

On the Pressure-Induced Phase Transformation in the Structure II Clathrate Hydrate of Tetrahydrofuran*

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Abstract. A high-pressure phase of the clathrate hydrate of tetrahydrofuran was prepared by freezing a liquid phase of overall composition $\text{THF} \cdot 7 \text{H}_2\text{O}$ under a pressure of 3.0 kbar, or by pressurizing the solid structure II THF hydrate at 255K to 3.4 kbar. Unfortunately, the products recovered at 77K were always mixed phase materials as shown by X-ray powder diffraction. A number of diffraction lines could be indexed in terms of the cubic structure I hydrate with a slightly expanded lattice parameter, 12.08 Å, giving some support to Dyadin's idea that the high pressure phase transition involves a conversion of Structure II to Structure I. Other phases observed in the recovered product include Ice IX and amorphous materials. The reversion of the high pressure sample to the structure II hydrate was followed by differential scanning calorimetry. At ambient pressure, the high pressure sample converts slowly back to Structure II hydrate even at 77K.

Key words: Tetrahydrofuran clathrate hydrate, high pressure, phase transition, structure II clathrate hydrate.

1. Introduction

Clathrate hydrates are host-guest materials where the guests are trapped in individual cages in an ice host lattice. There are three main families of structures, the cubic structures I and II [1, 2] and structure H for which a hexagonal structure has been proposed [3, 4]. The structure type is determined by the size of the largest guest incorporated in the structure.

There is considerable interest in the high pressure modification of hydrate structures and also the guest-free parent material, in this case ice. A recent development is the ready conversion of ice and some hydrates to high-density amorphous phases on the application of a pressure of about 13 kbar at 77K, a process already well documented and understood [5, 6]. A much less well studied process is the conversion of structure II hydrates to other phases at modest pressures of 3 kbar at 260K (Figure 1) [7–11]. For many different guest templates G, the conversion of structure II hydrate of composition $G \cdot 17 \text{H}_2\text{O}$ to lower hydrates $G \cdot m \text{H}_2\text{O}$ with $m = 7, 5$, etc. has been followed by calorimetry, and the hydration number of

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about 7 has been interpreted as being due to the conversion of structure II to a structure I hydrate [10, 11]. In this contribution we use X-ray powder diffraction to study the nature of the quenched high pressure product, and follow the reversion to structure II hydrate on annealing.

2. Experimental

Two different approaches were used to prepare a high pressure hydrate of tetrahydrofuran. The first involved the application of pressure to a sample of stoichiometry 7 H₂O : THF. The sample was placed in a Teflon-lined indium cup, frozen, loaded into a piston-cylinder apparatus and pressed cold (258K) to make a good seal. The pressure was then released and the sample allowed to melt. Subsequently the liquid sample was pressurized to 3.0 kbar at 285K and quenched to 77K, then annealed by cycling the temperature between 271 and 274K for 48 h by means of a programmable temperature controller (Haake PG40). Further annealing was carried out at 271K for 18 h, and finally the sample was cooled to 77K where the pressure was released and the sample recovered. The piston displacement as a function of applied pressure was used to follow the progress of the reaction and the final condition of the sample.

The second method was employed to see the actual conversion of a structure II hydrate to the high pressure hydrate, presumably along with conversion of the excess water to a high pressure ice. In this case, a solution of composition THF · 17 H₂O was placed in the Teflon-lined indium cup, sealed, and the temperature cycled between 269.5 and 276.5K for 48 h to induce homogeneous nucleation of structure II hydrate. This was followed by 24 h annealing periods at 263K and 252K. The temperature was then increased to 255K and the sample was pressed to 4 kbar, again recording the piston displacement as a function of applied pressure. The sample temperature was then cycled between 261 and 251K for 48 h at 3.4 kbar, and the sample cooled to 77K before the pressure was released and the sample recovered. A third sample was made using the same thermal treatment but without the application of high pressure to serve as a reference structure II material. The recovered hydrate samples were kept in liquid nitrogen for grinding and loading into a cold X-ray powder diffractometer sample cell. X-ray powder diffraction patterns were obtained with Co radiation on a Rigaku θ - θ diffractometer equipped with an Anton-Parr low temperature camera and a graphite monochromator. A DSC2910-TA2100 system (TA Instruments) equipped with a liquid nitrogen cooling accessory was used for characterizing all of the samples. Temperature and energy scales were calibrated by using high purity mercury, water, indium, tin and zinc. The accuracy in determining phase transition temperatures was about 0.3K and for heats of transition about 1–2%. Most scans were made at 10K min⁻¹ under a dry nitrogen gas flow rate of 50 mL min⁻¹.

