Re-entrant Structural Phase Transition in a Frustrated Kagome Magnet, $Rb_2SnCu_3F_{12}$

Electronic Supporting Information

Lewis J. Downie[a], Stephen P. Thompson[b], Chiu C. Tang[b], Simon Parsons[c] and Philip Lightfoot*[a]

Synchrotron X-ray Powder Diffraction

All synchrotron X-ray powder diffraction was performed at Diamond Light Source, Ltd., Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK. Beam-line I11 (High-resolution powder diffraction)[1] was used with monochromatic X-rays of either λ = 0.826128 Å (Run 1) or λ = 0.827168 Å (Run 2). These values (as well as zero point errors) were derived before each group of runs using a silicon standard. The temperature of the sample environment was controlled using an Oxford Cryosystem 700+ cryostream. The rate of temperature change was at a maximum of 10 °C min^{-1} with a minimum 5 minute equilibration time except in cases where the system was precooled and the sample cooled quickly. In such cases the minimum equilibration time was 20 minutes. A typical room temperature fit is shown in Fig. S1.

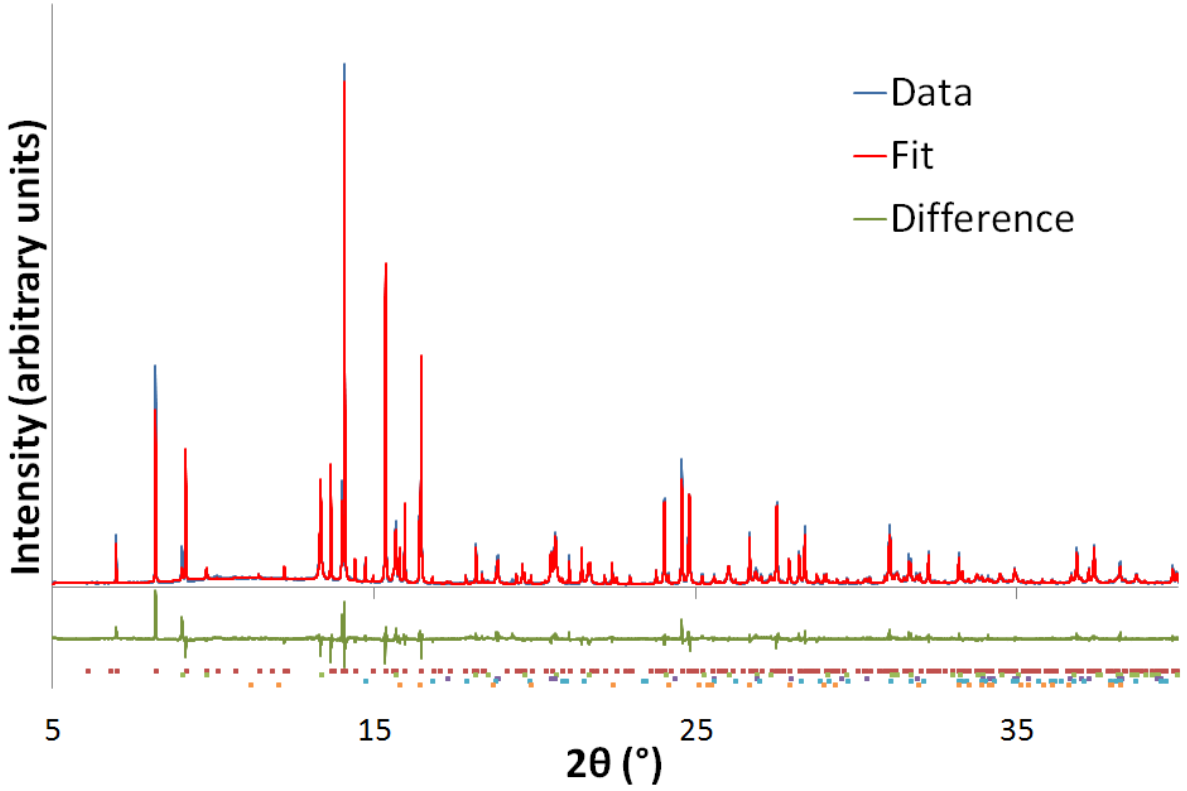


Fig S1: Rietveld fit at 300 K (tick marks: red = $Rb_2SnCu_3F_{12}$, green = Rb_2SnF_6, purple = CuO, blue = CuF_2, orange = $RbCuF_3$)

The fit is found to be good at all temperatures despite the relative complexity of the sample. The refinement takes into account five separate phases given in Table S1.

Table S1: The phases used in the Rietveld refinement and their refined weight percentages.

Phase	Weight percentage
$Rb_2SnCu_3F_{12}$ ('Rhomb-2' phase)	71.9 (4)
Rb_2SnF_6	19.6 (7)
CuO	2.9 (3)
CuF_2	2.0 (5)
$RbCuF_3$	3.7 (5)

Lattice parameters, background, relative proportions of phases, and profiles were refined. The coordinates of the atoms in each phase were not refined but the thermal parameters were constrained by atom type or, for the less abundant phases,

constrained to be the same for the entire phase. In the case of the phase of interest the starting models in Table S2 were used – the triclinic model was derived using ISODISTORT[2] with the transformation matrix {(2/3,1/3,1/3),(-1/3,1/3,1/3),(-1/3,-2/3,1/3)}.

