

An Investigation of Non-stoichiometry in the Systems SrFeO_{3-y} and SrCoO_{3-y} by Iron and Cobalt *K*-Edge Extended X-Ray Absorption Fine Structure Spectroscopy†

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A series of samples in the SrFeO_{3-y} (perovskite and brownmillerite) and SrCoO_{3-y} (hexagonal and brownmillerite) systems has been studied by extended X-ray absorption fine structure spectroscopy. In the cobalt system, evidence has been found for the existence of face-sharing CoO_6 octahedra in the substoichiometric low-temperature phase $\text{H-Sr}_2\text{Co}_2\text{O}_{5+x}$, and for both face- and edge-sharing CoO_6 octahedra in $\text{H-Sr}_2\text{Co}_2\text{O}_{5+x}$. In the iron system, the perovskite phases show only corner-sharing polyhedra, and the short-range structure is seen to be more closely related to the brownmillerite structure.

There is currently a great deal of interest in the perovskite-related materials ABO_{3-y} , where A is Ca, Sr, or Ba and B is a first-row transition metal, because of their wide range of possible applications as electrode materials and as catalysts. The ability of the transition metal to exist as both B^{4+} and as B^{3+} , and of the anion sublattice to accommodate a high concentration of vacancies, frequently results in the adoption of perovskite-related structures over the composition range $0 \leq y \leq 0.5$. The relationship between the stoichiometry and the detailed structure of the material is often complex. Compounds having the exact composition ABO_3 usually consist of an infinite three-dimensional network of corner-sharing BO_6 octahedra with the A cations occupying twelve-coordinate sites, whereas the anion sublattice in materials having the formula $\text{ABO}_{2.5}$ usually consists of an ordered arrangement of oxide ions and vacancies. In manganese compounds, e.g. $\text{SrMnO}_{2.5}$ and $\text{CaMnO}_{2.5}$, the ordering is such as to leave the transition metal in five-co-ordination.^{1,2} However, $\text{CaFeO}_{2.5}$, $\text{SrFeO}_{2.5}$, and the high-temperature phase $\text{B-SrCoO}_{2.5}$ all adopt the orthorhombic brownmillerite structure,³ with equal numbers of trivalent transition-metal cations in alternate layers of distorted BO_6 and BO_4 corner-sharing polyhedra.⁴⁻¹⁰ The compound $\text{SrCoO}_{2.5}$ is unique in that it adopts, below 850 °C, a poorly characterised phase of supposedly hexagonal symmetry, $\text{H-SrCoO}_{2.5}$.^{7,8} The crystal structure of this phase is unknown, although we have recently investigated¹⁰ the two polymorphs of $\text{SrCoO}_{2.5}$ by extended X-ray absorption fine-structure (EXAFS) spectroscopy, and found the first clear evidence that $\text{H-SrCoO}_{2.5}$, or $\text{H-Sr}_2\text{Co}_2\text{O}_5$, is not merely a modified brownmillerite network of corner-sharing polyhedra, but that short Co-Co distances (2.46 Å) are present, consistent with the presence of a significant number of face-sharing CoO_6 octahedra.

In this paper we report the results of our EXAFS experiments on samples of the non-stoichiometric system SrCoO_{3-y} , $y \neq 0.5$, and compare them to results obtained for SrFeO_{3-y} .

Experimental

Samples of SrCoO_{3-y} were prepared from accurately weighed amounts of spectroscopic grade Co_3O_4 and SrCO_3 , ground together in a ball mill, pressed into a pellet, and fired under a

variety of conditions. The stoichiometries of the products were determined by volumetric analysis.⁹ Sample 1, $\text{SrCoO}_{2.63}$, was fired in air at 1 250 °C for a total of 10 d with one intermediate grinding, before being slowly cooled to room temperature. Sample 2, $\text{SrCoO}_{2.56}$, was prepared from sample 1 by annealing at 900 °C for 24 h before quenching to room temperature. Samples 1 and 2 were both doped with ca. 1% of iron isotopically enriched in ^{57}Fe , and their characterisation by Mössbauer spectroscopy has been reported previously.⁹ Sample 3, $\text{SrCoO}_{2.38}$, was heated under flowing argon at 1 200 °C for 1 d before annealing at 700 °C for 1 d, 670 °C for 3 d, and cooling to room temperature, always under argon. Samples of SrFeO_{3-y} were prepared in a similar manner from spectroscopic grade Fe_2O_3 and SrCO_3 . Sample 4, $\text{SrFeO}_{2.83}$, was annealed in air at 1 250 °C and cooled at 30 °C h⁻¹ to 200 °C, and sample 5, $\text{SrFeO}_{2.80}$, was annealed in air at 920 °C for 2 d before quenching to room temperature.

