Complex magnetic ordering in the oxide selenide Sr2Fe3Se2O3

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Complex magnetic ordering in the oxide selenide $Sr_2Fe_3Se_2O_3$

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Supplementary Material

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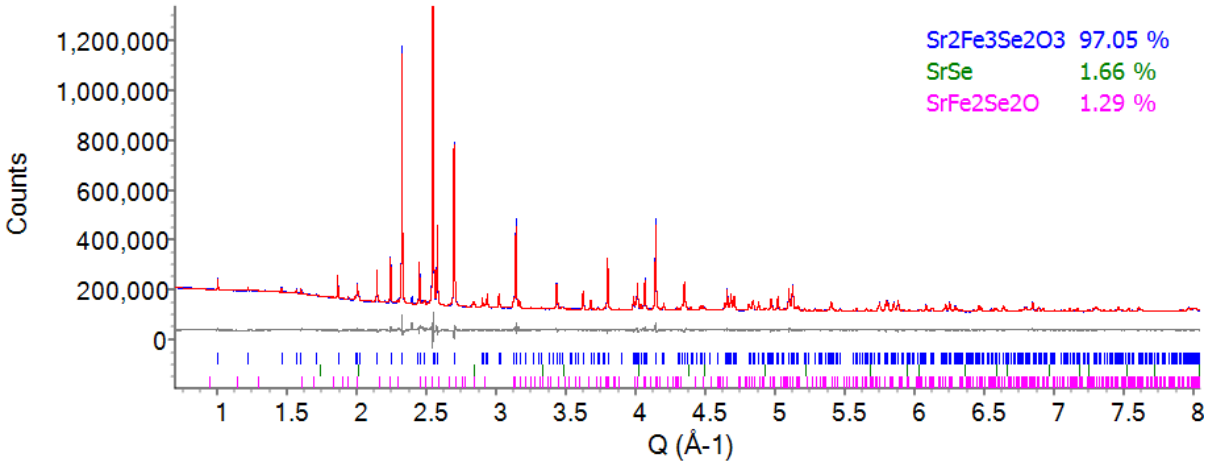

Figure S1 Rietveld refinement against PXRD pattern of $Sr_2Fe_3Se_2O_3$ sample ***A*** taken at room temperature using the Mythen detector of the I11 diffractometer at Diamond Light Source.

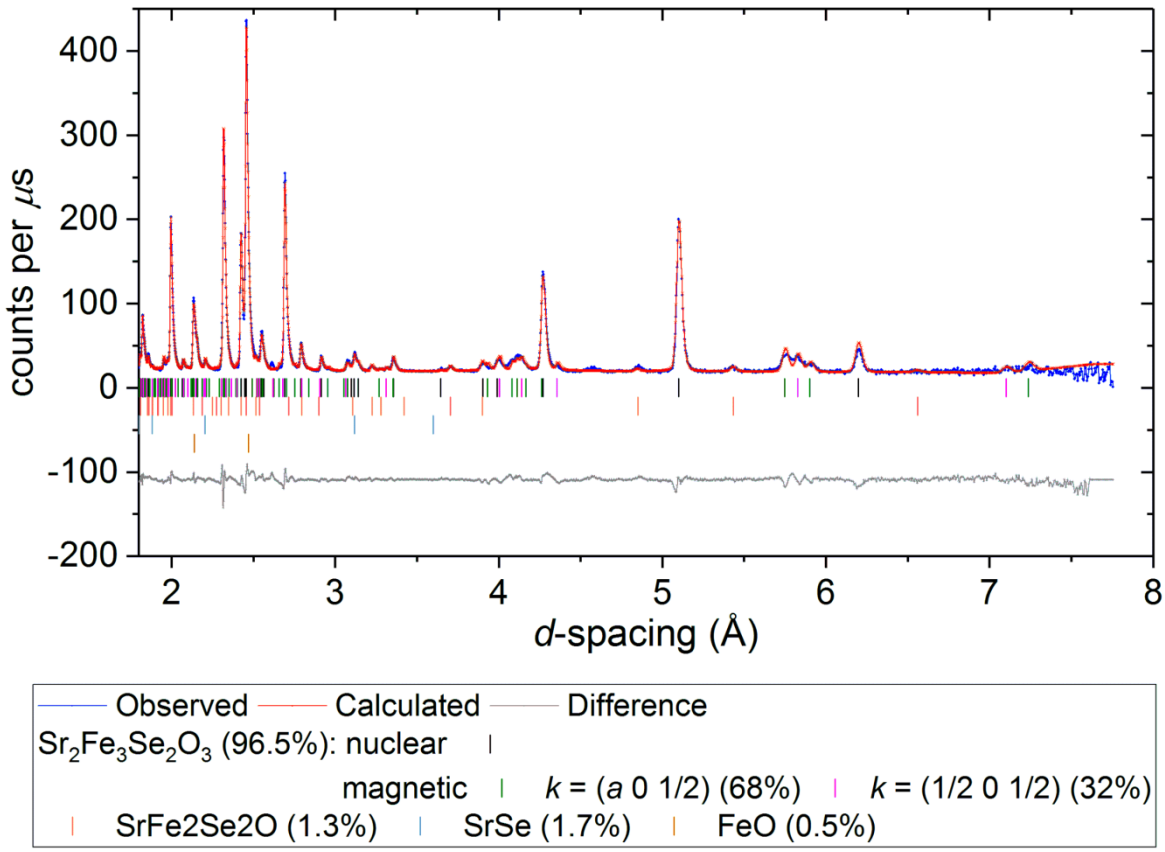

Figure S2 Rietveld refinement of $Sr_2Fe_3Se_2O_3$ sample A at 92 K showing the coexistence of the commensurate and incommensurate magnetic phases at T_{INC}. The material shows only the commensurate magnetic structure at and below 91 K, and only the incommensurate magnetic structure at 93 K up to T_{N1}.

Description of the magnetic models using ISODISTORT

As described in the main text, between 55 (T_{N2}) and 91 K (T_{INC}), one of the two Fe sites shows commensurate magnetic order with k-point U (½, 0, ½). The neutron diffraction data may be described with either the Fe2 sites; using mU2(a,0) modes with mU2[Fe2:h:mag]A'_1(a) constrained to be equal to minus mU2[Fe2:h:mag]A'_2(a), or the Fe1 sites; using the mU1(a,0) mode [Fe1:a:mag]mU1Ag(a). Equivalent fits can be achieved with either site, however using the Fe1 sites gives an ordered moment at 55K of 4.75 μ_B which is unrealistic for an Fe^{2+} ion. The conclusion that it is the Fe2 sites ordering in this regime is consistent with the Mössbauer data, which show the more abundant site to be the one that is ordered. An equivalent case occurs in the incommensurate region between T_{INC} and 118K (T_{N1}), in which the magnetic scattering occurs with k-point A (a, 0, ½) and can be described by either the Fe2 site with mA2 modes or Fe1 site with mA1 modes.

