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Fe doping in $La_{0.7}Sr_{0.3}MnO_3$ magnetoresistant perovskite

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Abstract

A series of samples of the GMR perovskite $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ system in the composition range $0.01 \leq x \leq 0.3$ has been prepared by the ceramic method. They have been characterised by X-ray diffraction, magnetic measurements and Mössbauer spectroscopy. This perovskite system crystallises in the space group $R\bar{3}c$. The substitution of Mn by Fe ions gives rise to a large decrease of the critical temperature of the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ system, suggesting the presence of a transition from ferro- to ferrimagnetic. Similar characteristics have been observed in the $La_{0.7}Pb_{0.3}Mn_{1-x}Fe_xO_3$ system. The Mössbauer spectra for all compounds measured in the paramagnetic region exhibit split peaks resulting from ions Fe^{3+} located in the distorted octahedral sites. The Fe quadrupole splitting increases with Fe^{3+} content increases. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnetically ordered materials; X-ray diffraction; Magnetic measurements; Mössbauer spectroscopy; Magnetoresistant materials

1. Introduction

Giant magnetoresistance (GMR) was known to occur in metallic bilayers and granular materials. This phenomenon of great technological importance is now found to occur in rare earth manganates of the formula $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = divalent cation) [1]. The presence of Mn^{3+}–O–Mn^{4+} units gives rise to ferromagnetism and the associated semiconductor–metal transition near the Curie temperature, T_c, because of the double-exchange mechanism. The substitution of the Mn ions by other transition metal ion, such as Fe, can give rise to important modifications in the magnetic and transport properties. ^{57}Fe Mössbauer spectroscopy is a powerful method for studying the crystal chemistry of iron in the perovskite structure. An additional advantage of the technique is that it 'sees' only the iron atoms, which is an important consideration when iron may constitute only a small fraction of the ions present in the structure. We describe in this work the Mössbauer measurements on Fe, which substitutes Mn in the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_{3-y}$ system ($0.01 \leq x \leq 0.3$).

2. Experimental

Polycrystalline samples of composition $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$, where $0.01 \leq x \leq 0.3$, were synthesised by the standard ceramic method. For $x > 0.05$ all phases were doped with 2% of ^{57}Fe of the total Fe content in the sample. The starting reagents, La_2O_3, $SrCO_3$, MnO_2 Fe_2O_3 and $^{57}Fe_2O_3$ were weighed in stoichiometric proportions and then milled for 30 min in acetone. The mixed powders were prefired at 900°C for 17 h then milled a second time, and finally heated at 1300°C for 18 h.

The different diagrams of X-ray diffraction were recorded on a PHILIPS X'PERT diffractometer using Cu K_α radiation. The analysis of the phases was carried out by the program FULLPROF [2] based on the method of Rietveld [3], using the option 'Profile Matching'.

Magnetic measurements were carried out in a Faraday balance and in a Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometer. The curves M(T) were obtained under an applied field of 10 mT and 1 T.

Mössbauer spectroscopy was performed in paramagnetic region in the transmission geometry using a conventional constant-acceleration spectrometer with a ^{57}Co–Rh source. The velocity was calibrated using Fe foil as standard

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Table 1
Crystallographic parameters obtained from the structural refinement of the synthesised compounds

Phase	a (Å)	c (Å)	V (Å^3)
$La_{0.7}Sr_{0.3}Mn^{57}_{0.99}Fe_{0.01}O_3$	5.511(3)	13.368(3)	351.67(1)
$La_{0.7}Sr_{0.3}Mn_{0.95}Fe_{0.05}O_3$	5.513(1)	13.367(2)	351.84(1)
$La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$	5.513(5)	13.366(2)	351.93(1)
$La_{0.7}Sr_{0.3}Mn_{0.8}Fe_{0.2}O_3$	5.516(1)	13.369(4)	352.29(1)
$La_{0.7}Sr_{0.3}Mn_{0.7}Fe_{0.3}O_3$	5.517(7)	13.373(2)	352.59(1)

material and the isomer shift is given with respect to Fe. The spectra have been fitted using the NORMOS program, developed by Brand et al. [4].

3. Results and discussion

3.1. X-ray measurements

The diffraction diagrams and crystallographic parameters for the synthesised oxides are very similar. The results are given in Table 1. The crystalline structure for all the compounds has been determined as rhombohedric, space group $R\bar{3}c$. These results are similar to those observed for the $La_{0.7}Pb_{0.3}Mn_{1-x}Fe_xO_3$ system [5].

The only consequence with the increase of the content of Fe is the expansion of the crystalline structure indicated by the increase in the volume of the unit cells. These results can be explained as due to the increase of both the Mn/Fe–O distances as was observed in the lead phases [5] obtained from the neutron diffraction data.

