Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Giant strain geared to transformable H-bonded network in compressed β-D-mannose

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Figures

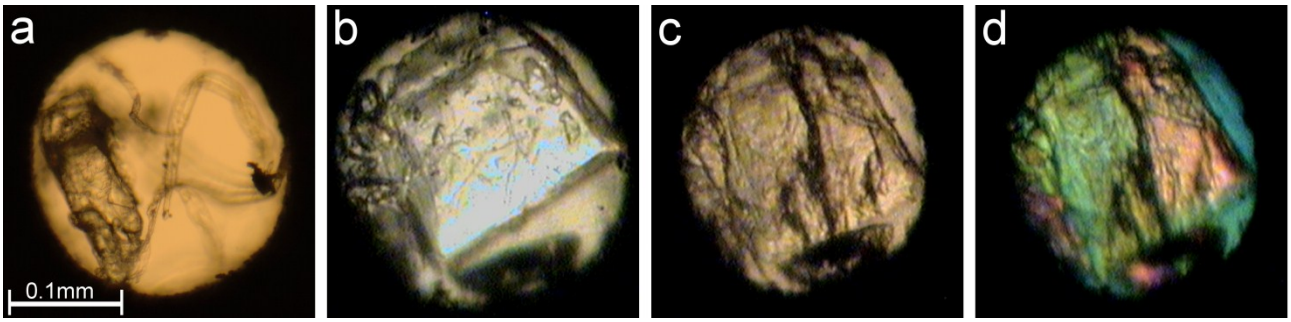

Figure S1. Crystals of β-D-mannose (a) Phase I at 0.48(2) GPa and (b) at ambient pressure just after closing the DAC, and (c,d) Phase II at 2.80(2) GPa shown without and with polarized light, respectively.

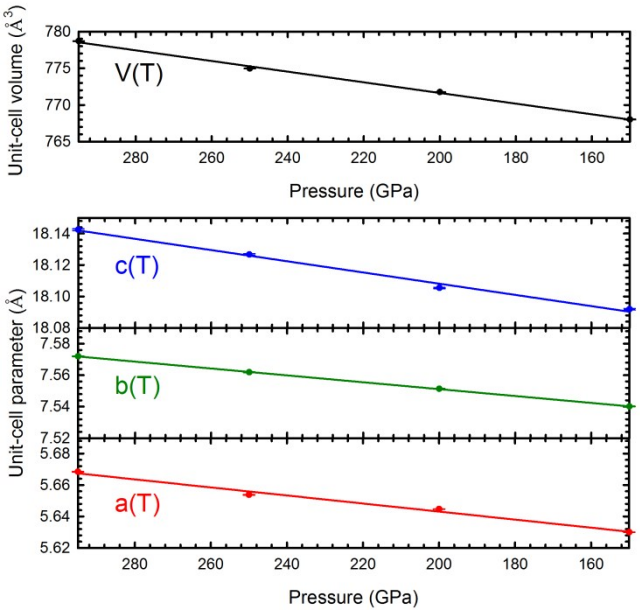

Figure S2. Temperature dependence of unit-cell volume and parameters of β-D-mannose Phase I.

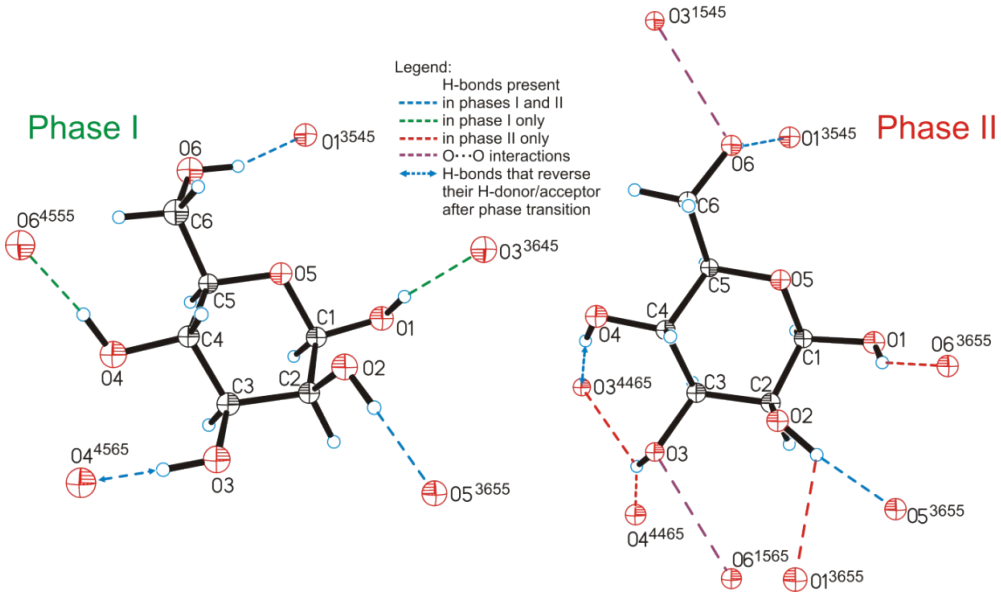

Figure S3. *β*-D-Mannose molecule in Phases I and II, viewed along axis *a* with hydrogen bonds marked on the donor site. H-Bonds existing in both phases, in Phase I only and in Phase II only are marked in blue, green and red, respectively. Unfavorable oxygen-oxygen contact O3···O6^{1565}/ O6···O3^{1545} present in Phase II is marked in purple and is shown from the perspective of both atoms O3 and O6 (thus only one of them is symmetry-independent). ORTEP symmetry code[1] is explicitly explained in Table S3.

