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Coupled electrical and magnetic properties in $(\text{La}, \text{Sr})\text{FeO}_{3-\delta}$

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This article is aimed at studying the temperature dependence oxygen nonstoichiometry, magnetic moments, Fe^{3+} fraction, Néel temperature and conductivity of $(\text{La}, \text{Sr})\text{FeO}_{3-\delta}$. It is found that the magnetic properties in $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ is determined by Fe^{3+} and its concentration, and the conductance is resulted from Fe^{4+} ions, which act as electron holes. Both of magnetic and electrical properties were directly governed by oxygen nonstoichiometry (δ). When $\delta=0.2$, the compound has maximum Fe^{3+} , the saturation magnetic moments and Néel temperature are $3.8 \mu\text{B}$ and $410 \text{ }^\circ\text{C}$, both at the highest level, whereas the total carrier concentration is at the minimum. © 2005 American Institute of Physics. [DOI: 10.1063/1.1860911]

I. INTRODUCTION

Interest in the coupling between transport and magnetic properties has been stimulated by a variety of applications, such as colossal magnetoresistance (CMR),¹ high temperature superconductivity,² and spintronics.³ This coupling is ubiquitous in the hole doped perovskite type oxides with general composition $A'_{1-x}A''_x\text{BO}_{3-\delta}$, where A' is the rare earth cation (valence state 3+), A'' is alkaline earth cation (valence state 2+), and B is a multivalent transition metal cation, such as Cr, Mn, and Fe.⁴ These materials are being used as interconnects,⁵ oxygen separation membranes,⁶ electrodes for solid oxide fuel cells,⁷ and magnetohydrodynamic power generators.⁸ The magnetic ordering is thought to arise from a superexchange interaction between the $3d$ orbital of transition metal ions and the $2p$ orbital of oxygen ions. Therefore, the magnetic moments will be mainly determined by unpaired $3d$ electrons on the transition metal ions. This is influenced by oxygen occupancy and Sr content in these compounds, as well as the electron neutrality principle. It is well-known that both the electrical and magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ are very sensitive to Sr-doping levels: For instance, the Néel temperature decreases with increasing Sr content (x). The oxygen nonstoichiometry in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (LSF) was found to play an important role in the magnetic structure of samples quenched from various gas atmospheres.^{4,9} Moreover, Fe valency and oxygen vacancies are of particular importance in transport properties (both electrical and ionic) of LSF. It is the intent of this article to correlate both the magnetic and electrical properties of

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ with the Fe valency and oxygen vacancies, with an emphasis on the properties as a function of temperature by using *in situ* Mössbauer spectrometry, impedance spectroscopy, and neutron diffraction.

II. EXPERIMENTAL

The modified Pechini method was used to synthesize nanocrystalline particles, followed by calcining, uniaxial pressing and sintering. A four-point-probe technique was used to measure electrical resistance on the rectangular samples ($2.00 \times 0.20 \times 0.20 \text{ cm}^3$) in the temperature range $150\text{--}1000 \text{ }^\circ\text{C}$ and oxygen activity in the range from 10^{-14} Pa to 10^5 Pa . Thermoelectrical power was measured on a similar rectangular sample. The potential difference (ΔV) across the sample was obtained as a function of temperature gradient (ΔT). The slope of a plot of ΔV vs. ΔT represents the apparent Seebeck coefficient, which was corrected by considering absolute thermopower for platinum to yield the Seebeck coefficient of the sample. Neutron diffraction was performed at room temperature on the sintered and quenched specimens. The quenching temperature was in the range between 700 and $1500 \text{ }^\circ\text{C}$. Rietveld refinement was carried out using FULLPROF code, which permits both multiphase and magnetic structure refinements. A conventional constant acceleration system was used to measure Mössbauer spectra with control over both the temperature and oxygen activity, with ^{57}Co as the source. The spectrometer was calibrated by using $\alpha\text{-Fe}$ at room temperature.

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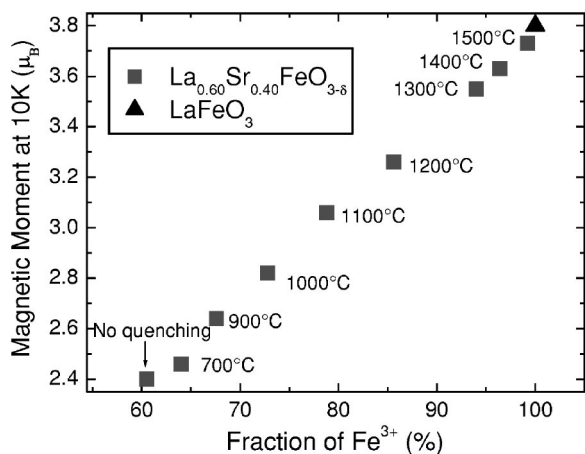


FIG. 1. Saturation moments vs the fraction of Fe^{3+} for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ quenched at various temperatures.

