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A Structural Comparison of the Two Polymorphs of $Sr_2Co_2O_5$ by Cobalt *K*-edge Extended *X*-Ray Absorption Fine Structure Spectroscopy†

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The high- and low-temperature forms of $Sr_2Co_2O_5$ have been studied by EXAFS spectroscopy. Evidence is presented to support the belief that the high-temperature phase is isostructural with $Sr_2Fe_2O_5$. Furthermore, the observation of a Co–Co distance of 2.46 Å in the low-temperature form is the first direct evidence for the existence of face-sharing CoO_6 octahedra in that phase.

The perovskite-related materials ABO_{3-y}, where A is Ca, Sr, or Ba and B is a first-row transition metal, have been the subject of much research activity because of their wide range of possible applications, for example as electrode materials and as catalysts. The fundamental property of the compounds that gives rise to many of these uses is the ability of the anion sublattice to accommodate a high concentration of vacant sites such that y can take values in the range $0 \leqslant y \leqslant 0.5$. This non-stoicheiometry depends upon the ability of the transition metal to exist as both B^{4+}, in the fully oxidised compound ABO_3, and B^{3+} in the fully reduced material $ABO_{2.5}$. Compositions for which $0 < y < 0.5$ can be regarded as mixed-valence compounds in which both B^{3+} and B^{4+} species are present.

The relationship between the stoicheiometry and the structure of the material can be very complex. The average co-ordination of the cations will decrease as reduction occurs, unless a major structural rearrangement takes place to eliminate anion vacancies. This rarely happens in the ABO_{3-y} compounds, where the change in co-ordination often leads to the adoption of a crystal structure which can be regarded as a perovskite derivative with an ordered arrangement of anion vacancies. The reduction of $CaMnO_3$ to $CaMnO_{2.5}$, for example, leads to a change in the co-ordination number from six (Mn^{4+}) to five (Mn^{3+});[1] the preference of Mn^{3+} for five-co-ordination can also be seen[2] in $SrMnO_{2.5}$. However, many of the fully reduced phases adopt a structure similar to that of the mineral brownmillerite,[3] in which equal numbers of transition-metal cations are in alternate layers of distorted octahedral and distorted tetrahedral sites. This structure is known to exist[4–6] for $BaFeO_{2.5}$, $SrFeO_{2.5}$, and $CaFeO_{2.5}$. Furthermore, it is clear from *X*-ray powder diffraction[7] and Mössbauer spectroscopy[8,9] on quenched samples that $SrCoO_{2.5}$ adopts an orthorhombic brownmillerite structure above 1 200 K (referred to as B–$Sr_2Co_2O_5$), although a full crystal-structure determination is not available. Unusually, the Co^{3+} ions in this material are in a high-spin state on both the tetrahedral and the octahedral sites. On slow cooling in air, the brownmillerite $SrCoO_{2.5}$ is oxidised[9] to $SrCoO_{2.63}$. However, the original composition is retained[7] when the sample is cooled in a sealed ampoule, with a phase transition occurring at 1 023 K. The uncertain structure of this low-temperature phase (referred to as H–$Sr_2Co_2O_5$) is the subject of the present paper. Grenier *et al.*[7] originally described it as a 2H hexagonal perovskite similar to $BaNiO_3$, but Rodriguez and Gonzalez-Calbet[10] have indexed their *X*-ray powder diffraction pattern, which is somewhat different to that reported by Grenier, in a rhombohedral unit cell. The 2H structure originally proposed by Grenier *et al.* consists of chains of face-sharing CoO_6 octahedra along the z axis of a hexagonal unit cell. More recently Grenier *et al.*[8] have proposed a new structural model in which the chains consist of Co^{3+} ions in O_h, C_{4v}, and D_{4h} geometries. The evidence for this model comes from Mössbauer spectroscopy and magnetic susceptibility measurements. The former, carried out on ^{57}Fe-doped samples, show clearly that there are two ^{57}Fe sites in the sample, one six-co-ordinate and one with a lower co-ordination number. We see no evidence in the published data for the existence of a third site. Grenier *et al.*[8] have chosen to interpret their susceptibility data in terms of a temperature-dependent magnetic moment for the Co^{3+} on the octahedral site, and a medium spin configuration at the D_{4h} and C_{4v} sites. We have previously[9] pointed out that the magnetic properties can be equally well explained by assuming that the transition at 1 023 K retains the octahedral and tetrahedral co-ordination found in the parent brownmillerite structure, but that the Co^{3+} ions on octahedral sites undergo a high-spin to low-spin transition, thus halving the average effective magnetic moment per Co^{3+} ion.

