Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 7.† A Study of the Non-stoicheiometric Phase $SrCoO_{3-y}$ by ^{57}Fe Mössbauer Spectroscopy‡

Peter D. Battle and Terence C. Gibb *

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The non-stoicheiometric phase $SrCoO_{3-y}$ has been studied by Mössbauer spectroscopy using ^{57}Fe as an impurity probe, and by *X*-ray powder diffraction. The fully reduced phase $Sr_2Co_2O_5$ contains high-spin Co^{3+} in both octahedral and tetrahedral sites, and has the same magnetic spin arrangement as the analogous iron compound. Oxidation produces a poorly defined 'hexagonal' phase which is apparently non-magnetic even at 4.2 K. There is evidence to suggest that the structure of this phase is related to that of the brownmillerite lattice with the retention of layers of tetrahedrally co-ordinated Co^{3+}, but with a high-spin to low-spin transition occurring on the octahedral sites. Slow relaxation effects have been observed for the iron impurities at low temperature, including a novel slow relaxation for Fe^{4+} ions.

The transition-metal perovskites are of particular interest because they can stabilize the higher oxidation states of the metal and also show a wide range of oxygen deficiency. The alkaline-earth metal perovskites AMO_3 (A = Ca, Sr, or Ba; M = Mn, Fe, or Co) contain the +4 oxidation state of the transition metal, and have been extensively studied with particular emphasis on the magnetic interactions. However, the iron and cobalt compounds are only stoicheiometric when prepared under high oxygen pressures, and readily lose oxygen. Interest in the oxygen-deficient phases has arisen more recently because it has been realized that complicated defect structures with regular arrangements of oxygen vacancies can exist, although they may not be revealed by the *X*-ray powder diffraction pattern. A major investigation of the system $SrFeO_{3-y}$ was described in Part 5 of this series.[1] Ordering of vacancies can occur to a degree which depends upon both the thermal history and the oxygen content of a given sample. The magnetic properties are very unusual and it was proposed that aggregation of oxygen vacancies produces layers of tetrahedrally co-ordinated Fe^{3+} cations. In this paper we report an investigation of the system $SrCoO_{3-y}$ and discuss its relationship to the iron system. During the preparation of this paper, two papers were published on the fully reduced composition $Sr_2Co_2O_5$, and as these partly overlapped our work the discussion has been expanded to include these new results.[2,3]

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. A small amount (*ca.* 1%) of α-Fe_2O_3, isotopically enriched to over 90% in ^{57}Fe, was incorporated in each sample to serve as a Mössbauer probe. A sample of $Sr_2Co_2O_5$ (or $SrCoO_{2.5}$) was obtained by quenching in air from 1 200 °C. Slow cooling in air gave $SrCoO_{2.63}$ (sample A) with an increased oxygen content. This was then annealed in air at 900 °C for 24 h before quenching to give $SrCoO_{2.56}$ (sample B) which, from Mössbauer data, was clearly different from sample A.

In addition, a sample of $Ca_2Fe_2O_5$ was prepared by firing appropriate amounts of $CaCO_3$ and Fe_2O_3 in air at 1 200 °C, and a sample of $Sr_2Fe_2O_5$ was prepared by firing a mixture of $SrCO_3$ and Fe_2O_3 at 1 400 °C under a stream of dry argon to prevent oxidation.

Initial characterization in each case was by *X*-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu-K_α radiation. The *X*-ray patterns from the brownmillerite samples were in good agreement with those published previously. Chemical analyses for Co^{4+} were carried out using a method described elsewhere.[4] Each sample was dissolved in hydrochloric acid in the presence of potassium iodide, and the iodine liberated was determined by titration with sodium thiosulphate in the presence of thyodene. The results obtained for y are considered to be accurate to within ±0.01.

Mössbauer spectra were recorded in the range 4.2—300 K with a $^{57}Co/Rh$ source matrix at room temperature; isomer shift values are relative to the spectrum of metallic iron. Temperatures below 80 K were obtained using liquid helium in an Oxford Instruments CF500 continuous flow cryostat controlled by a DTC2 digital temperature controller. The main spectrometer was an MS-102 microprocessor from Cryophysics Ltd. All data were processed using an Amdahl 580 computer.

