Evolution of cation and spin orders in the double–double-double perovskite series CaxMn2xFeReO6

Supplemental Material

Evolution of cation and spin orders in the double – double double perovskite series $Ca_xMn_{2-x}FeReO_6$

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Table S-I Refined structural parameters for Mn_2FeReO_6 in space group $P2_1/n$ from neutron data collected on the WISH diffractometer at the ISIS Neutron Facility. Sample size 70 mg.

T / K		1.5	20	40	60	80	100	125	150	175	200	225	250	275	300
Cell	a / Å	5.1985(4)	5.1988(4)	5.1989(4)	5.1991(4)	5.1995(4)	5.2002(4)	5.2004(4)	5.2011(4)	5.2020(4)	5.2027(4)	5.2041(4)	5.2051(4)	5.2066(4)	5.2087(4)
	b / Å	5.3590(4)	5.3593(4)	5.3589(4)	5.3589(4)	5.3589(4)	5.3597(5)	5.3600(5)	5.3611(5)	5.3624(5)	5.3634(4)	5.3650(4)	5.3660(4)	5.3670(4)	5.3687(5)
	c / Å	7.5867(6)	7.5871(6)	7.5878(6)	7.5890(6)	7.5902(6)	7.5913(6)	7.5914(6)	7.5925(6)	7.5935(6)	7.5941(6)	7.5956(5)	7.5964(5)	7.5979(6)	7.5998(6)
	β / °	90.114(8)	90.110(8)	90.098(9)	90.08(1)	90.07(1)	90.08(1)	90.08(1)	90.07(1)	90.07(1)	90.06(1)	90.06(1)	90.05(1)	90.06(1)	90.06(2)
	V / Å^3	211.36(3)	211.39(3)	211.40(3)	211.44(3)	211.49(3)	211.58(3)	211.60(3)	211.71(3)	211.82(3)	211.91(3)	212.07(3)	212.17(3)	212.31(3)	212.52(3)
Mn	x	0.490(2)	0.490(2)	0.490(2)	0.486(2)	0.483(2)	0.480(2)	0.478(2)	0.479(2)	0.479(2)	0.477(2)	0.481(2)	0.482(2)	0.482(2)	0.484(2)
	y	0.560(2)	0.560(2)	0.559(2)	0.560(2)	0.560(2)	0.560(2)	0.560(2)	0.560(2)	0.558(2)	0.559(2)	0.558(2)	0.556(2)	0.555(2)	0.553(2)
	z	0.755(3)	0.756(4)	0.756(4)	0.761(4)	0.761(4)	0.761(4)	0.759(4)	0.759(4)	0.761(4)	0.758(4)	0.755(4)	0.763(4)	0.768(3)	0.764(4)
O1	x	0.308(3)	0.308(3)	0.307(3)	0.307(3)	0.309(3)	0.306(3)	0.307(3)	0.305(2)	0.305(2)	0.304(2)	0.306(3)	0.305(3)	0.304(2)	0.310(4)
	y	0.317(3)	0.317(3)	0.318(3)	0.318(3)	0.320(3)	0.321(3)	0.322(3)	0.321(3)	0.320(3)	0.321(2)	0.320(3)	0.318(3)	0.315(3)	0.314(4)
	z	0.946(2)	0.946(2)	0.945(2)	0.943(2)	0.942(2)	0.942(2)	0.942(2)	0.943(2)	0.943(2)	0.943(2)	0.944(2)	0.940(2)	0.940(2)	0.941(3)
O2	x	0.329(3)	0.329(3)	0.331(3)	0.331(3)	0.330(3)	0.330(3)	0.330(3)	0.331(2)	0.332(2)	0.331(2)	0.329(3)	0.330(3)	0.332(2)	0.326(4)
	y	0.298(3)	0.299(3)	0.298(3)	0.299(3)	0.299(3)	0.297(3)	0.297(3)	0.298(3)	0.299(3)	0.299(3)	0.300(3)	0.302(3)	0.305(3)	0.309(4)
	z	0.568(2)	0.567(2)	0.566(2)	0.563(2)	0.562(2)	0.561(2)	0.561(2)	0.562(2)	0.562(2)	0.563(2)	0.565(2)	0.562(2)	0.562(2)	0.564(3)
O3	x	0.879(1)	0.879(1)	0.878(1)	0.879(1)	0.878(1)	0.876(1)	0.876(1)	0.876(1)	0.877(1)	0.876(1)	0.877(1)	0.878(1)	0.878(1)	0.876(1)
	y	0.439(1)	0.439(1)	0.439(1)	0.439(1)	0.441(1)	0.442(1)	0.442(1)	0.443(1)	0.443(1)	0.444(1)	0.444(1)	0.444(1)	0.444(1)	0.445(1)
	z	0.735(2)	0.734(2)	0.733(2)	0.731(2)	0.728(2)	0.729(2)	0.728(2)	0.727(2)	0.727(2)	0.726(1)	0.730(2)	0.730(2)	0.732(2)	0.734(2)
Mn, B_{iso} / Å^2		1.51(5)	1.52(5)	1.58(5)	1.4(3)	1.5(3)	1.4(3)	1.5(3)	1.6(3)	1.7(3)	1.9(3)	1.9(3)	1.8(3)	1.8(3)	2.3(3)
Fe/Re, B_{iso} / Å^2		1.67(2)	1.64(2)	1.67(2)	1.67(8)	1.64(8)	1.69(9)	1.69(9)	1.66(9)	1.75(9)	1.77(9)	1.81(9)	1.74(8)	1.74(8)	1.76(8)
O, B_{iso} / Å^2		0.86(2)	0.85(2)	0.81(2)	0.76(9)	0.69(9)	0.62(9)	0.58(9)	0.60(9)	0.62(9)	0.56(8)	0.70(8)	0.78(8)	0.94(9)	1.14(9)
R_{wp} / %		4.00	3.88	4.10	3.99	3.98	4.14	4.18	4.12	4.04	3.87	3.77	3.71	3.67	3.73
χ^2		5.01	3.57	3.47	3.31	3.32	2.58	2.31	2.27	2.19	2.03	1.93	1.88	1.77	1.67
Q / μA·h		60	40	40	40	40	29	25	25	25	25	25	25	24	22

Fe atoms are located at (0, ½, 0), with Re atoms at (½, 0, 0). Antisite disorder of Fe/Re is not refined due to poor neutron contrast. No site mixing between A and B-sites was found. Q, a measure of the total length of exposure of the sample to the neutron beam ($Q = I \cdot t$), is also tabulated.

