Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 8.* A Study of the Solid Solution $SrFe_{1-x}Co_xO_{3-y}$ by Iron-57 Mössbauer Spectroscopy

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An investigation of the oxygen-deficient phase $SrFe_{1-x}Co_xO_{3-y}$ has been carried out using ^{57}Fe Mössbauer spectroscopy and X-ray powder diffraction. Samples prepared under identical conditions show an increase in y as x increases. For $x \leqslant 0.2$ the solid solutions are tetragonally distorted perovskites and show the same defect structure and novel magnetic properties which were found earlier in $SrFeO_{3-y}$, but with an increase in the ordering temperature. Quenched samples show a higher degree of defect ordering than slow-cooled samples with the same Fe/Co ratio and which have a higher oxygen content. For $x \geqslant 0.3$ there is a major structural change which the X-ray powder data indicate is to a perovskite lattice of higher symmetry, although spectroscopic evidence suggests the presence of a much more disordered defect structure. At x = 0.9 the X-ray data show the simultaneous presence of perovskite, brownmillerite, and 'hexagonal' phases, and support the contention that the 'hexagonal' structure is closely related to the brownmillerite lattice.

The transition-metal perovskites are well known for their ability to stabilize the higher oxidation states of the metal and also to incorporate a wide range of oxygen deficiency. In Part 5 of this series[1] a major investigation of $SrFeO_{3-y}$ 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. Iron-57 Mössbauer data showed that this phase has very unusual magnetic characteristics. It was proposed that aggregations of oxygen vacancies result in layers of tetrahedrally co-ordinated Fe^{3+} which are very similar to the distorted tetrahedral layers of the fully reduced brownmillerite $Sr_2Fe_2O_5$. The latter, which contains alternate layers of octahedral (O) and tetrahedral (T) sites, is well known[1,2] to show long-range magnetic order with the spin axes of Fe^{3+} in the plane of the layers. An apparent long-range order involving only the tetrahedral sites was observed in $SrFeO_{3-y}$ below 220 K, with the magnetic spin axis now believed to be perpendicular to the layers instead of in the plane. It was tentatively proposed that electron delocalization in the intervening layers, which contain two distinct types of iron atom in octahedral co-ordination, is responsible for an effectively two-dimensional magnetic order in the tetrahedral sites with only a very weak magnetic coupling between the layers.

A study of the solid solution $SrFe_{1-x}Sn_xO_{3-y}$ showed[3] that the occurrence of the tetrahedral layers was suppressed by the tin substitution However, the supertransferred hyperfine field interaction at ^{119}Sn revealed a continuous distribution of fields consistent with a delocalized-electron behaviour in which the more usual near-neighbour interactions are obscured by longer-range effects. More recently,[2] a study of $SrCoO_{3-y}$ by ^{57}Fe Mössbauer spectroscopy found that the oxidized 'hexagonal' phase shows features which correlate strongly with $SrFeO_{3-y}$, and it was proposed that this 'hexagonal' phase is related to the brownmillerite lattice of reduced $Sr_2Co_2O_5$ with the retention of layers of tetrahedrally co-ordinated Co^{3+}, but with layers of low-spin Co^{3+} on the octahedral sites.

This paper reports an investigation of the solid solution $SrFe_{1-x}Co_xO_{3-y}$ in an attempt to throw further light on these defect structures.

Experimental

Samples of the phase $SrFe_{1-x}Co_xO_{3-y}$ were prepared at increments of 0.1 in x from accurately weighed amounts of spectroscopic grade Fe_2O_3, Co_3O_4, and $SrCO_3$, ground together in a ball mill, pressed into a pellet, and fired at 1 250 °C with intermediate grindings. The final heat treatment in each case was a slow cooling to room temperature in the furnace to maximize oxygen uptake. An aliquot of each sample was then annealed at 900 °C for 1 d and quenched to room temperature to prevent oxygen uptake.

