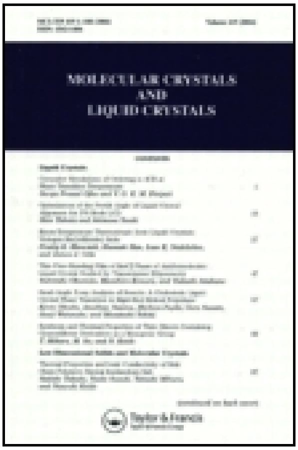

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Phase Behavior of Neohexanol up to Pressures of 300 MPa and Temperatures between 100 and 370 K

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Phase Behavior of Neohexanol up to Pressures of 300 MPa and Temperatures between 100 and 370 K

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The phase behavior of neohexanol has been studied at temperatures between 100 and 370 K and pressures up to 300 MPa with the aid of differential thermal analysis (DTA). The substance reveals three stable forms at atmospheric pressure (solid I, II, III) and a new high pressure modification (solid IV). Accordingly, two sets of triple point values have been established: (a) the (solid I + solid II + solid III) triple point at 70 MPa and 215 K; (b) the (liquid, solid I, solid IV) triple point at 88 MPa and 275 K. There is a further triple point (solid I, III, IV) expected immediately beyond the experimentally accessible pressure range (349 MPa, 251 K). Both phases solid I and IV are supposed to be orientationally disordered ("plastic") phases. Furthermore at least two metastable solid phases occur, denoted as solid III′ and III″ which are readily obtained on cooling.

Keywords: phase transitions, high pressure, plastic crystals, thermodynamics

1. INTRODUCTION

Some thermodynamic and dielectric properties of 2,2-dimethyl-butanol-1 (neohexanol) are reported in the literature.[1,2] After Dannhauser *et al.*,[1] neohexanol freezes at 241 K to a "soft, waxy solid" (plastic crystal). At lower temperatures of about 200 K neohexanol transforms into an ordinary molecular crystal. The reported dielectric behavior seems to be similar to that of cyclic-alcohols which have been characterized by low-frequency relaxations due to the hydrogen-bonded network. It is the aim of the present study to investigate the phase situation in more detail, using differential thermal analysis, and to include the high pressure phase behavior.

2. EXPERIMENTAL

Details of the high pressure DTA apparatus have been described elsewhere.[3,4] Phase transition temperatures have been determined at heating rates of 2 K min^{-1}.

Thermocouples of Chromel/Alumel have been calibrated against substances of known transition temperature. All transition temperatures were determined from the maximum of the slope of the DTA trace (inflection point) after the onset of the phase transition.

The limit of experimental error for the temperature measurement is 0.5 K. High pressure is generated by compressed rare gases and measured by using Bourdon gauges (Heise, Newton Connecticut, USA). The error of the pressure reading is supposed to be less than 5 bar (1 bar = 10^5Pa).

Neohexanol was not available commercially and therefore was synthesized from 2-chloro-2-methyl butane as described in the literature.[5] A purity of 99.9% was achieved by subjecting the sample to both distillation and gas chromatography.

3. RESULTS

Novel phases that have so far not been reported in the literature have been detected both at atmospheric (solid II) and elevated pressure (solid IV). The phase behavior is complicated by the occurrence of several metastable phases which render the determination of the stable phases extremely difficult (see Figure 1). Some features of the phase behavior are now described in more detail.

3.1 Measurements at atmospheric pressure

At atmospheric pressure neohexanol melts at 250.8 K. This value is considerably higher than reported in the literature, possibly due to the higher purity of the sample used in the present work. For example, Figure 2 shows the DTA-traces of a water-contaminated sample. The melting peak is not well defined and has been shifted significantly to lower temperatures.

