Electronic Supplementary Information

Magnetic ordering in a frustrated bow-tie lattice

Laura J. Vera Stimpson[1], Efrain E. Rodriguez[2], Craig M. Brown[3], Gavin B. G. Stenning[4], Marek Jura[4], Donna C. Arnold[1*]

[1] *School of Physical Sciences, University of Kent, Canterbury, Kent, CT1 7NH, UK*

[2] *Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742-2115, USA*

[3] *NIST Center for Neutron Research, 100 Bureau Drive, Gaithersburg, Maryland, 20899-8562, USA*

4 ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, OX11 0QX, UK

** Corresponding author, Donna C. Arnold, e-mail: d.c.arnold@kent.ac.uk, Tel: +44 (0)1227 827810*

Results and Discussion

Powder Neutron and X-ray diffraction data

X-ray and neutron diffraction data were refined using the model proposed by Ansell *et al.*[1] in the GSAS suite of programs.[2,3] Refinements were performed for 51 and 39 variables respectively which include lattice parameters, atom positions, zero point and 12 background coefficients fitted using a shifted Chebyschev polynomial function. Peak shape was determined using a Pseudo-Voigt function as described by Howard, and Thompson *et al.* (Type 2 in the GSAS suite of programs).[4,5] The U*iso* were allowed to refine in the powder neutron diffraction data but were fixed to 1.00 (U*i*/U*e**100) in the powder X-ray diffraction data since allowing them to refine resulted in physically unrealistic values. Fractional occupancies of the Ca and both Mn sites refined to be 1.0 within error and were thus fixed for subsequent refinements. Six spherical Harmonic order (ODF) terms were also refined in a cylindrical geometry in order to mitigate against surface roughness effects introduced by preparation of the sample for XRD analysis. In all cases the Texture Index was close to 1 indicating that the sample is randomly orientated. Refinement data and profiles for both X-ray and neutron diffraction data as a function of temperature are given in tables S1 through S4 and figures S1 through S4.

Table S1: *Rietveld refinement parameters for neutron diffraction data collected for $Ca_2Mn_3O_8$ as a function of temperature, refined using the space group C2/m and the model proposed by Ansell et al.*[1] *Values in parentheses indicate one standard deviation in the parameter.*

Parameter	**Temperature (K)**			
	4	**35**	**60**	**80**
χ^2	2.238	1.786	0.9412	0.9107
wRp (%)	9.58	8.85	6.23	6.11
Rp (%)	6.65	6.59	5.01	4.87
a (Å)	11.0077(3)	11.008(3)	11.009(2)	11.009(2)
b (Å)	5.8402(2)	5.841(1)	5.841(1)	5.840 (1)
c (Å)	4.937(2)	4.937(1)	4.9378(1)	4.9385(1)
β (°)	109.738(2)	109.735(2)	109.734(1)	109.734(1)
Cell Vol. (Å^3)	298.771(1)	298.813(8)	298.843(6)	298.882(6)
Ca (x,0,z)	0.7246(5) 0.6635(9)	0.7250(5) 0.6634(8)	0.7253(4) 0.6649(6)	0.7249 (3) 0.6664(6)
Ca $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	-0.1(2)	0.4(2)	0.4(2)	0.7 (2)
Mn1 (0,0,½)				
Mn1 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	1.4(4)	1.1(4)	0.3(3)	0.9(3)
Mn2 (0,y,0)	0.262(1)	0.262(1)	0.2594(7)	0.2599(7)
Mn2 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	-0.9(2)	-1.0(2)	0.6(2)	0.7(2)
O1 (x,y,z)	0.1012(3) 0.2222(5) 0.3935(6)	0.1007(2) 0.2229(4) 0.3933(5)	0.1005(2) 0.2229(3) 0.3919(4)	0.1002(2) 0.2222(3) 0.3925(4)
O1 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.30(12)	0.31(11)	0.45(9)	0.37(9)
O2 (x,½,z)	0.5954(5) 0.8998(8)	0.5961(4) 0.8998(8)	0.5963(3) 0.9000(6)	0.5962(3) 0.9017(6)
O2 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	1.0(2)	1.0(2)	0.4(1)	0.3(1)
O3 (x,0,z)	0.6033(4) 0.9609(8)	0.6033(4) 0.9609(7)	0.6051(3) 0.9626(5)	0.6044(2) 0.9624(5)
O3 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.3(2)	0.3(2)	06(1)	0.7(1)
Parameter	**Temperature (K)**			
	100	**150**	**200**	**300**
χ^2	0.9260	0.9022	0.8958	0.9822
wRp (%)	6.02	6.12	6.01	4.52
Rp (%)	4.79	4.95	4.91	3.69
a (Å)	11.010(2)	11.012(2)	11.015(2)	11.023(2)
b (Å)	5.841(1)	5.841(1)	5.842(1)	5.84629(8)
c (Å)	4.939(1)	4.940(1)	4.940(1)	4.94346(7)
β (°)	109.735(1)	109.746(1)	109.751(1)	109.771(1)
Cell Vol. (Å^3)	298.937(6)	299.04(1)	299.232(6)	299.785(6)
Ca (x,0,z)	0.7247 (4) 0.6662(6)	0.7247(4) 0.6641(6)	0.7245(3) 0.6645(6)	0.7248(3) 0.6661(5)
Ca $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.5(2)	0.3(2)	0.4(2)	0.4(1)
Mn1 (0,0,½)				
Mn1 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	1.1(3)	1.6(3)	1.3(3)	1.3(2)
Mn2 (0,0,z)	0.2607(7)	0.2605(7)	0.2607(7)	0.2577(6)
Mn2 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.7(2)	0.5(2)	0.7(2)	0.7(1)
O1 (x,y,z)	0.1001(2) 0.2232(3) 0.3926(4)	0.1003(2) 0.2226(3) 0.3925(4)	0.1006(2) 0.2231(3) 0.3923(4)	0.1005(2) 0.2228(3) 0.3919(3)
O1 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.41(9)	0.27(9)	0.54(9)	0.66(7)
O2 (x,½,z)	0.5970(3) 0.9016(6)	0.5969(3) 0.9013(6)	0.5963(3) 0.9016(6)	0.5967(2) 0.9011(4)
O2 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.4(1)	0.5(1)	0.3(1)	0.52(9)
O3 (x,0,z)	0.6042(3) 0.9618(6)	0.6039(3) 0.9605(6)	0.6040(3) 0.9610(6)	0.6041(3) 0.9605(4)
O3 $U_{(iso)}/U_{(e)}$ x 100 (Å^2)	0.7(1)	0.5(1)	1.0(1)	1.0(1)

