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Simultaneous Probing of the Fe and Co Sites in the CO$_2$-Absorber Perovskite Sr$_{0.95}$Ca$_{0.05}$Co$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$: a Mössbauer Study

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The Co and Fe sites have been probed in pristine and CO$_2$-treated Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ using emission (EMS) and transmission (TMS) Mössbauer spectroscopy and found to have different local oxygen coordination environments and, most probably, a layered arrangement in the lattice. The EMS and TMS spectra of the pristine material could be evaluated with a three-doublet model, with only one of the doublets being different in the two cases. The doublets were assigned to Fe species with localized and delocalized electronic states. Absorption of CO$_2$ at 650 °C resulted in magnetic ordering, which appeared to be static in EMS and rather dynamic in TMS spectra. This difference was attributed to the lower average oxygen coordination number of Co, and therefore ready absorption of CO$_2$ at O vacancies. CO$_2$ treatment at 950 °C triggered partial phase separation, confirmed also by scanning electron microscopy and X-ray microanalysis measurements. It was concluded that absorption of CO$_2$ occurs preferentially in Co-rich regions, where the oxygen vacancy concentration is higher. The Mössbauer data indicated a lower average valence state of Fe/Co atoms in the Co-rich region.

Introduction

ABO$_3$-type perovskites have attracted considerable interest recently because of their special physical and chemical properties. Some members of this family of compounds show such remarkable phenomena as ferroelectricity, colossal magnetoresistance, high-temperature superconductivity, and high catalytic activity.

Starting from the simple cubic lattice structure of CaTiO$_3$, substitution of Ca and Ti by various cations can result in tetragonal and orthorhombic unit cells and in even more complex layered structures. In the original perovskite of A^{II}B^{IV}O$_3$ stoichiometry, the A and B lattice sites can be occupied by metal ions of different valence states and the oxygen stoichiometry of the compound can also vary. These two parameters are obviously not independent of each other. Because the distance between nearest-neighbor cations is rather big and the perovskite structure is based on the close packing of oxygens, the magnetic properties are determined by oxygen-mediated exchange mechanisms such as superexchange[1] and double exchange.[2] As a consequence, any

physical properties of the perovskites that are related to the electron-exchange process are strongly influenced by the average number of oxygen vacancies as well as the binding electrons (related to the valence state of the cations) in a unit cell.

If the oxygen defects tend to get ordered in a special manner, it may promote absorption of small molecules such as CO$_2$.[3,4] This property may find technical application in reducing the industrial CO$_2$ output using these nonharmful perovskites as temporary storage materials for exhaust CO$_2$.

The selection of Ba, Sr, and Ca or a mixture of them for site A and Co and/or Fe for site B results in different CO$_2$ absorption abilities both in thermodynamical and kinetical terms.[4−6] This raises the question of the mechanism of the absorption.

Mössbauer spectroscopy is capable of monitoring the change of the local environment of the Fe atoms in the lattice when the compound absorbs CO$_2$. For example,

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Gibb[7] showed how complex Mössbauer spectra could be observed when only the oxygen stoichiometry was varied in a relatively narrow range in $SrFeO_{3-\delta}$. We have shown recently[6] that the CO_2 absorption abilities of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $Sr_{0.5}Ca_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ were markedly different in favor of the latter compound. Mössbauer spectroscopy could show in that case that $Sr_{0.5}Ca_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ has the structure of brownmillerite with ordered oxygen vacancy arrangement which is more or less preserved even during absorption, and this might be responsible for the easy CO_2 uptake. The brownmillerite structure could be easily recognized through the characteristic local hyperfine magnetic fields at the Fe sites. So, although the primary compositional difference between these compounds was the Sr-to-Ca ratio at site A, the difference in the properties of the compounds could be observed through the Fe atoms at site B, as a result of the structural changes induced by the different A site occupancy. These structural changes had a strong correlation with the oxygen stoichiometry of the compound.

The Fe-to-Co ratio at site B is also decisive in determining material properties, most characteristically the magnetic behavior.[8-10] For example, in $Ba_{0.95}Sr_{0.05}Fe_yCo_{1-y}O_{3-\delta}$, long-range magnetic order at room temperature could be observed only at $y < 0.8$, and the Co content sensitively affected also the catalytic selectivity for coupling of methane into C_2 hydrocarbons.[11] In this case, the probability of the alternative reaction, i.e., the burning of methane into CO_2 at the surface of the catalyst, is expected to depend on how easily the reaction product CO_2 may be accommodated in the perovskite lattice, and thus the complex correlations among the absorption, catalytic selectivity, defect structure, and Co content can be verified.

Using the emission version of ^{57}Fe Mössbauer spectroscopy, where the sample to be studied is doped with ^{57}Co, the parent nuclide of ^{57}Fe, information can be obtained about the environment of the Co atoms in the lattice. It does not, however, mean a direct information about the electronic structure of the Co ions because the Mössbauer spectrum is recorded with the help of the ^{57}Fe atom formed by the $^{57}Co(EC)^{57}Fe$ decay. Because the half-life ($\sim 10^{-7}$ s) of the 14.4 keV excited state of ^{57}Fe (that yields the Mössbauer γ quanta) is quite long as compared to the usual characteristic time of chemical bond vibrations ($10^{-12}-10^{-13}$ s), the "nucleogenic" ^{57}Fe atom accommodates itself in the chemical environment created formerly by the ^{57}Co and forms its own chemical bonds with the neighboring oxygens by the time the Mössbauer γ ray is emitted. This time, however, is certainly not enough for diffusion of lattice oxygens (at room temperature), so the coordination number of ^{57}Co is expected to be preserved for the nucleogenic ^{57}Fe. The newly formed chemical bonds may or may not reflect some hyperfine interactions of the Co parent (e.g., magnetic coupling), so the interpretation of the Mössbauer spectra needs careful consideration

in each case. Regarding the valence state, one expects it to be preserved also because the electron capture formally does not alter the charge balance between the nucleus and the electron shell. However, the electron capture of the ^{57}Co nucleus triggers an Auger cascade, and in certain cases (in highly ionic insulating materials), the presence of aliovalent charge states of the nucleogenic ^{57}Fe can be deduced from the Mössbauer spectra.[12] In perovskite systems, such a phenomenon has not yet been reported and is not even expected because of a high electron mobility in the lattice.

