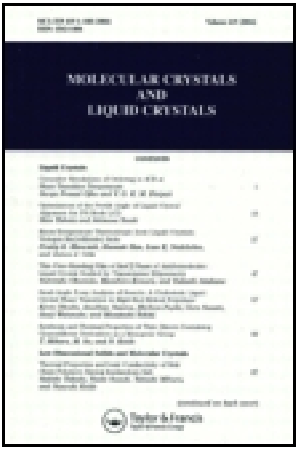

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Calorimetric Study of the Phase Transition of Para-Terphenyl

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Calorimetric Study of the Phase Transition of Para-Terphenyl

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INTRODUCTION

At 300 K crystalline para-terphenyl (PTP) may be considered to be planar, but the librational amplitude of the central ring is unusually high (16°). This behaviour has been explained by the occurrence of a double well potential for the central cycle which occupies at random one of the two possible positions and jumps continuously from one minimum to the other one.[1] When the temperature is lowered, a superstructure appears: an antiferro-reorientational ordering results from the stabilization of the central ring in one of the two possible wells.[2] A recent treatment of the diffraction data (neutron as well as x-ray) collected in the high temperature phase has confirmed this hypothesis: a double-peaked distribution function was obtained for the central ring librations.[3]

The Raman spectrum of PTP was recorded between 3 and 170 cm^{-1}.[4] When the temperature was raised from 15 to 300 K, no sudden change was noticed: all the Raman lines broadened progressively until the transition temperature was reached.

The transition has also been observed by electron diffraction,[5] IR spectroscopy[6] and neutron diffraction of a deuterated sample[7] in which the study of some superlattice reflections showed a continuous or nearly continuous phenomenon. Moreover a critical exponent could be associated with the

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variation of the relative intensities of these reflections as functions of $\varepsilon = (T - T_c)/T_c$. This exponent is small ($\beta \sim 0.15$) and corresponds either to a first-order transition close to a second order regime or to a two dimensional Ising model.

It was therefore valuable to complete these experiments by a study of the transitional heat capacity, which may also be expressed by a critical exponent as a function of ε.

EXPERIMENTAL

A sample of 0.199 mole of zone-melted PTP-h_{14} was studied between 10 and 300 K in an adiabatic calorimeter fully described previously.[8] Temperatures were measured with a Pt resistance thermometer (Leeds and Northrup) by a potentiometric method. The adiabatic shield temperature was kept automatically equal to that of the calorimeter within 0.3 K. The overall accuracy of the results obtained is estimated to be ±0.3 %.

RESULTS

A transition extending over 20 K was found with a C_p maximum at 193.33 K and a $\Delta S_t = 0.49$ J mole^{-1} K^{-1}, that seemed continuous for the resolution used ($\sim$0.8 K) (Figure 1). The transition temperature found by neutron diffraction[7] on a fully deuterated sample was 177.7±0.2 K.

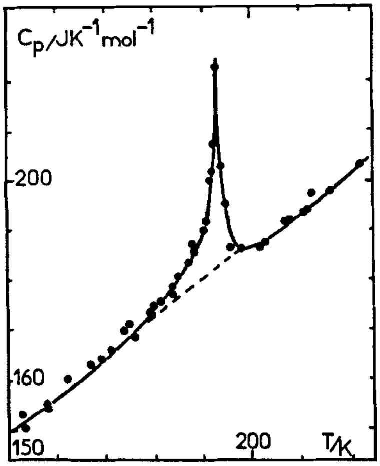

FIGURE 1 Heat capacity of *p*-terphenyl in transition region.