Table S2: Atomic coordinates (x10^4), equivalent isotropic displacement parameters (Å x 10^3), and site occupancies for starting models.

Rhombohedral[3] (*R*-3)					
Atom	*x*	*y*	*z*	U_{eq}	Occ.
Rb (1)	6667	3333	-647	25	1
Rb (2)	3358	1650	641	25	1
Cu (1)	5946	1665	1682	25	1
Cu (2)	3516	-723	1769	25	1
Sn (1)	5000	0	0	25	1
Sn (2)	6667	3333	3333	25	1
F (1)	6495	651	1700	25	1
F (2)	7409	2773	1439	25	1
F (3)	4581	693	2105	25	1
F (4)	7853	4443	2780	25	1
F (5)	4464	872	-460	25	1
F (6A)	4501	310	835	25	0.773
F (7A)	6389	1378	95	25	0.773
F (6B)	3861	-250	629	25	0.227
F (7B)	6066	1320	470	25	0.227
F (8)	2465	-2156	1462	25	1

Triclinic[2] (*P*-1)					
Atom	*x*	*y*	*z*	U_{eq}	Occ.
Rb (1)	3999	8933	8991	25	1
Rb (2)	8991	3999	8933	25	1
Rb (3)	8933	8991	3999	25	1
Rb (4)	6020	6020	6020	25	1
Cu (1)	7628	7401	17	25	1
Cu (2)	17	7628	7401	25	1
Cu (3)	7401	17	7928	25	1
Cu (4)	5285	7530	2492	25	1
Cu (5)	2492	5285	7530	25	1
Cu (6)	7530	2492	5285	25	1
Sn (1)	5000	5000	0	25	1
Sn (2)	0	5000	5000	25	1
Sn (3)	5000	0	5000	25	1
Sn (4)	0	0	0	25	1
F (1)	8195	5856	1049	25	1
F (2)	1049	8195	5856	25	1
F (3)	5856	1049	8195	25	1
F (4)	8848	6803	8666	25	1
F (5)	8666	8848	6803	25	1
F (6)	6803	8666	8848	25	1
F (7)	6686	8217	1412	25	1
F (8)	1412	6686	8217	25	1
F (9)	8217	1412	6686	25	1
F (10)	633	9370	8337	25	1
F (11)	8337	633	9370	25	1
F (12)	9370	8337	633	25	1
F (13)	4004	5948	8668	25	1
F (14)	8668	4004	5948	25	1
F (15)	5948	8668	4004	25	1
F (16A1)	5336	6644	525	25	0.773
F (16A2)	525	5336	6644	25	0.773
F (16A3)	6644	525	5336	25	0.773
F (17A1)	6484	5084	8717	25	0.773
F (17A2)	8717	6484	5084	25	0.773
F (17A3)	5084	8717	6484	25	0.773
F (16B1)	4490	6518	879	25	0.227
F (16B2)	879	4490	6518	25	0.227
F (16B3)	6518	879	4490	25	0.227
F (17B1)	6536	5724	9150	25	0.227
F (17B2)	9150	6536	5724	25	0.227
F (17B3)	5724	9150	6536	25	0.227
F (18)	3928	6842	3619	25	1
F (19)	3619	3928	6842	25	1
F (20)	6842	3619	3928	25	1

All refinements were performed using GSAS[4] with the EXPGUI interface[5]. Lattice parameters at all temperatures can be found in Tables S3, S4 and S5. Note that a mixed phase model (rhombohedral plus triclinic) provided the best fit at temperatures 160 - 225 K and 255 – 300 K. Outside these ranges only minor improvements in fit were observed by including the two phases.

Table S3: Lattice parameters for $Rb_2SnCu_3F_{12}$ during run 1 (heating).