3.2. Magnetic measurements

Fig. 1 shows magnetisation studies for the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ $(0 \leq x \leq 0.3)$ system. The samples with $x = 0.01$, 0.05, 0.1 present a behaviour purely ferromagnetic. The curves M vs. T for the compositions with $x = 0.2$, 0.3 indicated the existence of ferro- and antiferromagnetic contribution. The introduction of Fe in the samples causes an important decrease in the temperature of ferromagnetic ordering [6,7], following the same behaviour observed for the insulator–metal transition [8]. Fig. 2 shows the variation of critical temperature (T_{critic}) with different concentration of Fe in the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$, $(0 \leq x \leq 0.3)$ system. A clear difference in the values of T_{critic} as well as in the magnetic moments for all samples were observed. The T_{critic} of the samples $x = 0.01$, 0.05 and 0.1 was obtained as the minimum of the curve dM/dT, for $x = 0.2$, 0,3 the $T_{\text{critic}} = \theta p$ was found using the inverse susceptibility curve and the corresponding Curie–Weiss fit $[\chi = C/(T - \theta p)]$ in the high paramagnetic region, all values of T_{critic} were calculated from curves $M(T)$ measured at 10 mT. From these data it can be deduced that the presence of Fe favours a negative contribution to the double exchange mechanism. The presence of the Fe ions can induce an anisotropic deformation in the structure modifying both the Mn–O distance and Mn–O–Mn angles. This distortion leads to the increase of the canting angle of moments, by competition between double exchange ferromagnetism and superexchange antiferromagnetism, this latter also appears between Fe and Mn ions.

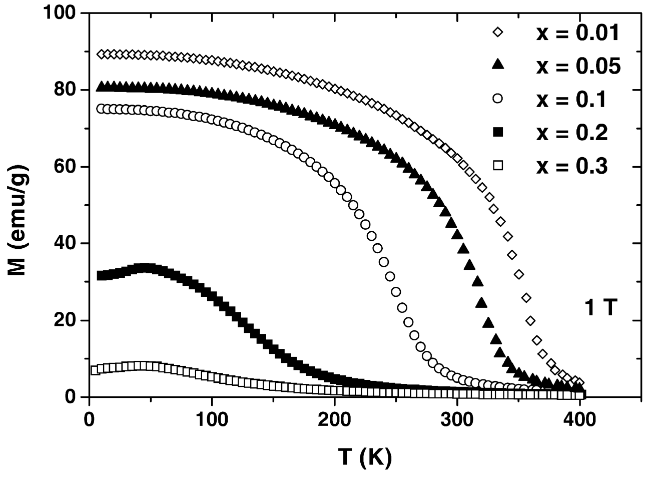

Fig. 1. Temperature dependence of magnetisation M in a 1 T field for the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ system.

3.3. Mössbauer measurements

Fig. 3 shows the Mössbauer spectra for the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_x$ system for $T > T_c$. Hyperfine parameters such as isomer shift (δ), quadrupole splitting (Δ) and the width at half height (Γ) for all the studied samples are listed in Table 2.

The Mössbauer spectra of the system discussed here

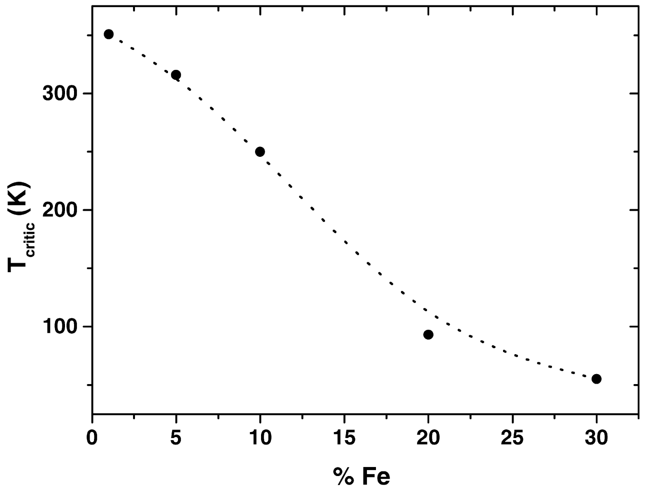

Fig. 2. Variation of critical temperature with different concentration of Fe in $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$, $(0 \leq x \leq 0.3)$ under an applied field of 10 mT. The line is a help to the eye.

Table 2
Mössbauer spectral hyperfine parameters for the studied compounds[a]

Compound	T (K)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)
$La_{0.7}Sr_{0.3}Mn^{57}_{0.99}Fe_{0.01}O_3$	410	0.370(6)	0.180(4)	0.380(9)
$La_{0.7}Sr_{0.3}Mn_{0.95}Fe^{57}_{0.03}Fe_{0.02}O_3$	365	0.300(6)	0.220(6)	0.360(9)
$La_{0.7}Sr_{0.3}Mn_{0.9}Fe^{57}_{0.08}Fe_{0.02}O_3$	300	0.360(2)	0.260(1)	0.320(1)
$La_{0.7}Sr_{0.3}Mn_{0.8}Fe^{57}_{0.18}Fe_{0.02}O_3$	300	0.360(0)	0.320(8)	0.330(6)
$La_{0.7}Sr_{0.3}Mn_{0.7}Fe^{57}_{0.28}Fe_{0.02}O_3$	300	0.340(7)	0.303(9)	0.300(9)
		0.340(6)	0.556(8)	0.290(9)

[a] Uncertainties for the last significant are given in brackets.

