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RECENT DEVELOPMENTS OF MICROCALORIMETRY AT HIGH PRESSURES

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ABSTRACT

With two high-pressure DSC microcalorimeters A (100 - 300 K, to 4 kbar) and B (300 - 600 K, to 6 kbar) phase transition temperatures and enthalpies along the transition lines up to a maximum pressure of 6 kbar were measured for some plastic crystals e.g. cyclohexane, 2-chloro-2-methylpropane, polyethylene, diamantane. Hence other thermodynamic quantities can be calculated e.g. phase transition entropies and volumes. The splitting of the phase transition entropy into a configurational and a volume part is discussed using the own data on diamantane.

INTRODUCTION

The melting transition from a positionally and orientationally ordered crystalline solid (s_1) to the positionally and orientationally disordered isotropic liquid (l) is a direct one in most cases. The corresponding changes of enthalpy $\Delta_s^l H_m$ and entropy $\Delta_s^l S_m$ are normally large. But the melting transition can also be effectuated on two different ways involving intermediate phases

1) via liquid crystalline phases (lc) exhibiting different degrees of positional disorder where, however, a considerable amount of orientational order is remaining (right hand side of Fig. 1; for contributions on liquid crystals to these Proceedings see refs. 1 - 3) or
2) via socalled plastic crystalline phases (e.g. s_2) where the positional order of a normal crystalline solid is widely maintained whereas a considerable amount of orientational disorder exists (left hand side of Fig. 1). Here the changes of enthalpy $\Delta_{s1}^{s2} H_m$ and entropy $\Delta_{s1}^{s2} S_m$ related to the solid (s_1) → solid(s_2) transition are often higher than the corresponding values for the subsequent melting transition $s_2 \rightarrow 1$.

This review deals with transition enthalpies $\Delta_{trs} H_m$ and transition temperatures T_{trs} for some selected substances involving plastic crystalline phases that have been determined recently in the author's laboratory at Bochum using high-pressure differential scanning calorimetry (DSC) up to 6 kbar. For first order transitions the transition entropies $\Delta_{trs}S_m$ can be calculated from the $\Delta_{trs}H_m$ and T_{trs} data determined experimentally according to the relation

$$\Delta_{trs}S_m = \Delta_{trs}H_m/T_{trs} \tag{1}$$

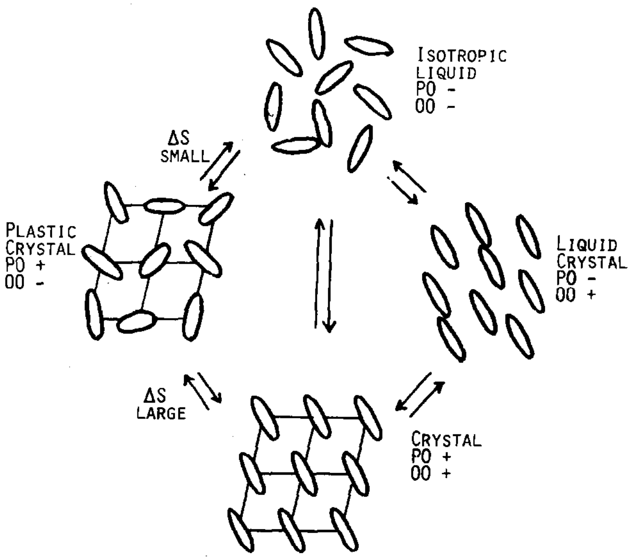


Fig. 1. Different ways for the phase transition ordered crystal → isotropic liquid (see text; PO = positional order, OO = orientational order)