Temperature (wRp %)	Phase **(% wt. if mix)**	a	b	c	α	β	γ
500 K (13.44 %)	Rhombohedral	13.94808(7)		20.53955(14)			
	Rhombohedral (Triclinic equiv.)	10.56998	10.56998	10.56998	82.56879	82.56879	82.56879
490 K (14.36 %)	Rhombohedral	13.94602(7)		20.52875(14)			
	Rhombohedral (Triclinic equiv.)	10.56674	10.56674	10.56674	82.58475	82.58475	82.58475
460 K (14.34 %)	Rhombohedral	13.93994(7)		20.49858(14)			
	Rhombohedral (Triclinic equiv.)	10.55755	10.55755	10.55755	82.62842	82.62842	82.62842
430 K (15.27 %)	Rhombohedral	13.93154(9)		20.47108(15)			
	Rhombohedral (Triclinic equiv.)	10.54793	10.54793	10.54793	82.65962	82.65962	82.65962
400 K (15.47 %)	Rhombohedral	13.92397(9)		20.44383(15)			
	Rhombohedral (Triclinic equiv.)	10.53872	10.53872	10.53872	82.69287	82.69287	82.69287
370 K (15.66 %)	Rhombohedral	13.91702(7)		20.41946(15)			
	Rhombohedral (Triclinic equiv.)	10.53040	10.53040	10.53040	82.72210	82.72210	82.72210
340 K (15.76 %)	Rhombohedral	13.90999(6)		20.38810(14)			
	Rhombohedral (Triclinic equiv.)	10.52055	10.52055	10.52055	82.76558	82.76558	82.76558
310 K (15.63 %)	Rhombohedral	13.90367(7)		20.35529(2)			
	Rhombohedral (Triclinic equiv.)	10.51070	10.51070	10.51070	82.81428	82.81428	82.81428
280 K (16.56 %)	Rhombohedral **(60.8 %)**	13.89777(7)		20.3240(2)			
	Rhombohedral (Triclinic equiv.)	10.50137	10.50137	10.50137	82.86117	82.86117	82.86117
	Triclinic **(39.2 %)**	10.5026(3)	10.4888(2)	10.5136(3)	82.808(2)	83.0201(15)	82.7436(19)
250 K (17.55 %)	Triclinic	10.49567(13)	10.47100(10)	10.50961(12)	82.7888(10)	83.1582(7)	82.7769(10)
220 K (17.39 %)	Rhombohedral **(21.2 %)**	13.8833(7)		20.2814(18)			
	Rhombohedral (Triclinic equiv.)	10.48583	10.48583	10.48583	82.90563	82.90563	82.90563
	Triclinic **(78.8 %)**	10.48901(11)	10.45747(10)	10.50346(11)	82.7510(9)	83.2737(8)	82.8137(9)
190 K (14.56 %)	Rhombohedral **(91.3 %)**	13.87539(7)		20.24422(17)			

	Rhombohedral (Triclinic equiv.)	10.47435	10.47435	10.47435	82.95884	82.95884	82.95884
	Triclinic **(8.7 %)**	10.4838(6)	10.4535(6)	10.4973(6)	82.676(4)	83.375(4)	82.806(5)
160 K (14.68 %)	Rhombohedral	13.86987(7)		20.21940(15)			
	Rhombohedral (Triclinic equiv.)	10.46658	10.46658	10.46658	82.99369	82.99369	82.99369
130 K (14.59 %)	Rhombohedral	13.86500(7)		20.19567(15)			
	Rhombohedral (Triclinic equiv.)	10.45934	10.45934	10.45934	83.02828	83.02828	83.02828
100 K (14.97 %)	Rhombohedral	13.86107(7)		20.17396(16)			
	Rhombohedral (Triclinic equiv.)	10.45294	10.45294	10.45294	83.06155	83.06155	83.06155

Table S4: Lattice parameters for $Rb_2SnCu_3F_{12}$ during run 2 (heating).

Temperature (wRp %)	Phase **(% wt. if mix)**	a	b	c	α	β	γ
300 K (10.17 %)	Rhombohedral	13.90136(4)		20.34751(8)			
	Rhombohedral (Triclinic equiv.)	10.50801	10.50801	10.50801	82.82338	82.82338	82.82338
270 K (10.06 %)	Rhombohedral **(43.5 %)**	13.89573(6)		20.3199(3)			
	Rhombohedral (Triclinic equiv.)	10.49959	10.49959	10.49959	82.86349	82.86349	82.86349
	Triclinic **(56.5 %)**	10.51158(16)	10.48354(11)	10.50333(19)	82.7775(17)	83.0485(9)	82.7769(16)
255 K (11.58 %)	Triclinic	10.50784(12)	10.47446(8)	10.49813(12)	82.7813(11)	83.1232(5)	82.7788(11)
240 K (10.74 %)	Triclinic	10.50599(10)	10.46618(7)	10.49444(10)	82.7960(9)	83.1932(5)	82.7640(9)
225 K (10.92 %)	Rhombohedral **(7.8 %)**	13.8968(2)		20.2692(11)			
	Rhombohedral (Triclinic equiv.)	10.48917	10.48917	10.48917	82.97182	82.97182	82.97182
	Triclinic **(92.2 %)**	10.50331(10)	10.45844(8)	10.49072(11)	82.8111(9)	83.2582(6)	82.7587(9)
210 K (10.86 %)	Rhombohedral **(63.1 %)**	13.87922(9)		20.2554(3)			
	Rhombohedral (Triclinic equiv.)	10.47844	10.47844	10.47844	82.97423	82.97423	82.97423
	Triclinic **(36.9 %)**	10.49948(19)	10.45565(17)	10.4861(2)	82.8171(18)	83.2928(12)	82.7512(16)
195 K	Rhombohedral	13.87647(5)		20.24273(10)			

(10.57 %)	Rhombohedral (Triclinic equiv.)	10.47451	10.47451	10.47451	82.96521	82.96521	82.96521
180 K (10.52 %)	Rhombohedral	13.87529(4)		20.23096(9)			
	Rhombohedral (Triclinic equiv.)	10.47146	10.47146	10.47146	82.98608	82.98608	82.98608

Table S5: Lattice parameters for $Rb_2SnCu_3F_{12}$ during run 2 (cooling).