Magnetic susceptibilities were measured at room temperature by the Gouy method.

Results and Discussion

The compound $Sr_2Co_2O_5$ (or $SrCoO_{2.5}$) can be prepared in air above 900 °C, and has been claimed[5,6] to have the brownmillerite structure with the space group *Icmm* and with antiferromagnetic ordering below the Néel temperature of 570 K. The structure is notionally derived from the perovskite lattice of $SrCoO_3$ by an ordering of oxygen vacancies, such that there are alternate layers of distorted octahedral and tetrahedral cation sites, and is thus analogous to $Sr_2Fe_2O_5$ and $Ca_2Fe_2O_5$ which show essentially the same magnetic-spin structure. However, no full crystal-structure determination has been published for $Sr_2Co_2O_5$; the magnetic structure was refined from neutron-diffraction data[5] under the assumption that the material is isostructural[7] with $Ca_2Fe_2O_5$ (which has the space group *Pcmn*) and the oxygen parameters of $Sr_2Co_2O_5$ itself were not refined. The structure of $Ca_2Fe_2O_5$ has subsequently been refined from single-crystal *X*-ray data by Colville[8] (as *Pcmn*) and by Berggren[9] (more conventionally as *Pnma*) to obtain more accurate oxygen positions. The structure of $Sr_2Fe_2O_5$ derived from powder neutron-diffraction data by Greaves *et al.*[10] features disordered 8*i* sites in the space group

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† Part 6, T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1986, 1447.

‡ *Non-S.I. unit employed*: B.M. = 9.274×10^{-24} J T^{-1}.

Icmm. A later single-crystal *X*-ray study by Harder and Muller-Buschbaum[11] gave the space group as *Ibm*2, although no standard deviations are given and the table of interatomic distances is clearly at variance with the table of atomic co-ordinates. Despite the difficulties in determining the precise space group, the three compounds are very closely related in structure and this general class of compound will be referred to as having the brownmillerite structure (although strictly this refers to Ca_2AlFeO_5, which is *Pcmn*). However, $Sr_2Co_2O_5$ is unusual in that cobalt occurs as high-spin Co^{3+} ($S = 2$), even on the octahedral sites where low-spin Co^{3+} ($S = 0$) might have been expected, producing an exceptionally strong exchange coupling. This is presumably related to the comparatively large unit-cell volume of the brownmillerite structure.

Preparation under oxygen above 900 °C results in perovskite phases which are said to progress from orthorhombic to tetragonal (*e.g.* $SrCoO_{2.77}$) to cubic symmetry (*e.g.* $SrCoO_{2.87}$) with increasing oxygen pressure.[5] Near-stoicheiometric $SrCoO_3$ is a cubic perovskite and is ferromagnetic,[12] with a Curie temperature of *ca.* 220 K, and makes an interesting contrast with $SrFeO_3$ which is antiferromagnetic. Both oxides are metallic. A later study[13] of the magnetic properties of the cubic perovskites $SrCoO_{3-y}$ ($0.05 < y < 0.26$) has shown that the Co^{4+} (d^5) is in the low-spin state ($S = \frac{1}{2}$) at 0 K. Increasing oxygen deficiency produces low-spin Co^{3+} (d^6, $S = 0$), so that the Curie temperature falls. However, it was suggested that an itinerant σ^* band overlaps the localized $t_{2g}{}^5$ level so that the paramagnetic susceptibility is anomalously high, and metallic character is seen.

