

## Charge Structure of the Combined System $(\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3)_{0.7}(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3)_{0.3}$ as Investigated by Mössbauer Spectroscopy

Young Rang Uhm, Sam Jin Kim and Chul Sung Kim\*

*Department of Physics, Kookmin University, Seoul 136-791, Korea*

(Received 14 December 2001)

The charge structures of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (LSMO) and of the combined system  $(\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3)_{0.7}(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3)_{0.3}$  are investigated by using Mössbauer spectroscopy. The antiferromagnetically ordered  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (LSFO) has possible charges of  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$ , which include a low-spin  $\text{Fe}^{4+}$  state at and above 230 K. The temperature dependences of the Mössbauer spectra for the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  system and for the combined  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$  system are fitted as three sets of Zeeman patterns corresponding to  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  below 230 K. At and above 230 K, the fitted Mössbauer spectra for the combined system are the same in all temperature ranges. Above 230 K,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  spectrum consists of two sets of six Lorentzians for  $\text{Fe}^{3+}$  and one line for low spin  $\text{Fe}^{4+}$ . It is worth noting that large fields are induced in the combined system.

**Key words :** Combined system, Mössbauer spectra,  $(\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3)_{0.7}(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3)_{0.3}$

### 1. Introduction

In recent years, much attention has been focused on the colossal magnetoresistance (CMR) of perovskite manganites [1]. For single crystals and epitaxial thin films, the magnitude of the CMR reaches a maximum only near the Curie temperature ( $T_c$ ). However, the fact that grain boundaries and interfaces can be an important source of low-field magnetoresistance (LFMR) has stimulated renewed interest in polycrystalline samples [2]. Several researchers have reported a large low-field CMR in a  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and  $\text{CoFe}_2\text{O}_4$  combined system [3], the magnetic properties related to the charge structure of  $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$  and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{FeO}_3$  have been investigated in recent years [2-5]. A charge disproportionation (CD) between  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$ , where  $\text{Fe}^{4+}$  ion is the low-spin (LS) state ( $^1T_g$ ), exists in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  with an orthorhombic structure [5]. A similar situation exists between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  [5]. The prototypical half metal with 100% spin polarized  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  has a low Curie temperature ( $T_c$ ) of 320 K, which was measured by using a superconducting quantum interference device (SQUID) magnetometer, and the antiferromagnetically ordered  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (LSFO) has a Néel temperature ( $T_N$ ) of 370 K.

In this research, a combined polycrystalline  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  (LSMO) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (LSFO) system was prepared by using the sol-gel process. We observed that magnetic properties of this combined system were sensitive to the charge structure.

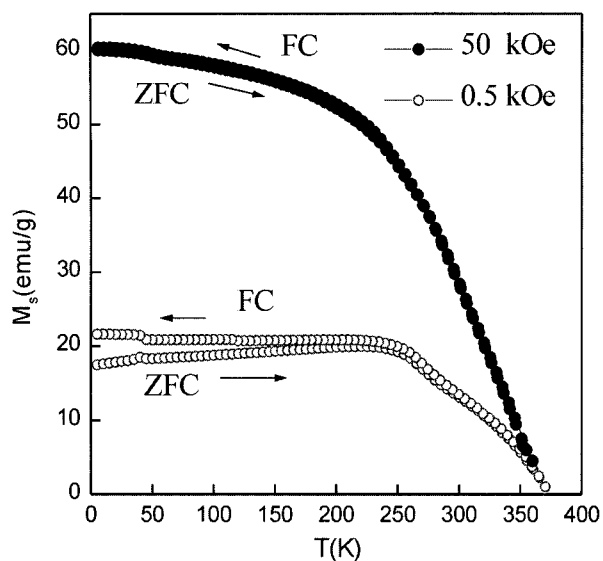
### 2. Experimental Technique

The  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$  combined samples were prepared in two steps. The  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  powders were prepared by using a sol-gel process. In the first step, stoichiometric amounts of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$  were dissolved in an aqueous solution. Then,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  powders were obtained by heat treatment at  $650^\circ\text{C}$ . The  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  powders were prepared by using a similar sol-gel process. Finally micrometer-scaled powders of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  were annealed at  $1100^\circ\text{C}$  for 1 hour. Second, the two samples were mixed in the composition  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$ . Chemically reacted grains of LSMO and LSFO did not exist in the combined system. For the measurements, a Mössbauer spectrometer of the electromechanical type was used in the constant-acceleration mode [6].