Table S-II Refined magnetic parameters for Mn_2FeReO_6 in space group $P2_1/n$ from neutron data collected using the WISH diffractometer at the ISIS Neutron Facility. Sample size 70 mg.

	T / K	1.5	20	40	60	80	100	125	150	175	200	225	250	275	300
Fe	mFe / μ_B	4.86(4)	4.82(4)	4.84(4)	4.77(4)	4.63(4)	4.54(4)	4.43(4)	4.33(5)	4.22(5)	4.04(4)	3.92(4)	3.78(4)	3.62(4)	3.39(5)
	φ_{Fe} / degrees	8(1)	8(1)	9(1)	8(2)	0	0	0	0	0	0	0	0	0	0
	θ_{Fe} / degrees	49(1)	49(1)	45(1)	38(1)	29(2)	24(2)	21(3)	23(3)	25(3)	24(2)	28(2)	29(2)	30(3)	18(4)
	φ_{FeFe} / degrees	16(2)	16(2)	17(3)	16(4)	0	0	0	0	0	0	0	0	0	0
	m_x / μ_B (FM)	3.64(6)	3.59(6)	3.41(7)	2.90(9)	2.3(1)	1.8(2)	1.6(2)	1.7(2)	1.8(2)	1.7(2)	1.9(1)	1.8(1)	1.8(2)	1.1(3)
	m_y / μ_B (AFM)	0.52(6)	0.50(6)	0.52(8)	0.4(1)	0	0	0	0	0	0	0	0	0	0
	m_z / μ_B (FM)	3.18(8)	3.19(9)	3.40(8)	3.77(8)	4.05(8)	4.15(8)	4.12(8)	3.97(8)	3.82(8)	3.68(8)	3.45(8)	3.31(9)	3.1(1)	3.22(9)
	θ_{Tilt} / degrees	24.5(1)	24.5(1)	24.5(1)	24.3(1)	24.1(1)	24.5(1)	24.6(1)	24.5(1)	24.3(1)	24.3(1)	24.5(1)	24.4(1)	24.5(1)	25.0(1)
	φ_{Tilt} / degrees	13.0(2)	12.9(2)	12.8(2)	12.7(2)	12.3(2)	12.1(2)	12.0(2)	11.7(2)	11.8(2)	11.5(2)	11.7(2)	11.8(2)	11.9(2)	11.8(2)
Mn	mMn / μ_B	3.84(3)	3.74(3)	3.31(3)	2.71(3)	2.06(4)	1.42(5)	1.10(6)	0.74(9)	0.6(1)	0	0	0	0	0
	φ_{Mn} / degrees	58(1)	58(1)	53(1)	46(2)	39(2)	40(4)	39(6)	50(20)	60(20)	-	-	-	-	-
	θ_{Mn} / degrees	55(1)	55(1)	51(2)	47(2)	49(3)	51(5)	54(9)	50(20)	60(30)	-	-	-	-	-
	m_x / μ_B (AFM)	1.67(8)	1.64(8)	1.56(8)	1.39(8)	1.20(7)	0.84(9)	0.7(1)	0.3(2)	0.3(3)	0	0	0	0	0
	m_y / μ_B (AFM)	2.65(4)	2.58(4)	2.06(5)	1.42(6)	0.98(8)	0.7(1)	0.6(1)	0.5(1)	0.5(1)	0	0	0	0	0
	m_z / μ_B (AFM)	2.22(6)	2.15(7)	2.07(6)	1.84(7)	1.35(6)	0.89(9)	0.6(1)	0.5(2)	0.3(3)	0	0	0	0	0
m_{tot} / μ_B f.u.$^{-1}$		3.87(8)	3.84(9)	3.9(1)	3.8(1)	3.7(1)	3.6(2)	3.5(2)	3.5(2)	3.4(2)	3.2(2)	3.1(2)	3.0(2)	2.9(2)	2.7(2)
R_{wp} / %		4.00	3.88	4.10	3.99	3.98	4.14	4.18	4.12	4.04	3.87	3.77	3.71	3.67	3.73
χ^2		5.01	3.57	3.47	3.31	3.32	2.58	2.31	2.27	2.19	2.03	1.93	1.88	1.77	1.67
Q / μA·h		60	40	40	40	40	29	25	25	25	25	25	25	24	22

Magnetic vectors for Fe and Mn are tabulated in both polar and Cartesian coordinate systems, in the polar system φ denotes the angle between the a and b axes (0° defined as parallel to a) and θ denoting the angle between the c and a axes (0° defined as parallel to c). The angles θ_{Tilt} and φ_{Tilt} reference the FeO_6 octahedra tilt angles between the c-axis and the a and b-axes, respectively. The angle φ_{FeFe} denotes the angle between Fe moments due to the antiferromagnetic component of Fe spin order along the b-axis. Magnitudes of Re moments are constrained as -0.2 × mFe, with the same magnetic symmetry as Fe. Total magnetisation due to ferrimagnetic Fe/Re order is shown as m_{tot}.

Table S-III Bond lengths, angles and BVS values for Mn_2FeReO_6 in space group $P2_1/n$ from the neutron profile fits at 1.5 K and 300 K.