Temperature (wRp %)	Phase **(% wt. if mix)**	a	b	c	α	β	γ
300 K (9.51 %)	Rhombohedral	13.90182(3)		20.34270(7)			
	Rhombohedral (Triclinic equiv.)	10.50715(3)	10.50715(3)	10.50715(3)	82.8347(2)	82.8347(2)	82.8347(2)
285 K (10.99 %)	Rhombohedral	13.89795(4)		20.33113(9)			
	Rhombohedral (Triclinic equiv.)	10.50298(4)	10.50298(4)	10.50298(4)	82.8470(3)	82.8470(3)	82.8470(3)
270 K (9.88 %)	Rhombohedral **(63.6 %)**	13.89442(4)		20.31730(12)			
	Rhombohedral (Triclinic equiv.)	10.49846(5)	10.49846(5)	10.49846(5)	82.8649(4)	82.8649(4)	82.8649(4)
	Triclinic **(36.4 %)**	10.5104(3)	10.5030(4)	10.4829(2)	82.770(3)	82.774(3)	83.0398(14)
255 K (10.68 %)	Rhombohedral **(38.3 %)**	13.89168(12)		20.3053(4)			
	Rhombohedral (Triclinic equiv.)	10.49466(14)	10.49466(14)	10.49466(14)	82.8814(12)	82.8814(12)	82.8814(12)
	Triclinic **(61.7 %)**	10.49834(15)	10.47361(10)	10.50877(13)	82.7739(12)	83.1284(8)	82.77772(13)
240 K (12.58 %)	Triclinic	10.49595(18)	10.46988(9)	10.50484(17)	82.7866(17)	83.1624(7)	82.7865(16)
225 K (11.60 %)	Triclinic	10.49236(14)	10.46205(8)	10.50251(13)	82.7638(12)	83.2292(6)	82.8099(12)
210 K (11.55 %)	Rhombohedral **(12.1 %)**	13.8793(3)		20.2582(8)			
	Rhombohedral (Triclinic equiv.)	10.4791(3)	10.4791(3)	10.4791(3)	82.942(3)	82.942(3)	82.942(3)
	Triclinic **(87.9 %)**	10.49897(13)	10.45388(10)	10.48708(14)	82.8243(12)	83.2972(7)	82.7588(11)
195 K (10.24 %)	Rhombohedral **(80.2 %)**	13.87635(6)		20.24240(16)			
	Rhombohedral (Triclinic equiv.)	10.47438(6)	10.47438(6)	10.47438(6)	82.9655(5)	82.9655(5)	82.9655(5)
	Triclinic **(19.8 %)**	10.4959(3)	10.4533(3)	10.4829(4)	82.826(3)	83.316(2)	82.737(3)

180 K (10.30 %)	Rhombohedral	13.87524(4)		20.23232(9)			
	Rhombohedral (Triclinic equiv.)	10.47173(4)	10.47173(4)	10.47173(4)	82.9831(3)	82.9831(3)	82.9831(3)
165 K (9.73 %)	Rhombohedral	13.87269(3)		20.21765(8)			
	Rhombohedral (Triclinic equiv.)	10.46745(3)	10.46745(3)	10.46745(3)	83.0059(3)	83.0059(3)	83.0059(3)

A plot of unit cell volume at different temperatures is given in Figure S2 and triclinic unit cell lengths and angles in Figures S3 and S4, respectively.

