

# Mössbauer spectroscopy and magnetoresistivity of $^{57}\text{Fe}$ substituted Mn in $\text{La}_{0.7-x}\text{Y}_x\text{Ca}_{0.3}\text{MnO}_3$ manganites

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We have studied the general physical properties of polycrystalline samples of  $\text{La}_{0.7-x}\text{Y}_x\text{Ca}_{0.3}\text{Mn}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_3$ ;  $x=0$  and 0.1; manganites prepared through sol-gel precursors. Characterization of these samples through electrical resistivity,  $\rho(T)$ , and magnetization,  $M(T)$ , measurements indicated a transition to a ferromagnetic state at  $T_C \sim 240$  and 100 K for  $x=0$  and 0.1, respectively. Mössbauer spectra taken from room temperature down to 4.2 K revealed the presence of two paramagnetic doublets from 300 to  $T_C$  having temperature independent hyperfine parameters and, that below  $T_C$ , the appearance of two ordered components that coexist with one paramagnetic phase. The coexistence between these phases is preserved from  $T_C$  down to  $\sim 20$  K. The highest magnetoresistance effect was found in the temperature range in which the change of volumetric fraction of these phases is maximum. © 2002 American Institute of Physics.

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The mixed-valence manganites with the general formula  $\text{Ln}_{1-x}\text{T}_x\text{MnO}_3$  (Ln=rare earth; T=Ca, Sr, or Ba) exhibit strong interplay between small lattice distortions, transport properties, and magnetic ordering.<sup>1-5</sup> In particular, the occurrence of colossal magnetoresistance (CMR) close to the Curie temperature,  $T_C$ , of these compounds is an object of great interest.<sup>1,2</sup> For example, the magnetic phase diagram of the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  system shows the existence of different phases with increasing Ca content.<sup>2</sup> In the low Ca doping region,  $x < 0.2$ , the compounds are found to be antiferromagnetic and insulating due to the superexchange interaction between  $\text{Mn}^{+3}$  ions. Increasing the Ca content  $x$  from 0.2 to 0.5 results in compounds that exhibit both ferromagnetic and metallic behavior below  $T_C$  due to the double-exchange interaction between  $\text{Mn}^{+3}$ - $\text{Mn}^{+4}$  pairs. Several experimental results<sup>6</sup> have suggested that the arrangement of these  $\text{Mn}^{+3}$ - $\text{Mn}^{+4}$  pairs is confined to small regions of these manganites with typical dimension of  $\sim 50$  Å. In fact, several spectroscopic and macroscopic measurements indicate that below  $T_C$ , at least two separated phases or regions coexist in these compounds.<sup>5-7</sup> It has been also argued that one of these phases has ferromagnetic and metallic (FM) character and the other is antiferromagnetic and insulating (AFI). Indeed, it was suggested that the CMR effect has its origin on the coexistence of these FM and AFI phases close to  $T_C$ .<sup>4</sup> These experimental results are in agreement with the phase separation scenario predicted theoretically by a number of models.<sup>8,9</sup>

In this work, we focus on Mössbauer, magnetic, and transport properties of  $^{57}\text{Fe}$  doped  $\text{La}_{0.7-x}\text{Y}_x\text{Ca}_{0.3}\text{MnO}_3$ ,  $x=0$  and 0.1, samples prepared through sol-gel precursors. The partial substitution of La by Y preserves the number of  $\text{Mn}^{+3}$ - $\text{Mn}^{+4}$  pairs and the  $^{57}\text{Fe}$  local probe was used to investigate the coexistence of phases below  $T_C$  in these manganites.

In order to produce homogeneous materials, polycrystalline samples of  $\text{La}_{0.7-x}\text{Y}_x\text{Ca}_{0.3}\text{Mn}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_3$  with  $x=0$  and 0.1 (hereafter referred as Y0 and Y10, respectively) were prepared through sol-gel precursors. Details of this chemical route for producing high-quality samples are described elsewhere.<sup>10</sup> The powders were heat treated at either 800 °C and 1000 °C in air for 30 h, subsequently pressed into pellets, and subjected to a final heat treatment at 1200 °C in air for 30 h. All samples were analyzed by x-ray powder diffraction using a Bruker<sup>TM</sup> Advanced D8 diffractometer. The x-ray patterns show that the orthorhombic structure (space group symmetry  $Pnma$ ) is preserved in all samples, with no vestiges of extra phases in any of the samples studied. Electrical resistance measurements in applied magnetic fields,  $H$ , up to 5 T were performed with a Linear Research LF-400<sup>TM</sup> ac resistance bridge operating at 16 Hz with variable excitation current.

