

# Single-Crystal to Single-Crystal Phase Transitions of Commensurately Modulated Sodium Saccharinate 1.875-Hydrate

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## Supporting information

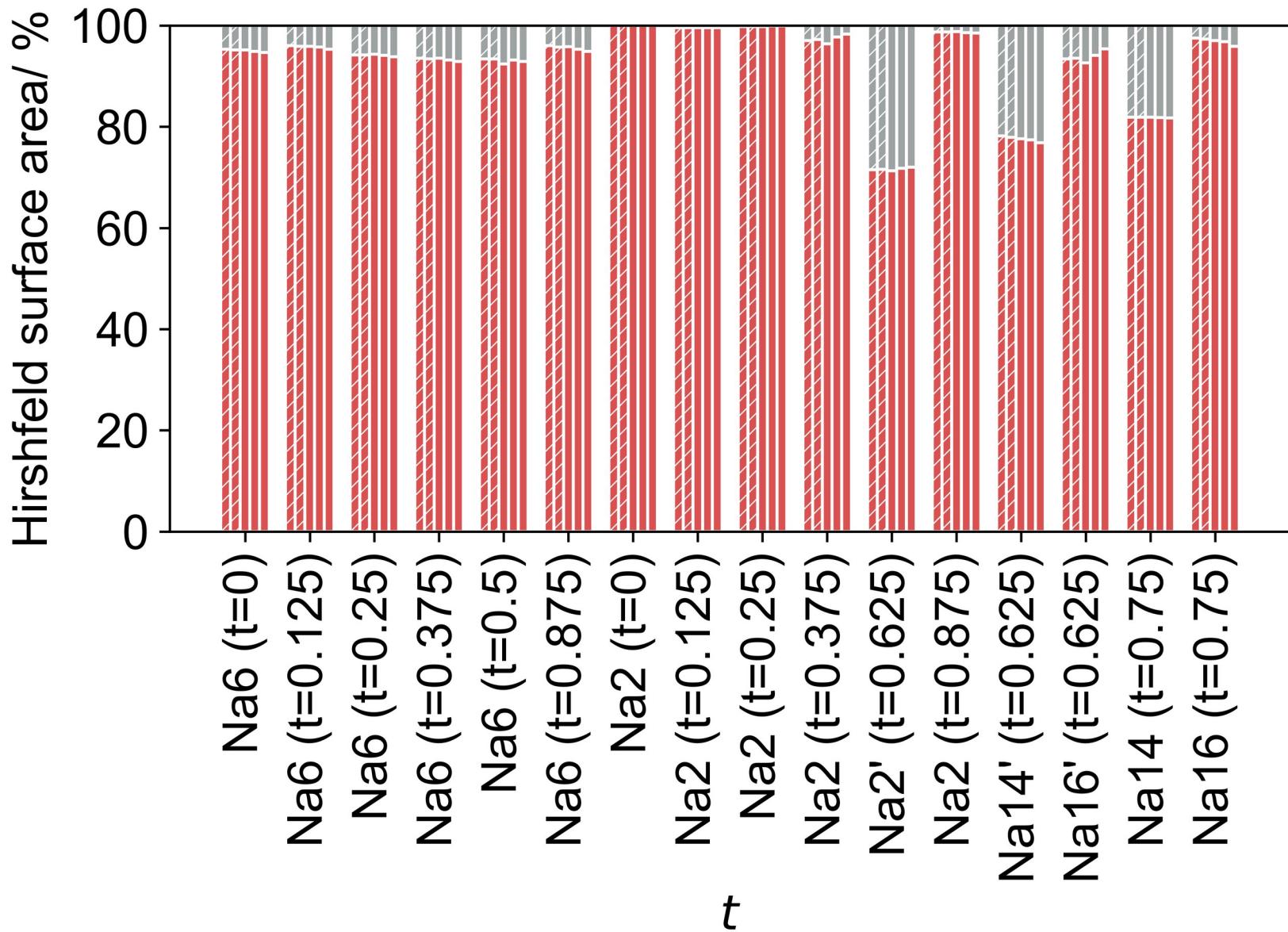
Phase	I	I	I	I	I	I	I	I
T/ K	298 <sup>2nd</sup>	298	270	250	210	170	140	130
<b>Crystal data</b>								
Formula	$\text{Na}(\text{C}_7\text{H}_4\text{NO}_3\text{S}) \cdot {}^{15}/_8 \text{H}_2\text{O}$							
Formula w.	238.94							
Crystal system	Monoclinic							
Space group	$C2/c(0,\sigma_2,0)s0$							
$\mathbf{q}, t_0$	(0, ${}^{3}/_4$ , 0), 0							
$a/ \text{\AA}$	18.74881(2)	18.74705(8)	18.72290(9)	18.70776(6)	18.67047(5)	18.62995(7)	18.60326(8)	18.59400(5)
$b/ \text{\AA}$	7.15262(4)	7.15189(8)	7.14263(9)	7.13587(8)	7.12303(9)	7.11507(8)	7.10726(6)	7.10397(7)
$c/ \text{\AA}$	29.18116(4)	29.18066(11)	29.16831(9)	29.15543(10)	29.12916(10)	29.12876(8)	29.11976(7)	29.11214(5)
$\beta/ {}^\circ$	93.77247(5)	93.77227(9)	93.75256(7)	93.73321(6)	93.66445(5)	93.55680(7)	93.49728(10)	93.48267(6)
$V/ \text{\AA}^3$	3904.80(2)	3903.97(4)	3892.34(4)	3883.88(4)	3865.98(4)	3853.68(4)	3842.99(3)	3838.36(3)
$Z, Z'$	16, 2	16, 2	16, 2	16, 2	16, 2	16, 2	16, 2	16, 2
$D_v/ \text{g cm}^{-3}$	1.6001	1.6004	1.6052	1.6087	1.6141	1.6213	1.6258	1.6278
$\mu/ \text{mm}^{-1}$	0.143	0.143	0.144	0.144	0.144	0.145	0.145	0.146
