

SPIN DYNAMICS INVESTIGATED BY MAGNETIC RESONANCE IN COLOSSAL MAGNETORESISTIVE MATERIALS

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The spin dynamics in colossal magnetoresistive manganites $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ (Di = Al, In; $x \leq 0.05$) has been analysed by ESR spectroscopy. The effect of the partial substitution of Mn by closed shell ions was evidenced. The temperature and x dependence of the resonance linewidth and integral intensity of the ESR signal have been investigated and discussed in terms of the bottlenecked spin relaxation and small polaron hopping models. The exchange coupling integral between Mn^{3+} and Mn^{4+} ions shows a decrease with increasing x due to the weakening of the double exchange interaction upon doping. A strong variation of the polaron activation energy with the doping level was also found and discussed in terms of the Mn - O distortion and the Mn^{3+} content.

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1. Introduction

The perovskite manganites ($\text{R}_{1-y}\text{A}_y\text{MnO}_3$ where R and A are trivalent rare-earth and divalent alkaline cations, respectively) are well known compounds for their colossal magnetoresistive properties (CMR). They are mixed valence compounds containing Mn^{3+} and Mn^{4+} ions. Coexistence of ferromagnetic and metallic conduction in these materials has been explained in terms of double exchange mechanisms (DE) [1]. However, DE interaction alone is insufficient to explain the observed CMR and an additional mechanism based on the polaronic effects was included. [2]. Here a strong electron – phonon coupling is expected because the electronic ground state of Mn^{3+} ions is degenerate giving rise to the Jahn – Teller effect (JT).

Despite the exhaustive study of the basic magnetic and structural properties of CMR manganites, the influence of the substitution at the Mn sites by closed shell ions is much less investigated. A better understanding of the underlying physical mechanisms could be achieved by destabilizing the Mn sublattice [3, 4, 5, 6, 7].

ESR spectroscopy is ideally suited for the investigation of the spin dynamics and magnetic correlations in manganese perovskites [8, 9, 10, 11, 12, 13]. The CMR materials show quite intense ESR signals and the corresponding parameters of interest are: the g – factors, the linewidth and the integral intensities. In contrast to the g - factors, which are nearly temperature independent in the paramagnetic regime, the linewidths and the integral intensities depend on both the temperature and the concentration of divalent alkaline cations [12]. A small number of contributions dealing with this subject have been published but limited space does not permit to review the literature here.

The main goal of this article is to point out the effects of the replacement of Mn by diamagnetic ions in colossal magnetoresistive perovskite $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ as seen by ESR.

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I will concentrate on the questions:

- (i) are the ESR data affected by the partial substitution of Mn by diamagnetic ions?
- (ii) is the bottlenecked spin relaxation model suitable to describe the magnetic interactions in the paramagnetic regime of substituted samples?
- (iii) can the adiabatic hopping motion of small polarons be influenced by non-magnetic doping level?

I will demonstrate in the following that the temperature and doping dependence of the two ESR parameters, integral intensity (I_{ESR}) and linewidth ($\delta H_{1/2}$) have revealed detailed information on the exchange coupling integral (J) between Mn spins and polaron activation energy (E_a) in this class of materials.

Some preliminary ESR results concerning the destabilisation of the Mn sublattice by aluminium (Al) and indium (In) have been already reported [14, 15, 16].

2. Experimental

We have chosen Al and In to make the substitution because these ions have: (i) a closed shell configuration, with no d electrons and no magnetic moments and (ii) the same valence with host manganese (+3). The only difference arises from their atomic radii, i.e. $\langle r \rangle_{Al} < \langle r \rangle_{Mn} < \langle r \rangle_{In}$. It has been recognized so far that the substitution for Mn with diamagnetic ions (Di) induces two types of randomness: (i) random potential fluctuation because the electronic configuration of Di ions is different from that of Mn^{3+} and Mn^{4+} (electrical randomness) and (ii) local cutoff of magnetic interaction between the t_{2g} spins (magnetic randomness) [6].