The thermograms also reveal an additional solid state transition to the plastic phase solid I. Below the plastic phase region there are two additional solid phases II and III. However, this sequence of phases is not observed on cooling. It occurs on heating after a thermal treatment for at least 30 h at approximately 170 K and higher pressures. The phase behavior is extremely complicated by the existence of metastable phases III′ and III″ which usually grow from supercooled phase I via phase II. Annealing for some hours favors the conversion from III″ to III′. Figure 3 also shows DTA peaks at considerably lower temperatures, probably due to a glass transition (Johari[2]: $T_g = 163$ K). Similar peaks have been observed at higher pressures and are represented by the dashed line of the phase diagram (Figure 1).

3.2 Measurements at higher pressures and lower temperatures

Annealing at higher pressures results in transformation from III″ to III′ as well as from III′ to III, however, at significantly faster rates than at atmospheric pressure. Examples of DTA-traces are shown in Figure 4, where the annealing time has been raised from 1 h (a) over 10 (b) to 26 hours (c). Comparing Figure 4a with 4b one notes the disappearance of the transition at 196.8 K (III″ to II) in favor of the transition at 206 K (III′ to II). At the beginning of the DTA studies the phase III′

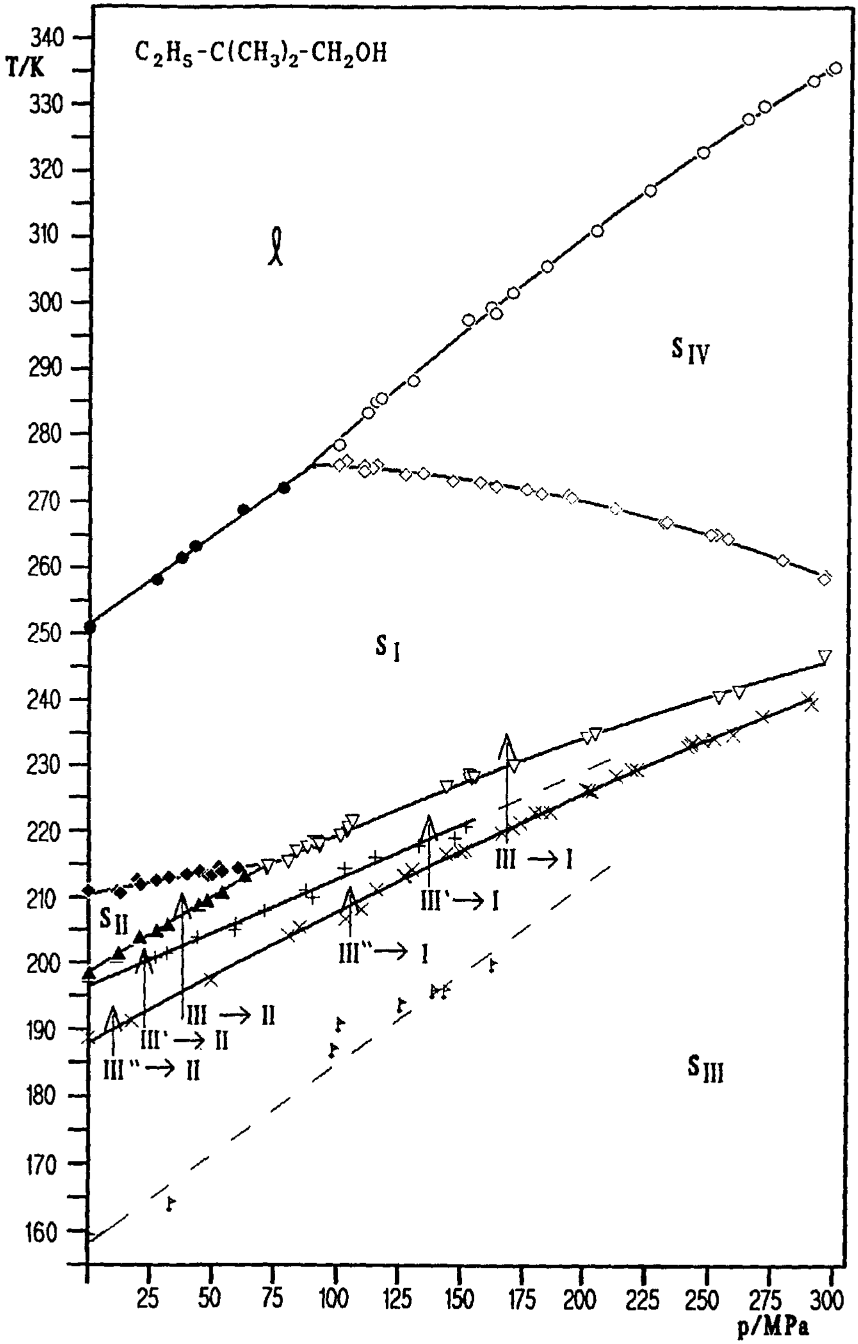

FIGURE 1 Phase diagram for neohexanol, showing the new phases solid II, IV and the metastable phases III' and III''.

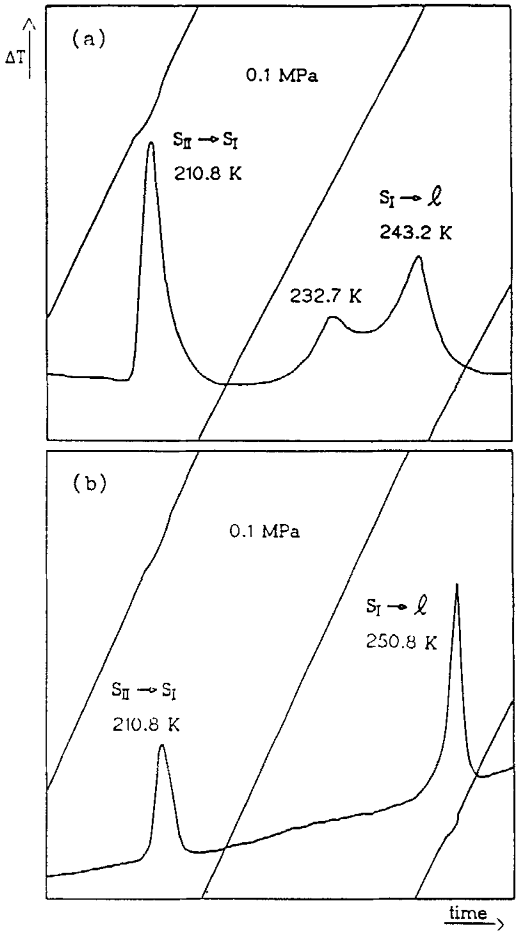

FIGURE 2 DTA traces for neohexanol containing different amounts of water.

was considered to be a stable solid phase. However, comparison of the Figures 4b and 4c clearly demonstrates its metastability: The peak corresponding to the III–II transition has been significantly increased at the expense of that from the III′–II transition.

The most convenient way for obtaining the phase transition III–II is first to anneal at moderate pressures of about 150 MPa and 200 K and then to remove the pressure at a temperature somewhat below the III–II transition line.

With increasing pressure the transition lines III–II and II–I converge, resulting in a triple point of 70 MPa and 215 K. The Figures 5a,b,c demonstrate how the III–II and the II–I transition temperatures come closer with increasing pressure. Only one peak is observed beyond the triple point pressure (Figure 5d).

Examples of coexisting phases III″, III′, and III are given in Figure 6. The exothermic peak in Figure 6 is probably due to the formation of III″ from super-

