Electronic Supplementary Material (ESI) for CrystEngComm.

Structural phase transitions in the kagome lattice based materials

$Cs_{2-x}Rb_xSnCu_3F_{12}$ (x = 0, 0.5, 1.0, 1.5)

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Supplementary Information

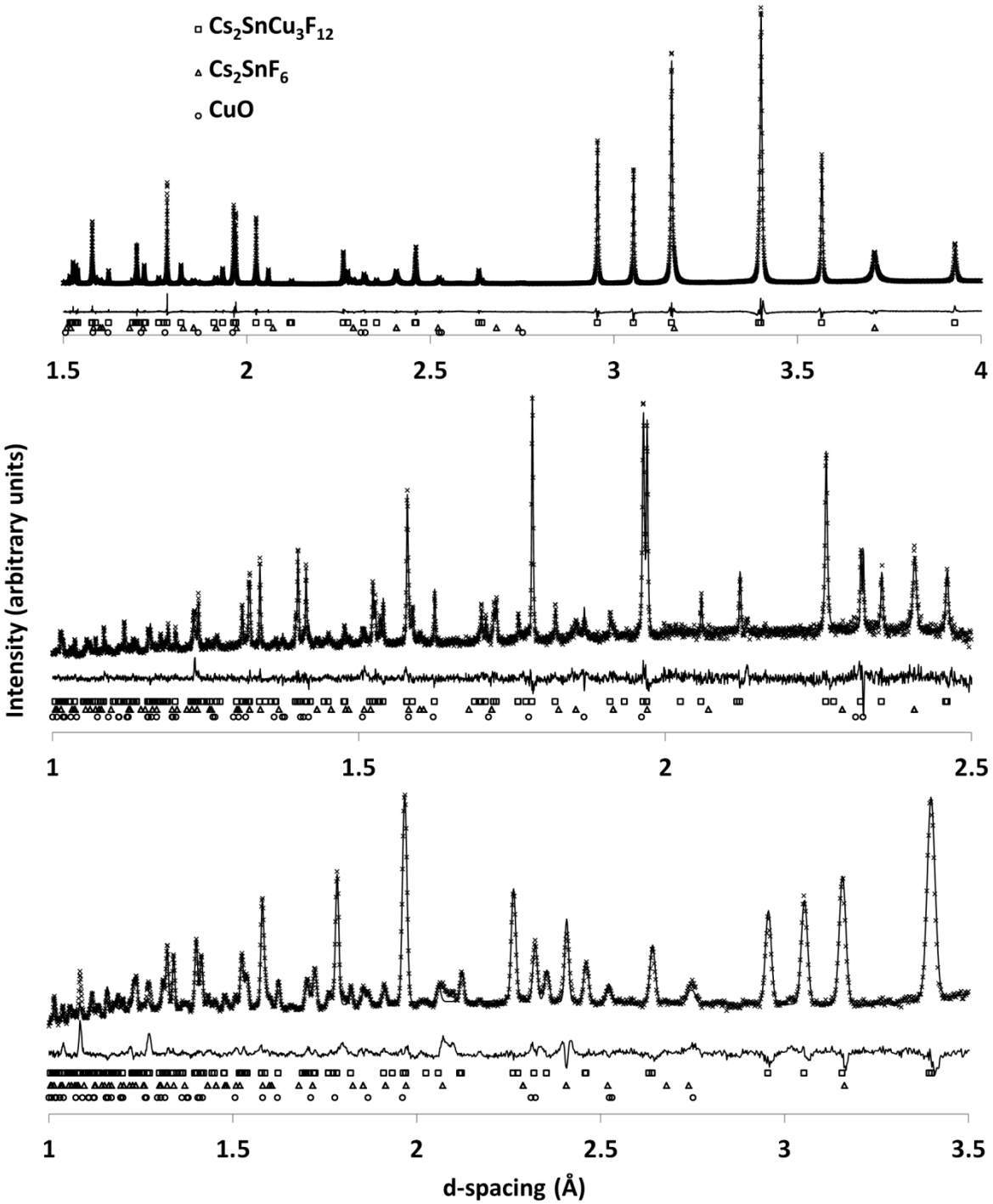

Figure S1: Rietveld fits for $Cs_2SnCu_3F_{12}$ at room temperature: SXPD (top) and NPD (lower two; middle is backscattering detector bank, bottom is 90 ° detector bank.)

Table S1: Comparison of fits of various monoclinic unit cell models to the NPD data for $Cs_2SnCu_3F_{12}$ at 100 K.

Fitted			-Bknd	
Space group	wRp (%)	Rp (%)	wRp (%)	Rp (%)
$P2_1/n$	4.34	3.49	4.70	3.42
$P2_1/m$	5.18	4.09	5.45	4.25
$P2/n$	5.12	4.30	6.10	4.67
$P2/m$	5.47	4.32	5.94	4.71

Table S2: Lattice parameters for $Cs_2SnCu_3F_{12}$ as a function of temperature derived from SXPD data ("run 1").

