

Supporting Information to

Ordering phase transition with symmetry-breaking from disorder over non-equivalent sites: Calorimetric and crystallographic study of crystalline D-sorbose

Sakiko Iwagaki¹, Hiroki Kakuta², Yasuhisa Yamamura¹, Hideki Saitoh², Mafumi Hishida¹, Kazuhiro Fukada³, and Kazuya Saito*¹

¹*Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, JAPAN*

²*Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, JAPAN*

³*Department of Applied Biological Science, Faculty of Agriculture, Kagawa University, Miki-cho, Kagawa 761-0795, JAPAN*

*Correspondence: kazuya@chem.tsukuba.ac.jp (K.S.)

Contents

Table S1	Experimental heat capacities of crystalline D-sorbose
Table S2	Standard thermodynamic quantities of crystalline D-sorbose at round temperatures
Table S3	Summary of structure analyses of D-sorbose at 100 K, 210 K, and 295 K

Table S1. Experimental heat capacities of crystalline D-sorbose.

$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$
Series 1		152.358	124.03	92.758	72.994	168.467	139.33
79.240	61.635	153.955	125.59	94.005	74.077	170.106	141.04
80.456	62.554	155.542	126.96	95.236	74.989	171.774	142.79
81.651	63.610	157.159	128.46	96.451	76.043	173.469	144.61
82.828	64.615	158.804	130.06	97.653	77.125	175.153	146.45
83.986	65.617	160.438	131.56	98.894	78.154	176.825	148.42
85.184	66.597	162.061	133.08	100.175	79.213	178.487	150.45
86.419	67.686	163.675	134.62	101.441	80.257	180.174	152.65
87.637	68.725	165.316	136.23	102.694	81.298	181.887	154.88
88.871	69.744	166.985	137.85	103.933	82.324	183.587	157.33
90.123	70.779	168.644	139.58	105.210	83.369	185.275	159.98
91.412	71.848	170.292	141.21	106.524	84.414	186.950	162.79
92.739	72.979	171.931	142.99	107.824	85.488	188.647	166.02
94.074	74.131	173.595	144.83	109.112	86.558	190.365	169.82
95.416	75.195	175.286	146.76	110.388	87.568	192.067	174.36
96.740	76.317	176.966	148.62	111.727	88.705	193.749	180.11
98.101	77.474	178.634	150.67	113.128	89.788	195.408	188.17
99.499	78.628	180.291	152.76	114.516	90.913	197.065	202.42
100.879	79.778	181.973	155.03	115.890	92.018	198.958	553.65
102.243	80.880	183.678	157.56	117.253	93.130	200.965	167.66
103.590	82.002	185.371	160.18	118.650	94.272	202.873	164.52
104.974	83.149	187.051	163.16	120.083	95.472	204.782	164.99
106.391	84.370	188.717	166.22	121.500	96.804	206.684	165.82
107.793	85.470	190.403	170.08	122.903	98.097	208.614	166.86
109.180	86.608	192.106	174.67	124.295	99.359	210.573	167.96
110.552	87.729	193.791	180.56	125.720	100.67	212.524	169.03
111.959	88.887	195.450	188.89	127.179	102.02	214.506	170.25
113.400	90.025	197.074	203.82	128.625	103.37	216.519	171.52
114.827	91.183	198.620	274.87	130.060	104.63	218.561	172.88
116.240	92.285	200.876	168.01	131.483	105.86	220.630	174.18
117.640	93.464	202.640	164.36	132.939	107.16	222.690	175.49
119.073	94.716	204.406	164.80	134.428	108.48	224.741	177.06
120.538	95.958	206.200	165.55	135.905	109.70	226.782	178.32
121.988	97.222	208.021	166.60	137.371	111.03	228.851	179.77
123.424	98.556	209.835	167.54	138.827	112.24	230.946	181.15
124.847	99.854	211.642	168.61	140.314	113.54	233.032	182.70
126.301	101.20	213.442	169.61	141.833	114.89	235.152	184.17
127.787	102.59	215.267	170.80	143.341	116.20	237.305	185.70
129.260	103.92	217.119	172.01	144.839	117.52	239.485	187.28
130.722	105.18	218.964	173.07	146.326	118.73	241.692	188.88
132.172	106.42	220.801	174.23	147.844	120.13	243.889	190.51
133.652	107.75	222.631	175.64	149.392	121.49	246.076	192.18
135.164	109.02	224.485	176.71	150.930	122.86	248.322	194.08
136.663	110.35	226.364	178.03	152.458	124.28	250.669	195.87
138.152	111.61	Series 2		153.976	125.63	253.042	197.97
139.658	112.91	200.644	164.09	155.525	127.02	255.401	200.77
141.224	114.28	202.346	164.13	157.102	128.57	257.745	204.23
142.820	115.61	204.044	164.74	158.670	129.96	260.077	204.32
144.404	117.05	Series 3		160.228	131.41	262.441	204.67
145.976	118.43	88.017	68.993	161.777	132.86	264.833	206.31
147.537	119.80	89.212	70.030	163.404	134.43	267.213	207.73
149.128	121.16	90.390	71.008	165.108	136.02	269.586	208.66
150.749	122.63	91.553	72.005	166.801	137.71	271.950	210.09

