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Charge disproportionation and ordering in $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$

J B Yang¹, X D Zhou², Z Chu³, W M Hikal⁴, Q Cai³, J C Ho⁴,
D C Kundaliya⁵, W B Yelon¹, W J James¹, H U Anderson²,
H H Hamdeh⁴ and S K Malik⁵

¹ Graduate Center for Materials Research and Departments of Chemistry and Physics,
University of Missouri-Rolla, Rolla, MO 65409, USA

² Center for Electronic Materials Research, University of Missouri-Rolla, Rolla, MO 65409, USA

³ Department of Physics, University of Missouri-Columbia, Columbia, MO 65211, USA

⁴ Physics Department, Wichita State University, Wichita, KS 67260, USA

⁵ Tata Institute of Fundamental Research, Colaba, Mumbai 400-005, India

E-mail: jinbo@umr.edu (J B Yang)

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Abstract

The perovskite $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ was investigated by neutron diffraction, magnetic and Mössbauer spectroscopy measurements. $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ undergoes magnetic ordering at $T = 190\text{--}200$ K accompanied by charge disproportionation. Magnetic peaks due to charge ordering are observed below 200 K. The charge ordering is gradually developed below 200 K along with a charge disproportionation, $2\text{Fe}^{4+} \Rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$. $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ shows an antiferromagnetic structure at low temperature. Magnetic moments of about 3 and $1.3 \mu_{\text{B}}$ were obtained from the neutron diffraction data refinement for Fe^{3+} and Fe^{5+} at 15 K, respectively, which suggest that both Fe ions are in a low spin state. These values are significantly lower than those reported by Battle *et al* for $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{2.98}$. Mössbauer spectra indicate that full charge ordering might be reached below 20 K with no Fe^{4+} .

1. Introduction

Perovskite compounds of the type $\text{RE}_{1-x}\text{A}_x\text{BO}_{3-\delta}$, where RE is rare earth, A is Ba, Ca or Sr and B is Fe, Mn, Co or Ni, are of considerable importance, due to their interesting electronic, magnetic and catalytic properties [1–8]. Depending on their compositions, they show a variety of magnetic and electronic phenomena, including ferromagnetic, antiferromagnetic, charge and orbital ordering. Among them, charge ordering (CO) transitions have been found to occur in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 2/3$), using Mössbauer spectroscopy measurements [9]. Neutron powder diffraction on the same compound by Battle *et al* [10] indicated a CO sequence

of $\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}$. . . along the body diagonal [111] with respect to the ideal perovskite structure. The magnetic moments were $3.6 \mu_{\text{B}}$ for Fe^{3+} and $2.7 \mu_{\text{B}}$ for Fe^{5+} at 50 K. A structural modulation accompanying the CO transition has been confirmed by electron microscopy [11]. CO is also observed in some other $\text{R}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ compounds with $\text{R} = \text{Pr}$ and Nd [12–15]. The CO was normally interpreted as the separation of a charge state into two different states as $2d^n = d^{n-1} + d^{n+1}$, where n is an integer. Takano *et al* [16] proposed a nonintegral oxidation state of iron in these materials as $\text{Fe}^{4+} \rightleftharpoons \text{Fe}^{4-\lambda} + \text{Fe}^{4+\lambda}$. Recently, Matsuno *et al* [17] suggested that the charge disproportionation can be correctly described as $2d^5\bar{L} \rightarrow d^5\bar{L}^2 + d^5$ rather than $2d^4 \rightarrow d^3 + d^5$, where \bar{L} denotes a hole in the oxygen 2p band. It has been shown that the charge disproportionation might be purely electronically driven and that the ordering of the oxygen holes plays an important role in $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ [18]. Although a neutron diffraction study has been reported for the $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{2.98}$ compound at 50 K and room temperature [10], no systematic study of the dependence of the crystal and magnetic properties of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ with temperature has been reported. Neutron diffraction can directly detect magnetic ordering and the structural modulation related to CO; therefore it is of considerable interest to investigate the relationship among structural, magnetic and CO in this system.

In this study, we report on the structural and magnetic properties of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ using data obtained from neutron diffraction, Mössbauer spectroscopy and magnetic measurements. The effect of temperature on the structural and magnetic properties and hyperfine interactions in this compound has been studied.