Mössbauer spectra were recorded in transmission geometry between 4.2 and 300 K using a 100 mCi  $^{57}\text{Co}$  (Rh matrix) source in constant acceleration mode. Lorentzian line-shapes were used to fit the spectra by means of a nonlinear least-squares program. Isomer shifts and velocity scales were referred to  $\alpha$ -Fe absorber at room temperature. Magnetization  $M(T)$  measurements were performed in a commercial superconducting quantum interference device magnetometer in both zero-field-cooling (ZFC) and field-cooling (FC) conditions between 5 and 300 K in applied fields up to 70 kOe.

It is useful to start this discussion by summarizing the  $M(T)$  behavior in both Y0 and Y10 samples (not shown). A sharp transition to a ferromagnetic state was observed at 237 K (sample Y0) and 100 K (sample Y10). Below these temperatures, a clear irreversibility in  $M(T)$  between ZFC and FC curves was observed. Regarding the Mössbauer data, the spectra for both Y0 and Y10 samples at room temperature could be fitted with two paramagnetic components, whose hyperfine parameters are listed in Table I. These parameters are very similar to those found for both  $^{57}\text{Fe}$  and  $^{57}\text{Co}$  doped LaCaMnO compounds.<sup>11,12</sup> The component with quadrupole

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TABLE I. Hyperfine parameters from Mössbauer spectra for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$  Y0 and  $\text{La}_{0.6}\text{Y}_{0.1}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$  Y10 samples at 300 and 4.2 K: QS, IS, and linewidth. Errors are given in parenthesis.

$T$ (K)	Sample	Site	B(T)	QS(mm/s)	IS(mm/s)	$\Gamma$ (mm/s)
300	Y0	P1	...	0.170(4)	0.366(2)	0.327(5)
		P2	...	1.36(4)	0.365(7)	0.52(9)
	Y10	P1	...	0.265(7)	0.369(2)	0.40(1)
		P2	...	1.34(4)	0.27(1)	0.57(7)
4.2	Y0	B1	52.2(6)	0.01(1)	0.49(1)	0.44(1)
		B2	48(1)	0.01(1)	0.34(1)	0.70(3)
	Y10	B1	52.2(7)	0.01(1)	0.34(1)	0.59(4)
		B2	49(1)	0.01(1)	0.32(1)	0.95(4)

splitting (QS)  $\sim 1.35$  mm/s corresponds to a minor fraction of a total resonant area and increases from 3(1) to 11(1)% with increasing Y content. The larger linewidth,  $\Gamma$ , of this component indicates a more disordered environment for the corresponding Fe site. The isomer shift (IS) values of all components are characteristic of a  $\text{Fe}^{3+}$  oxidation state.

When lowering the temperature from 300 K to  $T \sim T_C$ , the hyperfine parameters of the two paramagnetic sites and their relative population remain essentially constant. However, below  $T_C$  (for sample Y10), two magnetic components (sextets) start to develop and coexist with just one paramagnetic component (doublet). The magnetic components have broad lines and a complex structure characteristic of magnetic relaxing spectra. However, in contrast to an ordinary ferromagnetic transition, between 80 and 20 K both the paramagnetic doublet and the two magnetic sextets components coexist, suggesting the presence of competing phases even at  $T \ll T_C$ . At 4.2 K, only two magnetic sextets B1 and B2 are observed, with similar hyperfine fields but different linewidth and IS values (see Table I).

The distribution of iron population at the two magnetic phases at 4.2 K was close to 50%, in contrast with previously reported data on  $^{57}\text{Fe}$  doped  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  samples, where the low-field sextet is a minor fraction (or even absent) of the total resonant area.<sup>11,13</sup> From the data taken from 300 to 4.2 K, the temperature dependence of the relative populations of magnetic and nonmagnetic sites was extracted and is shown in Fig. 1. The data clearly indicate the presence of significant volume fraction of paramagnetic regions in the sample even

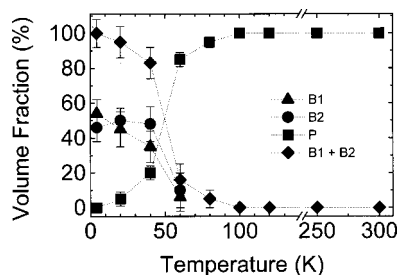


FIG. 1. Temperature dependence of the volume fraction of some phases in the  $\text{La}_{0.6}\text{Y}_{0.1}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$  sample. Circles and triangles denote two ordered phases, diamonds represent the sum of these ordered phases, and squares are associated with the paramagnetic component.