Meas. refl.	219920	219580	218918	218346	217545	216584	215953	216106
$[\sin(\theta)/\lambda]_{\max}/ \text{\AA}^{-1}$	0.75							
Unique refl.	53543	53580	53419	53302	53016	52778	52571	52512
Obs. refl.	23243	26775	27512	28963	30241	32872	34556	34771
$R_{\text{int}}(\text{obs.})$	0.0368	0.0388	0.0389	0.0383	0.0401	0.0371	0.0354	0.0353
<b>Refinement</b>								
Ref. method	Full-matrix least-squares on $F$							
No. of param.	1702	1702	1702	1702	1702	1702	1702	1702
$R_1$ (obs.)	0.0548	0.0539	0.0536	0.0534	0.0518	0.0499	0.0475	0.0471
$wR$ (all)	0.0567	0.0563	0.0559	0.0555	0.0544	0.0530	0.0517	0.0515
GoF (all)	1.74	1.95	1.95	2.03	2.04	2.14	2.21	2.22
$R_{m=0}$ (obs.)	0.0472	0.0498	0.0469	0.0474	0.0458	0.0442	0.0426	0.0426
$R_{m=\pm 1}$ (obs.)	0.0521	0.0504	0.0510	0.0496	0.0486	0.0471	0.0450	0.0451
$R_{m=\pm 2}$ (obs.)	0.0583	0.0565	0.0561	0.0567	0.0545	0.0521	0.0494	0.0486
$R_{m=\pm 3}$ (obs.)	0.0575	0.0557	0.0570	0.0557	0.0545	0.0524	0.0491	0.0488
$R_{m=\pm 4}$ (obs.)	0.0727	0.0677	0.0670	0.0681	0.0640	0.0610	0.0573	0.0558
H-atom treatment	constr.	constr.	constr.	constr.	constr.	constr.	constr.	constr.
Weighting sch.	$w = 1 / \sigma^2(F) + 0.0001F^2$							
$\Delta\rho_{\max}/ \text{e \AA}^{-3}$	1.10	0.86	1.03	1.22	1.42	1.26	1.41	1.17
$\Delta\rho_{\min}/ \text{e \AA}^{-3}$	-1.03	-0.91	-1.01	-0.93	-1.34	-1.56	-1.52	-1.53