Polycrystalline $La_{2/3}Ca_{1/3}Mn_{1-x}Di_xO_3$ (Di = Al, In; $x \leq 0.05$) were prepared with the conventional solid – state reaction method [3, 4]. The X – ray powder diffraction analysis confirmed that the samples are composed of a single – phase. Table 1 shows the Mn^{4+} content, as determined by redox titration and the transition temperature T_C defined as the inflection point of the a.c. magnetic susceptibility curves [3, 4, 16].

Table 1. Percentage of Mn^{4+} , critical temperature T_C , Curie – Weiss temperature θ and the ratio T_C / θ for $La_{2/3}Ca_{1/3}Mn_{1-x}Di_xO_3$.

	x	Mn^{4+} (%)	T_C (K)	θ (K)	T_C / θ
Al	0.00	30	263	339	0.78
	0.01	34	217	318	0.68
	0.03	34	203	260	0.78
	0.05	35	189	249	0.76
In	0.01	31	235	294	0.80
	0.03	32	190	220	0.86
	0.05	28	(65)	161	0.41

The samples with $x \leq 0.05$ and $x \leq 0.03$ for Al and In doping respectively, are nominally stoichiometric and, in order to preserve the charge equilibrium, the substitution of Di for Mn leads to an oxidation from Mn^{3+} to Mn^{4+} (Table 1). For $x = 0.05$ In, a cusp is developed in the susceptibility curve and the corresponding freezing temperature $T_f = 65$ K is given in Table 1. The T_C decreases with the increase of the Di content and implies weaker ferromagnetic interactions.

In the paramagnetic regime the ESR spectrum for all investigated samples consists of a single line with $g \approx 1.99$ [14]. The line shape of the powdered samples was found to be Lorentzian over the investigated temperature range and for all x. It confirms the presence of the exchange – narrowed Mn dipolar fields [15, 16]. Since the sample size effects due to magnetic losses affect the spectrum [11], we have used small amount of powder material, $m = 0.5$ mg, for each x. In order to evaluate the ESR parameters, the derivative spectra were fitted with a Lorentzian line shape with fit parameters being

the half – width at half – height, $\delta H_{1/2}$, of the corresponding absorption line and the resonance field, H_0 .

3. Spin dynamics in the paramagnetic regime

In the mixed valence manganites, Mn^{3+} ($3d^4$ with $S = 2$) and Mn^{4+} ($3d^3$ with $S = 3/2$) ions are in octahedral symmetry, their electronic configurations being $t_{2g}^3 e_g^1$ and $t_{2g}^3 e_g^0$ for Mn^{3+} and Mn^{4+} , respectively. The basic feature of the DE mechanism in the hopping of the e_g electron between neighbouring Mn^{3+} and Mn^{4+} ions through the Mn – O – Mn path [1]. It could also be looked upon as a transfer of a d – hole from Mn^{4+} to Mn^{3+} via the oxygen. The electron transfer is favoured when the spins of the t_{2g} electrons of Mn^{3+} are aligned with the t_{2g} spins of the adjacent Mn^{4+} ion since in this case, the carrier avoids the strong – site Hund exchange energy and hops easily. Therefore, e_g electrons are considered as mobile carriers being responsible for the electronic conduction and the ferromagnetism occurs simultaneously with metallic conduction. DE model provides a nice explanation for the existence of a strong coupling between the charge carriers and the localized manganese moments. The archetypal CMR compounds $La_{1/3}Ca_{1/3}MnO_3$ undergoes a ferro – paramagnetic (FM – PM) transition at $T_C \approx 260$ K accompanied by a metal – insulator (MI) transition.

The electronic ground state of the Mn^{3+} ions is degenerate (orbital doublet) and the spin – lattice relaxation is very strong [8]. This degeneracy is removed by the dynamic JT effect and one expects a very strong electron – phonon coupling. The mobile e_g electron is also expected to carry the lattice distortion with it and thus JT distortion of Mn^{3+} may assist polaron formation. Therefore, the polaronic effects have to be included in DE mechanism resulting in a polaronic contribution to the conduction in the paramagnetic regime of CMR materials [2]. ESR could provide experimental evidence of JT polarons in $La_{1-y}Ca_yMnO_3$ [8, 9, 17].