Initial characterization in each case was by X-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered Cu-K_α radiation. Single-phase material could not be obtained for x = 0.9, but the other compositions gave the powder pattern of the perovskite lattice with no other lines present. In some cases the lines were very sharp as if the structure were cubic; in others the lines were broader or even split by a small distortion which appeared to be tetragonal. The values for the lattice parameter a (and c where appropriate) and the overall nature of the pattern are summarized in Table 1. The oxygen content was found by chemical analysis for Fe^{4+} + Co^{4+} using a method described earlier.[2] Each sample was dissolved in hydrochloric acid in the presence of potassium

Table 1. Chemical composition and X-ray diffraction data for $SrFe_{1-x}Co_xO_{3-y}$

	Slow-cooled			Quenched		
x	y	a/c		y	a/c	
0	0.16	3.866, 3.852	Tetragonal	0.24	3.866	Split
0.1	0.18	3.858	Split	0.26	3.877, 3.849	Tetragonal
0.2	0.21	3.857	Split	0.28	3.875, 3.834	Tetragonal
0.3	0.23	3.863	Sharp	0.30	3.877	Sharp
0.4	0.24	3.863	V. sharp	0.32	3.879	Sharp
0.5	0.26	3.863	V. sharp	0.34	3.873	V. sharp
0.6	0.31	3.864	V. sharp	0.38	3.873	Sharp
0.7	0.35	3.864	V. sharp	0.40	3.87	Split
0.8	0.37	3.866	V. sharp	0.41	3.876	Split
0.9		Multi-phase			Multi-phase	
0.99	0.37	'Hexagonal'		0.44	'Hexagonal'	

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* Part 7 is ref. 2.

iodide, and the iodine liberated was determined by titration with sodium thiosulphate in the presence of thyodene. The results obtained for y are given in Table 1 and are considered to be accurate to within ± 0.01.

Mossbauer 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.

Results and Discussion

The cubic perovskite $SrFeO_3$ is unusual in being one of the few oxide phases to contain iron in the +4 oxidation state. It can be prepared[4,5] only under high pressures of oxygen, although an oxygen-deficient perovskite $SrFeO_{3-y}$ can be prepared over the range $0 \leqslant y \leqslant 0.28$, preparation in air giving $y > 0.14$. Stoicheiometric $SrFeO_3$ is metallic and an antiferromagnet with a Neel temperature, $T_N = 130$ K. Any attempt to reduce the oxygen content below that of $SrFeO_{2.72}$ leads to precipitation of the fully reduced iron(III) oxide $SrFeO_{2.5}$ (or $Sr_2Fe_2O_5$) which has a structure derived from the perovskite lattice but with alternate layers of distorted octahedral and tetrahedral iron sites. Several similar compounds exist and they are normally referred to as brownmillerites, although there is some confusion over the exact space group in some instances.[2]

The phase $SrCoO_3$ can also be prepared[6,7] at high oxygen pressure and is a metallic ferromagnet with a Curie temperature, $T_C = 220$ K. At lower oxygen pressures the perovskite progressively loses oxygen and distorts to tetragonal and then orthorhombic symmetry. The Co^{4+} in $SrCoO_3$ is in the low-spin (d^5, $S = \frac{1}{2}$) state, and reduction introduces Co^{3+} in the low-spin (d^6, $S = 0$) state so that the Curie temperature falls.[8] The fully reduced compound $Sr_2Co_2O_5$ has the brownmillerite structure[6,7] and is an antiferromagnet[9] with $T_N = 570$ K. It is unusual in that cobalt occurs as high-spin Co^{3+} ($S = 2$) on both sites, even though low-spin Co^{3+} ($S = 0$) might have been expected on the octahedral sites. This is a reflection of the comparatively large volume per formula unit of the brownmillerite lattice. Oxidation of the brownmillerite phase in air gives a poorly defined 'hexagonal' phase which is apparently[2] non-magnetic even at 4.2 K. Independent work[10-12] has shown that a 'hexagonal' phase is the stable form of $Sr_2Co_2O_5$ below 910 °C, although the X-ray characterization is not completely satisfactory.[2] The existence of $S = 1$ intermediate spin states for the Co^{3+} has been proposed.[11,12] However, data from this laboratory on oxidized samples have been interpreted[2] on the basis of a structure related in some way to the brownmillerite lattice with the retention of layers of tetrahedrally co-ordinated Co^{3+}, but with a change from high to low spin occurring on the octahedral sites.

