Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 6.[1] Iron-57 and Tin-119 Mössbauer Spectra of $SrFe_{1-x}Sn_xO_{3-y}$ ($0 \leqslant x \leqslant 0.7$)

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The oxygen-deficient perovskite phase $SrFe_{1-x}Sn_xO_{3-y}$ ($0 \leqslant x \leqslant 0.7$) has been studied using ^{57}Fe and ^{119}Sn Mössbauer spectroscopy and *X*-ray powder diffraction. The oxygen content of each sample depends on its thermal history, and magnetic ordering occurs at low temperatures. The aggregation of oxygen vacancies to produce layers of tetrahedrally co-ordinated Fe^{3+} cations which occurs for $x = 0$ appears to be suppressed by the tin substitution. The supertransferred hyperfine field interaction at tin reveals a continuous distribution of fields, and the spectroscopic data are consistent with a delocalised-electron behaviour in which the more usual near-neighbour interactions are obscured by longer-range effects.

The perovskite $SrFeO_3$ is of unusual interest, not only because it is one of the few oxide phases to contain iron in the +4 oxidation state, but also because it can be oxygen deficient. A preliminary study[2] in this laboratory some years ago of the solid solution $SrFe_{1-x}Sn_xO_{3-y}$ revealed the presence of large supertransferred hyperfine interactions in the ^{119}Sn Mössbauer resonance. However, a consistent interpretation of the data (obtained only for $x = 0.25$, 0.5, or 0.75) remained elusive. The subsequent observation of a novel charge disproportionation in $CaFeO_3$ at low temperatures which has been represented[3] as $2Fe^{4+} \longrightarrow Fe^{3+} + Fe^{5+}$ rekindled interest in the iron–tin solid solution. However, during the subsequent investigation some apparently anomalous data were obtained for the end-member, $SrFeO_{3-y}$. This resulted in a major reinvestigation of this phase which has already been published in considerable detail in Part 5 of this series.[1] The general background to the iron(IV) oxides was discussed at length in that paper, and therefore it will not be repeated here. In the present work specific references will be given only where directly relevant. This detailed study of $SrFeO_{3-y}$ ($0.15 < y < 0.25$) showed that ordering of oxygen vacancies can take place to a degree which depends upon both the thermal history and the oxygen content of a given sample. There is strong evidence to suggest that aggregation of oxygen vacancies results in layers of tetrahedrally co-ordinated Fe^{3+} cations, and that electron delocalisation takes place such that it may not be meaningful to assign an integral charge state to each and every iron site. It is therefore of interest to observe the effects on this unusual defect structure of substitution by tin.

Experimental

Samples of $SrFe_{1-x}Sn_xO_{3-y}$ [$x = 0(0.1)0.7$] were prepared from accurately weighed amounts of spectroscopic grade α-Fe_2O_3, SnO_2, and $SrCO_3$, ground together in a ball mill, and pressed into a pellet. After preheating at 1 200 K for 18 h to decompose the carbonate, the samples were fired in air at 1 510 K for 5 d, reground, and fired again at 1 530 K for 6 d. The final slow cooling was carried out in the furnace with a cooling time from 1 250 to 750 K of *ca.* 310 min (1° min^{-1} at 750 K). Quenched samples were obtained by annealing at 1 200 K for 24 h in air, and then quenching to room temperature in *ca.* 1 min.

Initial characterisation was by *X*-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu-K_α radiation. All samples with $x > 0$ gave a simple pattern from a cubic perovskite lattice. At $x = 0.8$ there was clear evidence for more than one phase, consistent with the earlier observations for $x = 0.75$ which showed slight traces of a second phase.

Chemical analysis was carried out to determine the oxygen deficiency using the method described earlier.[1] It was verified that the presence of tin(IV) did not affect the method. The results obtained were in good agreement with the loss in weight during sample preparation.

Mössbauer spectra were recorded 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 based upon a MS-102 microprocessor by Cryophysics Ltd. All data were processed using an Amdahl 470 computer.