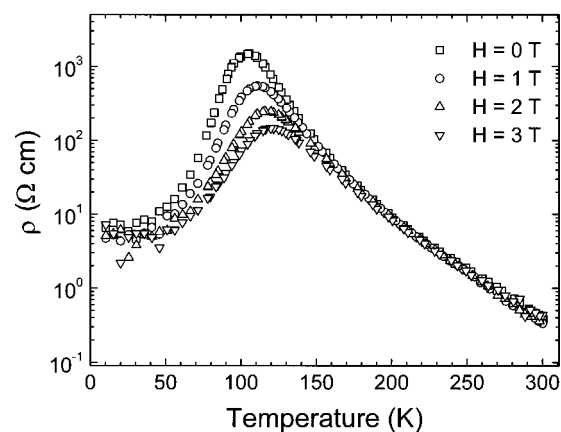


FIG. 2. Temperature dependence of the electrical resistivity  $\rho(T)$  of the  $\text{La}_{0.6}\text{Y}_{0.1}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3$  sample in several applied magnetic fields. The insulator–metal transition temperature,  $T_C$ , is defined as the temperature of the maximum in  $\rho(T)$  curves.

below  $T_C$ . Such a paramagnetic phase was observed to coexist with two ordered phases in a wide temperature range, roughly from 100 to 20 K. It has been argued that the development of paramagnetic regions [or superparamagnetic (SPM) islands] when approaching  $T_C$  from below could be due to increasing suppression of the long-range FM order towards  $T_C$ .<sup>14</sup> Indeed, our Mössbauer spectra exhibit typical features of a SPM transition when approaching  $T_C$  from the ordered state: (1) a gradual increase of the central doublet at expense of the magnetic component, and (2) an asymmetric (inward-curving) lineshape due to a distribution of phase volumes. It is worthwhile to mention that, to accurately characterize a SPM system, measurements of the blocking temperature, anisotropy constant, and fluctuation time must be performed as a function of both temperature and magnetic field. However, due to the intrinsic character of the SPM regions in manganites,<sup>14</sup> other effects are occurring close to  $T_C$ , making a separation of these contributions difficult. Nevertheless, if one assumes that these regions are SPM, their average volume can be estimated by using the expression  $\tau = \tau_0 \exp[KV/k_B T]$  for the dependence of the relaxation time. In this equation,  $V$  is the average volume of paramagnetic regions,  $\tau_0$  is the characteristic relaxation time ( $\sim 10^{-9} - 10^{-11}$  s for antiferromagnetic particles), and is  $K$  the total anisotropy of the region. The SPM-like behavior observed within the time window of Mössbauer spectroscopy ( $\sim 10^{-8}$  s) at  $T \sim 100$  K implies that  $KV \sim 200 - 400$  K. Assuming  $K \sim 10^6$  erg  $\text{cm}^{-3}$  (Ref. 15), these regions are estimated to have typical linear dimensions between 40 and 200 Å. Islands with similar dimensions were obtained from other techniques in these manganites.<sup>4,6</sup>

Some of the features discussed have their counterpart in transport properties of these compounds. Regarding the  $\rho(T)$  curves taken on the Y10 sample in  $H$  up to 3 T (see Fig. 2), the data exhibit a field independent semiconductor-like behavior of  $\rho(T)$  down to  $\sim 200$  K. Below this temperature, the curves slightly deviate from each other and the material undergoes an insulator–metal transition at  $T_C(H)$ . Increasing  $H$  results in an appreciable negative magnetoresistance CMR mostly in  $T \leq T_C$  and a careful inspection of these results

reveals that the changes in  $d\rho(T)/dT$  for  $T \leq 50$  K are negligible, even in fields as high as 3 T. This corresponds to the temperature region in which both ordered phases have constant volume fraction, as shown in Fig. 1. Also, the largest change in CMR is found to occur close to 90 K; near the temperature range in which the phases detected by Mössbauer spectroscopy coexist and compete with each other. This strongly suggests that the CRM effect has its origin in the coexistence of these phases, as proposed in similar systems.<sup>4</sup> It is important to notice that small differences in the temperature range where Mössbauer and  $\rho(T)$  data are uncorrelated can be explained by the application of  $H$  in the  $\rho(T)$  data. This shifts  $T_C$  to higher temperatures and certainly affects the volume fraction of these ordered phases close to  $T_C$ . Experiments of Mössbauer spectroscopy in applied magnetic fields up to 12 T are underway to better clarify this point.

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