Stoicheiometric $SrCoO_3$, doped with ^{57}Fe, shows a Mössbauer magnetic hyperfine field with a flux density of 29.6 T at 4.2 K, which is in the range expected for an Fe^{4+} cation. The spin structure is believed to be collinear.[14] The flux density at 4.2 K in $SrFeO_3$ is 33.1 T.[15]

When $Sr_2Co_2O_5$ is slowly cooled in air the resultant material adopts a structure which has been described[5] as being of the hexagonal $BaNiO_3$ type. Although the lattice parameter *a* was given as 5.47—5.48 Å, the *c* parameter was quoted as 4.2—4.3 Å, implying considerable uncertainty; no chemical analysis was given. In the present work a sample of $Sr_2Co_2O_5$ slowly cooled from 1 250 °C to room temperature had a composition of $SrCoO_{2.63}$. Reannealing at 900 °C and quenching altered the composition to $SrCoO_{2.56}$. Both samples gave essentially the same *X*-ray powder pattern but the number of diffraction lines observed was insufficient to determine the unit cell. Although a 'hexagonal' lattice seems possible, it is clear that the hexagonal two-layer $BaNiO_3$ lattice, which features face-sharing octahedra in chains along the *c* axis, cannot apply to this grossly oxygen-deficient phase because additional lines were present.

This 'hexagonal' structure has also been shown to occur below 910 °C in $Sr_2Co_2O_5$ cooled under argon to prevent oxidation.[2,3,16] Grenier *et al.*[3,16] tabulated *d* spacings for such a sample which correlate very well with our own data, but also failed to index the pattern. Rodriguez and Gonzalez-Calbet[2] have now claimed, on the basis of electron-diffraction and *X*-ray data which contain more reflections, that their pattern is due to a rhombohedral structure with $a_R = 6.853$ Å, $\alpha_R = 86.90°$ (hexagonal cell $a_H = 9.246$, $c_H = 12.495$ Å) which may be derived from a six-layer hexagonal lattice. They also note that the lines are broad and there is evidence that homogeneous crystallites are of a small size which would explain this. Although the powder-pattern *d* spacings[2] seem consistent with the rhombohedral lattice, we note, however, that both Grenier *et al.*[3] and ourselves record a line at $d = 2.427$ Å which is not included. Further work on the structural characterization of the 'hexagonal' phase is in progress.

Table. Calculated Mössbauer parameters

Compound	T/K	B/T	δ/mm s^{-1}	ε/mm s^{-1}	Site
$Ca_2Fe_2O_5$	295	51.4	0.34	−0.27	O
		43.8	0.17	0.35	T
	4.2	54.7	0.46	−0.28	O
		48.1	0.29	0.35	T
$Sr_2Fe_2O_5$	295	50.1	0.37	−0.35	O
		42.2	0.17	0.30	T
	4.2	53.9	0.50	−0.36	O
		46.4	0.28	0.31	T
$Sr_2Co_2O_5$	295	46.9	0.33	−0.29	O
		39.9	0.18	0.16	T
	4.2	51.0	0.48	−0.28	O
		45.2	0.30	0.12	T
$SrCoO_{2.63}$	295	—	0.38	1.20*	
(sample A)		—	−0.11	1.42*	
	4.2	46.4	0.50	−0.63	
		23.6	0.01	−0.47	
$SrCoO_{2.56}$	295	—	0.38	1.22*	
(sample B)	4.2	46.5	0.49	−0.63	
$SrFeO_{2.76}$	295	—	0.35	1.31*	
(X component)	4.2	46.6	0.47	−0.62	

* Quadrupole splitting.

Evidence that the production of the 'hexagonal' phase is associated with the comparative instability of the octahedral Co^{3+} cation in the unusual $S = 2$ high-spin configuration comes from the magnetic susceptibility data. Although tetrahedrally co-ordinated cations will tend to remain high-spin, because of the smaller crystal-field splitting, the octahedrally co-ordinated sites may readily revert to the more common $S = 0$ low-spin state. The paramagnetic moments at 300 K for samples A and B were found to be 2.45 and 2.44 B.M. respectively, which are broadly in agreement with other data.[5,16] Compared to the spin-only value for $S = 2$ of 4.90 B.M., these figures are compatible with the conversion of half of the cobalt to the low-spin $S = 0$ species. However, an alternative interpretation in terms of intermediate $S = 1$ spin states has been proposed,[3,16] and we shall return to a discussion of the structure of this phase later in the paper.