Table S2: *Rietveld refinement parameters for x-ray diffraction data collected for $Ca_2Mn_3O_8$ as a function of temperature, refined using the space group C2/m and the model proposed by Ansell et al.*[1] *Note U(iso) were fixed to 0.01 Å^2. Values in parentheses indicate one standard deviation in the parameter.*

Parameter	Temperature (K)						
	12	**20**	**30**	**40**	**50**	**60**	**70**
χ^2	0.8762	0.8598	0.9251	1.007	0.9272	1.043	0.8979
wRp (%)	14.66	14.51	15.04	15.68	15.06	16.02	14.8
Rp (%)	11.54	11.39	11.82	12.43	11.82	12.59	11.64
a (Å)	11.0047(4)	11.0069(4)	11.007(4)	11.0071(5)	11.007(4)	11.007(4)	11.008(4)
b (Å)	5.8395(3)	5.84016(3)	5.8400(2)	5.840(3)	5.840(2)	5.840(3)	5.840(3)
c (Å)	4.9370(2)	4.9371(3)	4.9372(2)	4.937(2)	4.937(2)	4.937(2)	4.938(2)
β (°)	109.737(3)	109.735(3)	109.741(3)	109.736(3)	109.736(3)	109.737(3)	109.734(3)
Cell Vol. (Å^3)	298.62(1)	298.62(1)	298.71(1)	298.72(1)	298.72(1)	298.73(1)	298.82(1)
Ca (x,0,z)	0.7250(7) 0.662(2)	0.7257(7) 0.665(2)	0.7261(7) 0.664(2)	0.7247(7) 0.665(2)	0.7223(8) 0.664(1)	0.7245(7) 0.665(2)	0.728(2) 0.670(4)
Mn1 (0,0,½)							
Mn2 (0,y,0)	0.258(1)	0.260(1)	0.258(1)	0.259(1)	0.258(1)	0.259(1)	0.258(2)
O1 (x,y,z)	0.098(1) 0.224(2) 0.396(3)	0.099(12) 0.2230(2) 0.397(3)	0.098(1) 0.226(2) 0.399(3)	0.098(1) 0.230(2) 0.403(3)	0.102(1) 0.225(2) 0.394(3)	0.101(1) 0.228(2) 0.395(3)	0.095(4) 0.223(6) 0.387(4)
O2 (x,½,z)	0.595(2) 0.888(5)	0.592(2) 0.882(5)	0.593(2) 0.879(5)	0.598(2) 0.887(4)	0.595(2) 0.896(4)	0.592(2) 0.897(4)	0.596(6) 0.88(1)
O3 (x,0,z)	0.599(2) 0.952(5)	0.603(2) 0.964(4)	0.599(2) 0.958(4)	0.600(2) 0.959(4)	0.596(2) 0.959(4)	0.599(2) 0.951(4)	0.617(5) 0.96(2)
Parameter	**Temperature (K)**						
	80	**90**	**100**	**110**	**120**	**130**	**140**
χ^2	0.9203	0.9235	0.9011	1.022	0.8910	0.8910	0.8803
wRp (%)	15.02	14.98	14.83	15.77	14.73	14.73	14.62
Rp (%)	11.9	11.8	11.52	12.56	11.58	11.58	11.60
a (Å)	11.007(4)	11.008(4)	11.008(4)	11.008(4)	11.008(4)	11.008(4)	11.010(4)
b (Å)	5.839(3)	5.840(3)	5.840(3)	5.840(3)	5.840(2)	5.840(3)	5.841(3)
c (Å)	4.938(2)	4.938(2)	4.939(2)	4.939(2)	4.939(2)	4.939(2)	4.939(2)
β (°)	109.735(3)	109.732(3)	109.741(3)	109.745(3)	109.741(3)	109.741(3)	109.742(3)
Cell Vol. (Å^3)	298.83(1)	298.82(1)	298.83(1)	298.81(1)	298.82(1)	298.82(1)	298.95(1)
Ca (x,0,z)	0.7253(6) 0.664(1)	0.728(1) 0.668(4)	0.726(1) 0.667(7)	0.728(1) 0.670(4)	0.727(1) 0.665(4)	0.727(1) 0.682(9)	0.728(1) 0.670(4)
Mn1 (0,0,½)							
Mn2 (0,0,z)	0.260(1)	0.259(2)	0.259(2)	0.258(2)	0.259(2)	0.259(2)	0.258(2)
O1 (x,y,z)	0.100(1) 0.228(2) 0.398(3)	0.095(4) 0.221(7) 0.387(4)	0.097(4) 0.228(7) 0.388(2)	0.095(4) 0.224(6) 0.386(4)	0.09(1) 0.229(7) 0.390(9)	0.090(4) 0.222(5) 0.380(3)	0.091(4) 0.225(6) 0.387(4)
O2 (x,½,z)	0.593(2) 0.901(4)	0.596(6) 0.89(1)	0.590(2) 0.89(2)	0.595(5) 0.88(1)	0.597(5) 0.88(1)	0.591(8) 0.879(9)	0.594(6) 0.88(1)
O3 (x,0,z)	0.602(2) 0.958(4)	0.614(6) 0.96(1)	0.614(6) 0.96(2)	0.617(5) 0.95(1)	0.623(4) 0.94(2)	0.617(5) 0.95(2)	0.617(5) 0.95(1)