A controversy exists regarding the interpretation of ESR data in CMR manganites. Three different models describing the linewidth dependence on T for $T > T_C$ have been discussed. Firstly, the observed linear temperature dependence of $\delta H_{1/2}$ in the paramagnetic regime was attributed to one – phonon spin – lattice relaxation [18]. Another mechanism is based on the conclusion that all Mn spins contribute to the resonance due to the spin – spin (exchange) interactions and so it is unrelated to any spin – lattice processes [11, 12]. This model was used to calculate the exchange integrals with the crystal field and anisotropic Dzyaloshinsky – Moriya (DM) terms taken into account [13]

According to the third model, the characteristic features of ESR intensity and linewidth in CMR manganites could be caused by spin – lattice relaxation of the entire exchange – coupled Mn^{3+} – Mn^{4+} spin system under the condition of a strong relaxation bottleneck [8, 9].

In the paramagnetic regime, it was observed a similarity between the temperature dependency of the ESR linewidth and that of the polaron hopping conductivity [9]. This indicates that the energy transfer in the relaxation mechanism is provided by the thermally activated hopping of small e_g polarons. Recently, the temperature dependences of both, longitudinal electron – spin relaxation time T_1 and transverse relaxation time T_2 were analysed in terms of the last two models described above [10].

In what follows we consider the ESR response of the system to contain three distinct components: Mn^{4+} ions; Mn^{3+} ions and the lattice. Here the spin – spin relaxation rates for the exchange coupled Mn^{3+} and Mn^{4+} ions are much larger than the spin – lattice relaxation rates.

In the bottlenecked spin relaxation scenario, the ESR integral intensity, I_{ESR} , is proportional to the total susceptibility, χ_{total} , of Mn^{3+} and Mn^{4+} spins [9]

$$I_{ESR} \propto \chi_{total} = \chi_s + \chi_\sigma \quad (1)$$

where χ_s and χ_σ are the renormalized static susceptibilities of the Mn^{4+} and Mn^{3+} spin systems, respectively.

$$\chi_s = \chi_s^0 \frac{1 + \lambda \chi_\sigma^0}{1 - \lambda^2 \chi_\sigma^0 \chi_s^0}, \quad \chi_\sigma = \chi_\sigma^0 \frac{1 + \lambda \chi_s^0}{1 - \lambda^2 \chi_\sigma^0 \chi_s^0} \quad (2)$$

Here χ_s^0 and χ_σ^0 are the bare (without exchange) susceptibilities of the Mn^{4+} and Mn^{3+} ions. The parameter λ is given by

$$\lambda = \frac{z J k_B}{N g_s g_\sigma \mu_B^2 \mu_0} \quad (3)$$

where $z = 6$ is the number of nearest neighbours, N is the total number of Mn spins per cm^3 , $g_s(g_\sigma)$ is the g factor of Mn^{4+} (Mn^{3+}) ions and J is the exchange coupling integral for the exchange interaction between Mn^{4+} and Mn^{3+} spins.

We assumed that the bare susceptibility of Mn^{4+} ions follows a Curie law $\chi_s^0 = C_s/T$ while that of Mn^{3+} is given by Curie – Weiss law, $\chi_\sigma^0 = C_\sigma/(T - \theta)$, where $\theta = -220$ K is taken to be the same as for undoped LaMnO_3 parent compound [19].

It is well established that in the paramagnetic regime of manganites, the conductivity σ is dominated by the adiabatic hopping motion of small polarons with the temperature dependence of the form $\sigma(T) \propto 1/T \exp(-E_\sigma / k_B T)$ [20].

Considering the proportionality between σ and $\delta H_{1/2}$, the temperature dependent part of the linewidth should arise from a thermally activated process involving the adiabatic hopping of small polarons. In this case, $\delta H_{1/2}$ can be expressed by [9]

$$\delta H_{1/2}(T) = \delta H_0 + A T^{-1} \exp(-E_a / k_B T) \quad (4)$$

where E_a is the polaron activation energy.

Obviously, from the experimental temperature dependencies of I_{ESR} and $\delta H_{1/2}$ one could evaluate J and E_a parameters in paramagnetic regime.