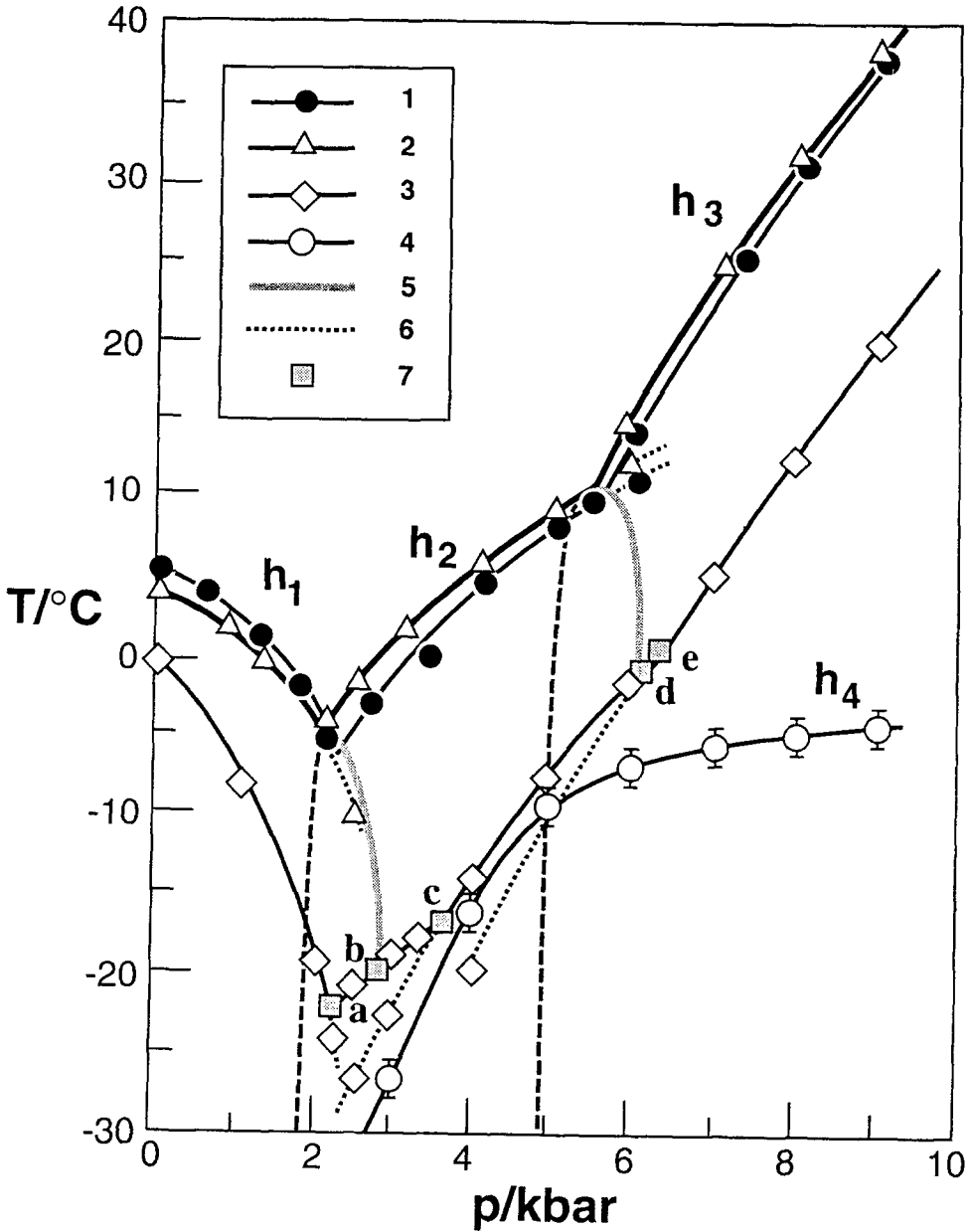


Fig. 1. P-T projection of the THF-H₂O diagram after Dyadin *et al.* [10]. (1,2) Melting curves of mixtures of the compositions THF · 17 H₂O (h₁) and THF · 7 H₂O (h₂), respectively; (3) three phase curve of ice (I, III, V or VI) + hydrate (h₁, h₂, or h₃ (THF · 4.6 H₂O)) + liquid (L); (4) three-phase peritectic decomposition curve for the hydrate (THF · 2.2 H₂O (h₄)); (5) three-phase curves for h₁ + h₂ + L and h₂ + h₃ + L; (6) metastable continuations of the branches; (7) four phase points (a, b, c, d, e).

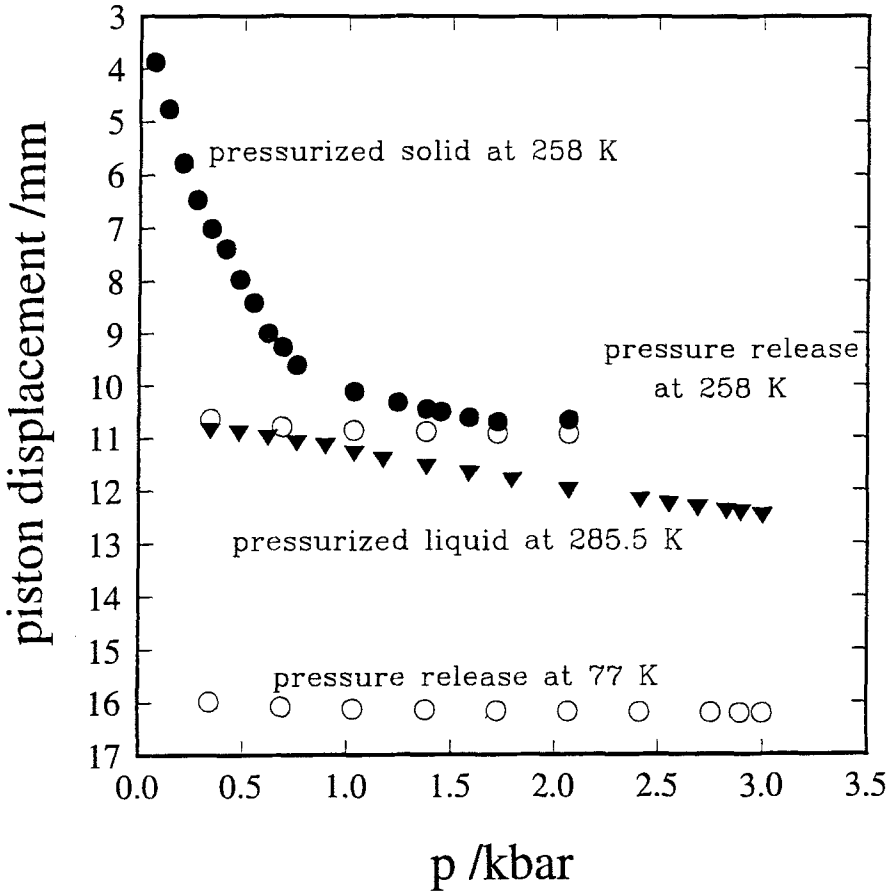


Fig. 2. Piston displacement d vs. nominal pressure p for making $\text{THF} \cdot 7 \text{H}_2\text{O}$ hydrate.

3. Results and Discussion

Piston displacement curves for the two high pressure sample preparations are shown in Figures 2 and 3. For the sample of composition $\text{THF} \cdot 7 \text{H}_2\text{O}$ it is confirmed that when the pressurized liquid is frozen, the volume of the solid is considerably smaller than that of the original frozen solid, and that the material can be recovered without volume change at 77K. For the second sample, which corresponds to a structure II hydrate, on application of pressure at 255K the expected volume change occurs at 3.4 kbar which we attribute to the conversion $\text{h1} \rightarrow \text{h2} + \text{liquid}$ (crossing of curve 5, shown nominally at 2.9 kbar in Figure 1). The small break in the curve at 1.8 kbar appears to correspond to the melting of a small amount of ice Ih under application of pressure (crossing of curve 3). Again, the sample can be recovered at 77K with minimal change in sample volume on release of pressure.