Results and Discussion

The solid solutions $SrFe_{1-x}Sn_xO_{3-y}$ at increments in x of 0.1 were prepared by a high-temperature synthesis in air at >1 500 K followed by slow cooling. Single-phase materials could not be obtained for $x > 0.7$ by this method, although it is still possible that a fast quench from high temperatures could yield a metastable phase. With the exception of the end-member $x = 0$ (which shows a tetragonal distortion), all samples gave a simple cubic-perovskite *X*-ray pattern. The lattice parameters are shown in Figure 1. Each sample was then annealed at 1 200 K in air and quenched, the *X*-ray pattern remaining essentially unchanged despite a considerable loss of oxygen from most samples, although the apparent slight increase in cell size may be significant. There is a substantial increase in the lattice parameter in a smooth progression between $SrFeO_{3-y}$ and $SrSnO_3$. This is consistent with the larger size of Sn^{4+}, but it is perhaps surprising that the lattice size is almost independent of the oxygen content. The *X*-ray pattern reveals nothing of the underlying complexities of the crystal lattice.

The oxygen content and the implied 'percentage of iron as Fe^{4+}' are shown in Figure 2. For the slow-cooled samples the addition of tin has very little effect on the oxygen content as shown by the parameter y which decreases slightly from 0.156 to 0.123. However, the ^{119}Sn Mössbauer resonance confirms beyond doubt that all the tin is in the +4 oxidation state, so that the iron is steadily reduced overall. It may be significant that single-phase material could not be prepared in a region where extrapolation suggests that the degree of oxidation of the iron would be very small. The quenched samples all show a sub-

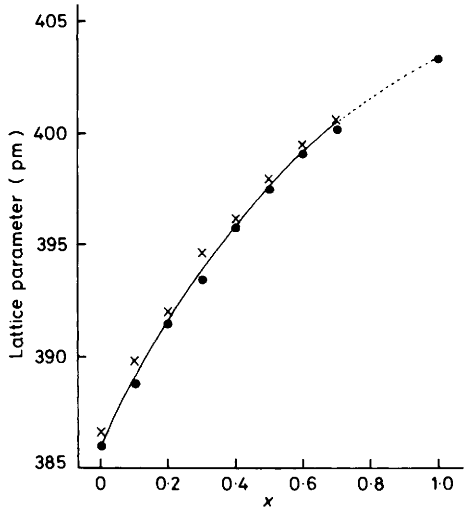

Figure 1. The cubic lattice parameter for the phase $SrFe_{1-x}Sn_xO_{3-y}$ as a function of x. The value for $x = 0$ is the averaged value, and that for $SrSnO_3$ is also included. The solid line is cosmetic only. The full circles represent slow-cooled and the crosses quenched samples

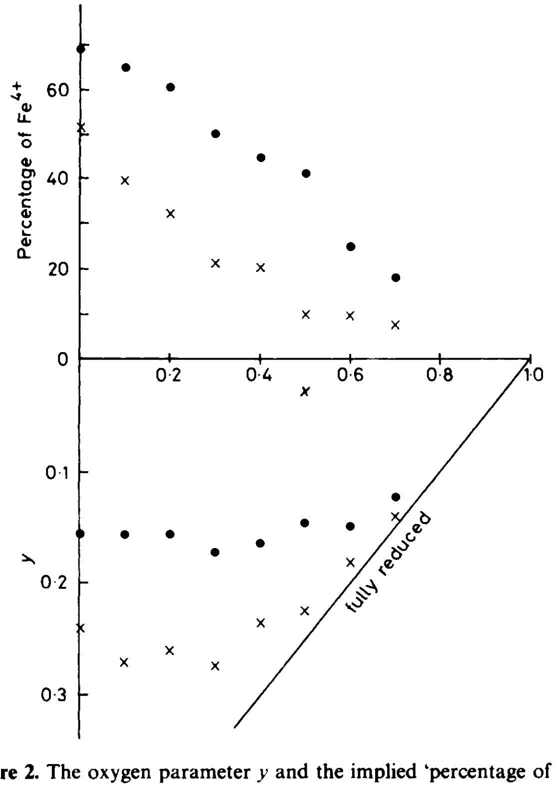

Figure 2. The oxygen parameter y and the implied 'percentage of iron as Fe^{4+}' as a function of x in $SrFe_{1-x}Sn_xO_{3-y}$. Symbols as in Figure 1. The 'fully reduced' line represents materials containing only Fe^{3+} and Sn^{4+}

stantial reduction in oxygen content and hence in the overall oxidation state of the iron compared to the slow-cooled samples.

