Supplementary information

Collection and refinement of diffraction data

X-ray data were refined with 6 background terms in function no 2 and Gaussian, Lorentzian and asymmetry terms in profile type 2. Lattice parameters, atom positions and isotropic temperature factors were refined to convergence.

The Osiris diffractometer at the ISIS spallation source was used to collect high d-spacing PND patterns. The collected data range was 13-140 μs (0.747-8.06 Å). Osiris data were refined with a linear absorption function, GSAS time-of-flight peak profile type no. 2 and 6 shifted Chebyshev (function number 1) background terms. Atom positions, magnetic moment and lattice parameters were freely refined but temperature factors could not be refined, presumably due to the lack of low d-spacing reflections. These were fixed at a small, positive value. The nuclear structures based on this data must therefore be considered of low resolution, though this does not affect the magnetic structure.

The high resolution diffractometer D2B at the Institut Laue Langevin was used to collect PND data for Sr_2FeO_3F at 3 K; data were collected at the optimum wavelength for instrumental resolution (1.59 Å) and at 2.40 Å to better resolve the high d-spacing reflections. Data sets at ambient temperature and 2 K were also collected on the $Sr_2Fe_{1-x}Co_xO_3Cl$ series with $\lambda = 1.59$ Å. All the D2B data was refined with 8 background parameters in a cosine Fourier series (GSAS function number 2) and constant wavelength peak profile type 2. Linear absorption, zero point, atom positions, magnetic moments and isotropic temperature factors were refined to convergence.

The very high intensity diffractometer D20 at the ILL was used to collect variable temperature diffraction data for Sr_2FeO_3F. The wavelength used was 2.40 Å and a graphite filter was used to remove harmonics. This data was refined with 4 background terms in

GSAS function no. 2 and peak profile type 2. Data sets were truncated (20-65° was used) to focus on the magnetic region and hence peak shape was refined once then fixed. Atom positions were fixed at the values obtained from the D2B data. For each phase lattice parameters, zero point, histogram scale factor, background and μ_x (= μ_y) were refined.

Representational analysis of the Sr_2FeO_3F magnetic structure

Representational analysis[1-8] allows the determination of the symmetry allowed magnetic structures that can result from a second-order magnetic phase transition, given the crystal structure before the transition and the propagation vector of the magnetic ordering. These calculations were carried out using the program *Sarah-Representational Analysis*[9] and magnetic structures based on this representational analysis were refined using the GSAS front end *Sarah-Refine*. Labelling of the propagation vector and the irreducible representations follows the scheme used by Kovalev.[10]

The crystallographic space group of Sr_2FeO_3F is *P4/nmm*. The set of magnetic peaks which persist to ambient temperature can be described with a propagation vector $\boldsymbol{k}$ = [½ ½ 0] – a doubling of the crystallographic axis along the *a* and *b* axes consistent with *xy* antiferromagnetic ordering. The decomposition of the magnetic representation Γ_{mag} in terms of the non-zero IRs of $G_{\boldsymbol{k}}$ for the iron site, and their associated basis vectors, ψ_n, are given in Table S1. Γ_1 describes the La_2NiO_4-type magnetic structure whereas Γ_2 is La_2CuO_4-type. Γ_3 describes structures with the moments pointing along *z*. Hence Γ_2 gives a good fit to the magnetic peaks which persist to room temperature (and also to the data from oxide chlorides and oxide bromides discussed previously). ψ_3 and ψ_4 both produce orthogonal structures if used individually; to produce collinear structures (which fit the data equally well) a mixture of ψ_3 and ψ_4 must be used.

Representational analysis was used to determine whether it was possible to describe the magnetic peaks with a single structural model. We showed previously,[1] though with lower resolution data, that a single model could apparently fit the peaks through an unusual rotation of the moments in the *xy* plane. The variable temperature data in Fig. 6 show that the peaks corresponding to $\boldsymbol{k}$ = [½ ½ ½] decay with temperature much more quickly than the remaining magnetic peaks. This was taken as evidence of a separate magnetic phase which was indistinguishable in nuclear structure, e.g. small changes in defect structure.

Table S1. Irreducible representations and associated basis vectors for the space group *P4/nmm* (setting 2) with $\boldsymbol{k}$ = [½ ½ 0].