### 3. Results and Discussion

The Scherrer relationship [7] of XRD for the combined

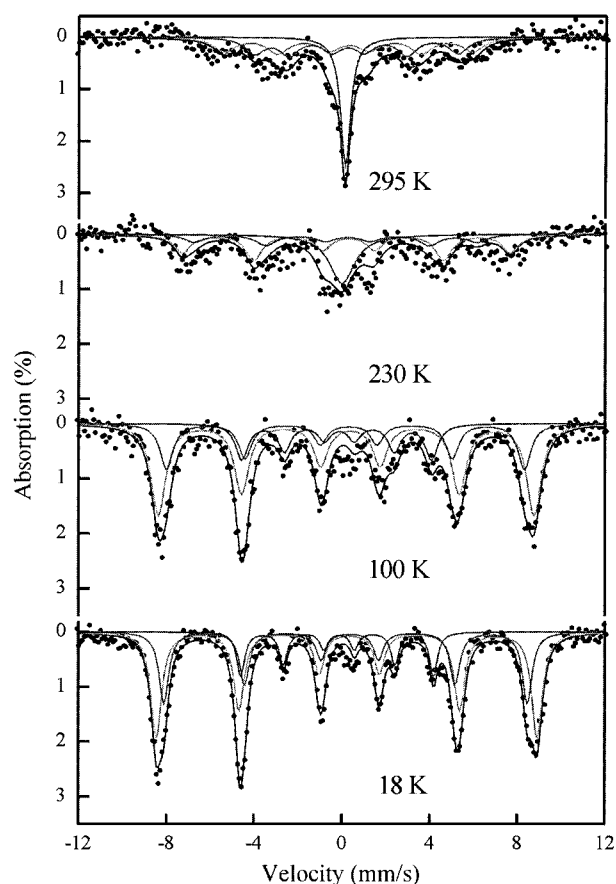
\*Corresponding author: Tel: +82-2-910-4752,  
e-mail: cskim@phys.kookmin.ac.kr



**Fig. 1.** Temperature dependence of the magnetization for the combined powder by measurement with a SQUID magnetometer.

(LSMO)<sub>0.7</sub>(LSFO)<sub>0.3</sub> system shows large grains for LSFO (1712 Å) and small grains for LSMO (622 Å). Figure 1 displays the temperature dependence of the magnetization, as determined by SQUID measurements, for the combined powder. Weakening of the ferromagnetism makes the resistivity higher and insulating. Unfortunately, we couldn't detect a large low-field CMR in the (LSMO)<sub>0.7</sub>(LSFO)<sub>0.3</sub> combined system. The magnetization at 500 Oe shows very different phases between the zero-field cooled and the field cooled measurements, below the room temperature. We deduce that the spontaneous magnetization in this combined system with a perovskite structure has an antiferromagnetic order of Fe<sup>3+</sup>-O-Fe<sup>4+</sup> and a ferromagnetic order of Mn<sup>3+</sup>-O-Mn<sup>4+</sup>. The value of the spontaneous magnetization is about 70% that of La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>. The magnetization of the combined different-grain-size sample (with 30 wt % LSFO) is lower (17 emu/g) than that of LSMO (27 emu/g) at 5 K in a field of 500 Oe. The Curie temperature (T<sub>C</sub>) for the combined system was determined to be 370 K by using a SQUID magnetometry, which is same as that of LSFO. This means that chemically reacted grains of LSMO and LSFO did not exist in the combined system. Upon mixing with LSFO, the T<sub>C</sub> and the magnetization at low temperatures are reduced.

