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Magnetic and Mössbauer spectral study of mixed valent $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ and related perovskites

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The $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskites are important because they are mixed electron and oxygen anion conductors and thus are able to serve as dense oxygen separation membranes. In order to better understand the mechanism for this separation a Mössbauer spectral study has been carried out to determine the ratio of iron(III) to iron(IV) in these mixed valent compounds. The Mössbauer spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ obtained between 4.2 and 78 K reveal that its Néel temperature is ~ 75 K and the two well-resolved magnetic sextets observed between 4.2 and 45 K indicate the presence of trapped valence iron(III) and iron(IV). At 4.2 K the respective hyperfine fields are 454 and 299 kOe and the isomer shifts are 0.388 and 0.057 mm/s. The iron(III) to iron(IV) ratio is 1.20, a ratio which yields a δ value of 0.32 and, if one assumes the presence of only copper(II), a corresponding stoichiometry of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$. © 1999 American Institute of Physics. [S0021-8979(99)54008-5]

The $(\text{La,Sr})(\text{Cu,Fe})\text{O}_{3-\delta}$ series of compounds are interesting because of their electrical and oxygen transport properties. More specifically, the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ compounds are interesting candidates for oxygen separation membranes, oxygen sensors, and solid oxide fuel cell applications, applications which result from the large number of oxygen vacancies combined with a relatively high electronic conductivity.¹⁻⁴ The La-Sr-Cu oxides exhibits several different phases with different stoichiometries, several of which exhibit superconductivity at low temperatures.⁵ Both the pure ferrite and pure cuprate compounds have been extensively studied, but there are fewer reports⁶ on the mixed copper-iron compounds.

Because it is important to know the relative amounts of iron(III) and iron(IV) in the $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ mixed valence oxides in order to understand their mechanism of oxygen anion transport, we have undertaken a Mössbauer spectral study of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and related compounds. Previous Mössbauer spectral work⁶⁻¹⁴ has shown that the hyperfine parameters of the iron(III) and iron(IV) ions will be quite different unless rapid electron exchange is occurring on the Mössbauer time scale.

The samples were prepared by a modified Pechini citrate process.¹⁵ The starting reagents were $\text{La}_2(\text{CO}_3)_3$ (s), SrCO_3 (s), $\text{Fe}(\text{NO}_3)_3$ (aq), and $\text{Cu}(\text{NO}_3)_2$ (aq), all standardized gravimetrically. The carbonates were dissolved in nitric acid, and the nitrate solutions were added in appropriate amounts. The solution was heated to ~ 360 K under stirring and 1.5 moles of citric acid and 1.5 moles of ethylene glycol per mole of metal ions were added. Heating and stirring was continued until nitrous oxide gas started to evolve and then the solution was evaporated to dryness in an oven for at least three hours. Homogeneity was ensured by milling a slurry of the solid in ethanol in a vibratory mill for 24 h after which the powders were dried and calcined at 970 K for 4 h followed by dry milling for 4 h. The powders were then pressed

with PVA as a binder and sintered at 1300 K in flowing oxygen on a bed of crushed sintered material of the same composition.

The oxygen stoichiometry of the samples was determined by titration in a nitric acid solution in which all the iron(IV) and copper(III) was first reduced to iron(III) and copper(II) through the addition of a measured amount of aqueous iron(II). Excess iron(II) was titrated with a standardized aqueous solution of KMnO_4 . The resulting oxygen deficiency was found to be 0.34 ± 0.02 .

The Mössbauer spectral absorbers contained 52 mg/cm^2 of powder and spectra were obtained between 4.2 and 295 K on a constant-acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with α -iron foil. The resulting paramagnetic spectra obtained at 78 and 295 K have been fit with the distribution method of Le Caër.¹⁶ The spectra obtained between 4.2 and 70 K have been fit with two sextets in which the components within each sextet had an area ratio of 3:2:1:1:2:3 and a linewidth ratio of $\Gamma + \Delta\Gamma : \Gamma + 0.5\Delta\Gamma : \Gamma : \Gamma : \Gamma + 0.5\Delta\Gamma : \Gamma + \Delta\Gamma$. It was not possible to fit the magnetic spectra with a single linewidth for each sextet, presumably because the oxygen vacancies in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ produce a small distribution of hyperfine parameters for each ion. The estimated errors are at most ± 2 kOe for the hyperfine fields, ± 0.005 mm/s for the isomer shifts, and ± 0.02 mm/s for the linewidths at 295 and 78 K and between 4.2 and 45 K. The errors are higher for the 53–70 K spectra.