Initial characterisation of the products was by X-ray powder diffraction. Samples 1–3 all gave similar but slightly different patterns with broad lines typical of the 'hexagonal' phase $\text{H-SrCoO}_{2.5}$. It has still not proved possible to index the patterns in a satisfactory way; there was no evidence of contamination by Co_3O_4 as has been suggested recently.¹¹ Samples 4 and 5 gave diffraction patterns characteristic of a tetragonally distorted perovskite structure. The latter two samples were also characterised by ^{57}Fe Mössbauer spectroscopy and it was clear that the local environment around the transition-metal ions in sample 4 was very similar to that in sample '1a' ($\text{SrFeO}_{2.84}$) discussed in an earlier publication,¹² and that the environment in sample 5 was very similar to that in sample '2b' ($\text{SrFeO}_{2.76}$), although sample 5 has a significantly higher oxygen content. Samples 4 and 5 thus represent the two extremes of the observed defect structure of the SrFeO_{3-y} phase.

Room-temperature EXAFS spectra of samples 1–3 were recorded at the cobalt *K* edge (1.608 11 Å, 7.710 keV) using the Daresbury synchrotron radiation source, running at an energy of 2.0 GeV and an average current of 190 mA. Similarly, spectra of samples 4 and 5 were recorded at the iron *K* edge (1.743 34 Å, 7.112 keV). In all cases data were recorded in the transmission mode on station 7.1, with the finely ground, undiluted samples contained between strips of adhesive tape. The data-reduction procedures, including background subtractions and phase-shift calculations, have been described previously.^{13,14} The reliability of the latter for the cobalt system has already been established.¹⁰ The compound FePO_4 , which has a well defined¹⁵ berlinite

† Non-S.I. unit employed: eV = 1.6×10^{-19} J.

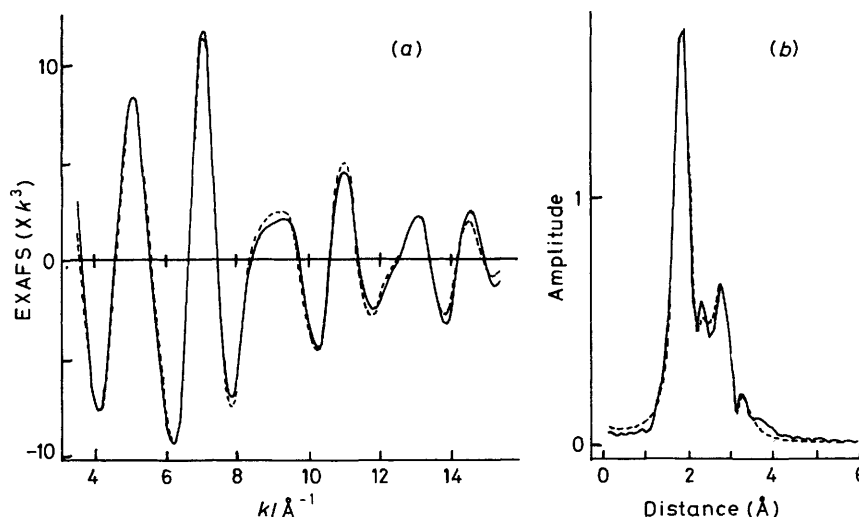


Figure 1. Observed (—) and calculated (---) Fourier-filtered EXAFS data (a) and the corresponding Fourier transforms (b) for sample 1, $\text{SrCoO}_{2.63}$

Table 1. Refined structural parameters of sample 1, $\text{SrCoO}_{2.63}$, from Co-K EXAFS data