4. Results and discussion

In what follows, the effects of the substitution of Mn with Di ions on the spin dynamics in paramagnetic regime are presented and discussed.

At high temperatures, the ESR integral intensity, I_{ESR} , for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ samples follows a ferromagnetic Curie – Weiss (CW) temperature dependence, $I_{ESR}(T) = C/(T - \theta)$, arising from the ferromagnetic coupling of the Mn^{4+} and Mn^{3+} subsystems. At lower temperatures in the paramagnetic regime there is a deviation from the CW law [15, 16]. From the linear behaviour for $T \geq 1.9 T_C$ and the extrapolation to lower temperatures, the CW temperatures θ could be obtained (Table 1). θ is reduced as x is increased showing a general weakening of DE interaction upon doping.

We can get an estimation of J by fitting Eq. (1) to the $I_{ESR} * T$ data (Figs. 1, 2). The multiplication of I_{ESR} by T eliminates the intrinsic temperature dependence of the ESR signal caused by the Boltzmann population of the Zeeman levels involved [8]. In both Fig. (1) and Fig. (2), the solid lines represent the best fit to Eq. (1) in the temperature range $1.5 T_C \leq T \leq 500$ K.

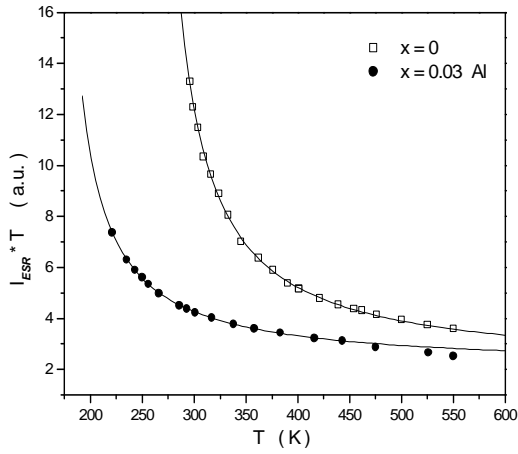


Fig. 1. Temperature dependence of $I_{ESR} * T$ for $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$ ($x = 0.00; 0.03$).

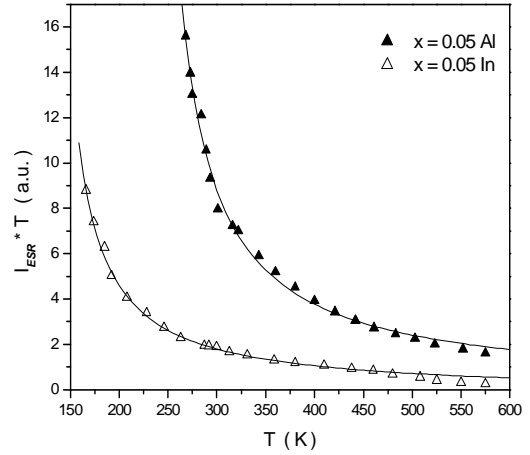


Fig. 2. Comparison of the temperature dependences of $I_{ESR} * T$ for $La_{2/3}Ca_{1/3}Mn_{0.95}Di_{0.05}O_3$.

The results can be found in Table 2. For the sample $x = 0.00$ the evaluated J value is of the same order of magnitude as the values obtained for $La_{0.8}Ca_{0.2}Mn^{16}O_{3+\delta}$ ($J = 78$ K) [9], $La_{0.8}Ca_{0.2}Mn^{18}O_{3+\delta}$ ($J = 71$ K) [9] and $Pr_{0.6}Ca_{0.4}MnO_3$ ($J = 154$ K) [21] from ESR measurements by using the bottleneck scenario.

Table 2. Exchange coupling integral J between Mn spins, polaron activation energy E_a and the residual linewidth δH_0 in the paramagnetic regime of $La_{2/3}Ca_{1/3}Mn_{1-x}Di_xO_3$.