2. Experimental details

The liquid-mix process was used to prepare $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$. An aqueous nitrate solution containing all the ingredient cations for each $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ composition was prepared from reagent-grade metal nitrates or carbonates. The cation content of each individual metal salt was determined by conversion to the respective oxide. A viscous polymeric precursor formed, when a mixture of citric acid and ethylene glycol (in 1:1 molar ratio) was mixed with a nitrate solution at about 75 °C upon evaporation of water and heating at 250 °C. The resulting porous resin intermediate was then pulverized and calcined at 800 °C for 6–8 h to yield oxide powders whose crystallite size was typically 50–500 nm. The powders were pressed at 207 MPa to form a dense bar. The bar was sintered at 1000–1200 °C for 24 h in the air and slowly cooled to room temperature. Powder x-ray diffraction using $\text{Cu K}\alpha$ radiation indicated that the symmetry of the samples remains rhombohedral (space group $R\bar{3}c$) at room temperature. The magnetization curves of the samples were measured using a SQUID magnetometer in a field of up to 6 T from 1.5 to 300 K. The powder neutron diffraction experiments were performed at the University of Missouri-Columbia Research Reactor (MURR) using neutrons of wavelength $\lambda = 1.4875 \text{ \AA}$. The data for each sample were collected over 24 h between 2θ angles of 5° and 105° on approximately 1 g of fine powders placed in a thin wall vanadium container. Refinement of the neutron diffraction data was carried out using the FULLPROF program [19], which permits multiple phase refinement as well as magnetic structure refinements. The Mössbauer spectra were measured using a conventional constant accelerated driver with a ^{57}Co (50 mCi) source in a Rh matrix. The spectrometer was calibrated using α -Fe and the isomer shift (IS) relative to α -Fe at room temperature.

3. Results and discussion

X-ray diffraction patterns of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ powders were obtained at a scanning speed of $0.2^\circ \text{ min}^{-1}$. The sample is single phase and the symmetry of the samples remains rhombohedral

