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LETTER TO THE EDITOR

An adiabatic calorimetry study of the polymorphism of 2,3-dimethylnaphthalene

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Abstract. Specific heat measurements for 2,3-dimethylnaphthalene (2,3-DMN) are presented for the temperature range 100–350 K. In the solid state, three anomalies in the specific heat curve are found, at 220 K, 275 K and 302 K. The anomalies at 275 K and 302 K are reported here for the first time. In the vicinity of the 220 K transition, interesting thermal effects are observed which might be connected with the existence of the modulated phase in 2,3-DMN.

2,3-dimethylnaphthalene (2,3-DMN) is an interesting molecular crystal. It belongs to the class of derivatives of naphthalene, a substance which is a well known, almost classical, molecular crystal. At room temperature the crystal structure of 2,3-DMN [1] is the same as that of naphthalene, i.e. monoclinic, space group $P2_1/a$ (C_{2h}^5) with two molecules per unit cell. The unit cell parameters are: $a = 7.916$ Å, $b = 6.052$ Å, $c = 10.017$ Å and $\beta = 105.43°$.

Such a structure requires that the molecules sit on a centre of symmetry. Because the 2,3-DMN molecule is acentric, this results in the presence of dipolar disorder, i.e. statistical up- and down-orientation of the dipolar molecule.

The heat capacity of 2,3-DMN has previously been measured in the temperature range 58–310 K by means of adiabatic calorimetry [2] but no solid–solid phase transitions were reported. However, x-ray studies [1] revealed the existence of two phase transitions, one of higher order from monoclinic to triclinic symmetry occurring around 220 K and the first-order one at about 100 K. The structures of the low-temperature phases are not known. The Raman spectra for fully deuterated 2,3-dimethylnaphthalene (2,3-DMN-d_{12}) measured at various temperatures also show differences consistent with the existence of polymorphism in the solid state [3]. In recent neutron diffraction measurements of 2,3-DMN-d_{12}, satellites were observed below 220 K, indicating the existence of an incommensurate phase below that temperature [4]. In view of these latter results, it seemed interesting to study the phase situation of 2,3-DMN using a highly accurate adiabatic calorimeter.

The measurements of the heat capacity were performed using the modernised version of the adiabatic calorimeter described in [5]. The sensitivity was better than 10 μK and the accuracy of the specific heat measurement was about 1%.

Two modes of operation were used. One of them was a classical specific heat measurement under adiabatic conditions. In the second mode (hereafter termed 'scanning mode'), the temperature difference between the sample and the adiabatic shield

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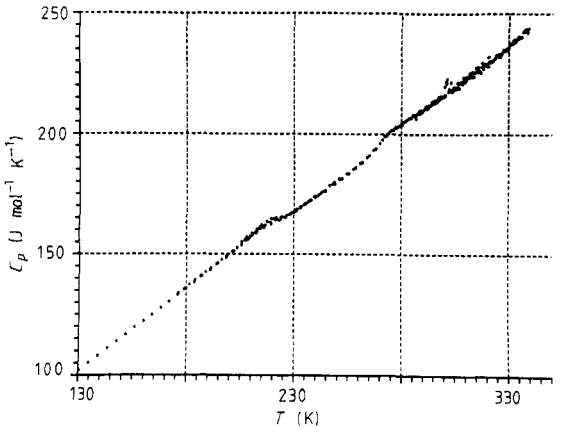

Figure 1. The specific heat of 2,3-DMN in the temperature range 130–340 K.

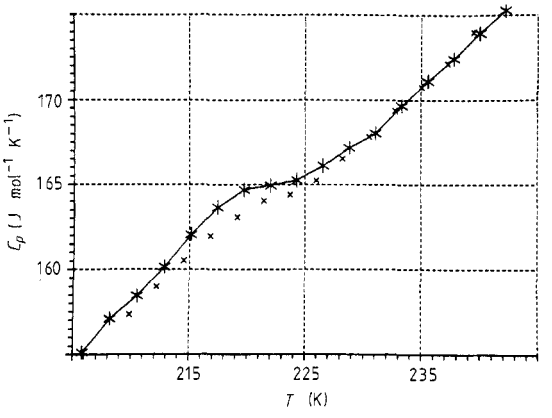

Figure 2. The specific heat of 2,3-DMN in the vicinity of the phase transition at 220 K.

was kept constant (positive or negative). The sample temperature was measured as a function of time. The anomaly in the heat capacity is then reflected by the anomaly in the cooling and heating rates. The details of this mode of operation are given in [6]. The temperature drift $\Delta T/\Delta t$, i.e. the cooling or heating rate, is hereafter abbreviated to 'drift'.

The sample used was a commercial powder sample. 33.85 g of 2,3-DMN were used, this being 0.217 mol. The measurements were performed in the temperature range 100–350 K. Several experimental runs were performed for each of the two modes of operation. Throughout the measurements we concentrated on the solid phase, as the transition to the liquid phase is well known from DSC measurements [7].