Below T_{N2} the Fe1 sites order, with k point S (k=½, ½, 0). In determining the model, the six ordering modes associated with this k-point for the Fe1 sites were tried: mS3+S4+ [Fe1:a:mag]Bg_1(a), mS3+S4+ [Fe1:a:mag]Bg_1(b), mS3+S4+ [Fe1:a:mag]Bg_2(a), mS3+S4+ [Fe1:a:mag]Bg_2(b), mS1+S2+ [Fe1:a:mag]Ag(a) and mS1+S2+ [Fe1:a:mag]Ag(b). Of these six, a combination of the four mS3+4+ modes: Bg_1(a,a) and Bg_2(a,a) gives a reasonable model, but does not give a satisfactory fit to the data, shown in Figure S3(a). The fit can be improved slightly by allowing all six terms to refine freely {mS3+S4+ Bg_1(a,b), mS3+S4+ Bg_2(a,b), mS1+S2+ Ag(a,b)} but even this gives a poor statistical and visual fit, which indicates that the data cannot be fitted with these modes alone, as shown in Figure S3(b). Inclusion of the Fe2 sites in the model was carried out by refining the combinations of the twelve modes associated with the S k-point for the Fe2 sites alongside those of the Fe1 sites. Of these twelve, only a combination of the mS3+S4+[Fe2:h:mag] modes gave significant improvement to the fit: refining mS3+S4+[Fe2:h:mag]A''_1(a,a) and mS3+S4+[Fe2:h:mag]A''_2(a,a) as well as mS3+S4+ [Fe1:a:mag]Bg_1(a,a) and mS3+S4+ [Fe1:a:mag]Bg_2(a,a). This produces a good statistical and visual fit, shown in Figure S3(c), with a reasonable magnetic model. If all 18 terms are allowed to refine freely of one another and produce a nonsensical model, only a minimal improvement in the agreement factor can be achieved (5.4 % vs 5.2 %), indicating the model represents a global minimum in the refinement.

The overall magnetic model uses five parameters to describe the ordering of the 32 Fe2 and 16 Fe1 atoms in the $2a_{nucl} \times 2b_{nucl} \times 2c_{nucl}$ magnetic cell: one for the major component of the Fe2 ordering (described by mU2[Fe2:h:mag]A'_1(a,0) = –mU2[Fe2:h:mag]A'_2(a,0)), two for the Fe1 ordering (described by mS3+4+[Fe1:a:mag]Bg_1(a,a) and mS3+4+[Fe1:a:mag]Bg_2(a,a)), and two for the Fe2 canting (described by –mS3+4+[Fe2:h:mag]A''_1(a,a) and –mS3+4+[Fe2:h:mag]A''_2(a,a)). Importantly, the mS3+S4+[Fe2] modes refine to have opposite sign to the mS3+S4+[Fe1] modes, which results in the Fe2 ions being antiferromagnetically aligned with respect to the nearest neighbour Fe1 ions.

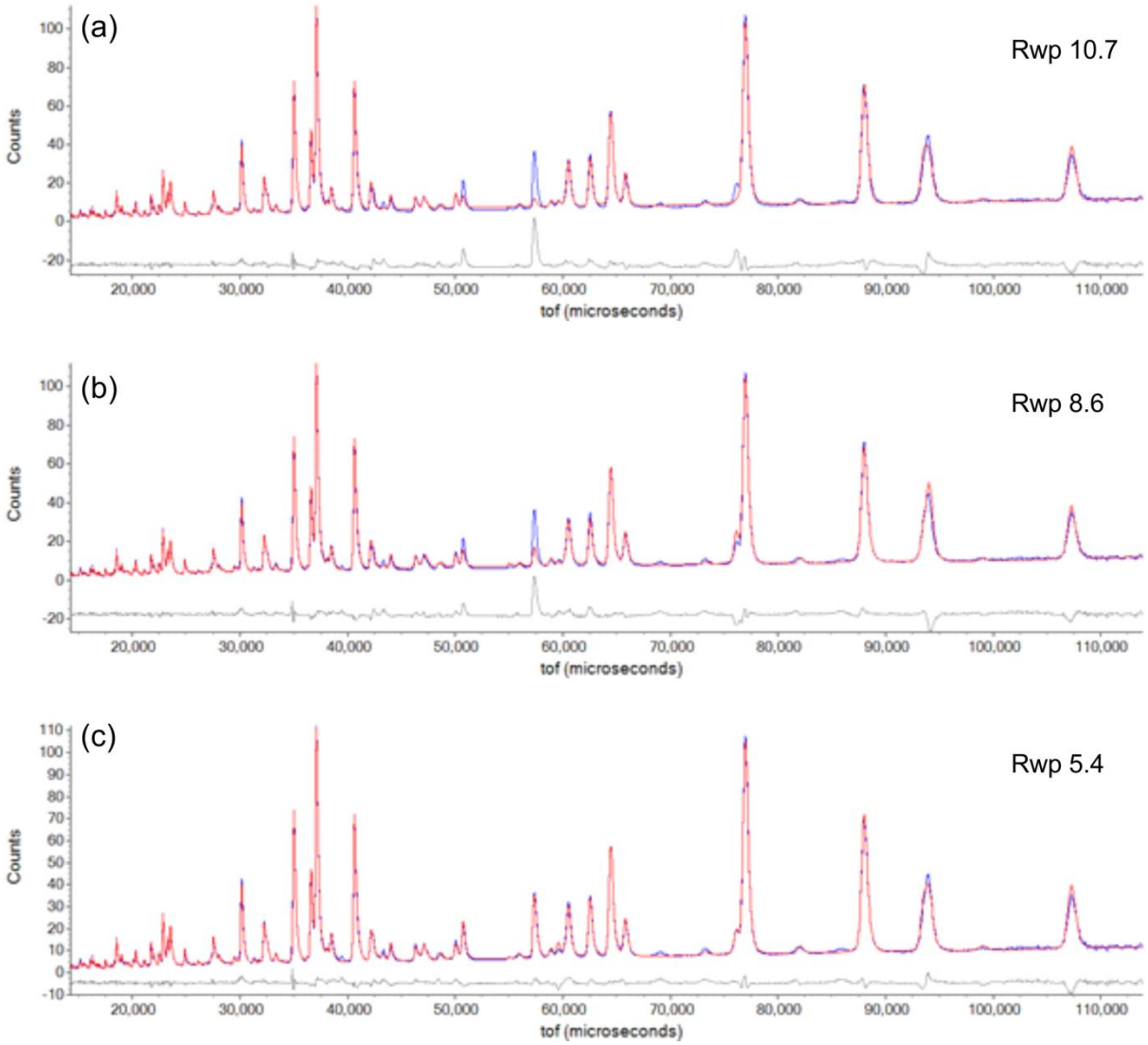

Figure S3 WISH bank 3/8 of a Rietveld refinement of the neutron diffraction pattern of sample ***A*** at 1.5K. **(a)** refinement of the model using only the Fe1 sites to account for the S-point magnetic scattering with all Fe1 atoms carrying the same moment. **(b)** Refinement of the model using only the Fe1 sites to account for the S-point magnetic scattering but allowing the free refinement of the parameters such that different atoms can have different moments. **(c)** Refinement of the model using both the Fe1 and Fe2 sites to account for the S-point magnetic scattering, using a sensible model.

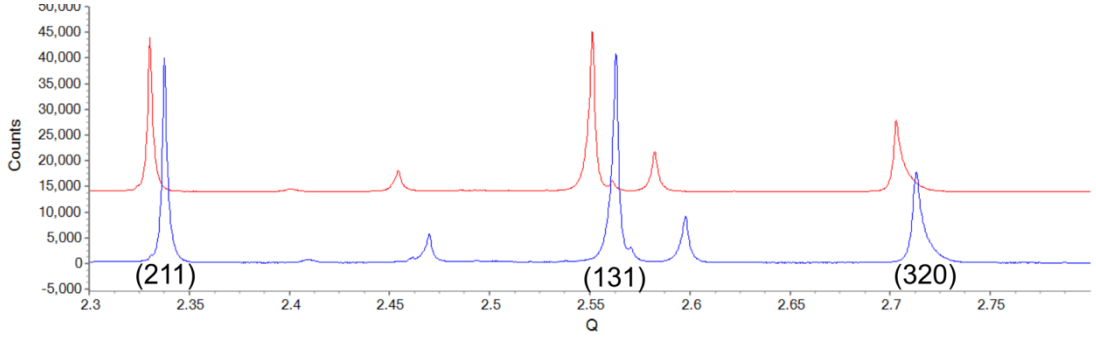

Figure S4 X-ray diffraction patterns of Sample A taken using the MAC detector of the ID22 diffractometer at the ESRF. The red pattern was taken at room temperature and the blue pattern at 5 K. No evidence of splitting in the strongest structural peaks is observed.