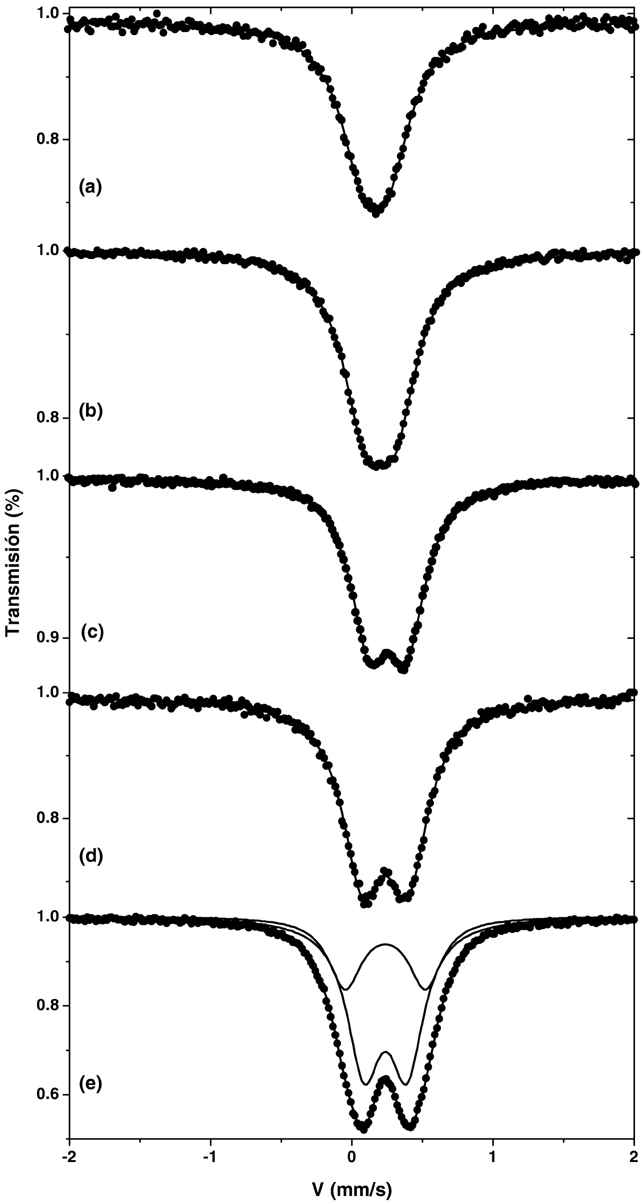

Fig. 3. Fitted Mössbauer data collected for the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ system in the paramagnetic region: (a) $La_{0.7}Sr_{0.3}Mn^{57}_{0.99}Fe_{0.01}O_3$; (b) $La_{0.7}Sr_{0.3}Mn_{0.95}Fe_{0.05}O_3$; (c) $La_{0.7}Sr_{0.3}Mn_{0.9}Fe_{0.1}O_3$; (d) $La_{0.7}Sr_{0.3}Mn_{0.8}Fe_{0.2}O_3$; (e) $La_{0.7}Sr_{0.3}Mn_{0.7}Fe_{0.3}O_3$.

show a doublet characteristic of a quadrupole effect Fe. The quadrupole splitting parameter measures the electric-field gradient at the Fe site, Δ is a sensitive reflection of local lattice symmetry. In our case, the Δ values increase with the amount of Fe^{3+} in the samples indicating a higher local distortion in the octahedral sites of the structure. The isomer shifts are characteristic of Fe (III) species (see Table 2) located on the octahedral sites of the structure. Therefore, the increase in the local distortion of the octahedra with increasing Fe content is directly related to the decrease of T_c in the studied compounds, as a consequence of the mechanism outlined above.

4. Conclusions

The substitution of Mn by Fe ions produces a local distortion not detected in the X-ray study. This distortion favours a decrease of the Curie temperature in the $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_{3-y}$ system probably due to the presence of antiferromagnetic couplings between Fe and Mn nearest-neighbours ions. The Mössbauer spectra for all compounds exhibit a doublet resulting from Fe^{3+} ions located in the distorted octahedral site. As the content of Fe^{3+} is increased the quadrupole splitting of Fe is increased. This arises from the anisotropic deformation of the environment of the Fe^{3+} located in the distorted octahedral sites. In this sense, Mössbauer spectroscopy turns out to be the most appropriate technique to study the environment of the Fe ions.

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