Table S3: *Rietveld refinement parameters for x-ray diffraction data collected for $Ca_2Mn_3O_8$ as a function of temperature, refined using the space group C2/m and the model proposed by Ansell et al.[1] Note U(iso) were fixed to 0.01 Å^2. Values in parentheses indicate one standard deviation in the parameter.*

Parameter	Temperature (K)						
	150	**175**	**200**	**225**	**250**	**275**	**300**
χ^2	0.9044	0.8928	0.8809	0.9085	0.8830	0.8866	0.9383
wRp (%)	14.88	14.74	14.67	14.92	14.70	14.75	4.98
Rp (%)	11.79	11.68	11.55	11.73	11.64	11.62	3.9
a (Å)	11.011(4)	11.011(4)	11.014(4)	11.016(4)	11.017(4)	11.019(4)	11.0131(1)
b (Å)	5.841(3)	5.842(3)	5.842(3)	5.843(3)	5.844(3)	5.845(3)	5.84160(9)
c (Å)	4.939(2)	4.940(2)	4.941(2)	4.941(2)	4.942(2)	4.943(2)	4.93926(8)
β (°)	109.743(3)	109.752(3)	109.753(3)	109.756(3)	109.762(3)	109.768(3)	109.78(1)
Cell Vol. (Å^3)	298.96(1)	299.062(1)	299.20(1)	299.34(1)	299.43(1)	299.59(1)	299.016(5)
Ca (x,0,z)	0.728(1) 0.670(4)	0.728(1) 0.668(4)	0.728(1) 0.669(4)	0.727(2) 0.667(5)	0.731(2) 0.660(5)	0.732(2) 0.650(8)	0.7244(3) 0.6656(1)
Mn1 (0,0,½)							
Mn2 (0,y,0)	0.258(2)	0.259(2)	0.259(2)	0.259(2)	0.263(2)	0.268(3)	0.2575(1)
O1 (x,y,z)	0.094(4) 0.224(6) 0.386(4)	0.095(4) 0.221(7) 0.387(4)	0.095(4) 0.221(7) 0.387(4)	0.089(3) 0.220(4) 0.380(8)	0.083(5) 0.207(7) 0.386(5)	0.081(5) 0.212(4) 0.38(1)	0.1004(2) 0.2296(2) 0.3982(2)
O2 (x,½,z)	0.594(6) 0.88(1)	0.596(6) 0.89(1)	0.596(6) 0.89(1)	0.599(6) 0.90(1)	0.61(1) 0.91(2)	0.61(1) 0.91(2)	0.5913(2) 0.8886(1)
O3 (x,0,z)	0.616(5) 0.95(1)	0.614(6) 0.96(1)	0.615(6) 0.96(1)	0.614(6) 0.95(1)	0.624(6) 0.96(1)	0.624(6) 0.95(2)	0.5984(2) 0.9609(3)

Table S4: *Bond lengths extracted from the Rietveld refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ as a function of temperature. Refinements were performed using the space group C2/m and the model proposed by Ansell et al.[1] Values in parentheses indicate one standard deviation in the parameter.*

Bond lengths (Å)	Temperature (K)							
	4	**35**	**60**	**80**	**100**	**150**	**200**	**300**
Mn_1 - O_1 (x4)	1.89511(3)	1.89521(3)	1.89776(2)	1.89157(2)	1.89411(2)	1.89450(3)	1.89945(2)	1.89646(2)
Mn_1 - O_2 (x2)	1.89978(6)	1.89990(6)	1.90005(4)	1.90732(4)	1.90943(4)	1.89450(3)	1.90736(4)	1.90959(3)
Mn_2 - O_1 (x2)	1.89934(6)	1.89663(6)	1.88895(4)	1.89176(4)	1.89292(4)	1.89223(5)	1.89245(4)	1.89201(3)
Mn_2 - O_2 (x2)	2.00368(4)	2.01189(3)	2.00408(2)	2.00215(2)	2.01284(2)	2.01034(3)	2.00785(2)	1.99960(2)
Mn_2 - O_3 (x2)	1.85770(4)	1.85240(3)	1.86870(2)	1.86170(2)	1.85728(2)	1.85895(3)	1.85755(2)	1.87106(2)
Ca - O_1 (x4)	2.40917(5)	2.41666(4)	2.41138(3)	2.41937(3)	2.42907(3)	2.41847(4)	2.41954(3)	2.42080(2)
Ca - O_2	2.37881(8)	2.37815(7)	2.37154(5)	2.36493(5)	2.36098(5)	2.37092(6)	2.37349(5)	2.36712(4)
Ca - O_3	2.29637(6)	2.29622(5)	2.28579(4)	2.28178(4)	2.28007(4)	2.28632(4)	2.28522(4)	2.28384(3)