		Fe at ¾,¾,0.22			Fe at ¼,¼,0.78		
IR	BV	m_x	m_y	m_z	m_x	m_y	m_z
Γ_1	ψ_1	1	0	0	0	-1	0
	ψ_2	0	1	0	-1	0	0
Γ_2	ψ_3	0	1	0	1	0	0
	ψ_4	-1	0	0	0	-1	0
Γ_3	ψ_5	0	0	0	0	0	-1
	ψ_6	0	0	1	0	0	0

For a second-order transition a powerful simplification to the number of possible structures arises as a consequence of the Landau theory – the ordering transition can involve only one irreducible representation becoming critical. Accordingly, the basis vectors[17] involved in the resulting structure are limited to those associated with a single IR and the number of "symmetry allowed" magnetic structures possible for a particular crystallographic site is simply the number of nonzero IRs in the decomposition of its magnetic representation. There

are two possibilities to describe the Sr_2FeO_3F magnetic structure. The first is that there are two distinct *P4/nmm* phases present, with indistinguishable nuclear structures but with magnetic ordering temperatures well above room temperature (***k*** = [*½ ½ 0*]) and around 60 K (***k*** = [*½ ½ ½*]). The second is that a further phase change occurs to the already ordered phase when cooled below *ca* 100 K, this would be described by the propagation vector ***k*** = [*0 0 ½*]) in the $P\bar{4}\,2_1m$ structure developed above.

The results of representational analysis to describe these cases are summarized in Tables S2 and S3. All symmetry allowed structures which describe a *c*-axis doubling have the moments in the top half of the cell exactly opposed to the moments of the corresponding atoms in the bottom half of the cell. Small rotations in opposite directions within the *xy* plane, as we described previously[1] when developing a single phase magnetic structure to describe Sr_2FeO_3F, are not symmetry allowed. Hence two magnetic phases must be present below *ca.*

Table S2. Irreducible representations and associated basis vectors for the space group *P4/nmm* (setting 2) with *k* = [*½ ½ ½*].

		Fe at *¾,¾,0.22*			Fe at *¼,¼,0.78*		
IR	BV	m_x	m_y	m_z	m_x	m_y	m_z
Γ_1	ψ_1	1	0	0	0	1	0
	ψ_2	0	1	0	1	0	0
Γ_2	ψ_3	0	1	0	-1	0	0
	ψ_4	-1	0	0	0	1	0
Γ_3	ψ_5	0	0	0	0	0	1
	ψ_6	0	0	1	0	0	0

100 K. The results of the representational analysis are actually the same, any one of ψ_1-ψ_4 in Table S2 and ψ_1, ψ_2, ψ_4 or ψ_5 in Table S3 describe a structure in which the layer stacking alternates between a La_2NiO_4-type sequence and a La_2CuO_4-type sequence. They result in intensity on the *½½½*, *½½3/2*, *½½5/2* and *½½7/2* magnetic reflections but no intensity on other magnetic peaks in this region of the diffraction pattern.

Table S3. Nonzero irreducible representations and associated basis vectors for the space group $P\bar{4}2_1m$ with $k = [0\ 0\ ½]$.

		Fe at *¼,¼,0.22*			Fe at *¾,¾,0.22*			Fe at *¼,¾,0.78*			Fe at *¾,¼,0.78*		
IR	BV	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z	m_x	m_y	m_z
Γ_1	ψ_1	1	1	0	-1	-1	0	1	-1	0	-1	1	0
Γ_2	ψ_2	1	-1	0	-1	1	0	-1	-1	0	1	1	0
	ψ_3	0	0	1	0	0	1	0	0	-1	0	0	-1
Γ_3	ψ_4	1	1	0	-1	-1	0	-1	1	0	1	-1	0
Γ_4	ψ_5	1	-1	0	-1	1	0	1	1	0	-1	-1	0
	ψ_6	0	0	1	0	0	1	0	0	1	0	0	1
Γ_5	ψ_7	1	0	0	1	0	0	0	0	0	0	0	0
	ψ_8	0	1	0	0	1	0	0	0	0	0	0	0
	ψ_9	0	0	1	0	0	-1	0	0	0	0	0	0
	ψ_{10}	0	0	0	0	0	0	-1	0	0	-1	0	0
	ψ_{11}	0	0	0	0	0	0	0	1	0	0	1	0
	ψ_{12}	0	0	0	0	0	0	0	0	1	0	0	-1

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