Comparatively few data are available for the solid solution $SrFe_{1-x}Co_xO_{3-y}$. Highly oxidized samples which are cubic perovskites have been made ($SrFe_{1-x}Co_xO_3$).[7] Although there is the implication of a complicated spin structure as the change from an antiferromagnet to a ferromagnet takes place with increase in x, the ^{57}Fe Mossbauer spectrum did not give any significant data[13] about this aspect. Oxygen-deficient samples in the phase appear not to have been studied. An attempt to prepare a brownmillerite compound of composition Sr_2FeCoO_5 was unsuccessful.[2]

Solid solutions of the phase $SrFe_{1-x}Co_xO_{3-y}$ were prepared by standard ceramic techniques. The oxygen content of the samples was found to depend on the thermal treatment. The initial preparations were slowly cooled in a furnace to room temperature to maximize the oxygen uptake. The end member, $SrFeO_{2.84}$, showed the powder X-ray pattern of a perovskite with a small tetragonal distortion, and the characterization of this sample has been described in detail elsewhere.[1] For samples with $0 \leqslant x \leqslant 0.8$ the X-ray powder pattern remained essentially that of a perovskite but with a significant narrowing of the lines to a simple cubic pattern for $x > 0.3$. It would be naive to assume that such a simple powder pattern indicates a random distribution of the oxygen vacancies which are shown to exist by the chemical analysis. However, the spectroscopic data reveal evidence for an ordered defect structure in at least part of the composition range, and recent work on other perovskite systems[14,15] for example has shown that materials which contain small microdomains of the order of 50—200 Å can give a simple cubic X-ray pattern because the wavelength of the radiation is too long to detect the short-range order in such a lattice.

Samples quenched from 900 °C contained less oxygen and showed significantly more splitting of the cubic perovskite pattern with a uniformly greater nominal cell volume. In this respect it is significant that the cell volume per formula unit for $SrFeO_3$ (57.07 Å^3) is significantly less than that for the reduced $SrFeO_{2.5}$ (61.10 Å^3). Preparations with $x = 0.9$ gave X-ray patterns with additional lines and were clearly multi-phase: lines attributable to perovskite, brownmillerite, and 'hexagonal' phases were observed.

The ^{57}Fe Mössbauer spectra at room temperature are shown in Figure 1 (slow-cooled) and Figure 2 (quenched samples). All data are of excellent quality, but for clarity only two spectra in each series are drawn in full, the remainder being shown as solid lines. The spectra for $x = 0$ have been analysed in considerable

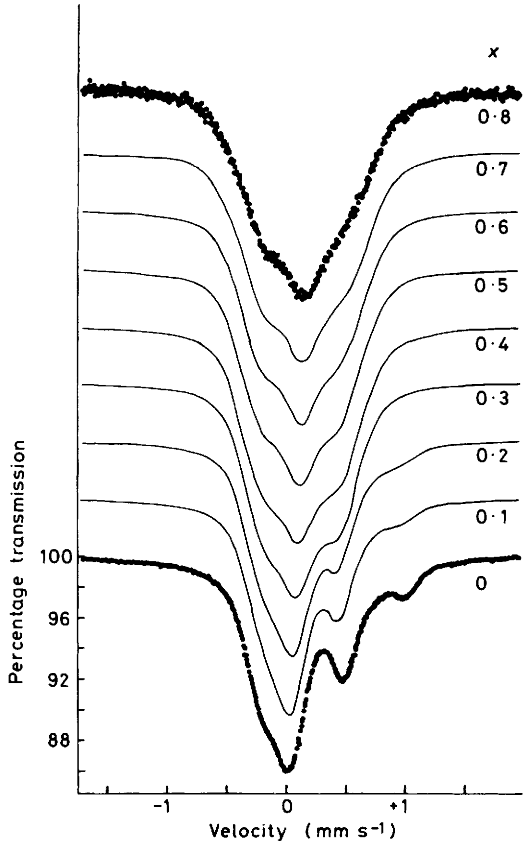

Figure 1. The ^{57}Fe Mössbauer spectra at 295 K of $SrFe_{1-x}Co_xO_{3-y}$ prepared by slow cooling for different values of x

Table 2. Parameters for the Mössbauer spectrum of $SrFe_{1-x}Co_xO_{3-y}$ at 295 and 4.2 K

