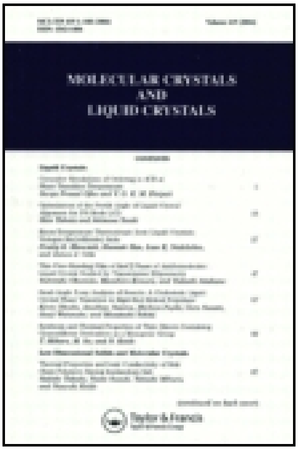

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A Characteristic Order-Disorder Molecular Phase Transition in 2-Chloronaphthalene

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A Characteristic Order-Disorder Molecular Phase Transition in 2-Chloronaphthalene

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An order–disorder phase transition has been studied in 2-Chloronaphthalene by both calorimetry and X-Ray diffraction. The transformation is reversible and does not destroy the single crystal. It extends over a large temperature range 253–309 K and can be considered as a "high order" transition: the high temperature form corresponds to a totally disordered phase and the low temperature form to a semi-ordered one.

I INTRODUCTION

The 2-Chloronaphthalene transition can be considered as a characteristic one for the series of $\beta(R)$ substituted naphthalene derivatives. It is particularly interesting by its continuous, reversible and "single crystal conservation" properties which allow a continuous investigation of the transition over its entire temperature range. The analysis methods which have been used are microcalorimetry measurements and X-ray diffraction on both single crystalline and polycrystalline materials.

II EXPERIMENTAL

The chemical products (MERCK C°) are purified by sublimation and zone melting methods in our laboratory. As a consequence of the easy syncrystallisation between 2-Chloronaphthalene and some homologuous compounds of the series, the final product contains a little residual amount of naphthalene (less than 0.5% as proved by mass spectrometry).

The measurements of heat capacities C_p are obtained with a low temperature differential Tian–Calvet microcalorimeter. The cooling system supplied by liquid nitrogen allows investigations in the temperature range 77–473 K. The detector sensitivity is approximately $E = 50\mu$ volt. mW^{-1}. The linear heating and cooling rates (dynamical method) are 4 degrees per hour in all experiments. C_p values ($\mathrm{J \cdot g^{-1}\,K^{-1}}$) are calculated from calorimetric curves according to:

$$C_p = \frac{1}{m}\cdot\frac{\Delta U}{E\,\mathrm{d}T/\mathrm{d}t}$$

where m = mass of the sample (g)
ΔU = observed deviation from zero line (V)
$\mathrm{d}T/\mathrm{d}t$ = rate of thermal treatment ($\mathrm{K \cdot s^{-1}}$)

X-Ray diffraction investigations are performed on single crystals and polycrystalline samples. In the first case, Weissenberg and precession cameras, equipped with freezing and heating regulation system are used. A Guinier–Lenné camera is used to study polycrystalline samples in the temperature

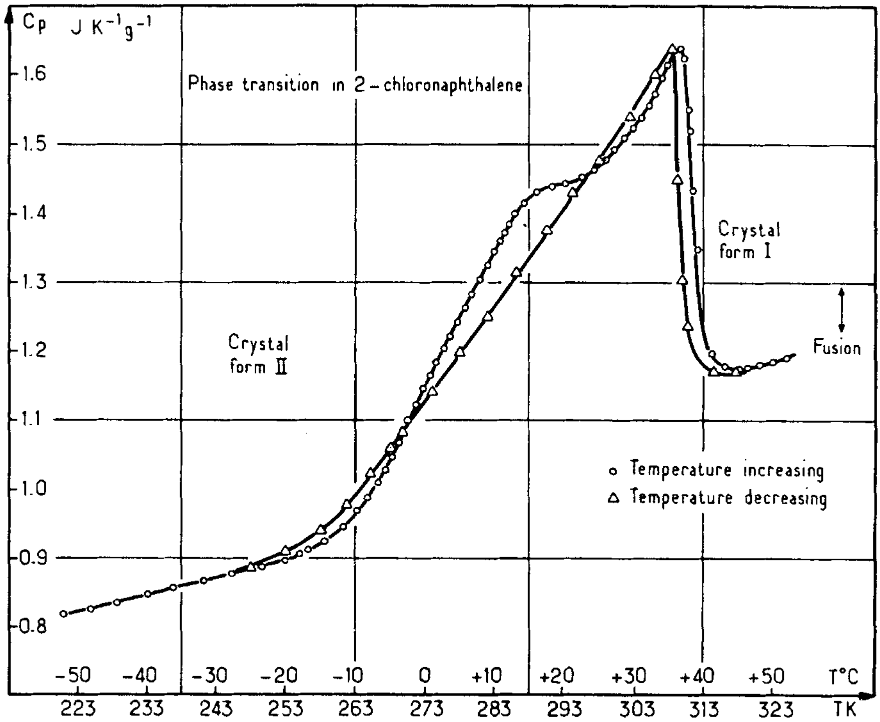

FIGURE 1 Variation of C_p throughout the transition.

