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**Supporting information for article:**

**Structural changes in Rochelle salt on phase transitions revisited in a multi-temperature single-crystal X-ray diffraction study**

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**Table S1** Relative displacement of atoms (which are symmetry-related in PE phases) in the FE phase with respect to the position of the pseudo-2-fold axis at 276 K. The atom with the largest relative displacement is highlighted in blue. See details on defining displacements in the main text, Section 3.3.

<i>Atoms</i>	<i>Corresponding atoms in LT/HT PE phases</i>	$\delta x$ (Å)	$\delta y$ (Å)	$\delta z$ (Å)	$\Delta$ (Å)
K1	K1	0.011 (2)	−0.005 (2)	-	-
K2	K2	−0.0001 (9)	0.003 (7)	-	-
Na1 / Na2	Na1	−0.001 (3)	0.000 (2)	0.009 (2)	0.010 (2)
O11 / O12	O1	−0.002 (4)	−0.000 (4)	0.004 (4)	0.004 (4)
O21 / O22	O2	0.007 (5)	−0.001 (4)	0.007 (4)	0.010 (4)
O31 / O32	O3	−0.019 (5)	−0.004 (5)	0.009 (4)	0.021 (4)
O41 / O42	O4	−0.006 (5)	−0.010 (5)	−0.001 (4)	0.012 (5)
O51 / O52	O5	0.002 (5)	−0.004 (4)	0.005 (4)	0.007 (4)
O61 / O62	O6	−0.006 (4)	−0.004 (5)	0.012 (5)	0.014 (5)
O71 / O72	O7	−0.0004 (4)	−0.000 (5)	−0.004 (6)	0.006 (5)
O81 / O82	O8	−0.005 (5)	0.006 (6)	0.005 (5)	0.009 (5)
O91 / O92	O9	0.005 (5)	−0.017 (8)	−0.004 (6)	0.019 (8)
O101 / O102	O10	−0.017 (5)	0.024 (6)	0.027 (6)	0.040 (6)
C11 / C12	C1	−0.001 (5)	0.001 (6)	0.006 (5)	0.006 (5)
C21 / C22	C2	−0.005 (7)	0.004 (6)	0.006 (5)	0.009 (6)
C31 / C32	C3	−0.006 (7)	−0.001 (6)	0.005 (6)	0.008 (7)
C41 / C42	C4	−0.010 (7)	−0.003 (3)	0.007 (6)	0.013 (7)

**Table S2** Interatomic distances at 253 K (LT PE), 276 K (FE) and 298 K (HT PE). For all temperatures anharmonic model was used. The distances with the largest difference in the monoclinic phase are highlighted in blue.

