Magnetic order in perovskite-related SrFeO$_2$F

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Abstract

Perovskite-related strontium orthoferrite, SrFeO$_{3-\delta}$, has been fluorinated by a low temperature reaction with poly(vinylidene fluoride) to give the compound SrFeO$_2$F. X-ray powder diffraction shows that fluorination leads to an expansion of the unit cell which is consistent with partial replacement of oxygen by fluorine and consequent reduction in the oxidation state of iron. Magnetometry experiments in the temperature range 10–400 K showed small aligned moments (0.003 ± 0.000 05 μ_B per Fe^{3+} ion at 2 T and 300 K), indicating the absence of ferro- or ferrimagnetism. The ^{57}Fe Mössbauer spectra recorded at temperatures below about 300 K show broadened, but unsplit, sextet patterns whilst spectra recorded above this temperature show clear splitting of the sextet structure and a magnetic ordering temperature of 685 ± 5 K. A model related to the pattern of substitution by fluorine on the octahedral arrangement of oxygen sites around iron is proposed in which SrFeO$_2$F undergoes a magnetic transition at about 300 K from a low temperature state with random spin directions to an antiferromagnetic state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of superconductivity in perovskite-related oxide fluorides of composition Sr$_2$CuO$_2$F$_{2+x}$ has stimulated considerable interest in the synthesis and characterization of other inorganic oxide fluorides with related structures [1–3]. The synthesis of such materials has usually been achieved by low temperature routes using gaseous fluorine, ammonium fluoride, xenon difluoride or the difluorides of metals such as copper, nickel or zinc. More recently a new method has been identified which entails heating the precursor oxide with the polymer poly(vinylidene fluoride) [4] to give high quality products without metal fluoride impurities which are often formed by other low temperature fluorination methods. We have used this method to fluorinate the oxygen deficient perovskite-related phase SrFeO$_{3-\delta}$ [5]. In this material strontium is coordinated by twelve oxygen atoms whilst iron

is located in an octahedral array of oxygen. The initial characterization [5] showed fluorination to induce a reduction of the oxidation state of iron from Fe^{4+}/Fe^{3+} in SrFeO$_{3-\delta}$ to Fe^{3+} in the compound SrFeO$_2$F.

We report here on the further examination of the fluorinated strontium orthoferrite, SrFeO$_2$F, principally by ^{57}Fe Mössbauer spectroscopy and magnetometry between 10 and 700 K, with a view to elucidating the magnetic properties of SrFeO$_2$F and how these might be related to the pattern of substitution by fluorine on the octahedral arrangement of oxygen sites around iron.

2. Experimental details

The oxygen deficient SrFeO$_{3-\delta}$ was prepared by the calcination of appropriate quantities of a well ground mixture of strontium (II) carbonate and iron (III) oxide at 1250 °C for 24 h in air. Fluorination was achieved by mixing the SrFeO$_{3-\delta}$

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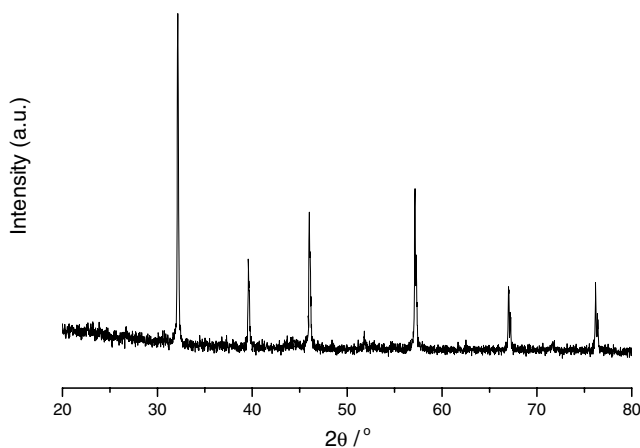
Figure 1. X-ray powder diffraction pattern recorded from SrFeO$_2$F at 298 K.

phase with poly(vinylidene fluoride) in a 1:0.75 molar ratio (precursor oxide:CH$_2$CF$_2$ monomer unit) and heating this mixture at 400 °C for 24 h in flowing nitrogen.