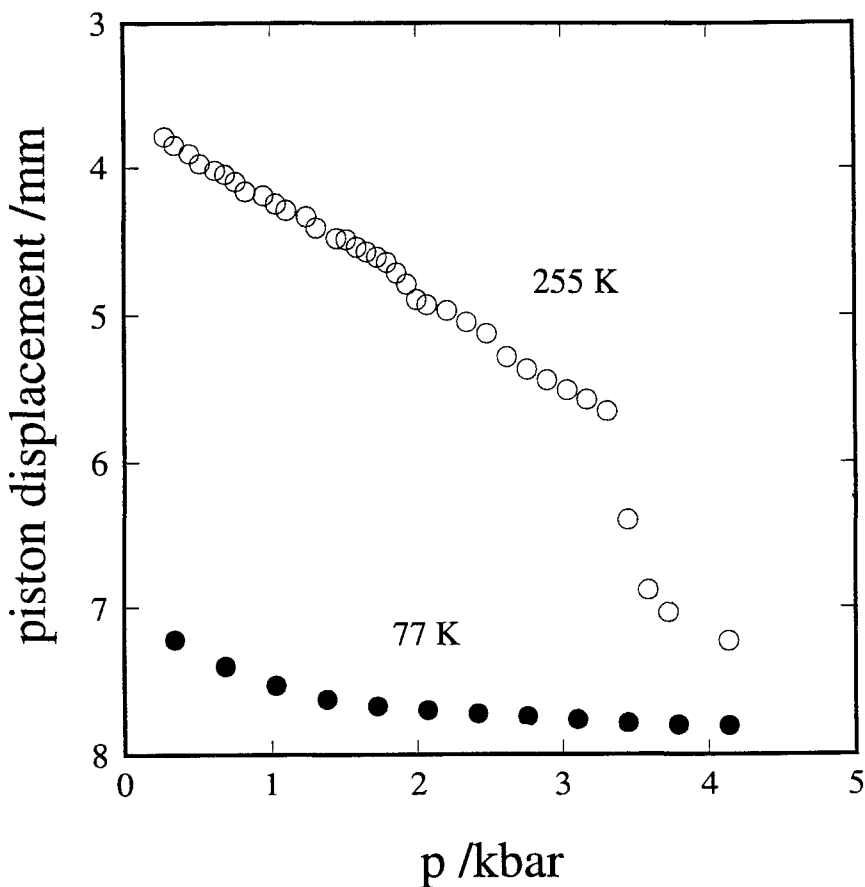


Fig. 3. Piston displacement d vs. nominal pressure p for transforming Structure II hydrate into Structure I hydrate.

Figure 4 shows X-ray powder patterns for samples 1–3. The most easily interpreted pattern is that of sample 3. Most of the pattern can be indexed in terms of structure II hydrate, as shown in Figure 4c, although there are significant quantities of Ice Ih. The strongest lines in the pattern for sample 2 can be assigned to ice III, as indexed in Figure 4b, although from the temperature and pressure history of the sample we conclude that in fact we have ice IX. Ice IX differs from ice III by proton disorder, and, therefore is indistinguishable from the latter by X-ray powder diffraction. This is also as expected, as the excess water which results on conversion of the structure II hydrate to the lower hydrate at 3.5 kbar is converted initially to the high pressure ice III when the pressurized sample is quenched in liquid nitrogen. The top pattern, Figure 4a, is for the THF · 7 H₂O sample which should correspond primarily to structure I hydrate. The pattern is much more complicated, and a number of different phases may be identified. The reflections which may be