Figure 1 presents the specific heat of 2,3-DMN as a function of temperature. In [2], the explicit value of C_p is given as 217.2 J mol K^{-1} at 298.15 K. At this temperature our value is lower by about 1%.

The present experiments found three anomalies in the specific heat curve. One broad transition appears at 220 K and another transition appears at 302 K. There is also a weak broad anomaly at around 275 K. The heat capacities in the vicinity of the 220 K and 302 K transitions are shown in figures 2 and 3, respectively. The experimental points in figure 2 come from different runs. We observed that the magnitude of the anomaly at

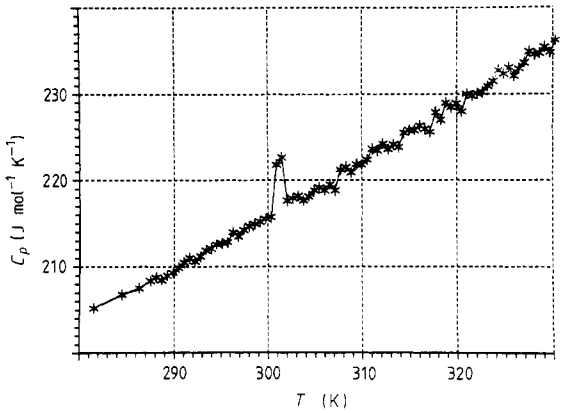

Figure 3. The specific heat of 2,3-DMN in the vicinity of the phase transition at 302 K.

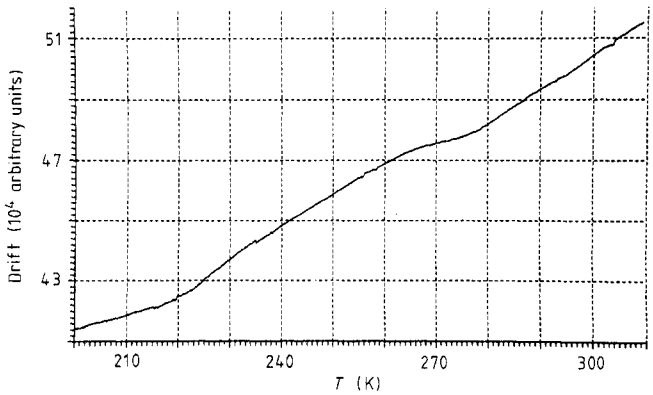

Figure 4. The results of the scanning mode applied on heating as described in the text. 'Drift' ($\Delta T/\Delta t$) means the temperature drift.

220 K depended to some extent on the temperature to which the sample was cooled prior to a given run.

Figure 4 presents the results of the measurements using a scanning mode on heating. All the anomalies are seen, although with the scale of the diagram the transition at 302 K is hardly visible. This transition has not previously been reported. In order to determine whether it is a first-order transition, its possible hysteresis was studied using the scanning mode. The results are shown in figure 5. By appropriate heating and cooling of the sample, the supercooling of the transition at 302 K was verified, and we may conclude that it is a first-order transition. Due to its weakness, its parameters could be only roughly estimated and are

$$T = 302 \text{ K}$$

$$\Delta H = 104 \text{ J mol}^{-1}$$

$$\Delta S = 0.35 \text{ J mol}^{-1} \text{ K}^{-1}.$$

The results of the measurements using the scanning mode on cooling are shown in figure 6. Around 293 K we see the supercooled 302 K transition. In the vicinity of the 220 K transition, very interesting and unusual behaviour was observed. In the

