Supplementary Information

Complex cation and spin orders in the high pressure ferrite $CoFe_3O_5$

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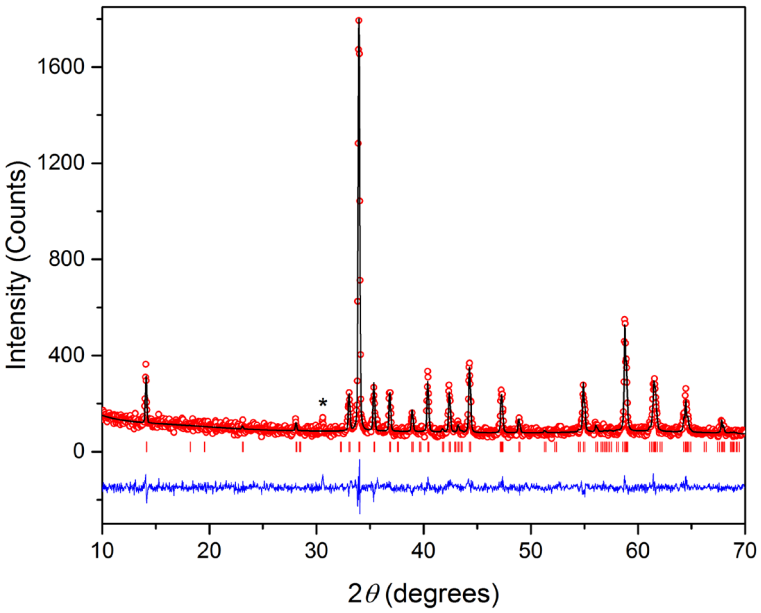

Figure S1. Rietveld fit to powder X-ray diffraction pattern of $CoFe_3O_5$ obtained using a Bruker D2 diffractometer at room temperature, with asterisk showing reflection from Cu K_β radiation. (χ^2 = 1.3, R_{wp} = 10.8 % and R_p = 8.4 %.

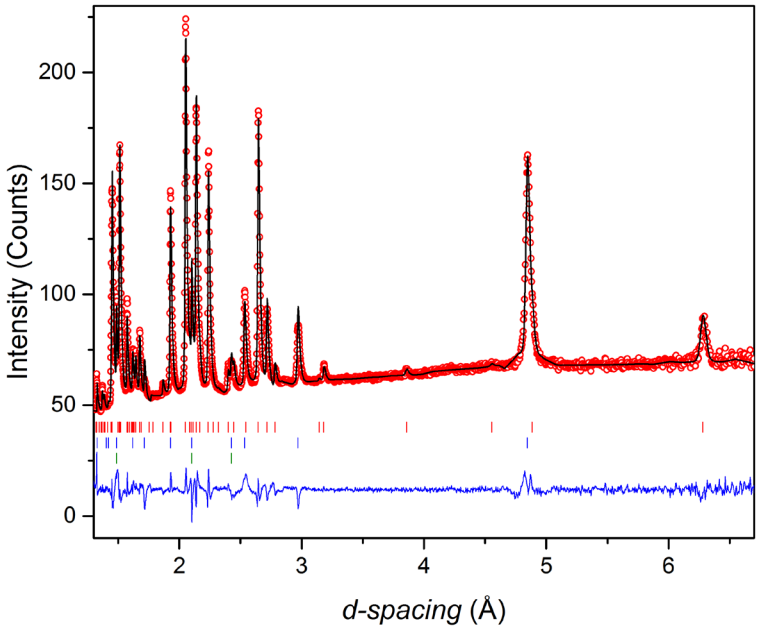

Figure S2. Rietveld analysis of high resolution neutron diffraction pattern of $CoFe_3O_5$ obtained at 400 K, with red tick marks presenting the nuclear reflections of $Co_{0.58}Fe_{3.42}O_5$, blue tick marks as $Co_{0.95}Fe_{2.05}O_4$ and the green tick marks indicate the nuclear peaks of $Co_{0.86}Fe_{0.14}O$. (χ^2 = 13.1, R_{wp} = 10.7 % and R_p = 12.9 %)

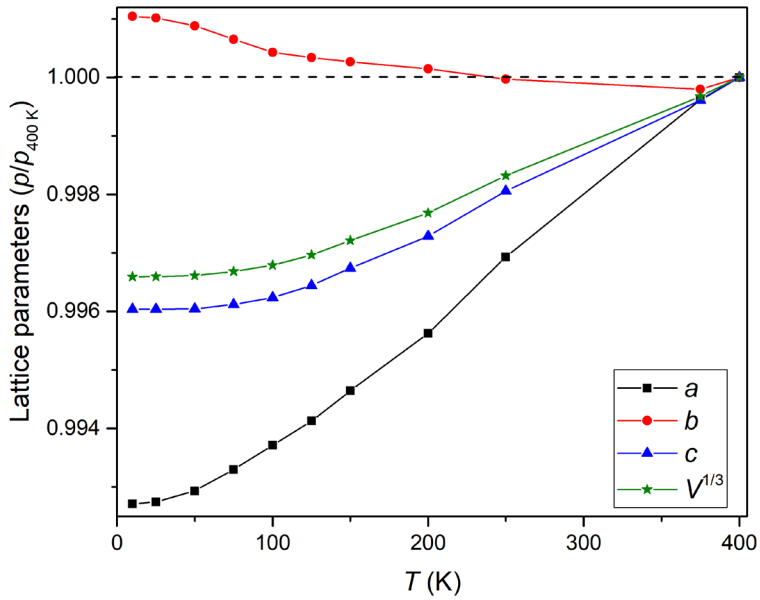

Figure S3. Changes in the lattice parameters relative to 400 K values obtained from PND ($a_{400\ K}$ = 2.9048(2), $b_{400\ K}$ = 9.7865(8) and $c_{400\ K}$ = 12.5884(6) Å).