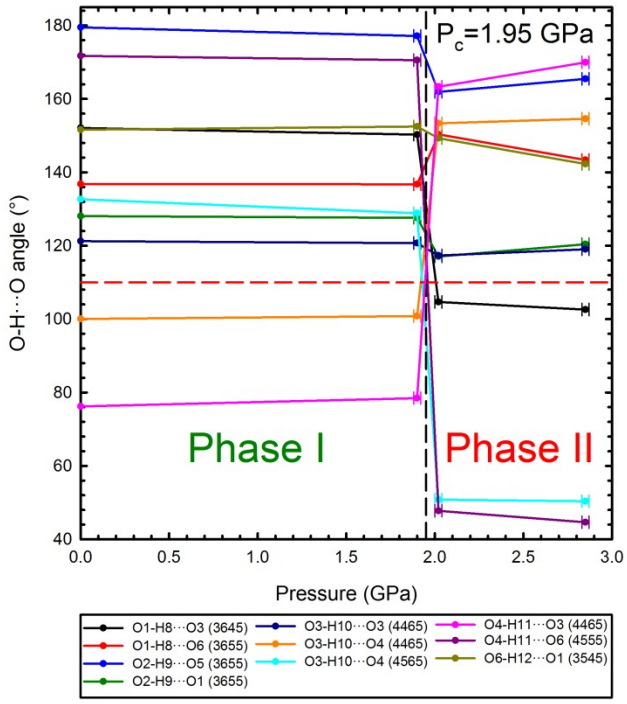

Figure S4. Pressure dependence of O-H···O angles in OH···O hydrogen bonds of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition and the limiting angle equal 110° (see Experimental) are marked with black and red dashed lines, respectively.

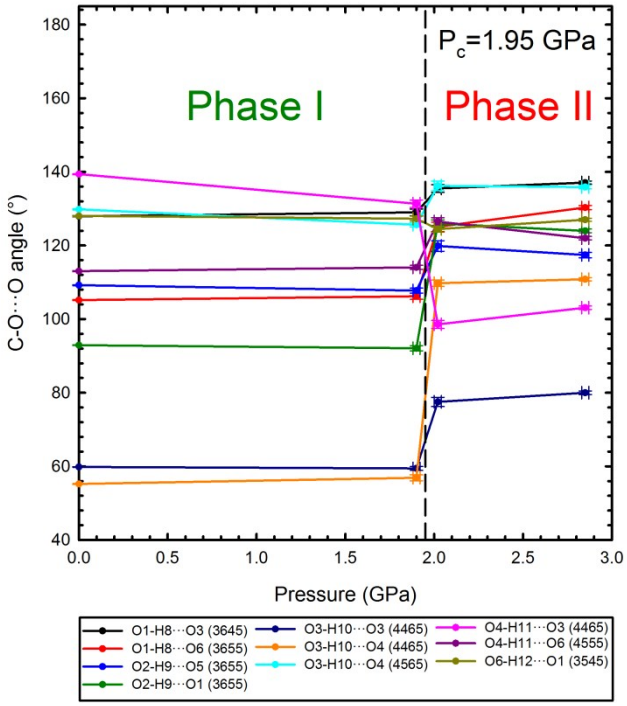

Figure S1. Pressure dependence of C-O···O angles in OH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition is marked with black dashed line.

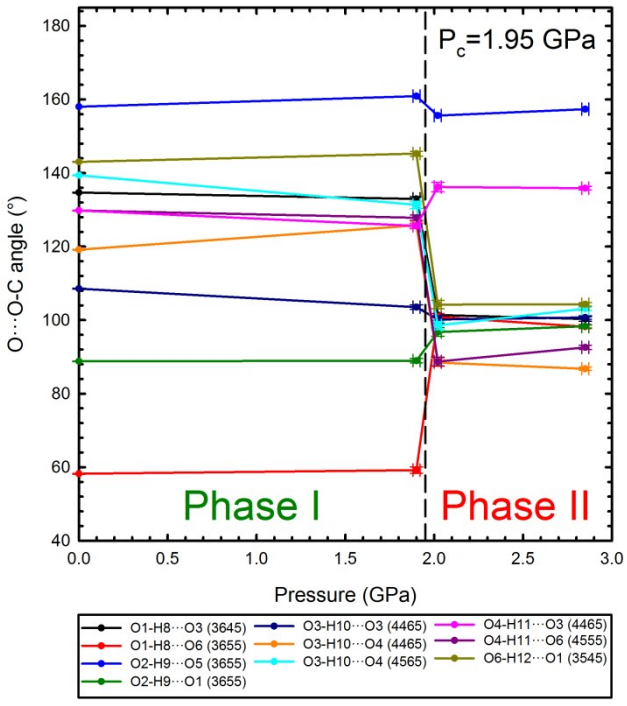

Figure S2. Pressure dependence of O···O-C angles in OH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition is marked with black dashed line.

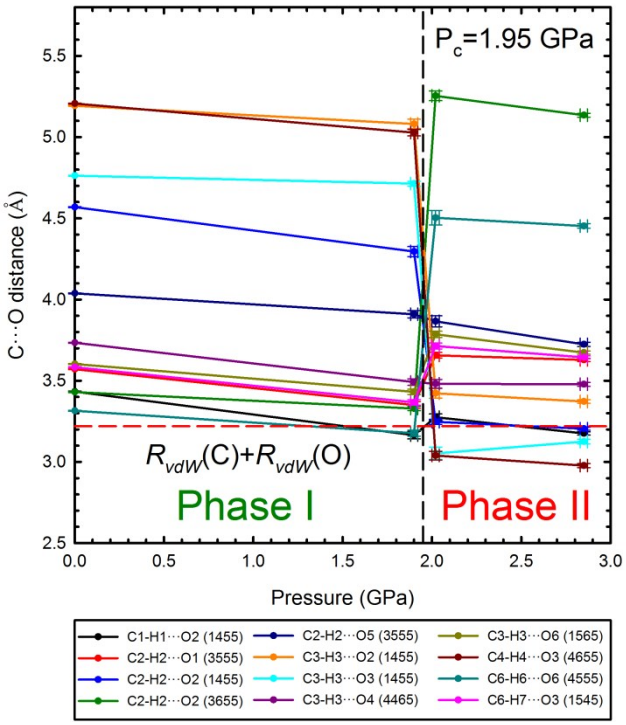

Figure S3. Pressure dependence of C···O distances in CH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition and sum of Van der Waals radii equal 3.22 Å of carbon and oxygen atoms[2] are marked with black and red dashed lines, respectively.