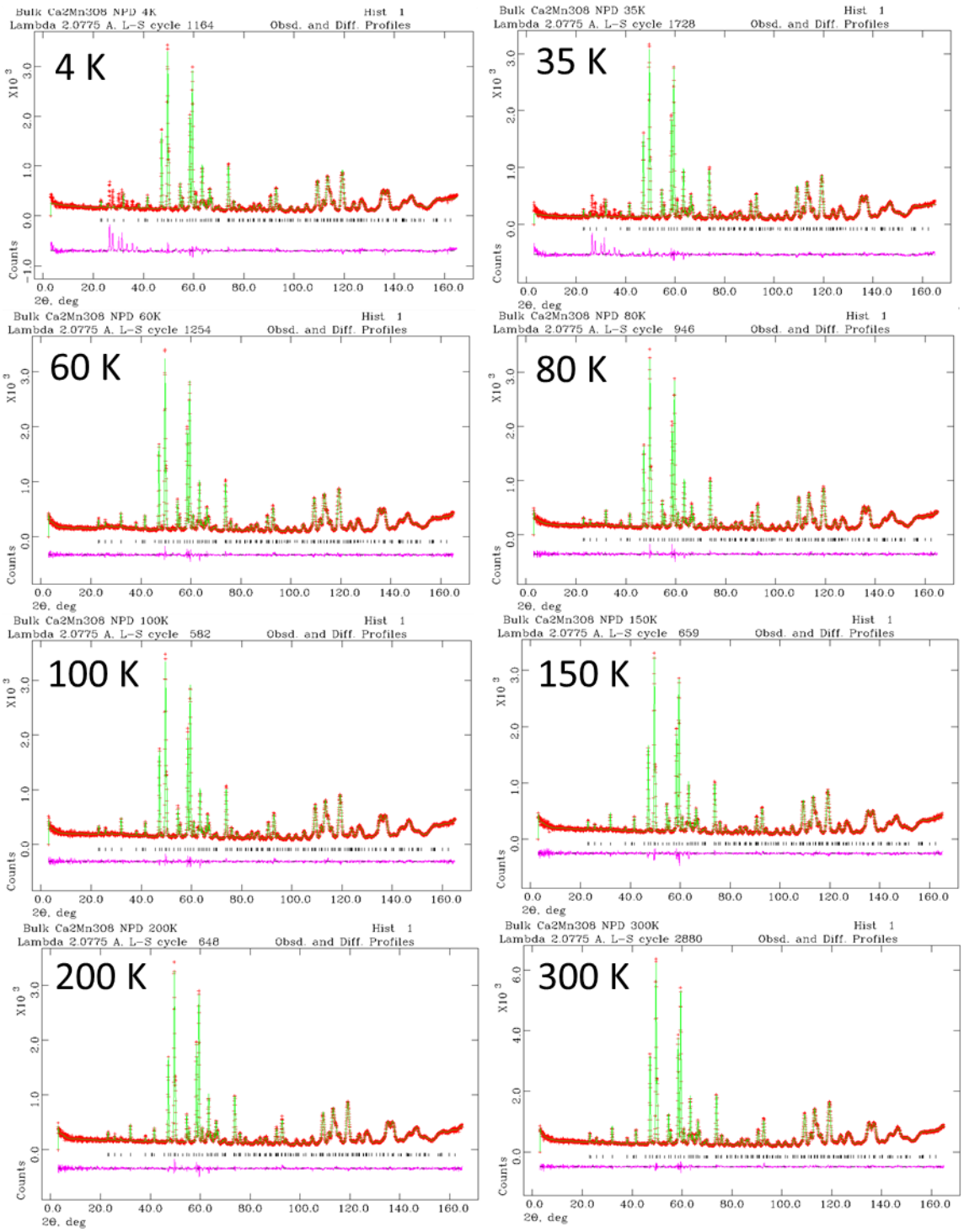

Figure S1: *Rietveld refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ at variable temperatures. Refined using the space group C2/m and the model proposed by Ansell et al.*[1] *where the red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