253 K	Length (Å)	276 K	Length (Å)	298 K	Length (Å)
K1 – O1	2.8294 (19)	K1 – O11	2.829 (3)	K1 – O1	2.835 (2)
		K1 – O12	2.835 (3)		
K1 – O8 <sup>i</sup>	3.094 (2)	K1 – O81 <sup>i</sup>	3.104 (4)	K1 – O8 <sup>i</sup>	3.122 (3)
		K1 – O82 <sup>i</sup>	3.109 (4)		
K1 – O9	2.923 (3)	K1 – O91	2.943 (4)	K1 – O9	2.963 (3)
		K1 – O92	2.939 (4)		
K1 – O10 <sup>i</sup>	3.389 (3)	K1 – O101 <sup>i</sup>	3.353 (4)	K1 – O10 <sup>i</sup>	3.366 (4)
		K1 – O102 <sup>i</sup>	3.403 (4)		
K2 – O4 <sup>ii</sup>	2.8451 (16)	K2 – O41 <sup>ii</sup>	2.847 (2)	K2 – O4 <sup>ii</sup>	2.8462 (18)
		K2 – O42 <sup>iii</sup>	2.847 (2)		
K2 – O5 <sup>iii</sup>	2.9881 (16)	K2 – O51 <sup>iv</sup>	2.993 (2)	K2 – O5 <sup>iii</sup>	2.9957 (17)
		K2 – O52 <sup>v</sup>	2.990 (2)		
K2 – O7 <sup>i</sup>	2.7931 (19)	K2 – O71 <sup>i</sup>	2.796 (3)	K2 – O7 <sup>i</sup>	2.802 (2)
		K2 – O72 <sup>vi</sup>	2.793 (3)		
K2 – O8 <sup>i</sup>	3.128 (2)	K2 – O81 <sup>i</sup>	3.114 (3)	K2 – O8 <sup>i</sup>	3.114 (3)
		K2 – O82 <sup>vi</sup>	3.126 (3)		
Na – O1	2.3651 (17)	Na1 – O11	2.368 (2)	Na – O1	2.3740 (19)
		Na2 – O12	2.366 (2)		
Na – O3 <sup>ii</sup>	2.4613 (19)	Na1 – O32 <sup>iii</sup>	2.463 (3)	Na – O3 <sup>ii</sup>	2.467 (2)
		Na2 – O31 <sup>vii</sup>	2.463 (3)		
Na – O5 <sup>ii</sup>	2.4893 (18)	Na1 – O52 <sup>iii</sup>	2.496 (3)	Na – O5 <sup>ii</sup>	2.499 (2)
		Na2 – O51 <sup>vii</sup>	2.498 (2)		
Na – O7	2.3347 (18)	Na1 – O71	2.335 (3)	Na – O7	2.342 (2)
		Na2 – O72	2.336 (3)		
Na – O8	2.3612 (19)	Na1 – O81	2.362 (3)	Na – O8	2.363 (2)
		Na2 – O82	2.365 (3)		
Na – O10	2.329 (2)	Na1 – O101	2.329 (3)	Na – O10	2.331 (2)

		Na2 – O102	2.327 (3)		
O1 – C1	1.262 (3)	O11 – C11	1.263 (4)	O1 – C1	1.258 (3)
		O12 – C12	1.261 (4)		
O2 – C1	1.242 (3)	O21 – C11	1.246 (4)	O2 – C1	1.244 (3)
		O22 – C12	1.243 (4)		
O3 – C4	1.251 (3)	O31 – C41	1.252 (4)	O3 – C4	1.252 (3)
		O32 – C42	1.254 (4)		
O4 – C4	1.258 (3)	O41 – C41	1.248 (4)	O4 – C4	1.255 (3)
		O42 – C42	1.253 (4)		
O5 – C2	1.422 (3)	O51 – C21	1.421 (4)	O5 – C2	1.420 (3)
		O52 – C22	1.423 (4)		
O6 – C3	1.417 (3)	O61 – C31	1.416 (4)	O6 – C3	1.418 (3)
		O62 – C32	1.416 (4)		
C1 – C2	1.533 (3)	C11 – C21	1.531 (4)	C1 – C2	1.531 (3)
		C12 – C22	1.530 (4)		
C2 – C3	1.527 (3)	C21 – C31	1.528 (4)	C2 – C3	1.524 (3)
		C22 – C32	1.529 (4)		
C3 – C4	1.528 (3)	C31 – C41	1.531 (4)	C3 – C4	1.532 (3)
		C32 – C42	1.528 (4)		

Symmetry codes for orthorhombic phases: (i)  $x, y, z - I$ ; (ii)  $-x + 1/2, y - 1/2, -z + I$ ; (iii)  $x + 1/2, -y + 1/2, -z$ .

Symmetry codes for monoclinic phase: (i)  $x, y, z - I$ ; (ii)  $x + 1/2, -y + 1/2, -z + I$ ; (iii)  $x + 1/2, -y - 1/2, -z + I$ ; (iv)  $x + 1/2, -y + 1/2, -z$ ; (v)  $x + 1/2, -y - 1/2, -z$ ; (vi)  $x + 1, y, z - I$ ; (vii)  $x - 1/2, -y + 1/2, -z + I$ .

**Table S3** The donor-acceptor distances in the hydrogen bonds in the RS structure at 100 K (LT PE), 276 K (FE) and 308 K (HT PE).

