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Supporting information for article:

Melilite-like modulation and temperature-dependent evolution in the framework structure of K2Sc[Si2O6]F

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Table S1 Interatomic distances [Å] and bond-valence sums [v.u.] $K_2Sc[Si_2O_6]F$ of the room temperature average structure and the high temperature normal structure of $K_2Sc[Si_2O_6]F$.

		Crystal I 21 °C	*Crystal II* 21 °C	*Crystal II* 200 °C
K1-O3	(4×)	2.809(2)	2.815(1)	2.821(2)
K1-O2	(2×)	3.012(2)	3.013(2)	3.014(2)
Bond-valence sum		0.827(2)	0.809(2)	0.807(1)
K1-F	(2×)	3.221(1)	3.225(1)	3.228(1)
Bond-valence sum		0.899(2)	0.880(2)	0.877(1)
K1-O3	(4×)	3.365(2)	3.366(2)	3.366(2)
Bond-valence sum		1.037(2)	1.088(2)	1.087(2)
K2-O1	(2×)	2.818(2)	2.816(2)	2.825(2)
K2-O2	(1×)	2.874(2)	2.881(2)	2.880(2)
K2-O3	(4×)	3.074(2)	3.074(2)	3.085(2)
Bond-valence sum		0.761(2)	0.749(2)	0.745(1)
K2-O3	(4×)	3.282(2)	3.2898(2)	3.284(2)
Bond-valence sum		0.939(2)	0.923(2)	0.923(1)
Sc-O3	(4x)	2.070(2)	2.0726(1)	2.073(1)
Sc-F	(2x)	2.062(2)	2.0742(1)	2.0688(3)
Bond-valence sum		3.075(5)	3.069(6)	3.053(4)
Si2-O1	(1x)	1.638(1)	1.6421(9)	1.642(2)
Si2-O2	(1x)	1.626(1)	1.6271(5)	1.627(1)
Si2-O3	(2x)	1.582(2)	1.585(1)	1.585(1)
Bond-valence sum		4.197(8)	4.156(10)	4.172(6)

Table S2 Interatomic distances [Å] of $K_2Sc[Si_2O_6]F$ in the (3+2) incommensurately modulated structure at 21, -50 and -100 °C

		Crystal II 21 °C	range	*Crystal III* -50 °C	range	*Crystal III* -100 °C	range
K1-O3	(4×)	2.734(2) – 2.909(2)	0.175	2.708(7) – 2.941(7)	0.233	2.701(7) – 2.951(7)	0.250
K1-O2	(2×)	2.925(3) – 3.140(4)	0.215	2.879(9) – 3.218(9)	0.339	2.863(8) – 3.250(8)	0.387
K1-F	(2×)	3.027(3) – 3.466(3)	0.439	2.934(6) – 3.586(7)	0.652	2.901(6) – 3.643(7)	0.742
K1-O3	(4×)	3.080(2) – 3.642(2)	0.562	2.961(7) – 3.734(7)	0.773	2.925(7) – 3.768(6)	0.843
K2-O1	(2×)	2.693(2) – 2.947(2)	0.254	2.650(6) – 2.996(5)	0.346	2.641(5) – 3.011(5)	0.370
K2-O2	(1×)	2.829(3) – 2.935(3)	0.106	2.802(9) – 2.952(9)	0.150	2.800(9) – 2.958(9)	0.158
K2-O3	(4×)	2.897(2) – 3.376(2)	0.479	2.812(7) – 3.569(7)	0.757	2.772(7) – 3.766(7)	0.994
K2-O3	(4×)	2.977(3) – 3.593(3)	0.616	2.832(7) – 3.716(7)	0.884	2.787(7) – 3.676(6)	0.889
Sc-O3	(4x)	2.069(2) – 2.093(2)	0.024	2.054(5) – 2.100(6)	0.046	2.051(5) – 2.104(5)	0.053
Sc-F	(2x)	2.065(1) – 2.074(1)	0.009	2.060(3) – 2.082(2)	0.022	2.062(2) – 2.087(2)	0.025
Si2-O1	(1x)	1.638(2) – 1.652(2)	0.014	1.630(4) – 1.664(4)	0.034	1.630(6) – 1.668(5)	0.038
Si2-O2	(1x)	1.625(1) – 1.634(1)	0.009	1.622(3) – 1.641(2)	0.019	1.624(2) – 1.648(2)	0.024
Si2-O3	(2x)	1.580(2) – 1.595(2)	0.015	1.572(6) – 1.608(6)	0.036	1.574(6) – 1.610(6)	0.036