1.5 K

Bond	M – O length / Å	Bond	M – O length / Å
Mn – O1	2.17(1)	Fe – O1	1.92(2) × 2
Mn – O1	2.57(2)	Fe – O2	1.90(2) × 2
Mn – O1	2.58(3)	Fe – O3	2.13(1) × 2
Mn – O2	2.16(2)	**<Fe – O>**	1.98(1)
Mn – O2	2.49(2)		
Mn – O2	2.73(2)	Re – O1	2.01(2) × 2
Mn – O3	2.13(1)	Re – O2	2.09(2) × 2
Mn – O3	2.14(1)	Re – O3	1.92(1) × 2
<Mn – O>	2.371(7)	**<Re – O>**	2.01(1)
Cation	**BVS**	**B – O# – B′**	**Angle / degrees**
Mn	1.83	Fe – O1 – Re	143.2(7)
Fe	3.38	Fe – O2 – Re	138.8(6)
Re	4.12	Fe – O3 – Re	138.9(6)

300K

Bond	M – O length / Å	Bond	M – O length / Å
Mn – O1	2.07(3)	Fe – O1	1.95(2) × 2
Mn – O1	2.59(3)	Fe – O2	1.95(2) × 2
Mn – O1	2.59(3)	Fe – O3	2.14(1) × 2
Mn – O2	2.17(3)	**<Fe – O>**	2.01(1)
Mn – O2	2.49(3)		
Mn – O2	2.78(4)	Re – O1	2.01(2) × 2
Mn – O3	2.14(1)	Re – O2	2.04(2) × 2
Mn – O3	2.23(1)	Re – O3	1.92(1) × 2
<Mn – O>	2.38(1)	**<Re – O>**	1.99(1)
Cation	**BVS**	**B – O# – B′**	**Angle / degrees**
Mn	1.83	Fe – O1 – Re	141.9(9)
Fe	3.09	Fe – O2 – Re	138.9(9)
Re	4.30	Fe – O3 – Re	138.9(6)

The program BondStr in the FullProf Suite was used to compute this data. The parameters used in BondStr for Re are not well defined and so the BVS computed is slightly lower than the expected value of 5.

Table S-IV Refined structure parameters for $x = 0.5$(M) in space group $P2_1/n$ and $x = 0.5$(T) in space group $P4_2/n$ phases at 300 K using synchrotron powder X-ray data. Phase ratio M:T: ReO_2 = 57.1(1):41.7(1):1.1 by mass.

$x = 0.5$(M)

Atom	*x*	*y*	*z*	Occupancy	B_{iso} / Å^2
Ca/Mn	0.0089(4)	0.0522(2)	0.2486(2)	0.25/0.75	0.305(7)
Fe/Re	0	½	0	0.942(1)/0.058	0.305
Re/Fe	½	0	0	0.942/0.058	0.305
O1	0.32404(8)	0.30386(9)	0.05414(9)	1	0.45(6)
O2	0.30080(8)	0.2966(1)	0.43867(9)	1	0.45
O3	0.60834(6)	0.96246(8)	0.24577(8)	1	0.45

Lattice parameters: a = 5.23676(1), b = 5.39465(1) and c = 7.61015(2) Å with β = 90.0615(2)°; residuals R_{wp} = 7.47 % and χ^2 = 7.66. Ca:Mn occupancy is fixed to the synthesis composition of 1:3

$x = 0.5$(T)

Atom	*x*	*y*	*z*	Occupancy	B_{iso} / Å^2
Ca/Mn	¼	¾	0.2804(5)	0.5/0.5	0.261(5)
Mn_{TD}	¾	¾	¾	1	0.261
Mn_{SP}	¼	¼	¾	1	0.261
Fe	0	0	½	0.950(1)/0.050	0.261
Re	0	½	½	0.950/0.050	0.261
O1	0.9323(2)	0.5410(2)	0.2568(1)	1	0.03(7)
O2	0.7291(1)	0.9581(1)	0.5734(1)	1	0.03(7)
O3	0.7444(1)	0.0572(1)	0.9584(1)	1	0.03(7)

Lattice parameters: a = 7.61368(1) and c = 7.60138(2) Å; residuals R_{wp} = 7.47 % and χ^2 = 7.66. Ca:Mn occupancy is fixed to the synthesis composition of 1:3.

Table S-V | Refined structure parameters for x = 0.5(M) phase at 2-300 K in space group $P2_1/n$ using neutron powder diffraction data from the WISH diffractometer at the ISIS Neutron Facility. Sample size 54 mg. The composition of this material is a two-phase mixture, including this phase (51(3) wt.%) and the phase described in **Table S-VII** (49(3) wt.%). This phase is found to have a chemical formula of $(Ca_{0.17(3)}Mn_{1.83})FeReO_6$.