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	7.131913(11)	=a	20.36532(5)	90	90	120	897.0858(28)
300 (monoclinic equivalent)	7.93962	7.13191	10.67248	90	98.25995	90	598.0572
280	7.130960(12)	=a	20.35025(5)	90	90	120	896.184(3)
280 (monoclinic equivalent)	7.93504	7.13096	10.66844	90	98.22747	90	597.456
260	7.129898(12)	=a	20.33456(5)	90	90	120	895.225(3)
260 (monoclinic equivalent)	7.93026	7.12990	10.66416	90	98.19415	90	596.817
240	7.128841(12)	=a	20.31934(5)	90	90	120	894.289(3)
240 (monoclinic equivalent)	7.92560	7.12884	10.66000	90	98.16200	90	596.193
220 (heating)	7.127702(13)	=a	20.30475(5)	90	90	120	893.362(3)
220 (heating) (monoclinic equivalent)	7.92111	7.12770	10.65589	90	98.13210	90	595.575
220 (cooling)	7.127737(13)	=a	20.30493(6)	90	90	120	893.379(3)
220 (cooling) (monoclinic equivalent)	7.92117	7.12774	10.65596	90	98.13231	90	595.586
210 (heating)	7.127123(13)	=a	20.29730(6)	90	90	120	892.889(3)
210 (heating) (monoclinic equivalent)	7.91881	7.12712	10.65380	90	98.11680	90	595.259
210 (cooling)	7.12720(13)	=a	20.29742(6)	90	90	120	892.913(3)
210 (cooling) (monoclinic equivalent)	7.91887	7.12720	10.65389	90	98.11654	90	595.275
200 (heating)	7.126498(13)	=a	20.28987(6)	90	90	120	892.406(3)
200 (heating) (monoclinic equivalent)	7.91651	7.12650	10.65167	90	98.10189	90	594.937
200 (cooling)	7.126651(13)	=a	20.28978(6)	90	90	120	892.440(3)
200 (cooling) (monoclinic equivalent)	7.91653	7.12665	10.65179	90	98.10050	90	594.960
190 (heating)	7.125861(14)	=a	20.28245(6)	90	90	120	891.920(4)
190 (heating) (monoclinic equivalent)	7.91420	7.12586	10.64953	90	98.08709	90	594.613
190 (cooling)	7.126027(13)	=a	20.28235(6)	90	90	120	891.329(3)
190 (cooling) (monoclinic equivalent)	7.91422	7.12603	10.64966	90	98.08558	90	594.219
180 (heating)	7.124463(15)	=a	20.27389(6)	90	90	120	891.193(4)
180 (heating) (monoclinic equivalent)	7.91135	7.12446	10.64647	90	98.07499	90	594.129
180 (cooling)	7.124969(14)	=a	20.27409(6)	90	90	120	891.329(4)
180 (cooling) (monoclinic equivalent)	7.91155	7.12497	10.64697	90	98.07172	90	594.219
170 (heating)	7.91261(8)	7.11983(8)	10.63580(12)	90	98.0341(6)	90	593.302(11)
170 (cooling)	7.91228(8)	7.12088(8)	10.63694(12)	90	98.0345(6)	90	593.428(11)
160 (cooling)	7.91058(8)	7.11723(7)	10.62982(11)	90	98.0103(5)	90	592.635(11)
140	7.90781(8)	7.10996(7)	10.61670(11)	90	97.9630(5)	90	591.160(10)
120	7.90443(8)	7.10505(7)	10.60627(11)	90	97.9189(5)	90	589.983(11)
100	7.90102(4)	7.10058(4)	10.59669(6)	90	97.8770(3)	90	588.885(6)

Table S3: Lattice parameters for $Cs_2SnCu_3F_{12}$ as a function of temperature derived from SXPD data ("run 2").

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	7.131728(14)	= a	20.36700(6)	90	90	120	897.113(4)
300 (monoclinic equivalent)	7.94005	7.13173	10.67267	90	98.26574	90	598.075
200	7.126750(16)	= a	20.29022(7)	90	90	120	892.484(4)
200 (monoclinic equivalent)	7.91668	7.12675	10.65197	90	98.10092	90	594.989
190	7.126132(16)	= a	20.28167(7)	90	90	120	891.953(4)
190 (monoclinic equivalent)	7.91406	7.12613	10.64961	90	98.08299	90	594.635
180	7.124720(16)	= a	20.27249(7)	90	90	120	891.196(4)
180 (monoclinic equivalent)	7.91102	7.12472	10.64641	90	98.06936	90	594.131
170	7.91245(4)	7.12068(4)	10.63520(7)	90	98.0288(3)	90	593.335(6)
165	7.91165(4)	7.11871(4)	10.63149(6)	90	98.0129(3)	90	592.927(6)
160	7.91081(4)	7.11689(4)	10.62815(6)	90	98.0008(3)	90	592.544(6)
150	7.90892(4)	7.11365(4)	10.62188(6)	90	97.9775(3)	120	591.817(6)
140	7.90691(4)	7.11072(4)	10.61611(6)	90	97.9541(3)	120	591.136(5)

Table S4: Lattice parameters for $Cs_2SnCu_3F_{12}$ as a function of temperature derived from NPD data.

