

EFFECTS OF In DOPING INVESTIGATED BY ESR IN COLOSSAL MAGNETORESISTIVE MANGANITE $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$

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The effects of the substitution for Mn with In in the colossal magnetoresistive manganites $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$ ($x \leq 0.05$) have been investigated by ESR. The temperature and x dependence of the resonance linewidth have been investigated and discussed in terms of the spin-spin (exchange) interaction scenario. In the paramagnetic regime, the exchange coupling integral, J, between Mn^{3+} and Mn^{4+} spins shows a decrease with increasing x. It could arise from the weakening of the double - exchange interaction upon doping, which reduces the exchange field at the Mn sites. The high temperature limit of the ESR linewidth does not depend on the doping level.

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1. Introduction

The manganite perovskites ($\text{R}_{1-y}\text{A}_y\text{MnO}_3$ where R – rare-earth; and A – Ca, B, Sr) have been widely studied since the discovery of colossal magnetoresistive (CMR) effects. They are mixed valence compounds containing Mn^{3+} and Mn^{4+} ions. Coexistence of ferromagnetism and metallic conduction in these compounds has been explained in terms of the double – exchange (DE) mechanism [1]. However, DE alone does not explain the CMR, and an additional mechanism based on the polaronic effects was included [2]. The basic magnetic and structural properties of CMR compounds were widely studied in the past. Despite the exhaustive study of the effects of rare-earth replacement, the influence of the substitution at Mn sites with diamagnetic elements is much less investigated [3, 4, 5].

ESR spectroscopy is a powerful tool for the study of the complex magnetic state in CMR compounds [6, 7, 8]. In order to obtain further insight into the effects of the replacement of Mn by In in the archetypal CMR compound $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, an X – band ESR investigation was carried out. In^{3+} - ion was chosen because it has no magnetic moment and its ionic radius is larger than the Mn one. Due to this difference in the ionic size, a strong effect of the substitution on the ESR data is expected. The results could be compared with the already reported ones for Al substitution [9, 10].

2. Experimental

Polycrystalline $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$ ($x \leq 0.05$) were prepared with the conventional solid-state reaction method. The Mn^{4+} content was determined by redox titration and the transition temperature T_C from the susceptibility curves (Table 1).

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The samples with $x \leq 0.03$ are nominally stoichiometric and in order to preserve the charge equilibrium the substitution of In for Mn leads to an oxidation from Mn^{3+} to Mn^{4+} . The lineshape of the powdered samples was found to be Lorentzian over the investigated temperature range and for all x . In order to evaluate the ESR parameters the derivative spectra were fitted with a Lorentzian lineshape 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 .

Table 1. Percentage of Mn^{4+} , critical temperatures T_C , Curie – Weiss temperature θ and the ratio T_C/θ for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$ manganites.

	x	Mn^{4+} (%)	T_C (K)	θ (K)	T_C / θ
In	0.00	30	263	339	0.78
	0.01	31	235	294	0.80
	0.03	32	190	220	0.86
	0.05	28	(65)	161	0.41

3. Spin dynamics for $T > T_C$

In CMR manganites, Mn^{4+} ($3d^3$ with $S_1 = 3/2$) and Mn^{3+} ($3d^4$ with $S_2 = 2$) ions are in the octahedral symmetry, their electronic configurations being $t_{2g}^3 e_g^0$ and $t_{2g}^4 e_g^1$ for Mn^{4+} and Mn^{3+} , respectively. The basic feature of the DE mechanism is the hopping of the e_g Jahn – Teller polarons between neighbouring Mn^{3+} and Mn^{4+} ions. The archetypal CMR compound $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$ undergoes a ferro - paramagnetic (FM - PM) transition at $T_C \approx 260$ K accompanied by a metal – insulator (MI) transition.

In the interpretation of our ESR data we have used the spin – spin (exchange) interaction scenario [7]. Here, all Mn spins contribute to the resonance because in the paramagnetic regime, $T > T_C$, a coincidence of dc magnetic susceptibility, χ_{dc} , with the integral intensity of the ESR spectrum, $I_{ESR} \approx \chi_{ESR}$, was found.

In the Weiss mean – field approximation for a system of two different spins, S_1 and S_2 , the Curie – Weiss (CW) temperature, θ , may be expressed by [7].

$$k_B \theta / J = (4z/3) y (1-y) S_1 (S_1+1) S_2 (S_2+1) / [y S_1 (S_1+1) + (1-y) S_2 (S_2+1)] \quad (1)$$

where $z = 6$ is the number of nearest Mn neighbours, x is the relative concentration of Mn^{4+} ions and J represents the exchange integral between Mn ions in the PM regime.

In order to describe the quasi-linear increase of $\delta H_{1/2}$ with temperature and tendency to saturation at higher temperatures, a single relaxation mechanism related to spin – only interactions was considered and resulted in [12]

$$\delta H_{1/2}(T) \propto [\chi_S(T) / \chi_{ESR}] \delta H_{1/2}(\infty) \quad (2)$$

where $\chi_S(T) = C/T$ is the single ion susceptibility, $\chi_{ESR} \propto I_{ESR}$ corresponds to the paramagnetic behaviour of the exchange coupled magnetic system and $\delta H_{1/2}(\infty)$ is identified with the high – temperature limit of the linewidth. This limiting value is independent of temperature and is related to the spin – only interactions.

In the exchange narrowing scenario, $\delta H_{1/2} \propto (\omega_p^2 / \omega_{ex})$, where ω_p is the frequency associated to anisotropic spin interactions and ω_{ex} is the frequency of isotropic exchange [11, 12]. As the effective FM coupling of the Mn ions could be described, in the PM regime, by an isotropic Heisenberg – like interaction [7], DE should contribute to the exchange narrowing.