100 K	D...A (Å)	276 K	D...A (Å)	308 K	D...A (Å)
O5—H5...O2	2.599 (2)	O51—H51...O21	2.603 (3)	O5—H5...O2	2.605 (3)
		O52—H52...O22	2.605 (3)		
O5—H5...O3 <sup>i</sup>	3.277 (2)	O51—H51...O31 <sup>i</sup>	3.350 (3)	O5—H5...O3 <sup>i</sup>	3.367 (3)
		O52—H52...O32 <sup>i</sup>	3.357 (3)		
O5—H5...O4 <sup>i</sup>	3.248 (2)	O51—H51...O41 <sup>i</sup>	3.265 (3)	O5—H5...O4 <sup>i</sup>	3.265 (3)
		O52—H52...O42 <sup>i</sup>	3.255 (3)		
O6—H6...O10 <sup>ii</sup>	2.812 (3)	O61—H61...O102 <sup>ii</sup>	2.897 (4)	O6—H6...O10 <sup>ii</sup>	2.947 (4)
		O62—H62...O101 <sup>iii</sup>	2.925 (4)		
O7—H17...O6	2.778 (2)	O71—H17...O61	2.795 (3)	O7—H17...O6	2.796 (3)
		O72—H37...O62	2.793 (3)		
O7—H27...O4 <sup>iii</sup>	2.853 (3)	O71—H27...O41 <sup>ii</sup>	2.883 (4)	O7—H27...O4 <sup>iii</sup>	2.891 (3)
		O71—H27...O41 <sup>ii</sup>	2.887 (3)		
O8—H18...O3 <sup>iv</sup>	2.697 (3)	O81—H28...O32 <sup>v</sup>	2.709 (3)	O8—H18...O3 <sup>iv</sup>	2.704 (3)
		O82—H48...O31 <sup>vi</sup>	2.703 (3)		
O8—H28...O1 <sup>v</sup>	3.346 (2)	O81—H18...O11 <sup>iv</sup>	3.385 (3)	O8—H28...O1 <sup>v</sup>	3.395 (3)
		O82—H38...O12 <sup>iv</sup>	3.382 (3)		
O8—H28...O2 <sup>v</sup>	2.746 (3)	O81—H18...O21 <sup>iv</sup>	2.750 (3)	O8—H28...O2 <sup>v</sup>	2.754 (3)
		O81—H18...O21 <sup>iv</sup>	2.754 (3)		
O9—H19...O2 <sup>vi</sup>	3.122 (3)	O91—H19...O22 <sup>vii</sup>	3.107 (4)	O9—H19...O2 <sup>vi</sup>	3.110 (3)
		O92—H39...O21 <sup>ix</sup>	3.118 (4)		
O9—H19...O3 <sup>vii</sup>	3.154 (3)	O91—H19...O32 <sup>viii</sup>	3.163 (4)	O9—H19...O3 <sup>vii</sup>	3.177 (3)
		O92—H39...O31 <sup>x</sup>	3.171 (4)		
O9—H19...O6 <sup>vii</sup>	3.102 (3)	O91—H19...O62 <sup>viii</sup>	3.145 (4)	O9—H19...O6 <sup>vii</sup>	3.148 (3)
		O92—H39...O61 <sup>x</sup>	3.144 (4)		
O9—H29...O4 <sup>viii</sup>	2.785 (3)	O91—H29...O42 <sup>i</sup>	2.816 (4)	O9—H29...O4 <sup>viii</sup>	2.818 (4)
		O92—H49...O41 <sup>i</sup>	2.818 (4)		
O10— H110...O1 <sup>ix</sup>	2.713 (2)	O101—H110...O12	2.732 (4)	O10—H110...O1 <sup>ix</sup>	2.738 (3)