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	7.13155(6)	= a	20.3610(3)	90	90	120	896.801(18)
300 (monoclinic equivalent)	7.93829	7.13155	10.67124	90	98.25131	90	597.867
165	7.8951(3)	7.1196(4)	10.6398(5)	90	98.0747(29)	90	592.13(5)
150	7.90569(17)	7.10976(18)	10.61490(29)	90	97.9377(16)	90	590.921(26)
100	7.89656(16)	7.09752(15)	10.58758(25)	90	97.8209(16)	90	587.871(22)

Table S5: BVS of $Cs_2SnCu_3F_{12}$ as a function of temperature.

	BVS			
Temperature (K)	Sn^{4+}	$Cu1^{2+}$	$Cu2^{2+}$	$Cs1^{+}$
300	4.626	2.016		1.039
165	4.508	1.926	2.050	0.887
150	4.502	2.106	1.972	0.908
100	4.554	2.030	2.002	0.942

Table S6: Bond lengths for $Cs_2SnCu_3F_{12}$ at 300 K and 100 K as derived from NPD data.

	Bond length (Å)	
Metal – fluoride bond	300 K	100 K
Cs – F3		3.058(11)
Cs – F1		3.161(10)
Cs – F1	3.115(4) (x3)	3.291(9)
Cs – F2	3.418(4) (x3)	3.042(10)
Cs – F4		3.265(11)
Cs – F5		3.303(11)
Cs – F5		3.388(10)
Cs – F6		3.367(11)
Cu1 – F2		1.934(8) (x2)
Cu1 – F1	1.8983(8) (x4)	1.874(8) (x2)
Cu1 – F6	2.3564(28) (x2)	2.304(7) (x2)
Cu2 – F3		1.976(11)
Cu2 – F1		1.925(9)
Cu2 – F2		1.878(10)
Cu2 – F3		1.839(11)
Cu2 – F4		2.351(8)
Cu2 – F5		2.355(9)
Sn – F6		1.940(7) (x2)
Sn – F4		1.945(7) (x2)
Sn – F5		1.950(6) (x2)
Sn – F2	1.9392(27) (x6)	

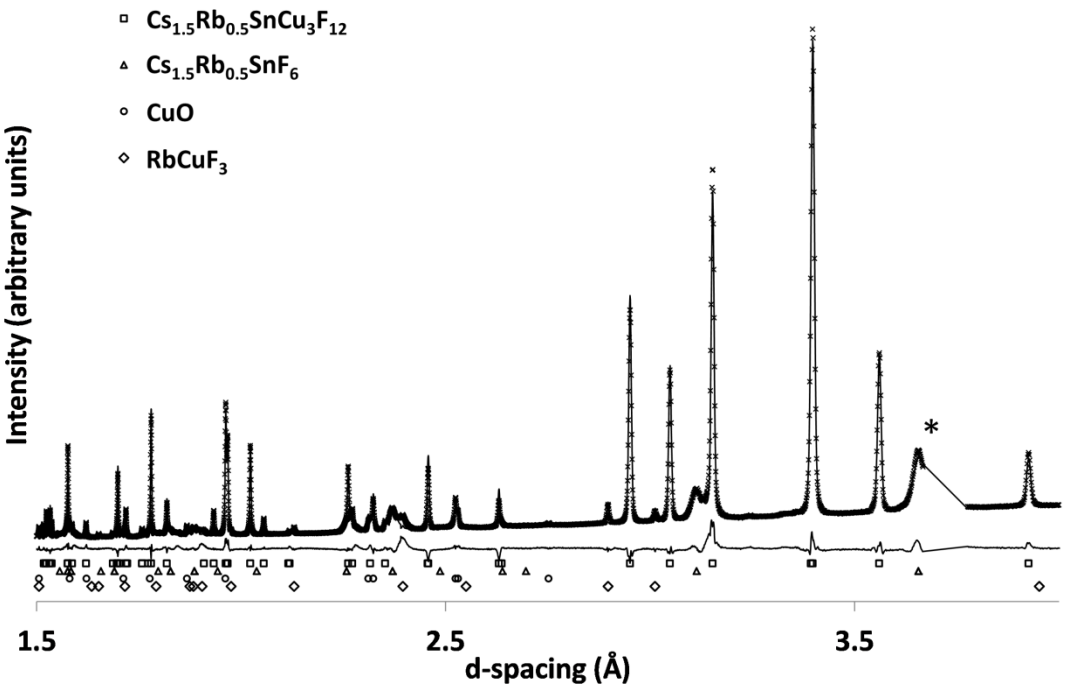

Figure S2: Rietveld refinement of SXPD data for $Cs_{1.5}Rb_{0.5}SnCu_3F_{12}$ at 300 K (* is an excluded area due to difficulty in fitting – most likely due to phase separation between the impurities Cs_2SnF_6 and Rb_2SnF_6).