The ^{57}Fe Mössbauer spectra of $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, and $^{57}Fe/Sr_2Co_2O_5$ have been measured at 295 and 4.2 K, and the data for the flux density of the hyperfine field, *B*, the chemical shift, δ, and the quadrupole perturbation, ε, are in the Table, and in the case of the strontium compounds are illustrated in Figure 1. The three compounds show very similar magnetic hyperfine spectra with two overlapping six-line patterns from the octahedral (O) and tetrahedral (T) sites. Only slight oxidation of $Sr_2Co_2O_5$ had occurred during the quenching, and this is borne out by the analysis, $SrCoO_{2.51}$, and the very small paramagnetic component in the central region of the spectrum. The data at room temperature agree within experimental error with those of Grenier *et al.*[3] The use of a first-order quadrupole interaction parameter, ε, is not strictly valid as the site symmetry for the tetrahedral site, in particular, is lower than axial in these phases, but computer simulations for various ranges of parameters have shown the second-order effects to be small. A detailed analysis[17] of the magnetic spectra for $Ca_2Fe_2O_5$ has shown that the quadrupole splitting from the tetrahedral site iron has a negative sign and that, while the principal value of the electric field gradient lies along the *b* axis of the crystal, the magnetic hyperfine field lies along the *c* axis, *i.e.* the two axes are perpendicular to each other, and that η is < 0.4.

The similarity of the spectra for $Sr_2Fe_2O_5$ and $^{57}Fe/Sr_2Co_2O_5$ (but with significantly different values for the flux densities)

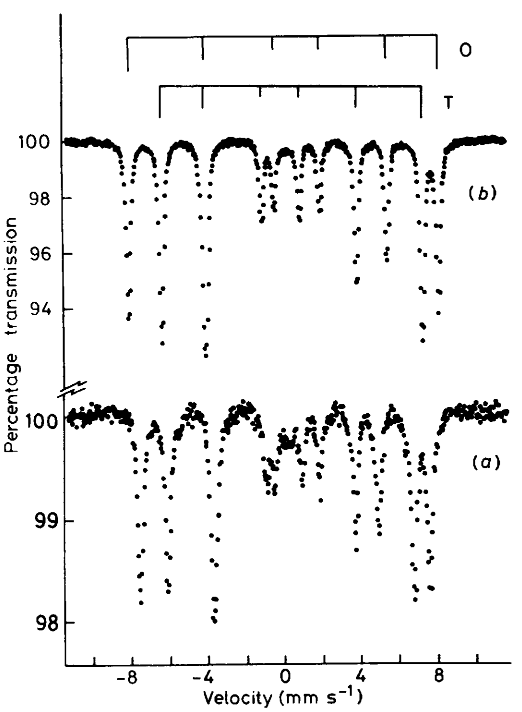

Figure 1. The ^{57}Fe Mössbauer spectra at 295 K of (*a*) ^{57}Fe/$Sr_2Co_2O_5$ and (*b*) $Sr_2Fe_2O_5$. The hyperfine splittings from the octahedral (O) and tetrahedral (T) sites are indicated

confirm that the ^{57}Fe is randomly distributed on both octahedral and tetrahedral sites of the cobalt compound. Furthermore, regardless of any uncertainty in the space groups, the structures of the two materials are sufficiently close to ensure similar site distortions and the same spin directions in the magnetically ordered state. This is in agreement with the neutron data.[5] The chemical shift of the tetrahedral site iron is uniformly lower than that for the octahedral site, as expected.