T / K		2	25	50	75	100	200	300
Cell	a / Å	5.2230(6)	5.2233(7)	5.2236(7)	5.2241(7)	5.2244(7)	5.2280(7)	5.2339(7)
	b / Å	5.3856(7)	5.3856(7)	5.3854(7)	5.3858(7)	5.3862(7)	5.3885(7)	5.3929(7)
	c / Å	7.5975(9)	7.5979(9)	7.5998(9)	7.602(1)	7.603(1)	7.606(1)	7.610(1)
	β / °	90.04(2)	90.03(2)	89.99(2)	89.96(2)	89.93(2)	89.92(2)	89.95(2)
	V / Å^3	213.71(5)	213.73(5)	213.79(5)	213.89(5)	213.95(5)	214.27(5)	214.80(5)
A	x	0.493(4)	0.495(4)	0.497(4)	0.492(4)	0.491(4)	0.496(4)	0.495(4)
	y	0.573(5)	0.571(5)	0.565(6)	0.564(6)	0.561(6)	0.554(6)	0.552(5)
	z	0.782(3)	0.784(3)	0.806(3)	0.821(3)	0.827(3)	0.828(3)	0.823(4)
O1	x	0.325(4)	0.323(4)	0.322(4)	0.320(4)	0.316(4)	0.315(5)	0.307(5)
	y	0.269(4)	0.269(4)	0.275(4)	0.274(4)	0.276(4)	0.288(5)	0.291(5)
	z	0.934(4)	0.935(4)	0.936(4)	0.938(3)	0.941(3)	0.937(4)	0.940(5)
O2	x	0.297(4)	0.297(4)	0.299(4)	0.301(4)	0.305(4)	0.311(5)	0.320(5)
	y	0.339(4)	0.340(4)	0.337(4)	0.338(3)	0.336(3)	0.325(4)	0.323(5)
	z	0.551(3)	0.553(3)	0.557(3)	0.559(3)	0.561(3)	0.564(4)	0.569(4)
O3	x	0.886(2)	0.885(2)	0.884(2)	0.881(2)	0.880(2)	0.880(2)	0.881(2)
	y	0.442(2)	0.442(2)	0.441(2)	0.441(2)	0.442(2)	0.444(2)	0.445(2)
	z	0.738(5)	0.738(5)	0.741(6)	0.742(5)	0.740(4)	0.740(4)	0.738(4)
θ_{Tilt} / degrees		23.6(1)	23.8(1)	24.1(1)	24.7(1)	24.8(1)	24.7(1)	24.3(1)
φ_{Tilt} / degrees		12.5(2)	12.5(2)	12.7(2)	12.8(2)	12.7(2)	12.1(2)	11.8(2)
mFe / μ_B		4.3(1)	4.3(1)	4.2(1)	3.9(1)	3.7(1)	3.56(1)	3.1(2)
φ_{Fe} / °		5(2)	8(2)	11(7)	21(31)	0	0	0
θ_{Fe} / °		63(4)	62(4)	48(5)	20(10)	9(11)	12(10)	14(18)
φ_{FeFe} / °		10(4)	15(5)	23(15)	42(63)	0	0	0
mFe_x / μ_B		3.8(2)	3.7(2)	3.1(3)	1.2(7)	0.6(7)	0.7(6)	0.7(10)
mFe_y / μ_B		0.3(1)	0.5(2)	0.6(4)	0.5(7)	0	0	0
mFe_z / μ_B		1.9(2)	2.0(3)	2.8(2)	3.6(2)	3.7(1)	3.5(1)	3.0(3)
mMn / μ_B		3.35(7)	3.05(8)	2.1(1)	1.4(2)	1.0(2)	0	0
φ_{Mn} / °		56(2)	58(3)	52(8)	44(20)	26(33)	-	-
θ_{Mn} / °		74(8)	66(8)	46(15)	38(28)	46(23)	-	-
mMn_x / μ_B		1.8(2)	1.5(2)	0.9(4)	0.6(5)	0.6(3)	0	0
mMn_y / μ_B		2.7(1)	2.4(1)	1.2(4)	0.6(6)	0.3(5)	0	0
mMn_z / μ_B		0.9(5)	1.2(4)	1.5(3)	1.1(3)	0.7(2)	0	0
mRe / μ_B		0.86(3)	0.85(3)	0.85(3)	0.77(3)	0.74(2)	0.71(2)	0.62(3)
m_{tot} / μ_B		3.4(4)	3.4(5)	3.3(6)	3.1(8)	3.0(3)	2.8(4)	2.5(10)
A/B	B_{iso} / Å^2	1.24(2)	1.25(2)	1.22(2)	1.24(2)	1.28(2)	1.30(2)	1.33(3)
O	B_{iso} / Å^2	0.35(2)	0.33(2)	0.46(2)	0.49(2)	0.55(2)	0.52(2)	0.69(3)
R_{wp} / %		3.61	3.61	3.52	3.43	3.42	3.47	3.44
χ^2		4.08	4.08	3.90	3.75	3.72	3.89	3.80
Q / μA·h		45	45	45	45	45	45	45

Fe atoms are located at (0, ½, 0), with Re atoms at (½, 0, 0). Antisite disorder of Fe/Re is not refined due to poor neutron contrast. Magnitudes of Re moments are constrained as -0.2 × mFe, with the same magnetic symmetry as Fe. Total magnetisation due to ferrimagnetic Fe/Re order is shown as m_{tot}. No site mixing between A and B-sites was found. A-sites are found to be 91.5(14) % Mn, with 8.5(14) % Ca. Q, a measure of the total length of exposure of the sample to the neutron beam ($Q = I \cdot t$), is also tabulated.

Table S-VI | Bond lengths, angles and BVS values for x = 0.5(M) phase in space group $P2_1/n$ from the neutron profile fits at 2 and 300 K.

2 K

Bond	A – O length / Å	Bond	B – O length / Å
Mn/Ca – O1	2.19(4)	Fe – O1	2.16(3) × 2
Mn/Ca – O1	2.51(4)	Fe – O2	2.15(3) × 2
Mn/Ca – O1	2.56(4)	Fe – O3	2.10(5) × 2
Mn/Ca – O2	2.44(4)	**<Fe – O>**	2.14(2)
Mn/Ca – O2	2.39(4)		
Mn/Ca – O2	2.8(4)	Re – O1	1.78(3) × 2
Mn/Ca – O3	2.19(3)	Re – O2	1.82(3) × 2
Mn/Ca – O3	2.09(3)	Re – O3	1.93(5) × 2
<Mn/Ca – O>	2.40(1)	**<Re – O>**	1.84(2)
Cation	**BVS**	**B – O# – B′**	**Angle / degrees**
Mn/Ca	1.78	Fe – O1 – Re	144(2)
Fe	2.17	Fe – O2 – Re	142(1)
Re	6.34	Fe – O3 – Re	140.8(6)

300 K

Bond	A – O length / Å	Bond	B – O length / Å
Mn/Ca – O1	1.93(4)	Fe – O1	2.01(3) × 2
Mn/Ca – O1	2.25(5)	Fe – O2	2.05(3) × 2
Mn/Ca – O1	2.86(5)	Fe – O3	2.11(3) × 2
Mn/Ca – O2	2.35(4)	**<Fe – O>**	2.06(2)
Mn/Ca – O2	2.47(5)		
Mn/Ca – O2	3.21(5)	Re – O1	1.78(3) × 2
Mn/Ca – O3	2.20(3)	Re – O2	1.82(3) × 2
Mn/Ca – O3	2.26(3)	Re – O3	1.93(5) × 2
<Mn/Ca – O>	2.44(2)	**<Re – O>**	1.84(3)
Cation	**BVS**	**B – O# – B′**	**Angle / degrees**
Mn/Ca	1.98	Fe – O1 – Re	145(2)
Fe	2.7	Fe – O2 – Re	136(2)
Re	4.69	Fe – O3 – Re	140.2(6)

The program BondStr in the FullProf Suite was used to compute this data.

Table S-VII Refined structure parameters for x = 0.5(T) phase at 2-300 K in space group $P4_2/n$ using neutron powder diffraction data from the WISH diffractometer at the ISIS Neutron Facility. Sample size 54 mg. The composition in this material is a two-phase mixture, including this phase (49(3) wt.%) and the phase described in **Table S-V** (51(3) wt.%). This phase is found to have a chemical formula of $(Ca_{0.74(2)}Mn_{0.26})MnFeReO_6$.