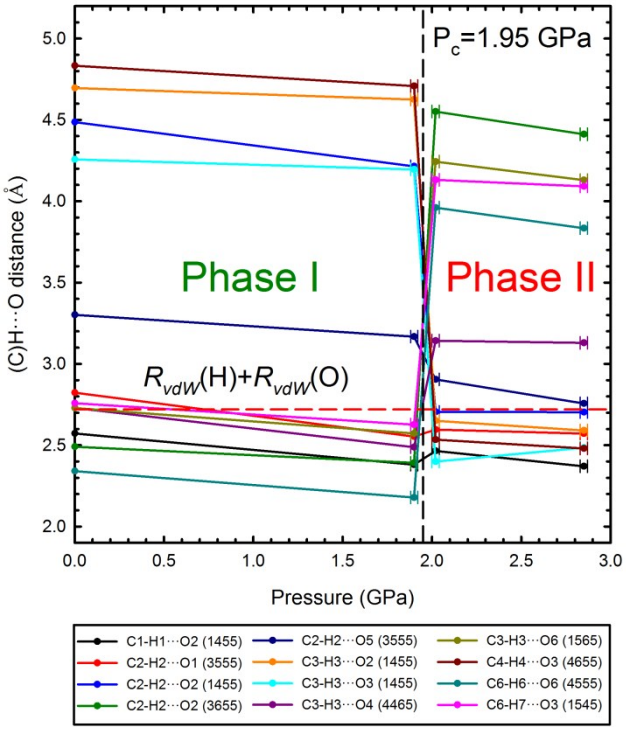

Figure S4. Pressure dependence of H···O distances in CH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition and sum of Van der Waals radii equal 2.72 Å of hydrogen and oxygen atoms[2] are marked with black and red dashed lines, respectively.

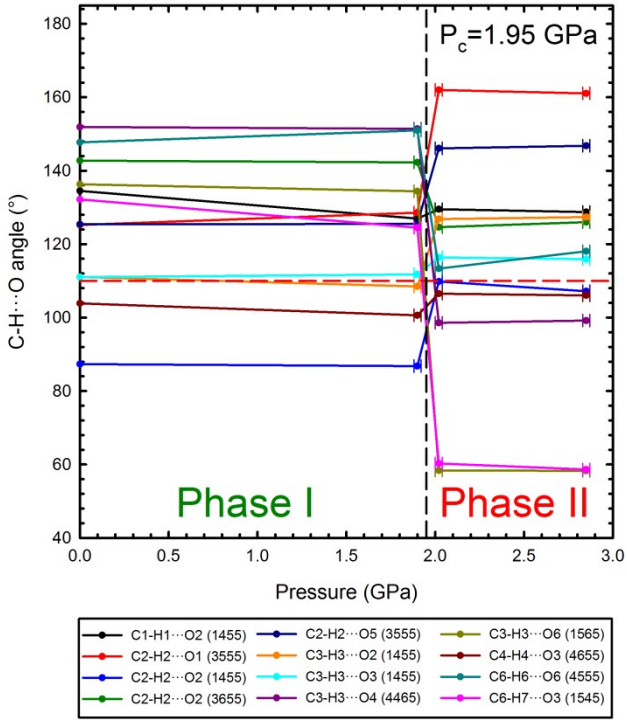

Figure S5. Pressure dependence of C-H···O angles in CH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition and the limiting angle equal 110° (see Experimental) are marked with black and red dashed lines, respectively.

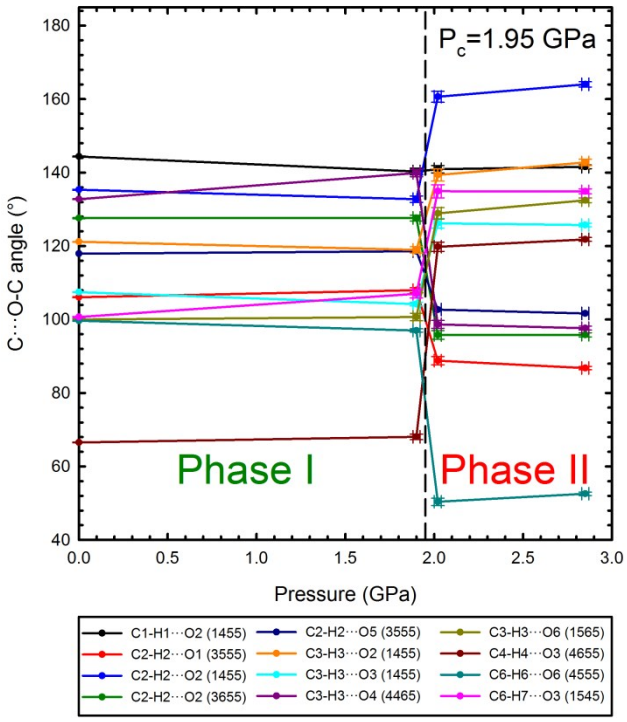

Figure S6. Pressure dependence of C···O-C angles in CH···O contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition is marked with black dashed line.