	295 K		4.2 K		
Component	δ/mm s^{-1}	Δ/mm s^{-1}	B/T	δ/mm s^{-1}	ε/mm s^{-1}
X	0.36	1.26	45.6	+0.43	−0.68
Y	0.27	0.46	44.1	+0.36	*ca.* 0
Z	−0.06	0.19	29.3	+0.03	*ca.* 0

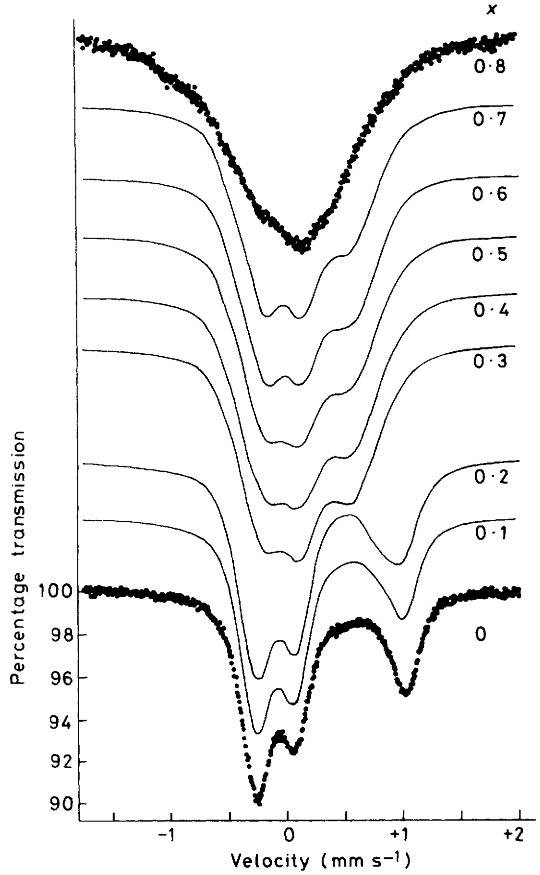

Figure 2. The ^{57}Fe Mössbauer spectra at 295 K of $SrFe_{1-x}Co_xO_{3-y}$ prepared by quenching from 900 °C for different values of x

detail in an earlier paper;[5] the reader is referred to that discussion, and only a brief summary is given here. It was clearly demonstrated that the spectrum for $x = 0$ in Figure 1 was made up of three overlapping quadrupole doublets, with the parameters given in Table 2. The line at +0.99 mm s^{-1} is one line of the quadrupole doublet referred to as the 'X component,' and attributed after detailed analysis to layers of Fe^{3+} in distorted tetrahedral co-ordination. Sites Y and Z are believed to belong to chemically distinct sites in a delocalized-electron system, rather than to specific localized-electron states, and indeed a thermally activated rapid electron-transfer process is seen to occur above 550 K resulting in a total collapse of the spectrum to a single narrow resonance line. In the quenched sample $SrFeO_{2.76}$ (Figure 2, $x = 0$), the X component is intensified at the expense of the Y component. In order to explain the observed disproportionation to brownmillerite which is normally seen for $y > 0.28$, it was proposed that the idealized structure $SrFeO_{2.75}$ contains the layer sequence TOOO. If one additional tetrahedral layer is inserted into a TOOOTOOOTOOO sequence, the resulting TOO(OTO-TOTO)OO configuration contains no less than seven layers in the correct sequence for $Sr_2Fe_2O_5$.