The Mössbauer spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ obtained at 295 and 78 K, are shown in Fig. 1 and several spectra, obtained between 70 and 4.2 K, are shown in Fig. 2. The hyperfine parameters associated with the fits shown in Fig. 2 are given in Table I. As is discussed below, the oxygen deficiency, δ , has been determined from the 4.2 K spec-

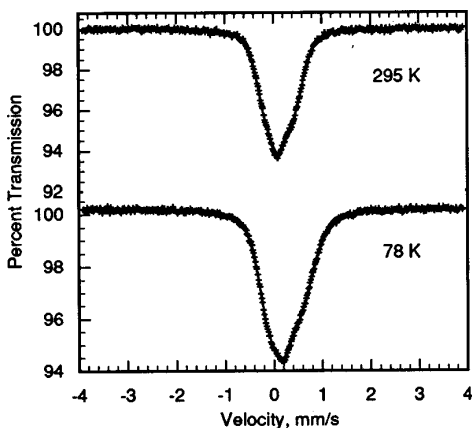


FIG. 1. Mössbauer spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ obtained at 295 and 78 K.

trum to be 0.32, a value which agrees well with the chemical analysis, and from this point the compound will be referred to as $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$.

As is apparent in Fig. 1, the 295 and 78 K nonmagnetic spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ are not symmetric, as was the case for the earlier spectra⁶ of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ and hence have been fit not with one singlet and two doublets,⁶ but rather the method of Le Caër¹⁰ has been used to fit each spectrum with a linearly correlated distribution of isomer shifts, δ , and quadrupole splittings, ΔE_Q . The distribution consisted of 20 doublets each with a linewidth, Γ , of 0.23 mm/s. At 78 K the fit, shown in Fig. 1, yields $\delta = 0.056\langle\Delta E_Q\rangle + 0.195$ mm/s and $\langle\Delta E_Q\rangle = 0.560$ mm/s, $\langle\delta\rangle = 0.226$ mm/s, and a distribution width, σ , of 0.39 mm/s. At 295 K, the fit yields $\delta = 0.027\langle\Delta E_Q\rangle + 0.120$ mm/s and $\langle\Delta E_Q\rangle = 0.445$ mm/s, $\langle\delta\rangle = 0.132$ mm/s, and a σ of 0.31 mm/s. These results agree almost perfectly with the equivalent 295 K values of $\langle\delta\rangle = 0.127$ mm/s and $\langle\Delta E_Q\rangle = 0.44$ mm/s, obtained⁶ for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ and are in good agreement with the values observed^{7-10,17} for $\text{SrFeO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. As will be shown below, the isomer shifts obtained for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ are exactly what would be expected for valence averaging, on the Mössbauer time scale, of the iron(III) and iron(IV) ions.

It is immediately apparent from Fig. 2 that $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ is antiferromagnetically ordered¹ at 70 K and below and that between 45 and 4.2 K the Mössbauer spectra reveal two resolved magnetic sextets. These spectra can be uniquely fit with hyperfine parameters that clearly correspond to iron(III) and iron(IV) for the sextet with the larger and smaller hyperfine fields, respectively. There is no evidence in the spectra for the presence of any iron(V) as has been noted in some cases in the past.^{11,12} As expected for cubic compounds, the observed quadrupole shifts are essentially zero for both oxidation states. At 25 and 4.2 K the relative areas of these two sextets yield an iron(III) to iron(IV) ratio of 1.20, a ratio which corresponds to, if one assumes the presence of only copper(II), an oxygen deficiency, δ , of 0.32 and a stoichiometry of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$. If some of the copper(II) has been oxidized to copper(III), as was the case⁶ for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.4}\text{Co}_{0.6}\text{O}_{3-\delta}$, then the oxygen deficiency of 0.32 represents an upper bound. The observed oxygen deficiency