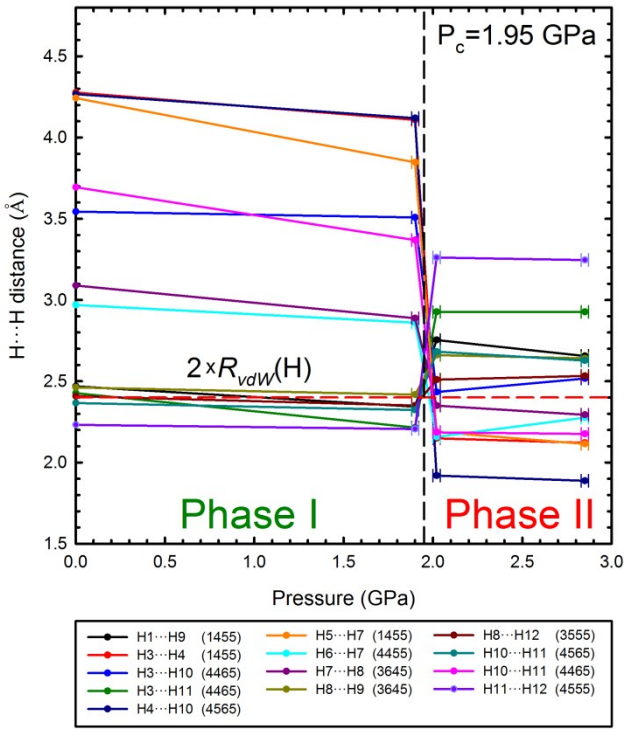

Figure S7. Pressure dependence of H···H distances in H···H contacts of *β*-D-mannose Phases I and II. Lines joining points are for guiding the eye only. Symmetry ORTEP codes[1] are explicitly explained in Table S3. The critical pressure (P_c=1.95 GPa) of the phase transition and sum of Van der Waals radii equal 2.40 Å of two hydrogen atoms[2] are marked with black and red dashed lines, respectively.

Tables

Table S1. Crystallographic and experimental data for *β*-D-mannose crystal structures in temperature range 150-295 K.

$C_6H_{12}O_6$	**Phase I**	**Phase I**	**Phase I**	**Phase I**
Pressure (GPa)	0.0001	0.0001	0.0001	0.0001
Temperature (K)	295	250	200	150
Formula weight	180.16	180.16	180.16	180.16
Crystal colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.23x0.10x0.08	0.23x0.10x0.08	0.23x0.10x0.08	0.23x0.10x0.08
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions (Å)				
a	5.6684(2)	5.6537(2)	5.64474(13)	5.62999(16)
b	7.5720(2)	7.5619(2)	7.55135(17)	7.5401(2)
c	18.1425(5)	18.1266(5)	18.1054(4)	18.0919(5)
Volume (Å^3)	778.69(4)	774.96(4)	771.75(3)	768.02(4)
Z	4	4	4	4
D_x (g cm^{-3})	1.537	1.544	1.551	1.558
Wavelength λ (Å)	1.54184	1.54184	1.54184	1.54184
Absorption coefficient (mm^{-1})	1.218	1.224	1.229	1.235
F(000) (e)	384	384	384	384
2θ max (°)	147.32	147.68	147.57	147.51
Min./Max. indices				
h	-6/7	-6/7	-6/7	-6/6
k	-9/8	-9/8	-8/9	-9/8
l	-21/22	-21/22	-22/21	-21/22
Reflections collected/unique	5200/1541	5225/1534	5239/1532	5219/1524
R_{int}	0.0268	0.0287	0.0238	0.0233
Observed reflections (I>4σ$_I$)	1434	1439	1483	1478
Data/parameters	1541/109	1534/145	1532 /109	1524/145
Goodness of fit on F^2	1.055	1.038	1.085	1.055
Final R_1 indices (I>4σ$_I$)	0.0319	0.0306	0.0283	0.0266
R_1/wR_2 indices (all data)	0.0354/ 0.0782	0.0330/0.0790	0.0293/0.0723	0.0274/0.0670
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.121, -0.163	0.172, -0.138	0.194, -0.258	0.166, -0.135
Weighting scheme[a]: x; y	0.0359; 0.1323	0.0420, 0.0972	0.0335, 0.1831	0.0334, 0.1913
Extinction coefficient	–	–	–	–
Absorption corrections	sample crystal	sample crystal	sample crystal	sample crystal
Sample transmission min/max	0.89 / 1.00	0.83 / 1.00	0.89 / 1.00	0.91 / 1.00

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$

Table S2. High-pressure crystallographic and experimental data for *β*-D-mannose crystal structures in 0.48-2.85 GPa pressure range. Due to the poor quality of data collected at 1.00 GPa, inhibiting the structure solution, this pressure point was excluded from the table and only unit-cell parameters were included in the Figure 2.

