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Mn-SITE DOPING EFFECTS IN THE GIANT MAGNETORESISTIVE PEROVSKITE $La_{2/3}Ca_{1/3}MnO_3$: AN EPR INVESTIGATION*

L. V. Giurgiu, M. N. Grecu[a], X. Filip, A. Darabont[b], E. Indrea, I. G. Deac[b], C. Filip, R. Ordean, G. D. Popescu[b], E. Surducan, J. Blasco[c], G. Papavassiliou[d]

National Institute for Research and Development of Isotopic and Molecular Technology, P.O. Box 700, R-3400 Cluj-Napoca, Romania
[a]National Institute of Materials Physics, 76900 Bucharest-Magurele, P.O.Box MG-7, Romania
[b]Physics Faculty, Babes-Bolyai University, R-3400 Cluj-Napoca, Romania
[c]Departamento de Fisica de la Materia Condensada, Universidad de Zaragoza, 50009 – Zaragoza, Spain
[d]Institute of Materials Science, National Center for Scientific Research, "Demokritos", 153 10 Athens, Greece

The effects of aluminium doping on Mn site in the magnetoresistive $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$ ($x \leq 0.05$) powders have been investigated by EPR. The temperature and x dependence of the resonance linewidth has been investigated and discussed in terms of exchange narrowing and spin-lattice relaxation. In the paramagnetic regime, the exchange coupling integral, *J*, between Mn^{3+} and Mn^{4+} ions shows a decrease with increasing x. It could arises from weakening of the double-exchange interaction by aluminium doping which reduces the exchange field at the Mn sites.

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1. Introduction

The manganese perovskites have been widely studied since the discovery of colossal magnetoresistance (CMR) effects. Coexistence of ferromagnetism and metallic conduction in these materials has been explained in terms of the double-exchange mechanism (DE) [1,2]. However, DE alone does not explain the CMR, and an additional mechanism based on the polaronic effects was included [3].

The archetypal CMR compound $La_{2/3}Ca_{1/3}MnO_3$ undergoes a para-ferromagnetic (PM-FM) transition at $T_c \approx 260$ K accompanied by a metal-insulator transition. The study of substitution of various metallic elements for manganese in this compound has shown that it was possible to modify its magnetic and transport properties [4,5]. For low replacement values of Mn by Al, which has no magnetic moment and its atomic radius is smaller than the Mn one, a decrease of the T_c with increasing Al content was observed, but the magnetoresistive properties do not change very much [4].

EPR spectroscopy is a powerful tool to study the complex magnetic state in the manganese perovskites [6,7]. In order to obtain further insight into the physical mechanisms related to the destabilization of the Mn sublattice by Al doping, an X-band EPR investigation of $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$ fine powders was carried out.

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2. Experimental

Ceramic samples of $La_{2/3}Ca_{2/3}Mn_{1-x}Al_xO_3$ (x = 0; 0.01; 0.05) were prepared by standard solid state reaction [4]. The X-ray powder diffraction analysis confirmed that the samples are composed of a single-phase. Table 1 shows the Mn^{4+} content, y, as determined by redox titration, and the values obtained for T_c defined as the inflection point of the susceptibility curves.

Table 1. Percentage of Mn^{4+} content and the critical temperatures T_c for $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$.

Parameter	x = 0	x = 0.01	x = 0.05
y(% Mn^{4+})	0.30	0.34	0.35
T_c (K)	263	217	189

The samples with $x \leq 0.05$ are nominally stoichiometric and in order to preserve the charge equilibrium; the substitution of Al for Mn leads to an oxidation from Mn^{3+} to Mn^{4+} (Table 1). The T_c decreases with the increase of the Al content and implies weaker ferromagnetic interactions.

In the paramagnetic regime the EPR spectrum for all investigated samples consists of a single line with $g \approx 1.99$. The line-shape of the ceramic samples reduced to fine powders 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. Since the sample size effects due to magnetic losses affect the spectrum [7] we have used small amount of powder material, m = 1mg, for each x. In order to evaluate the EPR parameters, the derivative spectra were fitted with a Lorentzian line-shape with fit parameters being the half-width at half-height, $\delta B_{1/2}$, of the corresponding absorption line and the resonance field, B_0.

3. Results and discussion

The temperature dependence of the EPR linewidth $\delta B_{1/2}$ up to 560 K is shown in Fig.1 for the samples with various Al concentrations x. The line-width decreases almost linearly with decreasing temperature, and goes through a minimum at $T_{min} \approx 1.1\ T_c$, the behaviour similar to that observed for undoped compound [7]. Its increase below T_{min} is attributed to the usual critical slowing down in ferromagnets. The temperature T_{min} shows a decrease with increasing x in accordance with the T_c variation.