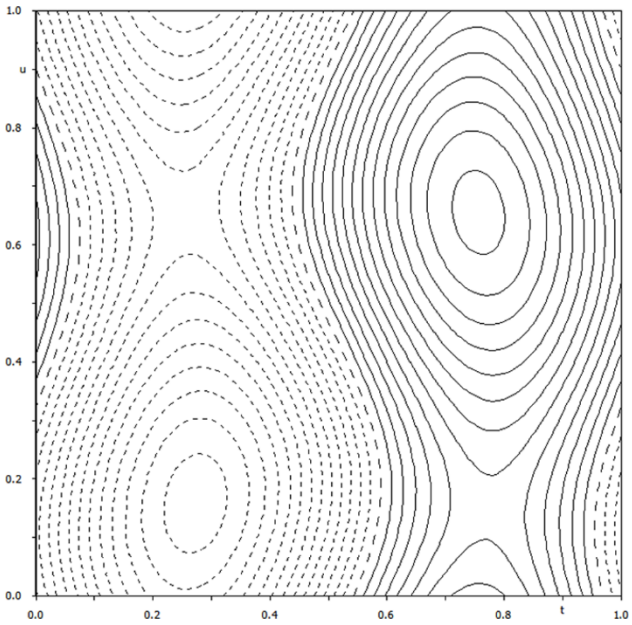
Table S3 Selected octahedral and tetrahedral angles of $K_2Sc[Si_2O_6]F$ measured from *crystal II* in the model of the average structure, in the (3+2)-modulated structure and in the high-temperature normal structure.

Temperature		21 °C	21 °C		200 °C
Structure		Average	(3+2)-IC modulated	range	N
Intra-octahedral					
F-Sc-F		180.0 (5)	178.2(1) – 180.0(5)	1.8	180.0 (5)
O3-Sc-O3		90.08(6)	88.7(1) – 91.5(1)	2.8	90.07(6)
O3-Sc-O3		175.72(5)	174.8(1) – 176.7(1)	1.9	176.1(1)
F-Sc-O3		92.14(3)	91.1(1) – 93.6(1)	2.5	91.95(3)
F-Sc-O3		87.86(3)	87.1(1) – 88.7(1)	1.6	88.05(3)
Inter-octahedral:					
Sc-F-Sc		180.0(5)	172.4(2) – 180.0(5)	7.6	180.0(5)
Intra-tetrahedral:					
O1 – Si – O2		105.9(1)	104.9(2) – 105.8(2)	0.9	105.7(1)
O1 – Si – O3	2x	107.9(1)	107.4(2) – 109.0(2)	1.6	108.2(1)
O2 – Si –O3	2x	110.4(1)	109.9(2) – 110.7(2)	0.8	110.2(1)
O3 – Si – O3		113.9(1)	113.2(2) – 115.0(2)	1.8	113.9(1)
O2 – O1 – O3		60.74(5)	60.4(1) – 61.0(1)	0.6	60.61(5)
O3 – O2 –O3		60.47(5)	60.2(1) – 61.0(1)	0.8	60.57(5)
O2 – O3 – O1		59.65(7)	59.0(1) – 59.9(1)	0.9	59.53(6)
O3 – O3 – O1		59.39(4)	59.0(1) – 59.8(1)	0.8	59.46(4)
O2 – O3 – O3		59.76(5)	59.5(1) – 60.1(1)	0.6	59.71(5)
Inter-tetrahedral:					
Si – O1 – Si		142.5(2)	141.4(1) – 143.6(2)	2.2	143.1(2)
Si – O2 – Si		174.3(2)	167.3(3) – 175.0(3)	7.7	174.6(1)
O2 – O1 – O2		68.78(8)	68.7(1) – 69.4(1)	0.7	69.21(7)
O3 – O1 – O3		118.91(9)	107.3(1) – 130.4(1)	23.1	118.92(5)
O3 – O1 – O3		179.6(1)	167.8(1) – 178.2(1)	10.4	179.8(1)
O1 – O2 – O1		111.22(7)	109.7(2) – 111.4(2)	1.7	110.79(8)
O3 – O2 –O3		108.78(7)	99.0(1) – 117.6(2)	18.6	108.6(1)
O3 – O2 –O3		146.08(1)	143.6(2) – 147.2(2)	3.6	145.92(9)

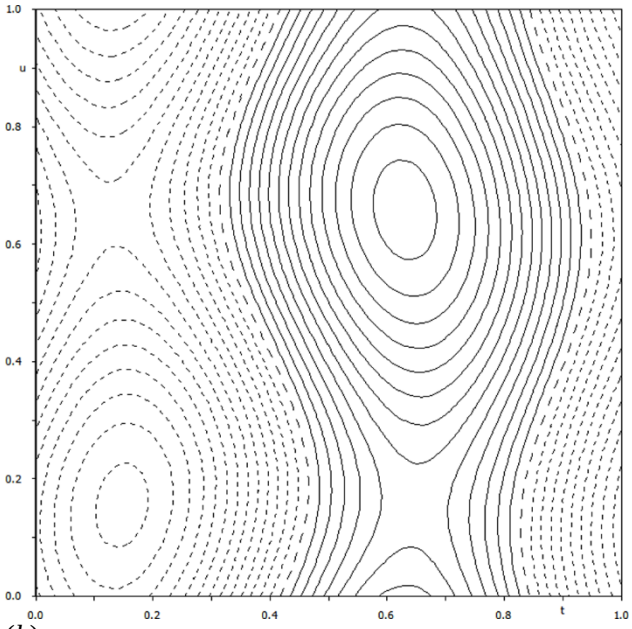
Table S4 Selected octahedral and tetrahedral angles measured from *crystal III* in (3+2)-modulated $K_2Sc[Si_4O_{12}]F$ at -50 and -100 °C.