attributed to structure I are indexed in the figure, the low-angle 222, 320 and 400 reflections being the most distinctive. A number of reflections may be assignable to structure II hydrate (311, 222, 400, 622, 733, 660) although the strong 511 and 440 structure II lines are absent. Some reflections suggest traces of ice Ih, which show up in a number of patterns where these were not expected, and we attribute these to small amounts of moisture which have condensed on the X-ray sample holder. The broad peak around $2\theta = 30^\circ$ in patterns 4a and 4b suggests that there may be some amorphous material as well. The weak structure I reflections also occur in pattern 4b, and we may conclude that structure I hydrate is present in both samples, although the reaction seems much more complex than suggested by the previous phase studies [9–11]. Also, since the reflections are broad the crystallite size appears to be very small despite the lengthy annealing procedure. The reflections attributed to structure I hydrate, 20 for the THF · 7 H₂O sample and 18 for the THF · 17 H₂O sample, were fitted with lattice constants of 12.0727 ± 0.0165 and 12.0815 ± 0.0196 Å. These values are rather larger than the usual structure I hydrate lattice constants, suggesting an expanded lattice for the larger than usual structure I guest. The structure II pattern in Figure 4c was fitted in terms of a lattice constant of 17.141 ± 0.0027 Å.

The pressure induced transformation observed at 3.4 kbar at relatively high temperature is clearly quite different from the pressure induced transition reported at 13 kbar and 77K [12]. In the former case the transformation involves a recrystallization with the breaking and reforming of hydrogen bonds. In the latter case, modelling calculations have shown that the O-O radial distribution function changes markedly on the application of pressure. For the related case of ice Ih it is known that the O-O distance increases and the H-H distance decreases as the material is transformed to high density amorphous ice due to water molecules taking up interstitial positions [12, 13].

In order to monitor the reversion of the high pressure structure I sample back to ambient pressure phases, scanning calorimetry was carried out to determine the transition temperatures. Figure 5 shows such a scan for the THF · 17 H₂O sample, with exotherms at 128K, 152K, 162K and 190K. The endotherms at 273 and 277K simply represent the melting of ice and THF hydrate, and will not be discussed further. In order to identify some of the phase changes, X-ray powder patterns were obtained at 83, 135, 160 and 200K (Figure 6). The pattern shown in Figure 6a is the original pattern after sample recovery, the others were taken 3 months later. The lines due to ice Ih seen in all patterns again are attributed to condensation of moisture during sample preparation. Even sample storage at 77K seems to have caused some changes after 3 months, there now being a number of lines attributable to Structure II hydrate. Evidently the high pressure hydrate is unstable even at 77K, although the conversion rate is slow. Pattern 6c, taken at 135K, shows additional changes, the main change being an increase in ice Ih content and a concomitant decrease in the amount of ice IX. By increasing the temperature, different forms of ice convert to ice Ic and later to ice Ih at various temperatures depending on