T / K		2	25	50	75	100	200	300
Cell Param	a / Å	7.600(1)	7.601(1)	7.602(1)	7.6035(9)	7.6040(9)	7.607(1)	7.612(1)
	c / Å	7.594(2)	7.594(2)	7.590(1)	7.590(1)	7.590(1)	7.594(1)	7.603(1)
	V / Å^3	438.6(2)	438.7(2)	438.6(1)	438.8(1)	438.9(1)	439.5(1)	440.5(1)
Ca/Mn	z	0.298(7)	0.301(7)	0.314(6)	0.331(7)	0.342(7)	0.358(7)	0.341(6)
O1	x	0.94(1)	0.94(1)	0.940(9)	0.93(1)	0.924(9)	0.915(4)	0.919(5)
	y	0.57(1)	0.57(2)	0.572(9)	0.57(1)	0.567(8)	0.555(3)	0.557(3)
	z	0.25(2)	0.25(2)	0.25(1)	0.265(5)	0.267(4)	0.266(4)	0.261(6)
O2	x	0.762(9)	0.76(1)	0.765(7)	0.76(1)	0.76(1)	0.749(8)	0.75(1)
	y	0.942(3)	0.941(3)	0.943(3)	0.948(2)	0.950(3)	0.951(2)	0.950(2)
	z	0.557(2)	0.558(2)	0.558(2)	0.555(2)	0.554(2)	0.553(2)	0.554(2)
O3	x	0.75(2)	0.75(2)	0.75(1)	0.74(1)	0.734(9)	0.731(6)	0.74(1)
	y	0.053(2)	0.052(2)	0.053(2)	0.054(2)	0.054(2)	0.053(2)	0.054(2)
	z	0.972(2)	0.972(2)	0.972(2)	0.970(2)	0.970(2)	0.972(2)	0.972(2)
mFe / μ_B		4.1(1)	4.2(1)	4.3(1)	4.5(1)	4.5(1)	4.22(9)	3.7(1)
mRe / μ_B		0.83(3)	0.83(3)	0.87(3)	0.90(2)	0.89(2)	0.84(2)	0.74(2)
mMn / μ_B		0.8(2)	0.8(2)	0.5(2)	0	0	0	0
m_{tot} / μ_B f.u.$^{-1}$		3.31(7)	3.33(8)	3.46(7)	3.60(5)	3.56(5)	3.37(4)	2.94(6)
A/B	B_{iso} / Å^2	1.24(2)	1.25(2)	1.22(2)	1.24(2)	1.28(2)	1.30(2)	1.33(3)
O	B_{iso} / Å^2	0.35(2)	0.33(2)	0.46(2)	0.49(2)	0.55(2)	0.62(2)	0.69(3)
R_{wp} / %			3.61	3.61	3.52	3.43	3.42	3.47
χ^2			4.08	4.08	3.90	3.75	3.72	3.89
Q / μA·h			45	45	45	45	45	45

Cation positions are as follows for A-sites: Ca/Mn (¼, ¾, z), Mn_{TD} (¾, ¾, ¾), Mn_{SP} (¼, ¼, ¾); and for B-sites: Fe (0, 0, ½) and Re (0, ½, ½). The 10-coordinate Ca/Mn site is found to have a site occupancy of 74(2) % Ca, 26 % Mn. Other sites are fixed at ideal occupancies of each ion. Magnitudes of Re moments are constrained as -0.2 × mFe, with the same magnetic symmetry as Fe. The tabulated value of m_{tot} refers to the total magnetisation of this phase, equivalent to: $m_{tot} = mFe - mRe$.

Table S-VIII $x = 0.5$(T) phase bond lengths, angles and BVS values in space group $P4_2/n$ from the neutron profile fit at 300 K.

Bond	M – O length / Å	Bond	M – O length / Å
Ca/Mn – O1	2.78(4) × 2	Fe – O1	2.12(5) × 2
Ca/Mn – O1	2.98(4) × 2	Fe – O2	1.99(9) × 2
Ca/Mn – O2	2.42(3) × 2	Fe – O3	1.86(8) × 2
Ca/Mn – O3	2.06(4) × 2	**<Fe – O>**	1.99(4)
Ca/Mn – O3	2.81(5) × 2	Re – O1	1.97(5) × 2
<Ca/Mn – O>	2.61(4)	Re – O2	1.98(9) × 2
Mn_{TD} – O2	2.13(2) × 4	Re – O3	2.06(8) × 2
Mn_{SP} – O1	1.95(3) × 4	**<Re – O>**	2.00(4)

Cation	BVS	Cation	BVS	B – O# – B′	Angle / degrees
Ca	2.37	Fe	3.37	Fe – O1 – Re	136.7(18)
Mn_{TD}	1.47			Fe – O2 – Re	147.2(9)
Mn_{SP}	2.36	Re	4.12	Fe – O3 – Re	152.6(9)

The program BondStr in the FullProf Suite was used to compute this data.

Table S-IX Refined structure parameters for $x = 1.5$(M) phase at 300 K in space group $P2_1/n$ using synchrotron powder X-ray data from ID22 at the ESRF.

Atom	*x*	*y*	*z*	Occupancy	B_{iso} / Å^2
Ca/Mn	0.0175(3)	0.0476(1)	0.2493(1)	0.75/0.25	0.270(3)
Fe/Re	0	½	0	0.948(2)/0.052	0.270
Re/Fe	½	0	0	0.948/0.052	0.270
O1	0.2978(7)	0.2918(7)	0.0520(7)	1	0.38(4)
O2	0.2959(7)	0.2944(7)	0.4524(7)	1	0.38
O3	0.5828(6)	0.9735(6)	0.2463(5)	1	0.38

Lattice parameters: $a = 5.38536(1)$, $b = 5.51731(1)$ and $c = 7.68841(1)$ Å with $\beta = 90.0456(2)°$; residuals $R_{wp} = 3.75$ % and $\chi^2 = 11.6$. Ca:Mn occupancy is fixed to the synthesis composition of 3:1. This monoclinic phase constitutes 88.0(2) % by weight of the refined sample, with another minority phase observed 11.88(6) %. This is assumed to be a tetragonal $P4_2/n$ phase, (as observed in $x = 0.5$ and 1.0) this is fit with lattice parameters: $a = 7.66839(6)$ and $c = 7.64770(7)$ Å, though insufficient data is present to adequately refine the structure of this phase. An impurity phase of 0.09 (1) % ReO_2 is also observed.