Table S1. (Continued)

$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$
274.424	211.43	147.769	119.81	249.486	194.84	99.468	78.653
277.004	213.37	149.358	121.27	251.970	197.02	100.901	79.863
279.572	215.26	150.979	122.73	254.482	199.35	102.316	81.011
282.127	217.15	152.632	124.21	257.077	203.39	103.714	82.112
284.729	218.75	154.273	125.71	259.714	204.51	105.096	83.306
287.414	220.70	155.903	127.16	262.342	204.67	106.519	84.473
290.127	222.78	157.521	128.68	264.959	206.53	107.981	85.690
293.173	224.94	159.171	130.21	267.608	208.03	109.428	86.888
296.551	227.38	160.852	131.74	270.289	208.97	110.858	88.019
Series 4		162.522	133.43	272.959	210.58	112.274	89.175
170.867	141.75	164.181	134.99	275.617	212.42	113.729	90.393
Series 5		165.829	136.64	278.263	214.32	115.222	91.640
88.238	69.259	167.507	138.28	280.938	216.23	116.700	92.810
89.428	70.254	169.215	140.08	283.641	218.21	118.163	93.889
90.603	71.273	170.911	141.81	286.571	220.33	119.611	95.219
91.786	72.229	172.597	143.65	289.799	222.51	121.096	96.559
93.034	73.280	174.271	145.49	293.082	225.06	122.617	97.909
94.326	74.399	175.973	147.44	296.348	227.33	124.123	99.252
95.600	75.403	177.704	149.56	299.595	229.54	125.617	100.62
96.858	76.475	179.423	151.66	Series 6		127.098	101.96
98.100	77.523	181.131	153.87	250.754	195.00	128.616	103.33
99.385	78.602	182.826	156.26	253.342	196.85	130.169	104.70
100.709	79.692	184.548	158.76	255.915	198.62	131.708	105.99
102.018	80.770	186.295	161.65	258.475	200.49	133.236	107.29
103.313	81.859	188.028	164.75	261.066	202.34	134.781	108.63
104.593	82.894	189.747	168.29	263.689	204.17	136.394	110.05
105.913	83.983	191.450	172.49	266.298	205.98	138.043	111.42
107.271	85.099	193.172	177.76	268.894	207.84	139.678	112.87
108.614	86.236	194.907	185.15	271.478	209.70	Series 8	
109.944	87.288	196.611	196.90	274.094	211.33	6.148	0.260
111.260	88.353	198.254	226.68	276.740	213.20	6.624	0.292
112.614	89.488	200.691	219.87	279.373	215.11	7.067	0.363
114.033	90.600	202.563	164.53	281.995	216.97	7.476	0.445
115.467	91.733	204.515	164.87	284.603	218.88	7.928	0.485
116.887	92.842	206.460	165.80	287.241	220.62	8.388	0.676
118.294	94.036	208.397	166.74	289.908	222.60	8.884	0.770
119.738	95.155	210.364	167.79	292.562	224.47	9.380	0.955
121.246	96.546	212.361	169.07	295.204	226.49	9.895	1.150
122.769	97.967	214.350	170.23	297.832	228.33	10.410	1.340
124.276	99.349	216.330	171.46	Series 7		10.948	1.543
125.769	100.73	218.302	172.67	80.595	62.758	11.530	1.774
127.298	102.10	220.302	174.00	81.922	63.873	12.096	2.092
128.863	103.53	222.397	175.35	83.226	64.992	12.615	2.360
130.415	104.87	224.547	176.86	84.507	66.079	13.126	2.673
131.953	106.16	226.687	178.27	85.836	67.197	13.622	3.070
133.478	107.50	228.817	179.71	87.213	68.386	Series 9	
135.039	108.81	230.975	181.23	88.568	69.513	14.048	3.270
136.633	110.22	233.163	182.81	89.902	70.620	14.442	3.577
138.215	111.57	235.412	184.33	91.216	71.743	14.850	3.851
139.784	112.93	237.726	185.91	92.576	72.914	15.287	4.192
141.342	114.29	240.027	187.60	93.980	74.081	15.756	4.503
142.932	115.64	242.358	189.42	95.364	75.246	16.241	4.922
144.556	117.04	244.719	191.25	96.730	76.364	16.745	5.319
146.168	118.46	247.069	192.87	98.078	77.509	17.279	5.691