		-50 °C			-100 °C		
		Min	Max	Range	Min	Max	Range
Intra-octahedral							
F-Sc-F		177.0(3)	180.0(5)	3.0	175.9(3)	180.0(5)	4.1
O3-Sc-O3		88.2(2)	91.8(2)	3.6	88.1(2)	92.0(2)	3.9
O3-Sc-O3		174.4(3)	176.9(3)	2.5	174.0(3)	177.3(3)	3.3
F-Sc-O3		90.3(31)	94.5(3)	4.2	89.7(3)	95.3(2)	5.6
F-Sc-O3		86.6(3)	89.2(3)	2.6	86.1(2)	89.4(3)	3.3
Inter-octahedral:							
Sc-F-Sc		167.9(3)	180.0(5)	12.1	165.8(3)	180.0(5)	14.2
Intra-tetrahedral:							
O1 – Si – O2		105.3(3)	106.6(3)	1.3	104.9(3)	106.6(3)	1.7
O1 – Si – O3	2x	106.7(3)	109.5(3)	2.8	106.9(3)	109.7(3)	2.8
O2 – Si –O3	2x	109.3(4)	110.8(4)	1.5	109.1(4)	110.9(4)	1.8
O3 – Si – O3		112.7(3)	115.4(3)	2.7	112.7(3)	115.5(3)	2.8
O2 – O1 – O3		59.8(2)	61.1(2)	1.3	59.9(2)	61.3(2)	1.4
O3 – O2 –O3		60.1(2)	61.5(2)	1.4	60.1(2)	61.4(2)	1.3
O2 – O3 – O1		58.9(2)	60.3(2)	1.4	58.8(2)	60.4(2)	1.6
O3 – O3 – O1		58.6(2)	60.1(2)	1.5	58.5(2)	59.9(2)	1.4
O2 – O3 – O3		59.2(3)	60.4(3)	1.2	59.1(2)	60.3(3)	1.2
Inter-tetrahedral:							
Si – O1 –Si		139.2(4)	143.3(5)	4.1	138.6(3)	143.6(4)	5.0
Si – O2 - Si		161.8(6)	175.9(6)	14.1	159.1(6)	176.2(6)	17.1
O2 – O1 – O2		68.5(3)	69.7(3)	1.2	68.2(2)	69.9(3)	1.7
O3 – O1 – O3*		103.1(3)	134.7(3)	31.6	101.7(2)	136.0(2)	34.3
O3 – O1 – O3**		163.1(3)	176.9(4)	13.8	161.9(2)	176.6(3)	14.7
O1 – O2 – O1		108.3(3)	111.4(3)	3.1	107.8(3)	111.8(3)	4.0
O3 – O2 –O3*		93.7(3)	123.0(4)	29.3	91.2(3)	124.7(4)	33.5
O3 – O2 –O3**		141.8(4)	148.3(4)	6.5	140.5(4)	148.6(4)	8.1

* O3 atoms on same side of ring plane ** O3 atoms on opposite sides of ring plane

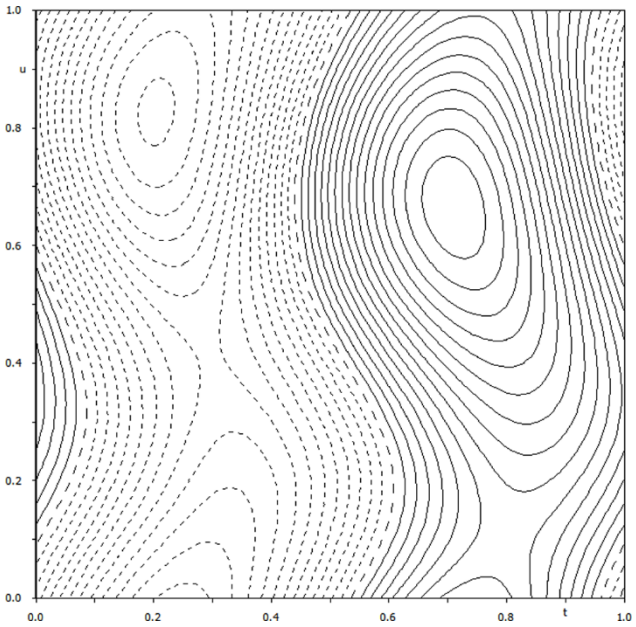


(*a*)

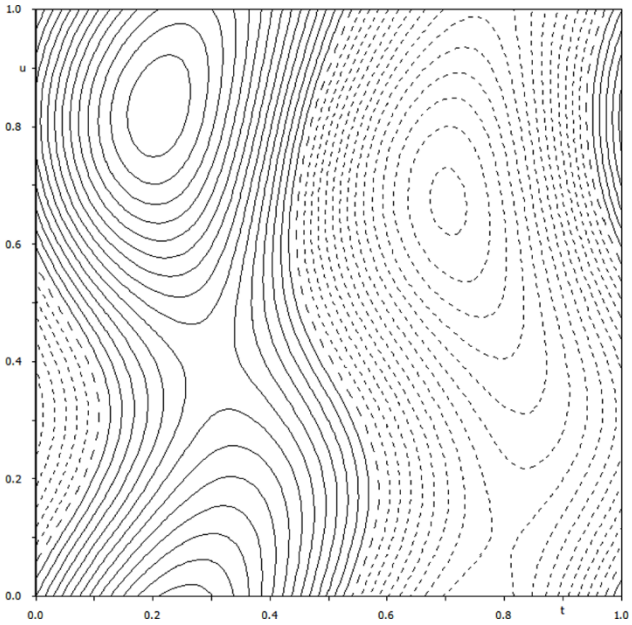


(*b*)

Figure S1 Displacement of (a) x(K1) and (b) y(K1) as a function of *t* and *u*. The displacement of z(K1) is zero. The contour lines are drawn with 0.01spacing.