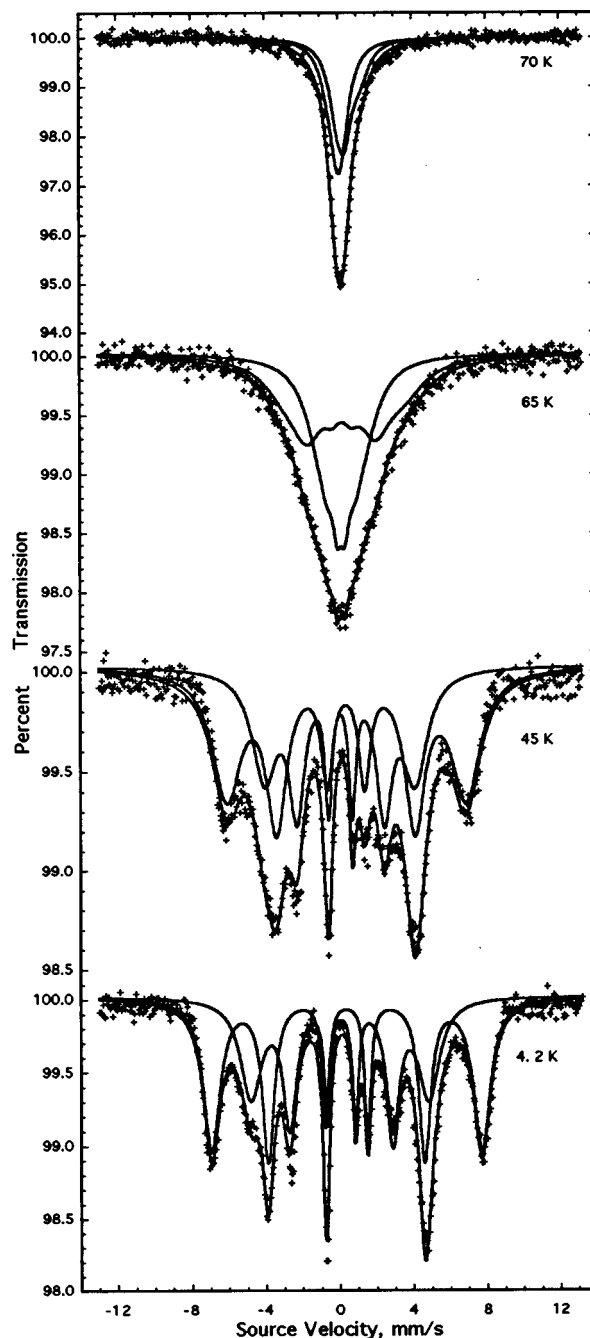


FIG. 2. Mössbauer spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ obtained at 70, 65, 45, and 4.2 K.

in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ falls in the rather narrow range of values which, depending upon the extent of oxygen heat treatment, ranged⁶ from 0.30 to 0.36 for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Co}_{0.6}\text{O}_{3-\delta}$. In contrast, an iron(III) to iron(IV) ratio of 0.67 was found⁶ for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$. Above 45 K, the Mössbauer spectra of $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$ broaden substantially and show less resolution, presumably because of the onset of magnetic relaxation on the Mössbauer time scale. However, as is shown in Fig. 2, between 4.2 and 65 K, two sextets are required to fit the spectra, and thus it appears that slow electron exchange between the two iron oxidation states persists up to at least 65 K and perhaps to 70 K.

The temperature dependence of the isomer shifts and hyperfine fields resulting from the spectral fits are shown in

TABLE I. Mössbauer spectral hyperfine parameters for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$.

Component	T (K)	H (kOe)	δ (mm/s ^a)	Γ (mm/s)	$\Delta\Gamma$ (mm/s)	% area
Iron(III)	70	9	0.260	1.64	0.23	55 ^b
	65	197	0.299	1.22	1.81	55 ^b
	60	303	0.342	1.31	1.94	55 ^b
	53	355	0.368	1.03	1.53	55 ^b
	45	398	0.378	0.70	1.03	52
	25	440	0.382	0.47	0.70	55
	4.2	454	0.388	0.44	0.66	55
Iron(IV)	70	4	0.200	1.06	0.15	45 ^b
	65	77	0.170	0.58	1.47	45 ^b
	60	150	0.134	0.65	1.64	45 ^b
	53	219	0.099	0.62	1.57	45 ^b
	45	254	0.076	0.48	1.19	48
	25	288	0.062	0.39	0.92	45
	4.2	299	0.057	0.39	0.98	45

^aThe isomer shifts are given relative to room temperature α -iron foil.

