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Magnetic and Mössbauer studies on oxygen deficient perovskite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$

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Samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{3-\delta}$ with varying oxygen vacancy contents were prepared by heating them in different gas flows. Magnetization measurement showed that samples with low oxygen vacancies have a magnetic ordering temperature in the range of 300–325 K while those with 9%–12% oxygen vacancies have a magnetic ordering temperature of 800 K and higher. Mössbauer spectra at 300 K exhibit paramagnetic or weak magnetic characteristics for the N_2 , O_2 , and air-quenched samples, whereas an average hyperfine field of 52 T is found for the CO/CO_2 reduced samples. The heat treatment in the reducing atmosphere creates oxygen vacancies and increases unit cell volume. However, the Fe–O bond length remains nearly constant, resulting in distortion/rotation of the oxygen octahedra which increases the Fe–O–Fe bond angle as much as 12 degrees. This dramatically affects the Fe–O–Fe superexchange coupling and plays a key role in the increase of the Néel temperatures. © 2002 American Institute of Physics. [DOI: 10.1063/1.1446128]

I. INTRODUCTION

There has been a great deal of contemporary interest in perovskite compounds of the type $\text{ABO}_{3-\delta}$, where A is La or Sr, B is a 3d transition metal such as Fe, Mn, Co, and Ni. In particular, the magnetic and transport properties of Fe and Mn compounds have been extensively studied. Mixed valence of the transition metal ions can be induced in these compounds by introducing divalent ions such as Ba, Ca, and Sr at the trivalent La site or by creating oxygen vacancies. The magnetic properties of these compounds are thought to arise from a superexchange mechanism involving 3d electrons of the transition metal ions and oxygen *p* orbitals. Thus oxygen plays a very important role in magnetic ordering of these compounds. Some perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{BO}_{3-\delta}$ (B = Mn, Fe, Co) compounds are strongly covalent antiferromagnetic metals while others are metallic with an enhanced Pauli paramagnetism and many are magnetic insulators. Upon substituting Sr^{2+} for La^{3+} , the orthorhombic structure becomes pseudocubic for $x \leq 0.4$ in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$.^{1,2} As for $x > 0.4$, the oxygen loss contributes to a decrease of the Fe^{4+} content, resulting in a maximum of about 40% for $x = 0.5$.² The Néel temperature decreases systematically with increasing Sr content.^{2,3} $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ are ferromagnetic when $x > 0.05$ and metallic when $x \leq 0.2$ because of hole doping.^{4–7} The modification of the chemical composition on the A sites and the concentration of the oxygen vacancies are effective for controlling the crystal structure and fundamental physical properties of the perovskite-type compounds.⁸ A previous study^{1,9} suggested that the structure and magnetic properties are strongly dependent on the heat treatment. However, no systematic studies, as a function of vacancy content, have been reported.

In this study, we report on the structure, magnetic properties, and the Mössbauer spectra of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{3-\delta}$ compounds prepared by varying heat treatment.

II. EXPERIMENTAL METHODS

The liquid-mixing method^{10,11} was used to prepare $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ fine powders. The powders were pressed at 207 MPa to form a dense bar. The bar was sintered at 1000–1200 °C for 24 h under O_2 , air, N_2 , and CO/CO_2 environments, followed by quenching to room temperature. The magnetization curves were measured using a SQUID magnetometer in a field of up to 6 T from 1.5 to 800 K. The crystal phase was identified by x-ray diffraction analysis using $\text{Cu K}\alpha$ radiation. The neutron diffraction experiments were performed at the University of Missouri-Columbia Research Reactor using neutrons of wavelength $\lambda = 1.4875 \text{ \AA}$. The neutron data were refined using the FULLPROF program.¹² The Mössbauer spectra were measured using a conventional constant accelerated driver at room temperature with a ^{57}Co (50 mCi) in a Rh matrix. The spectrometer was calibrated using $\alpha\text{-Fe}$ at room temperature and the isomer shift (IS) is relative to $\alpha\text{-Fe}$ at 300 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical x-ray diffraction patterns of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{3-\delta}$ powders at different heat treatment conditions. Similar patterns are observed for all samples, showing them to be single phase. The symmetry of the samples remains rhombohedral (space group $R\bar{3}c$) throughout the series, except that some peaks broaden in the highly reduced sample which might be due to distortion or the onset of decomposition. It is difficult to use XRD patterns to determine structural distortion. Accordingly, neutron diffraction was employed for structure analysis and to determine magnetic structure.¹³ An antiferromagnetic structure has been