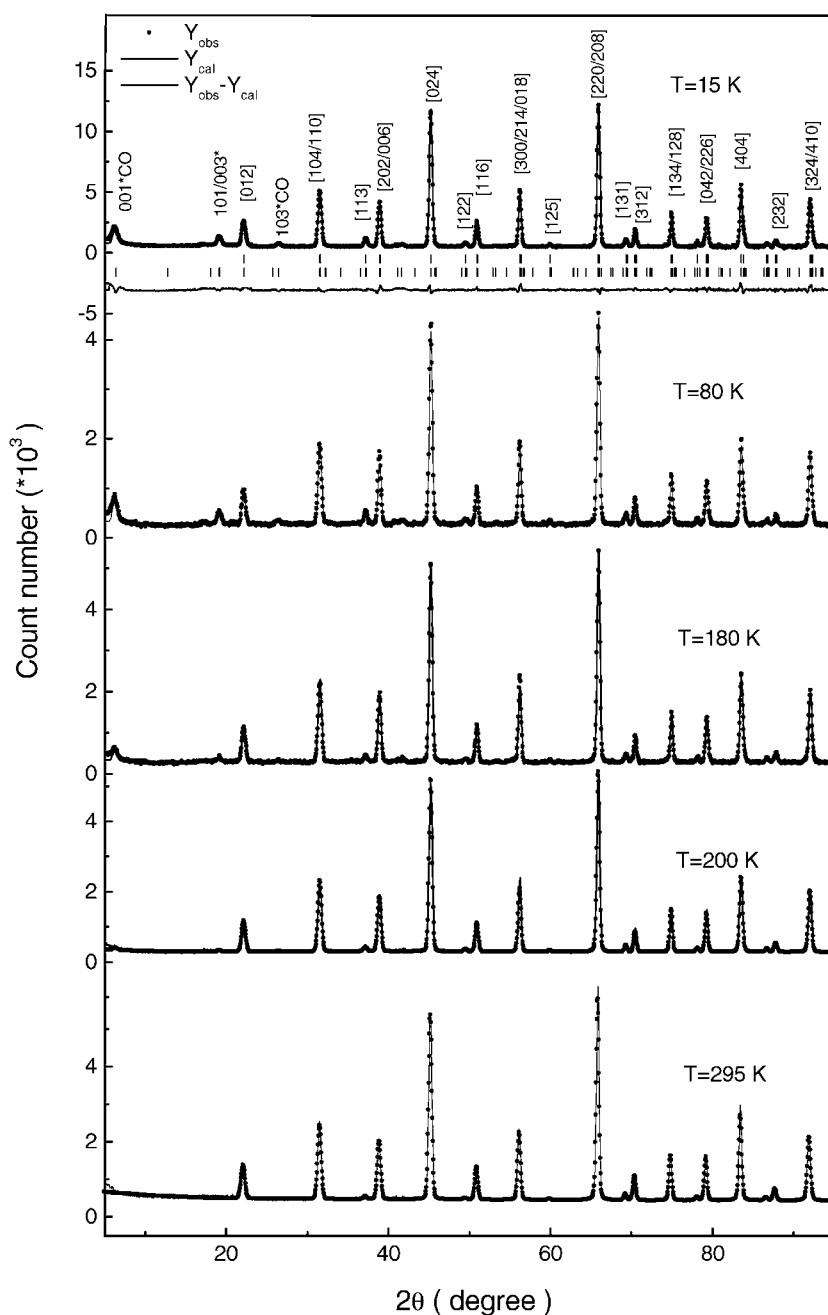


Figure 1. Neutron diffraction patterns of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures. (In the first pattern, the bottom curves ($Y_{\text{obs}} - Y_{\text{cal}}$) are the differences between experimental and refinement data. The vertical bars indicate the magnetic (bottom) and Bragg (top) peak positions.) *CO indicates the charge ordering peak.

(space group $R\bar{3}c$). In order to study the temperature dependence on the crystal and magnetic structure, powder neutron diffraction was employed to distinguish the phase transition, and to determine the magnetic structure. Figure 1 shows typical neutron diffraction patterns of the

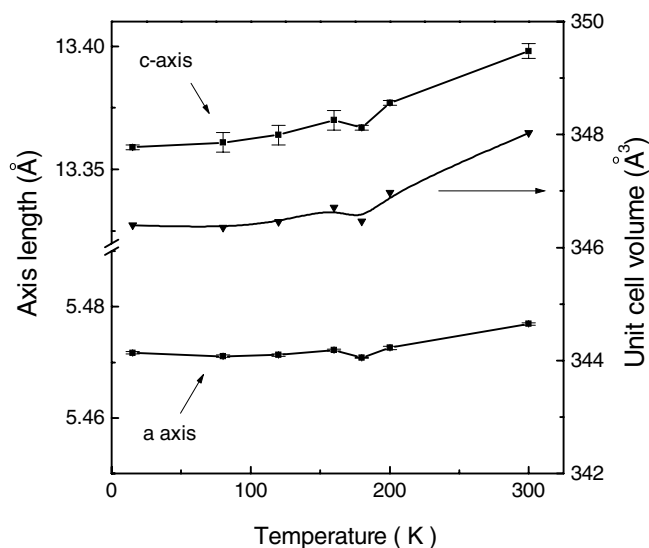


Figure 2. The lattice parameters of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures.

sample measured at different temperatures. At room temperature, all peaks of the pattern can be indexed by a unit cell $a = 5.477 \text{ \AA}$ and $c = 13.397 \text{ \AA}$, space group $R\bar{3}c$ in the hexagonal setting as reported by Battle *et al* [10]. Below 200 K, there are three extra peaks appearing at about 6.38° , 19.17° and 26.50° , which arise from the magnetic ordering. Accordingly, the crystal structure was refined using space group $R\bar{3}c$ from 10 K to room temperature. The lattice parameters of the $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ powders obtained from neutron diffraction data refinement at different temperatures are shown in figure 2. As can be seen from the curve, the lattice parameters a and c remain almost constant below 120 K and a fluctuation around 180 K is observed, which corresponds to charge disproportionation and magnetic ordering. Above 200 K, the lattice parameters increase almost linearly. It is suggested that there is an abrupt change of lattice parameters due to the charge disproportionation and ordering. The Fe–O–Fe bond angle decreases from 173.29° to 172.89° as temperature decreases from RT to 15 K. The Fe–O bond length changes from 1.939 \AA at RT to 1.936 \AA at 15 K. It is noted that the symmetry of the crystal structure might be lower than $R\bar{3}c$ due to distortion of the structure. We attempted to refine the crystal structure in lower symmetry space groups, such as $P\bar{3}c1$. However, there is no improvement in the refinement. Space group $R\bar{3}c$ leads to a reasonable refinement due to the overall small distortion of the crystal structure. This might indicate that we are unable to distinguish the localized structural distortion within the resolution of our experimental data. Another possibility would be related to that, if the charge states are believed to be nonintegral, then the electrons would be at least in part itinerant [10].