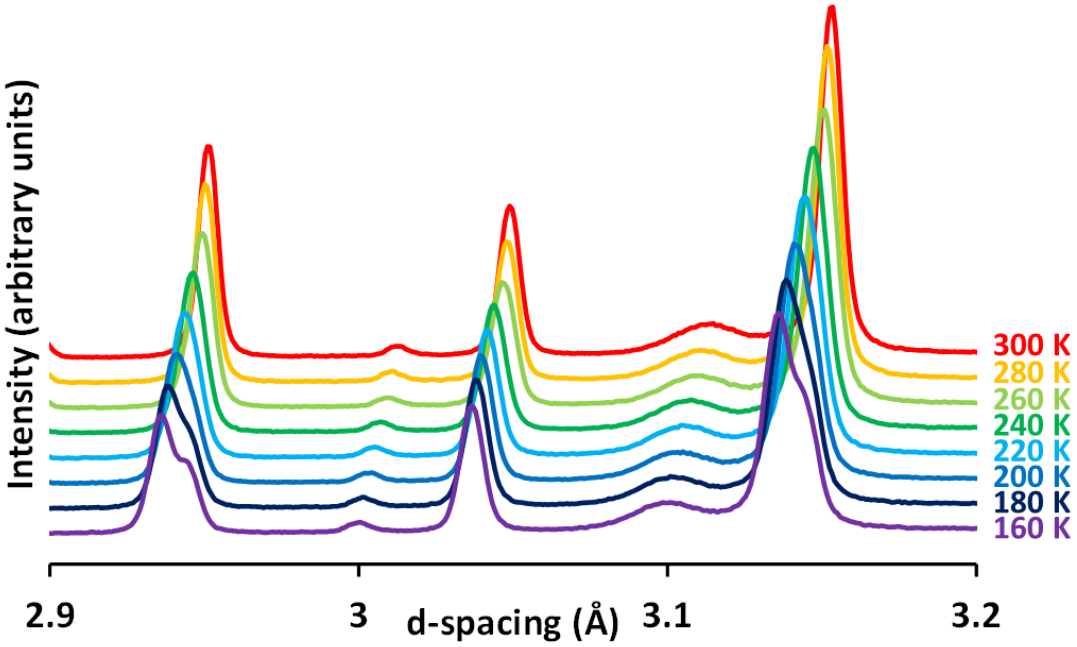

Figure S3: SXPD patterns for $Cs_{1.5}Rb_{0.5}SnCu_3F_{12}$ over the temperature range 300 – 160 K.

Table S7: Lattice parameters for $Cs_{1.5}Rb_{0.5}SnCu_3F_{12}$ as a function of temperature derived from SXPD data.

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	7.12113(2)	= a	20.35953(10)	90	90	120	894.120(6)
300 (monoclinic equivalent)	7.93475	7.12113	10.66165	90	98.3255	90	596.080
290	7.12030(2)	= a	20.35171(9)	90	90	120	893.569(6)
290 (monoclinic equivalent)	7.93227	7.12030	10.65925	90	98.3115	90	595.713
280	7.11915(2)	= a	20.34356(10)	90	90	120	892.924(6)
280 (monoclinic equivalent)	7.92960	7.11915	10.65650	90	98.2986	90	595.283
270	7.11738(3)	= a	20.33477(11)	90	90	120	892.092(7)
270 (monoclinic equivalent)	7.92657	7.11738	10.65305	90	98.2888	90	594.728
260	7.11636(3)	= a	20.33190(13)	90	90	120	891.711(9)
260 (monoclinic equivalent)	7.92544	7.11636	10.65154	90	98.2887	90	594.474
250	7.92512(7)	7.10748(6)	10.64518(11)	90	98.2227(5)	90	593.453(9)
240	7.92649(6)	7.10836(6)	10.63926(10)	90	98.2094(5)	90	593.319(9)
230	7.92065(5)	7.10332(5)	10.62659(8)	90	98.1951(5)	90	591.778(7)
220	7.91831(5)	7.10094(5)	10.61998(7)	90	98.1779(4)	90	591.062(7)
210	7.91596(5)	7.09596(4)	10.61376(7)	90	98.1582(4)	90	590.363(6)
200	7.91366(4)	7.09596(4)	10.60799(7)	90	98.1364(4)	90	589.696(6)
190	7.91148(4)	7.09358(4)	10.60274(6)	90	98.1151(4)	90	589.075(6)
180	7.90935(4)	7.09126(4)	10.59762(6)	90	98.0823(5)	90	588.472(6)
170	7.90729(4)	7.08902(4)	10.59274(6)	90	98.0705(4)	90	587.895(6)
160	7.90525(4)	7.08694(4)	10.58807(6)	90	98.0487(4)	90	587.343(6)
150	7.90335(4)	7.08493(4)	10.58370(6)	90	98.0272(4)	90	586.824(6)
140	7.90139(4)	7.08305(4)	10.57952(6)	90	98.0060(4)	90	586.316(6)
130	7.89947(4)	7.08120(4)	10.57533(6)	90	97.9852(4)	90	585.824(6)
120	7.89764(4)	7.07951(4)	10.57135(6)	90	97.9650(4)	90	585.358(6)
110	7.89575(4)	7.07788(4)	10.56755(6)	90	97.9447(4)	90	584.901(6)
100	7.89388(4)	7.07631(4)	10.56384(6)	90	97.9246(4)	90	584.456(6)

