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Note

HIGH-RESOLUTION DIFFERENTIAL THERMAL ANALYSIS AT HIGH PRESSURES. APPLICATION TO LIQUID CRYSTALS

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It is well known that there are many phase transitions with extremely low transition enthalpy values. As the thermal conductivity increases with increasing pressure the signals become even weaker under high pressure and may obtain the same order of magnitude as the noise, i.e., the signals can no longer be detected. Therefore increased sensitivity is especially important for high-pressure DTA devices. In the present work it is shown that by means of peak differentiation the sensitivity of DTA detection can be improved to such an extent that it is possible to detect phase transitions over a large pressure range even for extremely small transition enthalpies.

Figure 1 shows the principle of peak differentiation. Here the time-constant RC plays an important role in the differentiator equation that gives the output voltage of the differentiator

$$U_{\text{diff}} = \text{RC}(\mathrm{d}U/\mathrm{d}t)$$

where U is the electromotive force of the thermocouple. The value of RC in

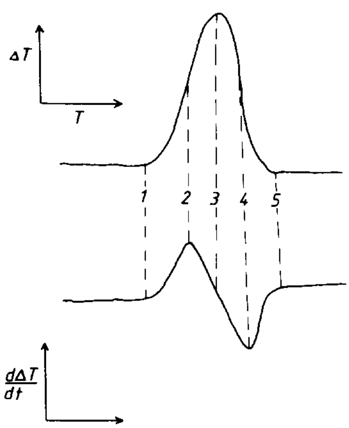

Fig. 1. Principle of peak differentiation, 1, Start; 2, 4, inflection points of normal signal; 3, maximum of normal signal; 5, end (see text).

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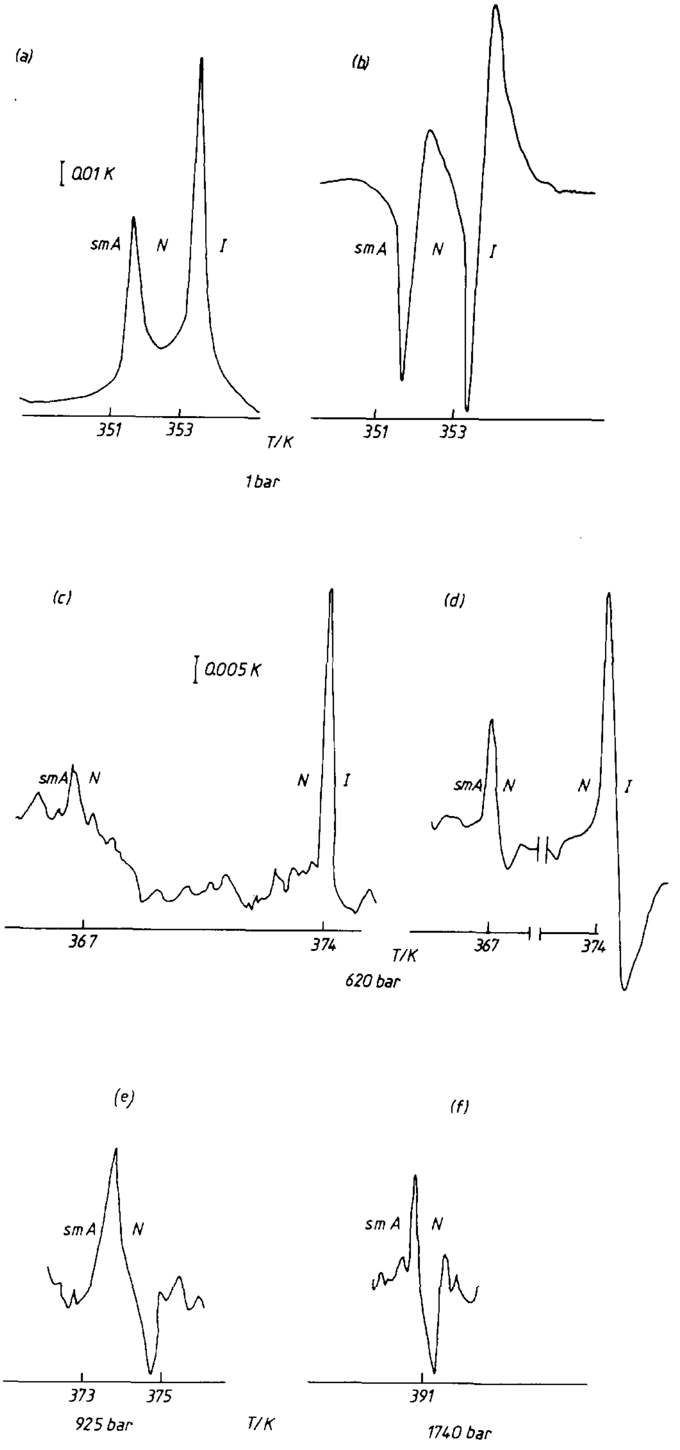