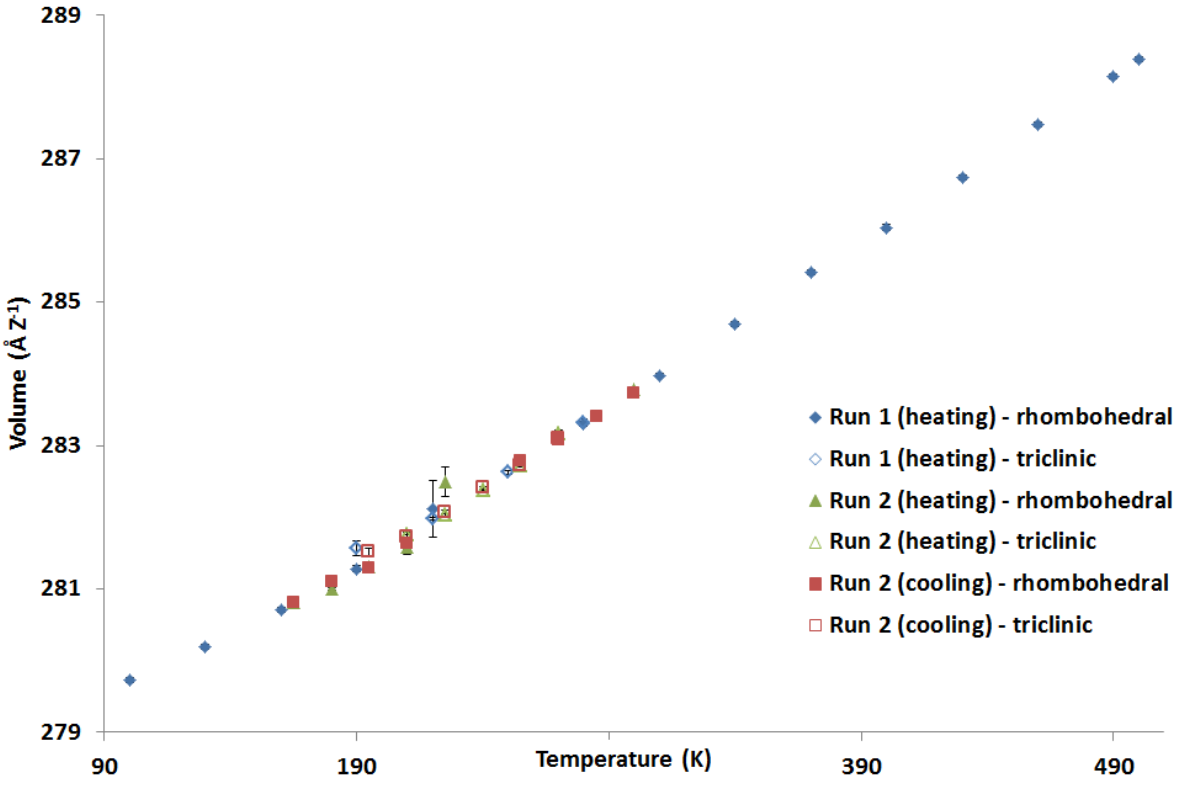


Figure S2: Unit cell volumes per formula unit for all three experiments

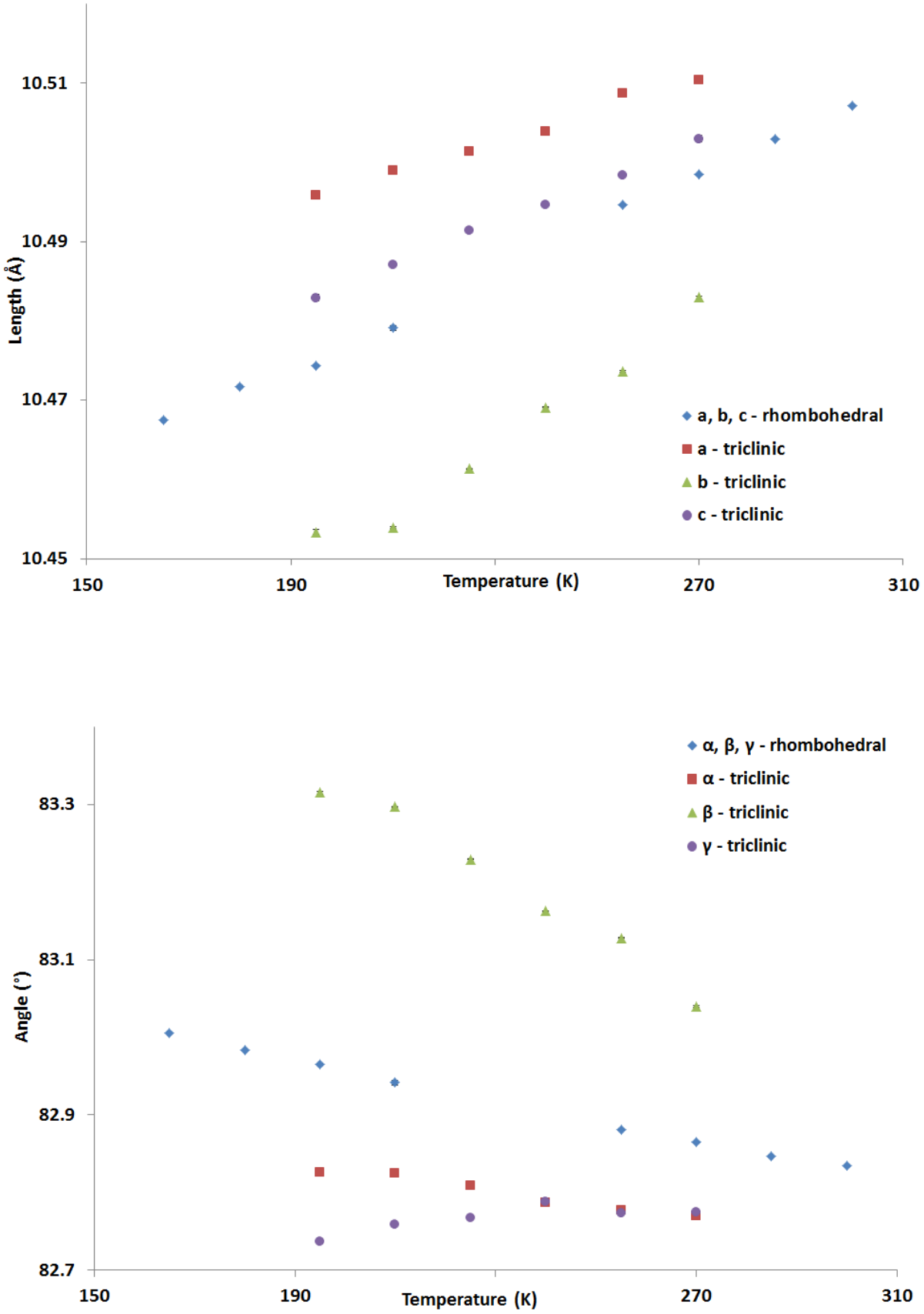
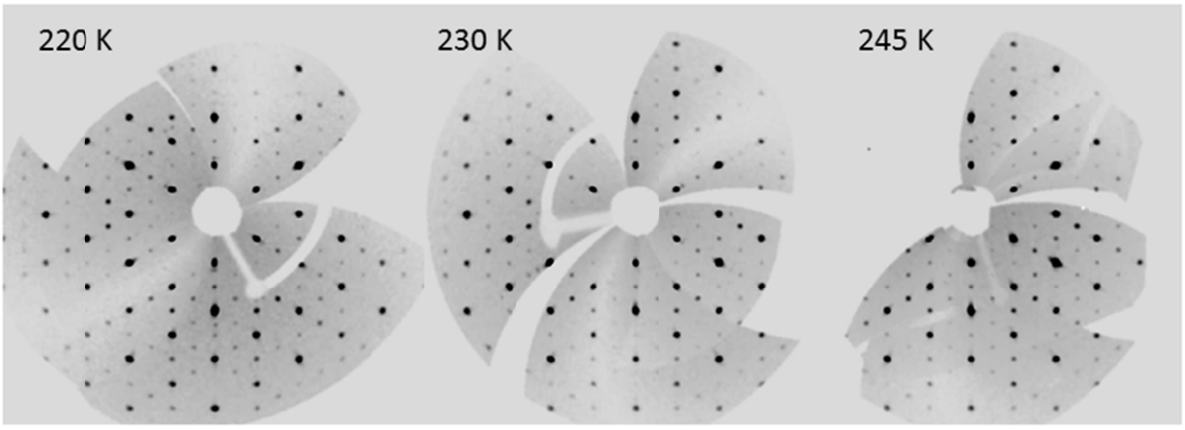