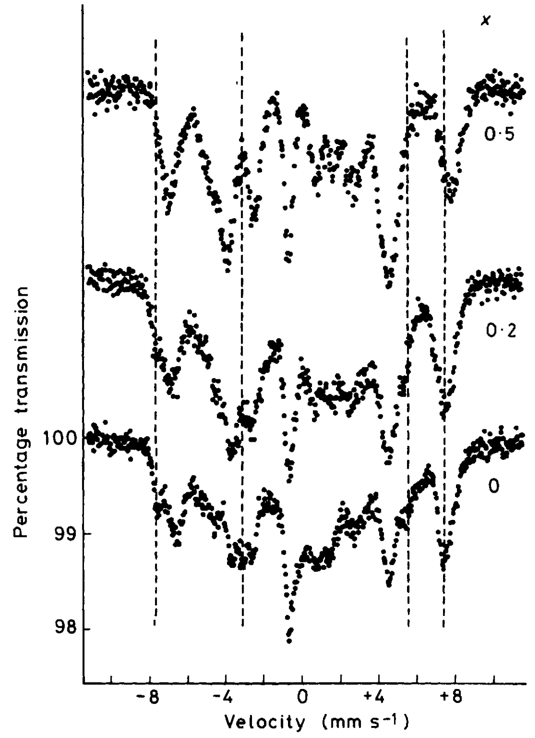

Figure 3. The ^{57}Fe Mössbauer spectra at 4.2 K of $SrFe_{1-x}Co_xO_{3-y}$ prepared by slow cooling for different values of x

The X component is still clearly present for $x = 0.1$ and 0.2, in both the slow-cooled and quenched samples, although there is some degree of broadening. However, for $x \geqslant 0.3$ the X component appears to be completely absent. At the same time the X-ray powder pattern becomes much sharper and loses the tetragonal splitting, and it may be assumed that with increased cobalt content the lattice becomes either more disordered or adopts a different defect structure. The change is most noticeable in the quenched samples as the oxygen content falls below about $SrMO_{2.72}$. For $x \geqslant 0.3$ there is very little change in the ^{57}Fe spectrum with composition despite the significant loss of oxygen, and although a full analysis of the data has not been attempted, it seems clear that the reduction must be more significant at the cobalt sites. This is fully consistent with the higher oxygen content for the iron phase ($x = 0$) compared to the cobalt phase ($x = 0.99$). The quenched sample with $x = 0.8$ alone shows a significantly different spectrum, and it is possible that superparamagnetic microdomains of a brownmillerite structure (which would be magnetic at room temperature) are appearing. In this respect the quenched sample with $x = 0.9$ showed positive X-ray evidence of perovskite, brownmillerite, and 'hexagonal' phases.

An extensive investigation of all the samples as a function of temperature was not attempted. However, selected spectra were obtained at low temperatures to monitor the effect of the cobalt on the defect structure exemplified by the X component in the spectra. Typical spectra at 4.2 K for the slow-cooled and quenched samples are shown in Figures 3 and 4. The data for $x = 0$ have been discussed in detail.[1] The four outermost line positions of the X component in the quenched samples are

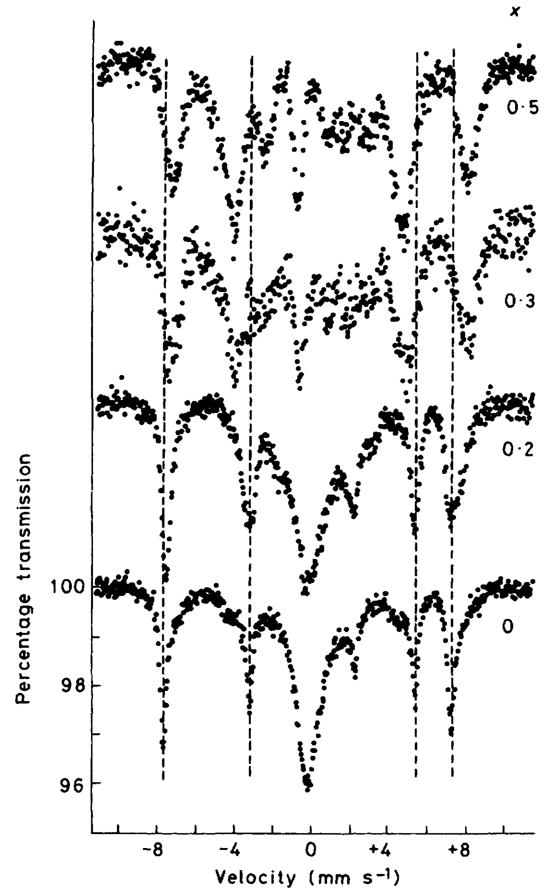

Figure 4. The ^{57}Fe Mössbauer spectra at 4.2 K of $SrFe_{1-x}Co_xO_{3-y}$ prepared by quenching from 900 °C for different values of x

drawn as dashed lines to enable a visual comparison of the spectra. In the slowly cooled sample (Figure 3) lines are identifiable from three hyperfine fields due to X, Y, and Z (see Table 2), and the spectrum is already partially collapsed by some kind of relaxation process at 4.2 K, even though the X component remains magnetic up to at least 200 K and follows a more normal Brillouin behaviour. This is accentuated in the quenched sample (Figure 4) where the X component gives a hyperfine splitting against a broadened but largely collapsed central feature. Again a Brillouin behaviour is shown below a temperature of *ca.* 220 K