Battle *et al* [10] indexed the magnetic peaks using the same size nuclear unit cell, but with space group $P\bar{3}m1$. However, as the magnetic peaks appearing in the neutron diffraction pattern showed the easy axis of magnetization to be in the basal plane, (in the xy plane of the structure rather than along the z axis, thus removing the $\bar{3}$ symmetry) we refined the magnetic structure using space group $P1$. The unit cell of the magnetic structure is the same as that of the crystalline structure, which has six iron atoms in the positions $(0, 0, 0)$, $(1/3, 2/3, 1/6)$, $(2/3, 1/3, 1/3)$, $(0, 0, 1/2)$, $(1/3, 2/3, 2/3)$ and $(2/3, 1/3, 5/6)$ with a charge sequence of $\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}$ In the refinement, the magnetic

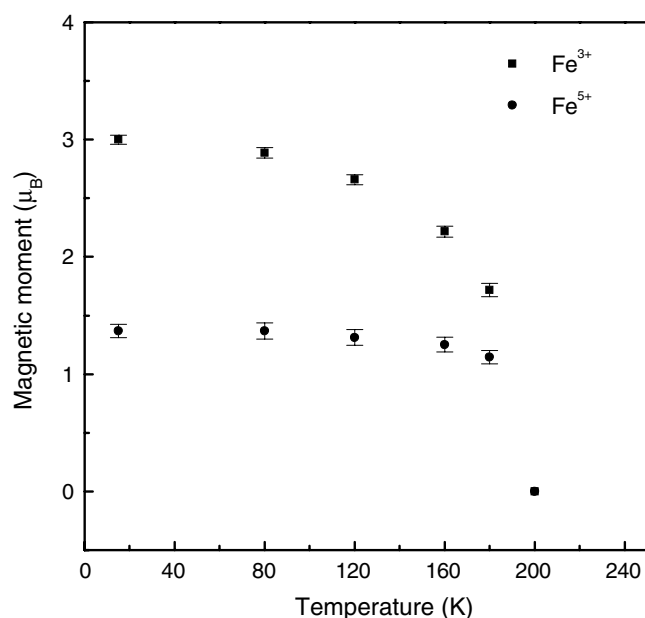


Figure 3. The refined magnetic moments of Fe^{3+} and Fe^{5+} at different temperatures for $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$.

moments of the iron atoms were constrained as two groups (Fe^{5+} and Fe^{3+}) to form an antiferromagnetic structure and the absolute values of the magnetic moments were kept the same for each group. The magnetic moments entirely lie in the basal plane. Several magnetic spin configurations were used to refine the magnetic structure. The magnetic spin configuration of $5 + (\uparrow)3 + (\uparrow)3 + (\downarrow)5 + (\downarrow)3 + (\downarrow)3 + (\uparrow)$ gives the lowest χ^2 and the best refinement. The coupling between Fe^{3+} and Fe^{5+} is ferromagnetic; on the other hand, the coupling between Fe^{3+} and Fe^{3+} , and between Fe^{5+} and Fe^{5+} is antiferromagnetic. The data refinement shows that the intensity of the first peak at 6.38° depends on the Fe^{3+} and Fe^{5+} CO and magnetic ordering, and the peaks at 19.17° and 26.50° arise from antiferromagnetic ordering at temperatures below 200 K. The intensities of these three peaks decrease as the temperature increases. They disappear at temperatures between 186 and 194 K. This is consistent with the magnetic ordering transition temperature [13, 20], which is also confirmed by our magnetic measurements. The Néel temperature of the compound is about 190 K, which is a response to the charge disproportionation and ordering. The refined magnetic moments of Fe^{3+} and Fe^{5+} at different temperatures are shown in figure 3. The magnetic moment of Fe^{3+} is about $3 \mu_B$ at 15 K and decreases gradually to $1.7 \mu_B$ at 180 K, and the magnetic moment of Fe^{5+} changes slightly from $1.3 \mu_B$ at 15 K to $1.1 \mu_B$ at 180 K. Above 200 K, both magnetic moments drop to zero. Our magnetic moments are smaller than those reported by Battle *et al* [10]. If the moments are fixed in their values, the calculated first peak, which is not shown in their neutron diffraction pattern, mismatches significantly with the experimental data both in the $P\bar{3}m1$ and $P1$ space groups. Thus it is possible that their exclusion of the first magnetic and CO peak may have led to higher magnetic moments in their refinement. Based upon our refinement of the magnetic structure one might conclude that, since the magnetic moment of Fe^{3+} is about $3 \mu_B$ at 15 K, the Fe^{3+} must have a low spin (LS) state of $t_{2g\uparrow}^3 t_{2g\downarrow}^1 e_{g\uparrow}^1$ or $t_{2g\uparrow}^4 t_{2g\downarrow}^1 e_{g\uparrow}^0$ rather than the high spin (HS) state $t_{2g\uparrow}^3 e_{g\uparrow}^2$, and the Fe^{5+} a $t_{2g\uparrow}^2 t_{2g\downarrow}^1 e_{g\uparrow}^0$ LS state.