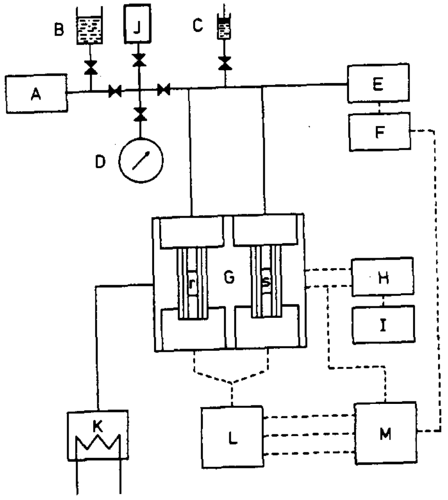


Fig. 2. High-pressure DSC microcalorimeter B (schematical; A handpump, B silicon oil, C oil syringe, D manometer, E strain gauge, F amplifier, C tempering jacket, H temperature regulator, I temperature program transmitter, K oil cooler, L DSC-1B control unit, M recorder, r reference, s sample; refs. 12,13)

From $\Delta_{trs}S_m$ some knowledge about the degrees of freedom that are involved in the crystal (s_1) → plastic crystal (s_2) transition can be obtained.

EXPERIMENTAL

Calorimetry at high pressure is in principle difficult because of the high heat capacities of the autoclaves and heat conductivities of the pressure transmitting media. Promising results have recently been obtained from differential scanning calorimetry (DSC) where heat losses are more or less balanced since sample and reference are always maintained at about the same temperature.

In our laboratory two high-pressure DSC microcalorimeters are in operation both being based on a preceding construction by Kamphausen (refs. 4,5). The essential parts of both are two identical high-pressure autoclaves each containing one original sample holder of a Perkin-Elmer DSC-2 microcalorimeter for the sample and the reference respectively.

- Calorimeter A has been constructed for measurements from 100 to 300 K and at pressures up to 4 kbar (Arntz; refs. 9,10)
- Calorimeter B can be used between 300 and 600 K and up to 6 kbar; the whole apparatus is schematically given in Fig. 2 (Sandrock; refs. 11,12). Details of the experimental set-up (e.g. of the gas-tight pans), the calibration procedure and the measuring technique are discussed elsewhere (refs. 12,13).

RESULTS

During the initial period of the high-pressure DSC investigations in the beginning of the seventies some long-chain alkanes and liquid crystals were studied (refs. 4 - 8). During the last few years the activities were concentrated on substances involving plastic crystalline phases.

With Calorimeter A phase transition temperatures and enthalpies have been measured for some selected plastic crystals e.g. cyclohexane (refs. 9,11), 1,3-dimethyladamantane (refs. 9,11). 1,3,5-trimethyladamantane (refs. 9,11), and 2-chloro-2-methylpropane (refs. 15,16). Some selected results are given in Figs. 3 - 7.

In Fig. 3 some original DSC traces are represented. Here the electrical power P to balance the temperature difference between the reference and the sample cell respectively is plotted against time t; from the position of the peaks the transition temperatures

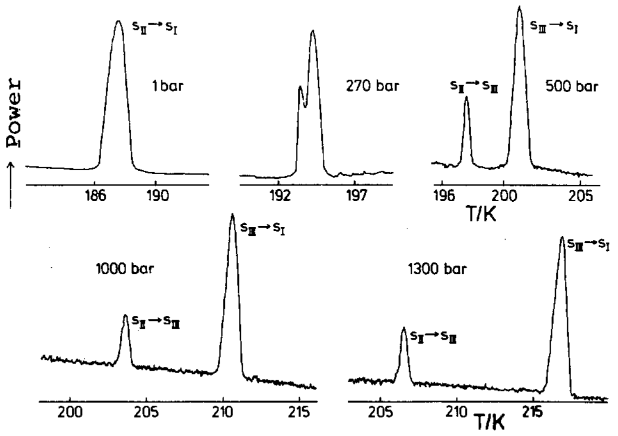


Fig. 3. Original DSC traces for cyclohexane (refs. 9,11)

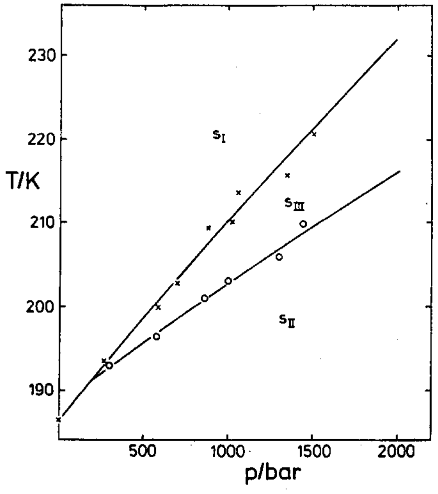


Fig. 4. T(p) phase diagram of cyclohexane (refs. 9,11)

