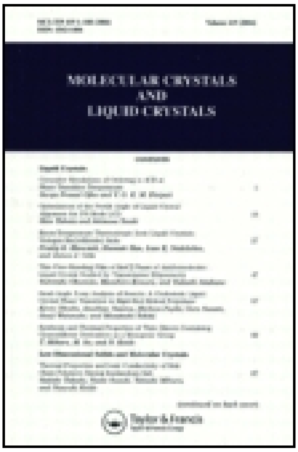

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Non-Equilibrium Phase Transitions: Metastable Phase → Stable Phase, Studied by Adiabatic Calorimetry

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Version of record first published: 24 Sep 2006.

To cite this article: Małgorzata Rachwalska (1993): Non-Equilibrium Phase Transitions: Metastable Phase → Stable Phase, Studied by Adiabatic Calorimetry, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 151-162

To link to this article: http://dx.doi.org/10.1080/10587259308030131

*Mol. Cryst. Liq. Cryst.*, 1993, Vol. 237, pp. 151–162
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# Non-Equilibrium Phase Transitions: Metastable Phase → Stable Phase, Studied by Adiabatic Calorimetry

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*(Received January 10, 1992; in final form September 2, 1992)*

The work studies metastable phases of some liquid crystal substances by adiabatic calorimetry. The process of transformation between metastable and stable phases is described quantitatively. The conclusions obtained deal with stability of metastable phases and energy difference between a metastable phase and a stable one.

*Keywords: NPOB, $\bar{7}$S5, MBBA, HOAB, adiabatic calorimetry, non-equilibrium phase transitions*

## 1. INTRODUCTION

Substances which in some temperature regions show liquid crystal properties, are characterised by the existence in the solid phase of one or many metastable phases. As examples let us take: (a) 4-nitrophenyl-4′-octyloxybenzoate (NPOB); (b) 4-*n*-pentylphenyl-4′-*n* heptyloxythiobenzoate ($\bar{7}$S5); (c) *N*-(*p*-methoxybenzilidene)-*p*-butyl aniline (MBBA); and (d) 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB). All these substances are the main subject of this work.

One of the methods used to discover metastable phases is adiabatic calorimetry. The above mentioned substances easily produce a metastable phase during fast cooling of a sample from one of the liquid crystal phases or from the isotropic phase. The fact that metastable phases can be easily formed can be associated with the structure of liquid crystal molecules. NPOB, $\bar{7}$S5, MBBA, HOAB molecules have a rod-like shape with shorter or longer lateral chains. Those chains can occur in various conformations which differ one from another energetically. Fast cooling of a liquid crystal can lead to the formation of a solid phase in which conformation of the molecules is energetically less favoured. The process is connected with internal degrees of freedom. In the creation of metastable phase external degrees of freedom play an important and a dominant role. Depending on rate of cooling we can get one or more metastable phases for any of the given substances.

It is well known that other substances i.e. those showing no liquid crystal properties, can easily be supercooled at 1st order phase transitions (especially during crystallization). The supercooled substance is in a metastable state and its specific heat values are higher than those observed for the stable modification. A similar situation can be observed while dealing with Gibbs energy vs temperature dependence.

A metastable phase is not a stable modification. It transforms to a stable modification at a temperature dependent on the type of substance and on its thermal history. The thermal effect connected with the process can be estimated in the adiabatic calorimeter. This is due to temperature dependence vs time during passing from a metastable phase to a stable one. The process can be quantitatively described, particularly, if we define a time constant $\tau$. This work deals with those problems, on the basis of experimental data published in References 1–4.

## 2. MONOTROPISM. KINETICS OF MONOTROPIC PHASE TRANSITIONS

The phenomenon of monotropic phases is illustrated in the G(T) dependence shown in Figure 1. Here one can see that phase II below $T_2$ is metastable and the phenomenon is monotropism. Phase I between $T_1$–$T_2$ is also metastable however. The 2 modifications (below $T_1$ and below $T_2$) differ energetically one from the other. The modification of higher energy (the metastable one) can easily pass into the stable modification or into another metastable one (if many metastable modifications exist in a sample) and the kinetics are facile. The effect is called a monotropic phase transition. The characteristic feature of a monotropic transition is the fact that such a transition occurs in one direction only: a metastable phase → a stable one. After such a transition, the metastable phase can be obtained again only by bringing the substance to the high temperature enantiotropic phase (in Figure 1 it is phase I) and then cooling it to a considerably low temperature.