X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using Cu Kα radiation at 298 K. The ^{57}Fe Mössbauer spectra were recorded between 10 and 700 K with a constant acceleration spectrometer using a Co/Rh source of about 25 mCi. The spectra between 10 and 317 K were recorded with a liquid helium flow cryostat and spectra between 285 and 700 K were recorded *in situ* using a specially designed furnace [6]. The ^{57}Fe Mössbauer chemical isomer shift data are quoted relative to metallic iron at room temperature. Magnetometry experiments were performed with a Quantum Design MPMS SQUID magnetometer equipped with a 6.0 T superconducting magnet over a temperature range of 10–400 K.

3. Results

3.1. X-ray diffraction

The x-ray powder diffraction pattern recorded from the fluorinated strontium orthoferrite is shown in figure 1.

Heating the sample in air at 400 °C resulted in no further changes to the x-ray powder diffraction pattern. The result is consistent with the partial replacement of oxygen by fluorine and consequent filling of the anion sites as opposed to a simple reduction in oxygen content. The x-ray powder diffraction pattern recorded from SrFeO$_2$F indexed to a cubic unit cell, $a = 3.956$ Å. The x-ray powder diffraction peaks shifted to lower angles on fluorination, consistent with an increase in unit cell size related to the partial replacement of O^{2-} by F$^-$, leading to a reduction in the oxidation state of iron from Fe^{4+}/Fe^{3+} [5] and consequently longer bond distances.

3.2. Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectra recorded between 80 and 700 K are shown in figure 2 whilst those recorded over the temperature range 10–317 K are collected in figure 3. The ^{57}Fe Mössbauer parameters are collected in tables 1 and 2.
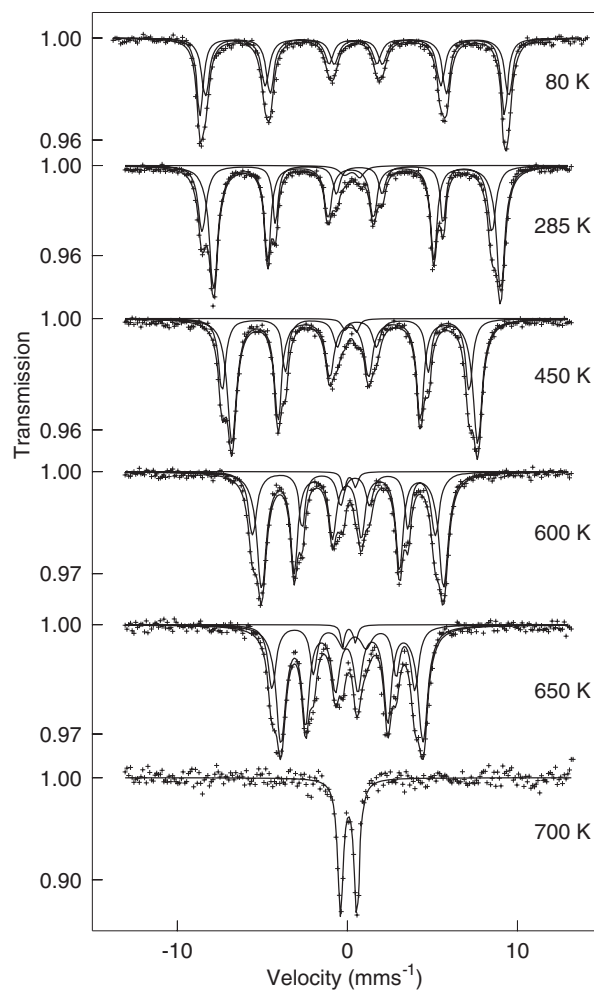
Figure 2. Mössbauer spectra recorded from SrFeO$_2$F between 80 and 700 K.

The interpretation of the shapes of the spectral profiles and the fitting procedures are discussed in detail later. There are, however, two features which are readily amenable to interpretation from the results presented in tables 1 and 2 and figures 2 and 3. Firstly, all the spectral components have chemical isomer shift values characteristic of the presence of Fe^{3+} ions. The variation of chemical isomer shift with increasing temperature is consistent with that expected from the second order Doppler shift. The absence of evidence from any iron oxidation state different from Fe^{3+} together with the presence of Sr^{2+}, O^{2-} and F$^-$ is consistent with a composition SrFeO$_2$F.