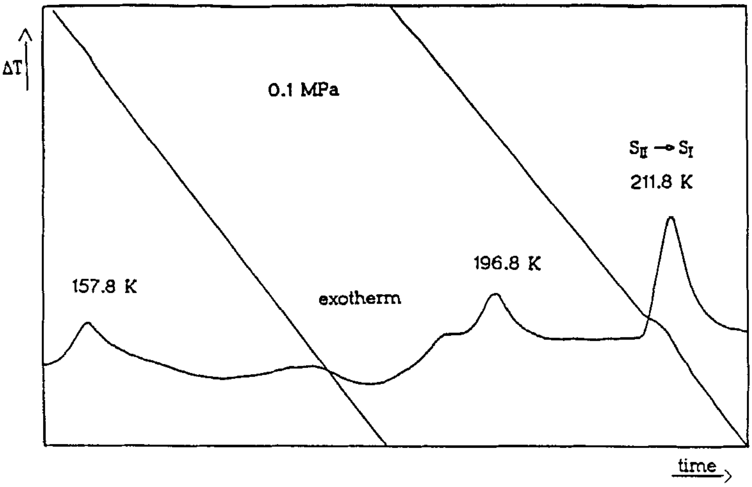

FIGURE 3 DTA traces for neohexanol showing phase transitions at low temperatures.

cooled solid I. However, the metastability of III″ is evident from the DTA-traces (Figure 7), although III″ will only reluctantly transform into the stable form III, even after annealing for 50 hours. Indeed Figure 7 clearly demonstrates that the large peak at 225.9 K disappeared completely in favor of the solid III–I transition. The conversion from III″ to III can be accelerated, if the sample is annealed in two steps: First a thermal treatment is performed in order to obtain a mixture of III″, I and III, similar to the stage between the two peaks of Figure 7a. Then the sample is cooled again to continue the thermal treatment. Subsequent heating leads to the thermogram shown in Figure 7b.

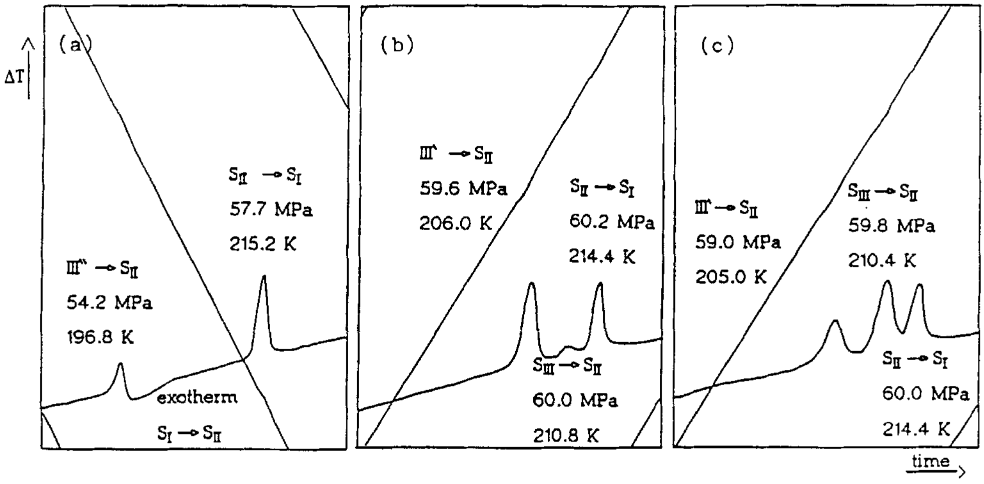

FIGURE 4 DTA traces for neohexanol showing the metastable phases III′ and III″.