Table S8: Comparison of standard rhombohedral model fits for $CsRbSnCu_3F_{12}$

	Fitted		-Bknd	
	wRp	Rp	wRp	Rp
$R\bar{3}$	4.87	3.08	11.41	6.33
$R\bar{3}m$	4.69	2.97	10.61	5.88
$P2_1/n$	3.85	2.51	7.96	4.67

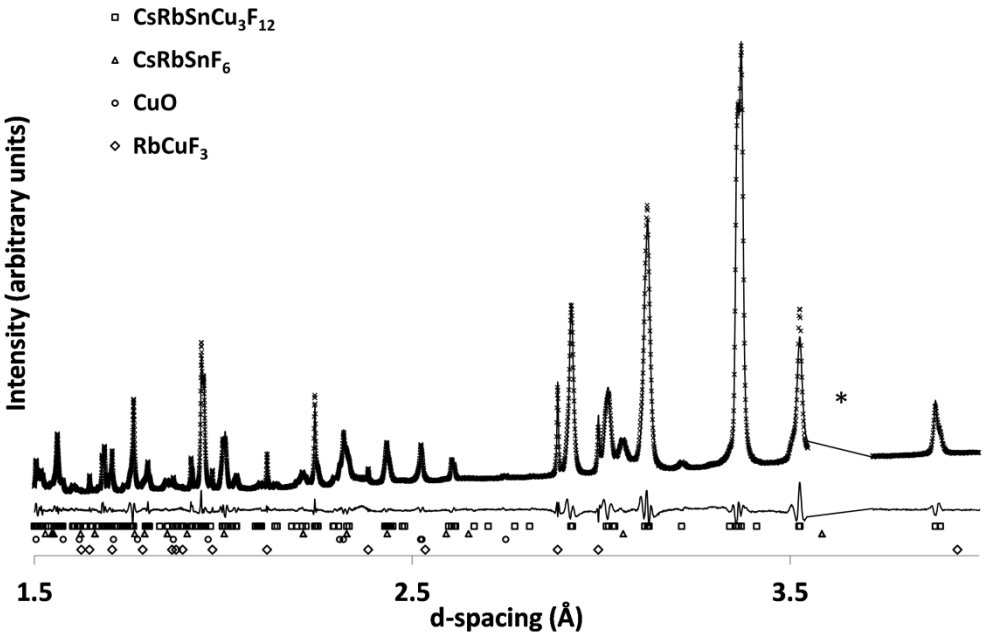

Figure S4: SXPD data and Rietveld refinement for $CsRbSnCu_3F_{12}$ at 100 K (* is an excluded area due to difficulty in fitting – most likely due to phase separation between the impurities Cs_2SnF_6 and Rb_2SnF_6).