Secondly, the spectra recorded at temperatures exceeding 285 K (figure 2, table 1) show increasing line-widths and decreasing magnitudes of magnetic hyperfine field until, at 700 K, the magnetic hyperfine field collapses to a quadrupole split absorption indicative of the paramagnetic state. The variation of the average magnetic hyperfine field with increasing temperature is shown in figure 4 and, from these data, a magnetic ordering temperature for SrFeO$_2$F of 685 ± 5 K can be deduced. The variation of the average magnetic hyperfine field with temperature is also compared in figure 4 with that calculated from the magnetic mean field

Table 1. ^{57}Fe Mössbauer parameters recorded from SrFeO$_2$F between 285 and 700 K.

Temperature (K)	$\delta \pm 0.02$ (mm s^{-1})	$e^2Qq/2 \pm 0.04$ (mm s^{-1})	$\Gamma \pm 0.04$ (mm s^{-1})	$B_{\text{hf}} \pm 0.8$ (kG)	Area ± 2 (%)
285	0.39	0.38	0.61	523	64
	0.34	−0.72	0.58	528	33
350	0.35	0.42	0.54	499	62
	0.30	−0.74	0.51	503	36
400	0.31	0.37	0.59	475	64
	0.26	−0.69	0.53	479	35
500	0.22	0.29	0.67	418	68
	0.20	−0.60	0.57	419	30
600	0.14	0.33	0.68	332	67
	0.12	−0.66	0.59	333	31
650	0.11	0.31	0.68	259	67
	0.10	−0.67	0.57	260	31
700 (doublet only)	0.07	0.96	0.39		100

Table 2. ^{57}Fe Mössbauer parameters recorded from SrFeO$_2$F between 10 and 317 K.

Temperature (K)	$\delta \pm 0.02$ (mm s^{-1})	$e^2Qq/2 \pm 0.02$ (mm s^{-1})	$\Gamma \pm 0.02$ (mm s^{-1})	$B_{\text{hf}} \pm 2$ (kG)	Area ± 2 (%)
10	0.48	−0.05	0.53	537	36
	0.47	−0.23	0.53	557	34
	0.49	0.19	0.53	560	30
80	0.47	−0.05	0.46	550	36
	0.48	−0.48	0.46	549	34
	0.49	0.49	0.46	549	30
200	0.41	−0.05	0.41	536	34
	0.41	−0.47	0.41	537	31
	0.42	0.49	0.41	537	28
	0.33	0.83	1.20	0	5
300	0.36	0.02	0.41	515	34
	0.36	−0.54	0.41	517	32
	0.36	0.49	0.41	516	28
	0.34	0.83	1.20	0	6
317	0.34	0.01	0.43	506	33
	0.35	−0.56	0.43	507	31
	0.36	0.5	0.43	506	28
	0.34	0.88	1.20	0	6