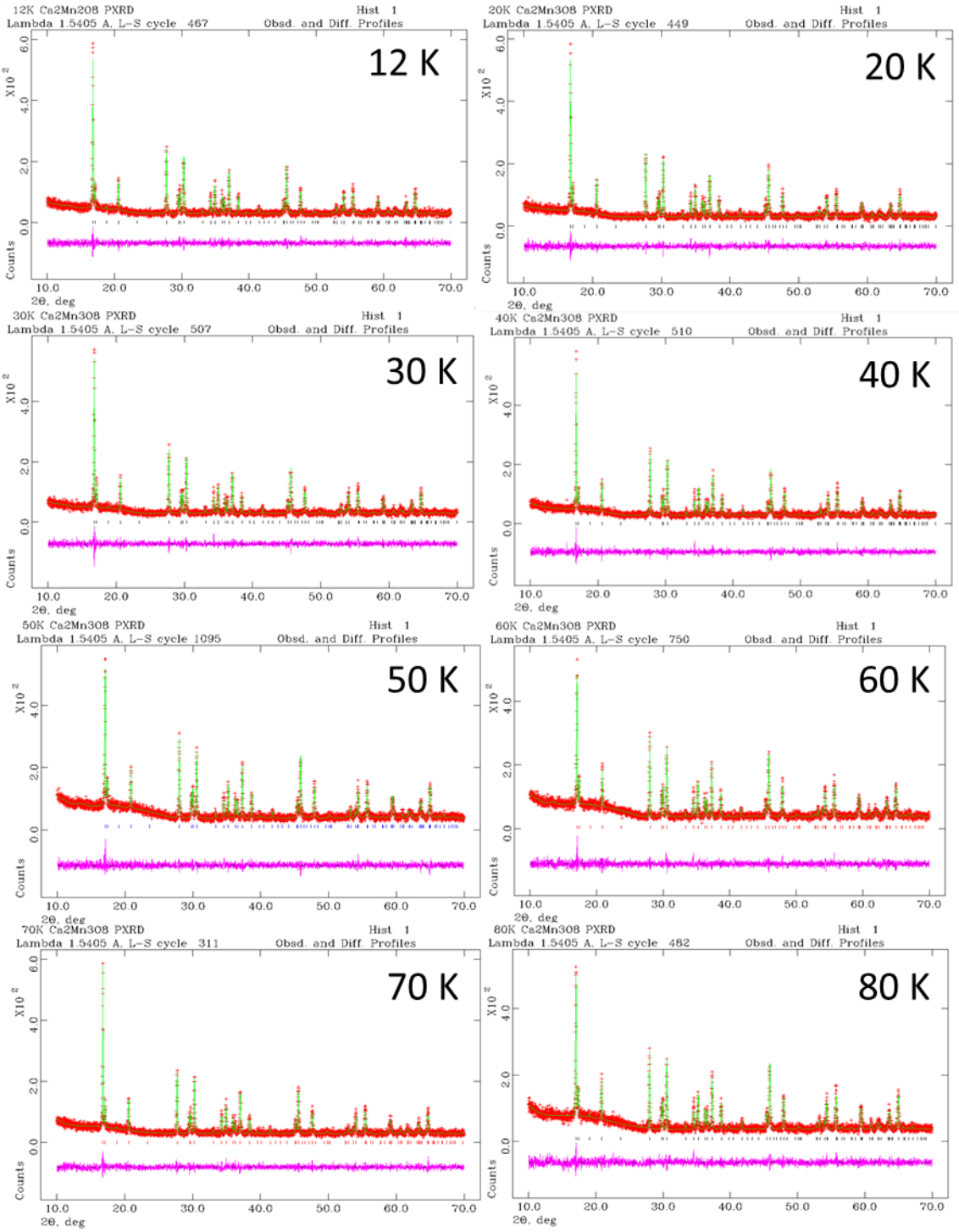

Figure S2: *Rietveld refinement of X-ray diffraction data collected for $Ca_2Mn_3O_8$ at variable temperatures between 4 K and 80 K. Refined using the space group C2/m and the model proposed by Ansell et al.*[1] *where the red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

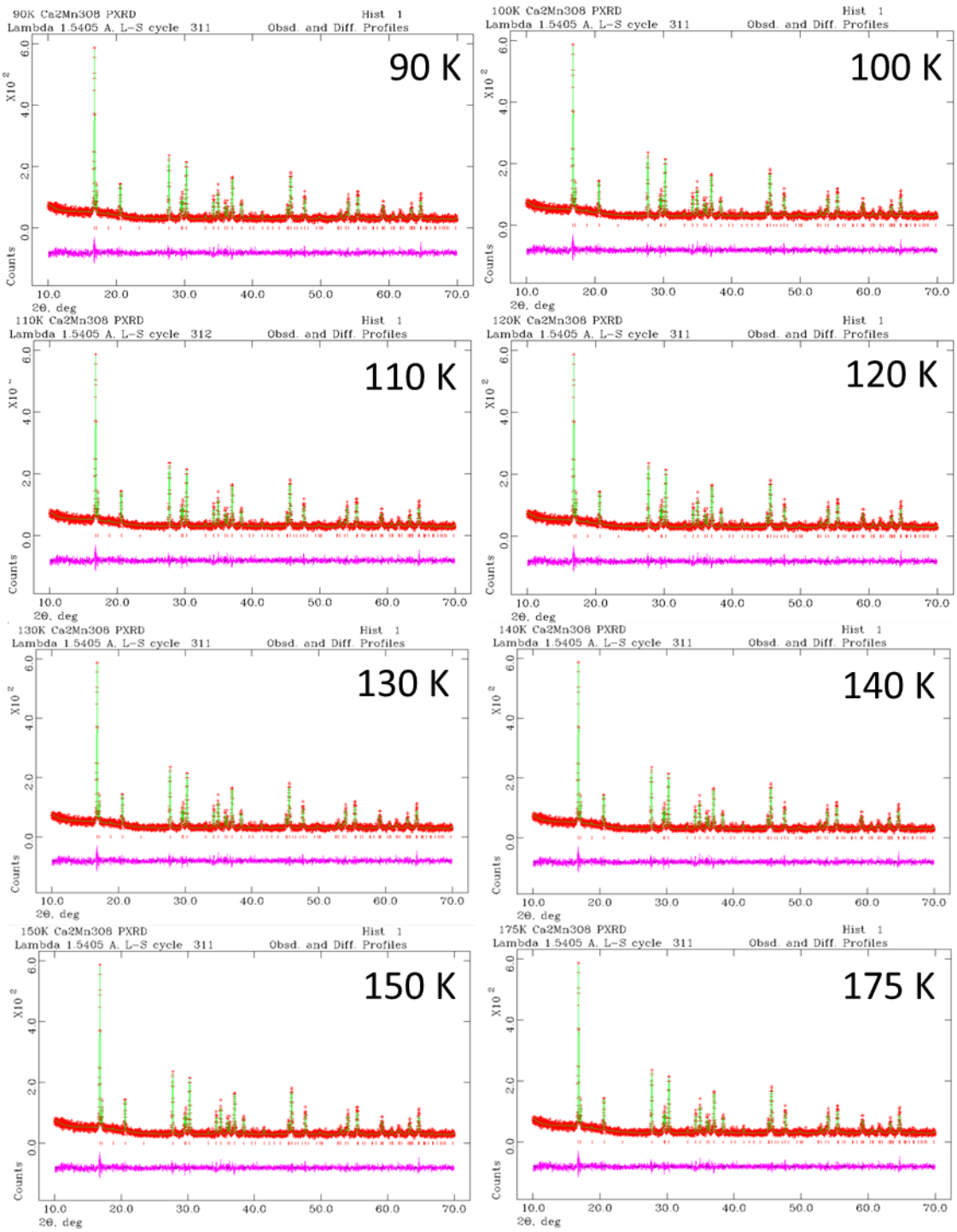

Figure S3:*Rietveld refinement of x-ray diffraction data collected for $Ca_2Mn_3O_8$ at variable temperatures between 90 K and 175 K. Refined using the space group C2/m and the model proposed by Ansell et al.*[1] *where the red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