The ^{57}Fe Mössbauer spectra at 295 K of the slow-cooled samples are shown in Figure 3. Data points are plotted for $x =$ 0 and 0.7 as examples representing the strongest and weakest absorptions, and the general shapes of the remaining spectra are shown as solid lines. The spectrum for $x = 0$ has already been interpreted in detail.[1] The weak line at more positive velocity is one of a quadrupole pair labelled X which has been attributed to

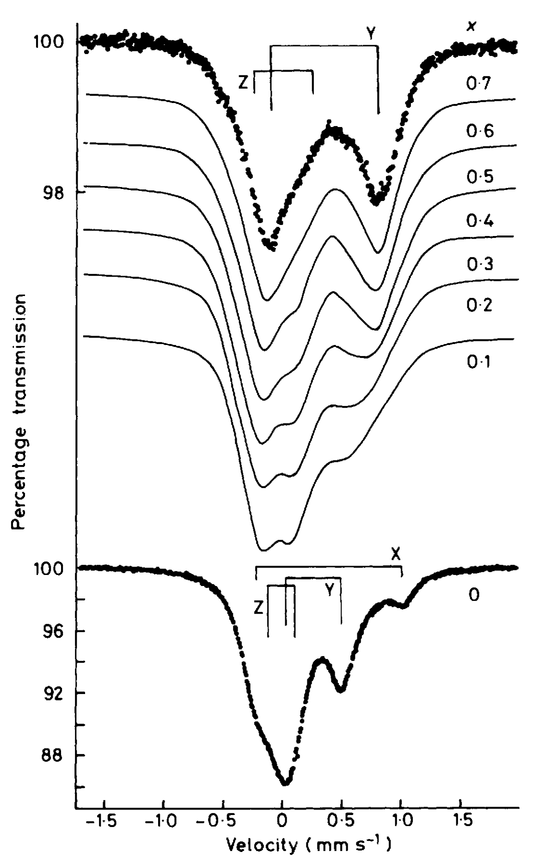

Figure 3. The ^{57}Fe Mössbauer spectra at 295 K of the slow-cooled samples of $SrFe_{1-x}Sn_xO_{3-y}$

Fe^{3+} cations in layers of tetrahedral sites. Components Y and Z are from chemically distinct sites which are believed to be part of a delocalised-electron system.

It is interesting that the X component as such appears to have disappeared at $x = 0.1$. This implies that the planar defect found in $SrFeO_{3-y}$ becomes unstable in the presence of a small amount of tin. On the other hand, work currently in progress has shown that with certain other substituents the X component is sometimes retained up to $x > 0.2$.

The Y component is now more intense and much broader, and with increasing x there is a gradual increase in the quadrupole splitting. Although the model is undoubtedly a gross simplification, each spectrum has been curve-fitted with a pair of quadrupole doublets which will be labelled as Y and Z to indicate their possible parentage. The curve fits are not very good for small x, but improve substantially as x increases so that the model is more significant for the later spectra. The quadrupole splitting of Y increases gradually from 0.68 mm s^{-1} at $x = 0.1$ to 0.90 mm s^{-1} at $x = 0.7$, while the chemical shift also increases from 0.24 mm s^{-1} with respect to metallic iron at $x = 0.1$ to 0.35 mm s^{-1} at $x = 0.7$. These changes are illustrated in Figure 4. The area of the Y component remains essentially *constant* at about 70% despite the significant reduction of the iron which is taking place. The chemical shift of Z remains constant at -0.05 mm s^{-1} from $x = 0.1$ to 0.5, and then increases rapidly to -0.01 mm s^{-1} at $x = 0.7$. These values are more negative than that for $SrFeO_3$ (+0.054) or $CaFeO_3$ (+0.073 mm s^{-1}) at the same temperature. Following the arguments expressed in Part 5,[1] it seems highly likely that Y and Z are chemically distinct species with non-integral charge states in a delocalised-electron structure. At low x it is possible that the Y and Z components in the spectra are no longer strictly

