

Electronic Supplementary Information for:

**Magnetic ordering of the cryogenic magnetic cooling mineral
gaudfroyite.**

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The supplementary information contains a table of crystallographic information and some figures which are referenced in the main paper. They provide useful additional information but are not essential to the main conclusions of the study.

Table S1.

Structural parameters of gaufroyite from NPD at 15 K and 0.1 K.

Refined atomic parameters of gaufroyite from NPD at 15 K

Atoms	Occ.	x	y	z	Uiso
Ca1	1	1/3	2/3	1/4	0.046(5)
Ca2	1	0.1307(7)	0.8277(7)	1/4	0.008(2)
Mn	1	0	1/2	0	0.0001 ^a
B	1	0.2153(5)	0.7608(6)	3/4	0.003(1)
C	0.5	0	0	0.074(1)	0.0001 ^a
O1	1	0.0970(5)	0.4795(5)	1/4	0.012(2)
O2	1	0.3127(6)	0.9077(5)	3/4	0.005(1)
O3	1	0.3023(4)	0.4750(4)	0.5459(5)	0.021(1)
O4	0.5	0.0516(9)	0.9134(7)	0.5701(8)	0.012(2)

Space Group: $P6_3/m$, $a = 10.5914(4)$ Å, $c = 5.8829(2)$ Å. $R_{wp}=0.0641$ (Bank $2\theta=121.66^\circ$), $R_{wp}=0.0497$ (Bank $2\theta=58.33^\circ$).

Refined atomic parameters of gaufroyite from NPD at 0.1 K

Atoms	Occ.	x	y	z	Uiso
Ca1	1	1/3	2/3	1/4	0.041(4)
Ca2	1	0.1318(7)	0.8279(7)	1/4	0.012(2)
Mn	1	0	1/2	0	0.0001 ^a
B	1	0.2133(5)	0.7603(6)	3/4	0.008(2)
C	0.5	0	0	0.074(1)	0.0001 ^a
O1	1	0.0977(5)	0.4800(5)	1/4	0.018(2)
O2	1	0.3119(6)	0.9064(5)	3/4	0.008(1)
O3	1	0.3027(4)	0.4764(4)	0.5435(5)	0.022(1)
O4	1	0.0506(8)	0.9135(7)	0.5705(8)	0.012(2)

Space Group: $P6_3/m$, $a = 10.5916(3)$ Å, $c = 5.8840(2)$ Å. $R_{wp} = 0.0613$ (Bank $2\theta=121.66^\circ$), $R_{wp}=0.0464$ (Bank $2\theta=58.33^\circ$); Shubnikov magnetic space group $P6_3'/m'$: $m_x=3.28(5)$ μ_B

^a U_{iso} for the C and Mn atoms were slightly negative and were therefore constrained to the small positive value, 0.0001.

