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Spin dynamics of Cr-doped $La_{0.67}Ca_{0.33}MnO_3$ in the paramagnetic regime

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Abstract

We report DC magnetization and electron paramagnetic resonance (EPR) measurements in ceramic samples of $La_{0.67}Ca_{0.33}Mn_{1-y}Cr_yO_3$ ($0 \leqslant y \leqslant 0.1$). We have observed a decrease of T_C with doping, which reveals a continuous dilution of the ferromagnetic exchange interaction. On the other hand, although the EPR linewidth (ΔH_{pp}) depends on the doping level, its high-temperature limit value ($\Delta H_{pp}(\infty)$) remains constant around 0.25 T. This implies that dynamic double exchange (DE) interaction is too slow to contribute to the exchange narrowing process.

Keywords: Colossal magnetoresistance; Double exchange interaction; $La_{0.67}Ca_{0.33}MnO_3$

Colossal magnetoresistance (CMR) in mixed valence manganites has attracted a large amount of interest in the last few years [1]. Substitution of Mn by Cr^{3+} could be of particular interest, as it is isoelectronic with Mn^{4+} and could be implicated in the DE interaction. Very recently, antiferromagnetic insulating-to-ferromagnetic metallic transition was induced in $Sm_{0.5}Ca_{0.5}Mn_{1-y}Cr_yO_3$, $0.05 \leqslant y \leqslant 0.09$ [2]. This has stimulated us to study the influence of Cr substitution in the CMR archetypal compound $La_{0.67}Ca_{0.33}MnO_3$. We have found that Cr doping reduces the ferromagnetic DE interaction of the pristine compound. This is manifested by a continuous decrease of both T_C and Curie–Weiss temperature (Θ_{CW}) with doping. We have also investigated the spin dynamics in the paramagnetic zone through the thermal evolution of the linewidth (ΔH_{pp}) for each level of doping.

$La_{0.67}Ca_{0.33}Mn_{1-y}Cr_yO_3$ ($y = 0.0$, 0.025, 0.05, 0.075, 0.10) were synthesized by conventional solid-state reaction. After several heating and grinding steps, pelletized samples were annealed at 1573 K for 100 h. In order to accurately determine the value of T_C, magnetization versus temperature was measured under an applied field of 10 Oe in field-cooled conditions using a VSM. For EPR measurements, a Bruker EMX spectrometer operating at 9.5 GHz (X-band) between 100 and 700 K was employed.

Replacement of 10% of Mn by Cr produces a decrease in T_C of nearly 60 K (Fig. 1). The same effect has been observed over Θ_{CW} extracted from the high-temperature fit of the paramagnetic susceptibility to the Curie–Weiss law. Using the Weiss mean-field approximation and Θ_{CW} we have derived the FM exchange constant J for doped samples [3]. We have observed a continuous reduction in the parameter J/k_B with doping (2.5% of Cr produces a reduction of nearly 20% in J). The observed dilution of J might be explained by a low degree of participation of Cr^{3+} in the DE interaction. The different effect of the crystal field on Mn^{4+} and Cr^{3+} probably causes energetic differences between e_g levels of Mn^{3+} and Cr^{3+} strong enough to make electronic exchange between them difficult.

$\Delta H_{pp}(T)$ was measured between $1.1T_C \leqslant T \leqslant 2.85T_C$ for all doping levels. Causa et al. [3] showed that $\Delta H_{pp}(T)$ for $A_{0.67}B_{0.33}MnO_3$ (A=La, Pr: B=Ca, Sr,

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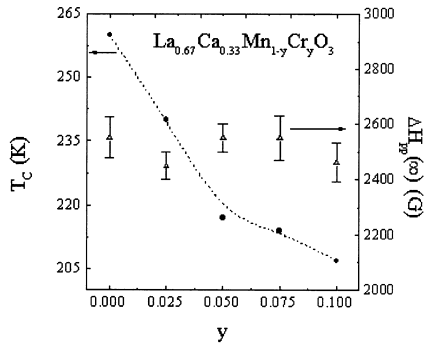

Fig. 1. Doping dependence of the Curie temperature (●) and of the high-temperature linewidth (△).

Pb) in the paramagnetic regime is described by $\Delta H_{pp}(\infty)C/T\chi_{DC}(T)$, where χ_{DC} is the magnetic susceptibility and $\Delta H_{pp}(\infty)$ is the high-temperature limit linewidth. This limiting value is independent of temperature and is related to spin only interactions. We have fitted $\Delta H_{pp}(T)$ with the experimental susceptibility and extracted $\Delta H_{pp}(\infty)$ for each case. The results are plotted in Fig. 1. Although $\Delta H_{pp}(T)$ is strongly influenced by doping this does not occur with $\Delta H_{pp}(\infty)$, which remains nearly constant around 0.25 T. The temperature and doping dependence of ΔH_{pp} are a direct consequence of the variations produced in the term $T\chi_{DC}(T)$ by the reduction of the DE coupling when doping with Cr.

Within the exchange-narrowing theory, $\Delta H_{pp}(\infty)$ is given by the ratio ω_p^2/ω_{ex} between anisotropic (ω_p) and isotropic (ω_{ex}) spin interactions. As the effective FM coupling between Mn ions can be described, in the paramagnetic regime, by an isotropic Heisenberg Hamiltonian [3], DE should contribute to the exchange narrowing. However, $\Delta H_{pp}(\infty)$ is unaffected by the changes in the DE interaction. This can be explained considering the time scale associated to the exchange narrowing. Huber et al. [4] estimated a characteristic time of $\sim 10^{-13}$ s for this process. If this time is considerably shorter than the characteristic time for electron transfer between Mn ions, $\Delta H_{pp}(\infty)$ is not changed by dynamic DE, as happens in these manganites. From the DC electrical conductivity associated with incoherent small polaron hopping at $T > T_C$, an estimation of the jump frequency (γ) between Mn^{3+}–Mn^{4+} ions can be made [5]: $\sigma = x(1-x)N(e^2a^2\gamma/6kT)\exp(-W_H/kT)$. Taking into account the relative concentration of Mn^{3+} and Mn^{4+} (x and $(1-x)$, of total concentration N), a mean Mn–Mn hopping distance (a) of 4 Å, and the hopping activation energy of the polaron mobility W_H, this jumping time gives a value of about $\sim 10^{-11}$ s.

In summary, we have proved that the high-temperature limiting value of EPR linewidth is determined by the frequency of the spin–spin exchange interactions, and DE does not affect this relaxation because it occurs on a different time scale.

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