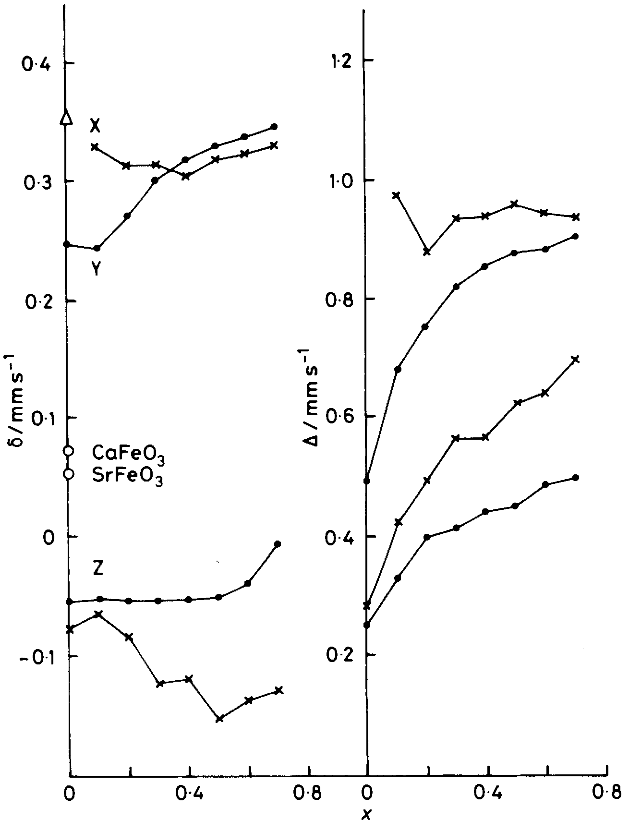

Figure 4. The chemical shift, δ, and quadrupole splitting, Δ, for $SrFe_{1-x}Sn_xO_{3-y}$ as a function of x. Symbols as in Figure 1. The lines are only for visual clarity

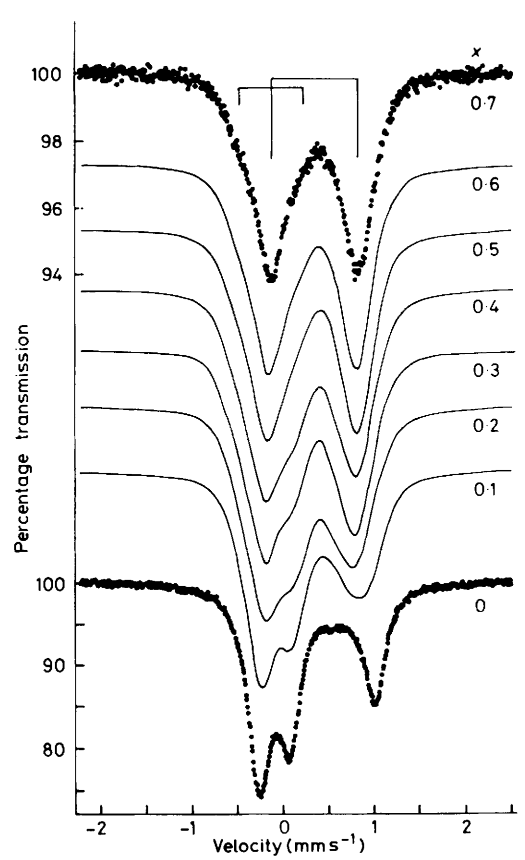

Figure 5. The ^{57}Fe Mössbauer spectra at 295 K of the quenched samples of $SrFe_{1-x}Sn_xO_{3-y}$

independent of each other because of electron transfer. The increase in the shift of Y with increasing x approaches that of the original X component which is considered to be due to a localised-electron Fe^{3+} cation. The observed narrowing of the Y component and broadening of the Z component with increasing x may also reflect the degree of variation in local atomic environment, but clearly, a more detailed interpretation is not possible.

The ^{57}Fe Mössbauer spectra at 295 K of the quenched samples are shown in Figure 5. The strong X component for $x = 0$ from layers of tetrahedrally co-ordinated Fe^{3+} has been replaced by a very broad quadrupole doublet which for small x is not Lorentzian in profile and may be comprised of several overlapping components. With increasing x the spectrum tends towards a symmetrical doublet, and the contribution from the Z component at lower velocities decreases from about 30% at $x = 0.1$ to 10% at $x = 0.7$. Parameters computed on a simple model of two quadrupole doublets (Figure 4) show that the chemical shift of the dominant doublet remains in the region of 0.31—0.32 mm s⁻¹ with a quadrupole splitting of about 0.95 mm s⁻¹. The splitting of the Z component also increases, but the apparent negative shift should be viewed with caution because of the decreasing intensity of this component. It appears that quenching produces a spectrum which is much closer to that of a localised-electron iron(III) material, and is similar to that of the slow-cooled sample with highest tin content ($x = 0.7$).