Mössbauer spectra of La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub> were taken at various temperatures ranging from 18 K to room temperature. Figure 2 shows the temperature dependence of the Mössbauer spectra for La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub>. With a least-squares computer program, three sets of six Lorentzian lines were



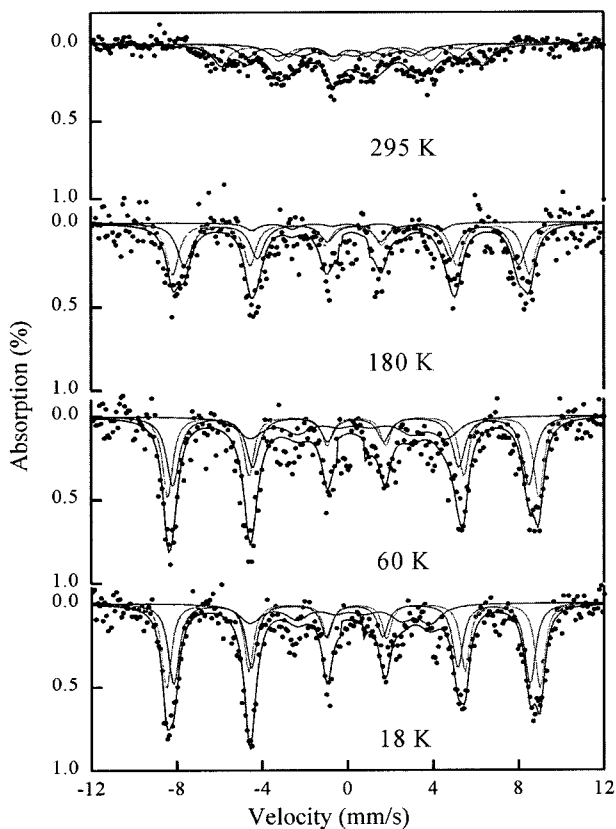
**Fig. 2.** Temperature dependence of the Mössbauer spectra for La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub>.

fitted to the Mössbauer spectra of La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub> at 18 K due to Fe<sup>3+</sup> in the octahedral site and the fivefold coordinated site and to Fe<sup>4+</sup>. The isomer shifts  $\delta$  of the three sub-spectra revealed that the two main components were Fe<sup>3+</sup> and that the other was Fe<sup>4+</sup>. The broad single line around 0 mm/s can be assigned to tetravalent iron, which reveals a low-spin (LS) state [4, 8]. The La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub> includes a low-spin state of Fe<sup>4+</sup> at and above 230 K. The valence states of iron Fe<sup>3+</sup> and Fe<sup>4+</sup> exist in all the samples. The Mössbauer parameters and the ratio of the three kinds of iron are given in Table 1. In the Mössbauer spectra, the magnetic hyperfine field of Fe<sup>4+</sup> is 273 kOe at 18 K, though the valence state belongs to the LS state. We detected similar effects in another distorted perovskite, Gd<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-y</sub> (x = 0.5 and 0.75) [8]. This means that the Mössbauer spectrum of the tetravalent iron ion has of Zeeman pattern with a fine structure when the enhanced high field (for example, the Fe<sup>3+</sup> ion at low temperature) affects Fe<sup>4+</sup>, though the stable state is a nuclear-resonance singlet.

Figure 3 shows the temperature dependence of the

**Table 1.** Mössbauer parameters for  $(\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3)_{0.7}(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3)_{0.3}$  and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ .  $H_{\text{hf}}$  is the magnetic hyperfine field,  $\Delta E_Q$  is electric quadrupole split, and  $\delta$  is the isomer shift