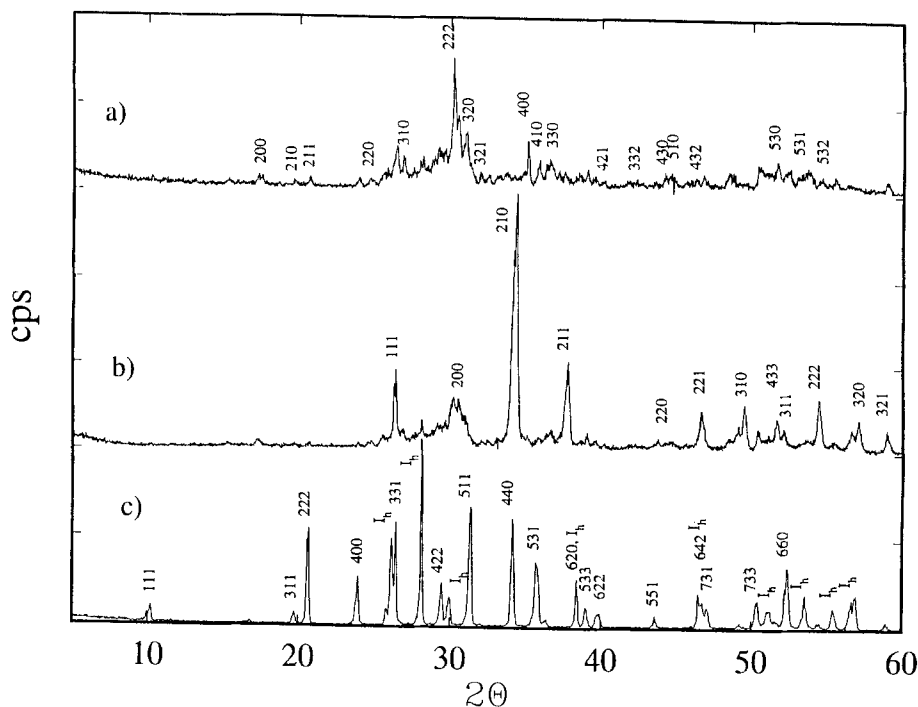


Fig. 4. The X-ray powder pattern taken at 83K. (a) Powder pattern of the sample of THF · 7 H₂O composition crystallized under a pressure of 3 kbar (19 Structure I peaks are indexed); (b) powder pattern of the sample of THF · 17 H₂O composition pressed up to 4 kbar at 253K (Ice III (IX) peaks are indexed); (c) powder pattern of a sample of THF · 17 H₂O composition crystallized at ambient pressure (Structure II peaks are indexed).

the origin of the sample [14]. The temperature position of the 190K exotherm we attribute to the Ic to Ih transformation. With increase of temperature, the ice IX reflections became significantly weaker and some Ih reflections became stronger. The Ih reflections which became more intense are 002, 110 and 112 and correspond to Ic peaks 111, 220 and 311, respectively, suggesting a partial ice IX to Ic phase transformation. The ice IX reflections are still present since according to the very weak exotherm at *ca.* 128K the transition is not yet finished. The Structure I 222 and 320 reflections become visible after being buried under the Ice IX peak 200, which is now gone. On the short timescale of the experiments there appear to be relatively small changes in the amounts of structure I and structure II hydrates. The broad bands around $2\theta = 28^\circ$ and 50° , attributed to amorphous material, also do not appear to change very much.

The biggest change in the diffraction pattern occurs between 135 and 160K, where the remaining structure I hydrate reflections as well as the ice IX and most of the ice Ih reflections disappear, and the sample seems to have converted almost completely to structure II hydrate. These changes appear to coincide with the two