Compound	J (K)	E_a (meV)	δH_0 (G)
$La_{2/3}Ca_{1/3}MnO_3$	116	120	24
$La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$			
$x = 0.01$	93	109	111
$x = 0.03$	84	103	126
$x = 0.05$	73	98	133
$La_{2/3}Ca_{1/3}Mn_{1-x}In_xO_3$			
$x = 0.01$	85	106	77
$x = 0.03$	71	97	138
$x = 0.05$	50	84	298

As one can see, the effect of Di doping is to perturb DE coupling between Mn^{4+} and Mn^{3+} ions, causing a continuous reduction in J with doping level (Fig. 3). The dilution of J in In - substituted samples is higher than the corresponding one for Al substitution [14, 16].

It is well established that the DE interaction depends on both the Mn - O distance and Mn - O - Mn bond angle [22]. The bending of the Mn - O bonds in the (a - b) plane suppresses the DE and promotes the antiferromagnetic contributions. In the substituted samples, the average Mn - O distance varies, depending on the Di - atomic radius compared to that of Mn, with the increase of doping level [3, 4]. On the other hand, the average Mn - O - Mn angle is rather constant in Al - substituted samples [3] while it decreases in In - substituted ones [4]. An enhanced bending of the Mn - O - Mn bond due to the large ionic size of In^{3+} is expected to slow down the charge - transfer and weaken the ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions. This could be the

reason for the observed larger reduction in J with In doping in comparison with the corresponding one for Al - substitution (Fig. 2).

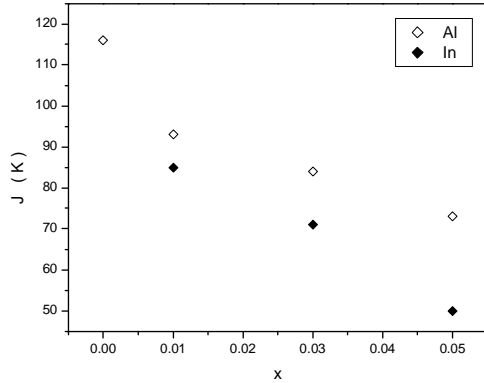


Fig. 3. Doping dependence of the exchange coupling integral J between Mn spins in $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ manganites.

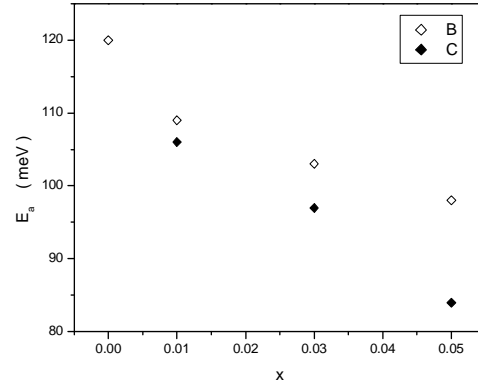


Fig. 4. Polaron activation energy, E_a , as a function of doping level x in $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$.

Therefore, the DE mechanism which is a process consisting of a Mn – Mn indirect exchange through the oxygen orbitals is very sensitive to the presence of Di impurities. The structural changes upon doping ($x \leq 0.05$) could qualitatively explain the decrease of J in $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ samples because they weaken the DE interaction. A similar effect in Cr – doped $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ was observed by ESR [23]. Here, a reduction of 20 % in J for $x = 0.025$ was evaluated by means of the spins – only interactions scenario [11].

In the following we discuss the temperature dependencies of the ESR linewidth $\delta H_{1/2}$, which are shown in Fig. 5 and Fig. 6 for samples with various Al and In concentration x , respectively.

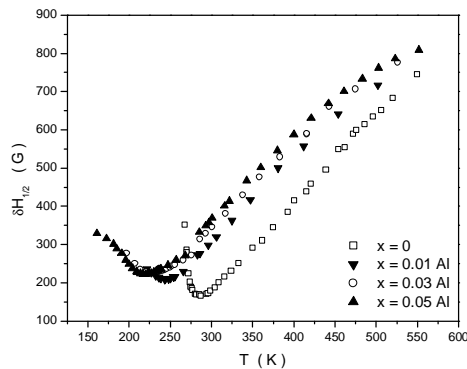


Fig. 5. Temperature dependence of the linewidth $\delta H_{1/2}$ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$.