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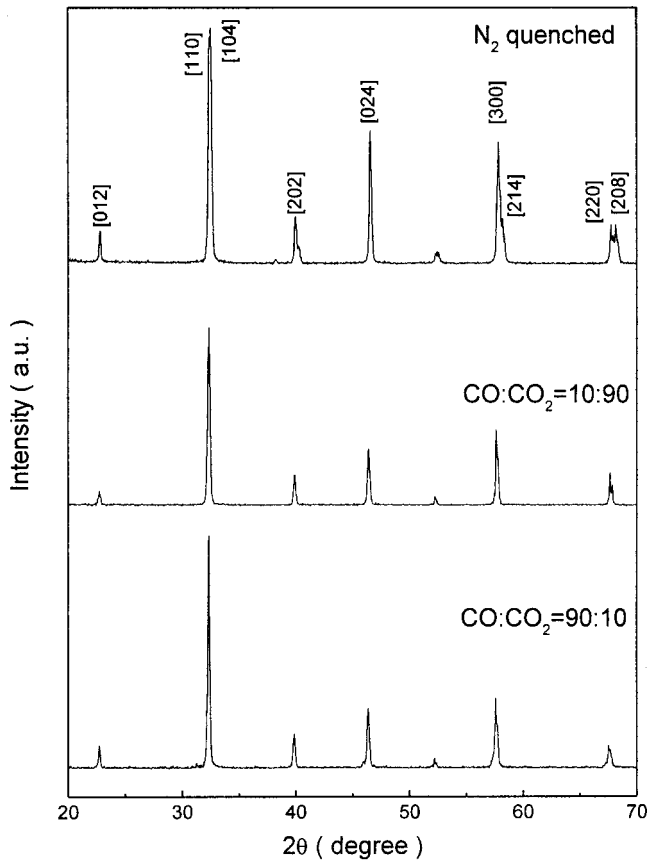


FIG. 1. Typical x-ray diffraction patterns of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ quenched in different atmospheres.

confirmed for all five samples. The Fe atoms show a magnetic moment of about $1.2\text{--}1.4 \mu_B$ for N_2 -, air-, and O_2 -quenched samples at 290 K. The CO/CO_2 quench results in a large unit cell and reduced rhombohedral distortion. A magnetic moment of $3.8 \mu_B$ for Fe atoms is found for the CO/CO_2 quenched samples. Oxygen vacancies were determined from iodometric techniques. The air-, O_2 -, and N_2 -quenched samples show 2%–6% vacancies on the oxygen sites. The oxygen vacancy concentration is around 9%–12% for the samples quenched in the CO/CO_2 mixtures. In Table I, we list the average bond length between atoms and the Fe–O–Fe bond angle. It is found that the Fe–O and Fe–Fe bond lengths remain nearly constant (change less than 0.6%), while the bond angle of Fe–O–Fe linkage changes from 162° to 174° . Since the Fe–Fe and the Fe–O distances do not change, the increase in the Fe–O–Fe bond angle in-