Table S-X Refined structure parameters for x = 1.5(M) phase at 2-300 K in space group $P2_1/n$ using PND data. Sample size 49 mg. This phase is found to have a chemical formula of $(Ca_{1.73(8)}Mn_{0.27})FeReO_6$.

T / K		2	25	50	75	100	200	300
Cell	a / Å	5.3736(8)	5.3738(8)	5.3739(8)	5.3738(8)	5.3739(8)	5.3782(8)	5.3843(7)
	b / Å	5.5094(8)	5.5095(8)	5.5102(8)	5.5120(8)	5.5153(8)	5.5162(8)	5.5168(7)
	c / Å	7.674(1)	7.675(1)	7.675(1)	7.675(1)	7.674(1)	7.677(1)	7.683(1)
	β / °	89.963(3)	89.996(3)	89.987(3)	89.969(3)	90.0500	90.040(3)	89.996(5)
	V / Å^3	227.20(6)	227.22(6)	227.27(6)	227.32(6)	227.45(6)	227.76(6)	228.22(5)
A	x	0.991(3)	0.993(3)	0.995(3)	0.996(3)	0.994(3)	0.996(2)	0.997(2)
	y	0.958(2)	0.960(2)	0.959(2)	0.959(2)	0.957(2)	0.956(2)	0.957(2)
	z	0.263(4)	0.265(3)	0.267(3)	0.267(3)	0.267(3)	0.266(3)	0.264(3)
O1	x	0.301(3)	0.302(3)	0.302(3)	0.305(4)	0.313(3)	0.313(3)	0.305(6)
	y	0.300(4)	0.302(4)	0.303(4)	0.290(4)	0.288(3)	0.290(4)	0.293(6)
	z	0.945(2)	0.944(2)	0.946(2)	0.947(2)	0.949(2)	0.949(2)	0.961(2)
O2	x	0.308(3)	0.306(3)	0.306(3)	0.304(3)	0.294(3)	0.295(3)	0.305(6)
	y	0.291(4)	0.291(3)	0.291(3)	0.304(4)	0.303(3)	0.302(4)	0.299(7)
	z	0.534(2)	0.533(2)	0.533(2)	0.535(2)	0.537(2)	0.537(2)	0.550(2)
O3	x	0.912(1)	0.913(1)	0.913(1)	0.912(1)	0.911(1)	0.9118(9)	0.9125(9)
	y	0.464(1)	0.466(1)	0.467(1)	0.467(1)	0.466(1)	0.4665(9)	0.4668(9)
	z	0.730(2)	0.729(2)	0.729(2)	0.732(2)	0.735(2)	0.739(3)	0.743(4)
θ_{Tilt} / degrees		8.6(2)	8.4(2)	8.3(2)	8.1(2)	8.2(2)	8.0(2)	7.8(2)
φ_{Tilt} / degrees		20.9(1)	20.8(0)	20.8(1)	20.7(1)	20.8(1)	20.2(1)	19.8(1)
mFe / μ_B		4.32(4)	4.29(4)	4.28(4)	4.22(4)	4.06(4)	3.75(4)	3.34(4)
φ_{Fe} / °		125(1)	125(1)	126(1)	131(1)	0	0	0
θ_{Fe} / °		76(12)	89(33)	85(25)	77(12)	35(2)	34(2)	18(4)
mFe_x / μ_B		-2.4(2)	-2.5(1)	-2.5(2)	-2.7(2)	2.3(1)	2.1(1)	1.1(2)
mFe_y / μ_B		3.4(1)	3.50(5)	3.4(1)	3.1(1)	0	0	0
mFe_z / μ_B		1.0(9)	0.08(254)	0.4(19)	1.0(8)	3.3(1)	3.1(1)	3.16(9)
mRe / μ_B		0.864(7)	0.858(7)	0.856(7)	0.844(8)	0.812(8)	0.749(8)	0.667(8)
m_{tot} / μ_B		3.46(3)	3.43(3)	3.42(3)	3.38(3)	3.25(3)	3.00(3)	2.67(3)
A/B	B_{iso} / Å^2	0.756(1)	0.79(1)	0.78(1)	0.79(1)	0.82(1)	0.85(1)	0.95(2)
O	B_{iso} / Å^2	0.49(2)	0.51(2)	0.52(2)	0.56(2)	0.56(2)	0.60(2)	0.69(2)
R_{wp} / %		4.18	4.14	4.10	3.98	3.91	3.55	3.28
χ^2		3.33	4.10	4.03	3.83	3.74	3.52	3.12
Q / μA·h		36	45	45	45	45	50	50

Fe atoms are located at (0, ½, 0), with Re atoms at (½, 0, 0). Antisite disorder of Fe/Re is not refined due to poor neutron contrast. Fe and Re sublattices are ferromagnetically ordered, and Re components are constrained to equal -20% of Fe values. The total magnetic moment determined from neutron diffraction, m_{tot}, is defined as mFe - mRe. No site mixing between A and B-sites was found. A-sites are found to be 86.5(4) % Ca, with 13.5 % Mn. Q, a measure of the total length of exposure of the sample to the neutron beam ($Q = I \cdot t$), is also tabulated.