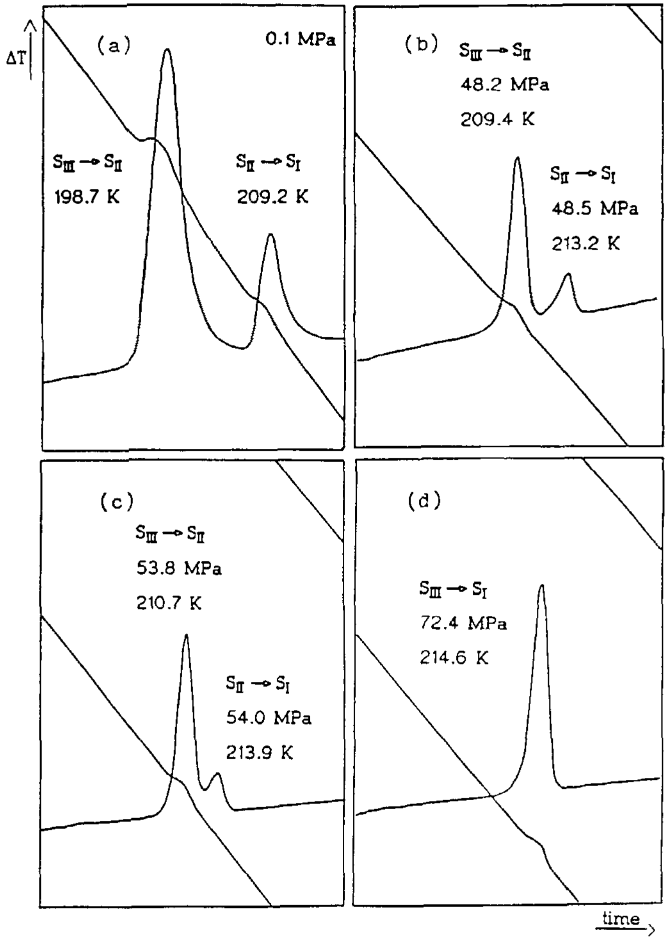

FIGURE 5 DTA traces for neohexanol in the coexisting region of phase II.

3.3 Measurements in the coexisting region of solid IV

A second plastic phase has been found (solid IV) at high pressures implying the occurrence of a triple point of liquid, solid I, solid IV at 88 MPa and 275 K. Surprisingly, the transition line solid I–solid IV has a negative slope. Therefore, a further triple point solid I–solid IV–solid III is expected just beyond the experimental pressure range (349 MPa, 251 K). Some selected DTA-traces are shown in the Figures 8 and 9 which include the melting and the solid III–I transition, respectively.

Neither the liquid nor the solid phase IV revealed a strong tendency to supercooling.

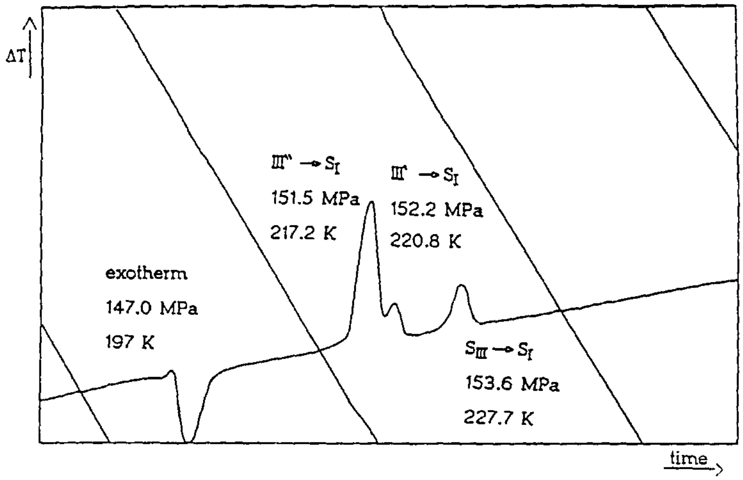

FIGURE 6 DTA traces for neohexanol showing the coexistence of III' and III''.

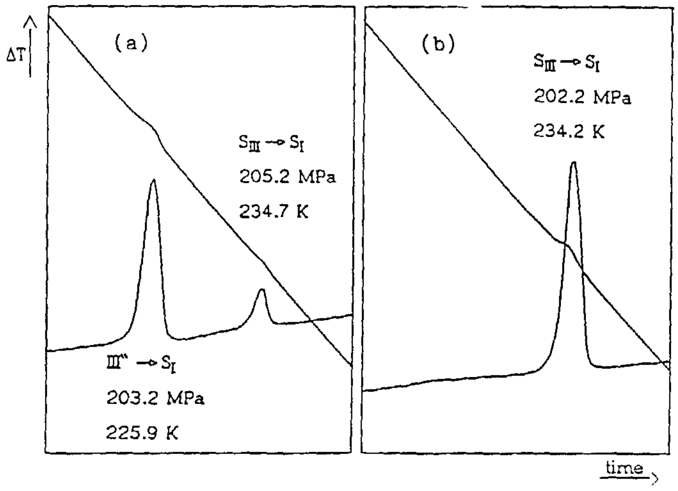

FIGURE 7 DTA traces for neohexanol showing the transformation from III'' to III.