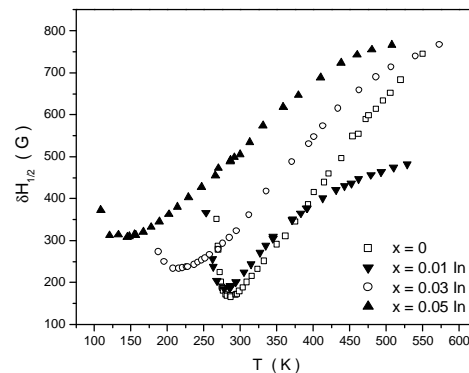


Fig. 6. $\delta H_{1/2}$ vs T for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$ manganites.

The linewidth goes through a minimum at $T_{\min} \approx 1.1 T_C$ and the temperature T_{\min} shows a decrease with increasing x in accordance with T_C variation, the behaviour similar to that observed for undoped compounds [14]. Its increase below T_{\min} is attributed to the usual critical slowing down in ferromagnets.

In the paramagnetic regime, $T > T_{\min}$, the temperature dependence of $\delta H_{1/2}$ for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ compound was found to be similar to that of the electrical conductivity and could be well described by the small polaron hopping model [9]. We have observed an alike behaviour for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ manganites.

Fig. 7 shows a comparison between the linewidth and the conductivity plotted as $\ln(\delta H_{1/2} * T)$ and $\ln(\sigma * T)$, respectively, vs $1000/T$ for $x = 0.00$ sample. The σ data are taken from Ref. 20 and correspond to a $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_{3+\delta}$ thin film having the highest annealing temperature. The solid lines are linear fits demonstrating that both $\delta H_{1/2}$ and σ follow the temperature dependence characteristic for the adiabatic small polaron hopping model with a similar value of the activation energy.

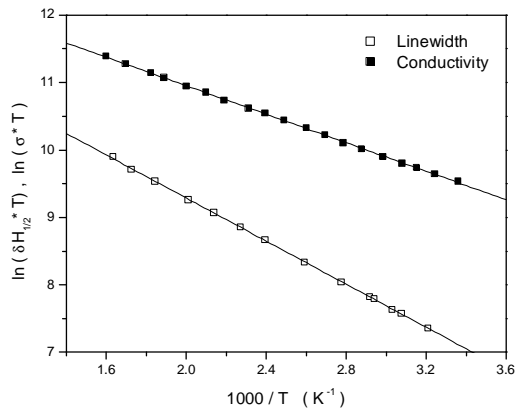


Fig. 7. The temperature dependence of $\delta H_{1/2}$ and σ in the paramagnetic regime of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$.

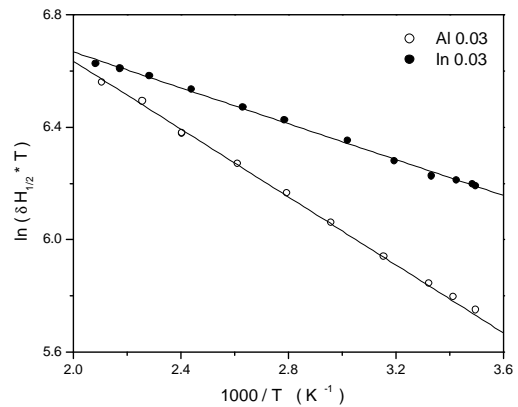


Fig. 8. $\ln(\delta H_{1/2} \times T)$ vs $1000/T$ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{0.97}\text{Di}_{0.03}\text{O}_3$. The solid lines are linear fits demonstrating the applicability of the small polaron model.

As shown in Fig. 8 the polaron model could also describe the temperature dependence of $\delta H_{1/2}$ for the substituted manganites. Here, the linear fits indicate that the polaron activation energy depends on the nature of the doped element: for a specific doping level the activation energy is higher for the Al - substitution than for the replacement of Mn with In.

In the temperature range $T > 1.5 T_C$, $\delta H_{1/2}(T)$ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ samples ($x \leq 0.05$) increases and could well be described by Eq. (4).