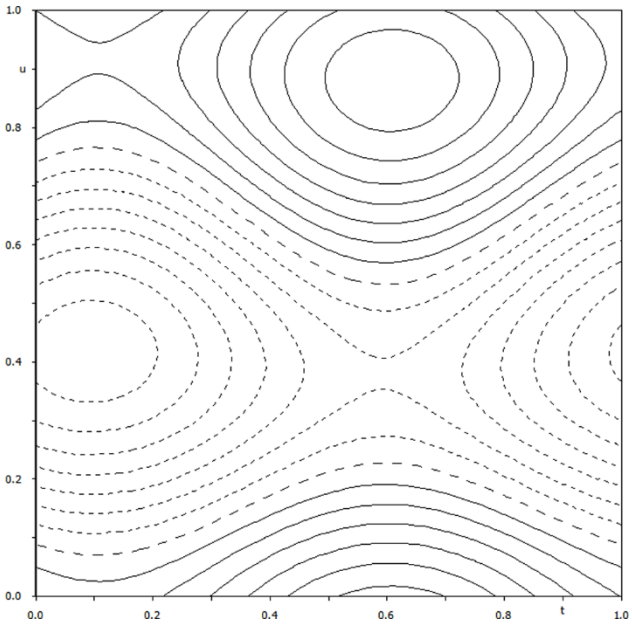


(*a*)

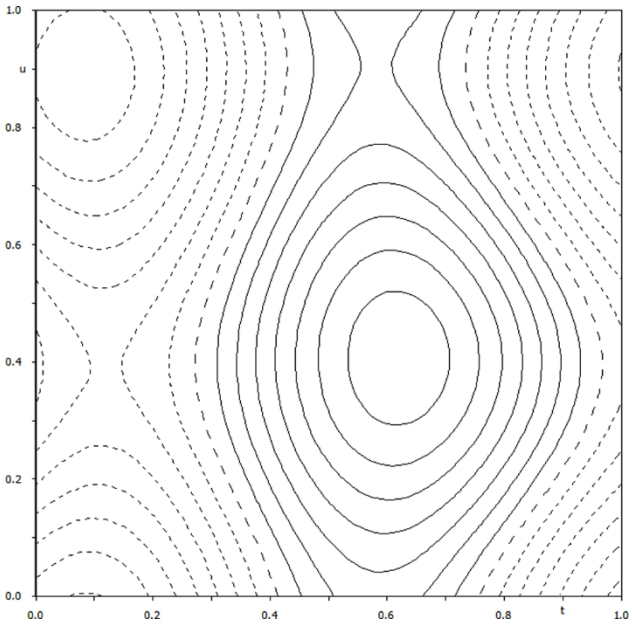


(*b*)

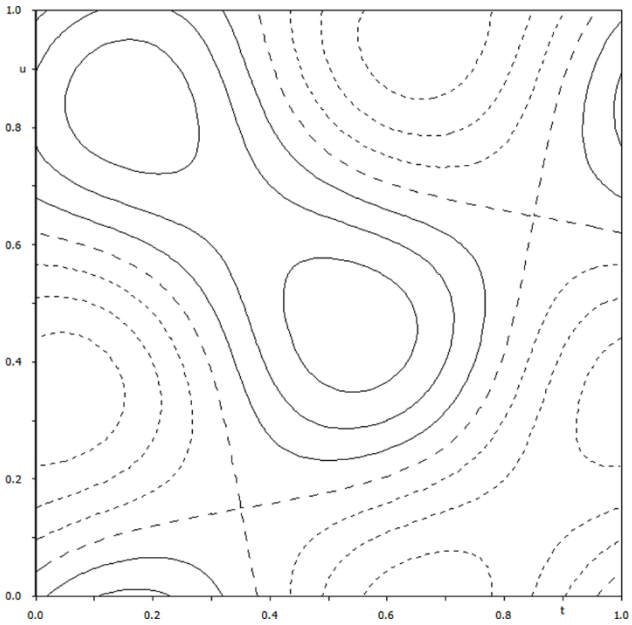
Figure S2 Displacement of (a) x(K2) and (b) y(K2) as a function of *t* and *u*. The displacement of z(K2) is zero. The contour lines are drawn with 0.01spacing.