range 100–470 K. Crystals and polycrystalline samples are sealed into Lindemann capillaries in order to avoid sublimation of the product. Precise determinations of crystallographic parameters are performed on a powder diffractometer, the thermal regulation system of which provided a stability of the temperature better than one degree. Internal standard (quartz) is included in the samples, so that the precision of θ values (Bragg diffraction angles) is 0.01 degree.

III RESULTS AND DISCUSSION

Thermal results for the temperature range 223–328 K are given in Figure 1. An anomaly of C_p is detected with both increasing and decreasing temperature. This phenomenon which occurs over a large temperature range (about 60 degrees) corresponds to a reversible phase transition in the solid state. The delay observed on the cooling curve is very weak: 2 degrees. The integration of C_p values (with H_{233K} as origin) leads to the curve shown on Figure 2.

Diffraction patterns corresponding to each temperature do not show any changes from the beginning to the end of long exposure times (five days or more) so that each diffraction pattern is actually characteristic of a stable state. The thermal evolutions of the (*h*0*l*) and (*h*1*l*) diffraction planes have been recorded. The directions of the crystallographic axes are the same along the transition high temperature form I ↔ low temperature form II.

Form II corresponds to a substructure of form I along the *c* axis of the monoclinic cells with $c_{II} \simeq 2c_I$ whereas $a_{II} \simeq a_I$, $b_{II} \simeq b_I$ and $\beta_{II} \simeq \beta_I$. The space group $P2_1/n$†, $Z = 4$ (form II) changes into $P2_1/a$, $Z = 2$ (form I). In order to illustrate these crystallographic variations, three characteristic cell parameter values are given in the following table.

T°(K)	*a*(Å)	*b*(Å)	*c*(Å)	β(°)	space group	*Z*	$V_{(Z=4)}$Å^3	Crystalline form
313	7.730	5.962	10.665	120.00	$P2_1/a$	2	2 × 426	I
299	7.680	5.956	21.316	120.22	$P2_1/n$	4	843	(transition phase)
248	7.596	5.930	21.240	120.34	$P2_1/n$	4	827	II

The transition may be interpreted by reorientational molecular motions on the crystallographic sites. As a consequence, the "molecule" in the high

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† We have chosen the formalism $P2_1/n$ which is not a conventional one (it corresponds to the space group $P2_1/c$) because it allows a description of this continuous transition. With this formalism, the crystallographic axis are the same in low and high temperature forms.

