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Effect of oxygen vacancies on the magnetic structure of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ perovskite: A neutron diffraction study

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Magnetic interactions in perovskite compounds of the type $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ ($M = 3d$ transition such as Mn and Fe) are presumed to arise through a super exchange between $3d$ electrons of the magnetic ions via oxygen orbitals. The magnetic structure of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ has been studied with neutron diffraction. Oxygen vacancies were created by annealing samples under various gases including N_2 , air and mixtures of CO/CO_2 . All $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ compounds maintain the rhombohedral structure (space group $R\bar{3}c$). The air- or oxygen-annealed samples have almost no oxygen vacancies while those made in the reducing atmosphere show 7%–11% oxygen vacancies. The rhombohedral distortion decreases in the reduced samples. All the samples exhibit antiferromagnetic ordering at room temperature, although a small ferromagnetic moment may also be present. The samples with little or no oxygen vacancies show a room temperature magnetic moment of $\sim 1.4 \mu_B$ at the Fe site while those having $>7\%$ oxygen vacancies show a moment of $\sim 4.0 \mu_B$. Magnetization measurements reveal a much higher magnetic ordering temperature in samples with oxygen vacancies © 2002 American Institute of Physics. [DOI: 10.1063/1.1455613]

I. INTRODUCTION

Perovskite oxides, $(\text{RE}_{1-x}\text{A}_x)\text{BO}_{3-\delta}$ where RE is rare earth, A=Sr or Ba; B=Cr, Mn, Fe, Co or Ni, are of considerable importance, due to their interesting electronic, magnetic and catalytic properties.¹ Fe and Mn are two interesting choices for B due to their specific electronic state in ABO_3 . With these two elements, a large variety of compounds can be synthesized by varying stoichiometry and heat treatments, which result in a large range of properties that may be tailored to specific applications. A comprehensive review of manganites has been given by Tokura.² Dann had synthesized ferrite compounds ($\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$) using a variety of annealing and slow cooling techniques for ($0 < x < 1$) and ($0 < \delta < 1$). They found the compounds are orthorhombic for $0 \leq x \leq 0.2$, rhombohedral for $0.4 \leq x \leq 0.7$, and cubic for $0.8 \leq x \leq 1.0$.³ Later, Shimony and Knudsen synthesized $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ annealed at 760°C in 335 atm of oxygen for seven days. Their measurements showed that the Néel temperature decreases from 750 to about 100 K as x changes from 0 to 1, and is around 300 K when $x = 0.4$.⁴ Sathe *et al.* have reported that $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ is an antiferromagnetic insulator with a rhombohedral structure having a magnetic moment of $4.6 \mu_B$ on Fe at 5 K.⁵

In the present work, five samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, subjected to different heat treatments, were studied using neutron diffraction at the University of Missouri Research Reactor.

II. EXPERIMENT

The five samples were all derived from the same starting material and were subsequently heat treated at 1000°C in flowing gas (N_2 , air, and three CO/CO_2 mixtures: 10%, 50% and 90% CO). They were then rapidly cooled to room temperature. Samples were contained in 3 mm V cells and neutron data were collected at 1.4785 \AA over a range of 96° (2θ). Rietveld refinement⁶ was carried out using the FULLPROF code and a number of different models were tested based on the parent cubic perovskite structure. The neutron measurement showed all samples to be single phase, except that the 90% CO-reduced sample is beginning to show peak broadening and asymmetry, suggesting the possibility of incipient decomposition of the sample.

Four models were found to give “reasonable” fits to the data, and each was tested for each sample. The statistical tests, however, show that the preferred model is different for the reduced samples than for the air- and N_2 -quenched samples. There are some notable differences between the neutron diffraction diagrams for the reduced samples and the other two (Fig. 1). The diffraction peak splitting for the reduced samples is dramatically reduced compared to the N_2 - and air-treated samples. No satisfactory fits could be achieved with cubic groups, and the rhombohedral models are the highest symmetry that can satisfactorily fit any (and all) of the data sets. The first diffraction peak (at about 19°) is much stronger in the reduced samples than in the air- or