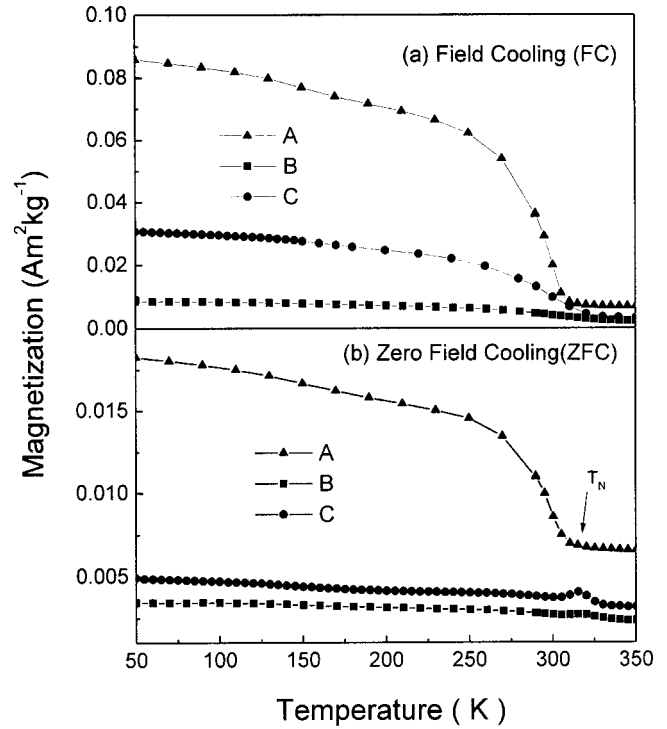


FIG. 2. Temperature dependence of the magnetization curves under zero field cooling (ZFC) (a) and field cooling (FC) (b) for $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ quenched in N_2 (A), air (B) and O_2 (C). A magnetic field of 50 Oe was used for the field cooling (FC) and zero field cooling (ZFC).

creases the overlap between the Fe–O atomic states and leads to a strong superexchange interaction between Fe–Fe. The increase in the oxygen vacancy concentration changes the valence state of the Fe and results in large magnetic moments of the Fe atoms in the CO/CO_2 treated samples.

Figure 2 shows the temperature dependence of the magnetization curves, under zero-field cooling (ZFC) and field cooling (FC) using an applied field of 50 Oe, for $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ powders with varying vacancy concentration. The difference between the FC and ZFC curves indicates the appearance of irreversibility for all compounds, suggesting the possibility of spin glass-like behavior. In particular for the N_2 -, O_2 -, and air-quenched samples, a large difference exists in the FC and ZFC curves below 300 K suggesting some spin glass-like behavior. The Néel temperatures T_N , 305, 325, and 325 K for the N_2 -, O_2 -, and air-quenched samples, respectively, have been determined from magnetization curves. The difference in the magnetization between

TABLE I. Néel temperatures, the average bond length between different atoms (bond length <math> < 4.0 \text{ \AA}</math>) and the Fe–O–Fe bond angles in $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ quenched in different environments.

	T_N (K)	Fe–O (\AA)	Fe–O–Fe bond angle ($^\circ$)	La–O (\AA)	Fe–Fe (\AA)	O–O (\AA)	La–La (\AA)	La–Fe (\AA)
N_2	315	1.972(1)	162.86	2.755(1)	2.789(3)	3.900(1)	3.900(1)	3.371(1)
Air	325	1.964(2)	166.17	2.762(2)	2.777(4)	3.899(1)	3.899(2)	3.371(1)
O_2	325	1.960(3)	166.85	2.759(3)	2.772(3)	3.895(4)	3.895(2)	3.367(5)
$\text{CO}=\text{CO}_2=10=90$	790	1.961(4)	173.28	2.771(5)	2.774(4)	3.916(3)	3.916(3)	3.391(1)
$\text{CO}=\text{CO}_2=50=50$	800	1.962(4)	173.20	2.772(4)	2.775(5)	3.918(1)	3.918(1)	3.392(3)
$\text{CO}=\text{CO}_2=90=10$	>810	1.963(3)	174.35	2.774(1)	2.777(4)	3.922(1)	3.922(1)	3.396(2)

TABLE II. Hyperfine field (B_{hf}), isomer shift (IS), and quadrupolar splitting (QS) of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ quenched in different environments.

