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Electron spin resonance study of Fe doping effect in $La_{0.67}Ca_{0.33}MnO_3$

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ABSTRACT

Electron spin resonance (ESR) study was carried out on $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ ($x = 0.0$, 0.04) samples. The temperature dependence of the ESR spectra indicates the presence of phase separation above and below T_C in $x = 0.0$ and 0.04 sample, respectively. The increase of the g-value in the high-temperature region indicates the existence of local spin correlations even in the paramagnetic state. The activation energy obtained from both the temperature dependence of the ESR intensity and linewidth exhibits a smaller value in the Fe-doped sample. Our study suggests that the ferromagnetic spin correlations would be significantly weakened by a slight doping of Fe ions on Mn sites.

1. Introduction

The magnetic and resistive behavior in the colossal magnetoresistance manganites is well known to be sensitive to the doping on Mn sites [1,2]. A number of studies have been made on the effects of the replacement of Mn by various transition elements, such as Mg [3], Cu [4], Co [5], Cr [6], Fe [7,8], etc. Attention has been paid especially to the doping of Fe because Mn^{3+} and Fe^{3+} have similar ionic radius and only minor lattice distortions are expected by the substitution. It has been generally observed that the Curie temperature T_C decreases with increasing Fe doping level [8]. Especially, Ogale et al. [9] found that the Fe-doped samples showed a marked decrease in T_C at the 4% doping level and attributed this to the average Fe–Fe separation approaching the size of the charge carriers (polarons) at this concentration.

Electron spin resonance (ESR) is a powerful tool for the study of magnetic correlation in manganites. Valuable information can be obtained regarding the interplay of different interactions through a study of the temperature dependence of various ESR parameters, such as the resonance field, g-value, peak-to-peak linewidth and resonance intensity. A number of ESR studies have been carried out on some manganites. Although several ESR studies on $La_{0.67}Ca_{0.33}MnO_3$ have been reported [10], there have been no detailed ESR studies on the Fe-doping effect. Here we report the ESR study of $La_{0.67}Ca_{0.33}Mn_{1-x}Fe_xO_3$ ($x = 0.0$, 0.04) at temperatures between 100 and 400 K. The analysis and comparison of the ESR spectra of both samples clarify the effect of Fe doping.

2. Experiments

The ESR experiments were carried out on a JEOL JES-FA200 ESR spectrometer at X-band frequencies ($\nu \approx 9.4$ GHz) with temperature range from 100 to 400 K. The samples used for the experiment were single crystals prepared by the floating-zone technique in an optical image four-mirror furnace. The magnetization was measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7). The magnetizations show sharp changes at $T_C = 218$ and 214 K, for $x = 0.0$ and 0.04, respectively, as shown in the inset of Figs. 2(b) and 3(b), being consistent with the reported results. In order to eliminate the demagnetization effect and internal field, which could distort the ESR spectra as temperature approaches T_C, we grind the single-crystal samples into powders and measured the ESR on the powder samples.

3. Results and discussion

Fig. 1 shows the temperature dependence of the ESR spectra for $x = 0.0$ (left panel) and $x = 0.04$ (right panel). For the $x = 0.0$ sample, the ESR spectra consist of a single paramagnetic resonance (PMR) line at high temperature. Below 250 K, a ferromagnetic resonance (FMR) line appears at the low-field side and shifts to lower fields with further cooling. Below Curie temperature $T_C \sim 220$ K, the PMR signal becomes very weak and undetectable. The coexistence of FMR and PMR signals between 220 and 250 K suggests a phase separation in the vicinity of T_C, in which the FM phase and PM phase coexist. This result is in agreement with the neuron scattering result of Teresa et al. [11]. Their small-angle neutron scattering experiments on $La_{0.67}Ca_{0.33}MnO_3$ demonstrated that small FM metallic clusters start to form in the paramagnetic insulating matrix slightly above T_C.

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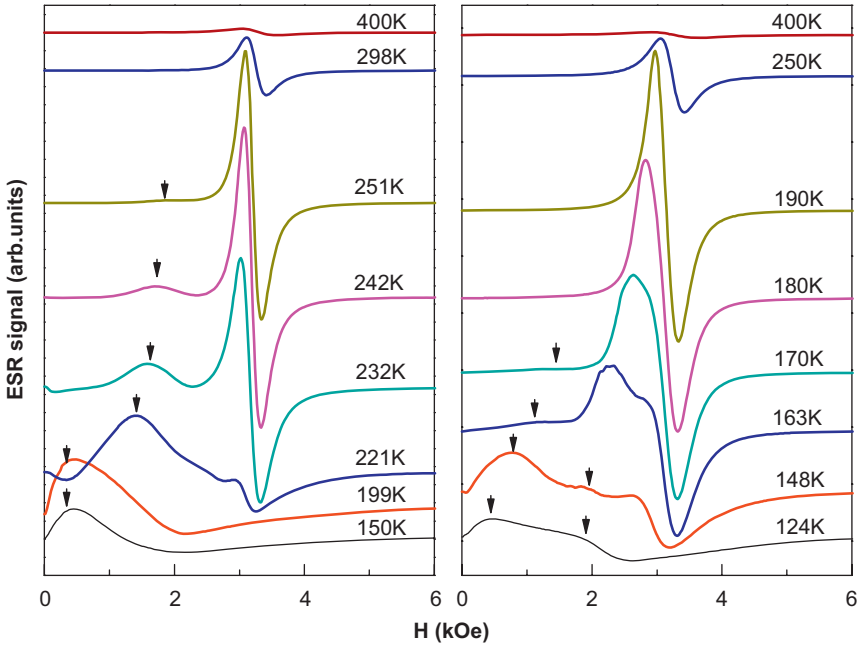

Fig. 1. Temperature dependence of the ESR spectra: (a) $x = 0.0$ sample and (b) $x = 0.04$ sample. The arrows mark the ferromagnetic resonance signals.