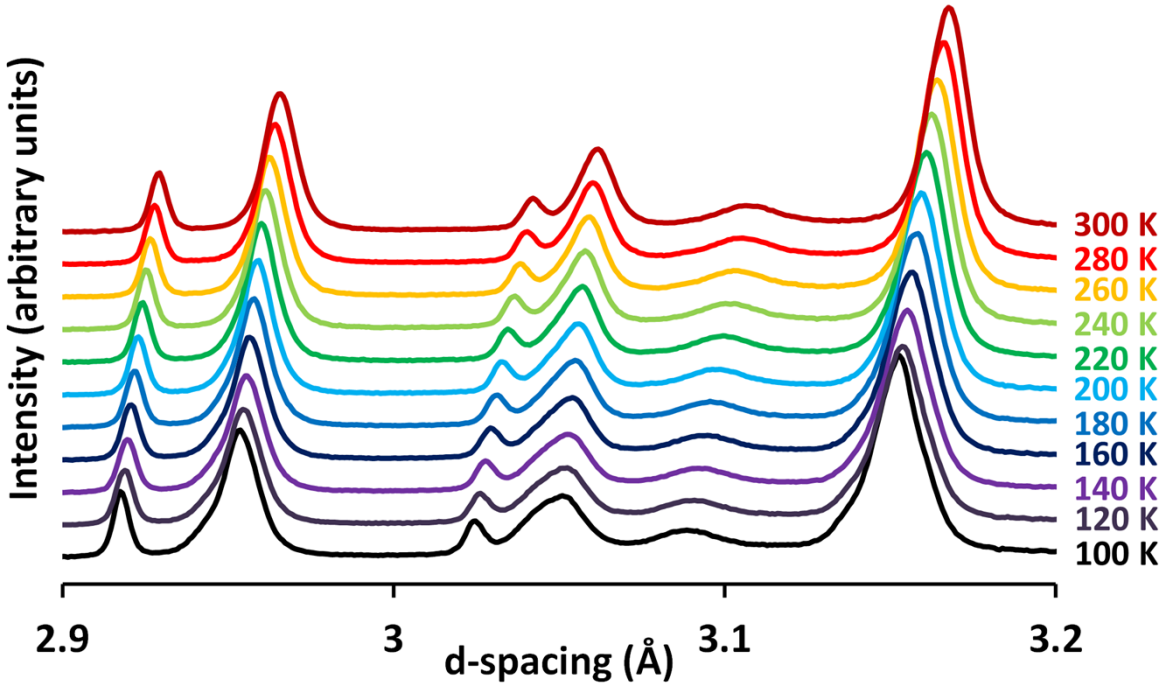

Figure S5: SXPD patterns for $CsRbSnCu_3F_{12}$ over the temperature range 300 – 100 K.

Table S9: Lattice parameters for $CsRbSnCu_3F_{12}$ as a function of temperature derived from SXPD data.

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	7.92369(9)	7.08376(7)	10.60375(12)	90	98.7057(8)	90	588.326(11)
290	7.92193(9)	7.08134(8)	10.59904(12)	90	98.6826(9)	90	587.769(11)
280	7.92011(9)	7.07871(8)	10.59437(12)	90	98.6567(9)	90	587.198(12)
270	7.91923(9)	7.07505(9)	10.59036(12)	90	98.6184(9)	90	586.666(12)
260	7.91779(8)	7.07177(8)	10.58685(12)	90	98.585(9)	90	586.145(11)
250	7.91536(8)	7.06978(8)	10.58305(12)	90	98.5642(9)	90	585.622(11)
240	7.91285(8)	7.06796(8)	10.57919(12)	90	98.4557(9)	90	585.102(11)
230	7.91030(8)	7.06634(8)	10.57542(12)	90	98.5268(9)	90	584.599(11)
220	7.90756(8)	7.06498(8)	10.57144(12)	90	98.5113(9)	90	584.088(11)
210	7.90484(8)	7.06356(8)	10.56758(12)	90	98.4945(9)	90	583.582(12)
200	7.90202(9)	7.06241(9)	10.56365(13)	90	98.4791(9)	90	583.085(12)
190	7.89935(9)	7.06121(9)	10.56007(13)	90	98.4641(10)	90	582.614(13)
180	7.89665(10)	7.06003(10)	10.55656(14)	90	98.4484(10)	90	582.148(13)
170	7.89392(10)	7.05902(10)	10.55307(14)	90	98.4352(11)	90	581.691(14)
160	7.89124(11)	7.05815(11)	10.54971(15)	90	98.4227(11)	90	581.256(15)
150	7.88868(11)	7.05724(11)	10.54652(16)	90	98.4090(12)	90	580.837(15)
140	7.88611(12)	7.05639(12)	10.54343(17)	90	98.3967(13)	90	580.426(16)
130	7.88363(12)	7.05546(13)	10.54053(17)	90	98.3830(13)	90	580.028(17)
120	7.88108(13)	7.05486(13)	10.53760(18)	90	98.3715(14)	90	579.647(17)
110	7.87887(13)	7.05384(13)	10.53484(18)	90	98.3573(14)	90	579.270(18)
100	7.87649(14)	7.05304(14)	10.53210(19)	90	98.3443(14)	90	578.898(18)