	Fe^{3+}			Fe^{4+}		
	B_{hf}	IS	QS	B_{hf}	IS	QS
	(T)	(mm/s)	(mm/s)	(T)	(mm/s)	(mm/s)
N_2		0.261(2)			0.180(4)	
Air	15.2(4)	0.263(2)	0.058(3)		0.170(3)	
O_2	19.1(3)	0.331(3)	0.047(3)		0.202(4)	
		I			II	
$\text{CO}=\text{CO}_2=10=90$	53.5(2)	0.324(4)	0.050(1)	50.1	0.236(4)	0.020(3)
$\text{CO}=\text{CO}_2=50=50$	53.3(2)	0.325(3)	0.056(3)	49.8	0.236(4)	0.021(5)
$\text{CO}=\text{CO}_2=10=90$	53.5(3)	0.324(3)	0.035(4)	50.4	0.272(3)	-0.063(2)

the ZFC and FC curves decreases as the CO/CO_2 ratio increases from 10% to 90% in the CO/CO_2 mixtures. Néel temperatures of the CO/CO_2 quenched samples have been found to be higher than 800 K for all samples, which is higher than that for LaFeO_3 ($T_N=750$ K), and much higher than the normal $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{3-\delta}$ compounds ($T_N\approx 300$ K).³ The increase of the Néel temperature is due to the increase of the superexchange interaction between the antiferromagnetic Fe ions. The increase in the oxygen vacancy concentration also changes the number of the oxygen neighbors with Fe. However, this effect makes only a small contribution to the superexchange interaction, thus having little effect on the Néel temperatures. The small changes in the Fe–O bond length have almost no effect on the Néel temperatures. It should be noticed that the temperature effect on the structure and composition of the samples is still not clear and a high temperature neutron diffraction experiment is in process.

The substitution of La^{3+} by Sr^{2+} will create some Fe^{4+} in the stoichiometric composition. The CO/CO_2 treated samples with high oxygen vacancy concentration have all Fe^{4+} reduced to Fe^{3+} (and even some Fe^{2+}) in order to keep charge balance in the compounds. ^{57}Fe Mössbauer spectra were taken of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{3-\delta}$. The hyperfine parameters are listed in Table II. The Mössbauer spectra of N_2 -, O_2 -, and air-quenched samples show a paramagnetic or weak magnetic behavior because the Néel point is quite close to room temperature. A relaxation of the hyperfine fields appears in the O_2 - and air-quenched samples, therefore a broadened sextet and singlet have been used in these samples. As for the N_2 -quenched sample, the Néel point is almost the same as the measured temperature (300 K). Thus two singlets give a reasonable fit. The hyperfine fields of the O_2 and air quenched samples are in the range of 14–19 T. The values of the isomer shift indicate Fe^{4+} and Fe^{3+} valence states in N_2 -, O_2 -, and air-quenched samples. The Mössbauer spectra of the CO/CO_2 quenched samples show a typical sextet. Two sextets have been used to account for the fitting of the entire spectra. The CO/CO_2 treated samples show an average hy-

perfine field of 52 T, which is of the same order as that of the Fe oxide. The isomer shifts of CO/CO_2 treated samples correspond to a valence state between Fe^{3+} and Fe^{2+} . According to the superexchange theory of Goodenough,¹⁴ the superexchange interaction between $3d^5(\text{Fe}^{3+})$ and $3d^5(\text{Fe}^{3+})$ cations are antiferromagnetic, and are stronger than that of Fe^{4+} and Fe^{3+} ions, as well as that of Fe^{4+} and Fe^{4+} ions. Thus, the reduction of the Fe^{4+} to Fe^{3+} or even Fe^{2+} ions also increases the strength of the superexchange interaction between Fe ions, which results in a large hyperfine field and high Néel point.

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