It is clear that our understanding of the structure of the low-temperature phase would benefit from a neutron diffraction study. However, the specimens we have prepared to date have always been poorly crystalline and both Grenier and ourselves have so far been unable to index the resulting *X*-ray powder diffraction patterns. We have therefore turned to extended *X*-ray absorption fine-structure (EXAFS) spectroscopy in order to gain a deeper insight into this complex structural problem, and we shall present here the first clear evidence that the low-temperature phase does not simply consist of a modified brownmillerite network of corner-sharing octahedra and tetrahedra.

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 compound $Sr_2Co_2O_5$ (or $SrCoO_{2.5}$) was obtained by quenching in air from 1 100 °C, and the composition, by iodometric analysis,[9] was $SrCoO_{2.496 \pm 0.005}$. Part of this material was annealed under dry argon at 800 °C for 3 d and then cooled at 10 °C h^{-1} to 300 °C and then more quickly to 160 °C, before removal from the argon atmosphere. Analysis gave $SrCoO_{2.508 \pm 0.005}$.

Initial characterisation was by *X*-ray powder diffraction; the pattern from the quenched sample was in good agreement with published data for the brownmillerite structure, while the

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

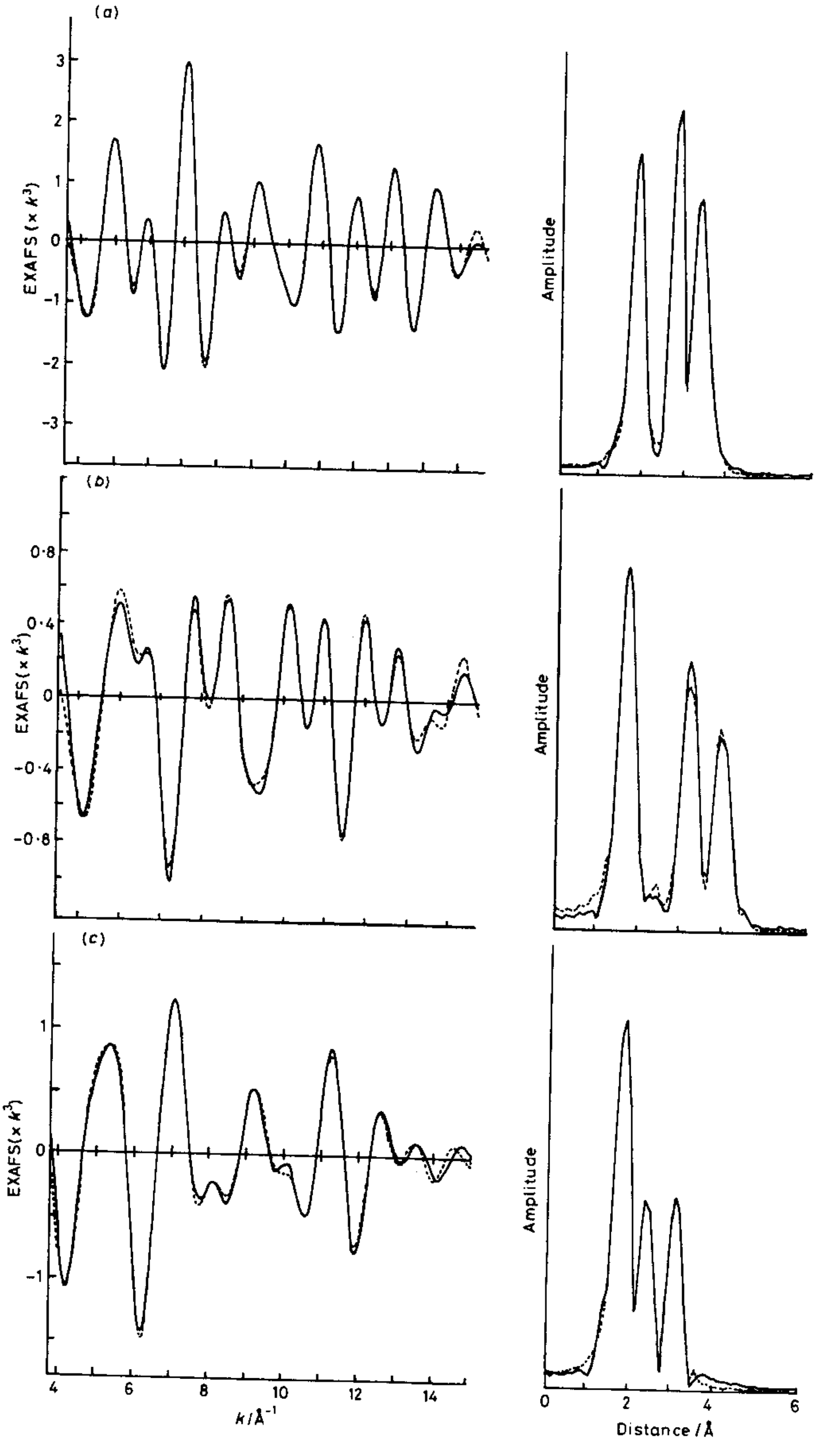

Figure 1. Observed (——) and calculated (– – – –) Fourier-filtered EXAFS data (left) and the corresponding Fourier transforms (right) for: (*a*) Co_3O_4; (*b*) B-$Sr_2Co_2O_5$; and (*c*) H-$Sr_2Co_2O_5$

annealed sample gave an ill defined pattern typical of the 'hexagonal' structure[9] with broad lines and some evidence for effects due to disorder or small particle size along the *c* axis.

Room-temperature EXAFS spectra were recorded at the cobalt *K*-edge (1.608 11 Å, 7.710 keV) using the Daresbury synchrotron radiation source, operating at an energy of 2.0 GeV and an average current of 190 mA. 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 (EXBACKI and MUFPOT programs available from the Daresbury suite of programs).