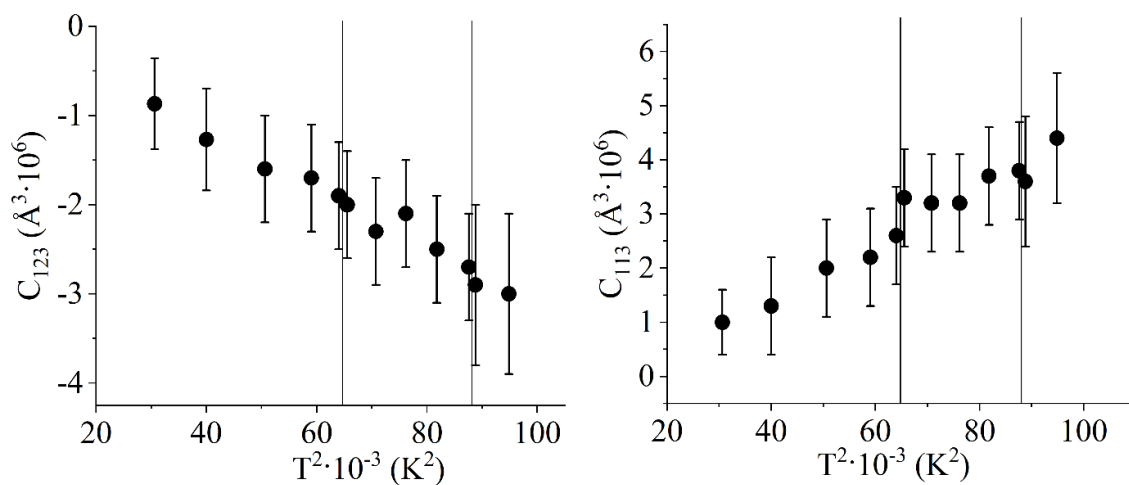
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		O102—H310...O11	2.729 (4)		
O10—	2.751 (3)	O101—H210...O91 <sup>iv</sup>	2.750 (4)	O10—H210...O9 <sup>v</sup>	2.759 (4)
H210...O9 <sup>v</sup>					
		O102—H410...O92 <sup>iv</sup>	2.758 (4)		