Atom type	Average co-ordination number	$2\sigma^2/\text{\AA}^2$	Radial distance (Å)
O	6	0.010	1.89
Co	1	0.013	2.43
Co	1	0.006	2.81
Sr	1.5	0.021	3.19

Table 2. Refined structural parameters of sample 2, $\text{SrCoO}_{2.56}$, from Co-K EXAFS data

Atom type	Average co-ordination number	$2\sigma^2/\text{\AA}^2$	Radial distance (Å)
O	6	0.010	1.89
Co	1	0.012	2.43
Co	1	0.009	2.82
Sr	3.5	0.023	3.19

structure, was used to demonstrate the validity of our calculated iron–oxygen phase shifts. The data on the cobalt-containing samples 1 and 2 were Fourier-filtered to include only the first four shells and those on sample 3 to include only the first three shells, cut-offs which can be made without causing large truncation effects and which are not complicated by overlapping Fourier-transform shells. The filtered data were fitted by a least-squares procedure in reciprocal space using the curved-wave approximation for $\chi(k)$, the EXAFS amplitude,¹⁶ which was weighted by k^3 , where k is the photoelectron wave vector. We estimate the following levels of accuracy in our refinements: co-ordination number, $\pm 50\%$; Debye–Waller factor, $\pm 50\%$; and radii, ± 0.02 Å. These are estimates of the errors arising from imperfect transferability of phase shifts and the fitting procedure described below. Statistical fitting errors are far smaller. The data on the iron-containing samples 4 and 5 are presented below simply as the phase-shift corrected raw, *i.e.* unfiltered, data and their Fourier transforms. No calculated curves are presented for the SrFeO_{3-y} system because the following discussion will focus on the structural properties of the SrCoO_{3-y} system, and the data for samples 4 and 5 will be used only to demonstrate that the two systems are very different.

Results and Discussion

Figure 1(a) and (b) show the observed and calculated Fourier-filtered cobalt EXAFS and their Fourier transforms for sample 1, $\text{SrCoO}_{2.63}$. In our previous work¹⁰ on $\text{B–SrFeO}_{2.5}$ we were able to use the known brownmillerite structure as a model to analyse the data with a high degree of confidence. However, there are no structural data available for these hexagonal

materials, nor any direct evidence regarding the co-ordination polyhedra. Therefore, the approximate occupation numbers of the various co-ordination shells were determined in preliminary fits by allowing the co-ordination number and Debye–Waller factor to refine. They were then held constant at the nearest half-integer value during final refinements of the shell radius and the Debye–Waller factor, thus leading to the rather high estimated error of 50% discussed above. The refined structural parameters are listed in Table 1. The first co-ordination shell, 1.89 Å distant from the central cobalt atom, is assigned as an oxygen shell and the second shell at a distance of 2.43 Å is a shell of Co atoms. These assignments are consistent with the previous work¹⁰ on $\text{H–SrCoO}_{2.5}$ where it was concluded that the structure contains face-sharing CoO_6 octahedra in addition to the corner-sharing polyhedra found in both the brownmillerite and perovskite structures. However, the co-ordination shell 2.81 Å distant from the central Co atom was not seen in $\text{H–SrCoO}_{2.5}$, and it can be attributed to the presence of edge-sharing octahedra in the partially oxidised sample 1. The assignment of the co-ordination shell at a radius of 3.19 Å as a strontium shell is totally consistent with a perovskite-related structure where the Co–Sr distance is ideally $\sqrt{3}a_0/2$ and the unit-cell parameter is $a_0 \approx 3.9$ Å.

The results of the data analysis on sample 2, $\text{SrCoO}_{2.56}$, are presented in Figure 2(a) and (b) and Table 2. A similar fitting procedure was used, and the results are very similar to those obtained for sample 1. Again the first two co-ordination shells contain oxygen and cobalt, at distances of 1.89 and 2.43 Å respectively, and the cobalt shell of 2.82 Å is clearly present. The peak at a radius of 3.19 Å has increased in intensity (the co-ordination number has doubled with a similar Debye–Waller