III. RESULTS AND DISCUSSION

Saturation magnetic moments as a function of fraction of Fe^{3+} (over total Fe concentration) are shown in Fig. 1. A datum of $\sim 3.8 \mu\text{B}$ for the LaFeO_3 refined from neutron diffraction, in which all Fe ions are in the 3+ state, is included. The fraction of Fe^{3+} was directly determined independently from the Mössbauer spectra and from measured oxygen occupancy. The oxygen occupancy was determined from refinements of the neutron diffraction data. From the charge neutrality principle, Fe is in the 3+ valence state for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{2.8}$ and Fe exhibits an average valence state of 3.4+ for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3.0}$. The oxygen occupancy around 2.8 was observed for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ quenched from 1500 °C in air, whereas full stoichiometry ($\delta \sim 0$) was determined for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ which was furnace cooled. Therefore, the magnetic moments are expected to be different for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3-\delta}$ with various δ values. The magnetic moment has also been determined by Rietveld refinement of neutron diffraction data. The antiferromagnetism is thought to arise from the superexchange interaction between $3d^5(\text{Fe}^{3+})$, $2p(\text{O}^{2-})$, and $3d^5(\text{Fe}^{3+})$ in the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ series. Either substitution of La^{3+} with Sr^{2+} or reduced oxygen vacancy density (δ from $x/2$ to 0) will generate Fe^{4+} in the compound, which, in turn, may decrease the antiferromagnetic interaction between Fe^{3+} ions. If the saturation magnetic moments for these two ions are significantly different, then a determination of the saturation moment (measurement at low temperature) can provide a direct determination of the ratio of the two species and, thus, of the stoichiometry. The saturation moment for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{2.8}$ is found to be $\sim 3.8 \mu\text{B}$, which is a typical moment for Fe^{3+} in LaFeO_3 system. The magnetic moment for $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{3.0}$ is $\sim 2.3 \mu\text{B}$ ($\sim 3.8 \mu\text{B} \times 60\%$), implying a near zero moment for Fe^{4+} ions. The magnetic moment is, as expected, linear with the fraction of Fe^{3+} and thus can be used to indirectly determine oxygen content somewhat more precisely than by direct crystallographic refinement. Oxygen deficiency can also be determined by Mössbauer studies.

If the interaction between Fe^{3+} and Fe^{3+} is stronger than both Fe^{3+} with Fe^{4+} and Fe^{4+} with Fe^{4+} , the magnetic ordering temperature will also change with the fraction of Fe^{4+} . In

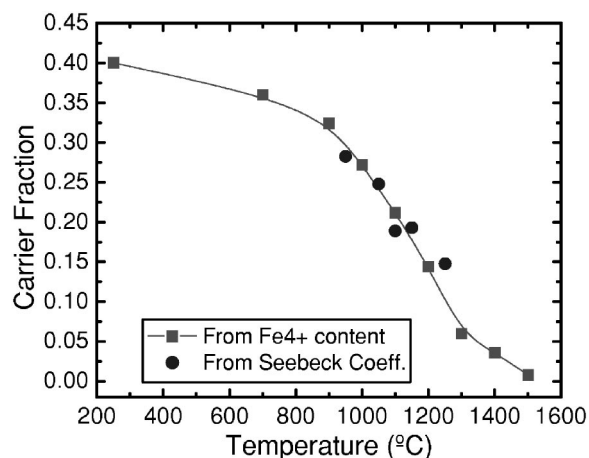


FIG. 2. Carrier concentration vs temperature, determined from Seebeck Coefficient and Fe^{4+} concentration.

the unquenched specimen, the fraction of Fe^{4+} is 40% (oxygen deficiency is nearly zero), which results in a rather low Néel Temperature (T_N) ~ 30 °C. T_N increases to ~ 410 °C for the specimen quenched from 1500 °C, which possesses a composition of $\text{La}_{0.60}\text{Sr}_{0.40}\text{FeO}_{2.8}$ and a saturation moment of $3.8 \mu\text{B}$. It is worth noting that T_N of LaFeO_3 , in which all Fe ions are in the 3+ valence state, is ~ 740 K (467 °C).¹⁰ Therefore, the magnetic ordering in LSF is dominated by the interaction between Fe^{3+} ions.