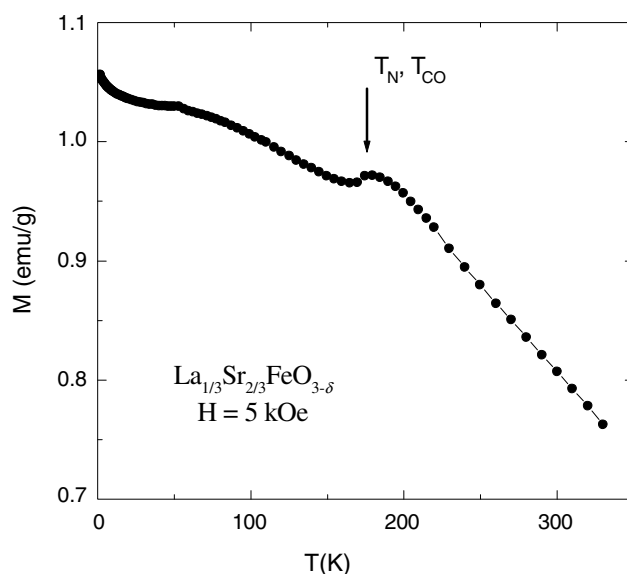


Figure 4. The temperature dependence of the magnetization for $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$.

Figure 4 shows the temperature dependence of the magnetization measured in a magnetic field of 5 kOe. A kink at about 180 K is found in the curve, corresponding to the Néel temperature of this compound [13, 20]. A ferromagnetic component is observed in the curves. This might arise from a tilting of the magnetic moment of Fe in the magnetic structure. This has been observed in some antiferromagnetic systems, where a parasitic ferromagnetic component appears in an antiferromagnetic structure [21–23]. The appearance of a weak ferromagnetic moment is not unexpected in the space group when the magnetic moments are not parallel to the *c* axis [24, 25]. No magnetic impurity was detected in the neutron diffraction and Mössbauer spectra measurements.

Figure 5 is the Mössbauer spectra of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ measured at different temperatures. The hyperfine parameters of the spectra are listed in table 2. The hyperfine field and IS are shown in figure 6. Using a least-squares computer program, two sets of Lorentzian sextet lines due to the Fe^{3+} and Fe^{5+} were fitted to the Mössbauer spectra at 20 K. Another sextet due to the Fe^{4+} was used to fit the spectra from 80 to 200 K. There is a single line of the Fe^{4+} above 180 K. The Mössbauer spectra consist of two single lines at, and above, 200 K. The ISs of the subspectra indicate that one is Fe^{3+} and the other Fe^{4+} at room temperature. The ratio of $\text{Fe}^{3+}/\text{Fe}^{4+}$ is about 35:65, corresponding to the stoichiometry of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{2.99}$ at room temperature. The amount of Fe^{4+} decreases from 65 to 5% as the temperature decreases from room temperature to 80 K. The charge disproportionation appears below 200 K, wherein the Fe^{4+} , Fe^{5+} , and Fe^{3+} valence states coexist. At 20 K, the ratio of Fe^{3+} to Fe^{5+} is about 2:1 due to the complete CO. The hyperfine field of Fe changes very slowly below the Néel temperature and quickly drops to zero at 200 K, a trend similar to that of the magnetic moments. This provides further evidence of charge disproportionation. There are some Fe^{4+} states appearing in the compound below the Néel point which indicates CO to be incomplete. This may be the reason that the CO peak in the neutron diffraction pattern is very broad and exhibits asymmetric features.

Since Fe^{4+} has very small magnetic moments at low temperatures, its presence in the compound decreases the average magnetic moment of Fe and disturbs the CO. Further it is

