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A Study of Charge Disproportionation in the Nonstoichiometric Perovskite $Sr_2LaFe_3O_{8+y}$ by Mössbauer Spectroscopy

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The cubic perovskite $Sr_2LaFe_3O_{8+y}$ ($0.6 < y < 1$) has been studied by Mössbauer spectroscopy, X-ray powder diffraction, and magnetic susceptibility techniques. The phase shows a first-order transition from a high-temperature paramagnetic averaged-valence state in which all Fe cations are electronically equivalent to a low-temperature antiferromagnetic mixed-valence state by the nominal charge disproportionation $2Fe^{4+} \rightleftharpoons Fe^{3+} + Fe^{5+}$. Mössbauer measurements show that both states coexist over a wide temperature range. Increasing oxygen vacancy concentration depresses the transition temperature by some 50 K, and causes a degree of relaxational collapse in the magnetic hyperfine patterns. There is evidence for electron-trapping in the vicinity of oxygen vacancies in the averaged-valence state. © 1988 Academic Press, Inc.

Introduction

The stoichiometric perovskite $CaFeO_3$ is a metallic paramagnet at room temperature (*1*). Below circa 115 K it undergoes a transition to a semiconducting antiferromagnetic phase, and Mössbauer data at 4.2 K have revealed (*2*) a charge disproportionation which was thought to be

$$2Fe^{4+} \rightleftharpoons Fe^{3+} + Fe^{5+}.$$

The single Mössbauer resonance line at room temperature with an isomer shift, δ, of 0.073 mm sec^{-1} is replaced at 4.2 K by two magnetic hyperfine patterns (magnetic flux density, B) of equal intensity with the parameters

	δ (mm sec^{-1})	B (T)
Fe^{3+}	0.34	41.6
Fe^{5+}	0.00	27.9
Mean	0.17	34.8

The symmetrical electron configurations of $t_{2g}^3e_g^2$ and t_{2g}^3 respectively are consistent with the absence of any significant quadrupole interactions. The mean values correspond very closely to those reported by Gallagher *et al.* (*3*) for $SrFeO_3$ ($\delta = 0.146$ mm sec^{-1}, $B = 33.1$ T at 4.2 K) which is a metallic antiferromagnetic perovskite. Although it has been suggested in a neutron diffraction study (*4*) that $SrFeO_3$ contains a (t_{2g}^4, $S = 1$) low-spin Fe^{4+} configuration, the large value of the hyperfine field is more in keeping with a high-spin ($t_{2g}^3e_g^1$, $S = 2$) configuration, with metallic conductivity arising from a delocalized σ^* band derived from the e_g

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electronic states, and thereby preventing a Jahn–Teller distortion.

A series of studies of the solid solutions $Ca_{1-x}Sr_xFeO_3$ $(0 < x < 0.75)$ and $Sr_{1-x}La_xFeO_3$ $(0 < x < 0.6)$ have shown (*5–7*) a similar disproportionation, but with a composition-dependent correlation between the isomer shift and the hyperfine field which is a universal curve for both solid solutions. This demonstrates convincingly the existence of effectively nonintegral valence states; i.e.,

$$2Fe^{4+} \rightleftharpoons Fe^{(4-\lambda)+} + Fe^{(4+\lambda)+}.$$

The first-order transition from antiferromagnetism to paramagnetism in $Sr_{0.7}La_{0.3}FeO_3$ takes place considerably below the anticipated Néel temperature (based on the observed temperature dependence of the hyperfine fields). Both phases coexist over a wide temperature range. In comparison, $CaFeO_3$ shows a more conventional second-order magnetic transition, the averaged valence state appearing above the Néel temperature.

The above observations all relate to samples prepared under high oxygen pressure in order to achieve a fully occupied anion sublattice. A similar disproportionation has been briefly reported (*8*) in the oxygen-deficient phase $Ca_xLa_{1-x}FeO_{3-y}$ $(0 < x < 0.5)$. However, the transitional region has not been investigated. During the course of a more wide ranging investigation into defect ordering in the system $Sr_2LaFe_3O_{8+y}$ $(0 < y < 1)$, we have been able to monitor the effect of an increase in the oxygen vacancy concentration on the temperature at which the transition occurs, and to establish the maximum vacancy concentration which can be achieved without the introduction of a further phase, and these results are reported in the present paper.