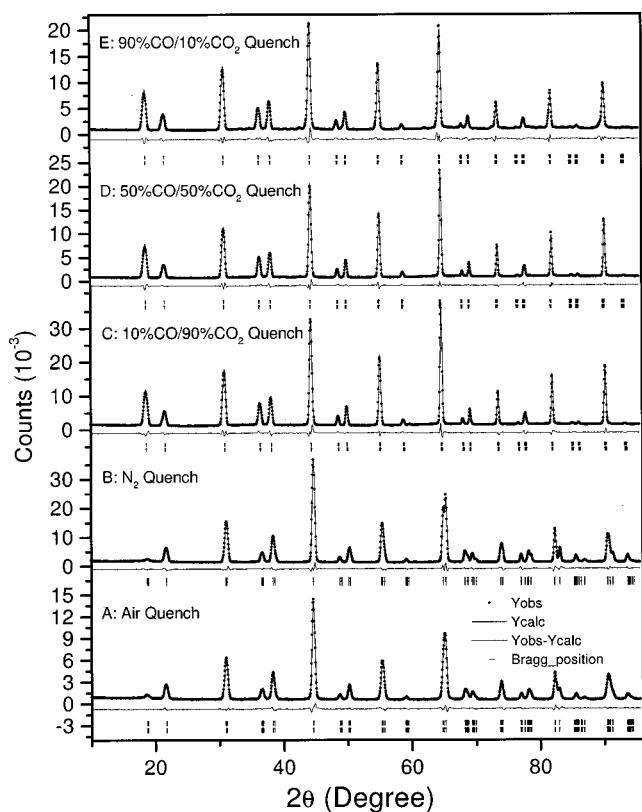


FIG. 1. Refined powder diffraction patterns for samples of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ under model 4.

N_2 -quenched samples. This change reflects a large increase in magnetic moment for the reduced samples.

III. MODELS

Model 1: The first model was found to apply to the air- and N_2 -quenched-samples. It has a pure rhombohedral ($R\bar{3}c$) space group with a unit cell volume around 360 \AA^3 for the tripled hexagonal setting of the cell, i.e., six times the volume of the basic cubic perovskite cell. In this model there is only one oxygen site at the position (0.54, 0, 0.25). Within all models the magnetic scattering was modeled as antiferromagnetic with moments along the hexagonal c axis, which reverse between the positions (0, 0, 0) and (0, 0, 1/2). The magnetic model has the symmetry $R\bar{3}$.

Model 2: Refinement of the reduced samples using model 1 left significant residuals in the difference between observed and calculated intensities. Fourier mapping showed that oxygen atoms appear to (partially) occupy additional positions. Model 2 introduces a second oxygen position [approximate coordinates (0.26, 0.39, 0.07)]. The occupation of both the normal position and this additional position were allowed to vary.

Model 3: The refinements in model 2 show significant occupation of both the oxygen sites, with a relatively small distance between them. Model 3 examines the possibility that the correct model has only a single oxygen site somewhere between the sites found by model 2. In principle Model 2 should show this directly, by reducing the occupa-

tion of the "ideal" octahedral site to zero while filling the second site to the net oxygen occupancy. However, it is not always possible to arrive at such a solution from the starting point for model 2 and thus model 3 is examined separately.

Model 4: To obtain more exact information about rotational distortion, we model FeO_6 as a rigid body that can rotate in three-dimensional space. In practice, the $P1$ space group is used to free coordinate constraints. The coordinates of La/Sr and Fe were constrained to get the same symmetry as in $R\bar{3}c$. The FeO_6 octahedron can freely rotate and expand. Taking into account opposite rotations of two rigid bodies sharing the same corner, two FeO_6 octahedrons were put in one unit cell. There are two formulas in the unit cell. The structural information is listed in Table I. This model gives the best χ^2 for all five samples.

IV. RESULTS

Table I shows some of the results of refinement using these four models. The unit cell volumes (using the $R\bar{3}c$ results) of the air- and N_2 -quenched samples differ by only 0.3 \AA^3 , a change of less than 0.1%, while the three reduced samples are larger by about 5 \AA^3 and differ among themselves by only about 0.15%. The c/a ratio changes from 2.432 for the air-quenched sample to 2.448 for the reduced samples. This change affects the peak positions and the apparent sharpness of the diffraction peaks.

For the air- and N_2 -quenched samples model 3 gives a slightly better result than model 1, suggesting that the oxygen atoms are slightly displaced from the ideal positions. The difference, however, is slight and may not be significant. All four models show that the oxygen concentration is 3 to within the experimental error of about 0.03. The two-site model fails for these cases.

For the three reduced samples a low χ^2 is observed for the two-site model (model 2). In this case the calculated vacancy concentration increases from 7.2% to 7.8% to 8.8% for the 10%CO, 50%CO and 90%CO samples, respectively. It is possible that the octahedra containing oxygen vacancies are distorted from the ideal position, while those that are fully occupied are close to ideal. It is very likely that correlated motion of adjacent octahedra is actually produced, which leads to model 4 to describe this movement in detail. Results of model 4 show the same tendency of vacancy concentration as that of model 2, but with a larger range (7%–11%).