Table S1. (Continued)

$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$	$\frac{T_m}{K}$	$\frac{C_p}{J K^{-1} mol^{-1}}$
17.856	6.271	53.390	39.165	108.211	85.880	198.133	222.02
18.429	6.632	54.185	39.861	109.767	87.142	199.383	881.87
18.960	7.202	54.974	40.567	111.304	88.396	200.554	269.67
19.477	7.463	55.763	41.305	112.825	89.590	202.253	164.48
19.993	7.956	56.556	41.932	114.383	90.930	204.091	164.74
20.513	8.491	57.358	42.618	115.978	92.158	205.959	165.52
21.044	8.995	58.168	43.334	117.556	93.414	207.917	166.46
21.581	9.511	58.986	44.079	119.118	94.704	209.926	167.54
22.135	9.998	59.806	44.765	120.663	96.008	211.927	168.73
22.699	10.492	60.622	45.522	122.242	97.455	213.918	169.90
23.272	11.039	61.443	46.239	123.855	98.973	215.938	171.22
23.840	11.567	62.275	46.960	125.452	100.42	217.987	172.49
24.399	12.111	63.114	47.704	127.034	101.89	220.092	173.84
24.962	12.719	63.941	48.413	128.602	103.30	222.253	175.31
25.533	13.159	64.750	49.127	130.203	104.71	224.404	176.75
26.103	13.742	65.545	49.846	131.839	106.11	226.584	178.25
26.671	14.427	66.327	50.481	133.461	107.47	228.794	179.72
27.243	14.856	67.151	51.261	135.069	108.84	230.992	181.29
27.818	15.486	68.016	51.979	136.662	110.27	233.180	182.78
28.382	15.996	68.868	52.745	138.290	111.63	235.360	184.31
28.944	16.518	69.706	53.437	139.951	113.06	237.568	185.92
29.522	17.133	70.531	54.154	141.598	114.52	239.805	187.50
30.094	17.574	71.395	54.889	143.233	115.90	242.105	189.18
30.664	18.092	72.317	55.707	144.855	117.32	244.467	190.92
31.251	18.677	73.246	56.513	146.509	118.79	246.818	192.69
31.846	19.302	74.160	57.306	148.196	120.27	249.197	194.56
32.457	19.920	75.062	58.049	149.870	121.76	251.603	196.62
33.090	20.485	75.997	58.875	151.531	123.19	253.996	198.94
33.745	21.066	76.968	59.685	153.181	124.67	256.374	202.17
34.420	21.768	77.949	60.552	154.862	126.24	258.735	204.72
35.107	22.366	78.955	61.387	156.574	127.81	261.127	204.08
35.802	23.081	79.964	62.265	158.274	129.40	263.552	205.29
36.502	23.727	81.007	63.176	159.962	130.96	265.966	207.18
37.204	24.407	82.086	64.051	161.639	132.53	268.370	208.23
37.908	25.001	83.176	64.927	163.346	134.20	270.819	209.20
38.626	25.650	84.276	65.960	165.083	135.87	273.352	210.95
39.370	26.394	85.362	66.843	166.808	137.63	275.973	212.67
40.131	27.089	86.481	67.772	168.521	139.35	278.703	214.65
40.867	27.807	87.634	68.795	170.223	141.12	281.514	216.65
41.589	28.515	88.771	69.720	171.953	142.97	284.410	218.67
42.343	29.181	89.893	70.564	173.712	144.89	287.405	220.89
43.118	29.901	91.001	71.575	175.460	146.89	290.544	223.10
43.898	30.614	92.142	72.565	177.196	148.87	293.779	225.45
44.680	31.350	93.315	73.554	178.920	151.05	296.995	227.77
45.459	32.009	94.473	74.525	180.671	153.37	300.195	230.00
46.246	32.779	95.618	75.507	182.448	155.74	303.425	232.32
47.042	33.522	96.750	76.444	184.212	158.25	306.684	234.59
47.837	34.251	97.913	77.364	185.963	161.05	309.925	236.88
48.634	34.897	99.106	78.284	187.700	164.07	313.147	239.20
49.433	35.687	100.286	79.298	189.460	167.71	316.350	241.51
50.232	36.385	101.454	80.350	191.240	171.95	319.584	243.77
51.029	37.089	102.640	81.291	193.001	177.20	322.847	245.91
51.812	37.790	105.101	83.288	194.740	184.32	326.091	248.30
52.595	38.451	106.637	84.571	196.447	195.24	329.317	250.53