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*a*)

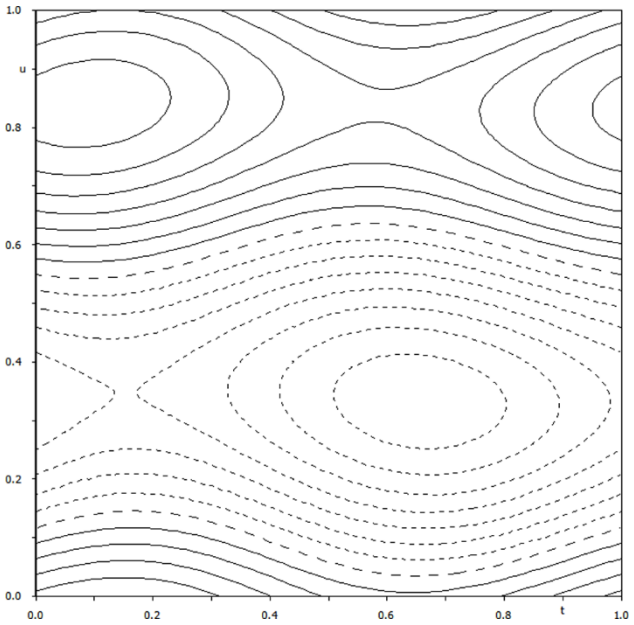

1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*b*)

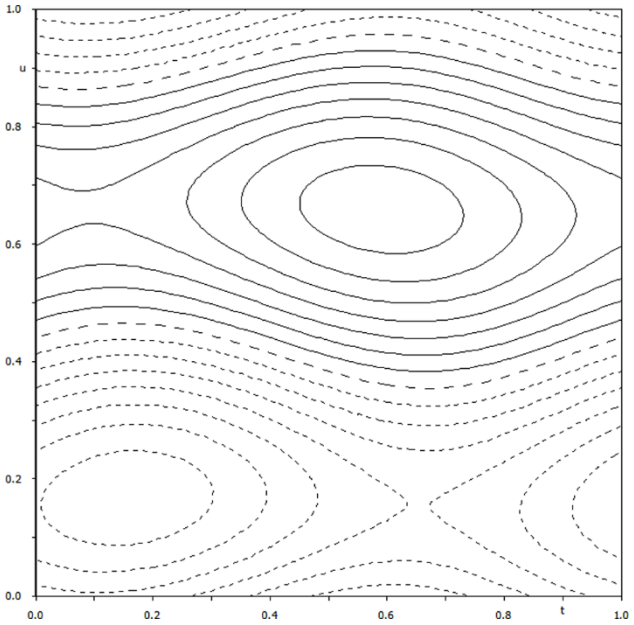


(*c*)

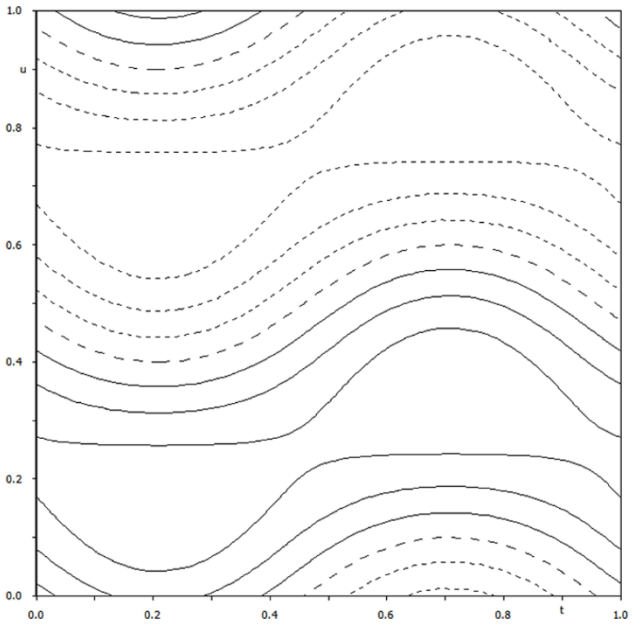
Figure S3 Displacement of (a) x(Sc), (b) y(Sc) and (c) z(Sc) as a function of *t* and *u*. The contour lines are drawn with 0.01spacing for dx and dy and with 0.0001 spacing for dz.


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*a*)

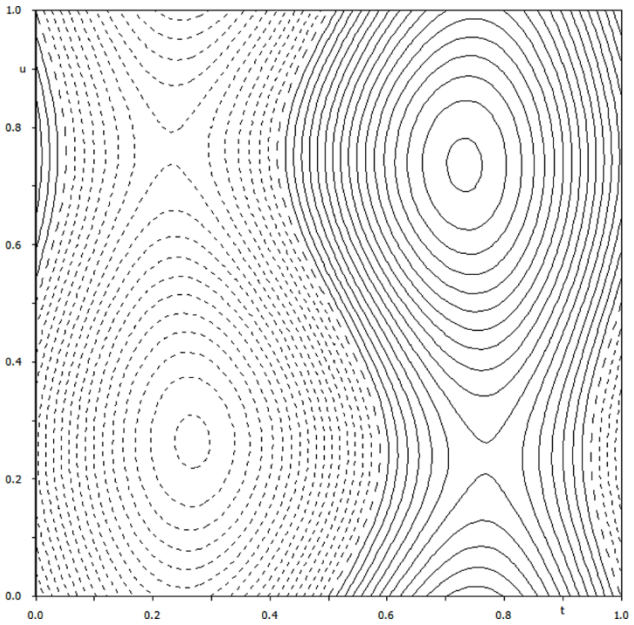

1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*b*)