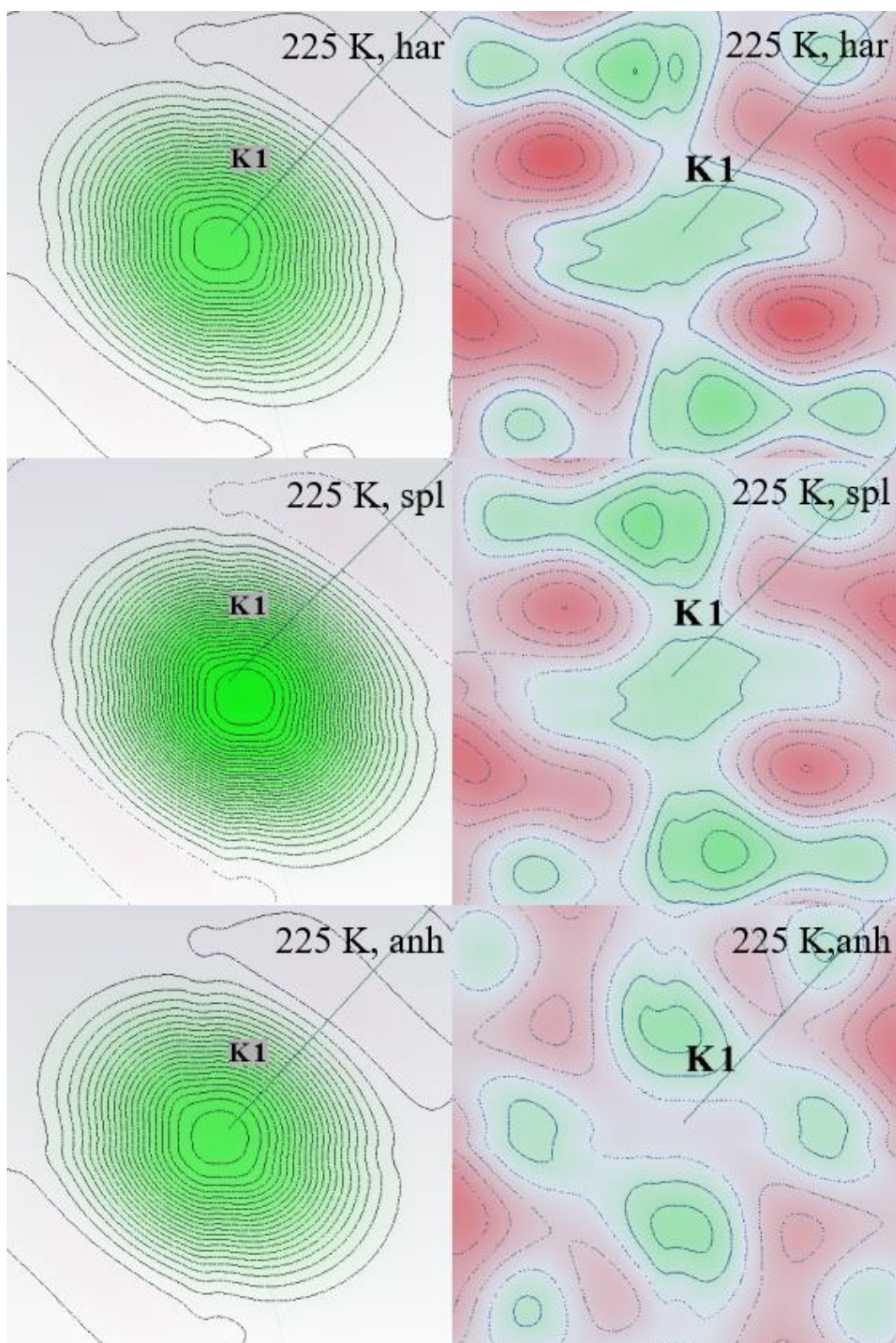
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Symmetry codes for orthorhombic phases: (i)  $x, y, z-1$ ; (ii)  $-x+1/2, y+1/2, -z+1$ ; (iii)  $x+1/2, -y+1/2, -z+1$ ; (iv)  $-x+1/2, y-1/2, -z+2$ ; (v)  $x, y, z+1$ ; (vi)  $-x+1/2, y-1/2, -z$ ; (vii)  $-x+1/2, y-1/2, -z+1$ ; (viii)  $-x, -y, z-1$ ; (ix)  $-x, -y, z$ .

Symmetry codes for monoclinic phase: (i)  $x, y, z-1$ ; (ii)  $-x+1/2, y+1/2, -z+1$ ; (iii)  $-x-1/2, y-1/2, -z+1$ ; (iv)  $x, y, z+1$ ; (v)  $-x+1/2, y-1/2, -z+2$ ; (vi)  $-x-1/2, y+1/2, -z+2$ ; (vii)  $-x+1/2, y-1/2, -z$ ; (viii)  $-x+1/2, y-1/2, -z+1$ ; (ix)  $-x-1/2, y+1/2, -z$ ; (x)  $-x-1/2, y+1/2, -z+1$ .