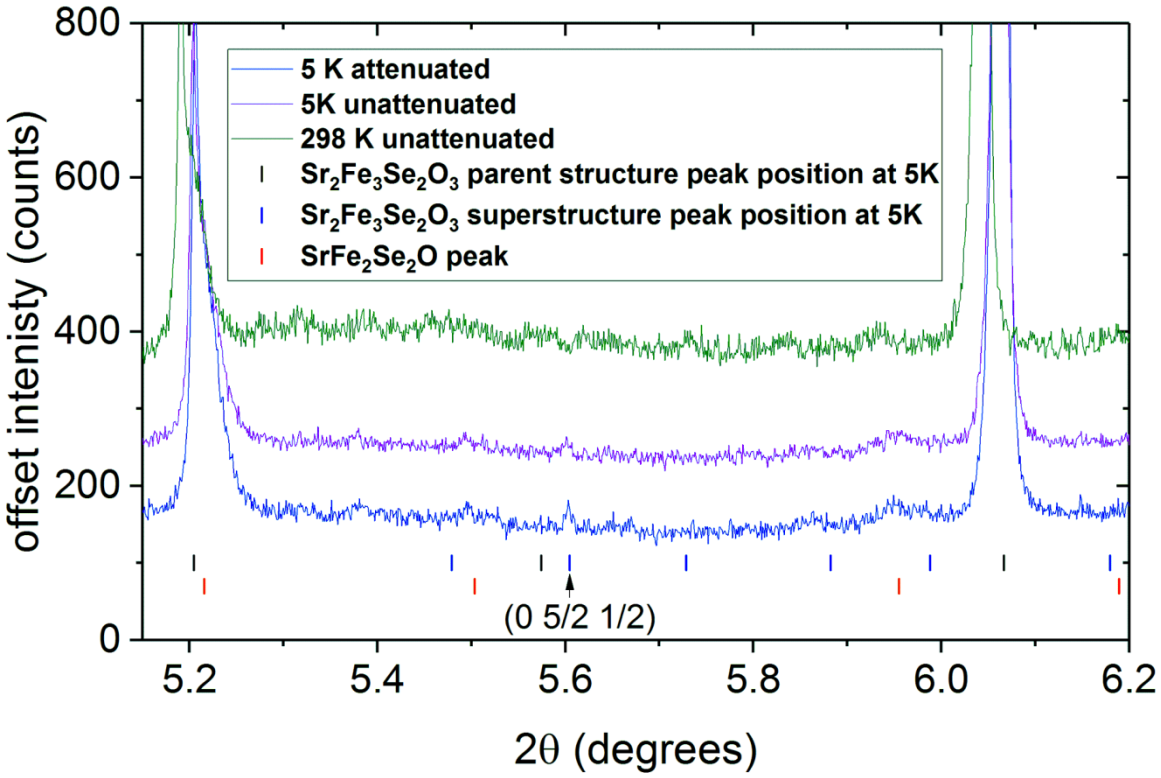

Figure S5 Powder X-ray diffraction of sample ***A*** taken at ID22 (λ=0.35440(Å)). The data taken at 5K (blue line) show the presence of a very weak peak at 5.6° coincident with the position of the 0 5/2 ½ reflection expected from the magnetic structure and symmetry analysis. This peak appears weaker in the pattern taken with the unattenuated beam (purple line), which while measured in the cryostat at 5K is estimated to be between 30 and 60 K based on the lattice parameters due to beam heating. The peak is absent in the room temperature diffraction pattern (green line).Note that the maximum peak height observed in the pattern was 40,000 counts.

Tables of unit cell information in the paramagnetic regime.

Table S1 Refined atomic parameters against synchrotron powder diffraction data for sample ***B***, corresponding to the data in Table 1 in the main paper. Peakshape asymmetry was observed in this high resolution data. Attempting to refine the asymmetry as 2 phases with different lattice parameters produced an improved fit, but no differences in the occupancies or positions of the atoms could be discerned between the phases. Since no physical origin for this asymmetry could be established, it was instead handled with an arbitrary asymmetric peakshape function.

Instrument	I11
Temperature	Room temperature
Nuclear symmetry	*Pbam* (55)
***a* (Å)**	7.8121(2)
***b* (Å)**	10.23747(9)
***c* (Å)**	3.99388(5)
V (Å^3)	319.413(7)
Density (g cm^{-3})	5.70486(9)
R_{wp} (%)	5.22
χ^2	1.56
R_{Bragg}	2.03

Atom	**Site**	***x***	***y***	***z***	**U_{11} (Å^2)**	**U_{22} (Å^2)**	**U_{33} (Å^2)**	**U_{12} (Å^2)**
Sr1	4*g*	0.09160(7)	0.34920(6)	0	0.0158(5)	0.0156(4)	0.0136(4)	–0.0007(4)
Fe1	2*a*	0	0	0	0.0136(8)	0.0191(7)	0.0141(8)	0.0002(6)
Fe2	4*h*	0.2588(1)	0.08825(8)	0.5	0.0129(6)	0.0188(4)	0.0120(5)	0.0010(4)
Se1	4*h*	0.40095(8)	0.33574(6)	0.5	0.0128(5)	0.0122(4)	0.0122(4)	0.0005(4)
O1	2*d*	0	0.5	0.5	0.004(2)	0.004(2)	0.004(2)	0*
O2	4*g*	0.2346(5)	0.0846(3)	0	0.017(1)	0.017(1)	0.017(1)	0*

* not refined: displacement ellipsoids for the oxide sites were refined as isotropic.

Table S2 refinement parameters from WISH at 135K for sample ***B***, corresponding to the data in Table 1 in the main paper.

Instrument	WISH
Temperature	135 K
Nuclear symmetry	*Pbam* (55)
***a* (Å)**	7.8003(2)
***b* (Å)**	10.2112(3)
***c* (Å)**	3.99121(9)
V (Å^3)	317.97(1)
Density (g cm^{-3})	5.7308(2)
R_{wp} (%)	4.10
χ^2	1.06
R_{Bragg}	1.37

Atom	**Site**	***x***	***y***	***z***	**U_{11} (Å^2)**	**U_{22} (Å^2)**	**U_{33} (Å^2)**	**U_{12} (Å^2)**
Sr1	4*g*	0.0908(3)	0.3494(2)	0	0.019(2)	0.017(3)	0.015(2)	0.004(2)
Fe1	2*a*	0	0	0	0.049(3)	0.023(3)	0.045(4)	0.024(2)
Fe2	4*h*	0.2604(2)	0.0897(2)	0.5	0.013(2)	0.025(2)	0.015(1)	–0.001(1)
Se1	4*h*	0.4003(3)	0.3330(2)	0.5	0.020(2)	0.014(2)	0.035(2)	0.001(2)
O1	2*d*	0	0.5	0.5	0.006(4)	0.008(4)	0.017(4)	–0.007(3)
O2	4*g*	0.2318(4)	0.0863(3)	0	0.050(4)	0.015(3)	0.035(2)	0.003(3)

Tables of structural information in the Fe2 ordered regime

Table S3 refinement parameters from WISH at 55K for the nuclear cell of sample ***B***, corresponding to the data in Table 1 in the main paper.