Sample	T (K)	$H_{\text{hf}}$ (kOe)	$\Delta E_Q$ (mm/s)	$\delta$ (mm/s)	Valence	ratio (%)	
$(\text{LSMO})_{0.7}$	18	1	542	-0.09	0.32	$\text{Fe}^{3+}$	53
		2	520	-0.07	0.26	$\text{Fe}^{3+}$	30
		3	296	-0.06	0.19	$\text{Fe}^{4+}$	17
$(\text{LSFO})_{0.3}$	293	1	380	-0.05	0.31	$\text{Fe}^{3+}$	45
		2	307	0.04	0.19	$\text{Fe}^{3+}$	27
		3	210	-0.09	-0.03	$\text{Fe}^{4+}$	28
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FO}_3$	18	1	539	-0.05	0.29	$\text{Fe}^{3+}$	43
		2	514	-0.09	0.27	$\text{Fe}^{3+}$	37
		3	273	-0.04	-0.02	$\text{Fe}^{4+}$	20
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FO}_3$	293	1	351	-0.01	0.28	$\text{Fe}^{3+}$	47
		2	287	-0.19	0.32	$\text{Fe}^{3+}$	29
		3	-	-	0.02	$\text{Fe}^{4+}$	31



**Fig. 3.** Temperature dependence of the Mössbauer spectra for the  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$  combined system.

Mössbauer spectra for the  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$  combined powder. The spectra consist of 3 sets of 6 Lorentzians, including a distorted oxygen vacancy site (fivefold coordinated). The  $(\text{LSMO})_{0.7}(\text{LSFO})_{0.3}$  combined system doesn't

show the broad single line around 0 mm/s assigned to the low-spin state of  $\text{Fe}^{4+}$ . The large grains of LSFO are well distributed and are surrounded by small LSMO grains. The magnetic hyperfine field of LSMO is much higher than that of LSFO. The large magnetic field of LSMO contributes to the field on the LSFO in the combined sample. Thus, the one Lorentzian line in the Mössbauer spectrum for  $\text{Fe}^{4+}$  changes to six Zeeman patterns over the entire temperature range from 18 K to room temperature. At 18 K, the magnetic hyperfine fields of the two  $\text{Fe}^{3+}$  are 542 and 520 kOe, and that of  $\text{Fe}^{4+}$  is 296 kOe. As shown in Table 1, the ratio of the tetravalent ion is 28% at the whole absorption line of Mössbauer spectra.

## 4. Conclusion

We prepared a combined system of  $(\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3)_{0.7}(\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3)_{0.3}$  by using a sol-gel process, and we studied its magnetic properties in terms of the charge structure. The mixed grains of LSMO and LSFO did not chemically react in the combined sample. In the Mössbauer spectra, the tetravalent iron showed Zeeman patterns, though the valence state belonged to the LS state, because the enhanced high fields of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  induced  $\text{Fe}^{4+}$ . In a combined system with different grain-sized samples (with 30 wt % LSFO), the high magnetic field (from LSMO) affected the charge structure of LSFO.

## Acknowledgment

This work has been support by the Korea Science and Engineering Foundation (R01-1997-00109).

## References

- [1] M. Imada, A. Fusimori and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
- [2] H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, *Phys. Rev. Lett.* **77**, 2041 (1966).
- [3] C. H. Yan, Z. G. Xu, T. Zhu, Z. M. Wang, F. X. Cheng, Y. H. Hunf, and C. S. Liao, *J. Appl. Phys.* **87**, 5588 (2000).
- [4] Y. R. Uhm, S. W. Lee, K. T. Park, C. S. Kim, Y. Tomioka, and Y. Tokura, *J. Appl. Phys.* **87**, 4873 (2000).
- [5] T. Ishikawa, S. K. Park, T. Katsufuji, T. Arima, and Y. Tokura, *Phys. Rev. B* **58**, R 13326 (1998).
- [6] Chul Sung Kim, Sung Yong An, Young Rang Uhm, Seung Wha Lee, Y. B. Kim and C. S. Kim, *J. Appl. Phys.* **83**, 6929 (1998).
- [7] P. Vaqueiro, M. P. Crosner-Lopez, and M. A. Lopez-Quintela, *J. Solid State Chem.* **126**, 161 (1996).
- [8] Y. R. Uhm, J. C. Sur, and C. S. Kim, *J. Magn. Magn. Mater.* **215-216**, 554 (2000).