Phase	II	II	II	II	II	II	II	III	III
T/ K	120	110	100	90	80	70	60	40	20
<b>Crystal data</b>									
Formula	Na(C <sub>7</sub> H <sub>4</sub> NO <sub>3</sub> S) · <sup>15</sup> / <sub>8</sub> H <sub>2</sub> O								
Formula w.	238.94								
Crystal system	Monoclinic						Triclinic*		
Space group	C2/c(0, $\sigma_2$ , 0)s0						C-1( $\sigma_1$ , $\sigma_2$ , $\sigma_3$ )0		
$\mathbf{q}_\parallel t_0$	(0, $\frac{3}{4}$ , 0), 0						(0, $\frac{3}{4}$ , 0), 0		
<i>a</i> / Å	18.60894(7)	18.60517(11)	18.60142(5)	18.59790(4)	18.59125(4)	18.58801(6)	18.58299(3)	18.57290(10)	18.57670(10)
<i>b</i> / Å	7.09612(5)	7.09471(7)	7.09359(7)	7.09217(5)	7.08808(6)	7.08802(8)	7.08624(6)	7.08190(10)	7.08640(10)
<i>c</i> / Å	29.07549(9)	29.07473(5)	29.07316(10)	29.07311(5)	29.06112(9)	29.06013(7)	29.04898(6)	29.02330(10)	29.04080(10)
$\beta/^\circ$	93.59123(8)	93.58434(12)	93.58574(7)	93.58194(6)	93.55830(5)	93.56348(5)	93.56293(4)	93.51100(10)**	93.53420(10)***
<i>V</i> / Å <sup>3</sup>	3831.92(3)	3830.31	3828.72(3)	3827.24(3)	3822.18(3)	3821.33(4)	3817.88(3)	3810.31(6)	3815.71(6)
<i>Z</i> , <i>Z'</i>	16, 2	16, 2	16, 2	16, 2	16, 2	16, 2	16, 2	16, 4	16, 4
<i>D<sub>v</sub></i> / g cm <sup>-3</sup>	1.6305	1.6312	1.6319	1.6325	1.6346	1.635	1.6365	1.6397	1.6374
$\mu$ / mm <sup>-1</sup>	0.146	0.146	0.146	0.146	0.146	0.146	0.146	0.147	0.146
Meas. refl.	215736	215742	215354	215114	215267	215148	214969	214582	214563
[sin( $\theta$ )/ $\lambda$ ] <sub>max</sub> / Å <sup>-1</sup>	0.75								
Unique refl.	52442	52402	52375	52326	52249	52249	52344	52280	52431
Obs. refl.	34304	34814	34863	35261	35241	35507	36098	34261	34027
<i>R</i> <sub>int</sub>	0.0360	0.0363	0.0370	0.0367	0.0403	0.0399	0.0367	0.0657	0.0793
<b>Refinement</b>									
Ref. method	Full-matrix least-squares on <i>F</i>								
No. of param.	1702	1702	1702	1702	1702	1702	1702	2045	2045
<i>R</i> <sub>1</sub> (obs.)	0.0492	0.0496	0.0491	0.0486	0.0489	0.0492	0.0482	0.0582	0.0665
<i>wR</i> (all)	0.0532	0.0535	0.0533	0.0534	0.0536	0.0537	0.0535	0.0610	0.0695
GoF (all)	2.25	2.29	2.28	2.32	2.31	2.32	2.39	2.49	2.77
<i>R</i> <sub>m=0</sub> (obs.)	0.0427	0.0439	0.0439	0.0434	0.0438	0.0437	0.0433	0.0544	0.0638
<i>R</i> <sub>m=±1</sub> (obs.)	0.0473	0.0467	0.0466	0.0460	0.0466	0.0467	0.0456	0.0564	0.0643
<i>R</i> <sub>m=±2</sub> (obs.)	0.0521	0.0521	0.0512	0.0511	0.0512	0.0520	0.0500	0.0597	0.0677
<i>R</i> <sub>m=±3</sub> (obs.)	0.0506	0.0518	0.0505	0.0502	0.0503	0.0501	0.0501	0.0595	0.0672
<i>R</i> <sub>m=±4</sub> (obs.)	0.0605	0.0602	0.0602	0.0593	0.0593	0.0605	0.0587	0.0655	0.0740
H-atom treatment	constr.	constr.	constr.	constr.	constr.	constr.	constr.	constr.	constr.
Weighting sch.	$w = 1 / \sigma^2(F) + 0.0001F^2$								
$\Delta\rho_{\text{max}}/\text{e } \text{\AA}^{-3}$	1.74	1.73	1.89	2.18	1.85	2.02	2.21	0.85	0.98
$\Delta\rho_{\text{min}}/\text{e } \text{\AA}^{-3}$	-1.57	-1.67	-1.80	-1.83	-1.80	-1.76	-1.79	-0.92	-0.91