Fig. 2. DTA traces for 9OCB at different pressures. (a), (c). Normal signals; (b), (d)–(f), differentiated signals (see text).

our case is RC $\geq$ 100 s. DTA signals can thereby be distinguished from noise by their slope and are therefore accentuated by the differentiator. Changes in the slope would be missed by an integrating filter only; in addition to that an integrating filter would be disturbed by a drifting baseline. By means of a special circuit arrangement high frequencies are suppressed and cannot influence the differentiator. (For details, see ref. 1.) This differentiator was used with a high-pressure DTA apparatus described elsewhere [2,3].

The equipment has been applied to the investigation of the phase behaviour of the liquid crystal 4′-*n*-nonyloxy-4-*n*-cyanobiphenyl (9OCB) at high pressures. This substance is of interest since it is expected to show the same re-entrant phenomena as 4′-*n*-octyloxy-4-*n*-cyanobiphenyl (8OCB) [4,5]. 9OCB exhibits three phase transitions at 1 bar: s/smA, smA/N and N/I, where s = solid, sm = smectic, N = nematic and I = isotropic liquid. In Fig. 2(a) and (c) typical DTA traces with normal detection are given at 1 and 620 bar, respectively. It follows that the smA/N transition is clearly detectable at normal pressure [Fig. 2(a)], but it is no longer distinguishable from the noise at pressures higher than about 620 bar [Fig. 2(c)]. Nevertheless the differentiated signal [Fig. 2(b), (d)–(f)] is still detectable at that pressure [Fig. 2(d)] and remains visible over the whole experimental pressure and temperature range [see Fig. 2(e) and (f)].

Figure 3 gives the $p-T$ phase diagram as determined from DTA runs. Whereas the s/smA and N/I transitions can be obtained from both detection methods (full lines) up to the highest pressures obtained, the smA/N

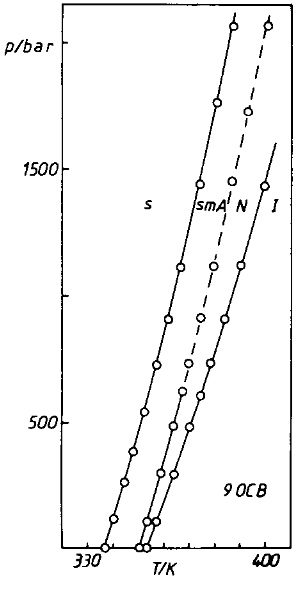

Fig. 3. $p-T$ phase diagram of the liquid crystal 9OCB. ———, Detected from normal and differentiated signals; – – –, detected from differentiated signals only (see text).

transition line could be detected above about 600 bar from differentiated signals only (see dashed line in Fig. 3). For details, see ref. 1.

These experiments demonstrate that the use of a differentiator might be indispensable in high-sensitivity DTA at high pressures. The investigations are continued.

ACKNOWLEDGEMENT

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