We have selected $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ for a simultaneous transmission and emission Mössbauer study. This compound is particularly suitable for such studies because, due to its own Co content, the external doping technique with radioactive ^{57}Co is free of any uncertainty of the localization of the dopant in the crystal lattice because only a simple isotopic exchange reaction is needed. Furthermore, this compound contains the same amount of Fe and Co, which makes the comparison of transmission Mössbauer spectroscopy (TMS) and emission Mössbauer spectroscopy (EMS) results easier. Some TMS data on $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ have already been published elsewhere.[6]

Experimental Section

$Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ was synthesized with the sol–gel method described elsewhere.[13] The last two sintering steps of the synthesis were performed at 850 °C for 10 h and at 1100 °C for 10 h in air. The samples were slowly cooled, uncontrolled, to room temperature in the furnace. X-ray diffractometry indicated phase-pure $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ with reflections nearly equal to those of cubic $Sr(Co_{0.5}Fe_{0.5})O_3$.[6] Two pellets were prepared. One was used for transmission Mössbauer measurements. For this purpose, the pellet was reground and the Mössbauer absorber was made from the resultant powder, keeping the sample thickness at about 20 mg/cm². The other pellet was used for the emission measurements. A total of 100 MBq of carrier-free $^{57}CoCl_2$ in an aqueous 0.1 M HCl solution was allowed to evaporate to dryness in a plastic vial, and then the $^{57}CoCl_2$ residue was transferred onto the surface of the pellet using about 200 mL of absolute ethanol. The doping was completed by heating the dry pellet in air at 950 °C for 2 h. As the pellet was allowed to cool in air slowly, we consider the two samples (the powder and the doped pellet) to be equal, i.e., to have the same oxygen stoichiometry. The quantity of the $^{57}CoCl_2$ "impurity" added was roughly 1 μg to compare with the 200 mg mass of the pellet.

The nonradioactive sample was used for oxygen deficiency determination by means of cerimetry. According to the titrations, the formula of the compound can be given as $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{2.67\pm0.02}$. More details have been published elsewhere.[6]

The transmission Mössbauer spectra were recorded with a conventional constant-acceleration-type spectrometer (Wissel) using $^{57}Co(Rh)$ as the standard source. For the EMS measurements, a moving standard PFC ($K_4[Fe(CN)_6]\cdot 3H_2O$) absorber was applied with a thickness of 0.5 mg of $^{57}Fe/cm^2$. The observed experimental line width for this absorber was 0.26 mm/s. All isomer shifts are given relative to α-Fe with the sign convention used in the TMS technique.

CO_2-absorption of the samples was carried out in a temperature controlled tube furnace in flowing CO_2. The duration of the treatment was determined on the basis of thermogravimetric analysis (TGA) measurements. It was concluded that a 2 h treatment is satisfactory for saturating the powdered

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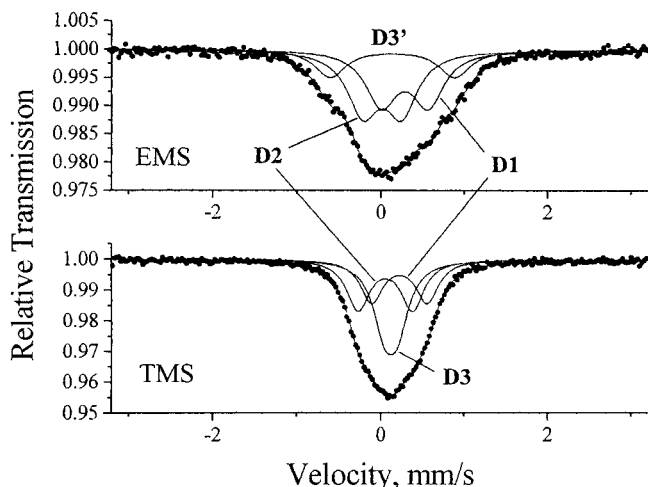
Figure 1. Emission (EMS) and transmission (TMS) Mössbauer spectra of pristine Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ recorded at room temperature, with three-doublet decomposition.

samples with CO$_2$ at all temperatures applied. It was, however, different for the compacted pellet. We observed that when treating the powdered material and the pellet simultaneously in the same furnace, the mass increase of the pellet was only a fraction of that of the powder.

Two temperatures were selected for the CO$_2$ treatments. At 650 °C, the CO$_2$ uptake begins, while at 950 °C, the saturated material already releases some absorbed CO$_2$, according to TGA. In the former case, the samples were slowly cooled in the furnace under CO$_2$. In the latter case, the treated samples were quenched in air by simply opening the furnace and removing the sample, to prevent re-uptake of CO$_2$ during cooling.

The amount of the absorbed CO$_2$ was checked by weighing the samples with an analytical balance. The CO$_2$ uptake proved to be anomalously low for the compacted pellet.

SEM combined with X-ray microanalysis was also used to show possible phase separation upon CO$_2$ treatments. X-ray mapping of 50 × 50 µm spots of the sample was performed in a wavelength dispersive mode.

Results and Discussion

Pristine Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$. The transmission and emission Mössbauer spectra of pristine Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ recorded at room temperature are shown in Figure 1. The spectra could be decomposed into three doublets. Simple Lorentzian line shapes were applied with common line-width parameters within one evaluation.