The magnetic model for all five samples is the same; antiferromagnetic Fe coupling of the Fe at (0,0,0) with that at (0,0,1/2) by a 180° rotation from up to down. However, the Fe moments for the three reduced samples refine between 3.72 and $3.82 \mu_B$ while the moments for the other two samples are much smaller (1.4 and $1.2 \mu_B$ for the air and N_2 quenched samples, respectively). This is a reflection of the super exchange through the oxygen atoms that is more effective when the Fe–O–Fe paths are very close to linear and Fe is in the Fe^{+3} state with a half full $3d$ band. As discussed in detail by Goodenough,⁷ the Fe–Fe super-exchange interaction is highly dependent on the Fe–O–Fe bond angle. Antiferromagnetic super-exchange interactions are stable for

TABLE I. Structural information for refinement of quenched and reduced samples using the four models. Cell parameters for models 2 and 3 are identical to those for model 1. Uncertainties are given in parentheses from the least significant digits.

Samples	A	B	C	D	E	
Temperature	1000°C	1200°C	1000°C	1000°C	1000°C	
Condition	Air	N ₂ quench	CO:CO ₂ = 10:90	CO:CO ₂ = 50:50	CO:CO ₂ = 90:10	
Model 1	χ^2	3.31	7.56	16.1	11.6	14.9
	% vac.	0.0(4)	0.0(4)	6.8(7)	8.1(7)	9.6(8)
	Fe M(u_B)	1.41(3)	1.17(3)	3.81(3)	3.84(3)	3.75(3)
	a (Å)	5.527(1)	5.531(1)	5.540(1)	5.542(1)	5.547(1)
	c (Å)	13.441(1)	13.434(1)	13.558(3)	13.564(3)	13.582(6)
	Vol. (Å ³)	355.6(1)	355.9(1)	360.4(1)	360.8(1)	361.9(2)
Model 2	χ^2	4.3	7	8.97	6.6	10.8
	% vac.	0.0(13)	0.0(12)	7.2(22)	7.8(21)	9.0(22)
	Fe M(u_B)	1.43(3)	1.18(3)	3.82(3)	3.82(2)	3.72(3)
Model 3	χ^2	3.1	7.38	9.7	7.06	11.1
	% vac.	0.0(4)	0.0(4)	7.51(6)	8.41(6)	9.14(7)
	Fe M(u_B)	1.42(3)	1.17(3)	3.86(2)	3.88(2)	3.77(3)
Model 4	χ^2	3.024	6.942	7.066	4.224	7.861
	% vac.	0.6(1)	0.4(1)	6.3(3)	7.2(4)	10.4(6)
	Fe M(u_B)	1.32(6)	1.07(6)	3.99(7)	4.05(7)	3.90(7)
	a (Å)	5.5057(16)	5.5011(11)	5.5418(5)	5.5452(5)	5.5545(14)
	b (Å)	5.5043(14)	5.5000(18)	5.5420(5)	5.5446(5)	5.5461(8)
	c (Å)	5.5020(10)	5.5020(13)	5.5410(4)	5.5424(8)	5.5593(8)
	α (degree)	60.33(2)	60.378(15)	59.933(5)	59.884(6)	59.925(15)
	β (degree)	60.377(13)	60.358(16)	60.027(3)	60.030(6)	59.825(7)
	γ (degree)	60.254(11)	60.377(9)	59.863(4)	59.920(8)	59.932(9)
	vol. (Å ³)	118.75(6)	118.69(6)	120.171(19)	120.345(27)	120.81(5)

bond angles close to 180°. This crosses over to ferromagnetic exchange for 125° < Fe–O–Fe < 150°. ⁷ In the present case all Fe–O–Fe angles are greater than 150°. For the reduced samples those angles are significantly larger than for the others.

V. CONCLUSIONS

The air- and N₂-quenched samples are close to stoichiometric with less than 1% vacancies on the oxygen lattice. The magnetic moment of the Fe is small, around 1.3 μ_B .

The oxygen vacancy concentration increases from 7% to 11% as the reducing treatment changes from 10%CO to 90%CO (model 4). These are in good agreement with Iodometric titration results.

The differences between the data (and the resulting refinements) for the reduced samples versus the air- and N₂-quenched samples are quite significant. The best fits are obtained with different models. Although model 3 gives reasonable results for all specimens, the resulting oxygen coordinates are significantly different, reflecting crystallographically distinct arrangements. Likewise, there are significant differences in the magnetic ordering for the two types of samples. This is reflected both in the intensity of the first Bragg peak in the neutron data, and in the resulting fitted moments.

By comparing the magnetic properties of these five samples and those in the literature, ^{3–5} it can be clearly seen that the oxygen vacancy concentration strongly influences the magnetic structure. The dominant effect of the 7% vacancy concentration is to force most Fe to the Fe⁺³ state. Therefore, the Fe–Fe super-exchange interaction is strengthened and the moment increases. The magnetization measurements are consistent with these results. ⁸

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