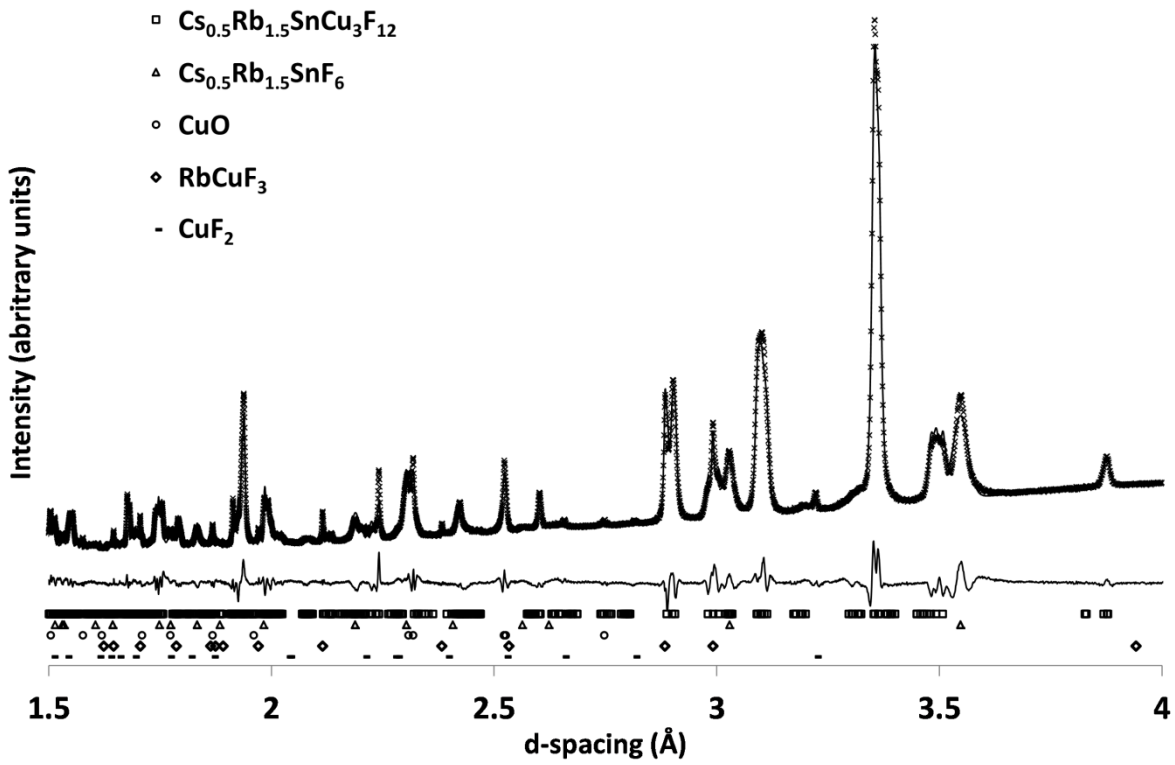

Figure S6: SXPD data and Rietveld refinement for $Cs_{0.5}Rb_{1.5}SnCu_3F_{12}$ at 100 K.

Table S10: Lattice parameters for $Cs_{0.5}Rb_{1.5}SnCu_3F_{12}$ as a function of temperature derived from SXPD data.

Temperature (K)	a (Å)	b (Å)	c (Å)	α °	β °	γ °	V (Å^3)
300	14.01939(12)	= a	20.35651(26)	90	90	120	3464.91(6)
300 (triclinic equivalent)	10.56280	10.56280	10.56280	83.16018	83.16018	83.16018	1154.97
290	14.01676(12)	= a	20.34747(26)	90	90	120	3462.07(6)
290 (triclinic equivalent)	10.55898	10.55898	10.55898	83.17094	83.17094	83.17094	1154.02
280	14.01399(12)	= a	20.33782(27)	90	90	120	3459.07(6)
280 (triclinic equivalent)	10.55569	10.55569	10.55569	83.18255	83.18255	83.18255	1153.02
270	10.54210(23)	10.56569(19)	10.55035(29)	83.2983(12)	83.1014(11)	83.1905(15)	1152.13(5)
260	10.53850(23)	10.56347(18)	10.54686(28)	83.3136(12)	83.1112(11)	83.2014(15)	1151.20(4)
250	10.53449(22)	10.56179(17)	10.54338(27)	83.3331(12)	83.1196(11)	83.2126(15)	1150.28(4)
240	10.53035(22)	10.56098(18)	10.53974(26)	83.3565(12)	83.1256(11)	83.2250(14)	1149.43(4)
230	10.52545(21)	10.56131(16)	10.53611(24)	83.3865(12)	83.1277(11)	83.2375(14)	1148.63(4)
220	10.52050(20)	10.56163(15)	10.53238(23)	83.4237(12)	83.1252(11)	83.2487(13)	1147.81(4)
210	10.51582(20)	10.56093(15)	10.52853(22)	83.4591(12)	83.1228(12)	83.2593(13)	1146.90(4)
200	10.51138(19)	10.55954(15)	10.52476(21)	83.4920(12)	83.1201(12)	83.2652(13)	1145.93(4)
190	10.50734(19)	10.55796(15)	10.52121(21)	83.5193(12)	83.1206(12)	83.2716(12)	1145.00(4)
180	10.50338(19)	10.55607(15)	10.51787(20)	83.5455(12)	83.1227(12)	83.2776(12)	1144.07(4)
170	10.49971(18)	10.55405(15)	10.51474(20)	83.5687(12)	83.1266(12)	83.2845(12)	1143.18(3)
160	10.49620(18)	10.55204(15)	10.51195(20)	83.5882(12)	83.1333(12)	83.2921(12)	1142.35(3)
150	10.49307(18)	10.54984(15)	10.50924(20)	83.6069(12)	83.1392(12)	83.2987(13)	1141.45(3)
140	10.48993(18)	10.54764(15)	10.50657(20)	83.6236(12)	83.1479(12)	83.3061(13)	1140.74(3)
130	10.48699(18)	10.54547(15)	10.50415(20)	83.6387(12)	83.1566(12)	83.3137(13)	1139.99(3)
120	10.48430(18)	10.54328(15)	10.50172(20)	83.6526(12)	83.1663(12)	83.3213(13)	1139.26(3)
110	10.48171(18)	10.54113(15)	10.49960(19)	83.6637(12)	83.1761(12)	83.3282(13)	1138.58(3)
100	10.47920(18)	10.53895(15)	10.49737(19)	83.6769(12)	83.1853(12)	83.3358(13)	1137.89(3)