4. Results and discussion

The effect of In substitution is to broaden, progressively, the resonance line and the linewidth at a fixed temperature shows an increase with increasing x (Fig. 1). It could arise from the weakening of the DE interaction by In doping which reduces the exchange field at the Mn sites and consequently an increase of the effective dipolar broadening would be expected.

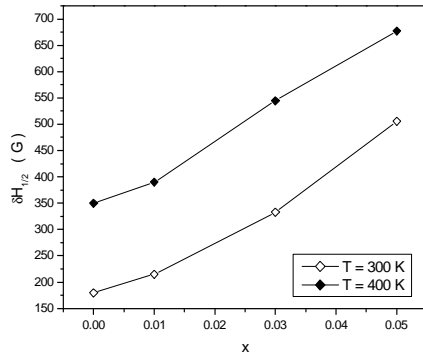


Fig. 1. Dependence of the ESR linewidth on concentration x with an implicit parameter of temperature.

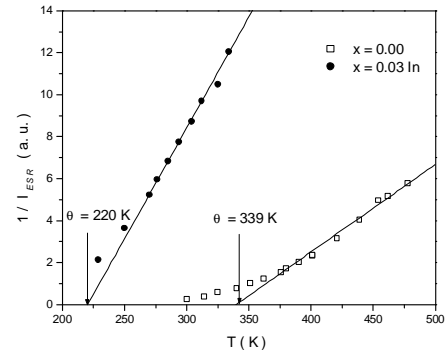


Fig. 2. $1/I_{ESR}$ as function of temperature for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$.

We have found that at high temperatures, the ESR integral intensity, I_{ESR} , follows a ferromagnetic 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. In Fig. 2 we show a plot of $1/I_{ESR}$ vs T for two selected In doped samples. From the linear behaviour for $T \geq 1.5 T_C$ and the extrapolation to lower temperatures, the CW temperatures θ could be obtained (Table 1). For $x \leq 0.05$, θ is reduced as x is increased showing a general weakening of DE interaction. We can get an estimate of J by using the measured values of θ in connection with Eq. (1). The results can be found in Table 2. For the sample $x = 0.00$ the evaluated J is very close to the value $J = 49$ K reported in [7].

As one can see, the effect of In doping is to perturb DE coupling, causing a continuous reduction in J with x (Fig. 3). It could arise from an enhanced bending of the Mn – O – Mn bond [4], which is expected to slow down the charge transfer and weaken the DE coupling.

Table 2. Exchange coupling integral J between Mn spin and the high – temperature limit of the linewidth $\delta H_{1/2}(\infty)$.

Compound	J (K)	$\delta H_{1/2}(\infty)$ (G)
$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$	48	1550
$\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$		
$x = 0.01$	40	1200
$x = 0.03$	30	1410
$x = 0.05$	24	1350

The temperature dependence of $\delta H_{1/2}$ in the paramagnetic regime of the substituted samples could be describe by means of the spin - spin (exchange) interaction scenario. The solid lines in Fig. 4 represent the best fit to the data corresponding to two typical doping levels. The fitting parameter $\delta H_{1/2}(\infty)$ for all investigated samples is given in Table 2. Within experimental resolution, $\delta H_{1/2}(\infty)$ does not depend on the doping level and, therefore, it is unaffected by the changes in the DE interaction.

A probable explanation for the absence of the influence of DE on $\delta H_{1/2}(\infty)$ can be related to the time scale associated to the exchange narrowing [8]. If this time is much shorter than the characteristic time for the hopping of e_g small polarons between Mn ions, the high - temperature limit of the ESR linewidth is not changed by dynamic DE process. A similar effect in Cr - doped $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ was identified by ESR [12].

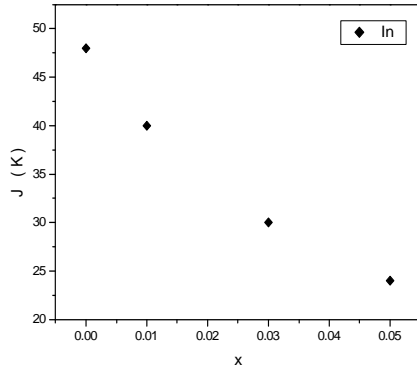


Fig. 3. Doping dependence of J in the paramagnetic regime of $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$.

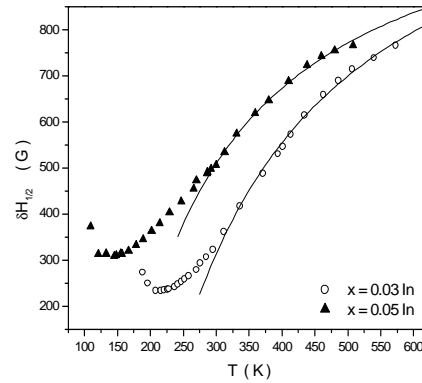


Fig. 4. $\delta H_{1/2}$ vs T for $\text{La}_{2/3}\text{Ca}_{1/3}\text{Mn}_{1-x}\text{In}_x\text{O}_3$ fitted with Eq. (2).

5. Conclusions

The effects of In substitution in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ have been investigated by ESR. The experimental results could well be described by a single relaxation mechanism related to the spin - only interaction. The weakening of the DE interaction upon doping results in a decrease of the exchange coupling integral J between Mn ions. It could arise from an enhanced bending of the Mn - O - Mn bond due to the large ionic size of In^{3+} . The high - temperature limit of the linewidth is unaffected by the changes in the DE mechanism and, therefore, is independent on the doping level.

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