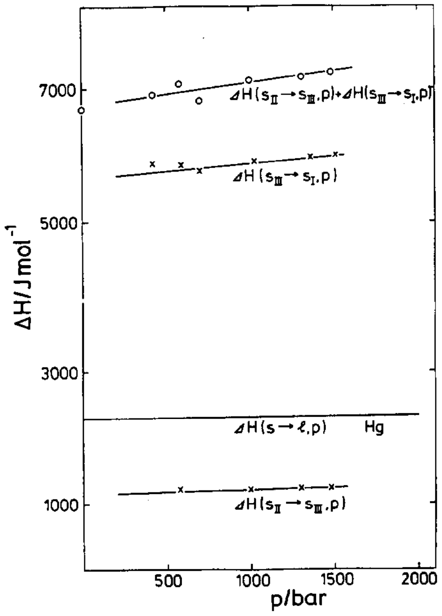


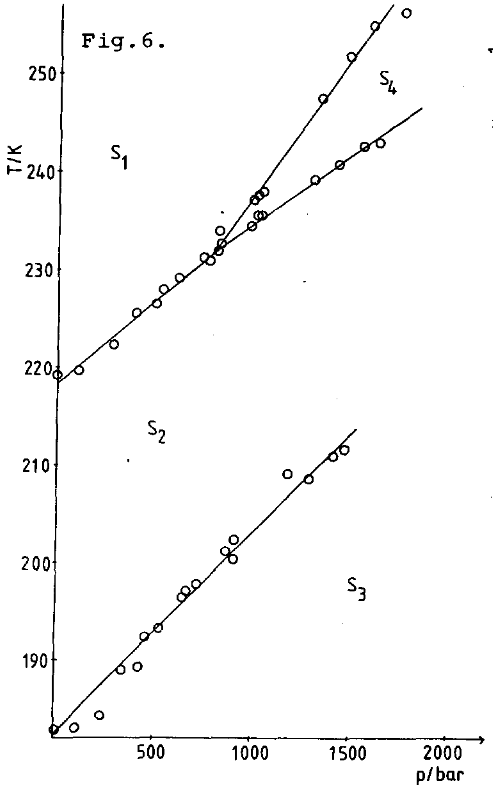
Fig. 5. $\Delta_{trs}H_m$ as a function of pressure along the transition lines for cyclohexane (refs. 9, 11; $\Delta_s^l H_m$ of mercury is also given; see text)

T_{trs} and from the peak areas the transition enthalpies $\Delta_{trs}H_m$ can be obtained. Fig. 3 shows DSC traces for cyclohexane at 1, 270, 500, 1000, and 1300 bar according to measurements by Arntz (refs. 9,11). With increasing pressure the s_{II}/s_I peak splits into two indicating the formation of a new pressure-induced phase s_{III}. This phase had been detected by Würflinger (ref. 17) for the first time; its existence could be confirmed by the present measurements. The p(T) phase diagram of cyclohexane obtained from our measurements is shown in Fig. 4 and in Fig. 5 the $\Delta_{trs}H_m$ data are plotted against pressure p on the coexistence lines. Here it is of interest that the enthalpy change for the $s_{III} \rightarrow s_I$ transition is much larger than that for the $s_{II} \rightarrow s_{III}$ transition; these facts give evidence for s_I being a plastic crystalline phase. In Fig. 5 the melting enthalpy of mercury is additionally given as a function of pressure along the melting pressure curve; the values were calculated from literature data and used for an internal enthalpy calibration (ref. 12).

Some results on 2-chloro-2-methylpropane (tert.butylchloride) are shown in Figs. 6 and 7 according to measurements by Wenzel (refs. 15,16). Here also a new pressure-induced phase was detected (triple point ca. 232 K, 805 bar).