Instrument	WISH
Temperature	55 K
Nuclear symmetry	*Pbam* (55)
***a* (Å)**	7.7963(2)
***b* (Å)**	10.2008(3)
***c* (Å)**	3.98951(9)
V (Å^3)	317.18(1)
Density (g cm^{-3})	5.7452(2)
R_{wp} (%)	4.55
χ^2	1.17
R_{Bragg}	1.55

Atom	Site	*x*	*y*	*z*	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)
Sr1	4*g*	0.0889(3)	0.3519(2)	0	0.019(2)	0.018(3)	0.019(2)	–0.001(2)
Fe1	2*a*	0	0	0	0.057(4)	0.015(3)	0.056(4)	0.023(2)
Fe2	4*h*	0.2569(2)	0.0893(2)	0.5	0.020(2)	0.027(2)	0.012(1)	0.003(2)
Se1	4*h*	0.4000(3)	0.3327(2)	0.5	0.021(2)	0.030(3)	0.030(2)	–0.008(2)
O1	2*d*	0	0.5	0.5	0.001(4)	0.002(4)	0.008(4)	0.001(3)
O2	4*g*	0.2278(3)	0.0862(3)	0	0.038(4)	0.009(3)	0.051(3)	–0.001(3)

Table S4 refinement parameters from WISH at 55K for the magnetic cell of sample ***B***, corresponding to the data in Table 1 in the main paper.

Instrument	WISH
Temperature	55 K
magnetic symmetry	B_ab2_1m (36.178)*
***a* (Å)**	15.5911(4)‡
***b* (Å)**	10.1997(3)‡
***c* (Å)**	7.9782(2)‡
***V* (Å^3)**	1268.72(5)‡
Density (g cm^{-3})	5.7452(2)
R_{wp} (%)	4.55
χ^2	1.17
R_{Bragg}	2.30

Atom	***site***	***x***	***y***	***z***		μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)
Fe2_1	8*a*	0.2569(2)	0.0893(2)	0		0	0	3.10(1)
Fe2_2	8*a*	0.5069(2)	0.4107(2)	0		0	0	3.10(1)

*This is a non standard setting of C_amc2_1, used in order maintain the same axis orientation as used for the nuclear cell. The unit cell is a $2a \times b \times 2c$ expansion of the nuclear unit cell.

Tables of structural information in the Fe1 and Fe2 ordered regime

Table S5 refinement parameters from WISH at 20K for the nuclear cell of sample ***B***, corresponding to the data in Table 1 in the main paper.

Instrument	WISH
Temperature	20 K
Nuclear symmetry	*Pbam* (55)
***a* (Å)**	7.7945(2)
***b* (Å)**	10.1979(3)
***c* (Å)**	3.9893(1)
***V* (Å^3)**	317.10(1)
Density (g cm^{-3})	5.7465(3)
R_{wp} (%)	4.61
χ^2	1.21
R_{Bragg}	1.99

Atom	**Site**	***x***	***y***	***z***	**U_{11} (Å^2)**	**U_{22} (Å^2)**	**U_{33} (Å^2)**	**U_{12} (Å^2)**
Sr1	4*g*	0.0898(3)	0.3487(3)	0	0.012(2)	0.022(3)	0.017(2)	0.001(2)
Fe1	2*a*	0	0	0	0.039(3)	0.018(3)	0.060(4)	0.015(2)
Fe2	4*h*	0.2599(2)	0.0900(2)	0.5	0.015(2)	0.025(2)	0.007(1)	0.003(2)
Se1	4*h*	0.4003(3)	0.3350(3)	0.5	0.022(2)	0.014(3)	0.024(2)	0.002(2)
O1	2*d*	0	0.5	0.5	0.017(5)	0.006(5)	0.006(4)	–0.007(3)
O2	4*g*	0.2317(4)	0.0860(3)	0	0.052(4)	0.010(3)	0.055(3)	0.008(4)

Table S6 refinement parameters from WISH at 20K for the magnetic cell of sample B, corresponding to the data in Table 1 in the main paper.

Instrument	WISH
Temperature	20 K
magnetic symmetry	$I_a b^*$ (9.40)
***a* (Å)**	15.5890(4)
***b* (Å)**	20.3958(6)
***c* (Å)**	7.9786(2)
γ(°)	90
V (Å^3)	2536.80(8)
R_{wp} (%)	4.61
χ^2	1.21
R_{Bragg}	2.27

Atom	***site***	***x***	***y***	***z***	***μ_x (μ_B)***	***μ_y (μ_B)***	***μ_z (μ_B)***
Fe1_1	4*a*	0	0	0	3.10(2)	-1.34(7)	0
Fe1_2	4*a*	0.5	0.5	0	3.10(2)	-1.34(7)	0
Fe1_3	4*a*	0.25	0.75	0	-3.10(2)	-1.34(7)	0
Fe1_4	4*a*	0.75	0.25	0	-3.10(2)	-1.34(7)	0
Fe2_1	*8a*	0.12995(11)	-0.04500(10)	0.75	-0.69(2)	0.59(5)	3.18(1)
Fe2_5	8*a*	0.37995(11)	0.79500(10)	0.25	0.69(2)	0.59(5)	-3.18(1)
Fe2_9	8*a*	0.12005(11)	0.70500(10)	0.25	0.69(2)	0.59(5)	-3.18(1)
Fe2_13	8*a*	0.87005(11)	0.04500(10)	0.75	-0.69(2)	0.59(5)	3.18(1)

*This is a non standard setting of space group $C_c c$ (9.40 in BNS notation), used in order maintain the same axis orientation as used for the nuclear cell. The unit cell is a $2a \times 2b \times 2c$ expansion of the nuclear unit cell.

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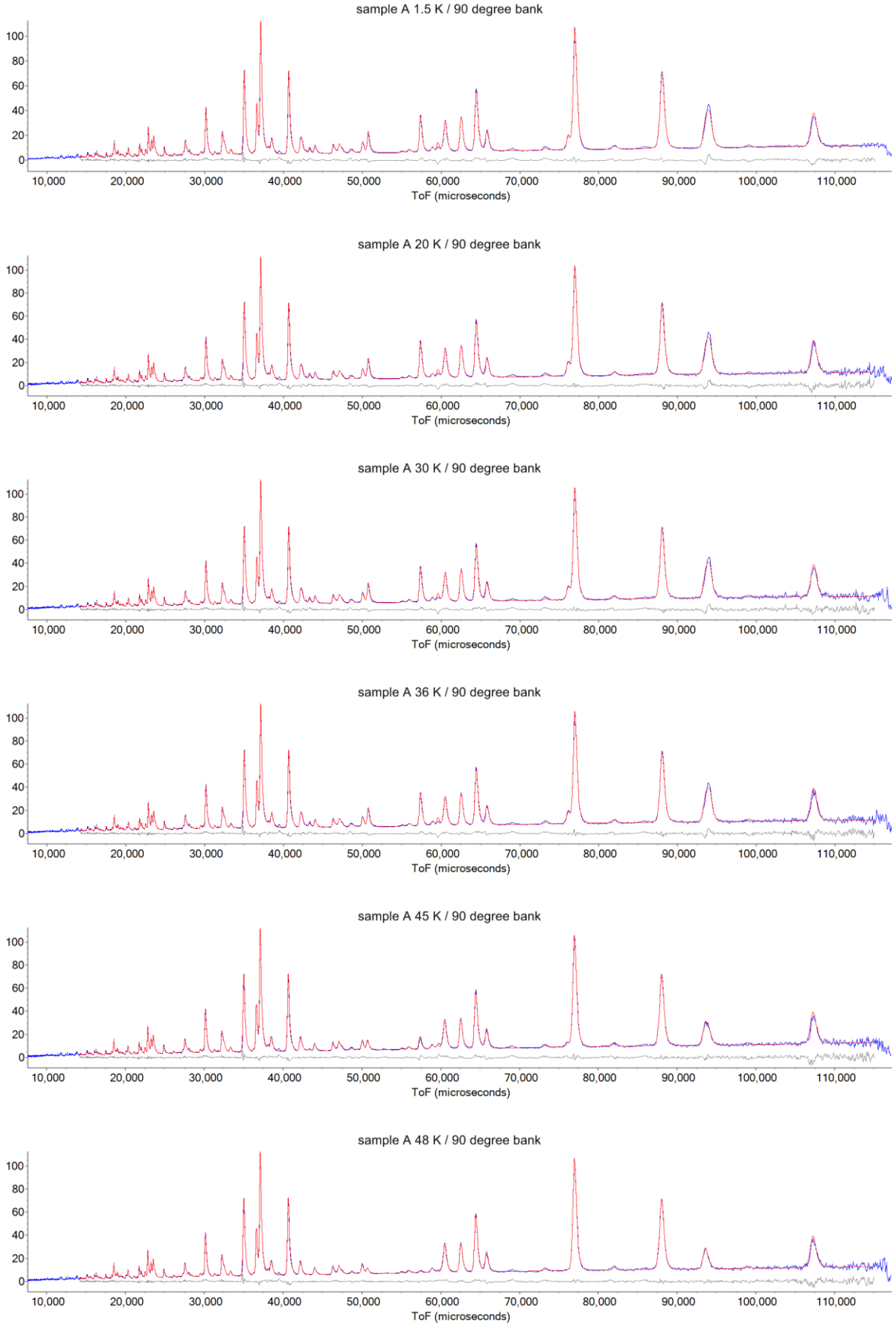
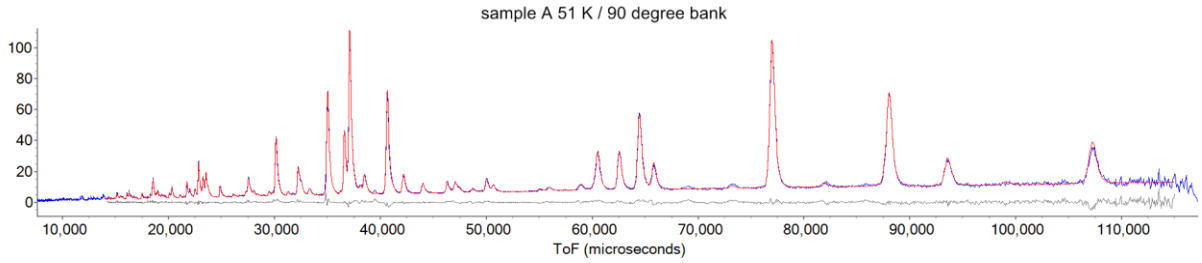
Figure S6. Rietveld refinements against Neutron Powder Diffraction data of Sample A. patterns at 1.5-91 and 125-150K were refined against with Topas Academic, patterns 92-119K were refined against with FullProf. The 150K refinement in Fullprof is also shown for comparison.