Experimental

Accurately weighed amounts of spectroscopic-grade Fe_2O_3, $SrCO_3$ and La_2O_3 with stoichiometric ratios appropriate for $Sr_2LaFe_3O_8$ were ground together in a ball mill, pressed into a pellet, and initially fired in a platinum crucible at 1400°C for 4–7 days with two intermediate grindings before quenching onto a metal plate in air. Aliquots of this material were then annealed in air at 1200°C for 2 days before cooling to a controlled temperature, annealing for a further 2 days to reach equilibrium, and finally quenching, usually into liquid nitrogen to minimize further uncontrolled oxidation. Initial characterization in each case was by X-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu$K\alpha$ radiation. Chemical analyses for nominal Fe^{4+} content were carried out by digestion in a standardized solution of ammonium iron(II) sulfate in the presence of HCl and titration with cerium(IV) sulfate using ferroin as indicator.

Magnetic susceptibility measurements were made in the temperature range $78 < T < 300$ K using a Newport Instruments Gouy balance. Mössbauer data were collected in the temperature range $4.2 < T < 290$ K using a $^{57}Co/Rh$ source matrix held at room temperature; isomer shifts were determined relative to the spectrum of metallic iron.

Results

Samples of $Sr_2LaFe_3O_{8+y}$ were quenched into liquid nitrogen after annealing in air at 700, 600, and 500°C; in air from 400°C; and slowly cooled to 200°C in air. In all cases the X-ray analysis at room temperature showed a simple cubic cell, although the high-angle lines were usually broader than one would expect from a highly crystalline material. The cell parameters and analytical results are given in Table I. The oxygen content decreases rapidly with increasing annealing temperature, and there is a concomitant slight but significant expansion of the unit cell. Mössbauer spectra were re-

TABLE I

CHARACTERIZATION OF THE $Sr_2LaFe_3O_{8+y}$ SAMPLES

Quench temperature (°C)	y	a (Å)
200	0.94	3.874
400	0.92	3.875
500	0.79	3.875
600	0.69	3.880
700	0.55	3.885

corded at temperatures between 78 and 295 K.

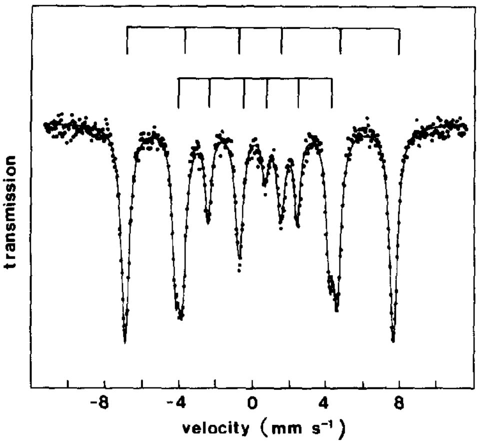

FIG. 2. Mössbauer spectrum at 78 K of $Sr_2La Fe_3O_{8.94}$ showing the analysis as two overlapping hyperfine sextets without quadrupole coupling (B = 45.1 and 25.9 Tesla, δ = +0.352 and −0.027 mm sec^{-1}, respectively).