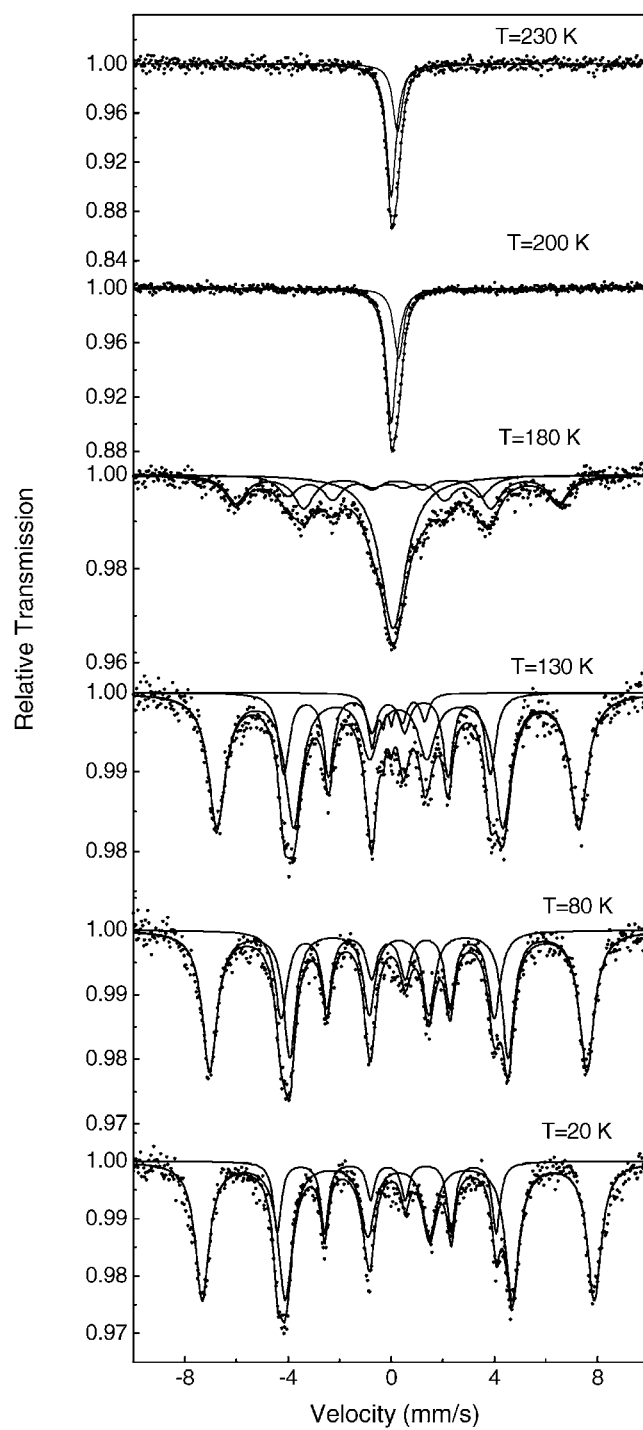


Figure 5. The Mössbauer spectra of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures.

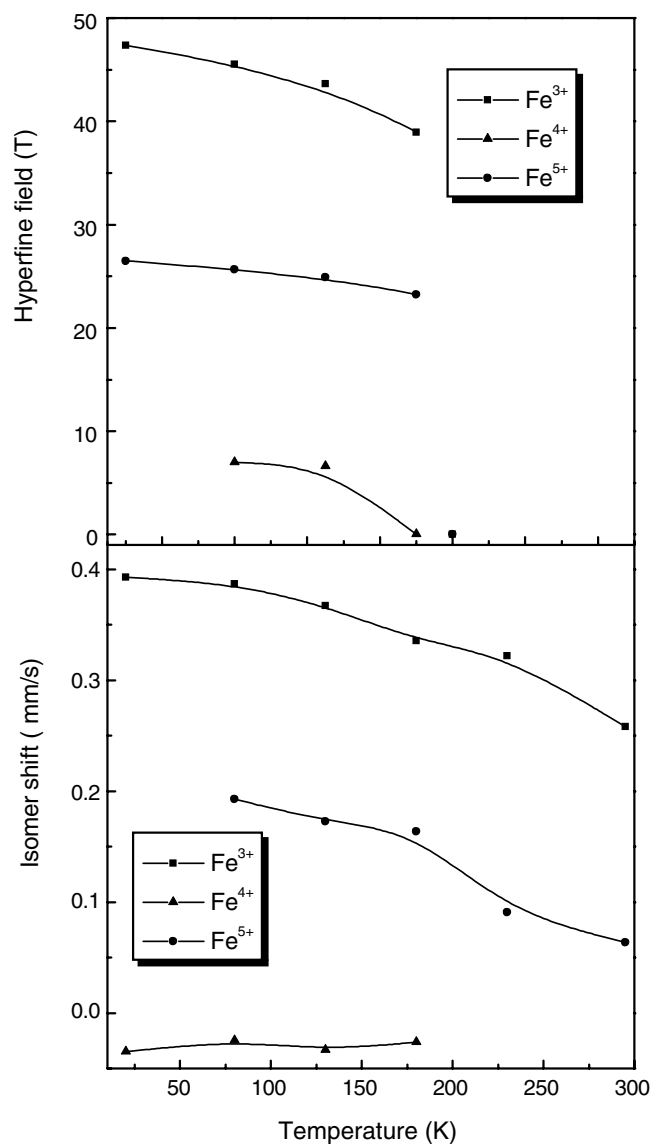


Figure 6. The hyperfine fields and isomer shifts of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures.