Questions still remain as to the behavior of electrons in Fe^{4+} ions. Information on multivalent Fe site cations and valency distribution can contribute to understanding conduction mechanisms in *p* type perovskite family oxides. At high temperature, LSF will lose oxygen to form oxygen vacancies, at the cost of decreasing hole concentration. This reaction can be represented in Kröger–Vink notation¹¹ as: $2\text{Fe}_{\text{Fe}}^{\bullet} + \text{O}_{\text{O}}^{\times} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{Fe}_{\text{Fe}}^{\times} + \text{V}_{\text{O}}^{\bullet\bullet}$, where $\text{Fe}_{\text{Fe}}^{\bullet}$ represents Fe ions in the 4+ valence state (similar to holes), $\text{Fe}_{\text{Fe}}^{\times}$ indicates Fe cations in 3+, and $\text{V}_{\text{O}}^{\bullet\bullet}$ represents the oxygen vacancy. Thus, the hole conductivity (σ) follows $\sigma = N\mu q$, where μ is the mobility, q is the carrier charge, and N is the hole concentration (Fe^{4+}). Because of the much higher mobility of the electrons or holes than that of oxygen ions, the total conductivity in ferrites is dominated by hole conduction. The carrier concentration can be directly determined from the measurements of Seebeck coefficient (Q). Figure 2 shows the plots of carrier density calculated from Fe^{4+} concentration, which is determined from the Seebeck coefficient and Fe^{4+} fraction in the system.

One would expect that a *p*–*n* transition occurs when the $\text{Fe}_{\text{Fe}}^{\bullet}$ concentration (functioning as holes) further decreases, and the average Fe valence drops below 3+, generating electron carriers. Theoretically, both increasing temperature and decreasing oxygen activity can drive this transition. However, resistivity measurements at 1600 °C are extremely difficult to perform. Therefore, we studied this phenomenon by decreasing oxygen activity (from 10^5 to 10^{-13} Pa) at 1000 °C. Figure 3 illustrates this transition. In the $p\text{O}_2$ region from 10^5 to 10^{-9} Pa, the total isothermal conductivity decreases due to decrease of $\text{Fe}_{\text{Fe}}^{\bullet}$ (hole) concentration as a result of generation of oxygen vacancies. At the minimum

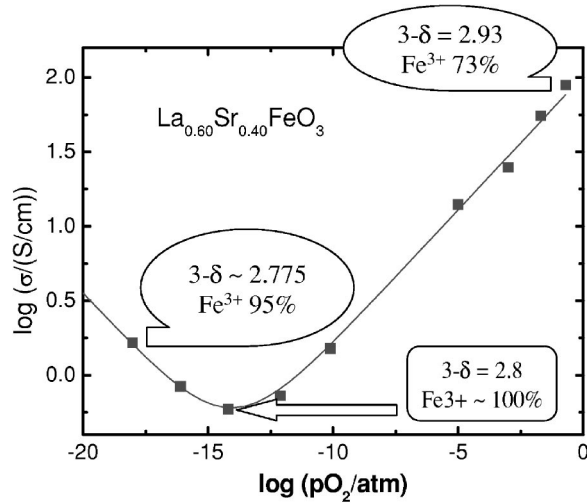


FIG. 3. $\log(\sigma)$ vs $\log(pO_2)$ with the fraction of Fe^{3+} and oxygen occupancy at 1000 °C for $La_{0.60}Sr_{0.40}FeO_{3-\delta}$.

conductivity, Mössbauer data on quenched samples show nearly all Fe cations are in 3+ valence state and oxygen occupancy ~ 2.8 , in agreement with the neutron results. Further decreasing oxygen activity increases the Fe^{2+} concentration, which functions as electrons. Thus, conductivity (n type) increases when $pO_2 < 10^{-9}$ Pa (shown in Fig. 3).

IV. CONCLUSIONS

Oxygen deficiency is nearly zero in the unquenched specimen; therefore, the fraction of Fe^{4+} is 40%, which results in a rather low Néel temperature (T_N) ~ 30 °C and a small room temperature moment ($\sim 1.3 \mu_B$) because the exchange interactions in this system are expected to be domi-

nated by the $Fe^{3+}-Fe^{3+}$ interactions. T_N increases to ~ 410 °C for the specimen quenched from 1500 °C, which possesses a composition of $La_{0.60}Sr_{0.40}FeO_{2.8}$ and a saturation moment of $3.8 \mu_B$. When the composition reaches $La_{0.6}Sr_{0.4}FeO_{2.8}$, it is expected that the system will reach its maximum average moment. Beyond this point Fe^{2+} is expected to appear, also with a smaller moment than Fe^{3+} , and the room temperature moment would then be expected to decrease, which indeed was observed in this study. Moreover, this point also corresponds to a $p-n$ transport transition in this system since Fe^{2+} acts as a donor and therefore the system changes from a p type conductor to an n type conductor.

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