Table S1. Lattice parameters, atomic coordinates and isotropic thermal displacements from powder synchrotron X-ray diffraction refinements in *Cmcm* space group of $CoFe_3O_5$ at 400 K (upper values) and 5 K (lower values). Estimated standard deviations in independent variables are shown in parentheses. χ^2 = 9.0 and 7.5, R_{wp} = 16.0 and 19.1 %, and R_p = 12.7 and 16.4 % at 400 and 5 K, respectively.

a /Å	*b* /Å	*c* /Å	Volume /Å^3
2.90423(3)	9.77325(8)	12.58173(11)	357.117 (5)
2.88002(2)	9.78467(7)	12.52485(9)	352.950(5)

Atom	Site	*x*	*y*	*z*	Occ Fe/Co[a]	B_{iso} /Å^2
M1	8*f*	½	0.2393(1)	0.1159(1)	1/0	0.44(2)
			0.2385(1)	0.1166(1)		0.28(1)
M2	4*a*	0	0	0	0.78/0.22	0.44
						0.28
M3	4*c*	0	0.4915(1)	¼	0.64/0.36	0.44
			0.4930(1)			0.28
O1	4*c*	½	0.3352(6)	¼	1	0.44
			0.3437(5)			0.28
O2	8*f*	0	0.3600(4)	0.0448(3)	1	0.44
			0.3626(4)	0.0450(3)		0.28
O3	8*f*	0	0.0923(5)	0.1422(3)	1	0.44
			0.0967(4)	0.1436(2)		0.28

[a] Occupancies were fixed using values from the fit to 400 K neutron data.

Table S2. Irreducible representations (IrReps) and basis vectors (BV) for M1, M2 and M3 spin order in $CoFe_3O_5$ with propagation vector (0 0 0). The magnetically independent atoms are M1 at (½, 0.242, 0.118), M2 at (0, 0, 0) and M3 at (0, 0.483, ¼). The symmetry related positions are generated by the operators 1: (x, y, z), 2: (x-½, -y+½, -z+1), 3: (-x+1, y, -z+½), 4: (-x+½, -y+½, z+½), 5: (-x, y, -z+½) and 6: (x, -y+1, -z+1). Magnetic structures at 100-250 K were fitted using basis vector $\Gamma_4\psi_6$ for M1 and M2 spins. Magnetic structures at 10-75 K were fitted using basis vectors $\Gamma_3\psi_4$ and $\Gamma_4\psi_6$ for M1 spins, $\Gamma_4\psi_6$ for M2 spins, and $\Gamma_3\psi_4$ for M3 spins. Refined components are shown in Table S3.

IrReps	Γ_1	Γ_2		Γ_3	Γ_4		Γ_5		Γ_6	Γ_7		Γ_8
BV	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ψ_7	ψ_8	ψ_9	ψ_{10}	ψ_{11}	ψ_{12}
Atoms	m_x	m_y	m_z	m_x	m_y	m_z	m_y	m_z	m_x	m_y	m_z	m_x
M1_1	+	+	+	+	+	+	+	+	+	+	+	+
M1_2	+	+	+	+	+	+	-	-	-	-	-	-
M1_3	-	-	+	+	+	-	+	-	+	-	+	-
M1_4	-	-	+	+	+	-	-	+	-	+	-	+
M2_1	+	+	+	+	+	+						
M2_5	-	-	+	+	+	-						
M3_1			+	+	+		+		+		+	
M3_6			+	+	+		-		-		-	

Table S3. Refined components and total magnetic moments (μ_B) at the three cation sites in $CoFe_3O_5$ between 10 and 250 K.

Sites	M1			M2	M3
T (K)	m_x	m_z	m_{Total}	$m_z = m_{Total}$	$m_x = m_{Total}$
10	1.82(3)	3.94(4)	4.34(3)	3.31(6)	2.56(5)
25	1.80(4)	3.95(5)	4.34(5)	3.34(8)	2.51(7)
50	1.68(4)	3.89(4)	4.24(4)	3.42(7)	2.20(7)
75	1.33(6)	3.85(5)	4.07(5)	3.41(8)	1.59(10)
100	0	3.53(5)	3.53(5)	3.80(8)	0
125	0	3.52(5)	3.52(5)	3.62(8)	0
150	0	3.40(4)	3.40(4)	3.45(7)	0
200	0	3.09(5)	3.09(5)	3.00(8)	0
250	0	2.54(5)	2.54(5)	2.21(8)	0