expression $B = B_0(1 - T/T_c)^\beta$ where B is the magnetic hyperfine field, B_0 is the magnetic hyperfine field at 0 K (57 T), T_c is the magnetic ordering temperature and the critical exponent, β, which is usually in the range 0.25–0.33 and in this calculation was taken as 0.25. The results displayed in figure 4 show good agreement between the experimentally determined data and those predicted theoretically.
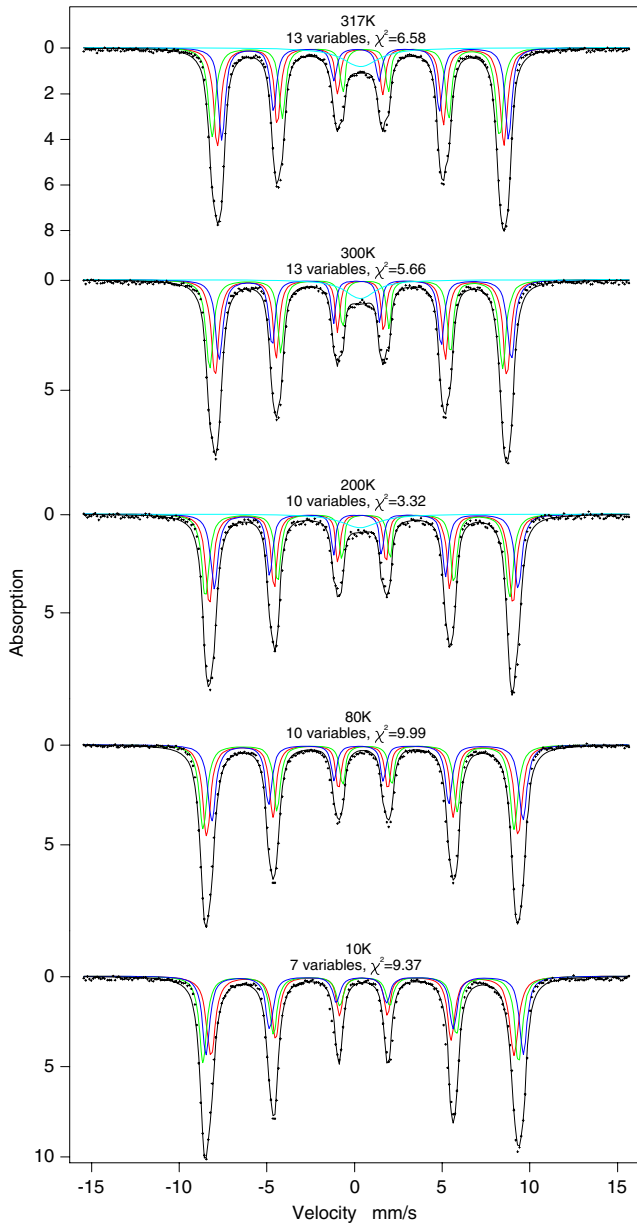
A comparison of the spectra contained in figures 2 and 3 shows a conspicuous difference in the shape of spectra recorded at low and high temperatures. The spectra recorded between 10 and 317 K in figure 3 and the spectrum recorded at 80 K in figure 2, show no splitting of spectral lines but significant broadening of each line contributing to the sextet pattern. In contrast, the spectra recorded between 285 and 650 K in figure 2 show clear splitting of all the lines constituting the overall profile of the sextet. The temperature of the change from the low temperature broad line spectra to the high temperature split line spectra appears not to be clear-cut in that all the spectra from 10 to 317 K recorded at increasing temperature are broadened (figure 3) whereas the spectrum recorded at decreasing temperature at 285 K

(figure 2) shows splitting of the spectral lines. This discrepancy may reflect thermal hysteresis or sample history, however the results contained in figures 2 and 3 do demonstrate that the spectra recorded at low and high temperatures have different profiles which (*vide infra*) has led us to an interpretation in terms of different magnetic states with a transition temperature around room temperature.

3.2.1. Fitting Mössbauer spectra in the range 285–700 K. Several models for the octahedral disposition of O^{2-} and F$^-$ ions around iron in the perovskite-related structure were considered during the fitting of the Mössbauer data. These included situations in which the random substitution of F$^-$ for O^{2-} gave differing numbers of F$^-$ ions in the six anion sites around iron. The spectra recorded in the higher temperature regime between 285 and 700 K were best fitted to a model in which each Fe^{3+} ion has four O^{2-} and two F$^-$ ions in the nearest neighbour anion shell, corresponding to charge neutrality within the perovskite-related unit cell.
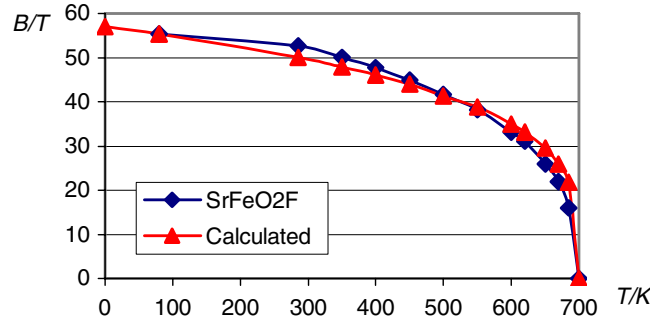
In this case there are two types of arrangements for the fluoride ions, that with the two F$^-$ ions at opposite corners

Figure 3. Mössbauer spectra recorded from SrFeO$_2$F between 10 and 317 K.