found that CO is sensitive to the homogeneity, chemical composition and the presence of defects in those compounds [26, 27]. The preparative history of Battle's and our samples are quite different: they used a conventional solid reaction method as compared to our liquid-mixing method, so our sample may have differed significantly in the extent of CO, electron–electron interaction, magnetic interaction and electron–lattice interaction in realizing CO. If so, a possible explanation for disparity in the moments is that it might result from differing degrees of ordering within the Fe³⁺ and Fe⁵⁺ layers. Our Mössbauer data indicate that, at the lowest temperature, the sample is fully charge disproportionated, yielding the ideal 2:1 ratio of Fe³⁺ to Fe⁵⁺. If, however, some Fe³⁺ is incorporated into the Fe⁵⁺ layers (and vice versa) then

Table 1. Refinement parameters of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures. x is the fractional position coordinates. a and c are the lattice parameters. V is the unit cell volume. B is the temperature factor. χ^2 is $[R_{\text{wp}}/R_{\text{exp}}]^2$, where R_{wp} is the residual error of the weighted profile.

T	15 K	80 K	160 K	180 K	200 K	RT
a (Å)	5.4717(2)	5.4711(2)	5.4722(6)	5.4708(2)	5.4726(3)	5.4769(2)
c (Å)	13.359(1)	13.361(1)	13.370(3)	13.367(1)	13.377(4)	13.398(4)
V (Å ³)	346.39	346.35	346.71	346.46	346.97	348.03
O, 18e, x	0.4780(2)	0.4775(2)	0.4770(4)	0.4783(2)	0.4793(4)	0.4816(7)
B (Å), Fe, 6b	0.43(5)	0.09(5)	0.36(4)	0.21(2)	0.23(4)	0.29(6)
B (Å), O, 18e	1.26(5)	1.07(7)	1.20(1)	1.02(2)	1.08(2)	1.10(8)
B (Å), La(Sr), 6a	0.48(4)	0.21(2)	0.51(5)	0.38(1)	0.34(3)	0.58(3)
χ^2 (%)	5.7	2.1	2.3	2.0	2.0	4.5

Table 2. The hyperfine field (B_{hf}), isomer shift (IS), quadrupole splitting (QS) and relative intensity (Int.) of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$ at different temperatures.

T (K)	Fe^{3+}				Fe^{4+}				Fe^{5+}			
	B_{hf} (T)	IS (mm s ⁻¹)	QS (mm s ⁻¹)	Int. (%)	B_{hf} (T)	IS (mm s ⁻¹)	QS (mm s ⁻¹)	Int. (%)	B_{hf} (T)	IS (mm s ⁻¹)	QS (mm s ⁻¹)	Int. (%)
300		0.258(1)		35		0.064(4)		65				
230		0.322(2)		42		0.091(3)		58				
180	38.9(2)	0.335(3)	0.002(3)	29		0.164(4)		47	23.2(2)	-0.026(4)	-0.066(4)	24
130	43.6(3)	0.367(4)	-0.022(1)	63		0.173(4)		11	24.9(1)	-0.033(2)	-0.043(1)	26
80	45.5(4)	0.387(1)	-0.026(3)	65	7.0(1)	0.193(2)	0.345(2)	5	25.7(3)	-0.025(2)	-0.032(1)	30
20	47.4(5)	0.393(2)	-0.036(1)	67					26.6(1)	-0.035(2)	-0.016(1)	33

the average moment in each type of layer will be decreased, since the incorporated species is expected to align antiferromagnetically, by virtue of the interactions with the six nearest-neighbour Fe atoms in the layers above and below. As the Fe^{5+} atoms will now be spread over two Fe^{3+} layers, the Fe^{3+} in the Fe^{5+} layers will be twice as concentrated as the Fe^{5+} in the Fe^{3+} layers, leading to a much greater affect on the average moment for the Fe^{5+} layer, as observed. This description assumes essentially localized moments that do not depend strongly on the near-neighbour environment. Such a picture is supported by Mössbauer data and by recent results obtained on $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ with $0 \leq x \leq 0.2$ [28]. The average Fe valence in these samples varies from 3.4 to 3.0 μ_{B} as δ increases. Mössbauer data on these samples at low temperature also show full charge disproportionation, but CO does not occur. The saturation magnetic moment varies linearly with δ , suggesting fixed, localized moments on the 3+ and 5+ sites equal to about 3.8 and 3.0 μ_{B} , respectively. Such values also fit Battle's and our results if one assumes roughly 5 and 25% disorder for the two cases, respectively.