It has to be mentioned that in our recent publication[6] we reported on a detailed study of the CO$_2$ absorption of this compound and recorded several transmission Mössbauer spectra at different CO$_2$ absorption levels. In that case we used a two-doublet model as a minimum requirement to achieve consistent fits for a series of spectra, all representing low levels of CO$_2$ absorption.

Our new results forced us to apply a more complicated model. Because of the highly overlapping lines, it is difficult to decide which type of evaluation is better because the χ^2 parameter is automatically lower if one uses a higher number of free fitting parameters. It is a fact, however, that when one more doublet was added to the model, the improvement of the relative χ^2 was substantial: it decreased from 1.61 to 1.19. Further-more, Gibb[7] earlier observed three distinct species in slightly oxygen-deficient SrFeO$_{3-\delta}$. Although one of his components with isomer shift δ = 0.36 mm/s was not

Table 1. Room Temperature Mössbauer Parameters of Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ Obtained in Transmission (TMS) and Emission (EMS) Modes^a

mode of measmt	subspectra	isomer shift, δ, mm/s	quadrupole splitting, Δ, mm/s	line width (fwhm, Γ), mm/s	relative area, %
TMS	D1	0.22	0.66	0.32	28.0
	D2	0.06	0.65	0.32	33.0
	D3	0.12	0.16	0.32	39.0
EMS	D1	0.25	0.56	0.45	37.7
	D2	−0.02	0.46	0.45	42.7
	D3'	0.11	1.49	0.45	19.7

^{a} Typical errors are ±0.005 mm/s for δ and Γ, ±0.01 mm/s for Δ, and ±4% for the relative areas.

found in our case, the two other doublets, Y and Z (following his notation) which had been assigned by the author to chemically distinct Fe states in a delocalized electron system, are very similar to our doublets D1 and D2, respectively (Table 1). The strongest argument to choose a three-doublet evaluation in our case is that the emission spectrum of the same compound could be fitted with a minimum of three doublets quite obviously. When the previous two-doublet model was kept for the TMS spectrum, the EMS spectrum would have contained three doublets, each very distinct from any one found in the TMS spectrum. This is very unrealistic. The three-doublet model, however, resulted in a consistent set of parameters to describe both cases, with only one parameter, the quadrupole splitting of the third doublet, being significantly different in TMS and EMS spectra (compare D3 and D3' in Table 1).

For the same reason, we discarded the idea of using a distribution fit for our spectra, although that has been found applicable by Long et al.[14] for the related perovskite La$_{0.2}$Sr$_{0.8}$Cu$_{0.2}$Fe$_{0.8}$O$_{2.68}$ with a Mössbauer spectrum very similar to our TMS spectra, at room temperature.

The common line width of the doublets was a constraint in the evaluations because the poor resolution of the lines did not permit us to evaluate them independently. This results also in rather large parameter correlations which should be taken into account when interpreting concrete values.

There are two important observations common in this family of compounds that should be taken into account in the assignment of the different doublets to appropriate lattice sites and Fe states. One is that there is a general trend that when these compounds are reduced, i.e., when more oxygen defects are introduced, long-range magnetic order appears. This can be explained by the diminished spin fluctuations due to missing oxygens, the concentration of which sets the conditions for the double-exchange coupling between Fe (and Co) spins. In our case, the magnetic structure could not be observed at room temperature, which indicates that the closest environment of Fe in the lattice is relatively oxygen-rich.

The other frequently observed phenomenon among these compounds is the charge disproportionation of Fe^{4+}:

$$2Fe^{4+} \rightarrow Fe^{5+} + Fe^{3+}$$
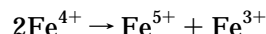
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This has been observed very clearly in $CaFeO_3$,[15,16] $Sr_3Fe_2O_7$,[17,18] $Sr_{2/3}La_{1/3}FeO_3$,[19] and $(Ba,Sr)FeO_3$,[20] although it was not found in $SrFeO_3$ down to 4.2 K.[21]

Gibb pointed out[7] that such a charge disproportionation may not result in integer valence states, but it is much closer to reality to consider it as

$$2Fe^{4+} \rightarrow Fe^{(4-d)+} + Fe^{(4+d)+}$$
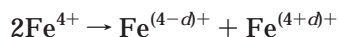
Such a charge disproportionation requires itinerant electrons in the system and results in an unbalanced charge distribution between originally identical lattice sites. In our spectra, it is remarkable that the intensities of doublets D1 and D2 in both the TMS and EMS experiments are roughly equal, and their isomer shifts almost symmetrically differ from that of doublet D3 (or D3′ in the EMS case) to negative and positive directions. Now there is a strong temptation to believe that the origin of doublets D1 and D2 is a process similar to the disproportionation of Fe^{4+}. D1 and D2 are certainly analogous to components Y and Z, respectively, reported in ref 7. Because typical isomer shifts for Fe^{4+} and Fe^{3+} states are around −0.1 and +0.4 mm/s, respectively, D3 cannot be considered as an Fe^{4+} species; its valence state is between +4 and +3, somewhat closer to the former. It follows from our interpretation that species D3 represents the average valence state of Fe in the compound, and its partial disproportionation leads to a state very close to (but lower than) Fe^{4+} (D2) and another one close to Fe^{3+} (D1).

The oxygen stoichiometry of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ was only 2.67 ($\delta = 0.33$) according to cerimetric titrations, which anticipates an average valence state of +3.34 for Fe and Co. Comparison of this value to the average valence state of Fe deduced from the isomer shifts clearly indicates that the valence state of Co should be lower than that of Fe in the pristine compound; it is presumably very close to +3.

The larger difference in the isomer shifts of D1 and D2 in the EMS experiment indicates a somewhat stronger "charge disproportionation" in that case.