The flux density of the hyperfine field is also smaller at the tetrahedral site. The various contributions to the hyperfine field have already been discussed extensively[18–21] in connection with the related rare-earth metal orthoferrites. There are several important contributions to the saturation flux density (*i.e.* the limiting value as the temperature tends towards 0 K, which in these compounds equates very well with the observed value at 4.2 K). In the specific case of Fe^{3+} ions, the largest contribution to the flux density derives from the intrinsic $S = \frac{5}{2}$ spin of the ion, which produces a large, negative hyperfine field by core polarization. In similar compounds with the same co-ordination it may be safely assumed that this term is a constant, although there may be a significant difference between octahedral and tetrahedral co-ordination due to covalent overlap. The $^6A_1$ configuration of Fe^{3+} is an S state, so that any orbital and dipolar contributions to the hyperfine field are usually small, although perhaps not negligible in distorted co-ordinations. However, these contributions are likely to be effectively constant in all three compounds.

A second major contribution is from the supertransferred hyperfine field (s.t.h.f.) which is produced by the spins at neighbouring cation sites by transfer and overlap effects, usually through the intervening anion. For a near-neighbour cation, M, with a half-filled or more than half-filled shell (*e.g.* Fe^{3+} and Co^{3+}) the s.t.h.f. produced at ^{57}Fe through a 180° Fe–O–M antiferromagnetic exchange linkage is expected to be negative so that the observed flux density of the hyperfine field increases. A third contribution is the zero-point spin deviation in antiferromagnets which may cause a significant difference between the flux density observed at ^{57}Fe in $Sr_2Fe_2O_5$ (magnetically concentrated in Fe) and in $Sr_2Co_2O_5$ (magnetically dilute in Fe), which is in addition to any s.t.h.f. effects. The s.t.h.f. and zero-point spin densities are difficult to measure separately. In $EuFe_{1-x}Co_xO_3$ the replacement of a neighbouring Fe^{3+} ion by a diamagnetic Co^{3+} results[18] in a reduction in the flux density of the s.t.h.f. of 1.02 ± 0.05 T at 0 K. In $EuFe_{1-x}Cr_xO_3$, the observed reduction[19] in the s.t.h.f. is only 0.82 ± 0.02 T at 0 K per nearest neighbour because of the contribution from Cr^{3+}. On the basis of these figures the contribution of the s.t.h.f. from six Fe^{3+} neighbours at an octahedral site is *ca.* 6 T, and from four neighbours at a tetrahedral site is *ca.* 4 T. All nearest neighbours have antiparallel spins. The reductions in field on going from $Sr_2Fe_2O_5$ to $Sr_2Co_2O_5$ are less than 2 T in all cases, which indicates a substantial s.t.h.f. from the Co^{3+} nearest neighbours of the sign expected, and thus provides further evidence that the Co^{3+} ions on octahedral sites are in a high-spin configuration. More precise measurements would require data from several samples in a solid solution. An attempt to prepare a brownmillerite compound of composition Sr_2FeCoO_5 was unsuccessful, and the corresponding calcium phases can only be prepared over a restricted composition range.[22]

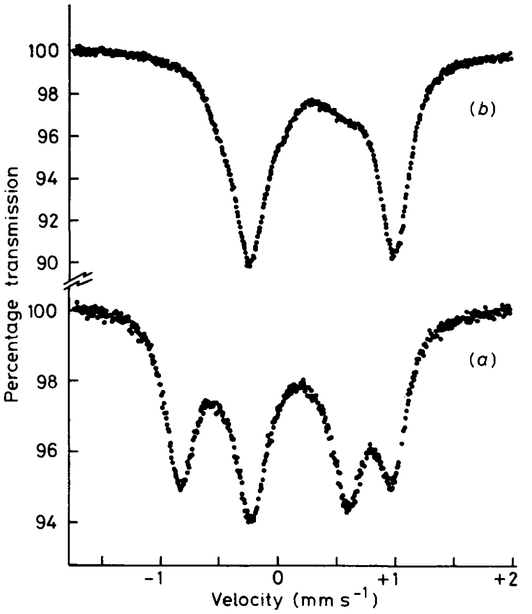

Figure 2. The ^{57}Fe Mössbauer spectra at 295 K of (*a*) sample A, $SrCoO_{2.63}$ and (*b*) sample B, $SrCoO_{2.56}$