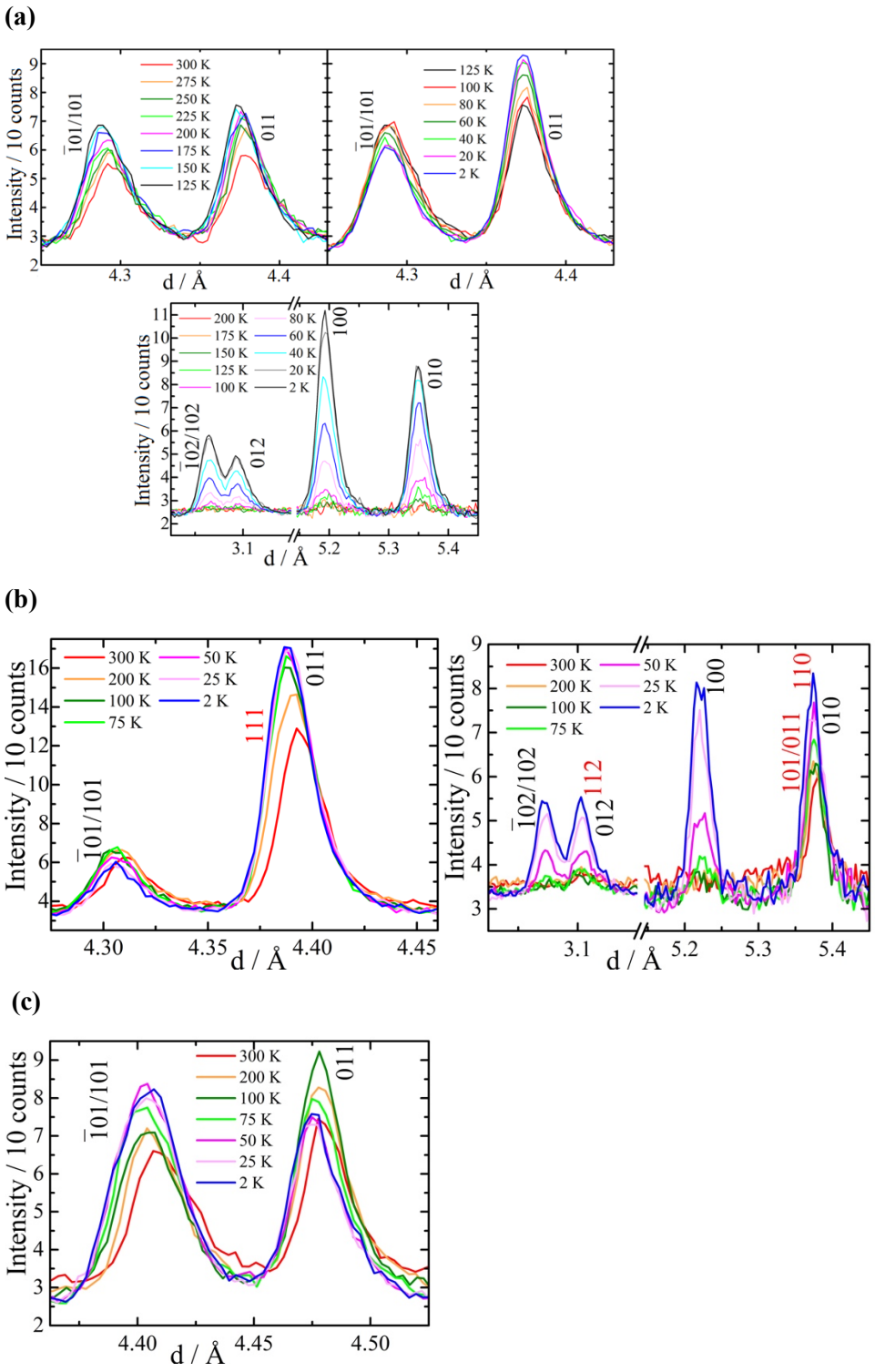

FIG. S-1. Selected powder neutron diffraction peaks for $Ca_xMn_{2-x}FeReO_6$ samples showing temperature evolution of magnetic intensities. (a) $x = 0$. Peaks sensitive to Fe/Re spin order are shown in the upper panels, and those arising from Mn spin order below 200 K are shown in the lower panel. Changes in the intensities of $\bar{1}$01/101 and 011 below 80 K evidence the spin canting transition at 75 K. (b) $x = 0.5$. Red/black labels show peaks from $x = 0.5$(T)/$x = 0.5$(M) phases. (c) $x = 1.5$(M) magnetic peaks.

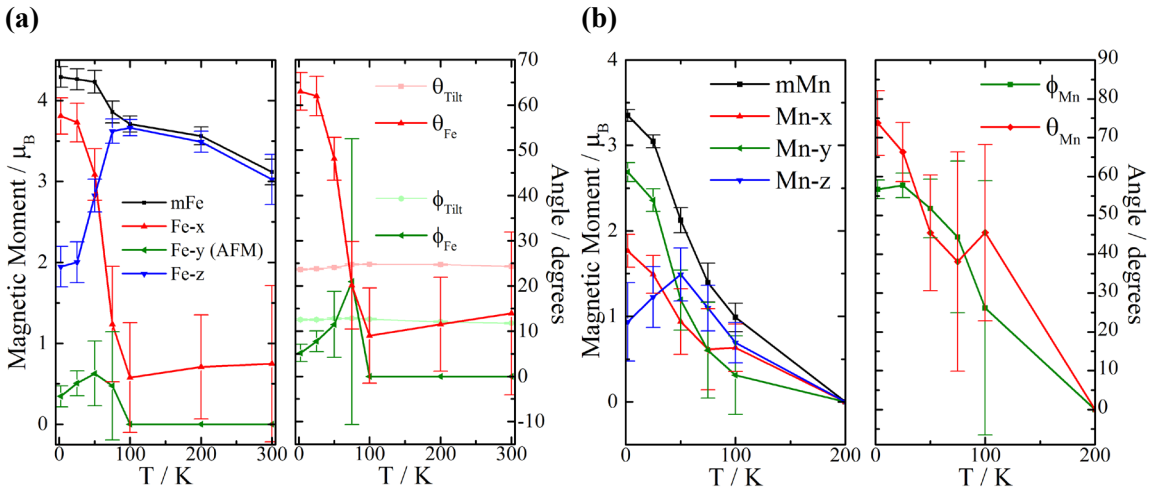

FIG. S-2. (Left) the total magnetic moment and cartesian components of x = 0.5(M) spin order, and (right) the tilt angles for (a) Fe and (b) Mn spins. Angles are defined in the caption to Fig. 3.