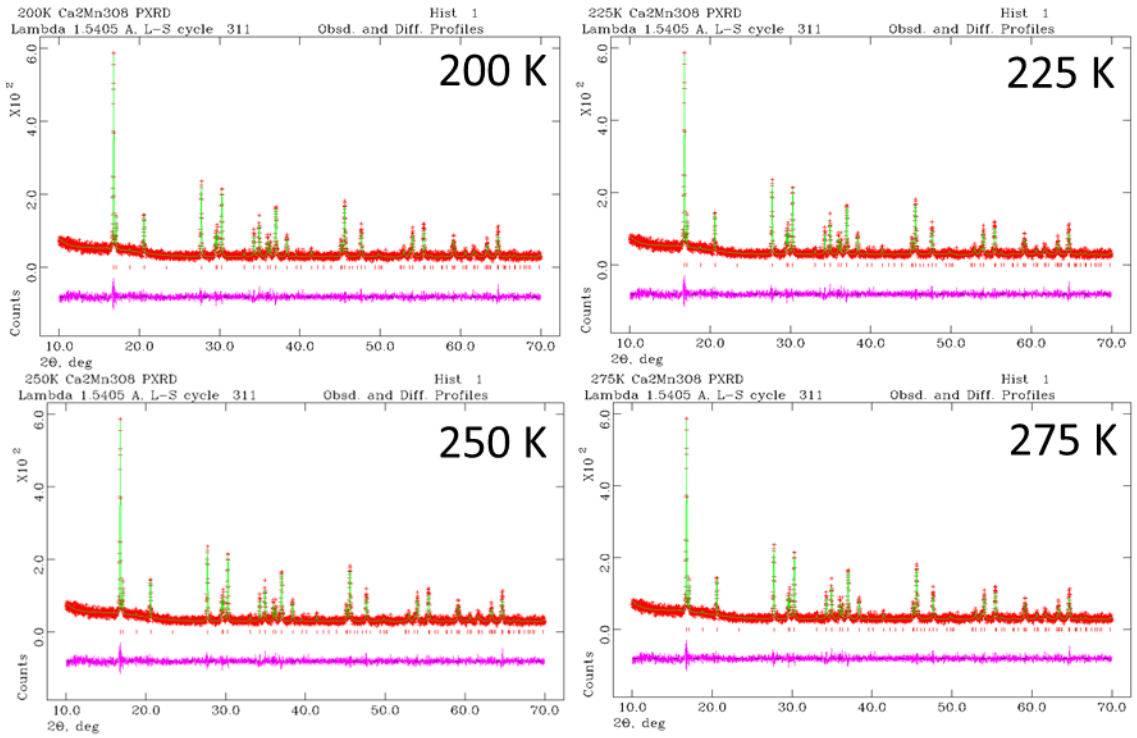

Figure S4: *Rietveld refinement of x-ray diffraction data collected for $Ca_2Mn_3O_8$ at variable temperatures between 200 K and 275 K. Refined using the space group C2/m and the model proposed by Ansell et al.*[1] *where the red circles are the observed data, the green line is the calculated model and the pink line is the difference curve.*

The Magnetic structure was determined using the Fullprof [6,7] suite and SARAh[8,9] programs. The propagation vector was first determined as, k = ½, ½, 0 using K-search. SARAh was then used to determine the irreducible representations of the propagation vector which were then evaluated using Fullprof. Goodness-of-fit parameters are detailed in table S5 with the refinement profiles given in figure S5. Figure S6 demonstrates that the fit (magnetic R factor = 192.5 %) obtained from the alternative irreducible representation suggestion does not accurately reproduce the magnetic Bragg peaks observed and thus cannot be the correct solution. Irreducible representations and their basis functions are given in table S6 and a fit to the second unsuitable model is given in figure S6.

Table S5: *Goodness-of-fit parameters determined from the magnetic structural refinement of neutron diffraction data collected for $Ca_2Mn_3O_8$ at temperatures of 4 K and 35 K.*

Parameter	**Temperature (K)**	
	4	**35**
χ^2	1.21	1.02
R_p (%)	11.1	10.4
R_{wp} (%)	11.7	11.6
Bragg R-factor (%)	3.352	2.252
RF-factor (%)	2.658	1.579
Magnetic R factor (%)	12.99	9.657

Table S6: *Irreducible representations Γ_1 and Γ_2 and their basis functions for the two Mn sites in $Ca_2Mn_3O_8$.*

Irreducible representation	**Basis functions for Mn1**	**Basis functions for Mn2**
Γ_1	(100); (010); (001) for *x,y,z*	(100); (010); (001) for *x,y,z* (100); (010); (001) for *-x,-y,-z*
Γ_2		(100); (010); (001) for *x,y,z* (-100); (0-10); (00-1) for *-x,-y,-z*