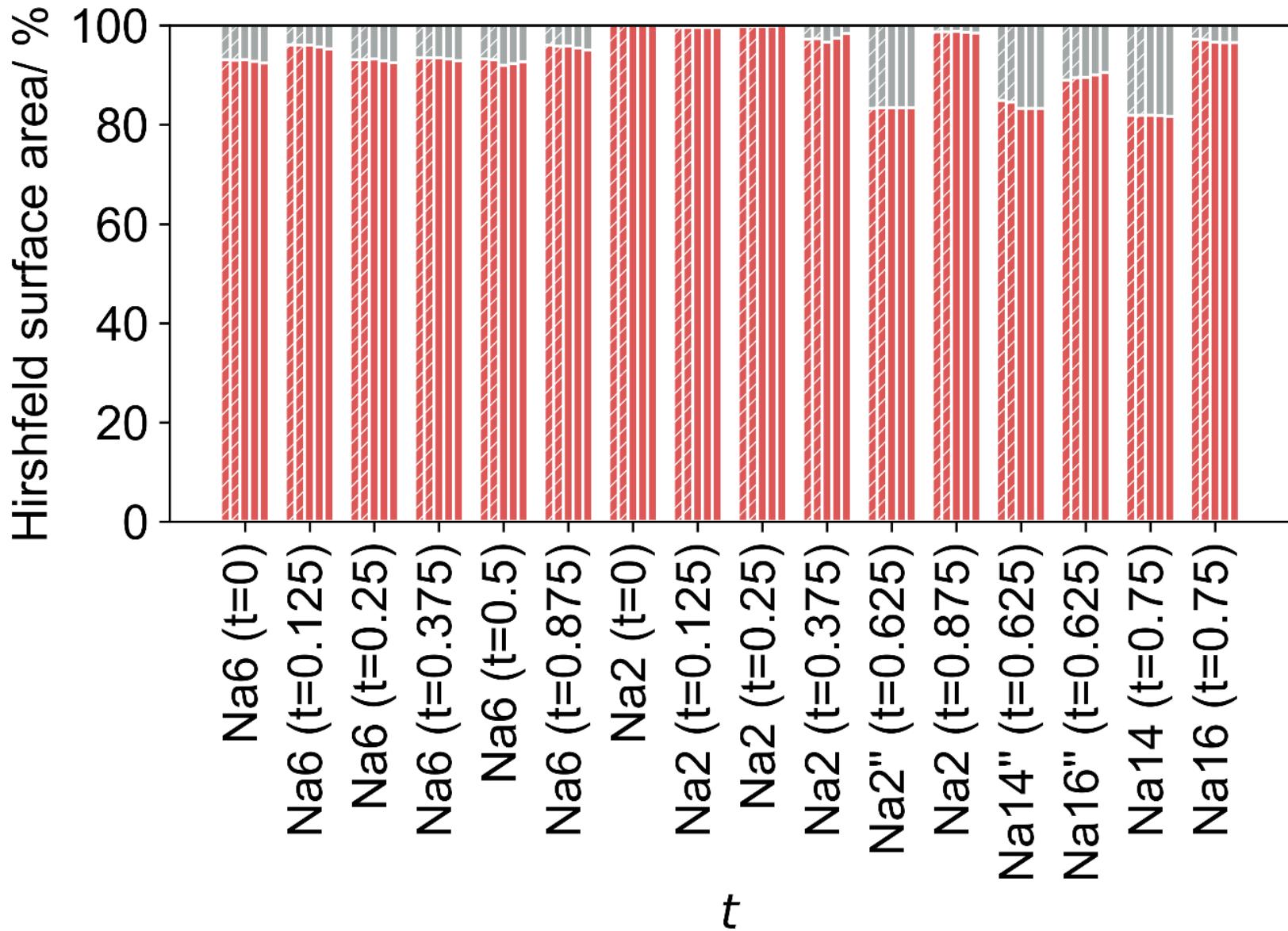
\* – pseudomerohedrally twinned with twin volume fractions virtually 0.5 : 0.5, therefore the data are averaged according to Laue class 2/m and the twin fractions are constrained to exactly 0.5 : 0.5

\*\* –  $\alpha = 89.9808(13)^\circ$ ;  $\gamma = 89.9763(14)^\circ$

\*\*\* –  $\alpha = 89.9392(2)^\circ$ ;  $\gamma = 89.9939(16)^\circ$



**Figure S1.** Hirshfeld surface area fractions defined by Na···O (red) and Na···other (gray) contacts of cations Na<sub>2</sub>. The five bars at each  $t$  value correspond to structures of primed disorder component at different temperatures (from right to left: 298, 210, 130, 120, and 60 K; phase I – regular, phase II – hatched).



**Figure S2.** Hirshfeld surface area fractions defined by Na···O (red) and Na···other (gray) contacts of cations Na<sub>2</sub>. The five bars at each  $t$  value correspond to structures of double-primed disorder component at different temperatures (from right to left: 298, 210, 130, 120, and 60 K; phase I – regular, phase II – hatched).