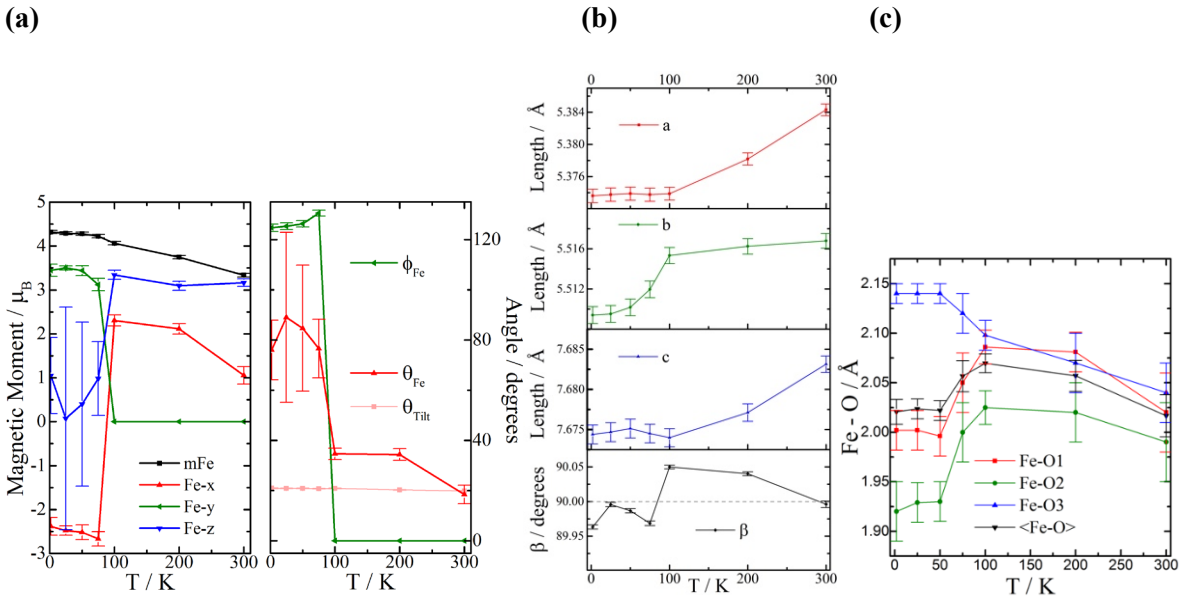

FIG. S-3. (a) (Left) the total magnetic moment and cartesian components of x = 1.5(M) spin order, and (right) the tilt angles for Fe spins. Angles are defined in the caption to Fig. 3. Thermal variations of (b) lattice parameters and (c) Fe-O distances for the x = 1.5(M) phase.

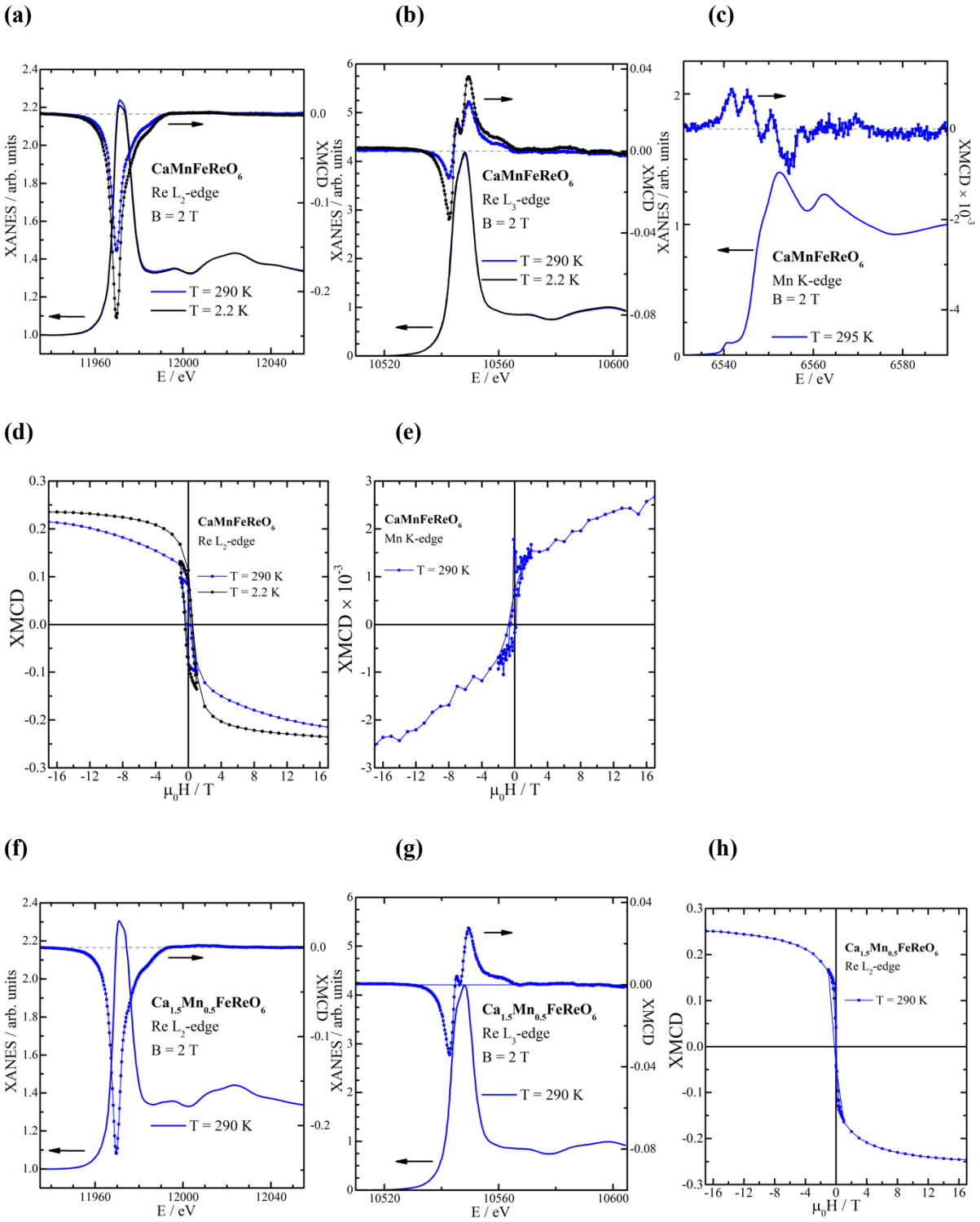

FIG. S-4. X-ray Absorption Near-Edge Spectra (XANES) and X-ray Magnetic Circular Dichroism (XMCD) for the $x = 1.0$ sample at (a) Re L_2-edge, (b) Re L_3-edge, and (c) Mn K-edge. (d) and (e) show hysteresis of the Re L_2 and (c) Mn K XMCD signals. XANES and XMCD data for the $x = 1.5$ sample at (f) Re L_2-edge and (g) Re L_3-edge, and (h) shows hysteresis of the Re L_2 XMCD signal.