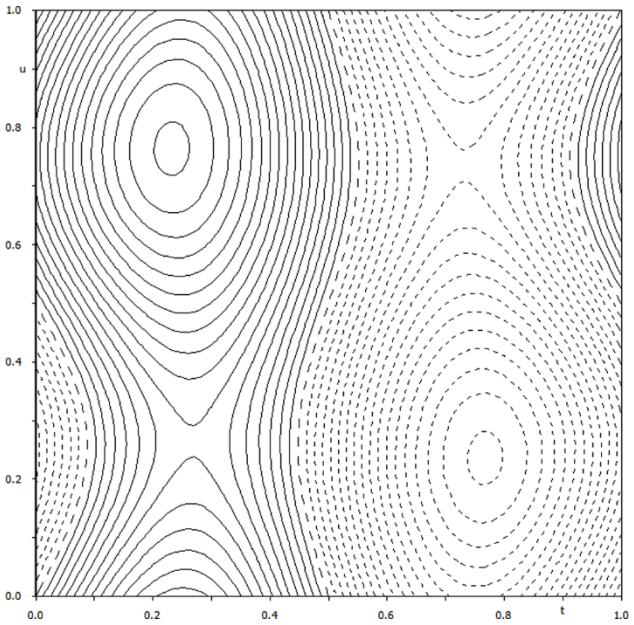


(*c*)

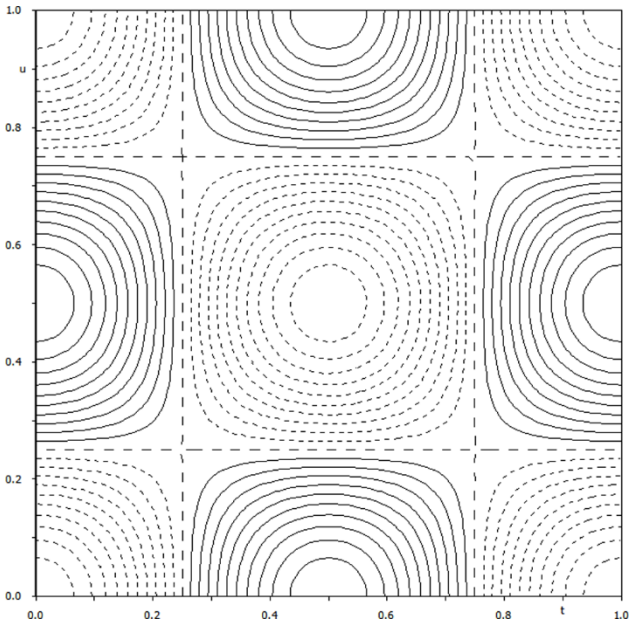
Figure S4 Displacement of (a) x(Si), (b) y(Si) and (c) z(Si) as a function of *t* and *u*. The contour lines are drawn with 0.01spacing for dx and dy and with 0.0001 spacing for dz.


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*a*)


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

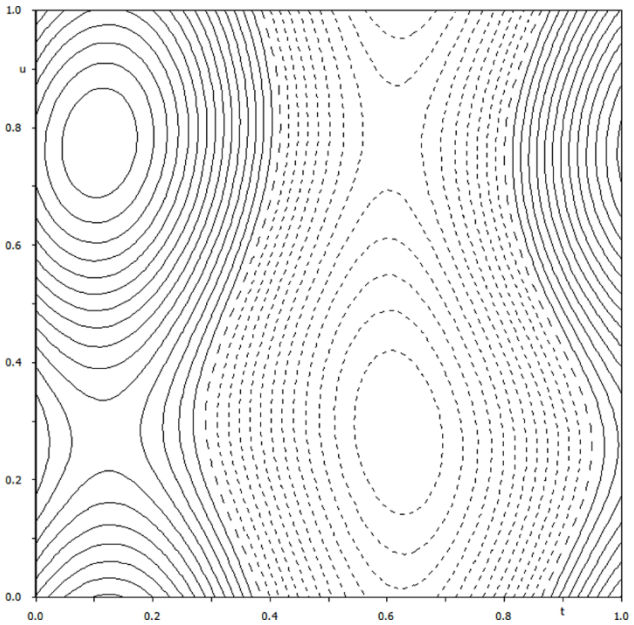
(*b*)



(*c*)

Figure S5 Displacement of (a) x(O1), (b) y(O1) and (c) z(O2) as a function of *t* and *u*. The contour lines are drawn with 0.01spacing for dx and dy and with 0.0001 spacing for dz.