Sample A which was slowly cooled in the furnace at a rate of 2.5° min^{-1} at 900 and 1° min^{-1} at 500 °C produced a 'hexagonal' phase with extra oxygen and an analysis of $SrCoO_{2.63}$. The Mössbauer spectrum at 295 K [Figure 2(*a*)] comprised an apparent four-line pattern, which was presumed to be two quadrupole doublets and showing that two major iron sites were present in approximately equal quantities. It seemed possible that these sites were derived from the original sites in the brownmillerite parent lattice. Various models for least-squares analysis of the data were tried, and it proved possible to fit two symmetrical quadrupole doublets of equal intensity only in the presence of a weaker third component with an appreciably smaller quadrupole splitting and a shift of *ca.* -0.1 mm s^{-1}. It is not proven, however, that only three distinct species exist in this material. A portion of sample A was annealed in air for 1 d at 900 °C and then quenched to give sample B ($SrCoO_{2.56}$). As well as a decrease in the oxygen content, there are now only two

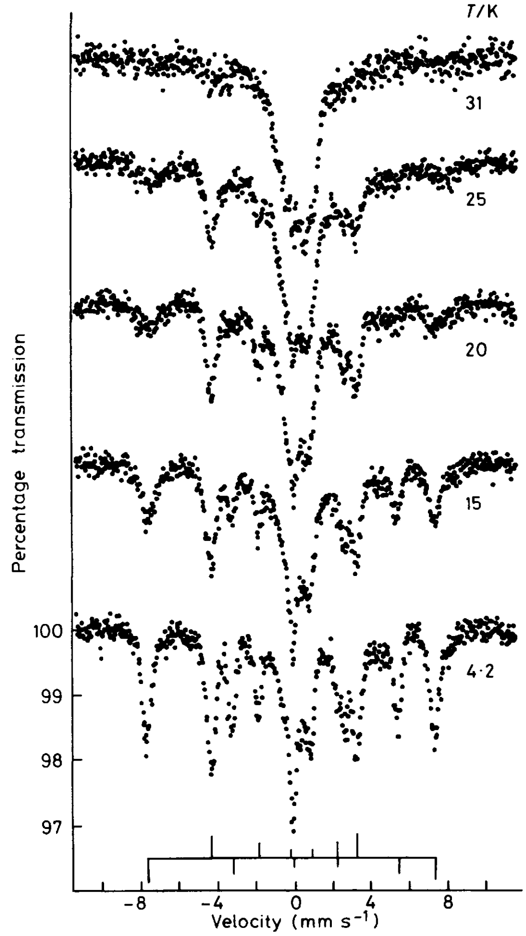

Figure 3. The ^{57}Fe Mössbauer spectrum of sample A ($SrCoO_{2.63}$) as a function of temperature

strong absorption lines corresponding to two lines of sample A (about 75% of the total area), with some less distinct features which are also difficult to analyse uniquely, but are attributable in part to a residue of the second major component [see Figure 2(*b*)]. Sample B had been held at just below the hexagonal–orthorhombic transition temperature for a much longer period than sample A, and it appears that a redistribution of ^{57}Fe takes place between different sites in the 'hexagonal' lattice. Using the two spectra of Figure 2 to assign pairs of lines, the parameters shown in the Table were obtained. Sample A at 4.2 K showed two superimposed magnetic hyperfine sextets (Figure 3), and the parameters for these are also given. The component at higher shift appears to compare well (apart from a systematic discrepancy in isomer shifts) with the major component described by Grenier *et al.*[3] for the fully reduced 'hexagonal' phase, and can be assigned to Fe^{3+} cations with a co-ordination lower than six. There is no evidence in sample A for the second, weaker component described by Grenier *et al.*[3] as due to Fe^{3+} in six-co-ordination. Sample B at 4.2 K shows a spectrum (Figure 4) in which the Fe^{3+} pattern dominates, but once again there is no evidence for any cations in octahedral co-ordination as seen by Grenier.