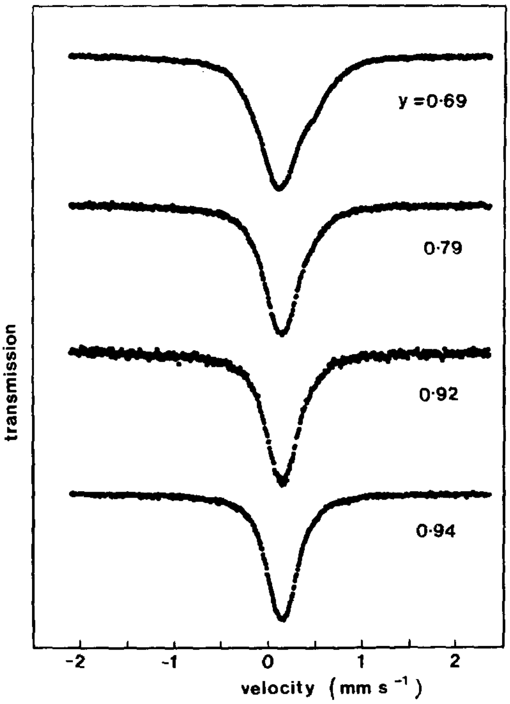

FIG. 1. Mössbauer spectra at 290 K of $Sr_2LaFe_3O_{8+y}$ (y = 0.94, 0.92, 0.79, and 0.69). Note the increasing asymmetry with decrease in y.

The stoichiometric composition $Sr_2La Fe_3O_9$ (which can only be obtained under high pressure of oxygen) is already a mixed-valence oxide with nominally two-thirds of the iron in the +4 oxidation state (or one-third in the +5 state). The spectrum for $Sr_2LaFe_3O_{8.94}$ (slow-cooled to 200°C) recorded at room temperature is shown in Fig. 1, and comprises a single symmetrical line. The lineshape is broad and slightly non-Lorentzian, with a width at half-height of 0.37 mm sec^{-1}, and an isomer shift of +0.141 mm sec^{-1}. This value is intermediate between the values expected for Fe^{3+} and Fe^{4+} or Fe^{5+}, and demonstrates the existence of a fast electron transfer resulting in an "averaged" valence state. At 78 K, the spectrum comprises two superimposed magnetic hyperfine patterns (Fig. 2) with magnetic flux densities of 45.1 and 25.9 Tesla, and isomer shifts of +0.352 and −0.027 mm sec^{-1}, respectively. There are no quadrupole interactions within experimental error. These parameters are completely consistent with the observations already made (7) for $Sr_{0.7}La_{0.3}FeO_3$, although in that instance there was no oxygen deficiency. It is clear that the same "mixed-valence" state is produced by a charge disproportionation into species approximating to Fe^{3+} and Fe^{5+}. The formula $Sr_2La Fe_3O_{8.94}$ indicates that 0.7% of oxygen is missing, and 31% of the iron can be present as Fe^{5+}. The experimental area ratios were

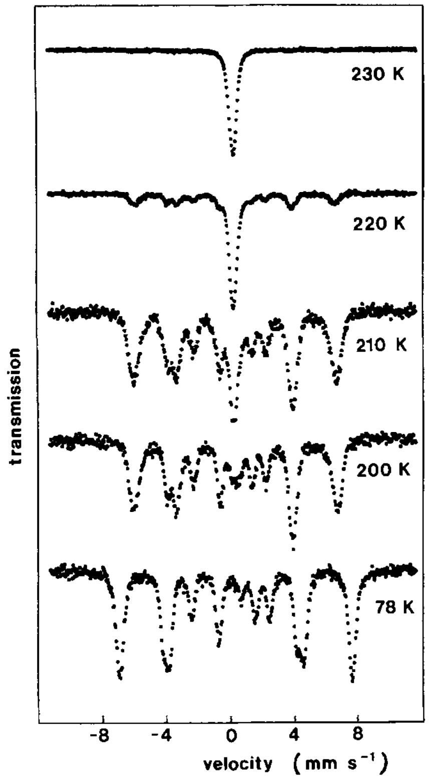

FIG. 3. Mössbauer spectra of $Sr_2LaFe_3O_{8.94}$ (slow-cooled to 200°C) as a function of temperature. Note the coexistence of the high-temperature paramagnetic averaged-valence state and the low-temperature antiferromagnetic mixed-valence state between about 200 and 225 K.

69 : 31, in excellent agreement. The large difference in the flux densities indicates a high degree of charge separation, greater than that found in $CaFeO_3$.

Figure 3 shows a selection of spectra at intermediate temperatures, and reveals the coexistence of the high-temperature averaged-valence state and the low-temperature mixed-valence state over a wide temperature range (approximately 200–225 K). This has also been reported in $Sr_{0.7}La_{0.3}FeO_3$, and is therefore not just a consequence of the oxygen deficiency. The temperature dependence of the hyperfine fields shows that the extrapolated Néel temperature of the mixed-valence state is substantially in excess of 225 K. It is clear that regions of the mixed-valence material make a first-order transition to the averaged-valence state (which is only paramagnetic) at significantly different temperatures.