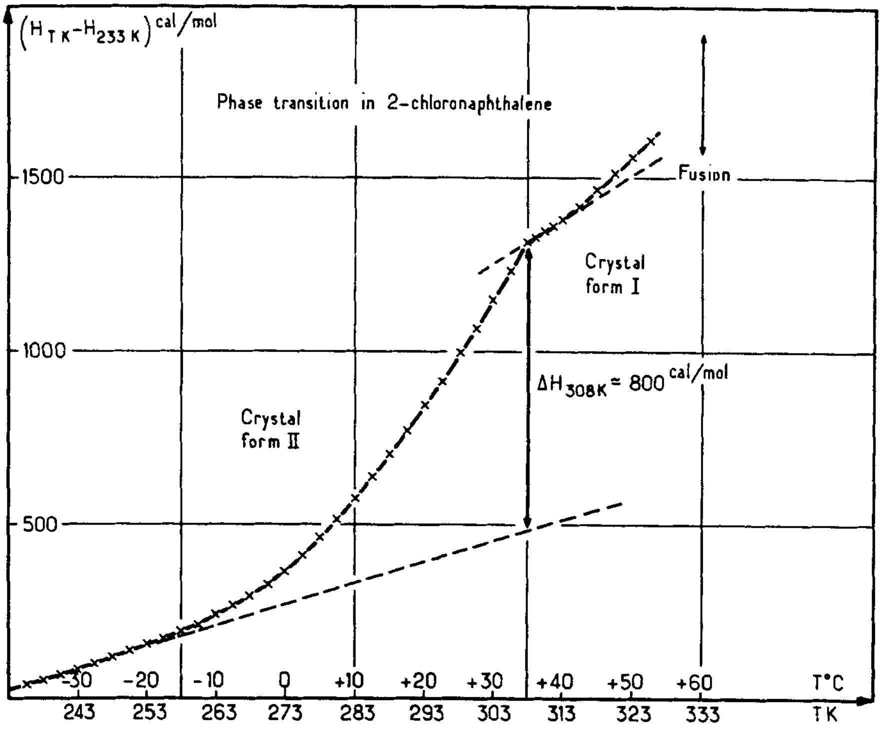

FIGURE 2 Relative variation of enthalpy values from C_p measurements.

temperature form appears to be completely centrosymmetrical with a statistical equidistribution of the chloride atom on the four β sites of the naphthalene ring (occupancy factor $f = 0.25$): the symmetry of the cell becomes the same as that of the pure naphthalene one†, with very similar crystallographic parameters. The structure of form I is totally disordered. On the other hand, form II appears to be semidisordered: crystal structure determinations all along this transition are in progress in our laboratory; first results show that the chloride atom is not equidistributed in the low temperature form.

A small and reproducible "hump" is detected near 290° K on the heating C_p curve (Figure 1). An interpretation of this phenomenon, based on a mechanism involving two near stages during the transition, can be submitted. Since the passage from the low temperature form (asymmetrical "molecule") to the high temperature one (centrosymmetrical "molecule") needs neces-

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† As regards to the crystal structure of naphthalene see Ref. 1.

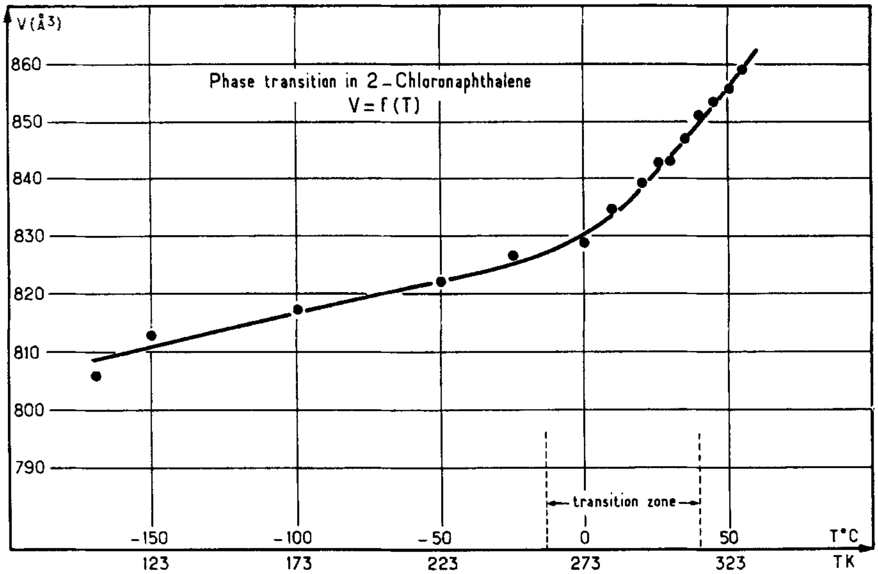

FIGURE 3 Cell volume variation (for 4 molecules) as regards to the phase transition.

sarily at least two types of reorientational motions around two pseudo binary axis of the molecule, it seems correct to assume that there are two competitive temperature dependent motions.

Both crystallographic and thermal results tend to prove that transition I ↔ II can be considered as a "high order" one and even as an "infinite order" one according to Allen and Eagles' approach of the continuous transition.[2] As a matter of fact, the enthalpy curve is continuous and shows only a weak break at 308 K (Figure 2). In the same way, the characteristic variation of the molecular volume plotted versus T (Figure 3) supports this assumption according to the conclusions of other works about specific volume studies.[3,4]

IV CONCLUSION

The 2-Chloronaphthalene, like several substituted naphthalene derivatives,[5–8] is affected by a crystalline phase transition induced by molecular disorder. This progressive and reversible transformation occurs in a large temperature range 253–309 K. Thermal analysis and X-Ray diffraction studies tend to show that the transition "total disordered form" I ↔ "semi-disordered form" II can be considered as a "high order" one.

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