In Calorimeter B polyethylene and diamantane were investigated. The p(T) phase diagram of polyethylene such as obtained from the DSC measurements is shown in Fig. 8; here the pressure-induced phase already found by other authors (ref. 18) could again be confirmed. For details (e.g. enthalpy changes, characterization of the material etc) see ref. 12.

Some results from a careful study of diamantane made by Sandrock (refs. 12, 14) are presented in Figs. 9 - 11. The original DSC traces in Fig. 9 demonstrate that even at high pressures the peaks are well resolved and have an excellent base line. In the T(p) phase diagram shown in Fig. 10 the very steep ascent of the melting pressure curve is remarkable ($dT/dp \approx 120\ K\cdot kbar^{-1}$). From the $\Delta_{trs}H_m$ and T_{trs} values obtained experimentally the transition entropies $\Delta_{trs}S_m$ were calculated; they are plotted in Fig. 11. The most interesting result is the large pressure dependence of the melting entropy.



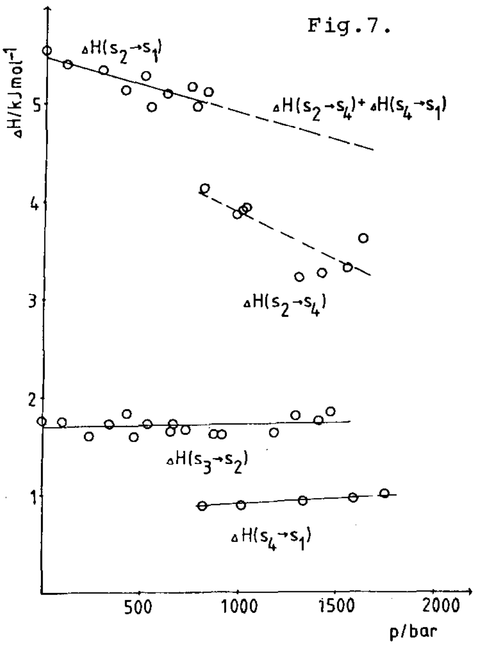


Fig. 6. T(p) phase diagram of 2-chloro-2-methylpropane (refs. 15,16)

Fig. 7. $\Delta_{trs}H_m$ as a function of pressure along the transition lines for 2-chloro-2-methylpropane (refs. 15,16)

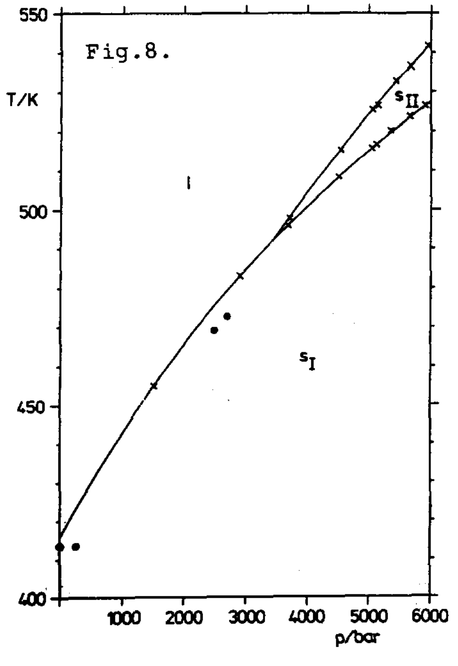


Fig. 8. T(p) phase diagram of polyethylene (ref. 12; ⊙ incompletely crystallized)

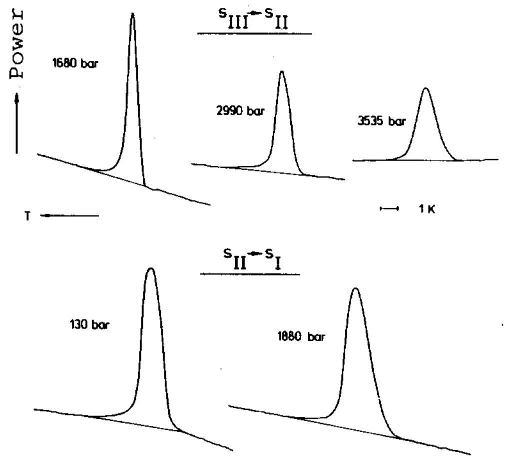


Fig. 9. Original DSC traces for diamantane (refs. 12,14)