For monotropic phase transitions the important problems are investigations of their kinetics i.e. the dependence of transition rate on such factors as the temperature of a transition or the so-called thermal history of a sample.

In an adiabatic calorimeter the process of transition from a metastable phase to the stable one can be easily observed because one can register a continuous increase

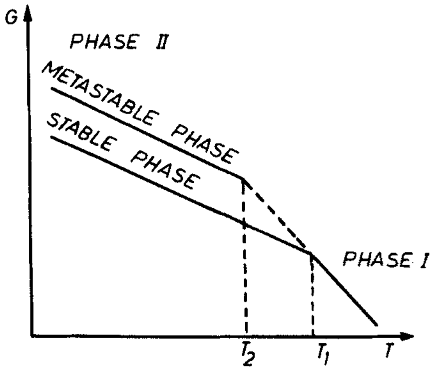

FIGURE 1 Gibbs' function vs temperature for monotropic set of phases.

of temperature, connected with passage of molecules from local minimum of energy (metastable state) to the absolute minimum of energy (stable state). On the way some portion of energy is released and the sample under adiabatic conditions must "selfheat". The rate of the heat production decreases in time and at the end of the process is equal to 0. Therefore we can see that investigation of temperature changes during such a transition can give us information about the kinetics of the process.

In order to pass from a metastable phase to a stable one, a sample needs to overcome the enthalpy of activation ($\Delta H'$). In such a way molecules can pass over an energy barrier (Figure 2). The higher degree of metastability the lower the energy.

The phase transition from a metastable phase to a stable one depends on the passage over the energy barrier. One can write it using the classical equation of an Arrhenius type[6]:

$$k = A \exp(-\Delta H'/RT) \tag{1}$$

where
$\Delta H'$ = the enthalpy of activation
$k$ = transition rate factor
$A$ = a transition constant

## 3. EXPERIMENT

The adiabatic low temperature calorimeter[5] used in the work was designed and made basing upon descriptions of calorimeters worked out at the Department of Chemistry of the University of Michigan. The calorimeter was intended for measurements in the temperature range from helium temperature to ca. 400 K.

Temperature measurements were performed with a Platinium resistance thermometer, which was carefully calibrated in a temperature range 90 K–550 K, on the basis of fundamental and secondary points of the International Temperature Scale. The calibration of the thermometer allowed temperature measurements with an accuracy of ca. 0.01 degrees, in respect to the International Temperature Scale.

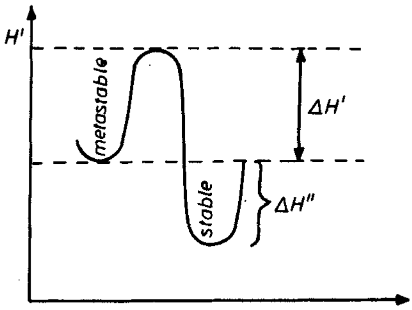

FIGURE 2 Energetical comparison of metastable and stable phases.

More details connected with the adiabatic calorimeter used in the work are presented in Reference 5. The sample mass amounted to 50.76 g in the case of HOAB, 54.15 g for $\bar{7}$S5, 52.06 g for NPOB, 62.05 g for MBBA. The mass of the calorimetric vessel was ca. 220 g.

In all the cases the investigated sample was heated from low to high temperatures (corresponding to isotropic liquid) during measurements of the specific heat. The portion of heat introduced into the calorimetric vessel increased its temperature by about 5 K in regions without anomalies. In regions of anomalies such portions of heat were correspondingly smaller. The time about 20 or 30 min. was needed to obtain $\Delta T = 5$ K, and nearly the same time was needed to obtain the temperature equilibrium in all experimental runs.