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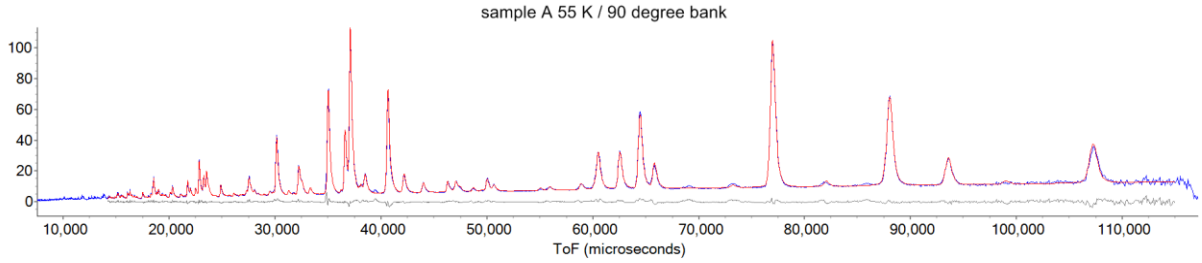
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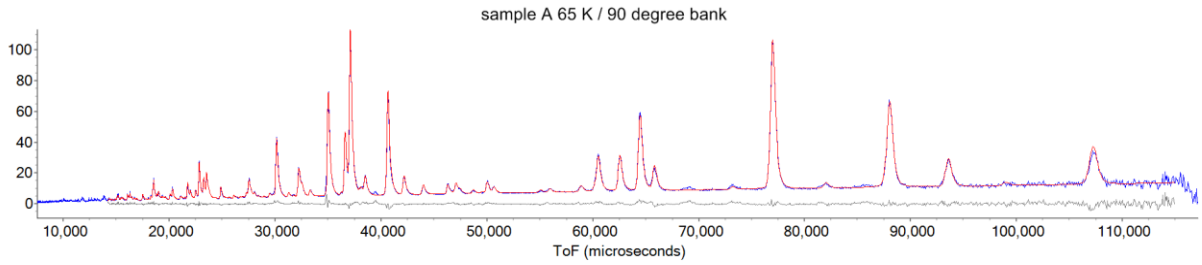
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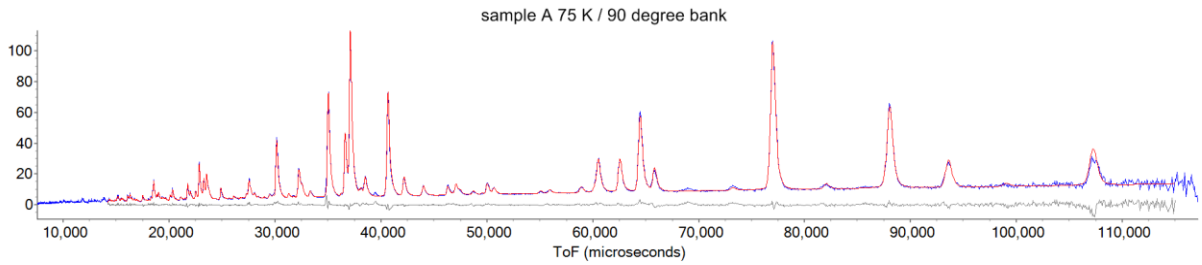
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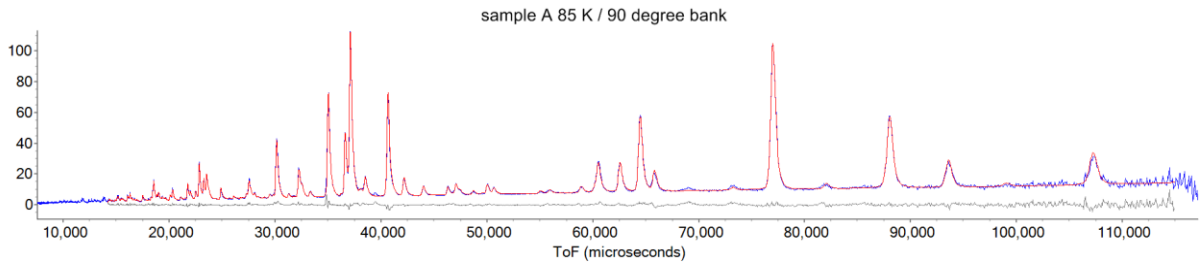
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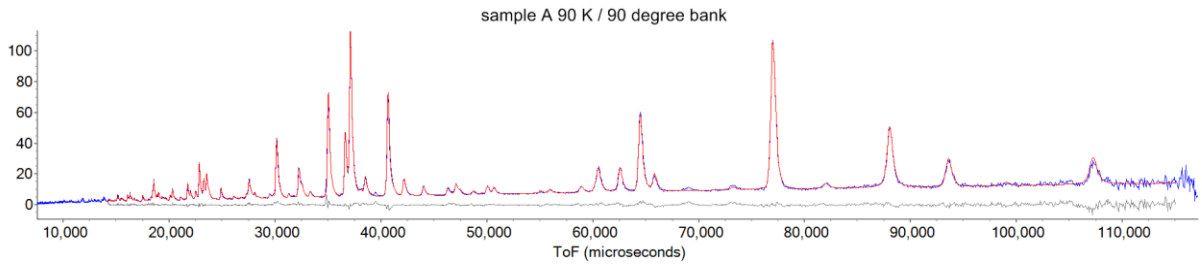
ToF (microseconds)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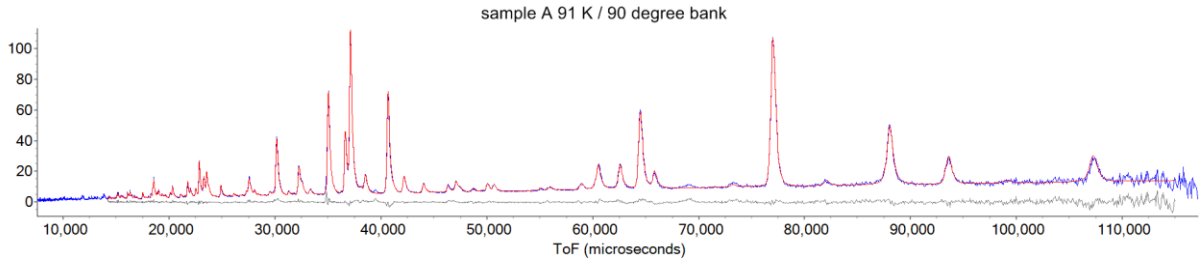