Figure 4. Variation of the magnetic hyperfine field in SrFeO$_2$F with temperature.

magnetic hyperfine field (B_{hf}), needs to be considered. In the present case, in which the magnetic interaction causes the main line splitting, the effect of the quadrupole interaction can be treated as a perturbation that yields energy shifts of $\Delta = \frac{1}{2}\Delta_0$ $(3\cos^2\theta - 1)$ where Δ_0 is the line splitting in the absence of hyperfine field and θ is the angle between the hyperfine field and V_{zz}. In table 1 it is seen that at 700 K the magnitude of the quadrupole splitting without magnetic hyperfine field, Δ_0, is 0.96 mm s^{-1}.

Given the above, it is possible to predict the quadrupole interactions of the two observed components. In almost all magnetically ordered perovskites the magnetic easy axis lies along a cube edge [7]. This is assumed here and the magnetic easy axis is denoted as the z axis. It is necessary to treat the *cis* and *trans* configurations separately. For the *cis* configuration there are two sub-arrangements according to whether the F$^-$ ions lie along the zx and zy axes, where V_{zz} makes an angle $\theta = 45°$ with the magnetic easy axis, or whether the F$^-$ ions are along the xy axes, where V_{zz} is at an angle of $\theta = 90°$ with the magnetic axis. The ratio of these sub-arrangements is 2:1. Using the value $\Delta_0 = +0.96$ mm s^{-1} the predicted quadrupole interaction values for the higher and lower area sub-arrangements are $+0.24$ and -0.48 mm s^{-1} respectively. In the case of *trans* coordinated sites there are again two sub-arrangements with $\theta = 90°$ (*trans* axis x or y) and $\theta = 0°$ (*trans* axis z) again with an area ratio of 2:1. For the *trans* configuration taking $\Delta_0 = -0.96$ mm s^{-1} (*cis* and *trans* configurations are expected to have opposite sign of EFG) we predict quadrupole interactions of $+0.48$ and -0.96 mm s^{-1} for the two sub-arrangements. Finally adding the *cis* and *trans* contributions—weighted in the *cis/trans* ratio of 4:1—we obtain predicted quadrupole interactions of $+0.29$ and -0.58 mm s^{-1} with area ratio 67%:33% for the two components. Comparison of these values with those of the fitted parameters in table 1 (mean values $+0.35$ and -0.68 mm s^{-1} with area ratio 65%:35%) show good, if not perfect, agreement. It seems that a model involving *cis* and *trans* arrangements of two F$^-$ ions per perovskite-related unit cell and a single magnetic (antiferromagnetic) axis is consistent with the spectra recorded in the temperature range 285–650 K.

3.2.2. Fitting Mössbauer spectra in the range 10–317 K. Several different models were initially used to fit the spectra

of the octahedron (*trans* arrangement) and that where F$^-$ is located at adjacent corners (*cis* arrangement). Random substitution of F$^-$ for O^{2-} (in the ratio 2F$^-$:4O^{2-}) gives a ratio of 4:1 for *cis:trans* configurations. The position (*cis* or *trans*) of the F$^-$ ion will be the major factor in determining the electric field gradient (EFG) at the spherical (3d)^5 ion. It is normally the case that V_{zz}—the principal axis of the EFG—is the axis of maximum symmetry at the Fe^{3+} ion and thus for the trans arrangement we expect V_{zz} to be along the F$^-$–Fe^{3+}–F$^-$ direction whilst for the *cis* arrangement V_{zz} is likely to be along the bisector of the two F$^-$–Fe^{3+} bonds.