The simultaneous presence of the "mother" and its disproportionated states may be explained by assuming that the disproportionation takes place at close to room temperature in this compound, and we observe an intermediate stage. It is worth mentioning that in $Sr_3Fe_2O_7$, which contains double-sheet layers of $[FeO_6]$ octahedra, the disproportionation reaction was observed at 300 K.[17] One can also assume that some microstructural inhomogeneity is responsible for this situation, and the conditions for disproportionation are not ful-

filled everywhere in the lattice. The inhomogeneity can be responsible for the large line widths, causing distribution of the isomer shifts and quadrupole splittings of each species.

When the room temperature data of the TMS and EMS experiments are compared, it is found that there is one significant difference, as has already been discussed in relation with the selected evaluation model: the quadrupole splitting of the central doublet (D3′) in the EMS spectrum is 1.49 mm/s, in sharp contrast with the value of 0.16 mm/s for doublet D3 observed in the TMS experiment.

The fact itself that EMS and TMS spectra of this compound are different (disregarding the model of evaluation) gives information about the spatial distribution of the Co and Fe atoms in the lattice. Taking into account that the compound contains Co and Fe in equal concentrations, there are four border cases which may be considered:

(i) Fe and Co have a perfectly random distribution in the lattice (i.e., at the B sites).

(ii) Fe and Co atoms have two-dimensional separation; i.e., they are ordered in alternating Co and Fe layers.

(iii) Fe and Co have a three-dimensional ordered structure with alternating occupancy of the B sites in all three directions of the lattice.

(iv) The Fe and Co atoms are found in microscopic but separate pockets in the lattice (phase separation).

All of these cases should be considered while keeping in mind that in EMS measurements one uses a nucleogenic ^{57}Fe probe with the coordination environment of the mother nuclide ^{57}Co preserved! The *nearest-neighbor (NN) metal* environments of the normal (TMS) and nucleogenic ^{57}Fe (EMS) are illustrated in Figures 2 and 3.

It can be seen that in case of randomness (i) the average number of NN Fe and Co ions is 3 for both normal and nucleogenic ^{57}Fe (Figure 2). Note that any distinction between the "Fe environment" and "Co environment" is meaningless in this case, and TMS and EMS spectra may be identical. If Co and Fe atoms form alternating layers in the lattice (ii), the Mössbauer spectra should be different. As shown in Figure 2, in the TMS case, the ^{57}Fe probe has 4 planar Fe neighbors and 2 axial Co neighbors. In the EMS case, the situation is reversed, there are 4 planar Co and 2 axial Fe neighbors. In case iii, the three-dimensional alternating occupancy at site B results in all Co neighbors in the TMS and all Fe neighbors in the EMS case (Figure 3). The situation is reversed in case iv, when separation of Co-rich and Fe-rich regions is assumed (Figure 3). TMS and EMS spectra are expected to be different in both cases.

Taking into account only the metal NNs is only a first approximation because the Mössbauer spectra are primarily determined by the oxygen neighbors of the ^{57}Fe probe. Now it follows that, because the oxygen coordination of ^{57}Co is preserved for the nucleogenic ^{57}Fe, one has to take into account the different degrees of oxygen occupancy at lattice sites between NN Fe, between NN Co, and between NN Co and Fe atoms. On the basis of this, some difference between TMS and EMS spectra can be expected also in case i because the original ^{57}Co environment contains 3 Co-Co and 3 Co-Fe NNs while the ^{57}Fe environment contains 3 Co-Fe and 3 Fe-Fe

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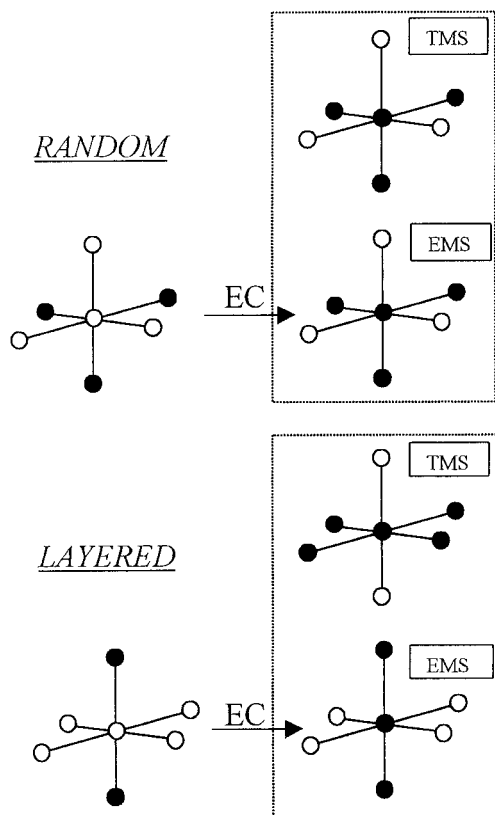
Perovskite Sr₀.₉₅Ca₀.₀₅Co₀.₅Fe₀.₅O₃₋δ

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Figure 2. NN metal environment of normal (TMS) and nucleogenic (EMS) ^{57}Fe atoms in the cubic lattice of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ in the cases of random and layered distribution of Fe/Co. Open and full circles represent Co and Fe, respectively. Oxygens located at the midpoints between metal atoms are not shown.

Figure 3. NN metal environment of normal (TMS) and nucleogenic (EMS) ^{57}Fe atoms in the cubic lattice of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ in the cases of three-dimensional alternating and phase-separated distributions of Fe/Co. Open and full circles represent Co and Fe, respectively. Oxygens located at the midpoints between metal atoms are not shown.