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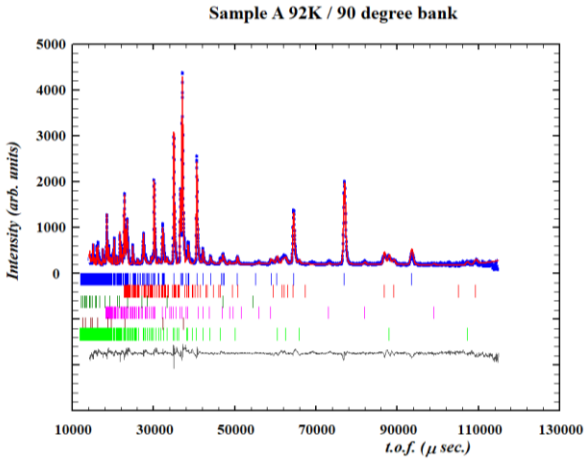
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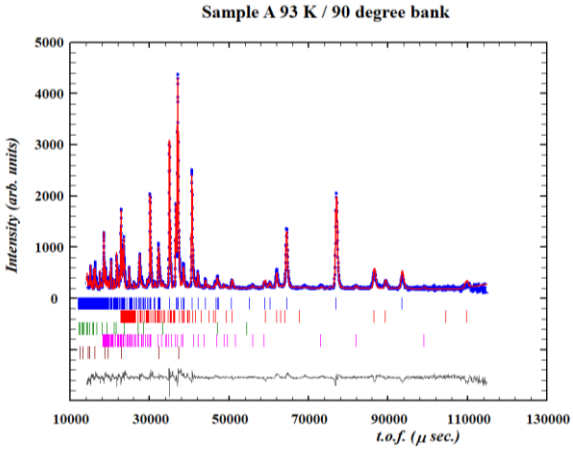
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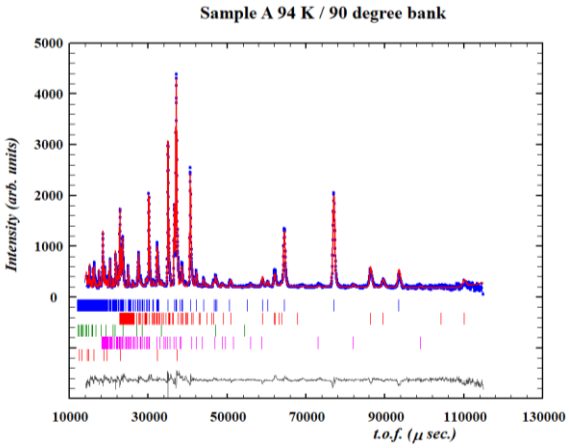
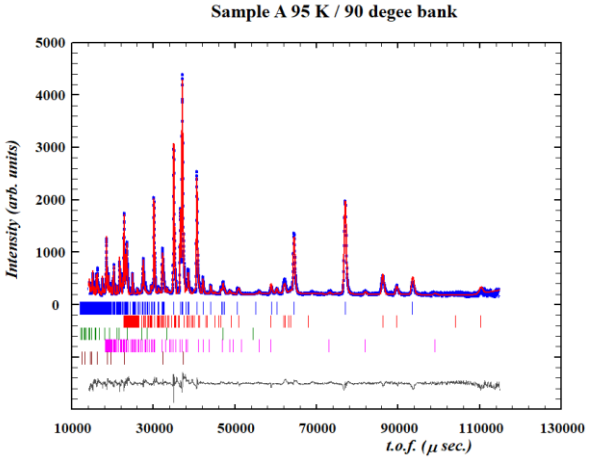
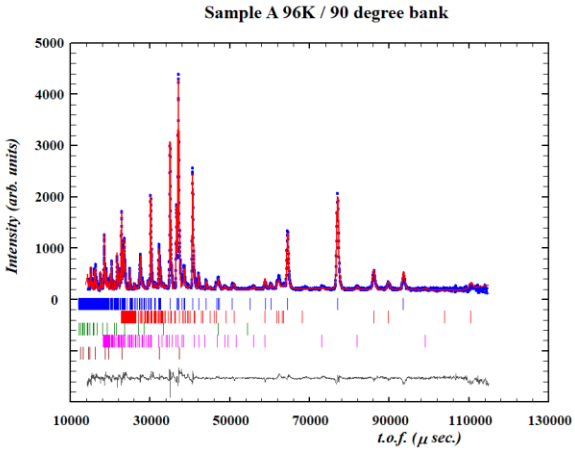
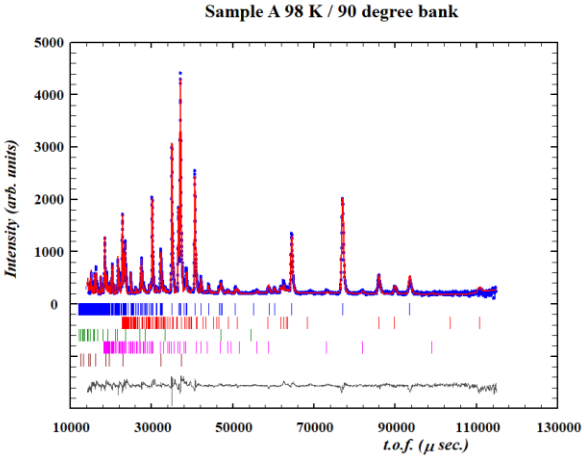
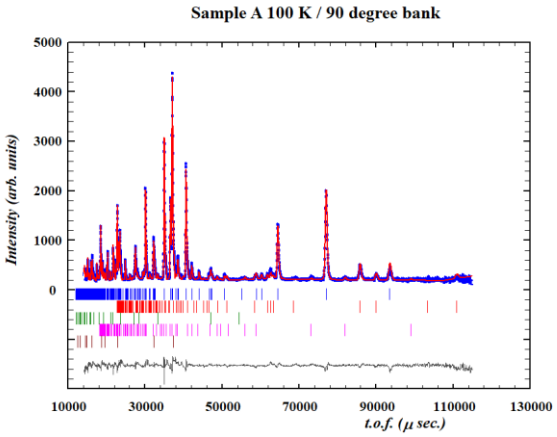
Intensity (arb. units)
t.o.f. (μ sec.)