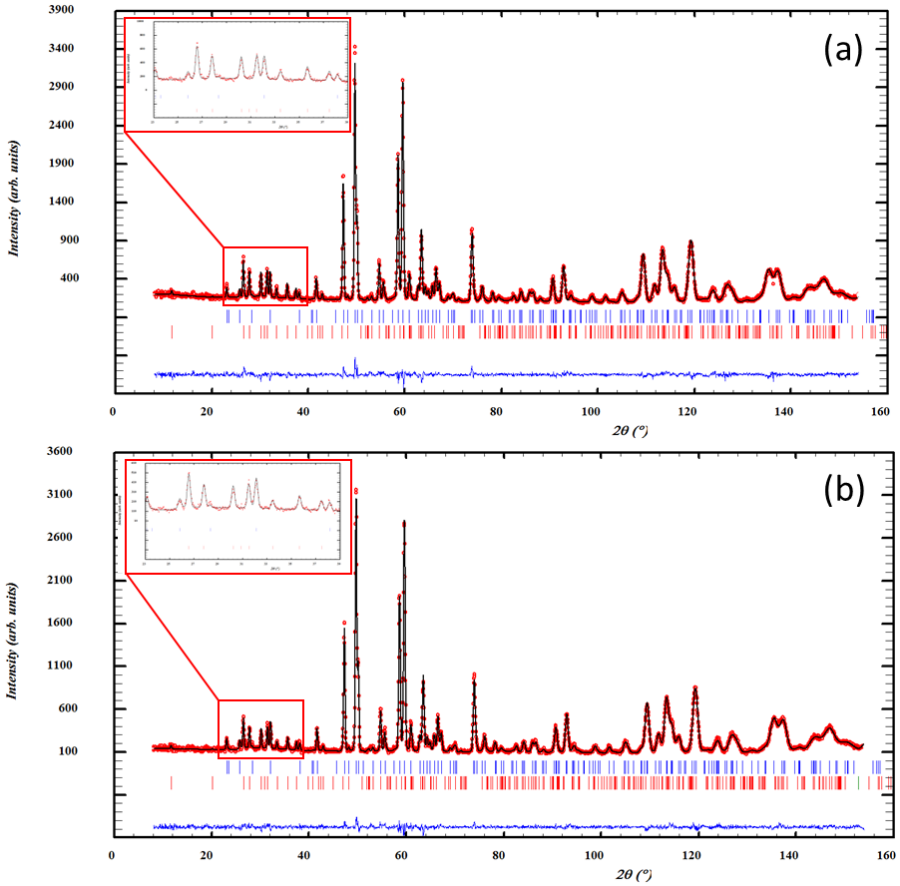

Figure S5: *Magnetic refinement profiles at (a) 4 K and (b) 35 K from neutron diffraction data collected for $Ca_2Mn_3O_8$. Inset shows an expanded region showing magnetic order. Where the black circles are the observed data, the red line is the calculated model and the blue line is the difference curve. Blue and red tickmarks represent the nuclear and magnetic phases respectively.*

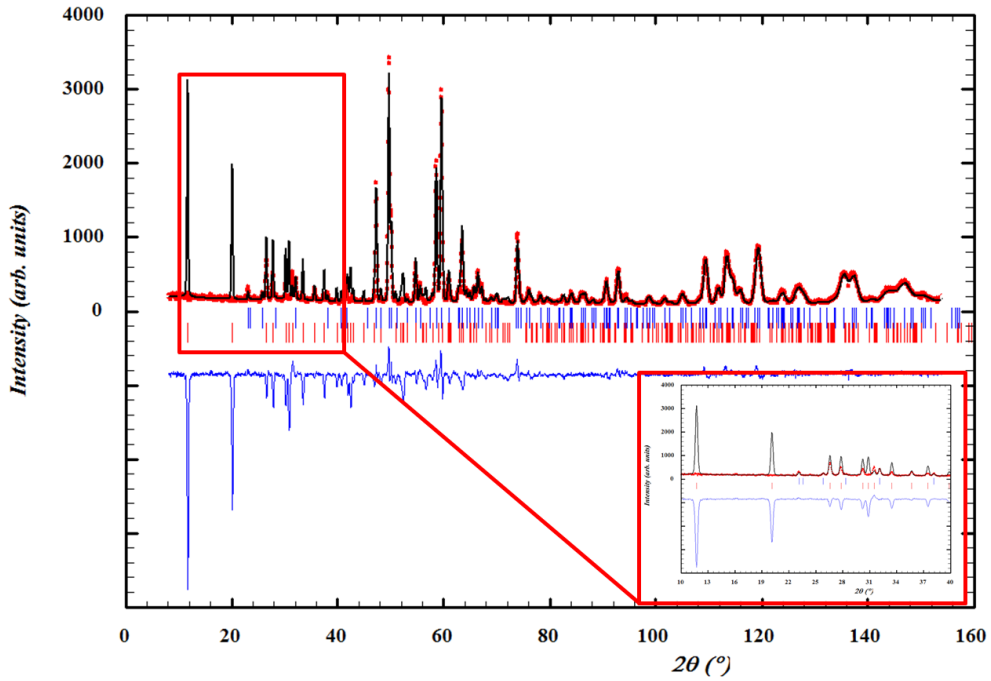

Figure S6: *Magnetic refinement profiles at 4 K from neutron diffraction data collected for* $Ca_2Mn_3O_8$ *demonstrating that the alternative irreproducible representation does not accurately model the magnetic Bragg data observed* (magnetic R factor = 192.5 %). *Inset shows an expanded region showing magnetic order. Where the black circles are the observed data, the red line is the calculated model and the blue line is the difference curve. Blue and red tickmarks represent the nuclear and magnetic phases respectively.*

Magnetic measurements

Field dependent SQUID magnetometry data is given in figure S7. The frequency dependence of the AC susceptibility was also investigated in order to probe the slight deviation between zero field cooled and field cooled data as shown in figure S8. These data ruled out a transition to a spin glass-like state consistent with the diffraction data.