The inverse magnetic susceptibility for $Sr_2LaFe_3O_{8.94}$ is shown in Fig. 4. There is an abrupt change at circa 200 K with a minimum indicative of a transition to antiferromagnetic ordering. Above this temperature the susceptibility is almost field independent; below it there is a pronounced field dependence which appears to be an intrinsic property of the phase. Using the standard relationship for the magnetic moment as a function of susceptibility χ and temperature T of $\mu = 2.83[\chi(T - \theta)]^{1/2}$, the data above 240 K lead to a magnetic moment of 5.55 Bohr magnetons per iron atom and a Curie–Weiss constant θ of circa −220 K.

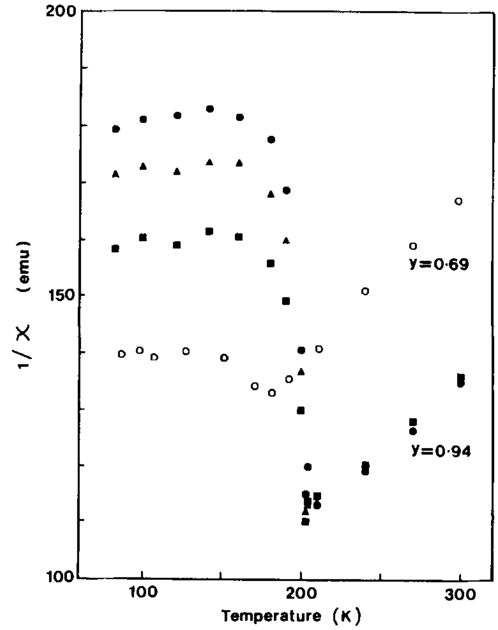

FIG. 4. The reciprocal susceptibility per mole of iron of $Sr_2LaFe_3O_{8.94}$ and $Sr_2LaFe_3O_{8.69}$ as a function of temperature. The magnet currents used corresponded to values of B_1^2–B_2^2 of circa 0.05 (squares), 0.12 (triangles), and 0.30 (circles) T^2.

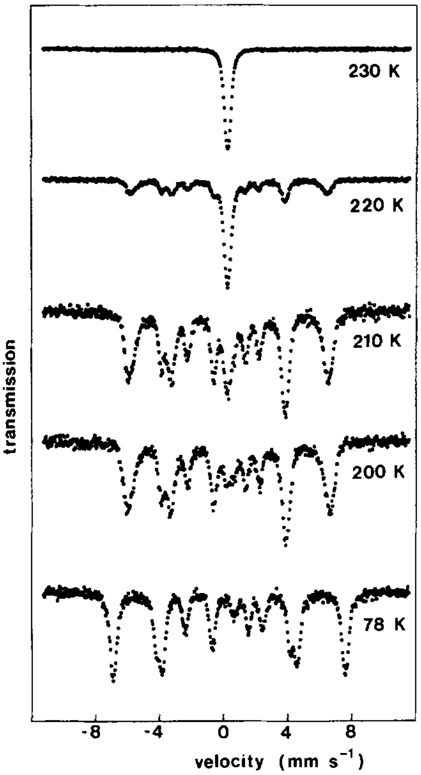

FIG. 5. Mössbauer spectra of $Sr_2LaFe_3O_{8.92}$ (quenched from 400°C) as a function of temperature.

The magnetic moment compares favorably with the average for $2Fe^{3+} + Fe^{5+}$ of 5.24 Bohr magnetons from the spin-only formula, and the large negative Weiss constant is consistent with essentially antiferromagnetic interactions. Thus the magnetic data are broadly in accord with a localized electron model, consistent with the existence of localized t_{2g} electrons and a narrow σ^* band. The small discrepancy in the observed transition temperature by Mössbauer spectroscopy (~225 K) and magnetic susceptibility (~200 K) may be due in part to a systematic error in the two temperature control systems, but a more likely possibility is that the two techniques respond differently within the timescale of processes occurring in the vicinity of the transition.