In sample A, the component at lower shift shows a much smaller hyperfine flux density at 4.2 K (23.6 T) and a shift of 0.01 mm s^{-1}. These values are much smaller than recorded[15] for Fe^{4+} in $SrFeO_3$ (33.1 T and 0.146 mm s^{-1}) and are closer to one of the species formed by charge disproportionation in $CaFeO_3$ (27.9 T and 0.00 mm s^{-1}).[23] Although originally presented as a disproportionation, $2\ Fe^{4+} \rightleftharpoons Fe^{3+} + Fe^{5+}$, there is now

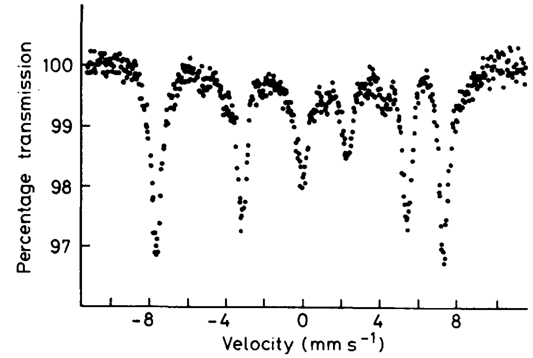

Figure 4. The ^{57}Fe Mössbauer spectrum of sample B ($SrCoO_{2.56}$) at 4.2 K

considerable evidence[1,24] in favour of non-integral charge states, $2\ Fe^{4+} \rightleftharpoons Fe^{(4-\lambda)+} + Fe^{(4+\lambda)+}$, in a number of phases which formally contain iron in the +4 oxidation state, but which have a high electrical conductivity. The observed electrical resistivity in the oxidized 'hexagonal' phase is fairly low,[5] and one cannot discount the possibility of delocalized electron interactions. It is not immediately obvious whether the Fe^{4+} ion in six-co-ordination would be in the high-spin ($S = 2$) or low-spin ($S = 1$) configuration. The comparatively large flux density observed in $SrFeO_3$ tends to support the $S = 2$ configuration.[1] However, in either case the large quadrupole interaction at this site will result in a large orbital and dipolar contribution to the hyperfine field at an Fe^{4+} ion as is often found in an analogous way for the Fe^{2+} ion. There are insufficient data concerning the higher oxidation states of iron to estimate these contributions, but they might be expected to produce a large decrease in the observed flux density. Accordingly, we consider that sample A should be regarded for the moment as containing an 'Fe^{4+}' species without defining the significance of this in terms of any specific localized-electron configuration.

The interpretation of the results presented above is not straightforward. It appears that in brownmillerite $^{57}Fe/Sr_2Co_2O_5$ the iron dopant is present as high-spin Fe^{3+}, distributed randomly over octahedral and tetrahedral sites which would otherwise accommodate high-spin Co^{3+} ions. When $Sr_2Co_2O_5$ is partially oxidized to 'hexagonal' $SrCoO_{2.63}$ by slow cooling, the Fe^{3+} ions on tetrahedral sites remain relatively unaffected, whilst those Fe^{3+} ions on octahedral sites are oxidized to Fe^{4+}. We suspect that this transition is brought about by the conversion of octahedral high-spin Co^{3+} to low-spin Co^{3+} and Co^{4+} on oxidation. This will considerably reduce the size of the octahedral sites such that they cannot accommodate high-spin Fe^{3+}, although the smaller Fe^{4+} ion is acceptable. Our model is consistent with the reduced magnetic moments measured for the oxidized samples. When $SrCoO_{2.63}$ is annealed for 1 d at 900 °C, the majority of the ^{57}Fe dopant migrates to the tetrahedral sites, where it can exist as high-spin Fe^{3+}, along with the high-spin Co^{3+}. It would be most unusual to find low-spin configurations on the tetrahedral site where the crystal-field splitting is relatively small. It is interesting that we are able to explain our data without invoking unusual $S = 1$ intermediate spin states for Co^{3+}. The magnetic data are reasonably close to expectation for a mixture of high-spin and low-spin Co^{3+}, and the similarity of the spectra for both the cobalt and iron compounds would suggest that there is a strong structural correlation.