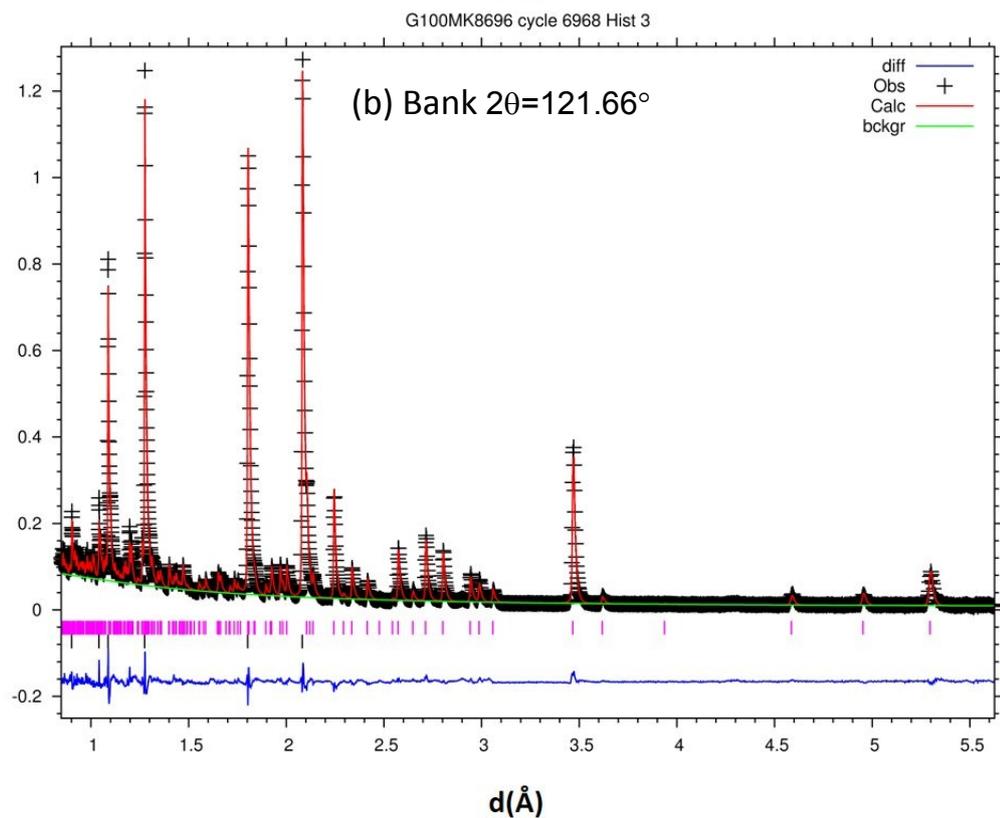
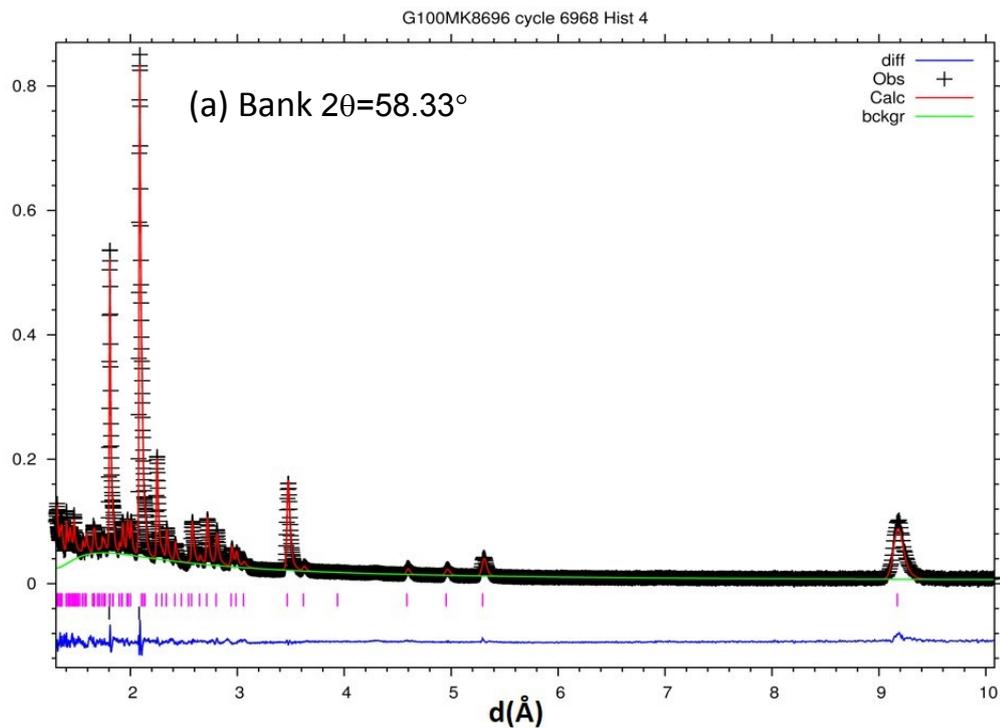


Fig.S1. The GSAS joint refined patterns of WISH data at 100 mK. Reflection positions are marked in magenta for gaudefroyite (nuclear and magnetic) and black for Cu.

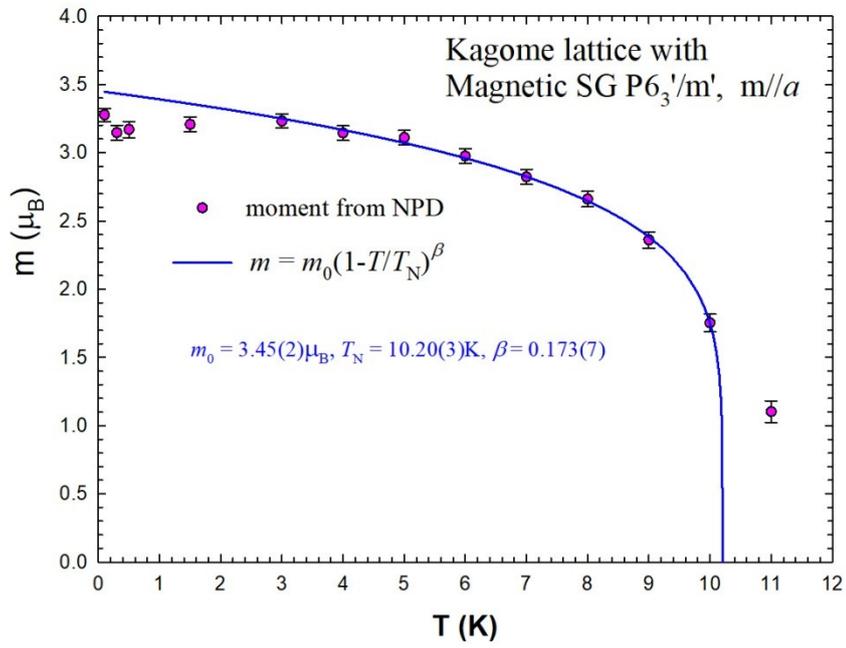


Fig.S2. Variation of magnetic moment with temperature for gaudefroyite at temperatures from 100 mK to 15 K and fitted to the scaling law shown. The parameters T_N and β agree with those obtained using integrated intensities and reported in the main paper.