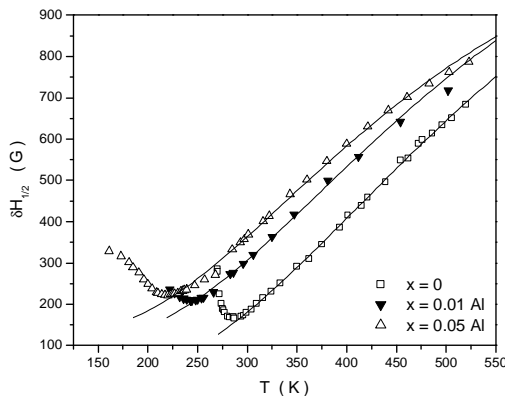


Fig. 9. Temperature dependence of $\delta H_{1/2}$ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ fitted with the small polaron model.

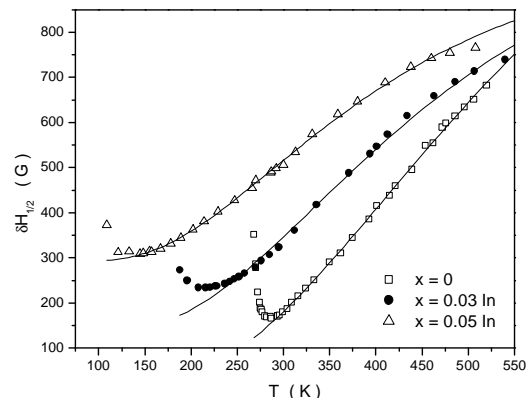


Fig. 10. $\delta H_{1/2}$ vs T for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$. The solid lines are the best fit to Eq. (4).

The solid lines in Fig. 9 and Fig. 10 represent the best fit to the data corresponding to some typical doping levels. The fitting parameters: the polaron activation energy, E_a , and the residual linewidth, δH_0 , for all investigated samples are summarized in Table 2. A fit to Eq. (4) was also used

to evaluate the activation energy from ESR measurements on polycrystalline $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ and $\text{Pr}_{0.65}\text{Ca}_{0.28}\text{Sr}_{0.07}\text{MnO}_3$ and results in $E_a = 106$ meV [9] and 110 meV [25], respectively.

An analysis of $\text{La}_{1-y}\text{Ca}_y\text{MnO}_{3+\delta}$ and $\text{LaMnO}_{3+\delta}$ series has shown a strong increase in E_a as the Mn^{3+} content increases [26]. It was argued that the polaron binding energy was proportional to the Mn – O distortion and there was a linear relationship between the Mn – O distortion and the Mn^{3+} content. Our results on $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{Di}_x\text{O}_3$ manganites are in agreement to that conclusion. From Fig. 4 one can see that E_a decreases with increasing doping level x , i.e. the decreasing Mn^{3+} content or similarly, increasing Mn^{4+} content (Table 1). A more pronounced decrease in E_a with In doping level is evidenced (Fig. 4).

In contrast to our findings, the nonmagnetic Ga (identical ionic radius with Mn) substitution at the Mn sites in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ implies an increase of E_a with increasing doping level [27]. It was suggested in this case, that the main influence of Ga doping is not on the lattice distortion but on local magnetic structure. Obviously, more experimental work has to be done in order to clarify the influence of Mn – site substitution of the transport and magnetic properties of CMR materials.

5. Conclusions

The effects of the substitution at Mn sites with Di – ions (Al, In) in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ manganites have been investigated by ESR. The temperature dependencies of I_{ESR} and $\delta H_{1/2}$ in the paramagnetic regime of the substituted samples can well be described by the bottlenecked spin relaxation scenario. The weakening of the DE interaction by Di – doping reduces the exchange field at Mn sites which results in a decrease of the exchange coupling integral J between Mn spins. Considering that the relaxation path is provided by thermally activated hopping of small e_g polarons, the activation energy E_a was evaluated from the temperature dependence analysis of the ESR linewidth. The observed decrease of E_a with increasing Di – doping level could be accounted for by the decrease of Mn^{3+} content and Mn – O distortion.

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