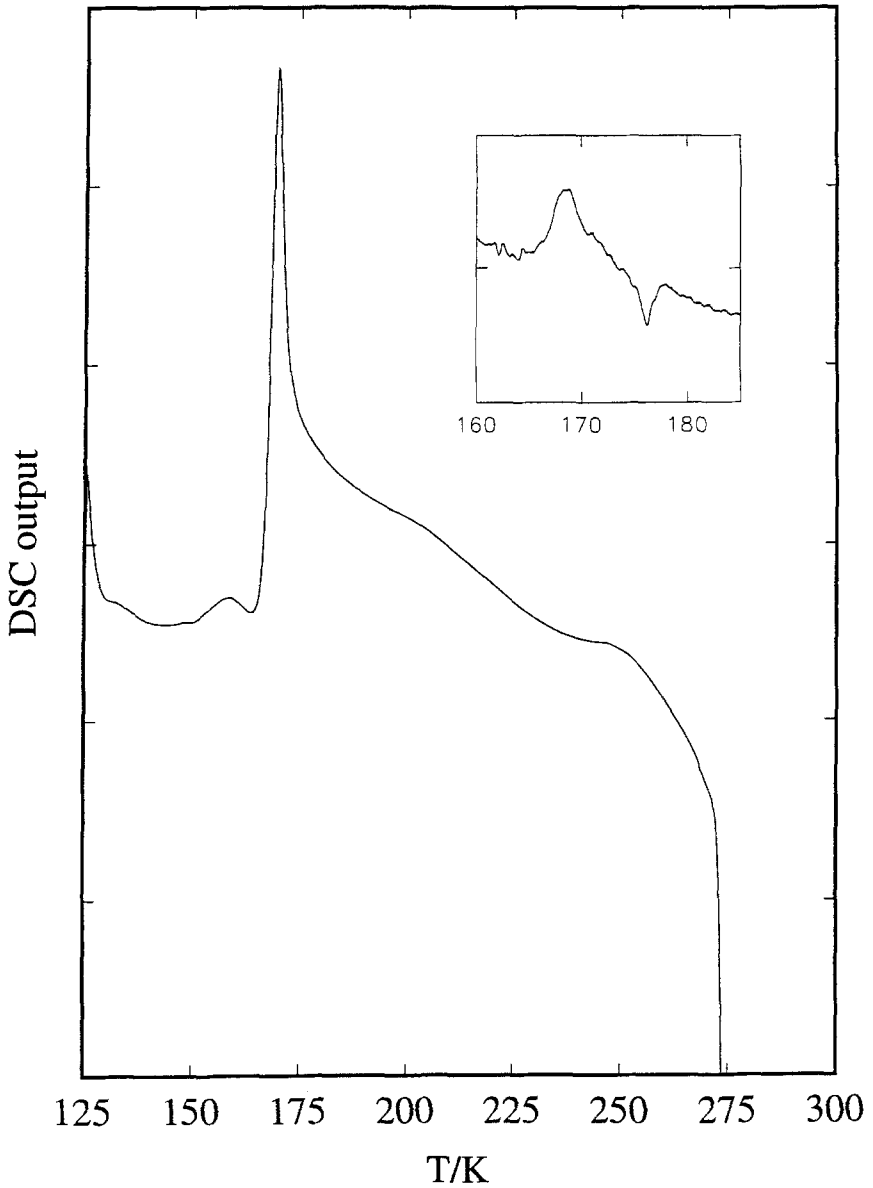


Fig. 5. A representative DSC run, at a scan rate of 10 K/min, of a THF·17 H₂O sample pressed up to 4 kbar and recovered at 77K. The melting of the THF hydrate is not shown. The inset represents a run of the same sample at a scan rate of 1K/min.

exotherms at 152K and 162K in Figure 5. The DSC scan of sample #1 showed a similar exothermic phase transformation at *ca.* 152K followed by melting of solid THF and the hydrate. Thus we conclude that the first of the transitions in question