[11] The reliability of the latter for cobalt and oxygen was established by measuring and analysing an EXAFS spectrum of the well characterised cubic spinel Co_3O_4. The lack of a suitable standard compound prevented an experimental check of the strontium phase shift, but it is known that neighbouring elements, with atomic numbers $Z + 1$ and $Z + 2$, have very similar back scattering phase shifts and the calculated strontium phase shift has been used, in place of a true zirconium phase shift, to fit the EXAFS from monoclinic ZrO_2 and zirconyl chloride ($ZrOCl_2$). There was good agreement between the zirconium–zirconium distances determined by diffraction methods and EXAFS [ZrO_2[12] diffraction (av.) 3.45, EXAFS 3.44; and $ZrOCl_2$[13] diffraction 3.56, EXAFS 3.55 Å] and it can thus be assumed that the calculated strontium phase shift is adequate. Furthermore, the prime concern of the present work is with the cobalt and oxygen environment of a given cobalt atom, and small errors in the cobalt to strontium distances will have no effect on the main arguments presented here. The data have been Fourier filtered to include only the first three shells, a cut-off which can be made without causing large truncation effects and one which is not complicated by overlapping Fourier-transform shells. It also eliminates complications in data analysis due to multiple scattering effects which could arise in more distant 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,[14] 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, ±20%; Debye–Waller factor, ±20%; and radii ±0.02 Å. These are estimated errors arising from imperfect transferability of phase shifts. However, in materials of unknown structure, *e.g.* H-$Sr_2Co_2O_5$, where the computed parameters may be based on an 'averaged' environment, the errors in the co-ordination number and Debye–Waller factor could be larger and care has to be taken to avoid unjustified overinterpretation of the results. Statistical fitting errors are far smaller.

Table 1. Radial distribution of atoms about Co in Co_3O_4

Atom type	Average co-ordination number	$2\sigma^2$ [a] (Å^2)	Average radial distance (Å)	
			EXAFS	Neutron
O	$5\frac{1}{3}$	0.006	1.930	1.923[b]
Co	4	0.006	2.863	2.858
O	$1\frac{1}{3}$	*c*	*c*	3.309
Co	8	0.012	3.355	3.351
O	4	0.010	3.432	3.390

[a] Debye–Waller factor determined from EXAFS. [b] Weighted average of 1.942 (tetrahedral) and 1.917 Å (octahedral). [c] Contribution to EXAFS too small to give reliable figure.

Table 2. Refined structural parameters of high-temperature brownmillerite, B-$Sr_2Co_2O_5$, from Co-*K* EXAFS data

Atom type	Average co-ordination number*	$2\sigma^2$ (Å^2)	Radial distance (Å)
O	2	0.004	1.83
O	2	0.008	1.97
O	1	0.009	2.16
Sr	4	0.021	3.24
Co	4	0.013	3.99
O	4	0.008	4.17

* Averaged over equal numbers of octahedral and tetrahedral sites.