3.4 Thermodynamic data

Some p,T data of the phase transitions are collected in Table I. The data have also been fitted to polynomials (available from Reference 3). This enabled us to calculate the initial slopes and the accompanying volume changes, see Table II. At elevated pressures the determination of the enthalpy change is much less accurate. This is mainly due to the limitations of the calibration procedure at high pressures. Approximate values are: solid IV–liquid: 1.4; solid I–IV: 0.3; solid III–I: 5.8 kJ mol^{-1}.

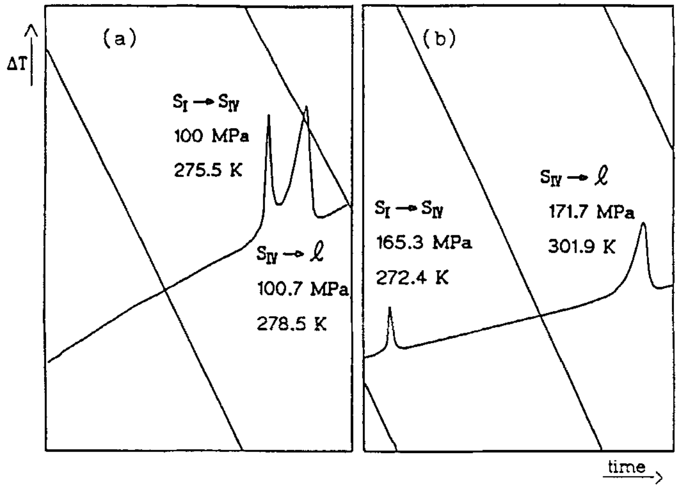

FIGURE 8 DTA traces for neohexanol showing transitions to phase IV and to the liquid.

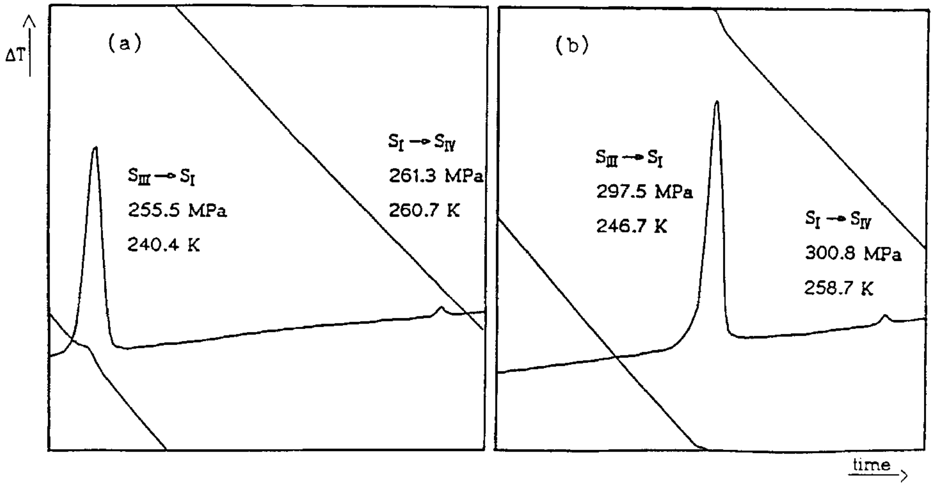

FIGURE 9 DTA traces for neohexanol showing the III–I and the I–IV transition.