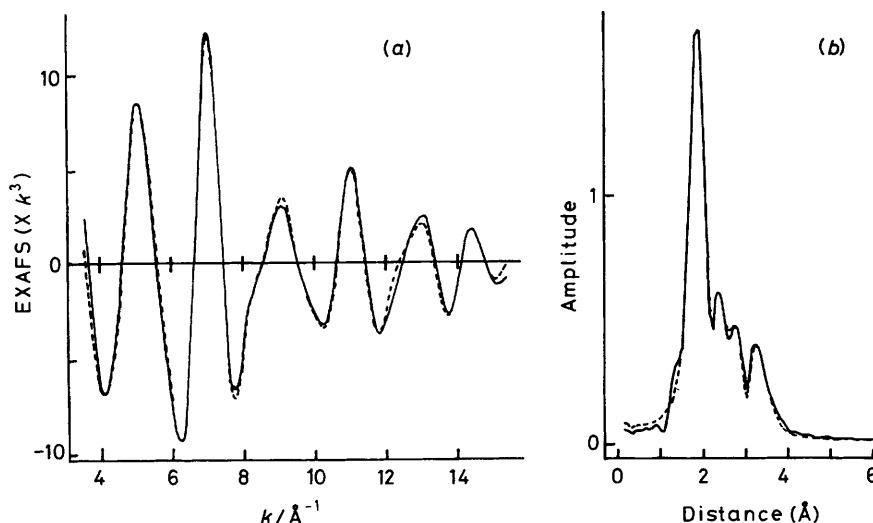


Figure 2. Observed (—) and calculated (---) Fourier-filtered EXAFS data (a) and the corresponding Fourier transforms (b) for sample 2, $\text{SrCoO}_{2.56}$

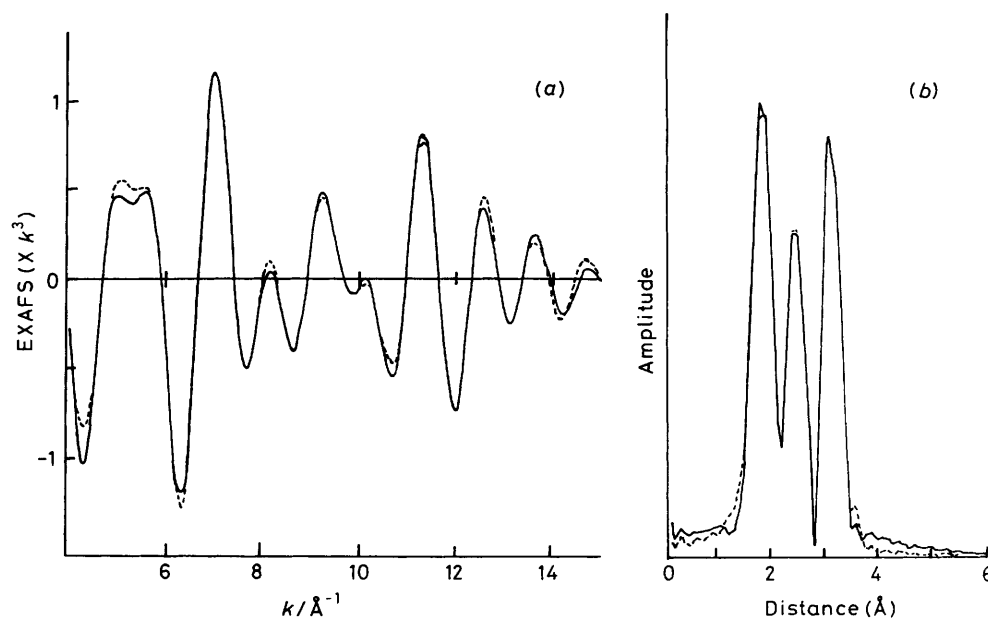


Figure 3. Observed (—) and calculated (---) Fourier-filtered EXAFS data (a) and the corresponding Fourier transforms (b) for sample 3, $\text{SrCoO}_{2.38}$

factor) compared to the corresponding peak for sample 1, thus implying that the strontium shell is more ordered in sample 2. However, it should be noted that in a true perovskite lattice the cobalt is surrounded by eight strontium cations, and the refined co-ordination numbers for the shell at 3.2 Å indicate that both samples have highly disordered structures.