Results and Discussion

The cubic spinel Co_3O_4 was adopted as a standard for phase shift determination because, although there are two distinct cobalt sites in the structure resulting in the observation of a cobalt environment which is a weighted average, there is only one variable crystallographic parameter, the co-ordinate of the oxygen atom at (u,u,u), which has been determined previously in an accurate neutron diffraction study.[15] In the analysis of the EXAFS of Co_3O_4, the Co–O and Co–Co distances and the corresponding co-ordination numbers were initially set to the values determined in the diffraction experiment, while the calculated back-scattering phase shifts of the cobalt and oxygen were refined, using two parameters for each phase shift, to optimise the agreement between the observed and calculated EXAFS. The phase shifts were then held constant at these refined values during a refinement of the co-ordination shell radii. Figure 1(*a*) shows the final observed and calculated EXAFS spectra of Co_3O_4 together with their Fourier transforms. The refined parameters, and those determined by Knop *et al.*[15] in the diffraction study are presented in Table 1. It was impossible to resolve the octahedral and tetrahedral cobalt sites in the EXAFS analysis, and the first oxygen co-ordination shell listed in Table 1 is thus an average over the two types of site. The second shell contains, on average, four cobalt atoms, a mean which derives from the presence of six cobalt atoms at a distance of 2.85 Å from the octahedral sites ($\frac{2}{3}$ of the total cobalt atoms). The significant contributions to the co-ordination shell at the greatest radius in Figure 1(*a*) come from an average of eight next-nearest neighbour cobalt atoms and four next-nearest neighbour oxygen atoms. The agreement between experiment and theory is clearly excellent [Figure 1(*a*)] and the refined radii of the co-ordination shells around cobalt are fully consistent with those calculated from the neutron diffraction data (Table 1). The level of agreement justifies the subsequent use of the refined values of the calculated phase shifts.

Figure 1(*b*) shows the observed and calculated Fourier-filtered EXAFS spectra, and the corresponding Fourier transforms, for brownmillerite B-$Sr_2Co_2O_5$. The three co-ordination shells apparent in the Fourier transform [Figure 1(*b*)] were assigned, in order of increasing radius, to oxygen, strontium, and a cobalt/oxygen mixture respectively. In fitting the EXAFS, a model involving a three-component first shell was used, along with a single-distance strontium shell, and a third shell with one cobalt distance and one oxygen distance. The use of a three-component first oxygen shell is consistent with a neutron diffraction study[5] of B-$Sr_2Fe_2O_5$ and is necessitated by the presence of both distorted octahedral and distorted tetrahedral sites for the transition-metal cation in the brownmillerite structure. The co-ordination numbers used in fitting the oxygen shells and the cobalt shell were arrived at from a consideration of the $Sr_2Fe_2O_5$ structure; that for the strontium shell was derived by initially allowing the co-ordination number and Debye–Waller factor to refine simultaneously and then fixing

Table 3. Refined structural parameters of low-temperature hexagonal $Sr_2Co_2O_5$, from Co-*K* EXAFS data

Atom type	Average co-ordination number	$2\sigma^2$ (Å^2)	Radial distance (Å)
O	5	0.011	1.89
Co	1	0.008	2.46
Sr	2	0.012	3.15
O	5	0.020	3.42

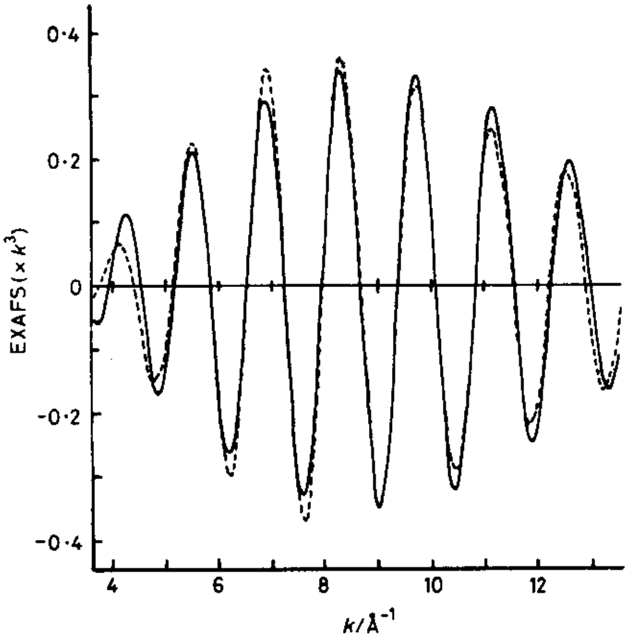

Figure 2. Fourier-filtered EXAFS of the second co-ordination shell (2.46 Å) in $H\text{-}Sr_2Co_2O_5$. (——) observed data, (- - - -) fit assuming the back-scattering atom to be cobalt