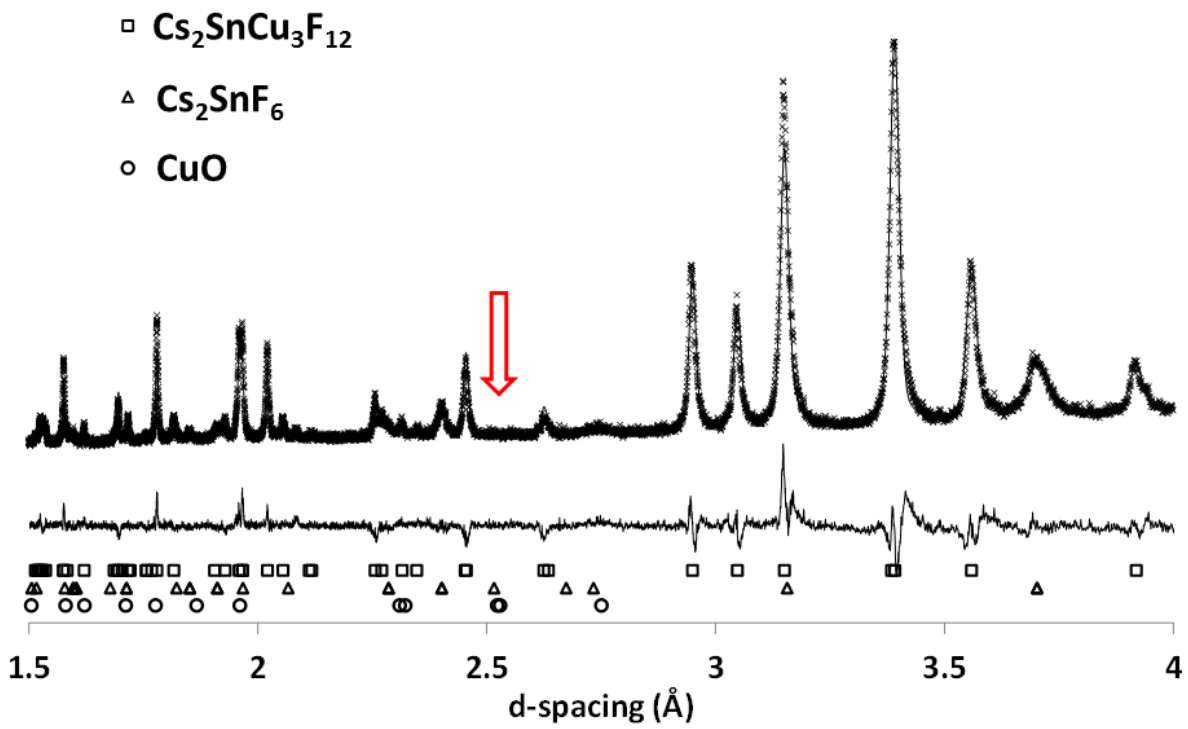

Figure S7: PXRD data and Rietveld refinement (at room temperature) for the sample of $Cs_2SnCu_3F_{12}$ used for the magnetic measurement . Tick marks are shown for CuO and the red arrow indicates the position of the strongest CuO reflection: this confirms that CuO is absent in this case, but is apparent in powders that have been synthesised by other methods.