(*a*)



(*b*)

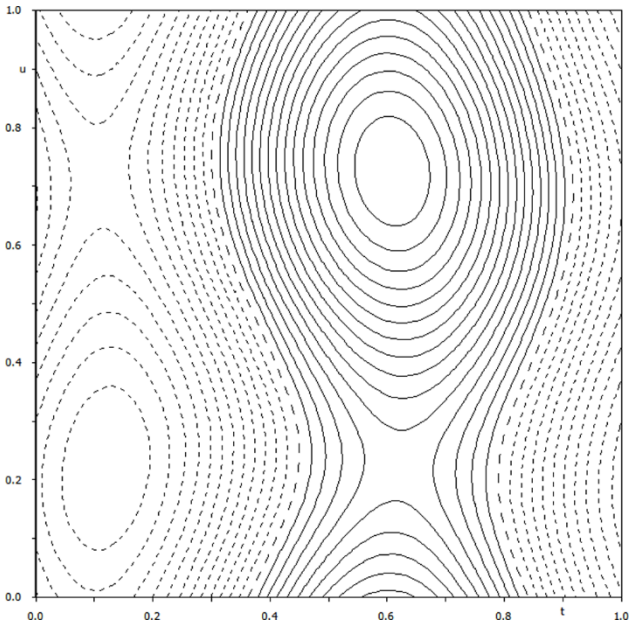
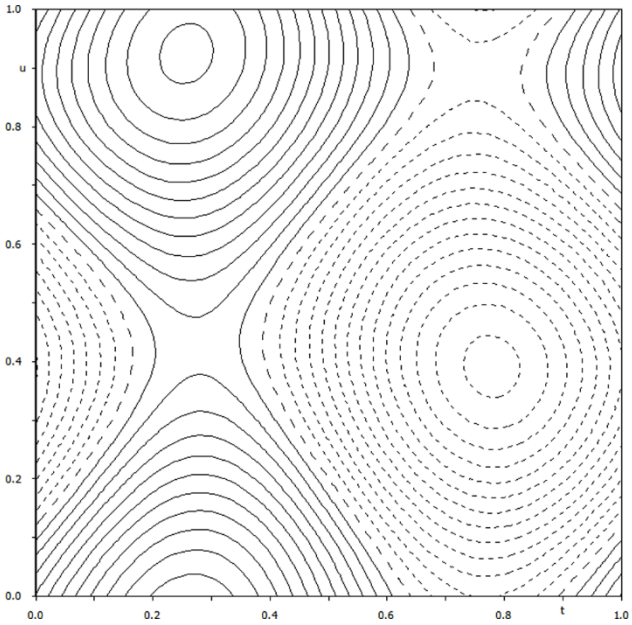
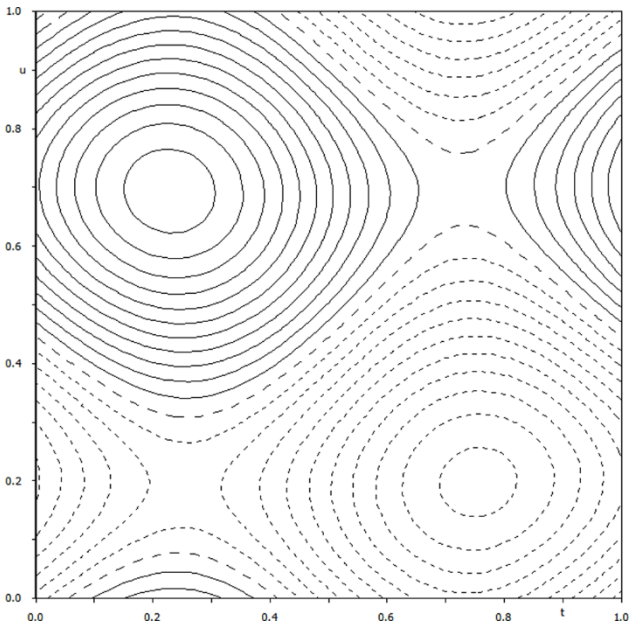


Figure S6 Displacement of (a) x(O2) and (b) y(O2) as a function of *t* and *u*. The displacement of z(O2) is zero. The contour lines are drawn with 0.01spacing.

(*a*)


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*b*)


1.0
u
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
t
1.0

(*c*)

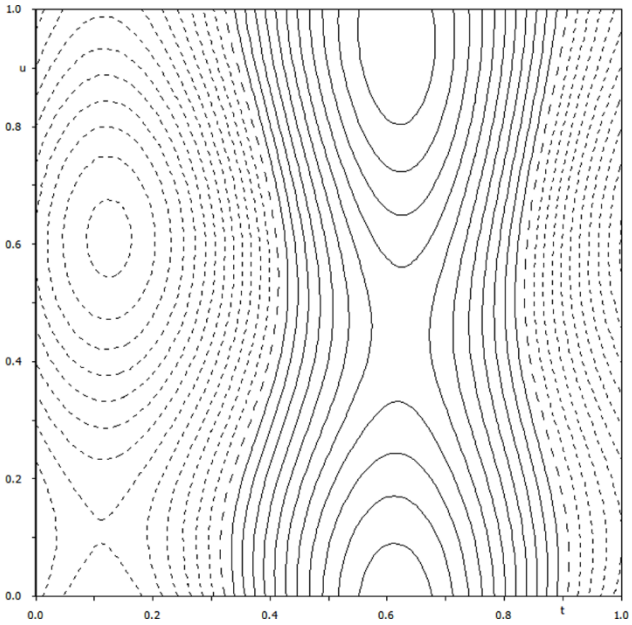
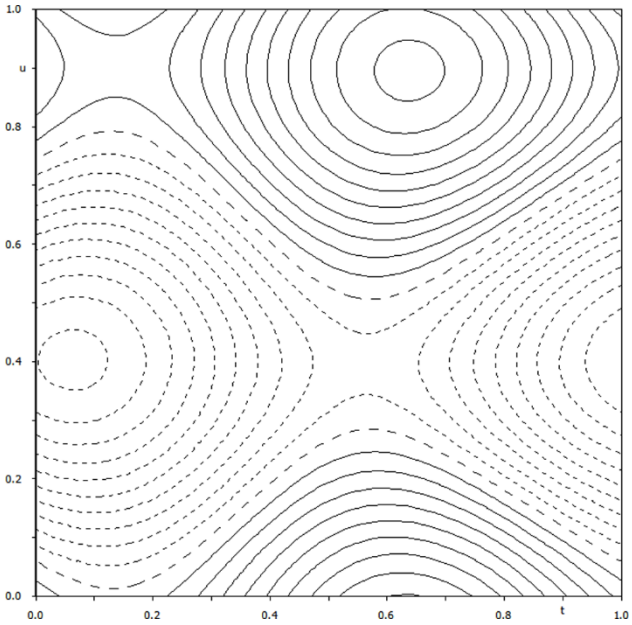