the co-ordination number to the nearest integer for further fits. This is a reasonable procedure to adopt in order to avoid the correlation effects that would otherwise occur. The results of these calculations are presented in Table 2. There should be a small contribution to the second shell from, on average, one cobalt atom, but this is far outweighed by that from the strontium and was not included in the final refinements. The tabulated data, and the excellent agreement between the experimental and theoretical spectra [Figure 1(*b*)], justify the assumption, made on the basis of Mössbauer spectroscopy and *X*-ray powder diffraction, that the high-temperature phase of $Sr_2Co_2O_5$ is isostructural with $Sr_2Fe_2O_5$, and further evidence of this will be presented below. The two compounds have a very similar spread of metal to oxygen distances in the first co-ordination shell, and the presence of a transition-metal shell at *ca.* 4 Å is always to be expected in a perovskite-related material. However, the refined value of 4 for the average number of strontium atoms surrounding a cobalt atom in $B\text{-}Sr_2Co_2O_5$ is rather low for such a material and may arise through destructive interference of back scattered waves from atoms at slightly different distances, leading to an apparent lowering of the EXAFS amplitude.[16]

Figure 1(*c*) shows the observed and calculated spectra and transforms obtained for the sample of 'hexagonal' $H\text{-}Sr_2Co_2O_5$.

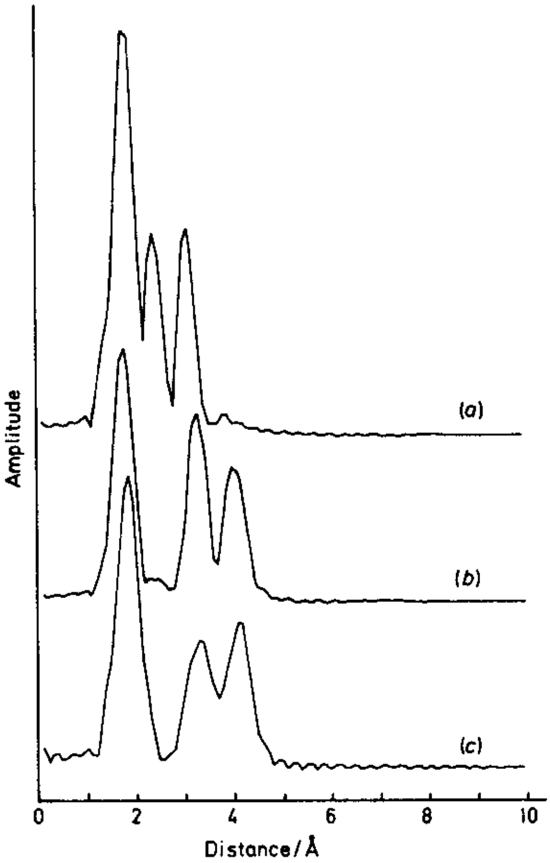

Figure 3. A comparison of the Fourier transforms of the Fourier-filtered EXAFS data for: (*a*) $H\text{-}Sr_2Co_2O_5$; (*b*) $B\text{-}Sr_2Co_2O_5$; and (*c*) $Sr_2Fe_2O_5$

In this case the number of distinct cobalt sites is unknown. The refined structural parameters are presented in Table 3. Although the first co-ordination shell again consists of, on average, five oxygen atoms, the spread of distances seen in $B\text{-}Sr_2Co_2O_5$ was not found in $H\text{-}Sr_2Co_2O_5$ and the maximum at *ca.* 2 Å in Figure 1 (*c*) is therefore narrower and of greater amplitude than that seen in Figure 1 (*b*). The appearance of the next-nearest neighbour shell at a radius of 2.46 Å is the most interesting feature of this work. Data analysis showed that it is best modelled as a shell of cobalt atoms with an average co-ordination number of one. Fitting with strontium or oxygen atoms, or with a combination of both, gave less satisfactory fits and made little chemical sense. Furthermore, a crude Fourier filter of this shell shows the correct back scattering amplitude envelope for cobalt (Figure 2). The third shell at a radius of *ca.* 3.3 Å was best modelled as being composed partly of strontium and partly of oxygen (Table 3), although this is not definitive.