In order to get the metastable phase, the sample was cooled from the smectic, nematic or isotropic phase by the direct thermal contact with the liquid nitrogen container. At the beginning of the cooling process its rate was fast (ca. 5.4 K/min.) and next it was diminishing. The average cooling was 2.6 K/min.

## 4. THE MATHEMATICAL DESCRIPTION OF THE PHASE TRANSITION IN WHICH A METASTABLE PHASE PASSES INTO A STABLE ONE

A metastable phase and a stable phase are subsystems between which heat may exchange. The two phases are in the same space. The interaction between those subsystems is described by a relaxation process. The system in which the relaxation process happens is isolated (it is in a calorimetric vessel).

During the process an amount of the energy is transferred from one subsystem into the other. Therefore the change of entropy of the whole system in time d$t$ is equal to:

$$\frac{dS}{dt} = \frac{1}{T'}\frac{dU'}{dt} + \frac{1}{T''}\frac{dU''}{dt} \tag{2}$$

where $U'$ and $T'$ stand for the one and $U''$ and $T''$ stand for the other subsystem.

From the law of the conservation of energy it follows:

$$dU' + dU'' = 0 \tag{3}$$

As a result of the fact that the system is isolated and the process metastable → stable phase is spontaneous, the rate of entropy increases and, consequently its source amounts to:

$$\frac{d_iS}{dt} = \left(\frac{1}{T'} - \frac{1}{T''}\right)\left(\frac{dU'}{dt}\right) = \left(\frac{1}{T}\right)\left(\frac{dU'}{dt}\right) \tag{4}$$

Hence flux $J_u = dU'/dT$ and impulse $X_u = \Delta(1/T)$. If we remember that $J_u = \sum_{k=1}^{n} L_{uk}X_k$ where $L_{uk}$ are phenomenological factors, we can write for the relaxation process the phenomenological equation:

$$\frac{dU'}{dt} = \frac{-L\Delta T}{T^2} \tag{5}$$

By introducing for $dU'$ the equation:

$$dU' = C\,dT \tag{6}$$

where $C$ means the specific heat of the first subsystem, we can write:

$$\frac{dT}{dt} = -\frac{L}{C}\left(\frac{\Delta T}{T^2}\right) \tag{7}$$

By denoting $-CT^2/L = \tau$, we get:

$$\frac{dT}{dt} = -\frac{1}{\tau}(\Delta T) \tag{8}$$

Hence

$$T = B \exp\left(\frac{-t}{\tau}\right) \tag{9}$$

where $B$ is a constant and $\tau$ is the so called relaxation time. Therefore we can write the Equation (8) in the following way:

$$T(\infty) - T(t) = B \exp\left(-\frac{t}{\tau}\right) \tag{10}$$

where $T(t)$ means a temperature at a moment of transition, $T(\infty)$ means the temperature after the transition, and $t$ – time. After finding the logarithm of (10) we get

$$\ln(T(\infty) - T(t)) = \text{const.} - \frac{t}{\tau} \tag{11}$$

$\tau$ denotes the time in which the temperature increase in moment $t$ is equal to $1/e$ of all the temperature increase.

We assume that the molar enthalpies of two phases and the heat capacity of the calorimetric vessel are constant during measurements. This has to be assumed in order to connect succeeding temperature increments with the relaxation process. The assumption is strongly supported because: (1) the transition is observed at a relatively high temperature and in that temperature region the inclination of the specific heat vs temperature curve is very small; and (2) the whole temperature increase is not large, it does not exceed several degrees.

From the $\ln(T(\infty) - T(t))$ vs time dependence, one can calculate for succeeding samples the slope as equal to $1/\tau$, for the phase transition: metastable phase → stable phase.

In drawing $\ln(T(\infty) - T(t))$ vs time dependence, the fact taken into consideration was that the error in the ordinate of succeeding experimental points increases if we approach the time equal infinity. For example if $T(\infty) - T(t) = 0.2$, the error of estimation of $\ln(T(\infty) - T(t))$ is about 7%. If $T(\infty) - T(t) = 0.01$ (such was the sensitivity of temperature measurement in the adiabatic calorimeter) the error of estimation of appropriate value of logarithm is 43%.