$C_6H_{12}O_6$	**Phase I**	**Phase I**	**Phase I**	**Phase II**	**Phase II**	**Phase II**	**Phase II**
Pressure (GPa)	0.48(2)	1.60(2)	1.90(2)	2.02(2)	2.10(2)	2.35(2)	2.85 (2)
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
Formula weight	180.16	180.16	180.16	180.16	180.16	180.16	180.16
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.20x0.15x0.10	0.20x0.15x0.11	0.16x0.15x0.10	0.18x0.15x0.10	0.20x0.11x0.10	0.20x0.10x0.07	0.19x0.18x0.10
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions (Å)							
a	5.577(2)	5.3889(10)	5.375(18)	4.609(3)	4.620(3)	4.58(3)	4.5744(6)
b	7.5481(7)	7.4568(8)	7.436(4)	8.438(6)	8.422(5)	8.401(8)	8.386(3)
c	18.060(3)	17.8288(19)	17.849(8)	17.40(9)	17.29(3)	17.20(5)	17.212(16)
Volume (Å^3)	760.3(3)	716.43(17)	713(2)	677(3)	672.9(14)	662(4)	660.3(6)
Z	4	4	4	4	4	4	4
D_x (g cm^{-3})	1.574	1.670	1.678	1.768	1.778	1.806	1.812
Wavelength λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.56087
Absorption coefficient (mm^{-1})	0.143	0.152	0.152	0.160	0.161	0.164	0.164
F(000) (e)	384	384	384	384	384	384	384
2θ max (°)	51.98	51.80	52.29	51.97	52.74	51.51	69.84
Min./Max. indices							
h	-4/4	-4/4	-2/2	-5/5	-5/5	-3/3	-7/7
k	-9/9	-8/8	-8/9	-10/10	-9/9	-10/9	-11/11
l	-17/17	-18/18	-19/19	-7/7	-11/11	-16/16	-13/13
Reflections collected/unique	2169/507	2318/623	2001/443	1599/333	1817/476	1474/331	4038/717
R_{int}	0.1296	0.0545	0.0984	0.1546	0.0879	0.2644	0.1028
Observed reflections (I>4σ$_I$)	358	483	299	198	288	144	469
Data/parameters	507/50	623/49	443/49	333/39	476/44	331 / 39	717/49
Goodness of fit on F^2	1.006	1.134	1.001	0.942	1.009	1.007	1.013
Final R_1 indices (I>4σ$_I$)	0.0744	0.0550	0.0737	0.0754	0.0614	0.1163	0.0706
R_1/wR_2 indices (all data)	0.0933/0.1591	0.0719/0.1386	0.1005/0.1403	0.1108/0.1173	0.0943/0.1220	0.1668/0.2857	0.0975/0.1697
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (eÅ^{-3})	0.243, -0.242	0.269, -0.223	0.171, -0.202	0.181, -0.156	0.177, -0.174	0.301, -0.307	0.258, -0.214
Weighting scheme[a]: x; y	0.0637; 0	0.0690, 0.2755	0.0485; 0	0.0037; 0	0.0438; 0	0.0989; 0	0.0749; 0
Extinction coefficient	0.10(2)	–	–	–	–	–	–

[a] $w = 1/(\sigma^2(Fo^2)+x^2P^2+yP)$, where $P=(\mathrm{Max}(Fo^2, 0)+2Fc^2)/3$

Table S3. ORTEP symmetry code.[1]

ORTEP code	Symmetry code
1455	-½-x, y, z
1545	x, -1+y, z
1565	x, 1+y, z
3545	-x, -½+y, ½-z
3555	-x, ½+y, ½-z
3645	1-x, -½-y, ½-z
3655	1-x, ½+y, ½-z
4455	-½+x, ½-y, -z
4465	-½+x, 1½-y, -z
4555	½+x, ½-y, -z
4565	½+x, 1½-y, -z

Table S4. Geometry of OH···H hydrogen bonds in *β*-D-mannose Phases I and II. Symmetry ORTEP codes[1] are explicitly explained in Table S3.