Figure S7 Displacement of (a) x(O3), (b) y(O3) and (c) z(O3) as a function of *t* and *u*. The contour lines are drawn with 0.02 spacing for dx and dy and with 0.001 spacing for dz.

(*a*)



(*b*)

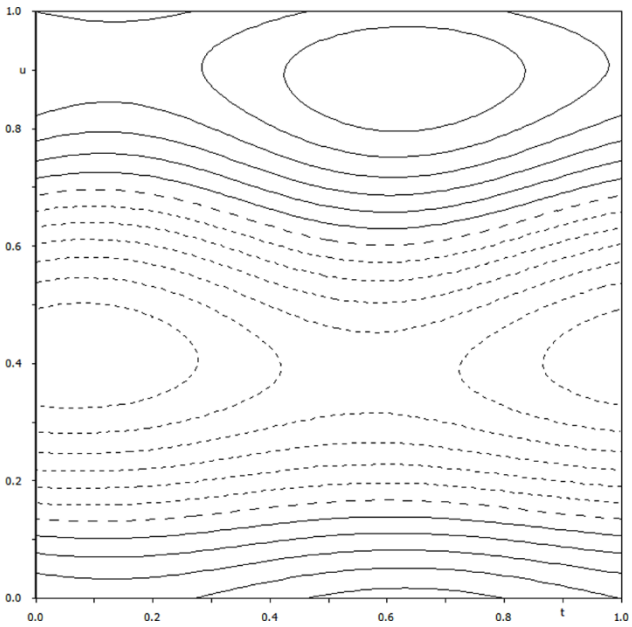


Figure S8 Displacement of (a) x(F) and (b) y(F) as a function of *t* and *u*. The displacement of z(F) is zero. The contour lines are drawn with 0.02 spacing.

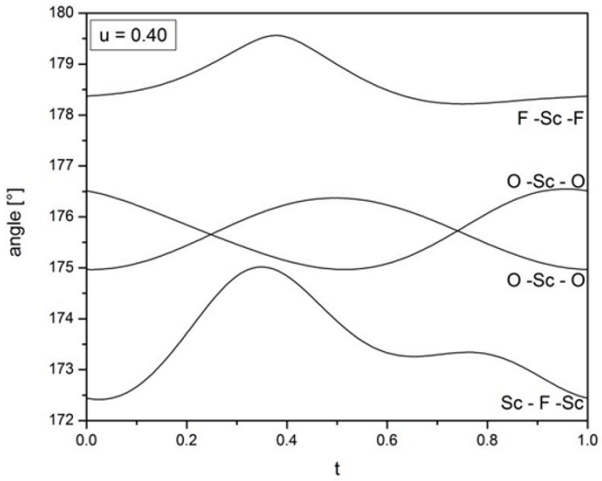


Figure S9 Inter- and intra-polyhedral angles in the octahedral ScO_4F_2-chain as a function of *t* at *u* = 0.4.

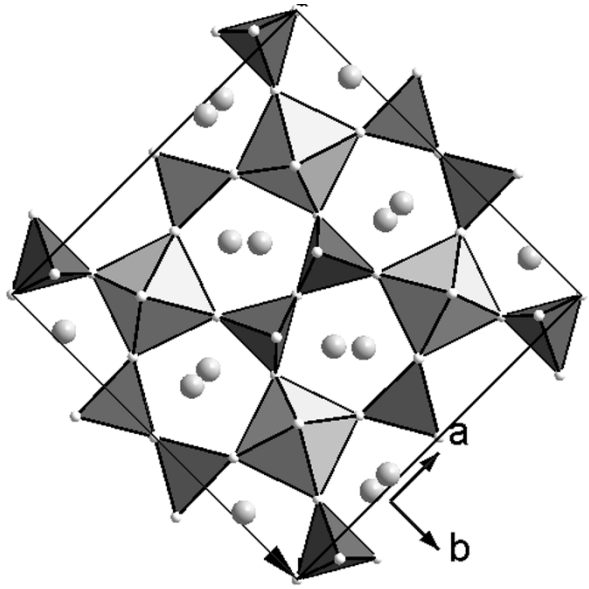


Figure S10 Crystal structure of $K_2Sc[Si_2O_6](OH)$ in a view along the *c*-axis (Pyatenko et al. 1979).