The results of the experiments on sample 3, $\text{SrCoO}_{2.38}$, presented in Table 3 and Figure 3(a) and (b), are quite different from those discussed above. The first oxygen co-ordination shell has a considerably lower amplitude and refinements of the occupation number resulted in an average co-ordination number of 3.4, whereas a best-integer value of 6 was found for samples 1 and 2. Furthermore, although this sample apparently contains face-sharing CoO_6 octahedra as indicated by the presence of a Co–Co distance of 2.47 Å, there is no evidence for a Co–Co distance of *ca.* 2.8 Å implying the absence of edge-

Table 3. Refined structural parameters of sample 3, $\text{SrCoO}_{2.38}$, from Co-K EXAFS data

Atom type	Average co-ordination number	$2\sigma^2/\text{Å}^2$	Radial distance (Å)
O	3.4	0.011	1.88
Co	1	0.008	2.47
Sr	2	0.010	3.14
O	5	0.013	3.37

sharing octahedra. However, the Fourier-transform peak corresponding to a co-ordination shell *ca.* 3.2 Å distant from the cobalt atom is considerably enhanced compared to the same feature in the spectra of samples 1 and 2. It has been treated as

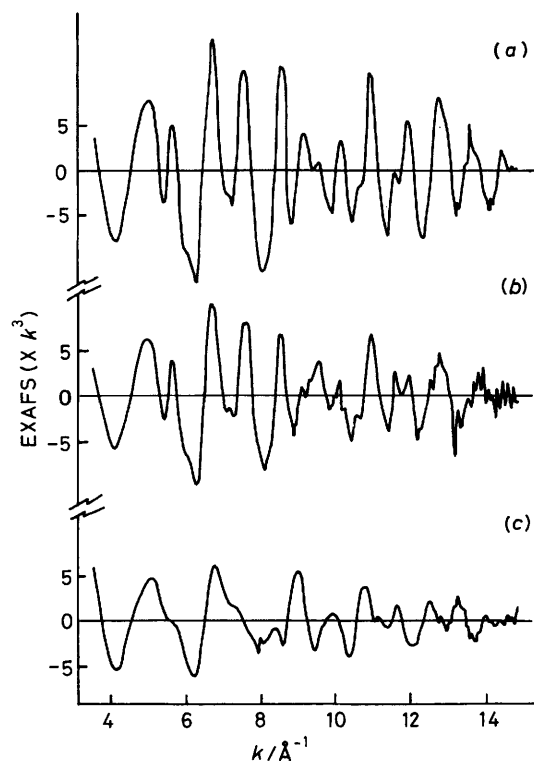


Figure 4. Observed k^3 -weighted EXAFS data (a) sample 4, $\text{SrFeO}_{2.83}$, (b) sample 5, $\text{SrFeO}_{2.80}$, and (c) $\text{SrFeO}_{2.5}$

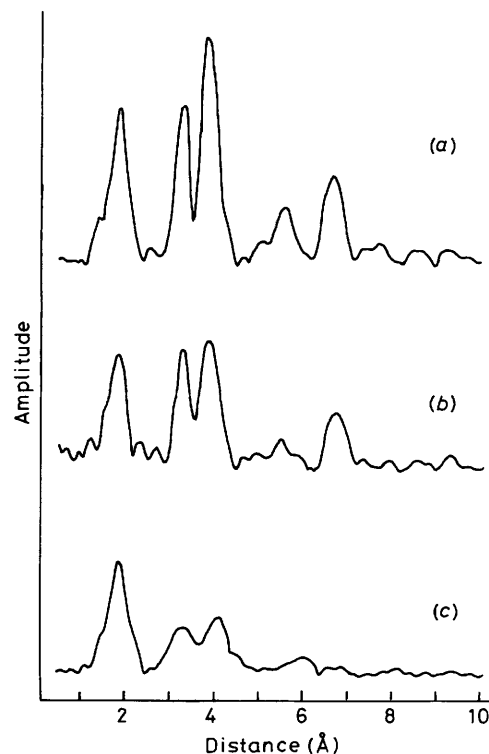


Figure 5. The Fourier transform of the observed EXAFS data for (a) sample 4, (b) sample 5, and (c) $\text{SrFeO}_{2.5}$

two overlapping peaks, one derived from a strontium shell at 3.14 Å and the other due to an oxygen shell at 3.37 Å. The results presented in Table 3 are thus very similar to those reported previously¹⁰ for $\text{H-SrCoO}_{2.5}$, with the exception of the reduced number of nearest-neighbour oxygen atoms around a cobalt atom, consistent with the lower oxygen analysis for this sample.