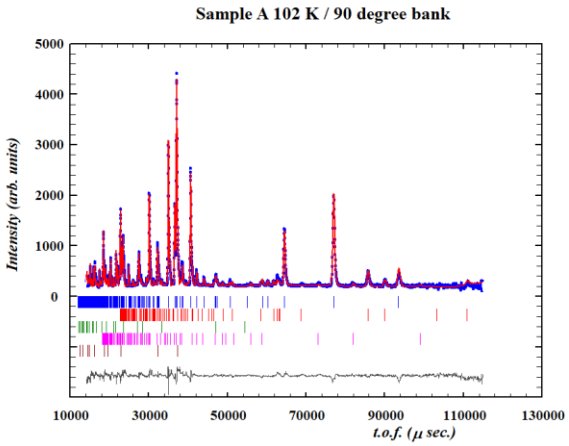

Sample A 94 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)

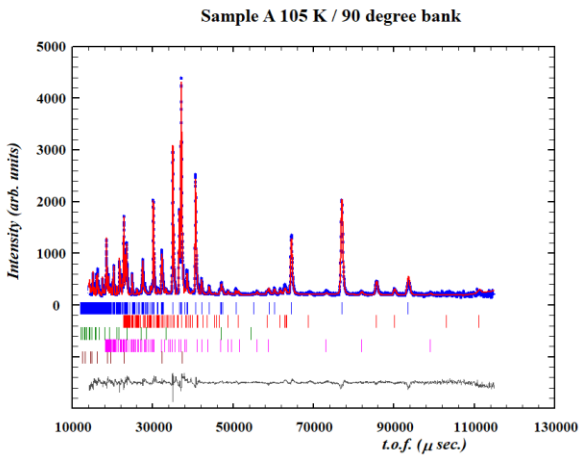

Sample A 95 K / 90 degee bank
Intensity (arb. units)
t.o.f. (μ sec.)

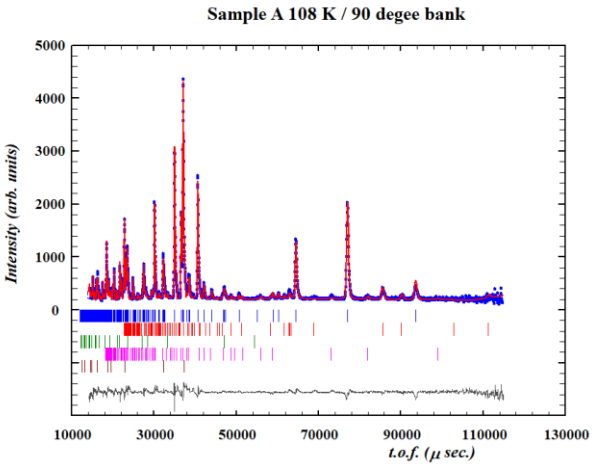

Sample A 96K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)

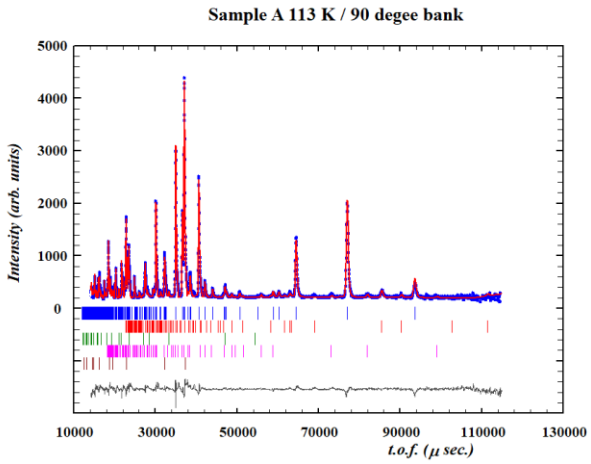

Sample A 98 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)

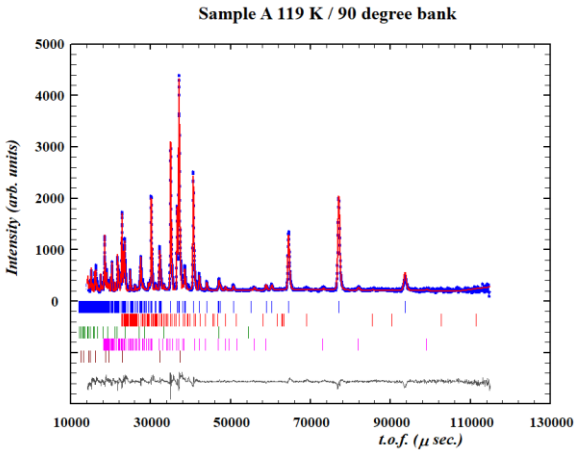

Sample A 100 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)

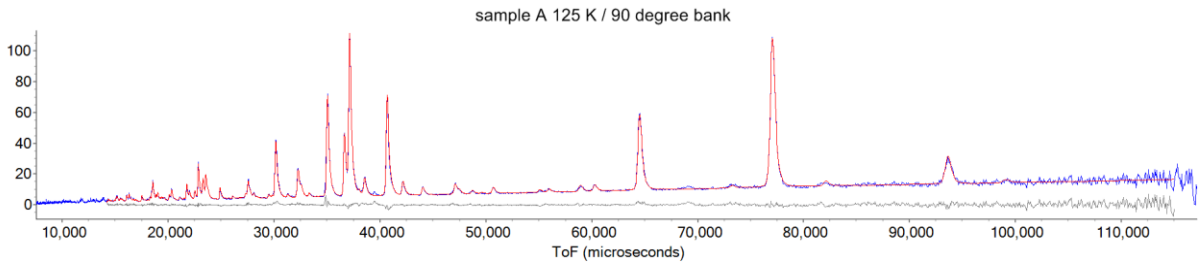

Sample A 102 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)

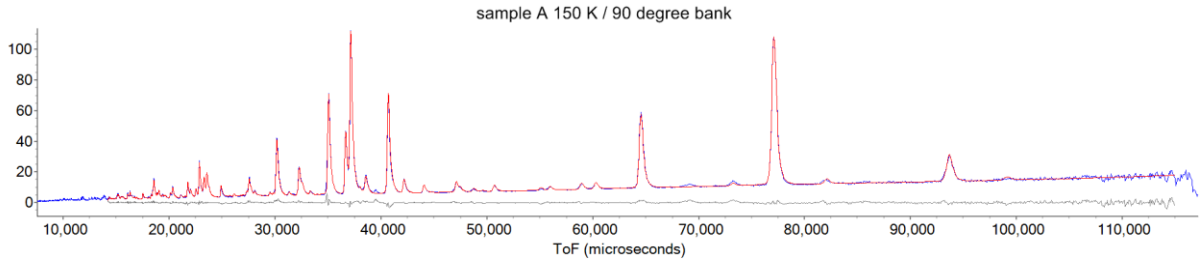

Sample A 105 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)


Sample A 108 K / 90 degee bank
Intensity (arb. units)
t.o.f. (μ sec.)


Sample A 113 K / 90 degee bank
Intensity (arb. units)
t.o.f. (μ sec.)


Sample A 119 K / 90 degree bank
Intensity (arb. units)
t.o.f. (μ sec.)


sample A 125 K / 90 degree bank
ToF (microseconds)


sample A 150 K / 90 degree bank
100
80
60
40
20
0
10,000
20,000
30,000
40,000
50,000
60,000
70,000
80,000
90,000
100,000
110,000
ToF (microseconds)