The results described above suggest that the topology of the octahedral/tetrahedral network has changed from being all corner sharing in $B\text{-}Sr_2Co_2O_5$ to include some face-sharing CoO_6 octahedra in $H\text{-}Sr_2Co_2O_5$. We have no conclusive evidence to prove that tetrahedral co-ordination persists into $H\text{-}Sr_2Co_2O_5$, although the mean nearest-neighbour oxygen distance of 1.89 Å is short enough to suggest that some fraction of the Co atoms retain a co-ordination number of less than six. Mössbauer spectroscopy also gives some indication that tetrahedral sites are present.[9] The structural differences between the two forms of $Sr_2Co_2O_5$ are emphasized in Figure 3 where the Fourier transforms of the filtered EXAFS data are compared directly. A pattern derived in a similar manner from

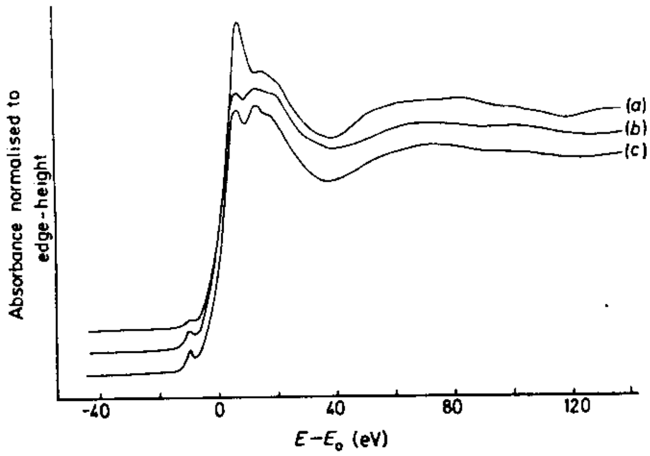

Figure 4. A comparison of the XANES region of: (*a*) H-$Sr_2Co_2O_5$; (*b*) B-$Sr_2Co_2O_5$; and (*c*) $Sr_2Fe_2O_5$

data collected at the Fe *K*-edge of $Sr_2Fe_2O_5$ is also shown in order to demonstrate once again the similarity between that compound and B-$Sr_2Co_2O_5$. Figure 4 shows the *X*-ray absorption near-edge structure (XANES) of the same three phases as a final demonstration of the similarities of B-$SrCo_2O_5$ and $Sr_2Fe_2O_5$ and their mutual differences with H-$Sr_2Co_2O_5$.

The structural features assigned to H-$Sr_2Co_2O_5$ in this work are very similar to those found previously[17] in 12 H-$BaCoO_{2.6}$. The structure of the latter compound consists of columns of four face-sharing CoO_6 octahedra, with the terminal octahedra sharing corners with CoO_4 tetrahedra. The average number of short cobalt distances is thus one per cobalt atom, in good but possibly fortuitous agreement with the value found in H-$Sr_2Co_2O_5$. The distances between the cobalt atoms in face-sharing octahedra (2.41 and 2.45 Å) are also in good agreement with the value found in H-$Sr_2Co_2O_5$ (2.46 Å) and it is tempting to believe that similar structural units exist in the two compounds. The Co–Co distance found in this work is slightly longer than that of 2.38 Å found[18] in the 2H-perovskite $BaCoO_3$, which contains only face sharing CoO_6 octahedra with all the transition-metal cations in an oxidation state of +4.

Finally it seems reasonable to postulate that the dramatic change in the co-ordination environment of some of the cobalt atoms on octahedral sites may well be accompanied by a change of spin state, from $t_{2g}{}^4e_g{}^2$ in B-$Sr_2Co_2O_5$ to $t_{2g}{}^6e_g{}^0$ in H-$Sr_2Co_2O_5$. This would be consistent with an earlier explanation[9] of the magnetic properties of H-$Sr_2Co_2O_5$.

Conclusions

The EXAFS technique has enabled us to elucidate the structure of the low-temperature 'hexagonal' form of $Sr_2Co_2O_5$ more thoroughly than has been possible to date. The structure contains short Co–Co distances (2.46 Å), strongly suggesting that there is some face sharing of CoO_6 octahedra, in contrast to the structure of the high-temperature brownmillerite phase where only corner-sharing polyhedra are found.

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