Mössbauer spectra were also collected at various low temperatures, using both the ^{57}Fe and ^{119}Sn resonances. All samples showed magnetic interactions, and approximate ordering temperatures were found to be 55 ($x = 0.1$), 48 (0.2), 38 (0.3), 32 (0.4), and 23 K (0.5) for the slow-cooled samples and 70 K ($x = 0.1$, quenched). At temperatures just below the ordering temperature the spectra usually showed some degree of collapse, although it was not immediately obvious as to whether this was due to relaxation narrowing or the usual behaviour predicted by molecular field theory in solid solutions or a combination of both. The magnetic behaviour of $SrFeO_{3-y}$ has already been shown to be exceedingly complex.[1] Consequently, more emphasis was placed on spectra at 4.2 K where both these factors should be substantially reduced in effect.

The ^{57}Fe spectrum of $SrFeO_{2.844}$ at 4.2 K (Figure 6) has already been analysed in detail.[1] It was shown that this spectrum is partially collapsed by some form of relaxation, although the three hyperfine components from X, Y, and Z could be readily identified. In contrast the spectrum for the slow-cooled $x = 0.1$ species (Figure 6) appeared to be a static spectrum, and could be analysed reasonably well in terms of two hyperfine fields of almost equal intensity with magnetic flux densities of 45.6 and 27.4 T and chemical shifts of +0.46 and −0.01 mm s⁻¹ respectively. The quadrupole parameters were small, but the comparatively broad linewidths of *ca.* 1 mm s⁻¹ and the overall spectrum profiles were consistent with a range of quadrupole perturbation rather than with a range of hyperfine field. The parameters obtained are reasonably close to those for the Y and Z components at $x = 0$ (45.6, 29.3 T and +0.43, +0.03 mm s⁻¹), and reinforce the assertion that the layer defect (or X component) is no longer present in high concentration. The spectrum for $x = 0.1$ (quenched) is basically similar but substantially broader. The spectra decrease in intensity with increase in x as expected, but also broaden further so that resolution is poor. However, the spectrum for $x = 0.7$ (slow-cooled) at 4.2 K in Figure 6 shows magnetic interaction with flux densities up to at least 44 T, despite the low ordering

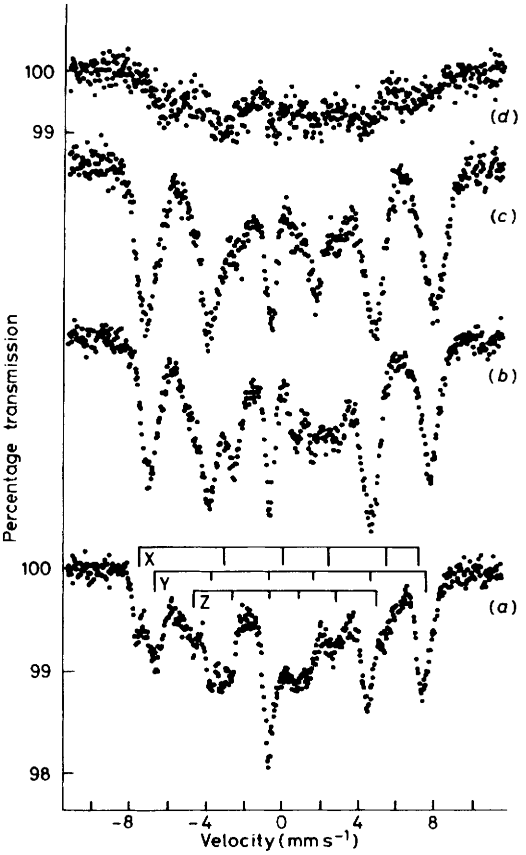

Figure 6. The ^{57}Fe Mössbauer spectra at 4.2 K of representative samples: (*a*) slow-cooled $SrFeO_{2.844}$; (*b*) slow-cooled $SrFe_{0.9}Sn_{0.1}O_{2.844}$; (*c*) quenched $SrFe_{0.9}Sn_{0.1}O_{2.729}$; (*d*) slow-cooled $SrFe_{0.3}Sn_{0.7}O_{2.877}$