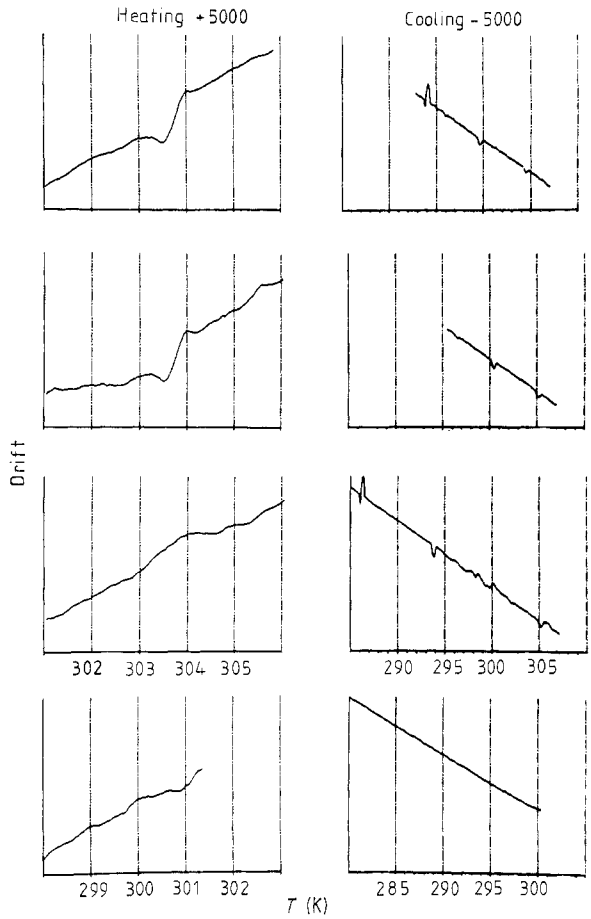

Figure 5. The results of the subsequent heating and cooling runs in the scanning mode showing the supercooling of the 302 K transition. The 1.5 K shift towards the higher temperatures of this transition is connected with the dynamic nature of the scanning mode and relatively high heating rate.

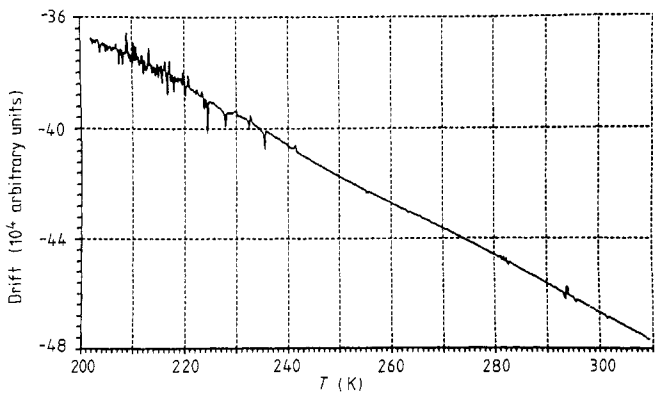

Figure 6. The results of the measurements in the scanning mode on cooling.

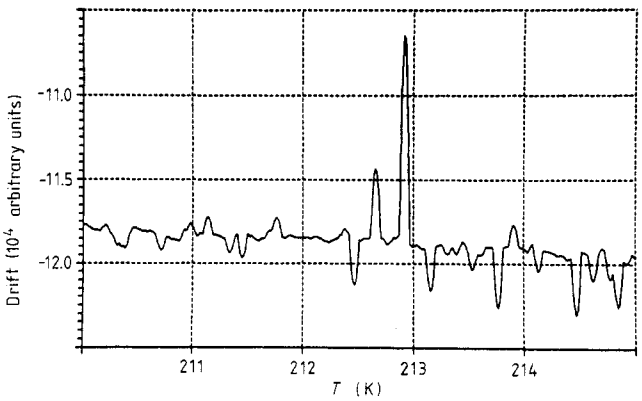

Figure 7. An enlarged-scale plot of the cooling rate fluctuations seen in figure 6.

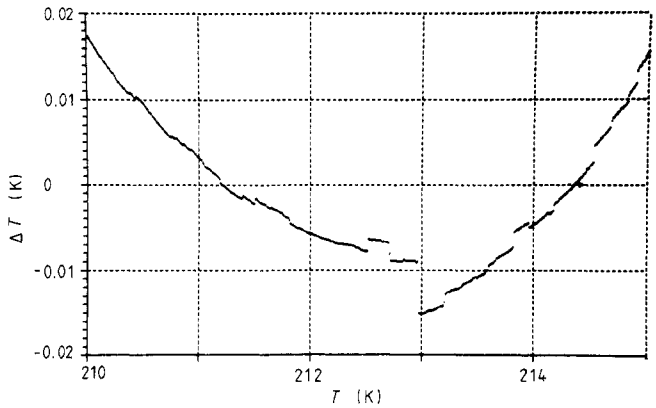

Figure 8. The same data in figure 7 in another representation. ΔT is means the deviation of the temperature from a linear dependence on time.

temperature range between about 230 and 200 K, strong fluctuations (both positive and negative) of the cooling rate were observed reflecting some thermal effects in the sample. In figure 7 they are shown on an enlarged scale. Numerous experimental runs were performed with different cooling rates and different thermal histories. In all runs the effects shown in figures 6 and 7 always appeared in the same temperature range, although their detailed structure was not identical from run to run. Strange behaviour in this temperature range was observed both in the 'fresh' sample consisting of small flakes packed tightly into the calorimetric vessel and in the sample obtained from the melt.

In order to estimate the magnitude of those thermal effects, the data of figure 7 are shown in another representation (figure 8). This presents the deviation (denoted in the diagram as ΔT) from a smooth line. In such a representation, it is seen that the jumps are of the order of mK, which gives an enthalpy change of the order of 0.1 J.

Although one cannot exclude other possible explanations, it seems that the fluctuations might be connected to the existence of the modulated phase in 2,3-DMN, as suggested by neutron diffraction results [4]. It is worthwhile noting that the observation of such subtle thermodynamic effects was possible because of the very slow cooling rates

and also due to the high sensitivity of our calorimeter, which was further enhanced by the large sample used.

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