TEMPERATURE DEPENDENCE OF BIREFRINGENCE OF β-NAPHTHOL CRYSTALS

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A statistical model of phase transition is proposed by the measurements of birefringence of the β-naphthol crystal as a function of temperature. The possibility to determine the lattice barriers of defect formation using these measurements is discussed.

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1. Introduction

There are very few literature data [1–5] on the temperature dependence of the birefringence of molecular crystals. They indicate the large sensitivity of birefringence to the microscopic changes in the crystal lattice. Especially great changes were observed near the phase transition point.

The phase transition of the β-naphthol crystal from low-temperature phase II to high-temperature phase I was first observed by Kofler [6]. This occurs at 391 K. Only very small changes in the crystal structure appear during phase transition. All the symmetry elements are ratained and only a four-fold decrease in the crystallographic c axis period appears [7]. Althought the structural changes are small, the positions of molecules in the crystal considerably change.

NMR, X-Ray and IR studies allow one to put forward a hypothesis that phase transition II → I could be explained as a result of the reorientation movements of half the quantity

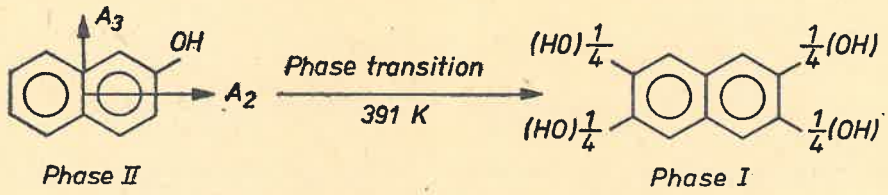

Fig. 1. Relation between phases of β-naphthol (schematic)

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of molecules by 180°, probably around the A_1 and A_2 molecular axes (Fig. 1). This reorientation gives the statistical structures in which the molecules became centrosymmetric [8].

Since birefringence is very sensitive to the reorientation of molecules in the crystal lattice, we started studies on the usefullness of the birefringence measurements of the β-naphthol crystal for establishing its structural changes near the phase transition point.

2. Experimental

Birefringence was measured using the interference method in polarized light [1]. The accuracy of these measurements was ± 0.0002. To assure better thermic contact, the samples were placed in silicon oil layers between glass plates. During the measurements the samples were placed in a sample-house, where temperature was kept stable by a tyrystoric temperature regulator (± 0.1 K). The temperature was controlled with a copper-constantan thermocouple.

β-naphthol was purified by the recrystallization and zone melting method and its melting point was 395–395.5 K, which is in a good agreement with the literature data [9]. The monocrystals examined obtained from the vapour phase, have a (001) orientation which was determined by optical and X-ray examinations.

3. Results and discussion

The birefringence of the β-naphthol crystal at the (001) cleavage plane as a function of temperature is shown in Fig. 2. The measurement dependence can be given analytically as

$$\Delta n_T = \Delta n_{293} - 1.06 \times 10^{-5}(T - 293) \qquad (1)$$

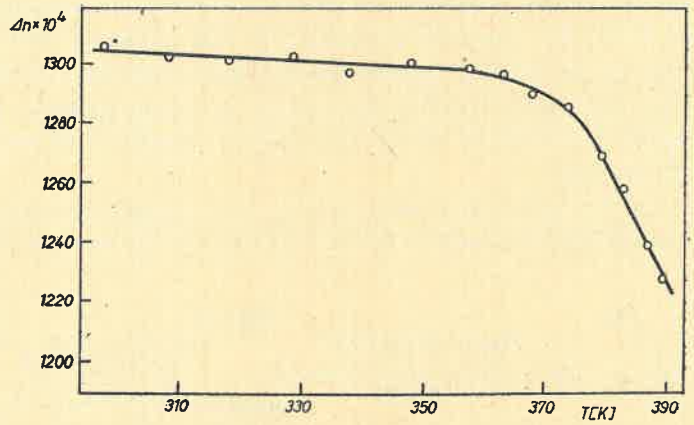

Fig. 2. Birefringence of β-naphthol crystals at the (001) cleavage plane as a function of temperature

in the 293 K–363 K range, where Δn_T and Δn_{293} are birefringence values at the temperatures equal to T and 293 K, respectively. The small value of the temperature birefringence coefficient for β-naphthol crystal equals -1.06×10^{-5} and appears as a result of strong

forces between molecules in phase II at the (001) cleavage plane. It is due to hydrogen bond chains of the O—H ... O type, 2.72 and 2.79 Å long, parallel to the crystallographic a axis [7]. So, there are very small birefringence changes in this temperature range, what confirms very small reorientations of the molecules.

However, 25 K below the phase transition point a strong decrease of the birefringence is observed, probably as a result of gradual breaking of the hydrogen bond and, consequently, an increase in the reorientation freedom of the molecules. Assuming the statistical character of the molecular reorientation processes, ΔH, called "lattice defects formation energy", can be estimated.

In our model, the probability for the formation of these defects $\theta(T)$ was assumed as

$$\theta(T) = \exp(-\Delta H/RT), \tag{2}$$

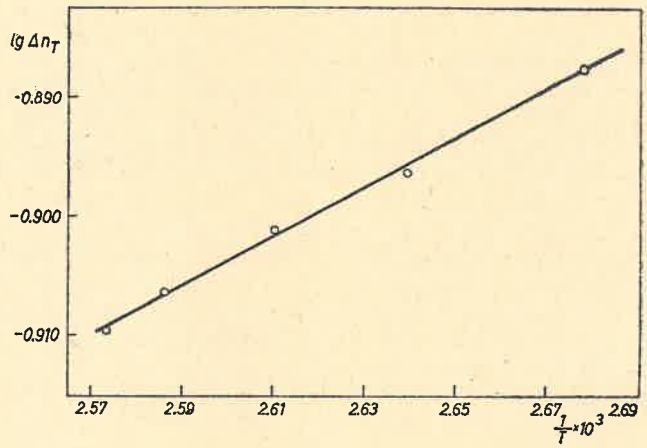

Fig. 3. Temperature dependence of birefringence as $\lg(\Delta n_T) = f(1/T)$ in the 368–388 K range

where $\theta(T) = \Delta n_T/\Delta n_0$, Δn_0 is a constant value and R is the gas constant. The logarithmical form of Eq. (2) in the 368 K–388 K range was graphically presented in Fig. 3. The least squares procedure applied to Eq. (2) leads to the calculation, ΔH, of the phase transition. From this value the entropy phase transition, (ΔS), can be estimated.

TABLE I

Thermodynamic properties of β-naphthol crystals from birefringence measurements

	According to Ref. [9]	Calculated in this work
ΔH phase transition (cal/mole)	1050	960
ΔS phase transition (cal/mole K)	2.80	2.53

The correctness of our model was confirmed by a comparison of calculated and literature data [9] (Table I). The entropy of phase transition of the order-disorder type can also be expressed according to the following equation [10]

$$\Delta S = R \ln N_{\mathrm{I}}/N_{\mathrm{II}}, \tag{3}$$

where $N_{\mathrm{I}}/N_{\mathrm{II}}$ is the ratio of possible arrangements of the OH group in the high- and low-temperature phases. The value $N_{\mathrm{I}}/N_{\mathrm{II}} = 3.6$ obtained from Eq. (3), is in a fair agreement with four arrangements of the hydroksyl group in the high-temperature phase obtained by Changh and Haget [8].

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