Substitution by cobalt ($x \leqslant 0.2$) produces no significant changes in the spectra other than a small degree of line broadening which could easily arise from a combination of small differences in hyperfine field and quadrupole interactions at nominally similar sites because of random replacement of Fe by Co. For $x \geqslant 0.3$ the magnetic spectra change markedly. The lines of the X component are now absent, and are replaced by a broadened hyperfine splitting of apparently the same overall average field but with a very much smaller quadrupole interaction as seen by the more regular spacing of the outer lines. The spectra are generally less collapsed by relaxation, but a detailed analysis is not feasible without a structural model, and more information about the overall distribution of iron and cobalt oxidation states and electronic configurations which cannot be deduced from the Mössbauer spectra alone. One can suggest that the broad lines are due to a more disordered structure, and that a significant change takes place between $x = 0.2$ and 0.3.

Spectra were also obtained for the quenched samples with $x = 0.1$ and 0.2 at a number of other temperatures to observe the temperature dependence of the X component. An essentially Brillouin behaviour was observed which corresponded closely to the data for $x = 0$ (Figure 19 in ref. 1). The only significant difference was that the magnetic hyperfine splitting finally disappeared at *ca.* 220 ($x = 0$), *ca.* 240 ($x = 0.1$), and *ca.* 260 K ($x = 0.2$). If the hyperfine field of the X component is indeed due to a two-dimensional order in layers of tetrahedral sites, then partial substitution by Co^{3+} is causing the ordering temperature to rise. This implies a strong exchange with high-spin (d^6, $S = 2$) Co^{3+}. The quenched sample with $x = 0.3$ gave a very broad partially collapsed magnetic hyperfine spectrum at 78 K, and was clearly quite different in behaviour. The combination of poorly resolved fine structure and relaxation broadening for the spectra of cobalt-rich samples prevents a more detailed analysis.

Conclusions

It has been shown that oxygen-deficient samples of the solid solution $SrFe_{1-x}Co_xO_{3-y}$ fall into two categories. For $x \leqslant 0.2$ there is clear evidence for the same defect structure which was observed earlier in $SrFeO_{3-y}$. The three distinct iron sites observed have been shown[1] to co-exist in the same compound because all three participate in rapid electron transfer at 700 K. The slow-cooled samples tend to be disordered because the low kinetic rate for atom diffusion (which appears to be of the order of hours at *ca.* 400 °C) prevents the establishment of an ordered defect structure in thermodynamic equilibrium in the final stages of oxygen uptake. On the other hand the samples quenched from 900 °C after a long anneal retain the equilibrium state at that temperature, which is more highly ordered and more closely related to the layer structure of the brownmillerite. Substitution by cobalt has little effect initially other than to raise the apparent ordering temperature of the tetrahedral site layers because of the partial replacement of Fe–O–Fe exchanges by Fe–O–Co. For $x \geqslant 0.3$ the structure changes drastically to a more disordered state which appears cubic to *X*-rays. The increasing oxygen deficiency with increase in x appears to result in preferential reduction at the cobalt sites. At $x = 0.9$ the perovskite *X*-ray pattern is replaced by a mixture of perovskite, brownmillerite, and 'hexagonal' phases, although it should be recognized that this may signify a growth in the size of microdomains which already exist at smaller values of x rather than a fundamental change in structure. The close relationship between the brownmillerite and perovskite structures supports the contention that the third phase present, the 'hexagonal' structure, is also closely related to both of them. Comparatively little is known with certainty about the co-ordination states and electron configurations of the defect sites in the solid solutions, and additional measurements are in progress using other techniques to resolve some of the outstanding questions on these unusual materials.

Acknowledgements

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