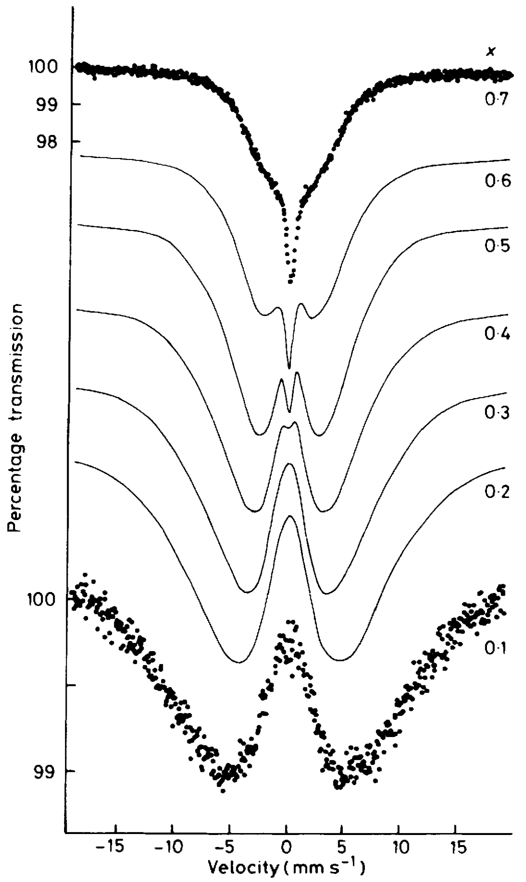

Figure 7. The ^{119}Sn Mössbauer spectra at 4.2 K of the slow-cooled samples of $SrFe_{1-x}Sn_xO_{3-y}$

temperature (<20 K). The magnetic spectra as a whole are consistent with the analysis in terms of two very distinct types of iron species in these phases, and although the values of the flux density are similar to those in $SrFeO_{2.844}$, it is difficult to assign a reliable charge state to these species for the reasons given in Part 5.[1]

The ^{119}Sn spectra at 4.2 K for the slow-cooled samples are shown in Figure 7, and reveal clear evidence for a large supertransferred hyperfine field. The quality of the data was high with the exception of those for $x = 0.1$ where the low tin content and extreme broadening were a problem. In an earlier paper in this series[4] it was found that ^{119}Sn spectra of a range of rare-earth iron perovskites containing tin were very sensitive to the near-neighbour environment of the tin nucleus and showed very complicated spectrum profiles due to the superposition of a number of sharp magnetic hyperfine patterns. Thus it was possible to resolve the hyperfine field for sites with six Fe^{3+} nearest-neighbour cations from that for sites with five Fe^{3+} plus one M^{3+} cation (M = Al, Ga, Sc, Cr, Mn, Co, or Ni). It was therefore disconcerting to find that in the present instance there was no evidence whatever for fine structure in the magnetic spectra. In view of the ^{57}Fe data, the possibility of partial collapse due to relaxation seems unlikely as an explanation for the whole series of spectra. The quenched sample with $x = 0.1$ was examined in the belief that this would show the largest change from a slow-cooled sample. Surprisingly the two samples gave apparently identical spectra at 4.2 K, although the ordering temperature seemed to be higher. It was concluded that each spectrum must comprise a large number of different hyperfine fields, *i.e.* there is a quasi-continuous hyperfine field distribution. A method of Fourier analysis to obtain the hyperfine field distribution has been developed by Window,[5] and was applied to the present problem. The data appear to be symmetrical with no significant quadrupole perturbation, and computed distributions using a six-term series are shown in Figure 8. Similar curves were obtained using series with an increased number of terms to check for distortions and artefacts in the results. Such effects were found to be small, and the curves are useful in determining the main features of the hyperfine field distribution. The lack of significant structure is particularly noteworthy. The curve for $x = 0.1$ shows a most probable value in the field distribution at a flux density of 12 T, but it is clear that values of over 20 T occur. The most probable value decreases significantly with increasing x, being only 6 T at $x = 0.4$ when there are also signs that some tin atoms experience a zero or very small hyperfine field. These trends continue to $x = 0.7$. As x increases so does the probability that a given tin cation will be surrounded by a cluster of other diamagnetic tin cations.