Table S1. (Continued)

$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T_m}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$
Series 10		Series 11		Series 12		Series 15	
220.535	174.36	240.682	187.97	210.787	167.76	240.552	187.83
222.833	175.65	243.045	189.78	212.779	169.12	242.914	189.47
225.119	177.17	245.396	191.30	214.763	170.40	245.265	191.14
227.395	178.75	247.737	192.90	216.739	171.35	247.605	192.83
229.700	180.34	250.107	194.74	218.743	172.97	249.933	194.45
232.036	181.97	252.506	196.31	220.777	174.09	252.250	196.01
234.360	183.61	254.893	197.94	222.803	175.19	254.557	197.77
236.673	185.25	257.269	199.84	224.885	176.86	256.854	199.35
238.973	186.79	259.635	201.23	227.021	178.42	259.140	201.09
241.304	188.49	262.029	203.13	229.187	179.83	261.415	202.96
243.664	190.23	264.452	203.92	231.383	181.35	263.678	205.48
246.012	191.90	266.860	206.12	233.568	182.70	265.929	207.25
248.350	193.70	269.259	208.50	235.743	184.60	268.171	208.57
250.676	195.49	271.648	209.96	237.979	185.96	270.406	209.18
253.030	197.42	274.066	211.58	240.317	187.97	272.635	210.49
255.412	199.69	276.512	213.37	242.685	189.27	274.856	211.86
257.778	202.62	278.947	215.07	245.042	191.17	277.107	213.50
260.130	204.18	281.371	216.82	247.386	193.09	279.425	215.14
262.476	204.74	283.785	218.41	249.719	194.87	281.809	216.91
264.851	206.23	286.225	220.38	252.080	196.82	284.257	218.74
267.254	207.89	288.691	222.40	254.468	199.34	286.815	220.40
269.649	208.73	291.147	223.90	Series 13		289.445	222.41
272.036	210.19	293.592	225.68	256.844	202.88	292.124	224.36
274.413	211.54	296.110	227.54	259.192	204.77	294.946	226.30
276.874	213.48			Series 14		297.999	228.63
279.504	215.30			261.536	203.28		

Table S2. Standard thermodynamic quantities of crystalline D-sorbose at round temperatures.

T K	C_p J K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(298.15 \text{ K})$ kJ mol ⁻¹	$S^\circ(T) - S^\circ(298.15 \text{ K})$ J K ⁻¹ mol ⁻¹
10	1.18	-36.020	-223.01
20	8.004	-35.979	-220.39
30	17.56	-35.851	-215.36
40	26.99	-35.628	-209.01
50	36.12	-35.313	-202.00
60	45.01	-34.907	-194.63
70	53.71	-34.413	-187.03
80	62.27	-33.833	-179.30
90	70.74	-33.168	-171.48
100	79.12	-32.419	-163.59
110	87.34	-31.586	-155.66
120	95.45	-30.673	-147.72
Glass transition around 120 K			
130	104.50	-29.673	-139.72
140	113.12	-28.584	-131.66
150	121.84	-27.410	-123.56
160	130.99	-26.146	-115.40
170	140.89	-24.788	-107.17
180	152.41	-23.323	-98.804
190	168.87	-21.725	-90.164
195	185.65	-20.844	-85.590
Phase transition at 199.5 K			
205	165.10	-18.282	-72.760
210	167.59	-17.451	-68.754
220	173.81	-15.744	-60.816
230	180.52	-13.973	-52.944
240	187.67	-12.132	-45.111
250	195.24	-10.218	-37.298
260	204.35	-8.2143	-29.440
270	208.83	-6.1505	-21.652
280	215.56	-4.0300	-13.941
290	222.70	-1.8388	-6.2527
298.15	228.53	0	0