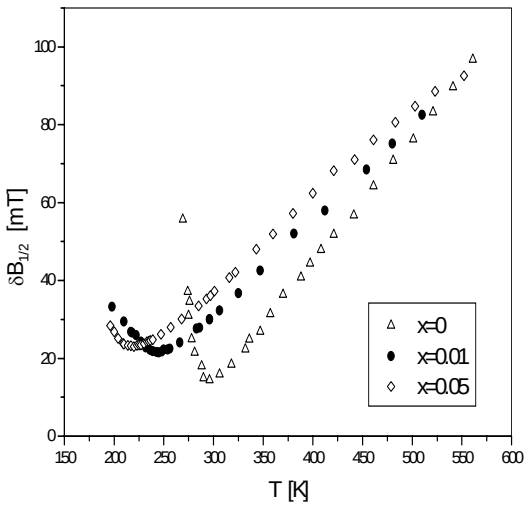

Fig. 1. Temperature dependence of the Al experimental linewidth $\delta B_{1/2}$ for $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$.

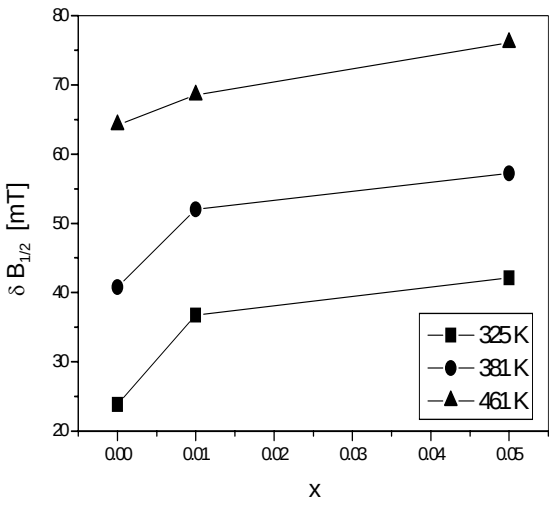

Fig. 2. Dependence of the linewidth on concentration x with an implicit parameter of temperature. The lines are only guides to the eye.

The effect of Al substitution is to progressively broaden the resonance line and the linewidth at a fixed temperature shows an increase with increasing Al concentration (Fig.2). It could arises from the weakening of the double-exchange ferromagnetic interaction by Al doping which reduces the exchange field at the Mn sites and consequently an increase of the dipolar broadening would be expected.

There is a debate considering the origin of the active ions responsible for the observed resonance in the paramagnetic regime. It was suggested that only Mn^{4+} ions ($3d^3$, $S_1 = 3/2$) having a weak spin-lattice relaxation give an EPR signal since the corresponding resonance of Mn^{3+} ions ($3d^4$, $S_2=2$) is unobservable due to a large zero field splitting and a strong spin-lattice relaxation [6]. In this case the T dependence of $\delta B_{1/2}$ could be explained by an exchange mechanism involving a bottleneck type regime between $Mn^{4+}$and Mn^{3+}magnetic subsystem. On the another hand, it was found that all Mn spins contribute to the resonance since $\chi_{ESR}(T)$ as determined by the spectrum integral intensity I(T) and $\chi_{dc}(T)$ coincide [7]. Appropriate to this model the linewidth behaviour can be described by a single relaxation mechanism related to spin-only interactions. In what follows we will assume that both Mn^{4+} and Mn^{3+} ions contribute to the EPR spectrum.

We have found that at high temperatures, I(T) for $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$ samples follows a ferromagnetic Curie-Weiss (CW) temperature dependence, $I(T) = C/(T-\theta)$, arising from the FM coupling of the S_1 and S_2 subsystems. At lower temperatures in the paramagnetic regime, there is a deviation from the CW law. Fig.3 shows a plot of 1/I vs T for the sample with x = 0.05. From the linear behaviour 1/I(T), for $T \geq 1.9\ T_c$, and the extrapolation to lower temperatures, the CW temperature θ can be obtained.