Such behaviour is not normally found for conventional localised-electron materials, where the short-range nature of the exchange mechanisms for the supertransferred hyperfine field results in obvious nearest-neighbour effects.[4] Although the hyperfine field is very sensitive to the Sn–O–Fe bond angle, it seems unlikely that the degree of variation should be so wide and uniform as to obscure all signs of structure in the distribution. However, it is possible that random oxygen vacancies would have a strongly disruptive effect on the superexchange. The behaviour is not dissimilar to that found in metallic alloys where the longer-range nature of the conduction-

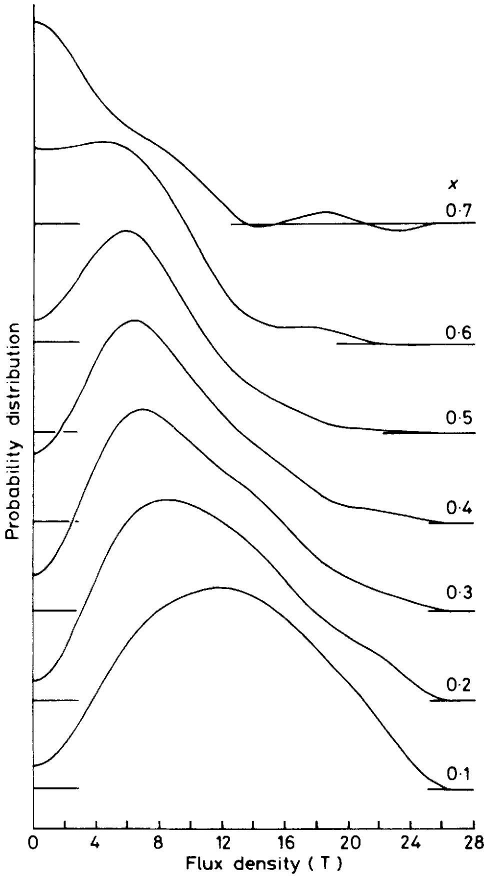

Figure 8. The hyperfine field distribution in the slow-cooled samples of $SrFe_{1-x}Sn_xO_{3-y}$. The most probable value is arbitrarily normalised to unity for convenience of plotting

electron superexchange results in a distribution of hyperfine fields. Nevertheless, in for example copper–manganese alloys[6] and palladium-based Heusler alloys,[7] structure is usually observable at some phase compositions.

Although the ^{119}Sn hyperfine spectra proved disappointing as a probe of the immediate atomic environment, they do lend some support to the postulation of delocalised-electron states in this phase.

Conclusions

A solid solution $SrFe_{1-x}Sn_xO_{3-y}$ with the perovskite structure has been found to exist for $0 \leqslant x \leqslant 0.7$. The oxygen content of each sample is dependent on the thermal history, and slow cooling produces a more highly oxidised material. Although the ideal perovskite structure ABO_3 features octahedral co-ordination of the B cations by oxygen, complete reduction of $SrFeO_3$ to $SrFeO_{2.5}$ results in half the Fe^{3+} cations having tetrahedral co-ordination. The defect structure of the oxygen-deficient perovskite phase has been shown[1] to feature planar aggregates of tetrahedral site cations. It is now clear that such large aggregates do not occur in the tin-substituted phase. However, if one assumes that the larger Sn^{4+} ion prefers octahedral co-ordination, then up to 50% of the iron sites (in fully reduced samples) must have four-co-ordination. The broad ^{57}Fe resonances probably reflect the disorder in the oxygen positions rather than the near-neighbour cation environment. However, the subtle changes in chemical shift with change in composition are indicative of delocalised-electron behaviour. It is not obvious as to how the two chemically distinct iron components in these phases are related in the structural sense. In particular it does not appear possible to apply the conventional binomial distribution model for site populations because near-neighbour interactions are obscured by longer-range effects. This is further borne out by the distribution of hyperfine fields in the supertransferred hyperfine interaction at tin. One may also conjecture that the upper composition limit of this phase is related to one or more of the following: the complete reduction of the iron, the disappearance of delocalised-electron behaviour, and the disappearance of long-range magnetic interactions, all of which seem imminent at $x > 0.7$.

Acknowledgements

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