It is interesting to compare the spectra of samples 1–3 with those of the iron-containing materials. EXAFS data for $\text{B-SrFeO}_{2.5}$ have been referred to in a previous paper,¹⁰ and were successfully analysed using the known crystal structure. This confirmed the validity of the data-reduction techniques which were applied to the new materials. The k^3 -weighted observed EXAFS spectra and the Fourier transforms are shown in Figures 4 and 5 for sample 4, $\text{SrFeO}_{2.83}$, and sample 5, $\text{SrFeO}_{2.80}$. In both cases, the observed spectra can be described in terms of a perovskite-related structure. The maxima at *ca.* 1.9, 3.3, and 3.9 Å can be assigned to iron–oxygen, iron–strontium, and iron–iron distances respectively. The relatively large width of the first maximum in the Fourier transform suggests that a broad spread of iron–oxygen distances is present, consistent with the occurrence of both octahedrally and tetrahedrally coordinated iron, as was predicted in an earlier Mössbauer study.¹² However, the spread of distances observed in these materials, whose structural details are unknown, renders a meaningful quantitative analysis of the EXAFS spectrum impossible. The spectra of brownmillerite $\text{SrFeO}_{2.5}$ are also shown for comparison. Although the Fourier-transform peaks do not shift in position on going from sample 4 to 5, there are large amplitude differences between the two spectra, both of which show marked differences from that of $\text{SrFeO}_{2.5}$. The change in the total intensity of the first maximum can be attributed to the increase in oxygen content on moving from $\text{SrFeO}_{2.5}$ to samples 4 and 5. The data for the last two samples,

but not for the first, include peaks of significant amplitude at radii greater than 5 Å. This increase in amplitude can be attributed to multiple scattering effects which increase in importance as the angle between one back scatterer and another approaches 180°, *i.e.* the structure approaches that of a cubic perovskite. The peak at *ca.* 3.9 Å (presumed to be due to Fe–O–Fe) and those at *ca.* 5.9 Å (Fe–O–Fe–O) and 6.8 Å (Fe–Sr–Fe) are considerably enhanced by this phenomenon. The presence of these high-radius features, which are not present in the data (not shown) for the SrCoO_{3-y} system, indicates that although the co-ordination distances around Fe in SrFeO_{3-y} show only slight changes upon oxidation, the angular distribution of the co-ordinating atoms changes markedly. This conclusion is consistent with an earlier Mössbauer study,¹² where samples 4 and 5 were found to have very different spectra (Mössbauer spectroscopy, *via* the quadrupole interaction, is strongly affected by the angular distribution and thus can be used to observe directly distortions in polyhedra). In view of the somewhat inadequate resolution of the EXAFS technique for this problem, any conclusions which are drawn must be qualitative in nature. The most striking contrast between the spectra of the cobalt samples 1–3 and those of the iron samples 4 and 5 is that there are no features above noise level in the latter indicative of either face- or edge-sharing polyhedra. It appears that the two systems SrCoO_{3-y} and SrFeO_{3-y} are structurally very different.

Conclusions

The EXAFS results described above lead to the conclusion that when the cobalt(III) oxide $\text{H-SrCoO}_{2.5}$ is partially oxidised so as to contain both Co^{III} and Co^{IV} , then the co-ordination polyhedra of the cobalt ions are linked by a mixture of corner-, edge-, and face-sharing, in contrast to $\text{H-SrCoO}_{2.5}$ where only

corner- and face-sharing are present and to the high-temperature brownmillerite phase $\text{B-SrCoO}_{2.5}$ where only corner-sharing is present. The partially oxidised system SrFeO_{3-y} contains only corner-sharing polyhedra. On reduction to an oxide containing Co^{II} , that is $\text{SrCoO}_{2.38}$, there is some loss of oxygen from the first co-ordination shell around cobalt. There is however no evidence for the presence of edge-sharing polyhedra at this composition.

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