		0.1MPa	0.48(2)GPa	1.60(2)GPa	1.90(2)GPa	2.02(2)GPa	2.10(2)GPa	2.35(2)GPa	2.85(2)GPa
O1-H8···O3^{3645}	O···O	2.768(3)	2.793(14)	2.700(10)	2.713(17)	4.210(27)	4.231(13)	4.140(33)	4.204(11)
	H···O	1.874	1.885	1.802	1.828	3.858	3.908	3.872	3.885
	O-H···O	152.1	154.8	152.7	150.3	104.7	102.9	99.3	102.6
	C-O···O	127.9(2)	126.2(8)	127.3(6)	129.0(9)	135.5(11)	137.0(6)	145.5(15)	137.1(4)
	O···O-C	134.7(1)	134.4(6)	133.4(4)	133.0(6)	101.4(17)	102.7(8)	106.3(15)	100.3(6)
O1-H8···O6^{3655}	O···O	5.223(3)	5.162(15)	5.018(10)	4.963(21)	2.582(20)	2.634(11)	2.628(37)	2.641(9)
	H···O	4.474	4.412	4.267	4.212	1.692	1.780	1.817	1.798
	O-H···O	136.8	136.8	136.8	136.7	150.3	144.9	139.0	143.4
	C-O···O	105.2(1)	103.0(8)	104.0(5)	106.2(8)	125.1(13)	129.3(8)	135.7(20)	130.3(6)
	O···O-C	58.2(1)	59.8(7)	60.2(5)	59.2(8)	100.9(9)	99.6(6)	105.7(17)	98.2(4)
O2-H9···O5^{3655}	O···O	2.894(2)	2.860(11)	2.824(8)	2.792(13)	2.884(28)	2.801(13)	2.905(30)	2.773(12)
	H···O	1.924	1.890	1.855	1.823	1.944	1.852	1.948	1.823
	O-H···O	179.5	178.7	177.9	177.2	161.9	165.2	168.5	165.5
	C-O···O	109.2(1)	108.6(6)	108.1(5)	107.7(7)	119.9(15)	117.9(7)	115.2(16)	117.4(7)
	O···O-C	158.0	156.5	157.8	160.9	155.6	160.0	163.2	157.4
O2-H9···O1^{3655}	O···O	3.563(2)	3.561(12)	3.531(9)	3.514(15)	3.045(17)	3.087(9)	3.061(27)	3.042(8)
	H···O	2.882	2.880	2.856	2.837	2.478	2.484	2.364	2.433
	O-H···O	128.1	128.1	127.5	127.6	117.1	120.1	128.3	120.4
	C-O···O	92.9(1)	92.7(6)	91.7(4)	92.1(7)	126.0(10)	123.3(6)	120.1(17)	124.0(5)
	O···O-C	88.8(1)	88.2(6)	87.5(4)	89.0(6)	96.8(12)	98.3(6)	108.2(14)	98.4(5)
O3-H10···O3^{4465}	O···O	5.317(3)	5.256(13)	5.233(10)	5.255(12)	3.014(28)	3.044(10)	3.036(25)	3.041(10)
	H···O	4.749	4.692	4.676	4.693	2.440	2.475	2.567	2.449
	O-H···O	121.2	120.9	120.3	120.7	117.3	117.2	109.8	119.0
	C-O···O	59.8(1)	59.6(5)	59.0(3)	59.4(5)	77.5(13)	77.2(7)	69.8(15)	80.0(5)
	O···O-C	108.6(1)	107.6(6)	105.7(4)	103.5(6)	100.2(11)	102.8(6)	108.2(15)	100.7(5)
O3-H10···O4^{4565} (T)	O···O	2.934(3)	2.905(15)	2.835(10)	2.910(18)	2.907(15)	2.883(10)	2.680(34)	2.865(8)
	H···O	2.189	2.171	2.113	2.201	3.421	3.365	2.975	3.385
	O-H···O	132.7	131.4	129.9	128.9	50.8	52.8	63.1	50.4
	C-O···O	129.8(1)	129.2(6)	127.0(4)	125.6(6)	136.2(13)	138.7(8)	152.3(20)	135.9(5)
	O···O-C	139.4(2)	137.9(8)	135.7(5)	131.4(10)	98.6(11)	101.2(6)	99.7(17)	103.1(5)
O3-H10···O4^{4465}	O···O	4.358(3)	4.270(17)	4.119(11)	4.041(20)	2.703(14)	2.722(10)	2.969(32)	2.707(8)
	H···O	4.083	3.989	3.839	3.745	1.800	1.814	2.077	1.799
	O-H···O	100.0	100.3	99.9	100.8	153.3	154.5	152.0	154.6
	C-O···O	55.2(1)	55.5(7)	54.3(4)	56.9(8)	109.8(9)	107.5(6)	97.3(19)	110.8(4)
	O···O-C	119.2(1)	120.4(7)	122.0(5)	125.8(10)	88.5(11)	88.5(7)	89.6(16)	86.8(5)
O4-H11···O3^{4465} (T)	O···O	2.934(3)	2.905(15)	2.835(10)	2.910(18)	2.907(15)	2.883(10)	2.679(34)	2.865(8)
	H···O	3.010	2.957	2.865	2.944	1.964	1.929	1.732	1.905
	O-H···O	76.2	77.5	78.5	78.5	163.3	167.2	164.5	170.0
	C-O···O	139.4(2)	137.9(8)	135.7(5)	131.4(10)	98.6(11)	101.2(6)	99.7(17)	103.1(5)
	O···O-C	129.8(1)	129.2(6)	127.0(4)	125.6(6)	136.2(13)	138.7(8)	152.3(20)	135.9(5)
O4-H11···O6^{4555}	O···O	2.700(2)	2.690(11)	2.642(8)	2.646(11)	3.303(25)	3.300(12)	3.415(36)	3.246(10)
	H···O	1.736	1.723	1.679	1.685	3.875	3.898	3.971	3.864
	O-H···O	171.7	173.8	171.7	170.5	47.8	46.1	49.1	44.6
	C-O···O	113.0(1)	113.2(6)	113.7(4)	114.0(6)	126.5(11)	124.4(6)	126.0(20)	122.0(5)
	O···O-C	129.8(1)	129.5(7)	128.3(5)	127.8(7)	88.7(12)	91.5(7)	88.8(17)	92.6(6)
O6-H12···O1^{3545}	O···O	2.695(2)	2.696(12)	2.629(8)	2.661(12)	2.556(18)	2.579(11)	2.679(38)	2.555(9)
	H···O	1.802	1.805	1.732	1.763	1.672	1.720	1.806	1.717
	O-H···O	151.6	151.2	152.1	152.5	149.3	145.6	148.2	142.3
	C-O···O	128.0(1)	128.3(7)	127.5(5)	127.3(7)	124.4(9)	125.1(5)	122.1(16)	127.0(4)
	O···O-C	143.0(2)	144.2(6)	146.2(5)	145.3(7)	104.2(12)	103.6(6)	100.5(18)	104.3(5)
O3···O6^{1565}/ O6···O3^{1545}	O···O	3.618(3)	3.538(15)	3.430(10)	3.355(17)	2.974(23)	2.920(10)	2.880(22)	2.866(9)
	C-O···O	78.0(1)/ 77.3(2)	79.1(8)/ 78.9(8)	77.9(5)/ 78.3(5)	81.7(10)/ 77.8(9)	112.4(19)/ 108.1(16)	113.5(8)/ 111.3(8)	112.9(13)/ 113.0(14)	113.5(6)/ 111.6(6)
	O···O-C	77.3(2)/ 78.0(1)	78.9(8)/ 79.1(8)	78.3(5)/ 77.9(5)	77.8(9)/ 81.7(10)	108.1(16)/ 112.4(19)	111.3(8)/ 113.5(8)	113.0(14)/ 112.9(13)	111.6(6)/ 113.5(6)

Bonds present in both, Phase I and II Bonds present only in Phase I Bonds present only in Phase II

O···O interactions Letter (T) indicates H-bonds reversing their polarity at the phase-transition

Table S5. Geometry of CH···H contacts in *β*-D-mannose Phases I and II. Symmetry ORTEP codes[1] are explicitly explained in Table S3.