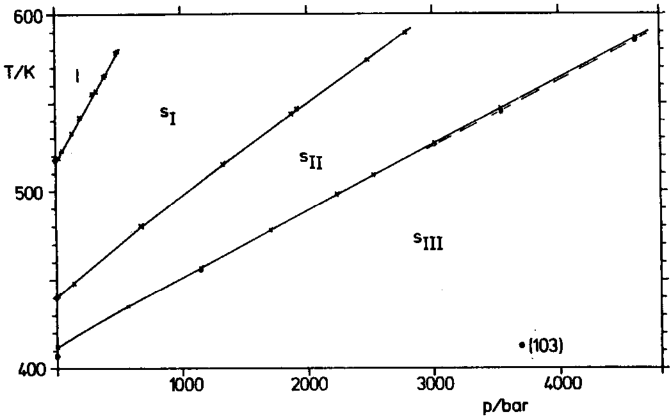


Fig. 10. T(p) phase diagram of diamantane (refs. 12,14)

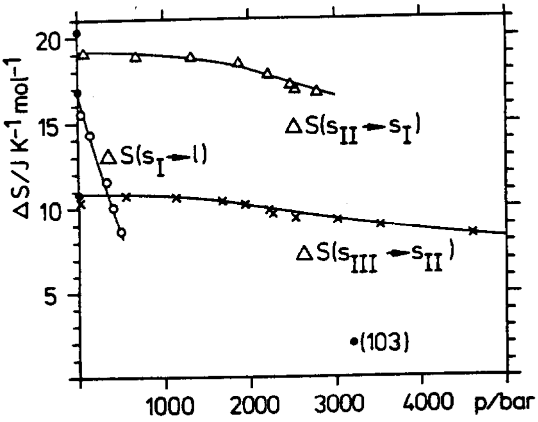


Fig. 11. $\Delta_{trs}S_m$ as a function of pressure along the transition lines for diamantane (see text; refs. 12,14)

DISCUSSION

In the present review transition temperatures T_{trs} (Figs.4,6,8, 10) as well as transition enthalpies $\Delta_{trs}H_m$ (Figs. 5,7) and transition entropies $\Delta_{trs}S_m$ (calculated from $\Delta_{trs}H_m$ and T_{trs} using Eq. (1)) (Fig. 11) were determined as a function of pressure along the coexistence lines. All transition temperatures increase with increasing pressure whereas different dependences on pressure are found for $\Delta_{trs}H_m$ and $\Delta_{trs}S_m$ according to substance and transition considered.

In the case of first order transitions the following differential equations hold for the curves shown in Figs. 4 - 8, 10, 11

$$\frac{dT_{trs}}{dp} = \frac{\Delta_{trs}V_m}{\Delta_{trs}S_m} = \frac{T_{trs}\Delta_{trs}V_m}{\Delta_{trs}H_m} \tag{2}$$

$$\frac{d\Delta_{trs}H_m}{dp} = \Delta C_{pm}\cdot\frac{dT_{trs}}{dp} + \Delta(V_m - T\cdot(\frac{\partial V_m}{\partial T})_p) \tag{3}$$

$$\frac{d\Delta_{trs}S_m}{dp} = \frac{\Delta C_{pm}}{T}\cdot\frac{dT_{trs}}{dp} - \Delta(\frac{\partial V_m}{\partial T})_p \tag{4}$$

where $\Delta X \equiv X' - X''$. From Eq. (2) $\Delta_{trs}V_m$ can be calculated as a function of pressure along the coexistence lines since T_{trs}, dT_{trs}/dp and $\Delta_{trs}H_m$ are known from the experiments. A typical example is shown in Fig. 12 where $\Delta_{trs}V_m$ is plotted against p for diamantane (Sandrock; refs. 12,14); here again the large decrease of $\Delta_s^1V_m$ is of particular interest. From Figs. 11 and 12 vanishing $\Delta_s^1S_m$ and $\Delta_s^1V_m$ values on the melting pressure line can be extrapolated at about 1 kbar; additional investigations are underway.