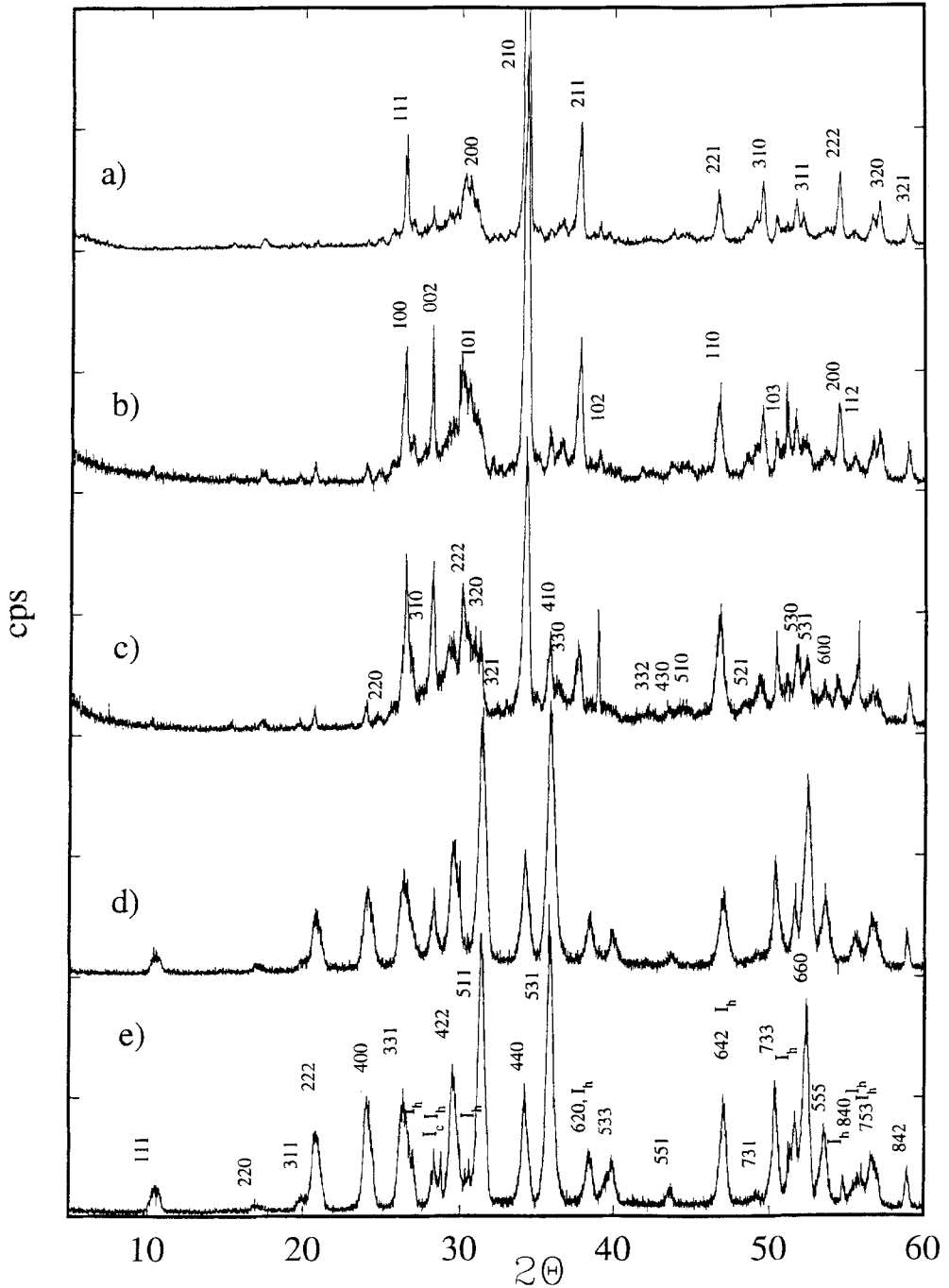


Fig. 6. A set of powder patterns of the THF · 17 H₂O sample pressed up to 4 kbar and recovered at 77K. (a) Freshly obtained sample examined at 90K as shown in Figure 4, curve (b), only the ice III (IX) peaks are indexed; (b) same sample examined at 83K after it had been stored in liquid nitrogen for 3 months, only the I_h peaks are indexed; (c) same sample at 135K, 21 Structure I hydrate peaks are indexed; (d) same sample at 160K; (e) same sample at 200K, only the Structure II peaks are indexed.

corresponds to a structure I to structure II transition. The second may be related to the formation of further structure II hydrate from the excess THF freed from structure I THF and ice. It should also be noted that the diffraction lines are very broad compared to those of a sample prepared at high temperatures, suggesting the presence of rather smaller crystals. The broad bands at $2\theta = 28^\circ$ and 50° also have disappeared. An additional line between two lines near $2\theta = 28^\circ$ could be attributed to the 111 ice Ic reflection, which suggests an amorphous ice \rightarrow ice Ic conversion, known to take place in this temperature region. A slow DSC scan over this temperature region showed that the 162K exotherm could be resolved into an exotherm, which at a slower scan rate appears at 164K, and an endotherm at about 173K. The endotherm probably corresponds to melting of THF. The instability at 77K of the structure I THF hydrate formed at high pressure suggests that a number of amorphous phases could be formed on decomposition, e.g. amorphous solid phases of ice and THF. Reaction to form structure II THF hydrate may be limited by transport and local availability of ice phases.

4. Conclusions

The above results show that it is difficult to prepare and recover high-quality single-phase products on application of 3.0–3.4 kbar pressure to either structure II hydrate, or a frozen mixed phase sample of composition $\text{THF} \cdot 7 \text{H}_2\text{O}$ near 260K. A number of weak, broad lines in the products recovered at low temperatures could be indexed in terms of a structure I hydrate which yielded lattice constants of 12.07 and 12.08 Å for the two samples prepared. These are slightly larger than those usually observed for structure I hydrate, as one might expect for a structure I hydrate with a larger than usual guest. The broadness of the diffraction lines suggests relatively small, poor quality crystals despite the extensive annealing cycles. Other phases identified in the recovered products include Ice IX, ice Ih, and amorphous materials. On the timescale of three months a small amount of product had reverted back to structure II hydrate, indicating its inherent instability at ambient pressure. On the shorter timescale of a calorimeter scan (minutes), the product reverts back to structure II hydrate above 150K.

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