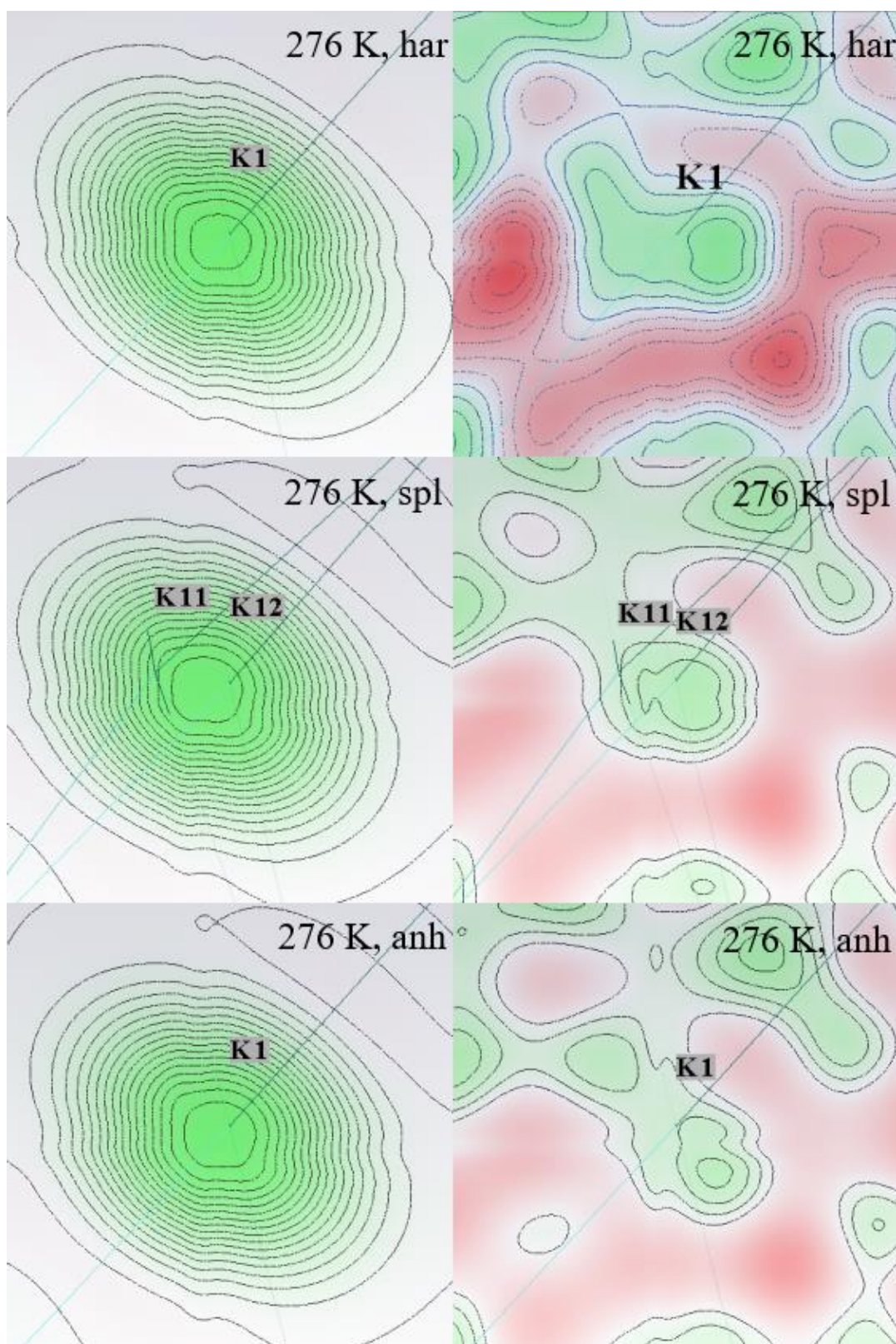


**Figure S1**  $C_{123}$  and  $C_{113}$  of K1 vs.  $T^2$ . Vertical lines correspond to phase transitions ( $T_1 = 255 \text{ K}$ ,  $T_2 = 297 \text{ K}$ ). The area between vertical lines corresponds to FE phase.  $C_{123}$  and  $C_{113}$  are 3<sup>rd</sup> order coefficients Gram-Charlier that are larger than  $3\sigma$ . The presence of significant coefficients justifies the application of 3<sup>rd</sup> order.

