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Electron spin resonance in iron-substituted manganites $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$

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Abstract

We report electron spin resonance (ESR) measurements on collosal magnetoresistive manganites $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ with $x = 0$, 0.01, 0.03, 0.06, 0.10 and 0.15, as well as on $LaMnO_3$ and $CaMnO_3$, in the vicinity of the magnetic transition temperatures T_C. ESR lines were fitted by Dysonian line shape. Temperature dependences of the linewidths exhibited a minimum value at $T^* \cong 1.25\,T_C$ followed by an increase of the width. We concluded that the ferromagnetic metallic clusters, exhibiting the double exchange interaction between Mn^{3+}–Mn^{4+} ions, play a dominant role in the resonance absorption.

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Keywords: Iron-substituted manganite; Electron spin resonance; Phase separation

1. Introduction

In the manganites $Ln_{1-x}A_xMnO_{3+\delta}$, where Ln = La, Nd, Pr, etc. and A = Ca, Ba, Sr, etc., the doping concentration introduces a mixed valence (Mn^{3+}, Mn^{4+}) which governs the magnetic and electric properties of the compounds. The electronic phase separation onto conducting ferromagnetic clusters, coupled via double exchange (D–E) interaction between Mn^{3+} and Mn^{4+} ions, with a characteristic lifetime exceeding $\tau \cong 10^{-5}$ s [1], was recently considered to be responsible for their colossal magnetoresistance [2].

We have performed electron spin resonance (ESR) studies, at 9.5 GHz ($\tau \cong 10^{-10}$ s), on the iron-substituted manganites, in order to search for dynamic properties of a mechanism of D–E interaction between the itinerant e_g electrons and the localised t_{2g} electrons forming the $S = \frac{3}{2}$ spins of the Mn^{4+} ions. Magnetic moments of the clusters and their concentration shall be responsible for the ESR signal and its linewidth.

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2. Experimental results and their analysis

Polycrystalline samples $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_{3+\delta}$ with $x = 0$, 0.01, 0.03, 0.06, 0.10 and 0.15 were prepared by the wet sol–gel method and solid-state reaction with $\delta \cong 0$ [3,4]. The overall stoichiometry was determined by a thermogravimetric method. The crystal structure and the exact stoichiometry were determined from precise X-ray diffraction by Siemens 5050 diffractometer, using the Rietveld procedure and "Full-proof" fitting programme. The lattice constants were extracted from the XRD data. Each of the investigated compounds was found to be single phase [3,4].

Magnetic and electric properties of the compounds were described previously [3,4]. ESR spectra were carried out at X-band microwave radiation, (ν = 9.5 GHz), in the temperature range between 4.2 and 300 K in magnetic fields up to 0.6 T, by a microwave spectrometer equipped with continuous gas-flow cryostat for He (Oxford Instruments). Bulk or powder samples were placed into quartz tubes in the cylindrical resonant cavity.

Here, we have restricted the analysis of our measurements to the electron paramagnetic spectra (EPR),

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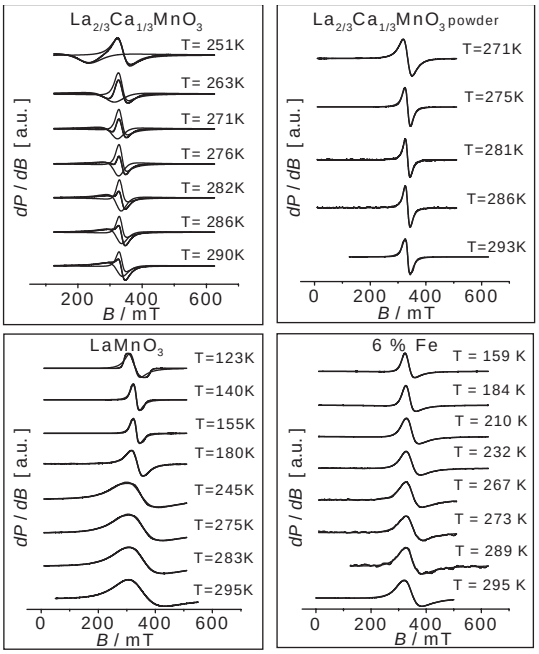

Fig. 1. Examples of temperature dependence of ESR spectra for $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ for $x = 0$ and 0.6 and for $LaMnO_3$. Solid lines show the fitting (see text).

shown in Figs. 1 and 2, in vicinity of the transition from paramagnetic insulator to ferromagnetic metal at temperature T_C. The transition temperatures were determined from our previous measurements of the susceptibility, magnetisation and specific heat [3,4]. T_C decreases from 262 K for $x = 0$, through 166 K for $x = 0.01$, 126 K for $x = 0.06$ and 103 K for $x = 0.1$, up to 80 K for $x = 0.15$. Below T_C, two or three lines were detected which may be attributed to different magnetic phases and the spectra are sample orientation dependent. The analysis of the ESR spectra will be presented elsewhere.

For Dysonian line shape in the form of the first derivative of microwave absorbed, power P with respect to the applied magnetic field B, linewidths ΔB and resonance fields B_r were derived by fitting the line to the proper combination of the absorptive and dispersive part of a Lorentzian shape line, following the method proposed in the paper [5]. The resonance field of all compounds under investigation yields a g-factor value, $g \cong 1.98-2.00$, slightly below the free electron value. For single run of measurements of bulk $La_{0.67}Ca_{0.33}MnO_3$, shown in the upper left panel in Fig. 1, we detected two-component resonant and antiresonant structure of the line due to the sufficiently high conductivity of the compound. The ratio of the dispersion to the absorption component of the lines changes from nearly zero to about 2 as x increases and obeys very similar temperature dependence as the absorption linewidth.

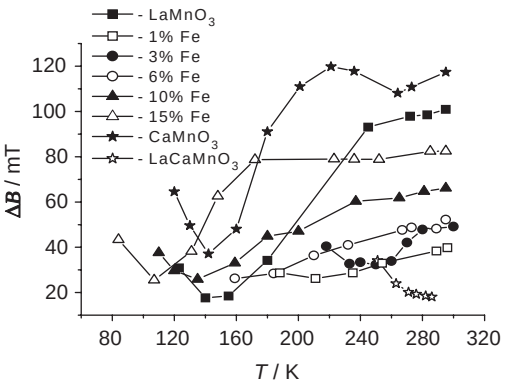

Fig. 2. Temperature dependence of the resonance linewidth.

The temperature dependences of the absorption linewidth in Fig. 2 exhibit minima at $T^* \cong 1.25\,T_C$. It was already established that the ESR signal comes from the ferromagnetic and metallic clusters Mn^{3+}–Mn^{4+}, coupled via D–E interaction between Mn^{3+} and Mn^{4+}, embedded into a paramagnetic matrix [6]. Above the minimum, the linewidth increases with temperature due to the spin lattice relaxation of the clusters.

Thus, we assume that the EPR line comes entirely from the clusters also because of the characteristic cluster lifetime $\tau \geqslant 10^{-5}$ s for $x = \frac{1}{3}$ [1] is much larger than the EPR Larmor time for our experiment, $\tau = 10^{-10}$ s. Thus, the EPR measures an average Mn^{3+}–Mn^{4+} state due to the jumping of an electron between them. With increasing concentration of Fe, which is in the Fe^{3+} ionic state [1,3], the concentration of the Mn^{3+} ions decreases mainly within the ferromagnetic clusters. Because the EPR linewidth increases with temperature and concentration of Fe, i.e. the cluster spin–lattice relaxation time decreases, we conclude that the substitution by iron weakens the D–E interaction.

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