NNs. Case ii is not very much affected by this new consideration, and there will be a sharp contrast between TMS and EMS spectra. In the three-dimensional alternating structure iii, there are only Fe–Co NNs in the whole lattice, so the TMS and EMS spectra may be identical. In this case, however, the fact of Fe or Co NN (our first approximation) will certainly introduce some disparity. Finally, in the case of phase separation iv, the difference between TMS and EMS spectra is trivial, just as in our first approximation.

We can summarize our considerations in three fairly reasonable assumptions (also for future use):

1. The Mössbauer isomer shifts and quadrupole splittings are primarily determined by the number and spatial arrangement of coordinated oxygens; the identity of the NN metal ion (Fe or Co) is of less importance.

2. The magnetic interaction as sensed by the Fe probe depends on the coordinated oxygens *and* the NN ions.

3. In EMS experiments, the relevant oxygen coordination environment of the Fe probe is that of the mother ^{57}Co nuclide, but for evaluating the magnetic interaction, the daughter ^{57}Fe matters.

Whichever approximation is applied, in cases i, iii, and iv the symmetry of the environment of the ^{57}Fe nucleus is basically the same as that in the TMS and EMS experiments. The major difference is found in the relative number of NN Fe and Co and in the occupancy of the six connecting O sites. These differences should be reflected first of all in the isomer shift of the central ^{57}Fe probe. It is only case ii where the environment of
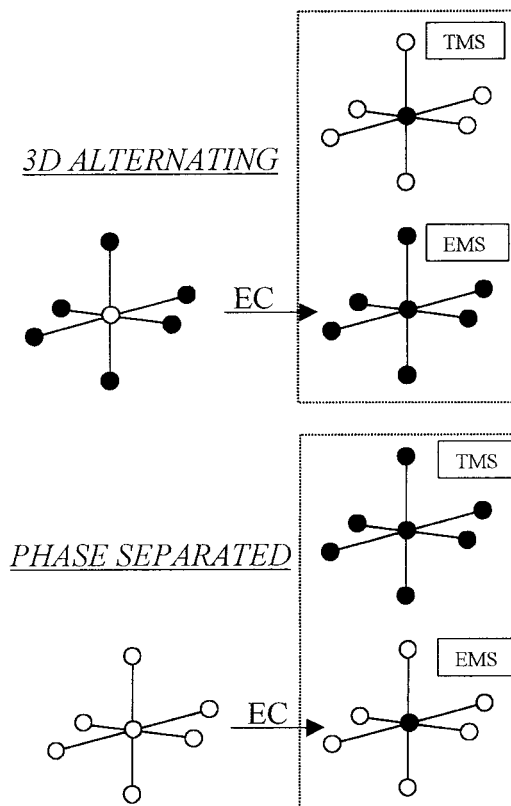
the normal and nucleogenic ^{57}Fe sharply differs in symmetry (opposite tetragonal distortion), and this should be seen in the quadrupole splitting of the corresponding species. (Let us note here that one may consider a fifth case of Fe–Co distribution in the lattice, when Co and Fe atoms are arranged in alternating chains, but this case is symmetrically analogous to case ii only the EMS and TMS cases are exchanged.)

It is interesting to return for a moment to case iv in light of transmission Mössbauer literature data on $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$. As we have discussed already, the TMS spectrum of $SrFeO_{3-\delta}$ contained three doublets at various oxygen stoichiometries ($\delta = 0.15-0.25$),[7] and only two of them seem to appear in the TMS spectrum of our $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{2.67}$ with somewhat different Mössbauer parameters. If phase separation occurs, our EMS spectrum may be compared to the TMS spectrum of $SrCo_{0.99}{}^{57}Fe_{0.01}O_{2.63}$ and $SrCo_{0.99}{}^{57}Fe_{0.01}O_{2.56}$.[22] Despite the very small difference in O stoichiometry of the quoted compounds, there is a big difference between their Mössbauer spectra; i.e., the former one contains two major doublets, and the latter contains only one of those, besides some minor ones (not discussed by the authors). Neither of the two major doublets reported corresponds to any of the doublets found by us in the EMS spectrum of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{2.67}$. This further supports the theory that major phase separation does not occur in our case.

(22) Battle, P. D.; Gibb, T. C. *J. Chem. Soc., Dalton Trans.* **1987**, 667.
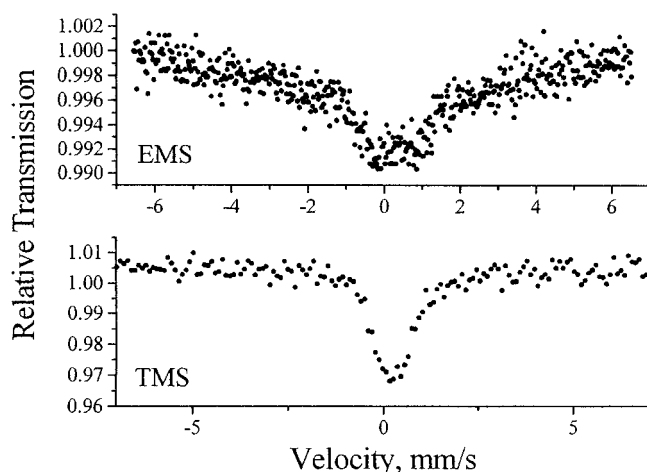
Figure 4. Emission (EMS) and transmission (TMS) Mössbauer spectra of pristine $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ recorded at 80 K.

Figure 5. Room temperature emission (EMS) and transmission (TMS) Mössbauer spectra of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ after CO_2 treatment at 650 °C.

On the basis of this argumentation, we can conclude that, most probably, the Co and Fe atoms form alternating layers in the $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ perovskite lattice, and this is the reason for the markedly different quadrupole splittings of species D3 and D3′ in the TMS and EMS spectra, respectively. It is noteworthy that $SrFeO_{2.5}$ has the brownmillerite structure with alternating layers of octahedrally and tetrahedrally coordinated Fe^{3+} sites. When half of the Fe is replaced by Co, which tends to acquire a lower valence state and, therefore, a lower coordination number than Fe, it is at least not very surprising to observe a layered structure. (This is the primary reason of why we do not consider seriously the "fifth" case briefly mentioned above, when the Co and Fe atoms are arranged in alternating chains instead of sheets.)