Figure S4: Triclinic unit cell angles for run 2 (cooling). The triclinic unit cell equivalent of the rhombohedral cell has been calculated (α = β = γ). Error bars are smaller than the data point size.

Single Crystal Diffraction

All crystals produced were pale green and had a plate-like morphology. Single crystal diffraction was performed using an Agilent SuperNova diffractometer for the first experiment and a Bruker Apex-II diffractometer device for the second

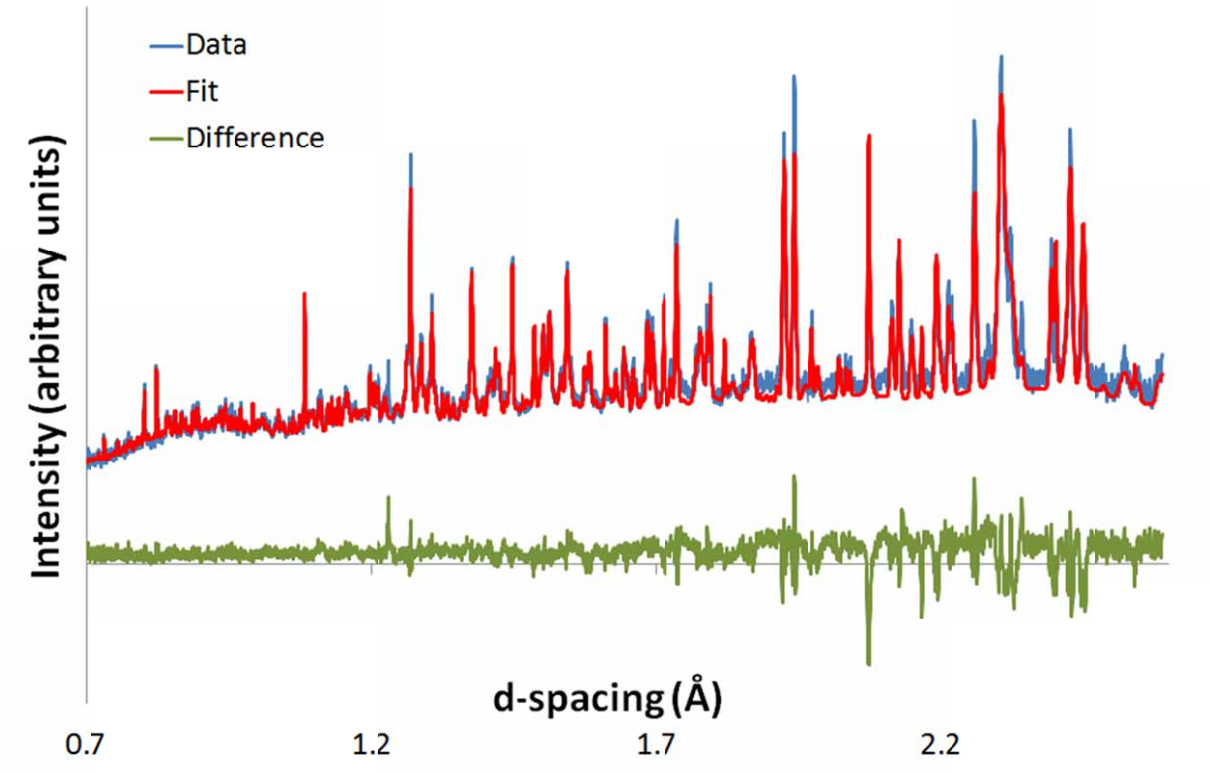
experiment both using Mo $K_{\alpha 1}$ radiation and the sample environment was controlled by an Oxford Cryosystems variable temperature. The data sets were analysed using the WinGX[6] package and SHELX[7]. Structure solution and refinement suggested a rhombohedral model analogous to that given in Table S2. CIF files for the single crystal refinements at 300 K, 245 K, 230 K, 220 K and 140 K are given as Supplementary.