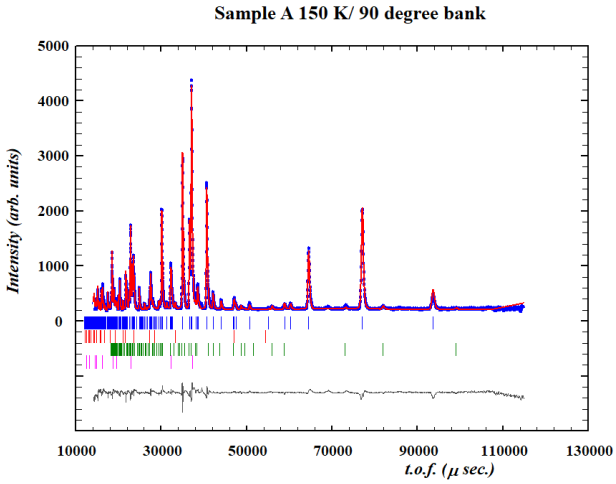
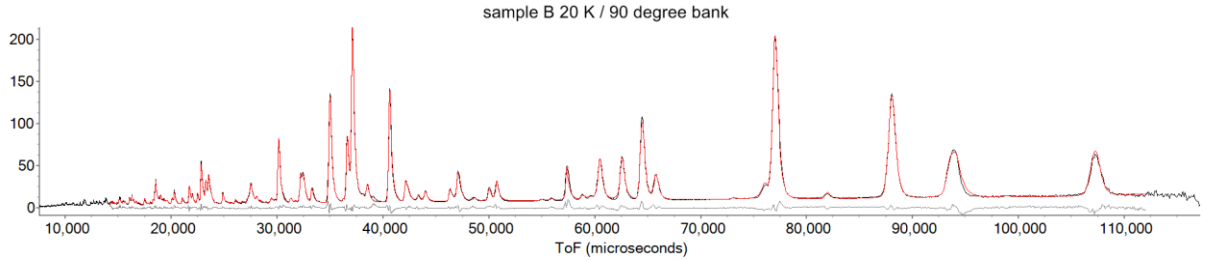
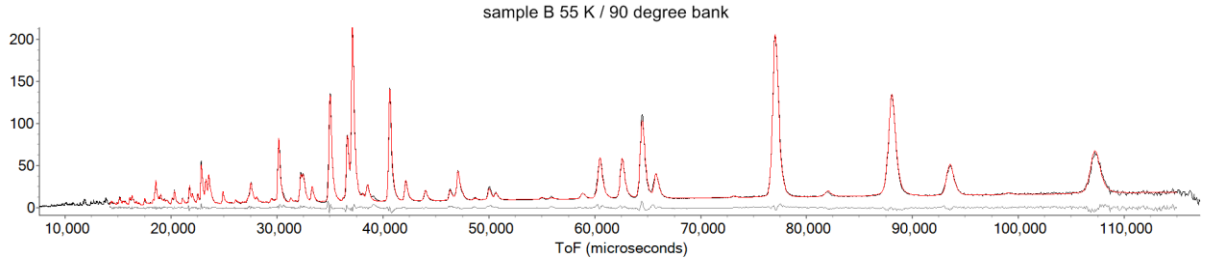
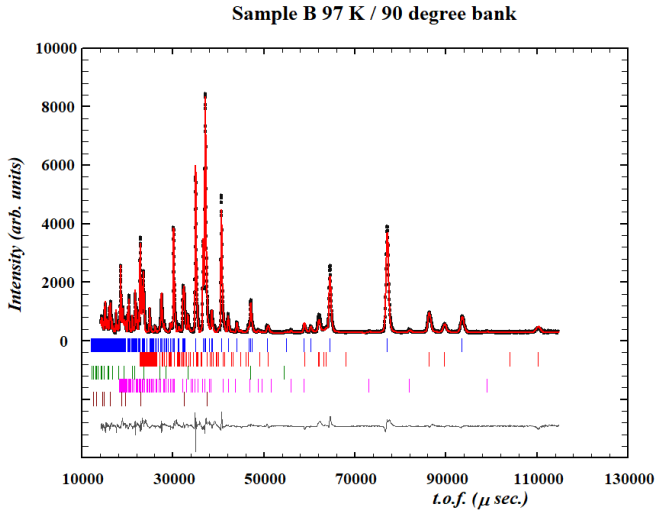

Sample A 150 K/ 90 degree bank
Intensity (arb. units)
5000
4000
3000
2000
1000
0
10000
30000
50000
70000
90000
110000
130000
t.o.f. (μ sec.)

Figure S7. Rietveld refinements for sample B (20, 55, and 97 K patterns are from the same refinements as in Figures 10, 6, and 9 in the main paper, respectively). See also Table 1 in the main text.







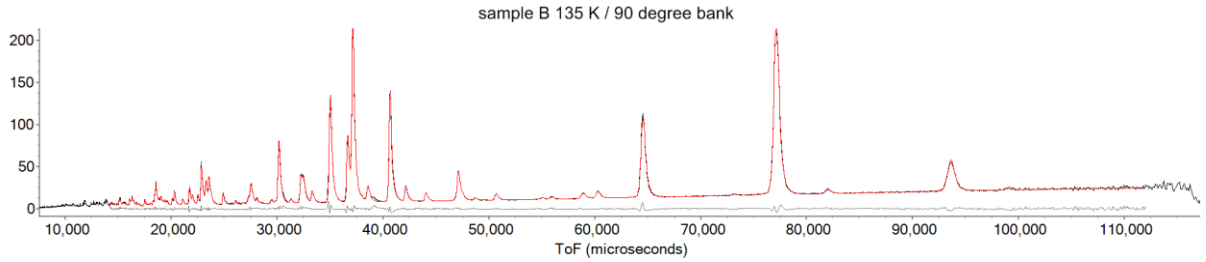


Table S7. Agreement factors for modelling of the neutron diffraction data of sample A

Temperature (K)	Rwp_bank1	Rwp_bank2	Rwp_bank3	Rwp_bank4	Rwp_bank5	Rwp_global	Refinement software
1.5	2.776	3.733	4.513	4.929	5.345	4.21	Topas Academic
20	4.141	4.639	4.855	5.397	5.529	4.88	Topas Academic
30	4.36	4.549	4.86	5.48	5.534	4.91	Topas Academic
36	4.097	4.658	4.75	5.347	5.497	4.85	Topas Academic
42	3.852	4.481	4.738	5.292	5.395	4.73	Topas Academic
45	3.815	4.324	4.711	5.338	5.419	4.68	Topas Academic
48	3.798	4.062	4.309	5.099	5.256	4.45	Topas Academic
51	3.913	4.243	4.341	5.121	5.208	4.53	Topas Academic
55	2.625	3.601	4.149	4.867	5.199	4.04	Topas Academic
65	3.758	4.083	4.455	5.171	5.304	4.50	Topas Academic
75	3.675	4.107	4.495	5.196	5.31	4.51	Topas Academic
85	3.681	4.251	4.467	5.164	5.385	4.55	Topas Academic
90	3.883	4.281	4.555	5.22	5.379	4.62	Topas Academic
91	4.496	4.697	4.782	5.348	5.262	4.89	Topas Academic
92	19.4	11.7	11.5	11.8	12.5	13.0	FullProf
93	19.7	12.1	11.6	12	12.4	13.2	FullProf
94	20	14.3	15.6	16.8	17.7	16.4	FullProf
95	18.5	11.8	11.6	11.9	12.5	12.9	FullProf
96	19.2	11.9	11.4	11.7	12.5	13.0	FullProf
98	18.8	11.6	11.5	11.7	12.5	12.8	FullProf
100	18.1	11.5	11.4	11.7	12.4	12.7	FullProf
102	18.9	11.4	11.5	11.8	12.4	12.8	FullProf
105	18.9	11.2	11.5	11.7	12.3	12.7	FullProf
108	19.7	11.2	11.3	11.7	12.3	12.8	FullProf
113	19.3	11	11.2	11.7	12.3	12.6	FullProf
119	19.7	10.8	11.3	11.6	12.2	12.6	FullProf
125	4.453	4.371	4.687	5.204	5.242	4.74	Topas Academic
135	3.588	3.98	4.4	5.04	5.13	4.38	Topas Academic
150	2.291	3.079	3.972	4.661	5.013	3.73	Topas Academic
150	14.2	10.5	11.1	11.5	12.1	11.6	FullProf

Figure S8. The cycloidal fits to PND data at 96 K show clear discrepancies with the experimental intensity in contrast with the incommensurate spin-density wave model shown in Figure 9 of the main text. Upper blue tickmarks: nuclear structure; lower red tickmarks: magnetic structure.