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COMPUTER ASSISTED DIFFERENTIAL THERMAL ANALYSIS AT HIGH PRESSURES: PHASE STUDIES ON LIQUID CRYSTALS

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Abstract: In the present work it is shown that phase transitions exhibiting very small transition enthalpies can be detected by computer assisted DTA especially at high pressures. The method is demonstrated on measurements for the liquid crystal 4-octyloxy-4'-cyanobiphenyl (8OCB) up to 2 kbar.

Detection of phase transitions exhibiting very small enthalpy changes (e.g. found in some liquid crystals) is difficult with thermal methods. In an earlier paper (1) the application of a differentiator was described in order to increase sensitivity of high pressure DTA. In the present work (2) it is shown that phase transitions exhibiting very small transition enthalpies can be investigated by computer assisted DTA especially at high pressures.

The high pressure DTA apparatus used here has been described elsewhere (3,4). The data have been recorded at equidistant time steps of about 750 ms with a microcomputer (hp 85). This technique is of some advantage in comparison with normal detection. It is not necessary to switch over to other sensitivity ranges during DTA runs. By digital data logging the signal/noise ratio has been improved by a factor of about 100 using some special computing procedures, e.g. digital smoothing and multiple scan. All computations such as integration, differentiation, temperature measurement etc. can be done offline with a desk-top computer (hp 9845). (For details see ref.2).

Fig.1 shows the complete phase diagram of 8OCB which exhibits a typi-

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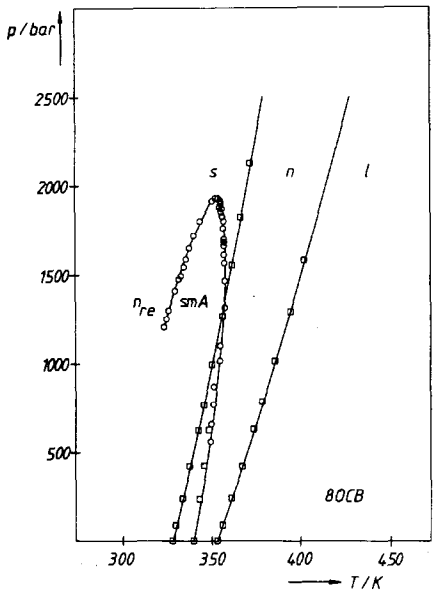

Fig. 1: Phase diagram of 8OCB

cal re-entrant smA/n transition with decreasing temperature between about 1200 and 1900 bar (5). The smA/n transition may still be followed beyond the intersection point with the freezing point curve at about 1300 bar, if the liquid crystalline phases are supercooled (6). There are some other interesting phenomena linked with the re-entrant behaviour (5,7,8).

The smA/n transition shows an enthalpy change of only ca. 120 J mol^{-1} ($\hat{=}$0.39 J·g^{-1} $\hat{=}$ 0.008 J·(cell content)$^{-1}$) at 1 bar that even decreases with increasing pressure. Concerning this phase transition high pressure experiments have been conducted so far by means of polarisation microscopy only. But even at normal pressure the transition can hardly be detected by a thermal method e.g. DSC (9). Fig.2a shows an original DTA trace of 8OCB for heating runs at normal pressure in order to demonstrate the ΔH ratios of the phase transitions involved. It is clarly seen that the smA/n transition is not detectable in this plot mainly due to the relatively large s/smA signal. But if an enlarged scale for ΔT is chosen, the smA/n transition becomes visible (Fig.2b-c). Fig.3a-c show an analogous sequence of DTA traces at 140 bar. If the pressure is increased to 820 bar and 1785 bar, respectively, the smA/n transition remains detectable in cooling runs even in the region that is supercooled with respect to the solid phase (Fig.4-5).