The total phase transition entropy $\Delta_{trs}S_m$ can generally be divided into two parts, a configurational entropy $\Delta S_{conf,m}$ and a volume entropy $\Delta S_{V,m}$

$$\Delta_{trs}S_m = \Delta S_{conf,m} + \Delta S_{V,m} \tag{5}$$

with

$$\Delta S_{V,m} \approx \frac{\alpha_p}{\kappa_T}\cdot\Delta_{trs}V_m \quad \text{and} \tag{6}$$

$$\Delta S_{conf,m} \approx R\cdot\ln(N_2/N_1) \tag{7}$$

Here α_p and κ_T are (mean) values of the cubic expansion coefficient and the isothermal compressibility and N_2 and N_1 the number of possible molecular orientations in the high and low temperature phases respectively. Combination of Eqs. (5), (6), and (7) results

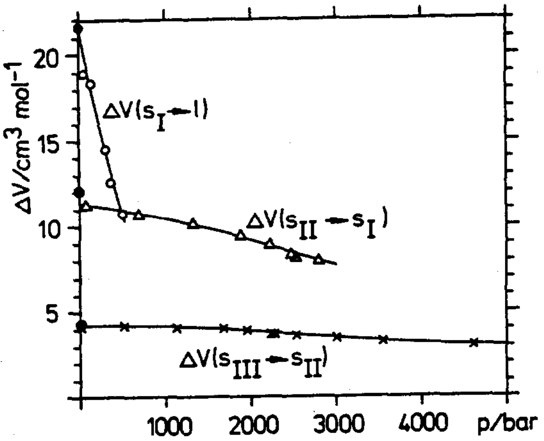


Fig. 12. $\Delta_{trs}V_m$ as a function of pressure along the transition lines for diamantane (see text; refs. 12,14)

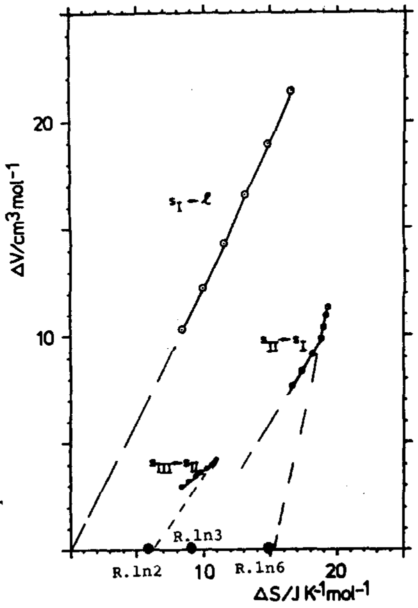


Fig. 13. $\Delta_{trs}V_m(\Delta_{trs}S_m)$ plots for diamantane for the determination of $\Delta S_{conf,m}$ (see text; refs. 12,14)

in

$$\Delta_{trs}V_m = \frac{\kappa_T}{\alpha_p}\left(\Delta_{trs}S_m - \Delta S_{conf,m}\right) \tag{8}$$

For the derivation of these equations and the assumptions made see refs. 12,14.

According to Eq. (8) a plot of $\Delta_{trs}V_m$ versus $\Delta_{trs}S_m$ will result in a straight line within the validity of the assumptions made, the intersection point with the abscissa giving $\Delta S_{conf,m}$. From the corresponding plot for diamantane in Fig. 13 $N_2/N_1 \approx 6$ results for the $s_{II} \rightarrow s_I$ transition and $N_2/N_1 \approx 2$ for the $s_{III} \rightarrow s_{II}$-transition when the extrapolation is made for the low-pressure branches (right hand side) of the curves. These findings can be interpreted by molecular rotations around the threefold axis in the s_{II} phase and by additional rotations around three twofold axes in the s_I phase. Smaller N_2/N_1 values are extrapolated from the high-pressure branches (left hand side) of the curves giving evidence for a change in the degrees of rotational freedom with increasing pressure (see refs. 12,14).

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