The sample annealed and quenched into air from 400°C, $Sr_2LaFe_3O_{8.92}$, gave spectra which were almost identical to those of $Sr_2LaFe_3O_{8.94}$ (see Figs. 1 and 5). The Fe^{5+} component at 78 K comprised 31% of the total area compared to 30% from the chemical analysis. This confirmed that the equilibration with oxygen was fast and essentially complete in the slow-cooled sample. The spectrum at room temperature shows evidence of a slight asymmetry on the positive velocity side, and this becomes much more pronounced in the 500 and 600°C quenched samples (Fig. 1). The temperature dependence of the Mössbauer spectrum in $Sr_2LaFe_3O_{8.79}$ (Fig. 6) is different from that described above. The spectrum at 78 K is little changed with the area of the Fe^{5+} component being 29% as against 26% by chemical analysis. The magnetic spec-

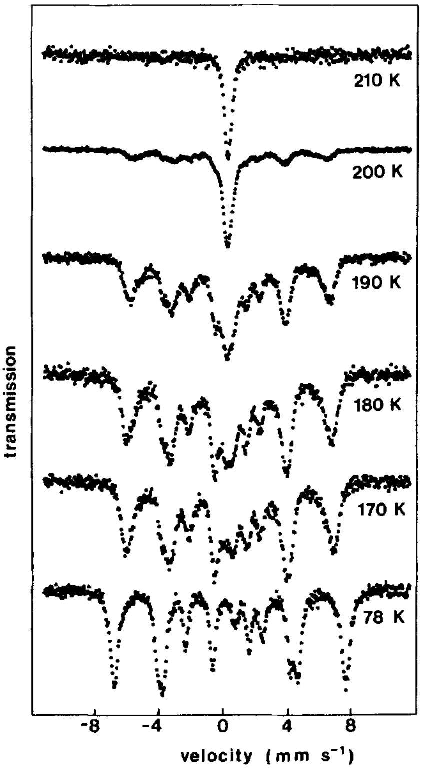

FIG. 6. Mössbauer spectra of $Sr_2LaFe_3O_{8.79}$ (quenched from 500°C) as a function of temperature.

trum collapses between 170 and 210 K, but the first-order characteristics of the transition are partly obscured by a degree of inward broadening and collapse more typical of relaxation. This trend continues in $Sr_2LaFe_3O_{8.69}$. Inward collapse is already in progress at 78 K (Fig. 7), although the spectrum is clearly derived from an Fe^{3+}/Fe^{5+} mixed-valence system, and the collapse is complete by 180 K.

The magnetic susceptibility data for $Sr_2LaFe_3O_{8.69}$ (Fig. 4) are distinctly different from that for $Sr_2LaFe_3O_{8.94}$. The susceptibility is almost field independent, and the transition which is now at a lower temperature (circa 180 K) is far less pronounced (data are shown at only one field). The reciprocal susceptibility in the paramagnetic region is significantly displaced to higher values, with a similar magnetic moment, but a much larger Weiss constant. This is consistent with the additional reduction to Fe^{3+} and the expected increase in the strength of the exchange interactions. In principle this could be confirmed by seeing a smaller temperature dependence of the hyperfine fields in the mixed-valence state, but the effect is obscured by the onset of relaxational narrowing.

$Sr_2LaFe_3O_{8.55}$ quenched from 700°C gave a cubic X-ray pattern which camouflaged a much more complex nature. The Mössbauer spectra (Fig. 8) reveal the presence of a second phase which is magnetically ordered at 290 K and comprises some 20% of the spectrum area. The remaining component is still the mixed/averaged valence