The enthalpy change due to the solid II–I transition is considerably lower than for the solid III–II transition. In addition the magnitude of the enthalpy change of the intermediate solid I–IV transition is fairly small. Such enthalpy behavior is quite common for plastic crystals that exhibit more than one disordered phase.[6] Indeed recent measurements of the dielectric constant confirm that solid I and IV are orientationally disordered phases. In contrast, only low values have been found for the permittivity of solid II.[3]

TABLE I

Transition temperatures as a function of pressure for neohexanol

p/MPa	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K
I–liquid		*II–I*		*III–II*		*III′–I*		*III″–I*	
0.1	250.8	0.1	210.8	0.1	198.5	0.1	197.0	0.1	188.8
27.7	258.2	11.8	210.8	11.2	201.0	27.0	200.8	17.5	191.2
37.3	261.5	12.8	210.5	12.3	201.4	31.7	201.4	49.5	197.4
43.0	263.2	20.0	212.7	20.5	203.9	44.0	204.0	80.3	204.2
61.6	268.7	21.0	211.9	27.4	204.9	59.0	205.0	85.0	205.5
78.0	272.0	27.7	212.4	32.0	205.9	59.6	206.0	103.4	206.8
		32.5	212.9	44.4	208.9	71.0	208.0	110.0	208.2
IV–liquid		40.0	213.4	48.2	209.4	87.8	211.2	116.0	211.2
		45.0	213.9	53.8	210.7	103.0	214.4	127.0	213.2
100.2	278.5	48.5	213.2	63.0	213.2	115.6	216.0	127.5	213.2
111.5	283.4	50.3	213.4			133.0	217.8	130.5	214.2
114.8	285.0	52.5	214.5	*III–I*		147.6	219.0	144.0	216.5
117.0	285.5	54.0	213.9			152.2	220.8	150.1	216.8
130.0	288.2	60.0	214.4	71.7	214.4			151.5	217.2
152.2	297.4			72.4	214.6			166.6	219.7
161.7	299.4	*I–IV*		80.4	215.2			171.0	220.5
163.4	298.4			83.7	216.9			174.0	221.2
170.2	301.6	100.0	275.5	88.0	217.4			180.0	222.8
183.8	305.7	103.2	276.2	90.6	218.2			182.9	222.8
204.3	311.0	110.4	275.3	91.7	218.2			186.2	222.8
225.3	317.0	113.5	275.0	92.8	217.7			200.8	226.2
246.8	322.9	115.6	275.5	93.0	217.9			202.0	226.2
264.6	327.9	127.0	274.0	101.5	219.2			203.2	225.9
271.3	329.9	134.2	274.1	104.0	220.0			214.0	228.4
290.8	333.8	146.0	273.2	104.5	220.5			220.4	229.5
298.0	335.6	156.7	273.2	106.0	221.4			222.5	229.5
299.4	335.9	163.6	272.3	144.2	226.6			242.8	232.9
		176.0	271.9	154.2	228.4			244.4	233.2
		181.9	271.2	154.3	227.9			244.6	233.5
		193.0	271.0	155.8	228.2			249.0	233.9
		194.4	270.7	172.0	229.8			253.5	234.8
		176.0	271.9	202.2	234.2			261.4	234.8
		181.9	271.2	205.5	234.7			272.8	237.7
		193.0	271.0	255.5	240.4			291.3	240.4
		194.4	270.7	263.4	241.2			292.6	239.5
		212.4	269.0	297.5	246.7				
		231.8	267.0						
		233.0	267.1						
		251.7	265.1						
		253.7	265.1						
		258.4	264.5						
		280.1	261.4						
		296.8	258.5						
		297.0	258.8						

TABLE II

Thermodynamic properties of neohexanol at 1 atm

transition	$\frac{T}{K}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{dT/dp}{\text{K MPa}^{-1}}$	$\frac{\Delta V}{\text{cm}^3\text{mol}^{-1}}$
melting	250.6	1.7	0.30	2.1
solid II/I	210.4	1.3	0.08	0.5
solid III/II	198.6	4.5	0.23	5.2
solid III′/II	196.4	2.6	0.16	2.1
solid III″/II	187.9	3.9	0.21	4.4

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