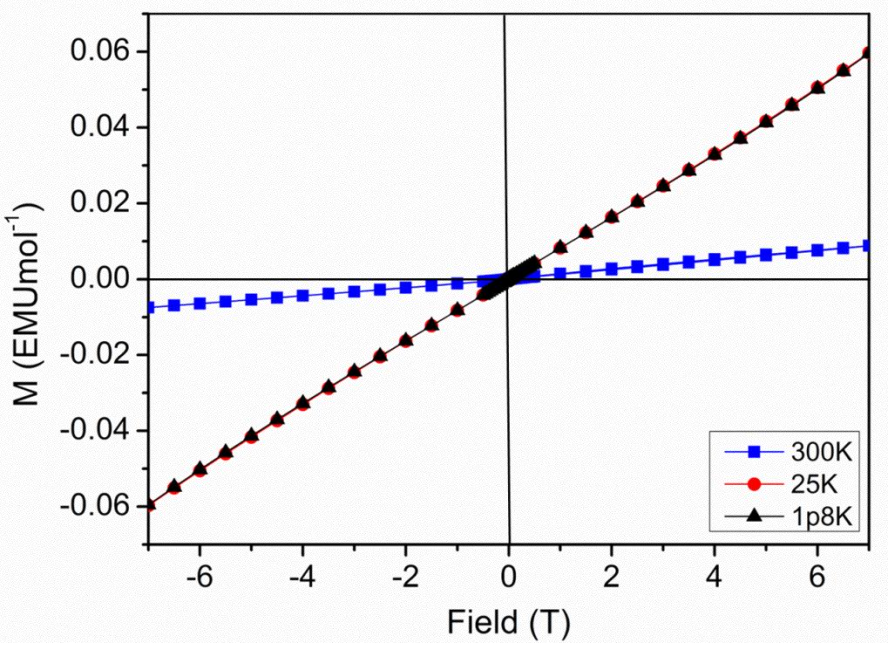

Figure S7: *Field dependent measurements of $Ca_2Mn_3O_8$ collected at 300 K (blue), 25 K (red) and 1.8 K (black).*

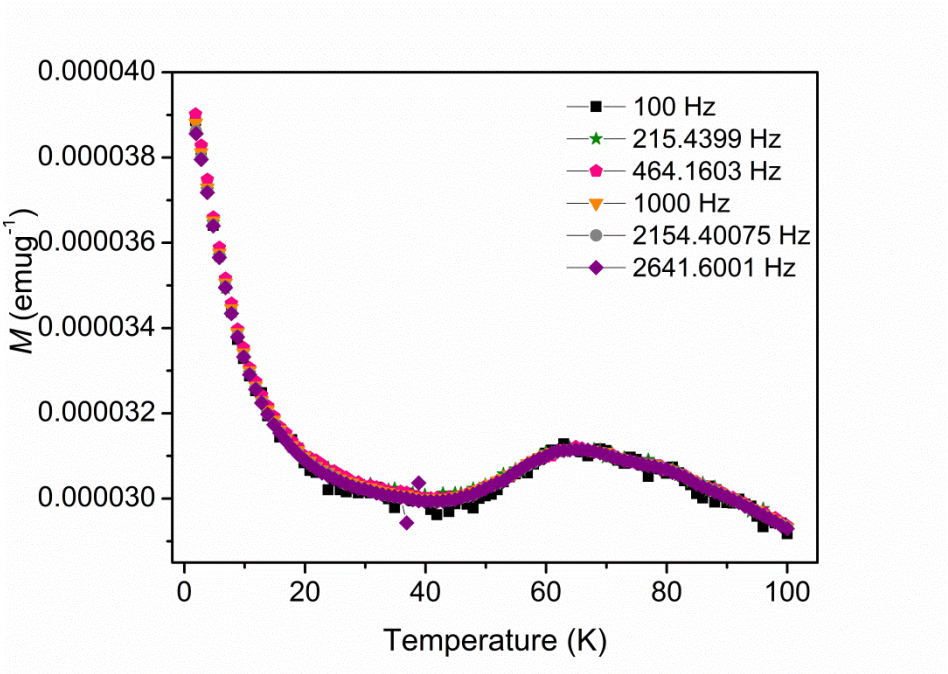

Figure S8: *AC magnetic susceptibility measurements of $Ca_2Mn_3O_8$ collected as a function of temperature and frequency at 0.1 T.*

Inelastic measurements

Figure S9 shows an energy slice through the elastic channel of the data collected at λ = 2.5 Å indicating that the Warren-like behaviour observed in the background of the diffraction data does not arise as a result of 1D or 2D static magnetic ordering.

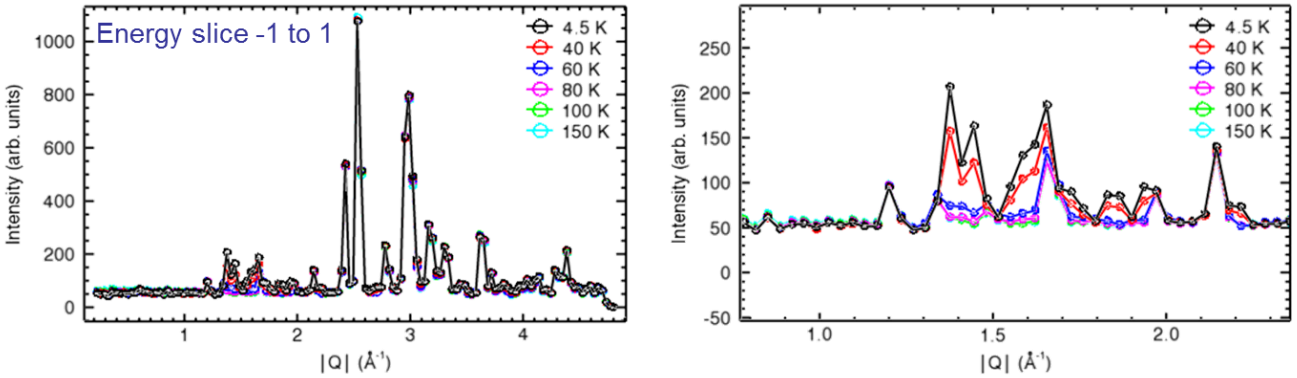

Figure S9: *Constant energy cut of the elastic channel between -1 meV and 1meV showing that there are no Warren-like features in the background and ruling out the possibility of static low dimensional ordering of magnetic spins between 130 K and* T_N.

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