For the Fe-doped sample, the spectra show a single Lorentzian resonance line above 180 K. The FMR signal appears just below $T_C \sim 174$ K, which indicates that the FM clusters do not form above T_C. Meanwhile, the PMR signals persist well below T_C. The coexistence of FMR and PMR signal also indicates a phase separation in the Fe-doped sample. However, in contrast to $La_{0.67}Ca_{0.33}MnO_3$, where the phase separation occurs above T_C, the phase separation in $La_{0.67}Ca_{0.33}Mn_{0.96}Fe_{0.04}O_3$ occurs mainly below T_C in the ferromagnetic state.

On comparing the spectra for $x = 0.0$ and 0.04, we found that the doping of Fe decreases the T_C and lowers the phase separation temperature range. It indicates the doping of Fe ions disrupts the FM correlation above T_C and it is consistent with the general trend in these systems, where doping with Fe tends to result in a weakened double-exchange interaction, thereby lowering T_C.

In order to obtain more information from the ESR spectra and further investigate the effect of Fe doping in $La_{0.67}Ca_{0.33}MnO_3$, we analyzed the ESR parameters after fitting the spectra by the equation

$$\frac{dP}{dH} = \frac{d}{dH} A\left(\frac{\Delta H_{pp}}{\Delta H_{pp}^2 + (x - H_r)^2} + \frac{\Delta H_{pp}}{\Delta H_{pp}^2 + (x + H_r)^2}\right), \quad (1)$$

where ΔH_{pp} is the peak-to-peak linewidth, H_r is the resonance field and A is the area under the absorption curve. The temperature dependence of various ESR parameters for both samples is shown in Figs. 2 and 3.

Figs. 2(a) and 3(a) show the temperature dependence of g-value for both samples. In the high-temperature region, the g-value obtained from the resonance field H_r shows weak temperature dependence. As temperature decreases close to T_C, the g-value increases gradually in the PM state. This indicates that the spin correlations are present even above T_C and gradually develops with decreasing temperature.

The temperature dependence of ESR intensity obtained through double integration of the spectra is shown in Figs. 2(b) and 3(b). For both samples, the intensity initially increases slowly with decreasing temperature, and then increases rapidly as the temperature approaches T_C. This behavior is qualitatively similar to the susceptibility data.

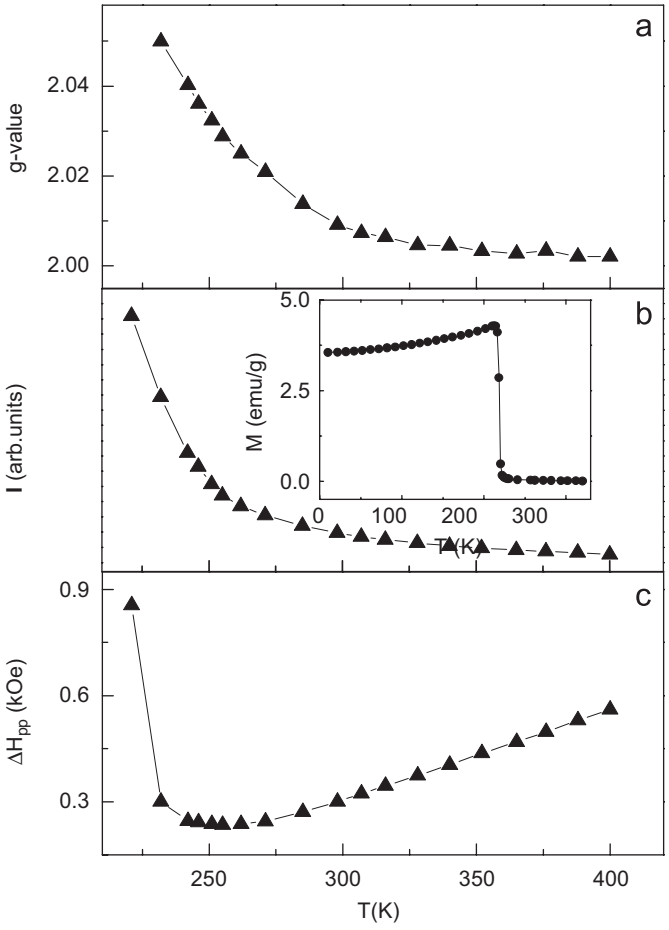

Fig. 2. Temperature dependence of the ESR spectra parameter for the $x = 0.0$ sample: (a) g-value, (b) intensity I and (c) linewidth ΔH_{pp}. The inset of (b) shows the temperature dependence of magnetization for the $x = 0.0$ sample.