4. Summary

Based on neutron diffraction, Mössbauer spectroscopy and magnetic measurements, it is found that magnetic ordering and charge disproportionation appear at a temperature below 200 K in $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$. However, CO develops slowly along with the charge disproportionation. A fully CO appears to occur below 20 K in polycrystalline $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_{3-\delta}$. We clearly observed a neutron diffraction peak around 6.38° due to the magnetic and CO below 200 K. Refinement of neutron diffraction data at 15 K gives magnetic moments of 3.0 and 1.3 μ_{B} for

Fe³⁺ and Fe⁵⁺, respectively, values significantly lower than in the literature. The disparity in the moments may arise from the fact that our sample differs significantly from Battle *et al* in the extent of CO.

Acknowledgments

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References

- [1] Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **334** 1
- [2] Tokura Y 1999 Fundamental features of colossal magnetoresistive manganese oxides *Contribution to Colossal Magnetoresistance Oxides, Monographs in Condensed Matter Science* ed Y Tokura (London: Gordon and Breach) pp 1–53
- [3] Salamon M B and Jaime M 2001 *Rev. Mod. Phys.* **73** 583
- [4] Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1039
- [5] Ramirez A P 1997 *J. Phys.: Condens. Matter* **9** 8171
- [6] Rao C N R and Raveau B (ed) 1998 *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides* (Singapore: World Scientific)
- [7] Coey J M D, Viret M and von Molnar S 1999 *Adv. Phys.* **48** 167
- [8] Kaplan T and Mahanty S (ed) 1999 *Physics of Manganites* (New York: Kluwer–Academic)
- [9] Takano M and Takeda Y 1983 *Bull. Inst. Chem. Res. Kyoto Univ.* **61** 406
- [10] Battle P D, Gibb T C and Lightfoot P 1990 *J. Solid State Chem.* **84** 271
- [11] Li J Q, Matsui Y, Park S K and Tokura Y 1997 *Phys. Rev. Lett.* **79** 297
- [12] Uhm Y R, Lee S W, Park K T, Tomioka Y, Tokura Y and Kim C S 2000 *J. Appl. Phys.* **87** 4873
- [13] Kajimoto R, Oohara Y, Kubota M, Yoshizawa H, Park S K, Taguchi Y and Tokura Y 2001 *J. Phys. Chem. Solids* **62** 321
- [14] Park S K, Ishikawa T, Tokura Y, Li J Q and Matsui Y 1999 *Phys. Rev. B* **60** 10788
- [15] Nowik I, Felner I and Awana V P S 1999 *J. Magn. Magn. Mater.* **192** 67
- [16] Takano M, Kawachi J, Nakanishi N and Takeda Y 1981 *J. Solid State Chem.* **39** 75
- [17] Matsuno J, Mizokawa T, Fujimori A, Takeda Y, Kawasaki S and Takano M 2002 *Phys. Rev. B* **66** 193103
- [18] Matsuno J, Mizokawa T, Fujimori A, Mamiya K, Takeda Y, Kawasaki S and Takano M 1999 *Phys. Rev. B* **60** 4605
- [19] Rodriguez-Carvajal J 1998 Program: FULLPROF, Version 3.d
- [20] Ishikawa T, Park S K, Katsufuji T, Arima T and Tokura T 1998 *Phys. Rev. B* **58** R13326
- [21] Yang J B, Yelon W B, James W J, Chu Z, Kornecki M, Xie Y X, Zhou X D, Anderson H U, Joshi A G and Malik S K 2002 *Phys. Rev. B* **66** 184415
- [22] Argyriou D N, Mitchell J F, Potter C D, Hinks D G, Jorgensen J D and Bader S D 1996 *Phys. Rev. Lett.* **76** 3826
- [23] Kawan H, Kajimoto R, Kubota M and Yoshizawa H 1996 *Phys. Rev. B* **53** 2202
- [24] Dzialoshinski I 1968 *J. Phys. Chem. Solids* **4** 241
- [25] Moriya T 1960 *Phys. Rev. B* **120** 91
- [26] Battle P D, Gibb T C and Nixon S 1988 *J. Solid State Chem.* **77** 124
- [27] Garcia-Gonzalez E, Parras M, Gonzalez-Calbet J M and Vallet-Regi M 1996 *J. Solid State Chem.* **125** 125
- [28] Yang J B, Zhou X D, Xie Y X, James W J, Yelon W B, Anderson H U, Chu Z, Hikal W M, Ho J C and Hamdeh H H 2002 *Proc. 7th Int. Workshop on Rare Earth Magnets and Their Applications (Newark, DE, Aug. 2002)* (Princeton, NJ: Rinton Press Inc.) p 245