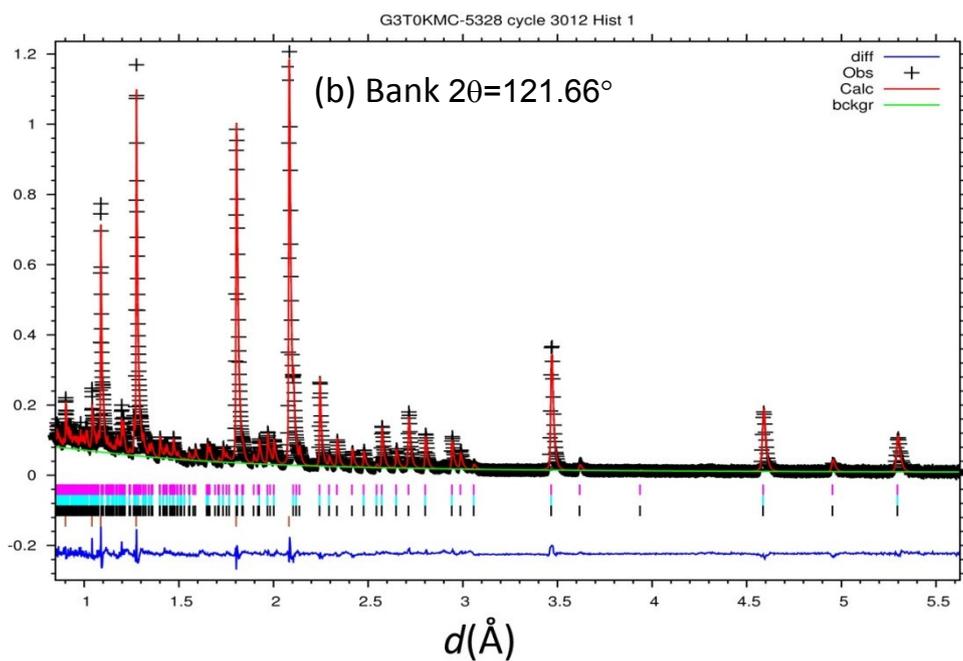
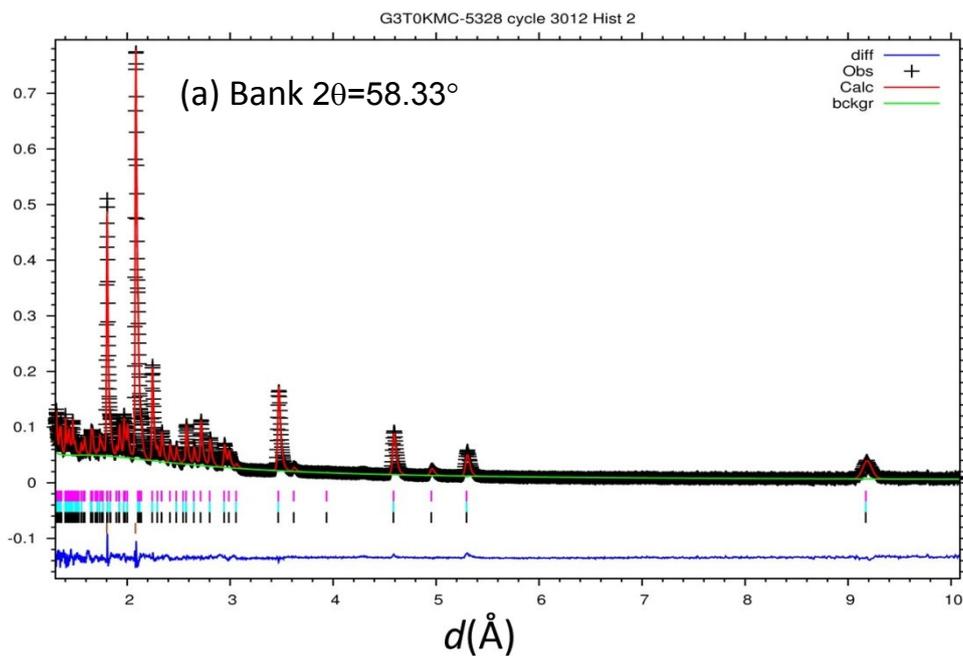


Fig.S3. The GSAS joint refined patterns of WISH data in a cryomagnet at 100 mK and an applied magnetic field of 3T. Reflection positions in magenta and black are for gaudfroyite (nuclear and AFM), cyan for FM and brown for Cu.