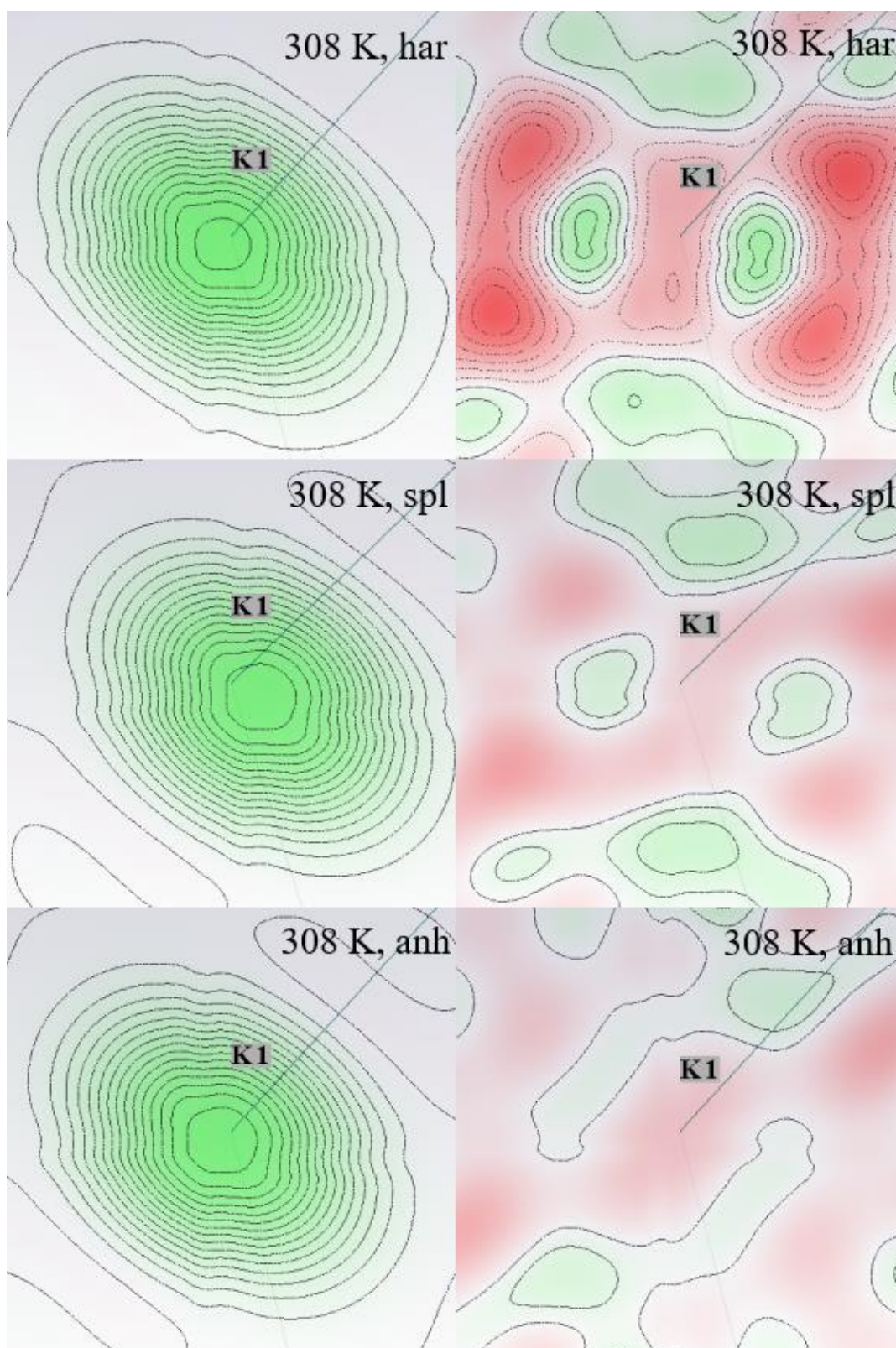


**Figure S2** Electron density (left, the contour interval is  $2 \text{ e}\text{\AA}^{-3}$ ) and residual electron density (right, the contour interval is  $0.05 \text{ e}\text{\AA}^{-3}$ ) maps at 225 K (LT PE phase). Three different models for describing K1 atom were used: *har* - Harmonic, no split; *spl* - Harmonic, split; *anh* - Anharmonic, non-split. Models *spl* and *anh* reduce the intensity of the residual electron density.