More interesting results are obtained for sample A in the temperature range 4.2—31 K (see Figure 3). The spectrum at 4.2 K comprises two hyperfine sextets as mentioned earlier, but there is also an excess of absorption in the central region of the spectrum, which may relate to the unidentified features in the paramagnetic spectrum. As the temperature is raised, this central absorption intensifies at the expense of the wings until at 31 K the collapse is almost complete. In principle this equates with the report[3] of a Néel temperature of 25 K in the 'hexagonal' phase of $Sr_2Co_2O_5$. However, one would expect that iron impurities coupled to a Co^{3+} magnetic lattice would show a Brillouin collapse in the hyperfine field with rise in temperature. This does not happen. The outer Fe^{3+} lines in the spectrum become broader and weaker but remain essentially in the same positions. Furthermore, the Fe^{4+} lines collapse in the same way but at a much higher temperature, as can be seen in the spectrum at 20 K. These effects are characteristic of slow relaxation of isolated paramagnetic ions, and there is no evidence in favour of long-range antiferromagnetic order in this material. A similar collapse of the hyperfine field by slow relaxation was observed at 20 K for sample B. The interpretation of the low-temperature Mössbauer spectra in terms of relaxation phenomena rather than long-range magnetic order must be reconciled with the observation[3] of an apparent Néel point (25 K) in the susceptibility of 'hexagonal' $Sr_2Co_2O_5$. We assume that antiferromagnetic order does occur in the fully reduced material, but that the increase in structural disorder which takes place on oxidation destroys the long-range magnetic interactions. An antiferromagnetic low-temperature phase is not inconsistent with our model of low-spin octahedral sites and high-spin tetrahedral sites: the spinel Co_3O_4 which has low-spin Co^{3+} on octahedral B sites and high-spin Co^{2+} on tetrahedral A sites has a Néel temperature[25] of 40 K, despite there being no direct A–O–A exchange path.

It is particularly noteworthy that the spectral parameters of the Fe^{3+} component are identical with those of the 'X component' observed[1] in $SrFeO_{2.76}$. In this compound it was proposed that aggregation of oxygen vacancies as a prelude to forming the brownmillerite structure produces layers of tetrahedrally co-ordinated Fe^{3+} cations which show two-dimensional long-range order below 220 K. If $SrCoO_{2.63}$ has a structure derived from the brownmillerite lattice, it may contain layers of tetrahedrally co-ordinated Co^{3+} ions which, because of the different spin configuration, may not show the two-dimensional order. Such a phenomenon can only occur in the case of uniaxial magnetic anisotropy (Ising magnet) and not in an isotropic (Heisenberg magnet) or two-dimensional (XY magnet) system. The Fe^{3+} ions in $SrFeO_{2.76}$ seem to be consistent with an Ising magnet. Nevertheless, in the cobalt compound the direction of the hyperfine field at ^{57}Fe in the limit of slow relaxation will tend to be the same, so that if the ground state approximates to a $\pm\frac{5}{2}$ Kramers' doublet an almost identical spectrum will result. The observation of slow relaxation for Fe^{4+} is novel, although without more structural data it is not possible to analyse the effect in more detail.

Conclusions

Mössbauer spectroscopy has confirmed that the structure and magnetic spin arrangement of $Sr_2Co_2O_5$ are very similar to those of $Sr_2Fe_2O_5$ and $Ca_2Fe_2O_5$. The 'hexagonal' phase produced by oxidation is difficult to characterize, but the similarity in data for this phase and the reduced iron perovskites suggests a strong correlation in the defect structures which we believe are derived from the alternate four- and six-co-ordination layer structure of brownmillerite. There is no evidence from Mössbauer spectroscopy for long-range magnetic order in the oxidized 'hexagonal' phase, but slow paramagnetic relaxation is seen for both Fe^{3+} and Fe^{4+} cations. The evidence favours a transition from high-spin to low-spin cobalt at the octahedral sites as the lattice transforms to the 'hexagonal' phase, and we can see no experimental justification for previous postulations of intermediate spin configurations of cobalt.

Acknowledgements

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