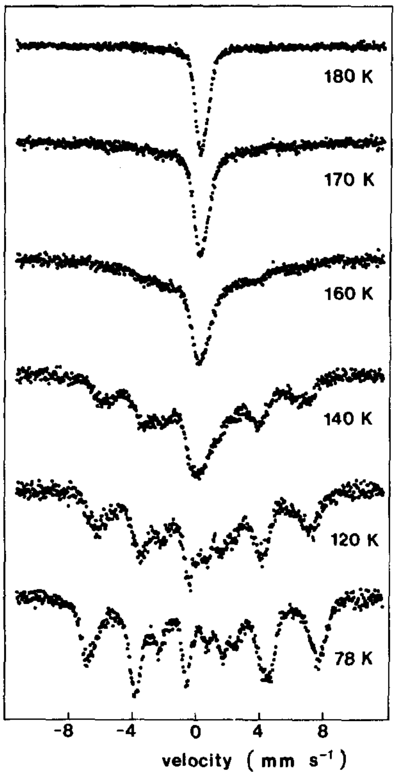

FIG. 7. Mössbauer spectra of $Sr_2LaFe_3O_{8.69}$ (quenched from 600°C) as a function of temperature.

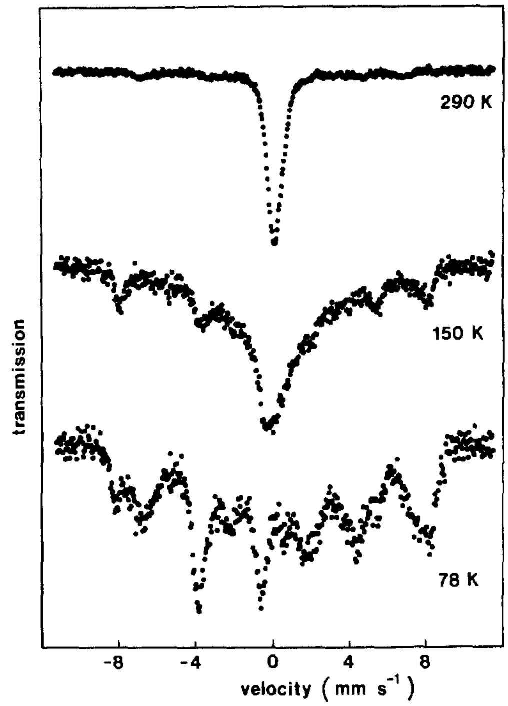

FIG. 8. Mössbauer spectra of $Sr_2LaFe_3O_{8.55}$ (quenched from 700°C) as a function of temperature. Note the weak magnetic lines from a second phase at 290 K. These lines are not in fact significantly more intense at the lower temperatures; the intensity scale is different for each spectrum.

phase. This new phase becomes the sole component at higher temperatures and is an ordered defect phase which will be discussed elsewhere.

Discussion

The early work on the oxygen-deficient perovskite solid-solution $Sr_{1-x}La_xFeO_{3-y}$ by Shimony and Knudsen (*9*) indicated the complexity of the system and the existence of iron in a high oxidation state, but has been largely superceded by later work. The existence of charge disproportionation was first described by Takano *et al.* (*5, 7*) as described above. An investigation of the electrical and magnetic properties of samples quenched from 400, 1100, and 1300°C has shown (*10*) that magnetic order occurs at a temperature which depends linearly upon the fraction of nominal Fe^{4+} present $(= 1 - x - 2y)$, but not on the La/Sr (or La/Ca) ratio, as replacement of Fe^{3+} by Fe^{4+} weakens the Fe–O–Fe exchange interactions. A case was argued for Fe^{4+} in a low-spin state, largely on the basis that the ordering temperature decreases faster with increasing Fe^{4+} content than expected. However, we have previously reported (*11*) that substitution of *paramagnetic* Cr^{3+} into $EuFeO_3$ depresses the ordering temperature faster than substitution by *diamagnetic* low-spin Co^{3+}, and therefore feel that this observation is not conclusive evidence for a low-spin state. Charge disproportionation was not studied by Grenier *et al.* (*10*), and it is difficult to reconcile this feature with the model. Indeed, the transfer

$$2(t_{2g}^3e_g^1) \rightleftharpoons (t_{2g}^3) + (t_{2g}^3e_g^2)$$

at nominally octahedral sites is inherently more plausible than

$$2(t_{2g}^4) \rightleftharpoons (t_{2g}^3) + (t_{2g}^3e_g^2).$$

The latter requires an overall excitation of electrons which would involve a large energy uptake, and would be more likely to occur upon heating rather than cooling. Later related work from the same group also seems to favor a high-spin Fe^{4+} configuration (*12*).