The difference in the transition temperature between PTP-d_{14} and PTP-h_{14} was attributed to an isotopic effect.[9] This hypothesis was checked by differential scanning calorimetry (Perkin Elmer DSC 2), which gave the following results:

PTP-d_{14} $T_c = 178.8$ K $\Delta S_t = 1.08$ J mole^{-1} K^{-1}

PTP-h_{14} $T_c = 191.0$ K $\Delta S_t = 0.45$ J mole^{-1} K^{-1}

DISCUSSION

The division of structural phase transitions into "displacive" and "order disorder" is not an absolute one: it has been theoretically shown[10] that intermediate types are possible. The transition of PTP seems to belong to such a case: the smallness of the transition entropy supports a displacive mechanism as in chloranil[11] but no soft mode has been observed;[4] on the other side the existence of a double-peaked distribution function of the central ring librations[2] is an argument for the order–disorder behaviour counter-balanced by the low value of the potential barrier height. Similar situations have been observed in other systems such as $SnCl_2 \cdot 2H_2O$[12] or *p*-diiodobenzene.[13]

The heat capacity results in the transition region were analyzed according to Salamon's procedure.[14] The data were introduced into expressions of the form

$$C_p^+ = A^+(\varepsilon^{-\alpha^+} - 1)/\alpha^+ + B^+ + D\varepsilon$$

and

$$C_p^- = A^-(|\varepsilon|^{-\alpha^-} - 1)/\alpha^- + B^- + D\varepsilon$$

where A and B are constants, $\varepsilon = (T - T_c)/T_c$, the signs + or − refer to the situations $T > T_c$ and $T < T_c$ respectively and D is a base line slope parameter easily determined far from T_c. The essence of the scaling argument lies in the basic symmetry of the critical properties with respect to T_c: if and only if the critical exponents α^+ and α^- are equal, C_p^+ and C_p^- can be combined, plotted on the same curve as a function of ε and fitted with a single power law (Figure 2).

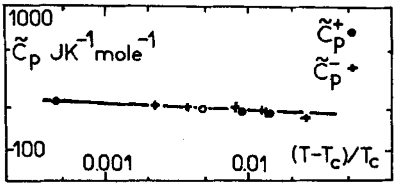

FIGURE 2 Determination of the critical exponent according to Salamon's procedure.

This method gave $\alpha^+ = \alpha^- = 0.049$ for $10^{-3} < \varepsilon < 10^{-2}$ with $T_c = 193.24$ K, but the number of relevant heat capacity results is very limited and needs to be substantially increased. A consequence of $\alpha > 0$ is that C_p becomes infinite at T_c: this has to be tested with a very small resolution ($\sim$0.1 K) in the neighbourhood of T_c. The magnitude of α is comparable to other exponents.[15]

The problem in such a treatment lies in the uncertainty about the true value of the excess heat capacity of the transition. Salamon takes into account the lattice contribution through a function of ε and not of T: this procedure lowers the correction near T_c and its purpose seems to aim at a flattening of the base line rather than a subtraction of the lattice contribution. If C^+ and C^- are corrected by the same function of T that was used for the determination of ΔS_t, α^+ and α^- remain equal but become very large, about 0.44 (Figure 3).

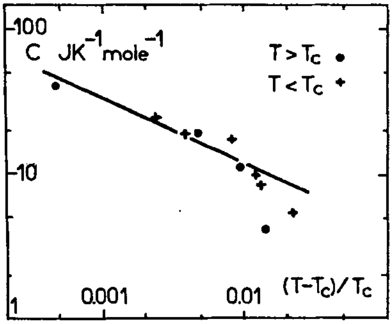

FIGURE 3 Other determination of the critical exponent.

CONCLUSION

In spite of its preliminary character, this study shows clearly that ideal situations seldom happen with molecular crystals. More work is needed, not only to clarify the particular problem of paraterphenyl but also to determine clear cut conditions for the calculation of excess properties.

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Note added on the proofs

During the Brandeis Conference, Professor E. F. Westrum Jr. has brought our attention to the fact that Dr. S. S. Chang had performed experiments on *p*-terphenyl. Dr. S. S. Chang kindly sent us his very precise results presented at the 7th. Symposium on Thermophysical Properties (American Society of Mechanical Engineers, N.B.S. May 1977) and at the American Chemical Society Meeting of Anaheim, March 1978. The agreement between both sets of results is very good.