^bParameter constrained to the value given.

Figs. 3 and 4, respectively. Clearly, above ~ 50 K the isomer shifts, which are very characteristic of discrete valence iron(III) and iron(IV) ions,¹¹ gradually approach the value obtained for the valence averaged isomer shift at 78 K. Further, the weighted average isomer shift is, as expected, virtually constant between 4.2 and 78 K. The iron(III) and iron(IV) hyperfine fields are typical of these oxidation states and follow the expected magnetization curve, see Fig. 4, and the reduced hyperfine fields show the expected Brillouin behavior. However, it should be noted that the 4.2 K iron(IV) hyperfine field of 299 kOe is somewhat smaller than the 331 kOe value found⁷ in SrFeO_3 , presumably because of the presence of copper(II) which replaces some of the iron and reduces the magnetic exchange interactions.

The Mössbauer spectra of a series of compounds, $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, where x ranges from 0.15 to 0.5, have also been measured at 78 and 295 K and the spectra in most cases resemble those shown in Fig. 1. However, in some cases the 78 K spectrum shows the initial onset of magnetic ordering. More specifically, for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ at 295 K, the La Caër fit yields $\delta = 0.049\langle\Delta E_Q\rangle + 0.107$ mm/s and $\langle\Delta E_Q\rangle = 0.416$ mm/s, $\langle\delta\rangle = 0.127$ mm/s, and a σ of 0.31 mm/s, values which

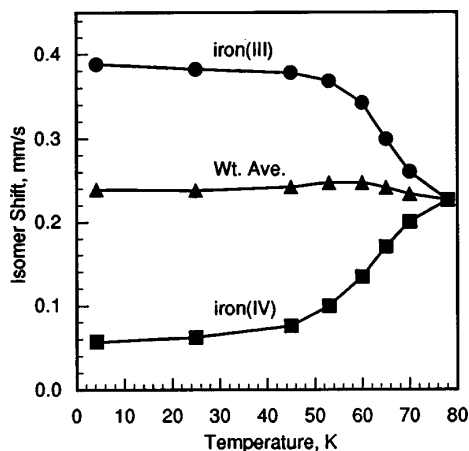


FIG. 3. Temperature dependence of the isomer shifts in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$.

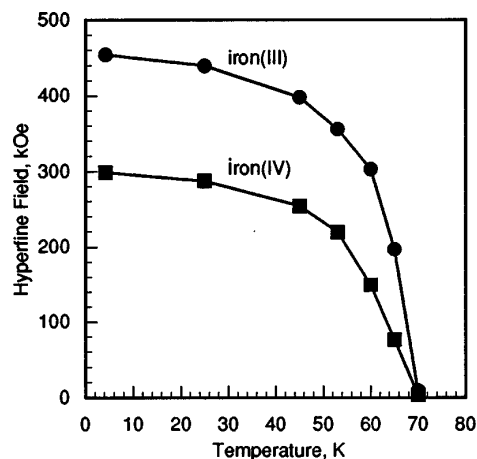


FIG. 4. Temperature dependence of the hyperfine fields in $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$.

are, as expected, quite similar to those given above for $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{2.68}$. In contrast, if $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cu}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ is annealed at 1300 K in an oxygen atmosphere for 12 h, there is a distinct change in the 295 K spectrum and a distribution fit yields $\delta = 0.0528\langle\Delta E_Q\rangle + 0.106$ mm/s and $\langle\Delta E_Q\rangle = 0.550$ mm/s, $\langle\delta\rangle = 0.135$ mm/s, and a σ of 0.38 mm/s. Thus it would appear that, whereas reducing the amount of copper in the compound has relatively little influence upon the local iron electronic environment, annealing in oxygen does have a major influence. At this time further studies between 4.2 and 295 K are in progress in order to determine the influence of the amount of copper and annealing upon the iron(III) to iron(IV) ratio and the magnetic ordering temperature in these compounds.

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