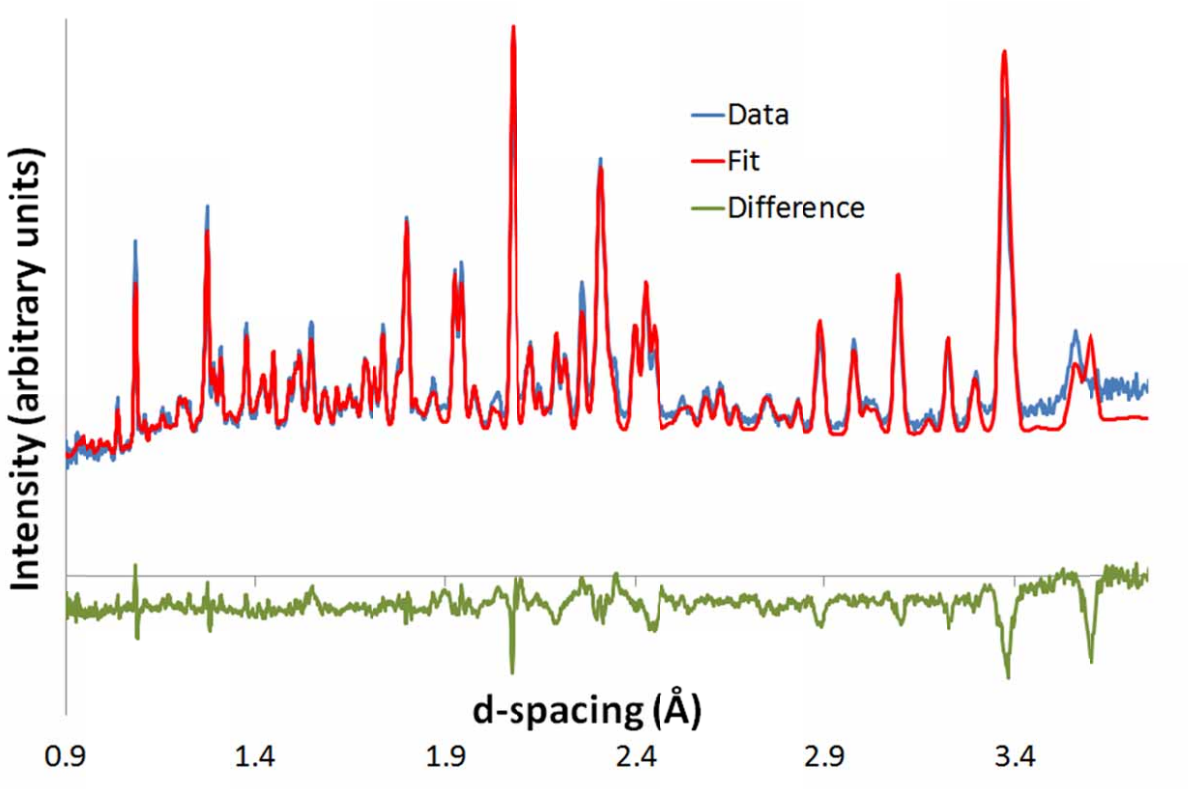
ention of 3-

Neutron Powder Diffraction

Neutron powder diffraction was performed at ISIS Neutron and Muon Source, STFC, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, OX11 0QX. The HRPD (High Resolution Powder Diffraction)[8] beamline was used with the sample (~5 g) held in flat plate geometry using a steel can with vanadium foil windows. Screws in the can were blanked with cadmium sheets. The sample holder was heated directly while using a cryostat within the sample station which was set to its lowest temperature achievable. For this reason the sample temperature was also measured directly at the sample. Measurements at a range of temperatures were taken but due to impurities it is difficult to extract the same detail that is present in the synchrotron X-ray data. We also find instrumental peaks in our data. An example of the data at room temperature is found in figure S6a and S6b.