It is remarkable that the difference in the quadrupole splittings (between EMS and TMS experiments) is not observed in the disproportionated states D1 and D2. A possible explanation is that charge disproportionation requires an extended covalency of the lattice, i.e., a long-range interaction in the Fe sublattice. Such an interaction may reduce local asymmetries in the electron density distribution around the Fe nuclei. It appears that species D3 (D3′) is sensitive to the local charge distribution because it corresponds to a local state, while species D1 and D2 are insensitive to it because of significant valence electron delocalization.

As was mentioned earlier, the observation of long-range magnetic order in these compounds can also be indicative of the local oxygen and metal environment of the Mössbauer probe atom. There was no sign of magnetism at room temperature, so the samples were measured also at 80 K (Figure 4). Despite the much poorer statistics as compared to the room temperature measurements, it is clear that the TMS spectrum still does not show any magnetism, while the formation of a magnetic structure is clearly under way in the EMS case at 80 K. Based on the observed tendency of magnetic ordering upon an increase in the number of oxygen vacancies in related compounds, this observation is practically in agreement with all models shown in Figures 2 and 3. Although it would be very difficult to make a quantitative statement about the tendency of magnetic ordering, based purely on the relative number
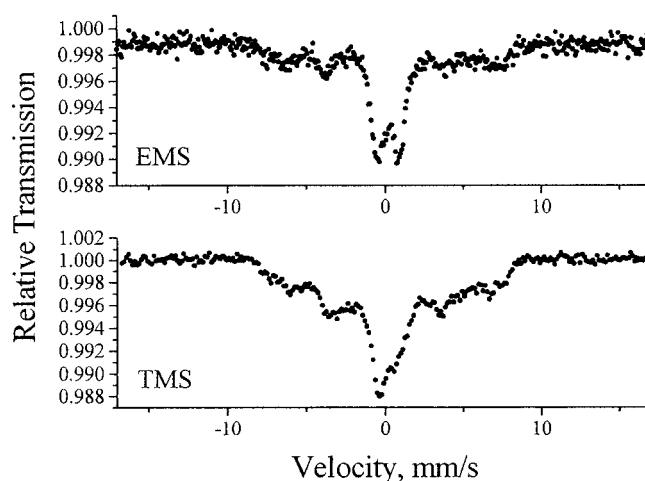
of Co−O−Fe and Fe−O−Fe exchanges, one may expect a more significant difference between the EMS and TMS experiments in the three-dimensional alternating iii and the phase-separated iv models and no difference at all in the random i model. Thus, our observation would also support the existence of Co and Fe layers in the lattice. However, the different oxygen occupancies complicate the picture, and a firm conclusion from this observation only should not be drawn.

In the case of a layered structure, one would anticipate a lower than cubic symmetry for the lattice. It is possible that the lattice is composed of a mixture of tetragonal or orthorhombic microdomains, while, macroscopically, the system appears to be cubic for X-ray diffraction (XRD). This behavior is not unknown for perovskites. It has been shown by theoretical calculations for Fe-doped $YBa_2Cu_3O_{7-\delta}$ that a macroscopically tetragonal structure (as seen by XRD) can originate from a randomly oriented ensemble of orthorhombic microdomains.[23]

CO_2-Treated $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$. Figure 5 shows the TMS and EMS spectra of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$, recorded at room temperature.

Before the two spectra are compared, let us recall that, although the TMS and EMS specimens were treated simultaneously in the same furnace, the observed mass increase for the EMS pellet was meaningless; i.e., the percentage increase was about one-tenth of that observed in the powdered sample (TMS). This means that the penetration of CO_2 into the compacted pellet was significantly hindered. However, Mössbauer emission spectroscopy is sensitive to the upper 20−30 μm thick surface layer of these samples because of the strong absorption of the 14.4 keV γ-rays. Thus, we assumed that a treatment similar to that used in the case of the powdered material corresponds to a saturation absorption in the surface layer of the pellet as well, and thus the transmission and emission Mössbauer spectra of the CO_2-treated samples are comparable.

According to the powdered material (TMS sample), the amount of the absorbed CO_2 was 0.43 m/m % only

(23) Baumgartel, G.; Jensen, P. J.; Bennemann, K. H. *Phys. Rev. B* **1990**, *42*, 288.
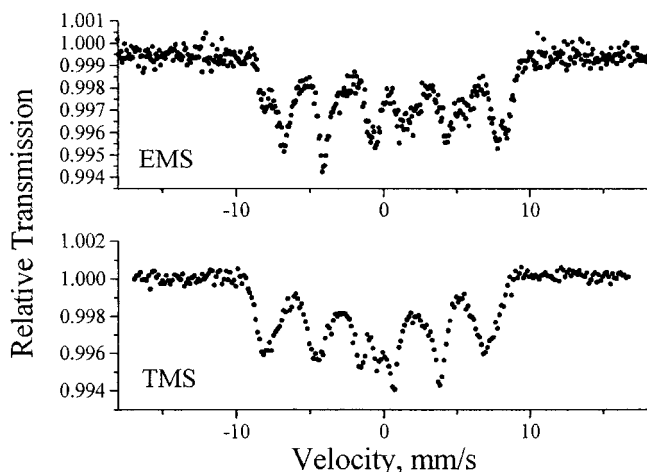
Figure 6. Emission (EMS) and transmission (TMS) Mössbauer spectra of Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ after CO$_2$ treatment at 650 °C, recorded at 80 K.

at 650 °C.[6] As can be seen, the TMS spectrum reveals a complicated magnetic structure, indicating relaxing species most probably combined with the distribution of a hyperfine magnetic field.