In table 1 it is seen that the fits comprise two components but that the area ratio is 2:1 rather than the 4:1 characteristic of *cis:trans* arrangements. In order to explain this, a further variable, the angle between V_{zz} and the direction of the

recorded at temperatures between 10 and 317 K shown in figure 3. It was found that at least three sextet components were required to achieve a reasonable fit to the spectra and that, for spectra recorded between 200 and 317 K, an additional non-magnetic doublet component was also required. The ^{57}Fe Mössbauer parameters resulting from the fitting of the spectra are contained in table 2. At each temperature the parameters show that the three magnetic components have similar areas and similar values of magnetic hyperfine field. The line broadening exhibited in the spectra is achieved in the fits by a pattern of values of quadrupole interaction in which one component has a value near zero whilst the other components have values that are approximately equal in magnitude but are opposite in sign. Such a set of fitting parameters may arise in a number of ways but in view of later magnetization results (*vide infra*) a model was considered in which the Fe^{3+} moments were randomly oriented with respect to (any) axis of maximum electric field gradient (EFG). Incorporating $\sin\theta$ weighting— where θ is the angle between the magnetic hyperfine field and the axis of the EFG—the angular ranges that give equal component areas are $0° < \theta < 48°$, $48° < \theta < 71°$ and $71° < \theta < 90°$. Evaluating the mean angular factor $\frac{1}{2}\{3\cos^2\theta - 1\}$ for the approximation of the quadrupole interaction in a magnetic spectrum over these angular ranges for a system of randomly oriented iron moments gives values of $+0.56$, -0.11 and -0.45 respectively. This set of values is similar to those from fits with three unrestricted magnetic components, showing that a random Fe^{3+} moment model is consistent with the magnetically split spectra in this temperature range.

The non-magnetic component, observed with an area of $\sim 6\%$ in spectra above 80 K, is likely to arise from an Fe^{3+} phase with an ordering temperature below 200 K.

3.3. Magnetization results

The variation of magnetization with increasing temperature from 10 to 400 K following cooling in (i) zero applied field (ZFC) and (ii) an applied field of $H = 100$ Oe (FC) is shown in figure 5(a). The results show a separation between the field cooled and zero field cooled data below 300 K. This behaviour is consistent with a spin glass magnetic state [8, 9].

The hysteresis cycle measured at 300 K and shown in figure 5(b) demonstrates negligible hysteresis and the absence of saturation up to the maximum applied magnetic induction $B = 2$ T. The low values of aligned magnetic moment per Fe^{3+} ion (about $0.003\mu_\beta$ per Fe^{3+} ion at 2 T) exclude the possibility of ferro or ferrimagnetic order in $SrFeO_2F$.

4. Discussion of the magnetic structure

The most reasonable approach to the arrangement of anions around Fe^{3+} in $SrFeO_2F$ derives from the assumption that charge neutrality is retained within the cubic perovskite-related unit cell in which the body-centred Fe^{3+} ion is surrounded by six anions in the face-centred sites. In such a situation two of the six anion sites will be occupied by fluorine ions and the remaining four by oxygen ions.

The results that bear on the magnetic structure of $SrFeO_2F$ for temperatures below the ordering temperature of 685 K are:
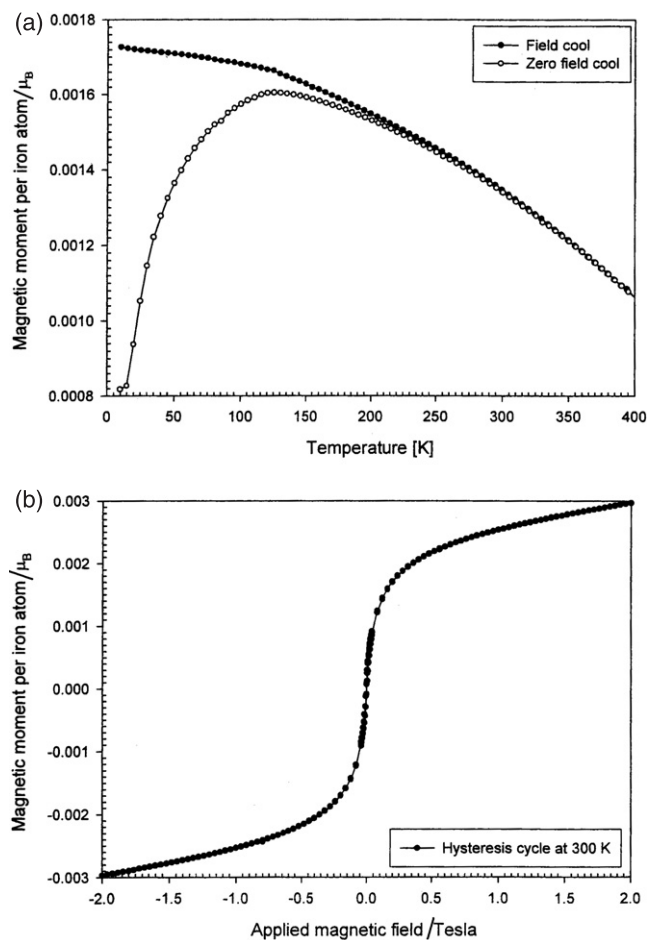
Figure 5. (a) Variation of magnetization between 10 and 400 K. Separate plots show field cooled and zero field cooled data. (b) Hysteresis cycle of $SrFeO_2F$ recorded at 300 K in a field of ± 2 T.