		0.1MPa	0.48(2)GPa	1.60(2)GPa	1.90(2)GPa	2.02(2)GPa	2.10(2)GPa	2.35(2)GPa	2.85(2)GPa
C1-H1···O2^{1455}	C···O	3.433(3)	3.404(18)	3.200(12)	3.165(24)	3.275(20)	3.190(13)	3.136(46)	3.175(10)
	H···O	2.573	2.564	2.407	2.381	2.465	2.366	2.299	2.370
	C-H···O	134.5	132.6	127.8	127.0	129.5	130.5	131.4	128.8
	C···O-C	144.4(1)	143.4(9)	140.3(5)	140.3(9)	140.9(10)	143.3(7)	145.6(17)	141.6(5)
C2-H2···O1^{3555}	C···O	3.571(3)	3.495(16)	3.368(11)	3.350(21)	3.657(18)	3.644(12)	3.569(43)	3.628(10)
	H···O	2.823	2.733	2.581	2.554	2.596	2.591	2.508	2.572
	C-H···O	125.2	126.2	127.9	128.6	162.0	160.5	162.2	161.0
	C···O-C	106.1(1)	108.9(6)	108.8(5)	108.0(7)	88.8(11)	87.3(6)	90.7(15)	86.8(4)
C2-H2···O2^{3655}	C···O	3.430(3)	3.407(13)	3.339(10)	3.329(13)	5.254(30)	5.144(16)	5.159(35)	5.135(12)
	H···O	2.491	2.468	2.399	2.392	4.551	4.410	4.396	4.412
	C-H···O	142.7	142.7	142.7	142.3	124.6	126.9	129.1	126.0
	C···O-C	127.6(1)	128.3(7)	127.6(5)	127.6(8)	95.8(12)	97.2(7)	98.7(17)	95.8(6)
C2-H2···O2^{1455}	C···O	4.569(3)	4.515(20)	4.336(12)	4.295(31)	3.247(16)	3.246(11)	3.208(52)	3.204(9)
	H···O	4.486	4.435	4.252	4.214	2.705	2.767	2.807	2.704
	C-H···O	87.3	87.1	87.0	86.8	109.8	106.0	101.2	107.2
	C···O-C	135.3(1)	134.3(8)	132.2(5)	132.8(9)	160.7(15)	164.8(8)	170.4(20)	164.0(7)
C2-H2···O5^{3555}	C···O	4.038(3)	3.995(17)	3.900(11)	3.909(22)	3.866(34)	3.746(16)	3.632(45)	3.724(13)
	H···O	3.301	3.264	3.150	3.168	2.904	2.786	2.680	2.757
	C-H···O	125.4	124.9	126.1	125.5	146.1	145.9	144.7	146.8
	C···O-C	117.9	118.5	120.8	118.6	102.7	104.4	107.0	101.6
C3-H3···O2^{1455}	C···O	5.193(3)	5.139(18)	5.022(12)	5.081(29)	3.422(31)	3.386(14)	3.262(46)	3.372(11)
	H···O	4.696	4.645	4.563	4.625	2.650	2.617	2.473	2.591
	C-H···O	111.1	110.8	108.5	108.5	126.8	126.4	127.6	127.4
	C···O-C	121.2(1)	120.1(8)	118.0(5)	119.0(9)	139.3(17)	142.1(9)	147.0(16)	142.8(9)
C3-H3···O3^{4465}	C···O	4.763(3)	4.697(15)	4.659(11)	4.714(15)	3.052(38)	3.062(20)	2.882(38)	3.125(15)
	H···O	4.257	4.188	4.167	4.195	2.400	2.418	2.278	2.485
	C-H···O	111.0	111.2	110.0	111.8	116.4	115.9	112.5	115.9
	C···O-C	107.4(1)	106.8(5)	104.7(3)	104.2(5)	126.2(13)	127.4(6)	130.4(12)	125.7(5)
C3-H3···O4^{4465}	C···O	3.734(3)	3.655(18)	3.481(12)	3.491(20)	3.481(27)	3.432(15)	3.482(31)	3.478(12)
	H···O	2.730	2.649	2.482	2.488	3.143	3.080	2.993	3.129
	C-H···O	151.9	151.9	150.7	151.4	98.6	99.3	107.3	99.2
	C···O-C	132.8(1)	134.3(8)	136.7(5)	139.9(10)	98.7(11)	98.8(7)	98.1(15)	97.7(5)
C3-H3···O6^{1565}	C···O	3.603(3)	3.555(15)	3.429(11)	3.431(16)	3.786(19)	3.727(13)	3.716(26)	3.673(10)
	H···O	2.728	2.702	2.575	2.572	4.243	4.191	4.096	4.130
	C-H···O	136.3	134.1	133.9	134.4	58.4	58.0	62.3	58.3
	C···O-C	100.0(2)	102.1(8)	102.5(6)	100.7(11)	128.9(16)	131.8(8)	133.2(14)	132.5(6)
C4-H4···O3^{4565}	C···O	5.207(3)	5.146(16)	5.024(11)	5.028(20)	3.039(27)	3.041(17)	3.247(42)	2.977(12)
	H···O	4.833	4.783	4.693	4.708	2.535	2.540	2.616	2.481
	C-H···O	103.9	103.2	101.3	100.6	106.5	106.6	115.7	106.1
	C···O-C	66.5(1)	66.8(7)	65.9(4)	68.1(8)	119.8(13)	117.8(8)	105.0(20)	121.8(5)
C6-H6···O6^{4555}	C···O	3.315(3)	3.247(17)	3.175(12)	3.177(18)	4.504(45)	4.478(18)	4.605(40)	4.453(14)
	H···O	2.341	2.287	2.198	2.178	3.960	3.889	4.068	3.834
	C-H···O	147.7	145.6	147.8	151.0	113.3	116.1	113.0	118.1
	C···O-C	99.7(1)	98.2(5)	96.6(3)	97.0(5)	50.4(10)	52.2(6)	50.6(14)	52.6(5)
C6-H7···O3^{1545}	C···O	3.583(3)	3.552(15)	3.443(11)	3.366(17)	3.713(19)	3.702(11)	3.632(25)	3.644(9)
	H···O	2.758	2.747	2.674	2.626	4.132	4.127	4.001	4.091
	C-H···O	132.2	130.3	127.0	124.5	60.3	59.9	62.7	58.6
	C···O-C	100.7(1)	102.4(9)	102.2(5)	107.0(11)	134.9(18)	134.9(8)	131.8(14)	134.9(7)