It is not possible to follow the whole re-entrant branch of the phase

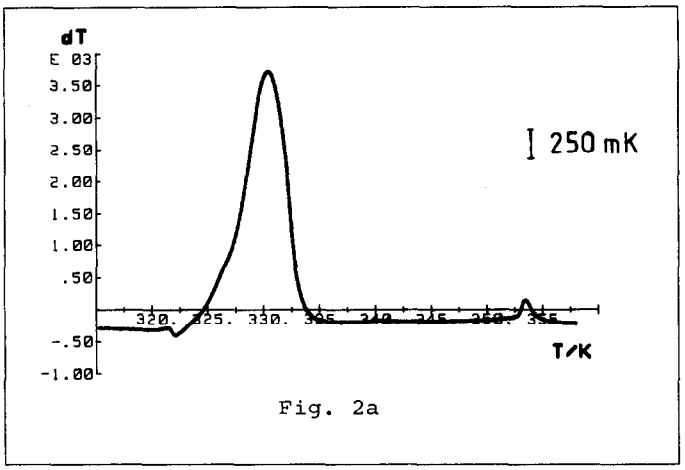

Fig. 2a

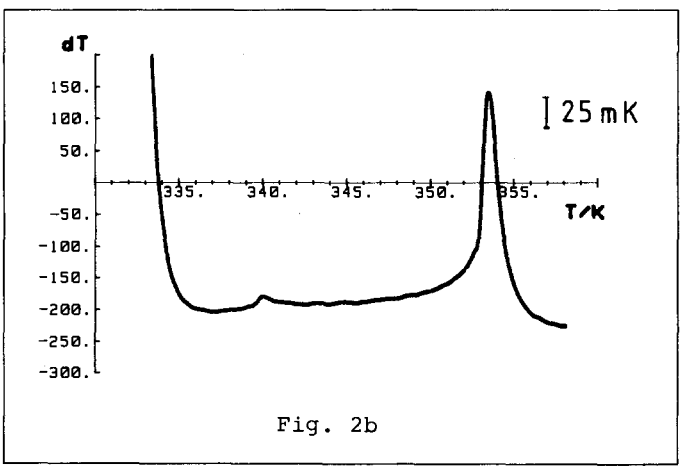

Fig. 2b

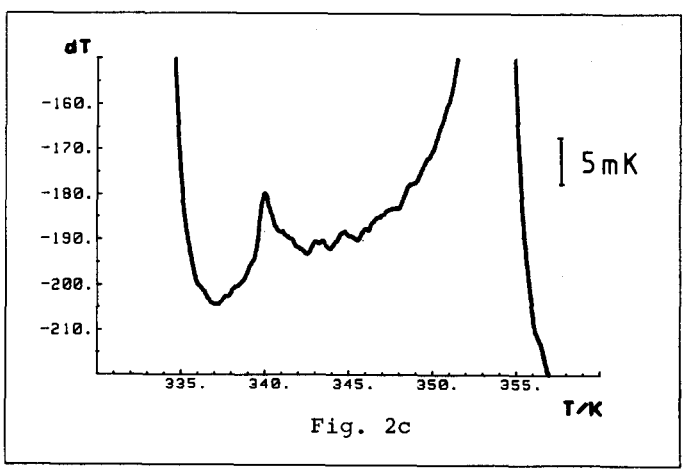

Fig. 2c

Fig. 2a-c: DTA traces at 1 bar

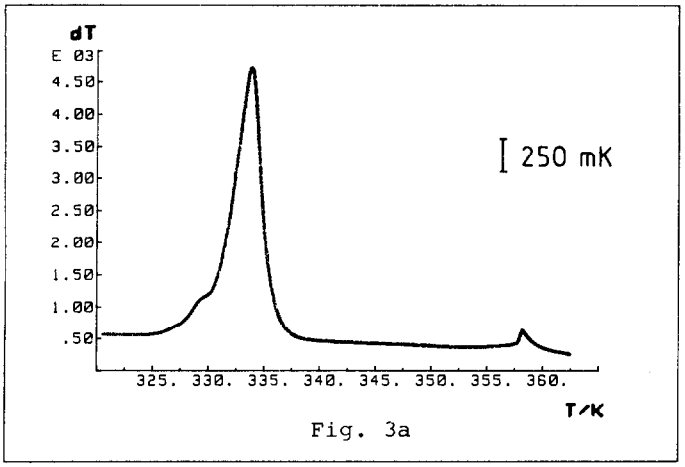

Fig. 3a

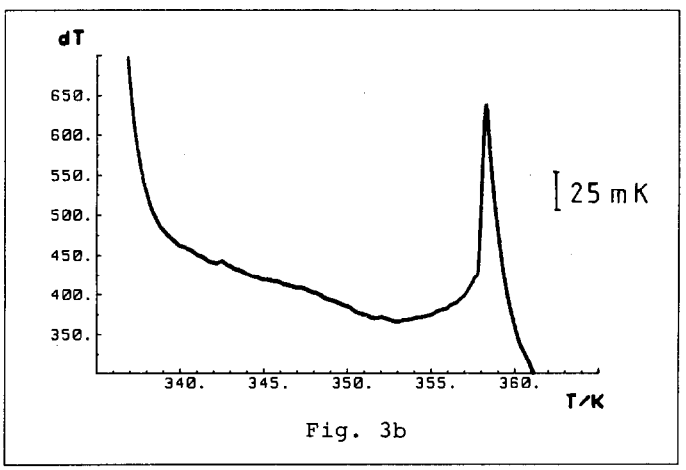

Fig. 3b

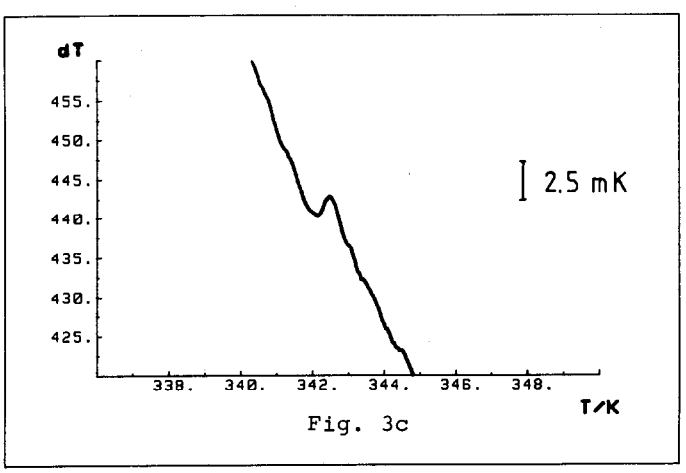

Fig. 3c

Fig. 3a-c: DTA traces at 140 bar

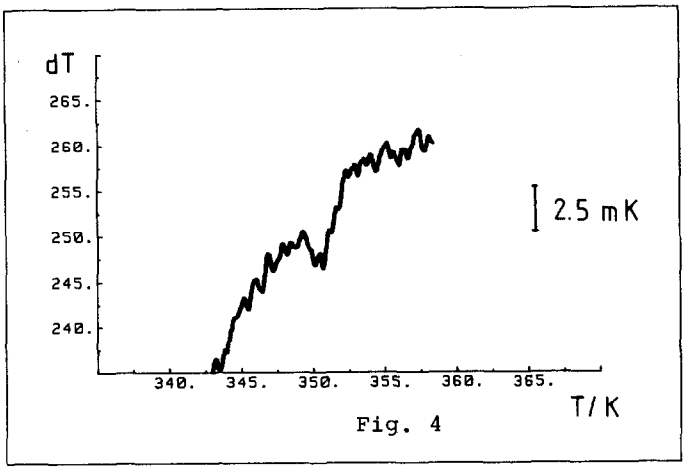

Fig. 4

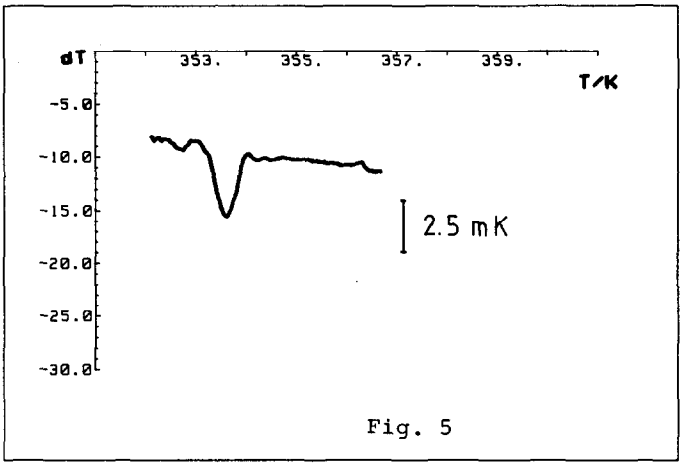

Fig. 5

Fig. 4 and 5: DTA cooling runs at 820 bar (Fig.4) and 1785 bar (Fig.5)

transition line by DTA since solidification takes place earlier for DTA detection than for polarisation microscopy. This difference in supercooling can be understood from the small amount of compound (~ 1 mg) and the well polished diamond window planes used in polarisation microscopy whereas in DTA 20-25 mg of substance are used and the inner walls of the high pressure cells are not well finished.

These experiments demonstrate that the use of electronic computers is most useful for increasing sensitivity and resolution in DTA especially at high pressures. The measurements are continued.

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