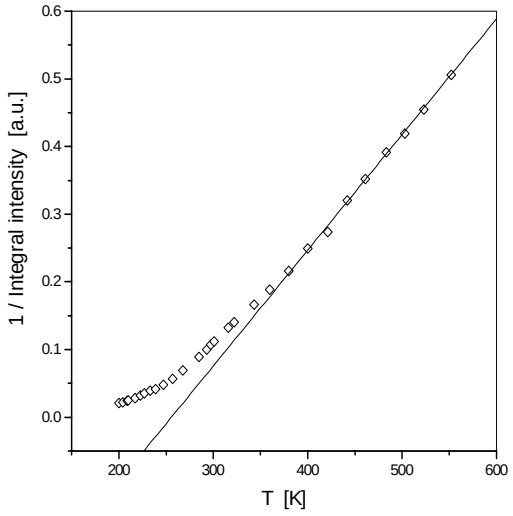

Fig. 3. 1/Intensity of EPR line as function of T for $La_{2/3}Ca_{1/3}Mn_{0.95}Al_{0.05}O_3$. The solid line represents the best fit to the CW law at high temperatures.

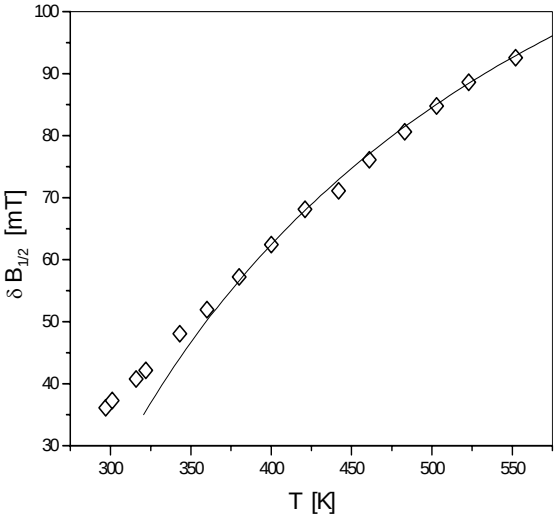

Fig. 4. Temperature variation of the $\delta B_{1/2}$ for sample with x = 0.05 and the fit with Eq. 2 (solid line).

In Table 2, we present θ values determined from high temperature region as function of Al concentration. For $x \leq 0.05$, θ is reduced as x is increased showing a general weakening of DE interaction.

In the Weiss mean-field approximation for a system of two different spins, S_1 and S_2, the θ temperature may be expressed as [7]

$$k_B\theta / J = (4z/3)y(1-y)S_1(S_1+1)S_2(S_2+1)/\left[yS_1(S_1+1)+(1-y)S_2(S_2+1)\right] \quad (1)$$

where z is the number of nearest Mn neighbours and J represent the exchange integral between Mn ions in the PM regime.

Table 2. Variation of θ, J and $\delta B_{1/2}(\infty)$ as function of Al concentration x in $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$. See text for definitions of the terms.

x	θ [K]	T_c/θ	J [meV]	$\delta B_{1/2}(\infty)$ [mT]
0	325	0.80	4	201
0.01	278	0.78	3.1	243
0.05	265	0.74	2.8	322

Using the measured values of θ, the exchange coupling integrals J evaluated by means of Eq.(1) are given in Table 2. As one can see, the effect of Al doping is to perturb DE coupling between Mn^{3+} and Mn^{4+} ions, causing a decrease in J [7]. It could arises from the bending of the Mn-O-Mn bonds in the (a-b) plane which is expected to slow down the carrier hopping and weaken the DE.

In order to describe the quasilinear increase of $\delta B_{1/2}$ with temperature and tendency to saturation at higher temperatures, a single relaxation mechanism was considered and resulted in [8].

$$\delta B_{1/2}(T) \propto \left[\chi_S(T)/\chi_{ESR}(T)\right]\delta B_{1/2}(\infty) \qquad (2)$$

Where $\chi_S(T)$ is the single-ion susceptibility and $\delta B_{1/2}$ corresponds to the spin-only interactions.As far as we can tell, the $\delta B_{1/2}(T)$ dependencies for different x could be reasonably described by Eq.(2) (see Fig. 4) and the limiting values $\delta B_{1/2}(\infty)$ are given in Table 2.

4. Conclusions

The effects of Al substitution in $La_{2/3}Ca_{1/3}Mn_{1-x}Al_xO_3$ ($x \leq 0.05$) powders have been investigated by EPR. The experimental results could be well described by a single relaxation mechanism related to the spin-only interaction. As x increases T_{min} shifts to a lower temperature. The weakening of the DE interaction by Al doping reduces the exchange field at Mn sites, which results in a broadening of the resonance lines and a decrease of the exchange coupling integrals J between Mn^{3+} and Mn^{4+} ions in the PM regime.

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