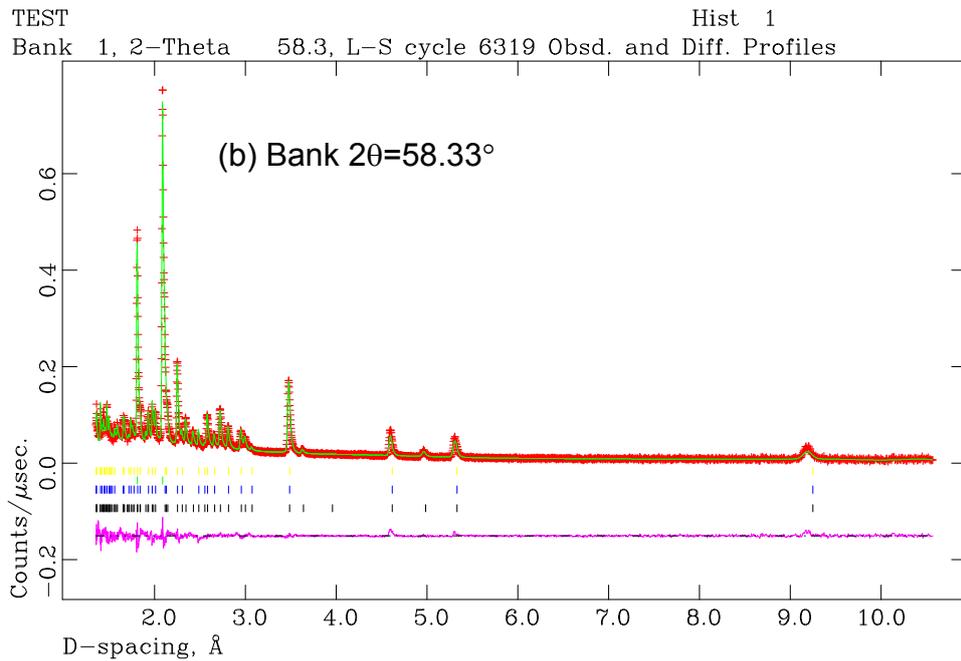
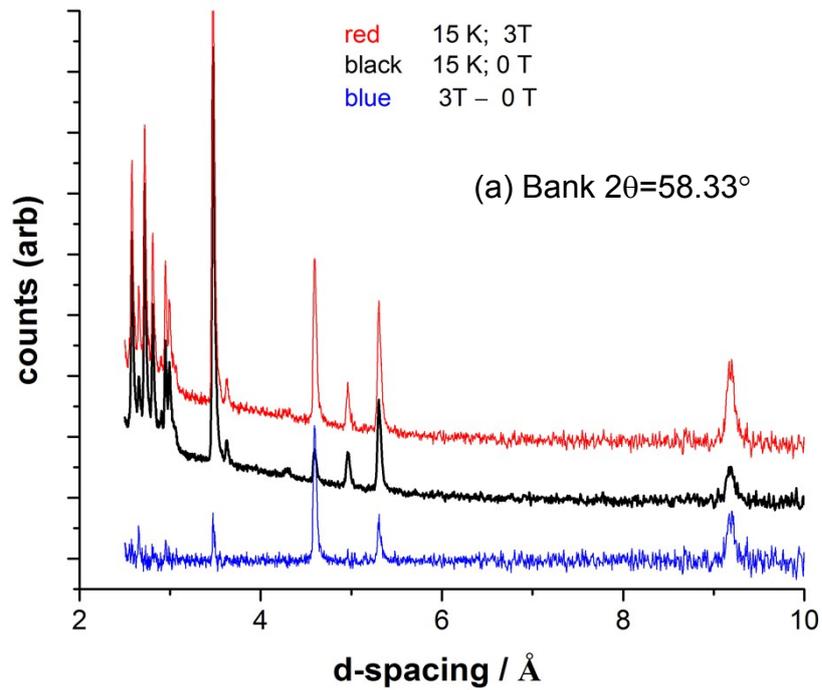


Fig.S4 (a) Profiles for gaufreyite at 15 K in fields of 0 T and 3 T and the difference indicating the FM neutron scattering. (b) The fitted profiles for 15 K, 3 T data. The reflection positions are: yellow and blue, the FM components; black, gaufreyite nuclear; green, Cu.