300	229.86	0.4240	1.4177
310	236.99	2.7583	9.0712
320	244.04	5.1635	16.707
330	250.95	7.6386	24.323

Standard thermodynamic functions of crystalline D-sorbose were obtained from the smoothed value of measured heat capacities of well equilibrated runs (Series 3 & 9 in Table S1), except for the narrow temperature region between 195.0 K and 205.0 K, within which the main phase transition occurs at 199.5 K. The enthalpy and entropy changes in the region were calculated directly from the measured heat capacities within 0.1 % in the accuracy.

The standard functions of enthalpy $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ and entropy $\{S^\circ(T) - S^\circ(298.15 \text{ K})\}$ were calculated as tabulated in Table S2, based on the smoothed heat capacity C_p according to the following equations:

$$H^\circ(T) - H^\circ(298.15 \text{ K}) = \int_{298.15}^T C_p dT$$

and

$$S^\circ(T) - S^\circ(298.15 \text{ K}) = \int_{298.15}^T \frac{C_p}{T} dT.$$

Note that the C_p , $[H^\circ(T) - H^\circ(298.15 \text{ K})]$, and $[S^\circ(T) - S^\circ(298.15 \text{ K})]$ are not proper but apparent thermodynamic quantities below ca. 130 K, because crystalline D-sorbose undergoes the glass transition around 120 K, below which the system is out of thermodynamic equilibrium.

Table S3. Summary of structure analyses of D-sorbose at 100 K, 210 K, and 295 K.

Empirical formula	C ₆ H ₁₂ O ₆		
Formula weight	180.16		
Absorption coefficient	0.149 mm ⁻¹	0.147 mm ⁻¹	0.146 mm ⁻¹
<i>F</i> (000)		384	
Radiation		Mo <i>K</i> α	
Wavelength		0.71073 Å	
Crystal size	0.16 x 0.10 x 0.06 mm ³	0.16 x 0.10 x 0.06 mm ³	0.20 x 0.10 x 0.04 mm ³
CCDC No.	1990268	1990267	1990266
<i>T</i> / K	100	210	295
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	6.4999(7)	6.5258(2)	6.5372(1)
<i>b</i> / Å	18.1977(20)	18.0150(6)	18.0528(3)
<i>c</i> / Å	6.1935(7)	6.2922(2)	6.3059(1)
<i>β</i> / °	93.562(5)	90	90
<i>V</i> / Å ³	731.18(14)	739.73(4)	744.19(2)
<i>Z</i>	4	4	4
<i>θ</i> range	2.24 ° < <i>θ</i> < 30.07 °	2.26 ° < <i>θ</i> < 30.08 °	2.26 ° < <i>θ</i> < 30.02 °
Index range	−9 < <i>h</i> < 9	−9 < <i>h</i> < 9	−9 < <i>h</i> < 9
	−25 < <i>k</i> < 25	−25 < <i>k</i> < 25	−25 < <i>k</i> < 25
	−8 < <i>l</i> < 8	−8 < <i>l</i> < 8	−8 < <i>l</i> < 8
Reflection collected	64544	37989	25714
Completeness in <i>θ</i> range	99.8%	99.8%	99.8%
Absorption correction	TWINABS	SADABS	SADABS
Max. and min. transmission	0.99, 0.95	0.99, 0.96	0.99, 0.93
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Hydrogens	difference map	difference map & calculated	difference map & calculated
Data/restraints/parameters	64544/1/314	2169/13/172	2173/14/171
Ratio of twin components	0.496(1) : 0.504(1)	—	—
Goodness-of-fit on <i>F</i> ²	1.059	1.132	1.176
Final <i>R</i> index [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> = 0.0279	<i>R</i> = 0.0286	<i>R</i> = 0.0302
Final <i>R</i> indices (all data)	<i>R</i> = 0.0287, <i>wR</i> = 0.0718	<i>R</i> = 0.0290, <i>wR</i> = 0.0828	<i>R</i> = 0.0325, <i>wR</i> = 0.0908
Largest diff. peak and hole	0.320/−0.259	0.310/−0.146	0.258/−0.134
Absolute structure			
Flack <i>x</i> (Parsons method)	0.04(7)	−0.05(8)	0.09(19)