(i) the small aligned moment per Fe ion that excludes a ferromagnetic or ferrimagnetic state;
(ii) the separation of field cooled (FC) and zero field cooled (ZFC) magnetizations at temperatures less than ~ 300 K;
(iii) the change in Mössbauer spectra at ~ 300 K.

The situation that seems to give the best agreement with the data is of ordering into an antiferromagnetic state at $T_N = 685$ K which persists as the temperature is decreased to ~ 300 K. Below this temperature a state characterized by random spin orientation sets in which shows different ground state alignments in FC and ZFC conditions. The Mössbauer spectra have been fitted with this situation in mind and reasonable agreement is found.

The analysis of the Mössbauer spectra point to a situation in which the Fe^{3+} magnetic spin system converts from an ordered to a random state as the temperature is decreased to room temperature. Such re-entrant phases with random spin configurations are not uncommon in magnetic systems with some inbuilt disorder [9]. This has recently been exemplified in the perovskite-related oxide of composition $La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3$ ($0.1 < x < 0.4$) in which the randomness arises from the competing magnetic interactions caused by the substitution by iron on the

manganese site [10]. In SrFeO$_2$F the randomness arises from the substitution by fluorine on the oxygen anion site causing different superexchange Fe^{3+}–O^{2-}–Fe^{3+} and Fe^{3+}–F–Fe^{3+} pathways which, to give rise to disorder, would need to have contrasting values, for example be of different sign.

In such a transition where the observed spin system goes from a state of order to a state of greater disorder with decreasing temperature there should be another coupled sub-system within the material in which disorder increases to ensure that the total entropy of the system decreases with decreasing temperature. It would be reasonable to envisage that such a temperature-dependent sub-system might correspond to a change in the lattice or an order–disorder transition which initiates the observed change in the spin system. In the case of SrFeO$_2$F, the strong ionic bonding associated with the presence of F$^-$ and O^{2-} ions renders any such order–disorder transition around room temperature as highly unlikely. Hence, the most likely scenario is that some lattice distortion away from the low temperature cubic state causes a change in the balance of the magnetic interactions and consequently in the observed change of the spin system. It is clear that this change in lattice symmetry is of insufficient magnitude to be observed directly in the Mössbauer spectra but is clearly inferred by the observed behaviour of the coupled magnetic system.

The results therefore show that the magnetic structure of SrFeO$_2$F is significantly more complex than that of antiferromagnetic structurally related PbFeO$_2$F [11] in which the *trans* configuration of fluorine in the distribution of anions around Fe^{3+} is favoured over the *cis*-arrangement. The differences may be related to the lower temperature synthesis route to produce SrFeO$_2$F, in contrast to the high pressure, high temperature synthesis route needed to produce PbFeO$_2$F.

5. Conclusion

The oxide fluoride of composition SrFeO$_2$F has a magnetic ordering temperature of 685 ± 5 K. At temperatures between 685 and about 300 K the material behaves as an antiferromagnet and, at about 300 K, undergoes a transition to a state with random spin orientation.

Acknowledgment

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