Contacts present in both, Phase I and II

Contacts present only in Phase I

Contacts present only in Phase II

Table S6. Distances OF H···H contacts in *β*-D-mannose Phases I and II. Symmetry ORTEP codes[1] are explicitly explained in Table S3.

	0.1MPa	0.48(2)GPa	1.60(2)GPa	1.90(2)GPa	2.02(2)GPa	2.10(2)GPa	2.35(2)GPa	2.85(2)GPa
H1···H9 ^{1455}	2.469	2.461	2.353	2.344	2.754	2.640	2.500	2.655
H3···H4 ^{1455}	4.277	4.167	4.017	4.108	2.149	2.117	2.228	2.121
H3···H10 ^{4465}	3.544	3.482	3.480	3.508	2.434	2.414	2.162	2.517
H3···H11 ^{4465}	2.427	2.386	2.210	2.215	2.927	2.870	2.786	2.927
H4···H10 ^{4565}	4.267	4.207	4.110	4.119	1.919	1.905	1.872	1.888
H5···H7 ^{1455}	4.243	4.108	3.891	3.847	2.189	2.198	2.181	2.115
H6···H7 ^{4455}	2.970	2.815	2.771	2.861	2.158	2.241	2.309	2.276
H7···H8 ^{3645}	3.089	3.079	2.963	2.888	2.350	2.332	2.483	2.294
H8···H9 ^{3645}	2.462	2.471	2.450	2.418	2.661	2.684	2.592	2.641
H8···H12 ^{3555}	2.408	2.375	2.294	2.351	2.510	2.553	2.655	2.533
H10···H11 ^{4565}	2.366	2.320	2.234	2.323	2.682	2.618	2.240	2.627
H10···H11 ^{4465}	3.694	3.630	3.467	3.369	2.186	2.219	2.535	2.176
H11···H12 ^{4555}	2.232	2.232	2.198	2.206	3.261	3.281	3.352	3.246

Table S7. Quadratic polynomial functions (Phase I) and exponential decay functions (Phase II) fitted to the experimentally obtained pressure dependences of unit-cell volume *V* and parameters *a, b, c* of *β*-D-mannose used for the calculation of the differential part of compressibility parameter $\beta_x = -\frac{1}{x}\frac{\partial x}{\partial p}$. *R* is correlation coefficient.

	Phase I	Phase II
a(*p*)	$a = 0.0456*p^2 - 0.2468*p + 5.6736$ (R= 0.9979)	$a = 2.7917*\exp(-1.9531*p) + 4.5623$ (R= 0.9148)
b(*p*)	$b = 0.0005*p^2 - 0.0751*p + 7.5753$ (R= 0.9950)	$b = 95.2396*\exp(-3.7094*p) + 8.3842$ (R= 0.9992)
c(*p*)	$c = 0.0402*p^2 - 0.2464*p + 18.1520$ (R= 0.9874)	$c = 27167968.950113068*\exp(-9.2695*p) + 17.2008$ (R= 0.9958)
V(*p*)	$V = 8.2077*p^2 - 51.5984*p + 780.0857$ (R= 0.9969)	$V = 198411.568564999*\exp(-4.6101*p) + 659.4821$ (R= 0.9935)

Table S8. Compressibility $\beta_x = -\frac{1}{x}\frac{\partial x}{\partial p}$, where *x* stands for unit-cell parameters *a*, *b*, *c* and volume *V,* in *β*-D-mannose Phases I and II. The differential part was analytically calculated based on a quadratic polynomial (Phase I) or exponential decay (Phase II) fitted to the experimentally obtained pressure dependences of unit-cell volume *V* and parameters *a, b, c.* Used functions are listed in Table S7.

Pressure [GPa]	β_a[GPa^{-1}]	β_b[GPa^{-1}]	β_c[GPa^{-1}]	β_V[GPa^{-1}]
0.0001	$43.54*10^{-3}$	$9.92*10^{-3}$	$13.58*10^{-3}$	$66.26*10^{-3}$
0.48	$36.40*10^{-3}$	$9.89*10^{-3}$	$11.51*10^{-3}$	$57.50*10^{-3}$
1.00	$28.46*10^{-3}$	$9.89*10^{-3}$	$9.25*10^{-3}$	$47.84*10^{-3}$
1.60	$18.72*10^{-3}$	$9.86*10^{-3}$	$6.61*10^{-3}$	$35.36*10^{-3}$
1.90	$13.68*10^{-3}$	$9.84*10^{-3}$	$5.25*10^{-3}$	$28.61*10^{-3}$
2.02	$22.89*10^{-3}$	$23.32*10^{-3}$	$106.80*10^{-3}$	$122.03*10^{-3}$
2.10	$19.53*10^{-3}$	$17.36*10^{-3}$	$51.20*10^{-3}$	$84.88*10^{-3}$
2.35	$12.08*10^{-3}$	$6.89*10^{-3}$	$5.07*10^{-3}$	$27.23*10^{-3}$

2.85	$4.56*10^{-3}$	$1.08*10^{-3}$	$0.05*10^{-3}$	$2.73*10^{-3}$

References:

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[2] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.