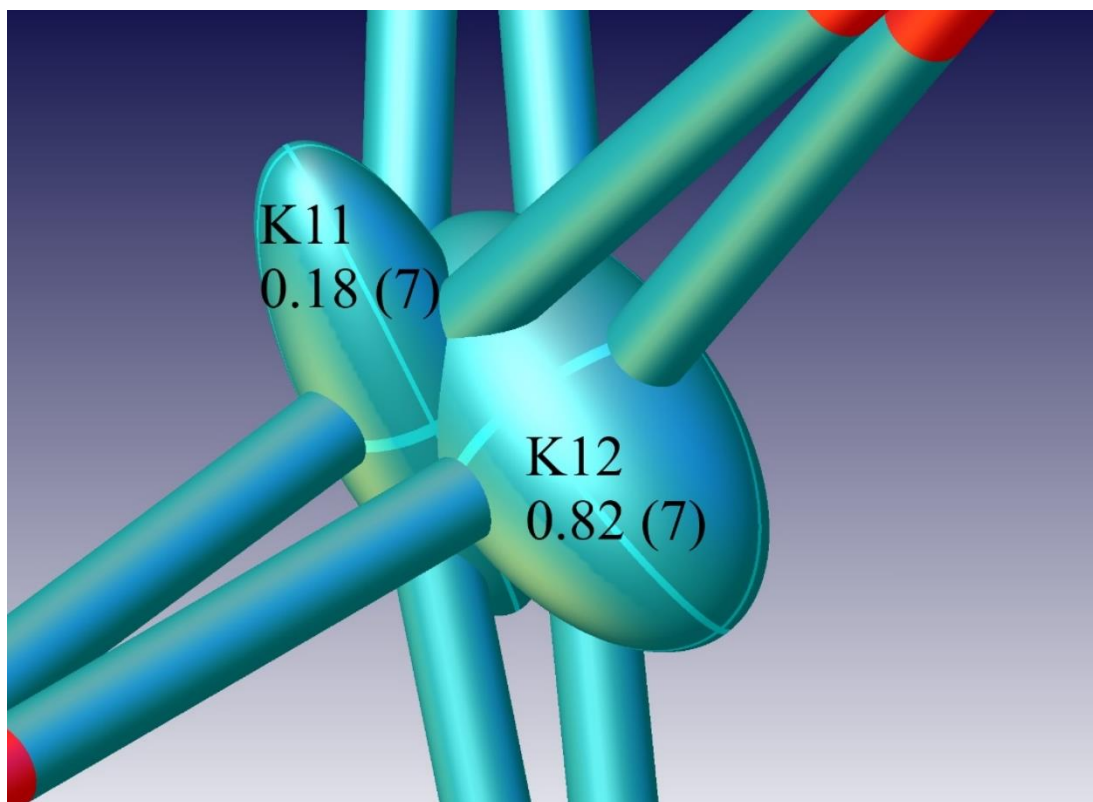


**Figure S3** Electron density (left, the contour interval is  $2 \text{ e}\text{\AA}^{-3}$ ) and residual electron density (right, the contour interval is  $0.05 \text{ e}\text{\AA}^{-3}$ ) maps at 276 K (FE phase). Three different models for describing K1 atom were used: *har* - Harmonic, no split; *spl* - Harmonic, split; *anh* - Anharmonic, non-split. Models *spl* and *anh* reduce the intensity of the residual electron density.



**Figure S4** Electron density (left, the contour interval is  $2 \text{ e}\text{\AA}^{-3}$ ) and residual electron density (right, the contour interval is  $0.05 \text{ e}\text{\AA}^{-3}$ ) maps at 308 K (HT PE phase). Three different models for describing K1 atom were used: *har* - Harmonic, no split; *spl* - Harmonic, split; *anh* - Anharmonic, non-split. Models *spl* and *anh* reduce the intensity of the residual electron density.





**Figure S5** Atomic displacement parameters, ADPs (50 % probability level) and occupancy of the K1 position split into two at 276 K (FE phase). In the split model (*spl*), one of position has a suspiciously small population and a strange ellipsoid shape.