The appearance of magnetic order is obviously due to the absorption of CO$_2$, as was already observed by us in (Ba,Ca)(Fe,Co)O$_{3-\delta}$ earlier.[24] However, at 650 °C, some oxygen loss is expected when the material is heated, and oxygen loss can also induce magnetic ordering. The most likely mechanism of CO$_2$ uptake at this level is the absorption of stick-shaped CO$_2$ molecules in channels of ordered O defects.[4] CO$_2$ seems to play a role similar to that of the absence of oxygen: it blocks fast electron transfer between metal ions, which inhibits magnetic fluctuations and helps form static long-range order of spins.

The EMS spectrum is basically different from the TMS one. The lines are broad (>1 mm/s), but the spectrum could be evaluated by static approximation, i.e., with Lorentzian doublets and sextets instead of a relaxational line shape. A very formal fit including one sextet and one doublet resulted in $\delta = 0.22$ mm/s and $\Delta = 1.25$ mm/s for the doublet and $\delta = 0.29$ mm/s and $B = 41.3$ T with quadrupole shift $\epsilon = -0.15$ mm/s for the sextet.

The low-temperature spectra (Figure 6) revealed the same difference. While the envelope of the TMS spectrum showed signs of magnetic relaxation or distribution of a hyperfine field, the EMS spectrum could be fitted with three sextets with reasonable Mössbauer parameters, isomer shifts of 0.19, 0.29, and 0.41 mm/s and magnetic fields of 36.9, 45.2, and 51.2 T, respectively. Some residual paramagnetic doublets were also present.

The most characteristic difference between the TMS and EMS experiments is, therefore, the appearance of dynamic (relaxing) or static magnetic interaction. It appears that the nucleogenic ^{57}Fe, with its heritage of the poorer oxygen environment of ^{57}Co, accommodates CO$_2$ molecules in its vicinity much more easily than the regular Fe and participates in long-range magnetic order more readily.
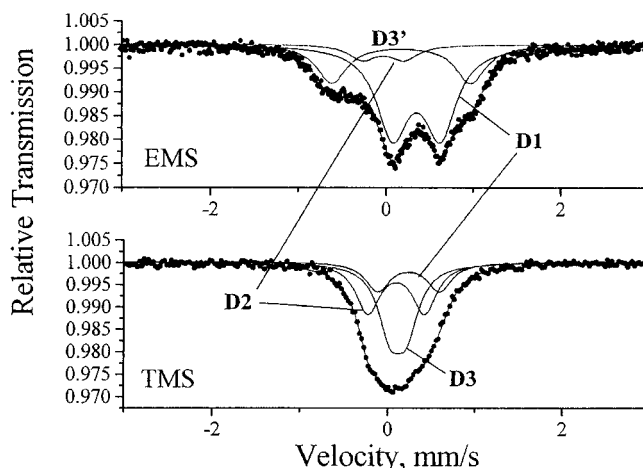
(24) Homonnay, Z.; Nomura, K.; Juhász, G.; Vértes, A.; Ujihira, Y. *J. Radioanal. Nucl. Chem.* **1999**, *239*, 291.

Figure 7. Room temperature emission (EMS) and transmission (TMS) Mössbauer spectra of Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ after CO$_2$ treatment at 950 °C followed by rapid cooling to room temperature.

Table 2. Room Temperature Mössbauer Parameters of Sr$_{0.95}$Ca$_{0.05}$Fe$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ Obtained in Transmission (TMS) and Emission (EMS) Modes after Treatment in CO$_2$ at 950 °C for 3 h^a

mode of measmt	subspectra	isomer shift, δ, mm/s	quadrupole splitting, Δ, mm/s	line width (fwhm, Γ), mm/s	relative area, %
TMS	D1	0.24	0.71	0.33	20.8
	D2	0.10	0.65	0.33	35.8
	D3	0.12	0.19	0.33	43.4
EMS	D1	0.32	0.55	0.41	60.4
	D2	−0.03	0.58	0.41	13.4
	D3′	0.14	1.62	0.41	26.2

^{a} Typical errors are ±0.005 mm/s for δ and Γ, ±0.01 mm/s for Δ, and ±4% for the abundances.
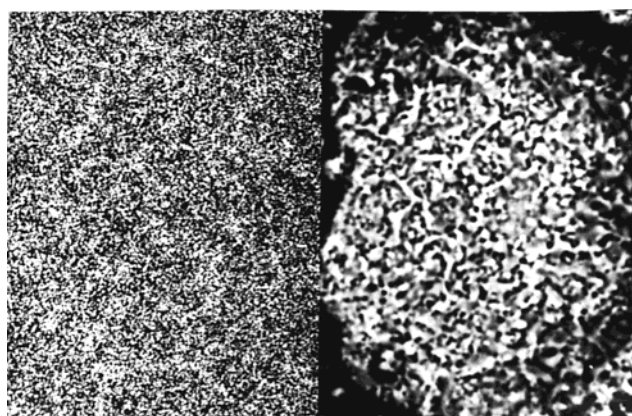
The samples heated in CO$_2$ at 950 °C for 2 h retained 4.37 m/m % CO$_2$ (according to the measurement of the powdered sample). Mössbauer spectra were recorded at room temperature only (Figure 7).

It can be seen already from the envelope of the spectra that, despite the more than 4% CO$_2$ absorbed, they look like those recorded before any absorption. Evaluation revealed three components with parameters similar to those found in the pristine compound but with different abundances (Table 2).