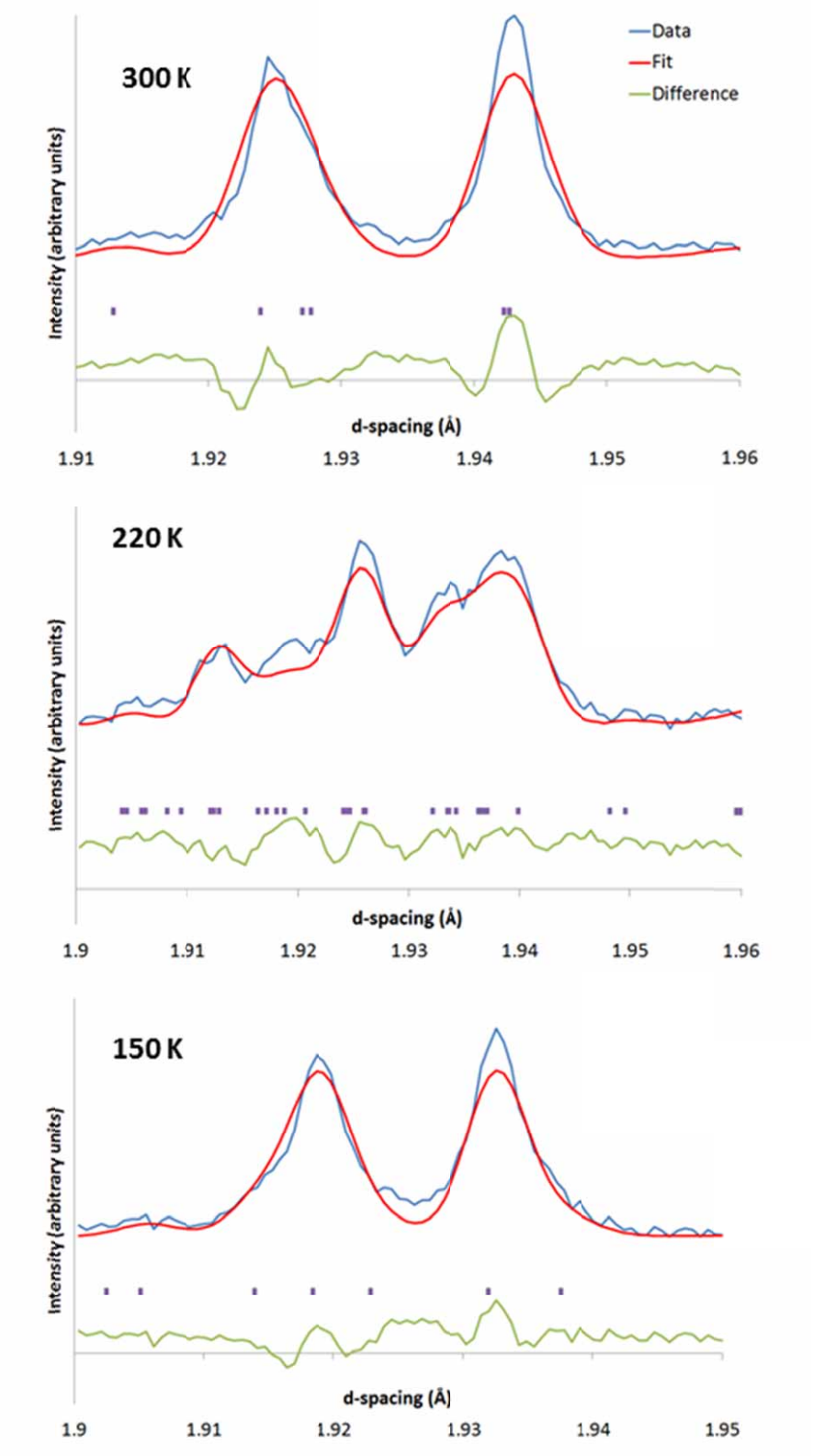


the
vith a Le



tion of the

Although the complexity of these patterns makes it difficult to ascertain the precise details of any phase transitions, there is an area where only the phase of interest is represented between d = 1.9 and 1.98 Å (figure S7). This region clearly shows the appearance and disappearance of peak splitting with lowering of temperature, corresponding to the same conclusion discussed for the synchrotron experiment



ıere are no

1 S. P. Thompson, J. E. Parker, J. Potter, T. P. Hill, A. Birt, T. M. Cobb, F. Yuan, C. C. Tang, *Rev. Sci. Instrum.*, 2009, **80**, 075107.
2 B. J. Campbell, H. T. Stokes, D. E. Tanner, D. M. Hatch, *J. Appl. Cryst.*, 2006, **39**, 607.
3 K. Morita, M. Yano, T. Ono, H. Tanaka, K.Fujii, H. Uekusa, Y. Narumi, K. Kindo, *J. Phys. Soc. Jpn.*, 2008, **77**, 043707.
4 A. C. Larson, R.B. Von Dreele, *Los Alamos National Laboratory Report*, 1994, **LAUR 86-748**.
5 B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210.
6 L. J. Farrugia, *J. Appl. Cryst*., 1999, **32**, 837.
7 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
8 M. W. Johnson, W. I. F. David, *Rutherford Appleton Laboratory Report*, 1985, **RAL-85-112**.