The present work was initiated largely to study the ordering of oxygen vacancies at the composition $Sr_2LaFe_3O_8$, to ascertain whether an orthorhombic phase analogous to $Ca_2LaFe_3O_8$ exists, and whether it can show microdomain behavior upon oxidation. These features will be the subject of a separate paper. Here we concentrate on the effects of a change in oxygen vacancy concentration upon the charge disproportionation at a fixed Sr/La concentration ratio.

It is now clear that the mixed/averaged valence phase extends from $Sr_2LaFe_3O_9$ to about $Sr_2LaFe_3O_{8.6}$ with over 6% of the oxygen sites vacant. At room temperature the X-ray symmetry is cubic with a slight increase in cell size upon reduction. There is no evidence for vacancy ordering or cation ordering, and it seems likely that the strontium and lanthanum are disordered. Electron transfer takes place between the nominal $Fe^{3+} + 2Fe^{4+}$ cations to produce an averaged-valence state within a timescale of $<10^{-7}$ sec. Increasing oxygen vacancy concentration results in the emergence of asymmetry in the Mössbauer resonance. We have been unable to analyze the spectra with any confidence as a small number of overlapping Lorentzian lines. It therefore seems more realistic to attribute the asymmetry to the partial trapping of electrons at Fe^{3+} cations in the vicinity of vacancies such that all cations are no longer electronically equivalent, as suggested by Grenier *et al.* (*10*) in explaining the electrical conductivity of the phase. However, there is no positive evidence for iron sites with tetrahedral coordination. In $Sr_2LaFe_3O_{8.69}$ some 19% of sites have one or more nearest neighbor vacancies assuming a random distribution. It may be the trapping of electrons combined with an increase in cation–cation distance which forces a transition to the new defect phase. At low temperatures the averaged-valence state undergoes a charge disproportionation to $2Fe^{3+} + Fe^{5+}$ with a high degree of charge separation. We considered it likely that there would be a concomitant change in crystal symmetry, although this has never been demonstrated in such a system. Accordingly we recently collected neutron powder-diffraction data for $Sr_2LaFe_3O_{8.94}$ at 5 K, and obtained clear evidence that the low-temperature phase is a noncubic antiferromagnet. We hope to present a full structure analysis in a future paper.

The magnetic susceptibility data show that the magnetic order is essentially antiferromagnetic, which would require there to be at least six iron atoms in the magnetic unit cell of stoichiometric $Sr_2LaFe_3O_9$. The field dependence below the transition region in $Sr_2LaFe_3O_{8.94}$ suggests a weak parasitic ferromagnetism due to spin misalignment in accord with the data for $Sr_{0.7}La_{0.3}FeO_3$. This effect is absent in $Sr_2LaFe_3O_{8.69}$, and it would appear that the increase in vacancy concentration destroys the subtle modification of the spin structure required. The observed relaxation broadening in the Mössbauer data is indicative of increasing short-range fluctuations in the spin structure. There is no sign in either case that the transition temperature is significantly affected by the magnetic field applied during the susceptibility measurement.

It is not obvious as to why the mixed/averaged valence transition takes place over a wide temperature range. This is not vacancy related, because the effect has also been reported in material prepared under high pressures of oxygen (*7*), and it has been suggested that the effect is related to a distribution in domain size. However, the nature of these domains was not specified. There is a clear reduction in the temperature of the critical region by some 50 K with increasing vacancy concentration; that is, the antiferromagnetic mixed-valence state becomes less stable thermally compared to the paramagnetic averaged-valence state. The charge disproportionation has been shown to involve nonintegral valence states (*6, 7*), and one might have expected to see a temperature dependence in the hyperfine fields of the two components consistent with a reduction in the charge separation at higher temperatures. There is no evidence for this, and the transition to an averaged valence state is discontinuous, at least at the composition studied here. Hopefully a determination of the low-temperature structure will throw new light onto these interesting phenomena.

Acknowledgments

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