The similarity of the TMS spectra before and after CO$_2$ absorption is especially striking. They can be considered to be equal within experimental error, and it looks as if some kind of a rejuvenation treatment of the sample occurred. Only the relative amount of species D2 seems to have increased a little bit at the expense of D1 in the TMS spectrum. This shift between the amounts of the species D1 and D2 is very high in the EMS spectrum, and this time it is in favor of D1. This may indicate a net transfer of charge between the Co and Fe sublattices.

However, the very fact that the EMS spectrum changed and the TMS spectrum did not shows that the absorbed CO$_2$ molecules got localized near Co atoms and not near Fe atoms. It is also interesting that these spectra do not indicate magnetism at more than a 4% absorption level while magnetic ordering occurred at 0.4% CO$_2$ already. We attributed this earlier to order/disorder processes of oxygen vacancies or Co/Fe atoms or absorbed CO$_2$ molecules, at high temperature.[6]
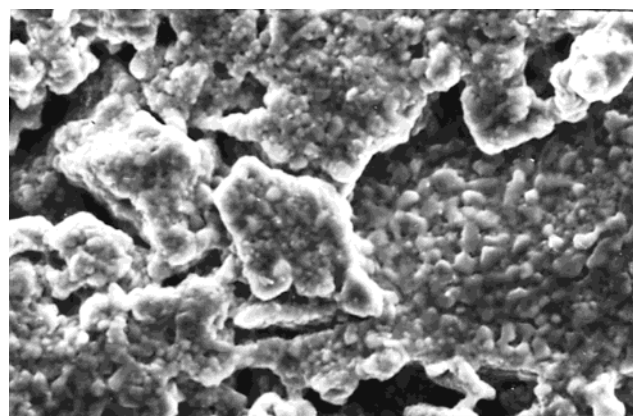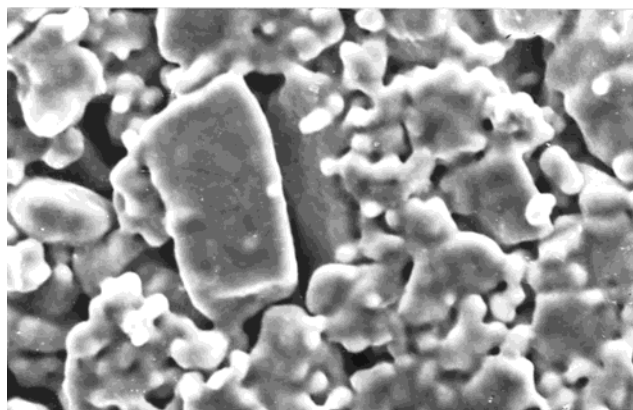
Figure 8. SEM image of $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ after absorption of CO_2 at 800 °C for 3 h (bottom) and at 950 °C for 3 h (top).

Figure 9. X-ray map of Co Kα (top left) and Fe Kα (bottom left) with the corresponding backscattered electron images (right) of the same $Sr_{0.95}Ca_{0.05}Fe_{0.5}Co_{0.5}O_{3-\delta}$ grain surface area. Separation of Co- and Fe-rich zones can be observed.

From among our models describing the distribution of Co and Fe in the lattice, neither i nor ii or iii could account for the different behavior of TMS and EMS spectra because, in these models, Fe and Co are finely dispersed in the lattice, and it would not be possible that only Co senses the effect of CO_2 while Fe does not. Therefore, phase separation must have occurred.

To verify this, we carried out SEM and X-ray microanalysis measurements on samples treated in CO_2 at 800 and 950 °C. (800 °C is still below the temperature of maximum absorption rate and capacity of the compound.[6]) The results are illustrated in Figures 8 and 9. The X-ray maps of Co Kα and Fe Kα radiation (recorded by a wavelength dispersive spectrometer) for the sample treated at 950 °C revealed a slight inhomogeneity in the Fe-to-Co ratio, which is a sign of the beginning of phase separation (Figure 9). Inhomogeneity was not observed after the 800 °C treatment.

There is one question yet to be answered, namely, if Co and Fe get separated in the lattice, how is it possible that only the EMS spectrum has a major change? The presence or absence of absorbed CO_2 is not enough explanation because the Fe-to-Co ratio in the environment of the Mössbauer probe changes for the normal Fe probe also (TMS). To resolve this controversy, one can assume that the oxygen coordination environment of the normal Fe probe, which primarily determines the Mössbauer parameters (our first assumption), is saturated in every case. It does not necessarily mean sixfold coordination; it may only correspond to the case of $SrFeO_{3-\delta}$. It is quite logical to accept that, in the sample treated at 950 °C, where CO_2 molecules are localized mainly in Co-rich regions, simultaneously, the Fe atoms in the Fe-rich regions retain the oxygen environment they have had in the layered structure, which is actually very similar to that in $SrFeO_{3-\delta}$. This assumption gives ready explanation for the close resemblance of the TMS spectrum of our pristine and CO_2-treated (at 950 °C) samples and that of pure $SrFeO_{3-\delta}$.[7]

Finally, according to the EMS measurements, the relative weight of species D1, which represents the lowest valence state, increased after the treatment at 950 °C (Table 2). It perfectly fits into our scenario because the Co-rich region is the one where a lower oxidation state is expected, and because this means more oxygen vacancies, it means also more room for CO_2 molecules to be accommodated.

Thus, when the effect of CO_2 absorption is summarized, it appears that CO_2 absorption at high temperature triggers decomposition of the layered structure and Co and Fe start precipitating into separate pockets. This is not seen in the TMS Mössbauer spectra because the oxygen coordination environment of Fe is saturated, and the Fe probe is not sensitive to changes in the lattice at a distance larger than the first coordination sphere. Because the average coordination number for Co was lower already in the pristine compound, the Co-enriched

regions have relatively large oxygen deficiency, so the average valence state decreases only here, and CO_2 absorption takes place also in this defect-rich lattice.