Dependence on $\ln(T(\infty) - T(t))$ of obtained results are shown in Figures 3, 4 and 5. In Figure 3 and 5 for long periods of time only half of the experimental error are marked. From Figures 3, 4 and 5 one can see that some straight line segments are clearly distinguishable. Experimental points which follow the straight line at the beginning of the transition deviate (downwards) from the line as the end of the transition is approached and the effect exceeds experimental errors. Such the behaviour seems to reflect more than one relaxation process responsible for the transition metastable → stable phase. To account for it, in the Equation (10) another time constants could be introduced, though it would be difficult to do because of the large experimental error at long times. Therefore in what follows I consider only one $\tau$ value.

## 5. AN APPLICATION OF RELAXATION MODEL FOR DESCRIPTION OF PHASE TRANSITIONS IN LIQUID CRYSTAL SUBSTANCES

The comparison of values calculated for the studied liquid crystal substances leads to the following conclusions: Bringing the sample to a temperature slightly higher than the one at which the transition started, causes an increase of the transformation

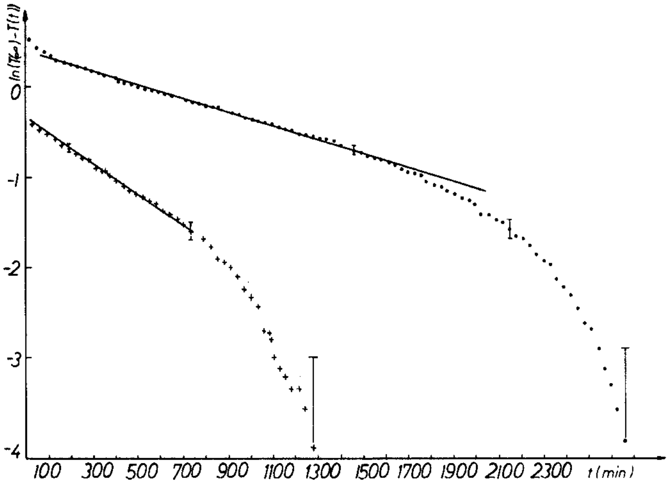

FIGURE 3 The $\ln(T(\infty) - T(t))$ vs $t$ dependence for HOAB. (+) = the sample was fast cooled from 410 K to 95 K and then heated during the measurement of the specific heat. The spontaneous phase transition metastable phase I → metastable phase II was observed at average temperature 335.8 K. (·) = next the sample was cooled down to a room temperature then measurements of the specific heat were performed in the same manner as for (+). The spontaneous phase transition metastable phase II → stable I was observed at average temperature 343.7 K.

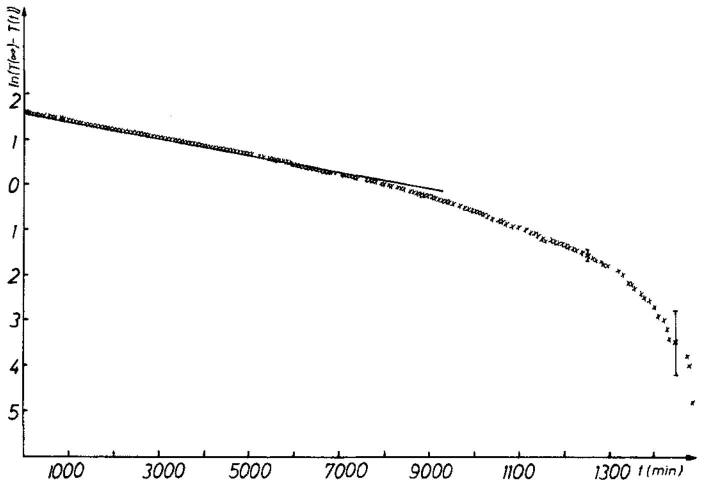

FIGURE 4 The $\ln(T(\infty) - T(t))$ vs $t$ dependence for HOAB. The sample was cooled from 410 K to 333 K and then heated during the measurement of specific heat. The spontaneous phase transition metastable phase II → stable one was observed at average temperature 344.4 K.

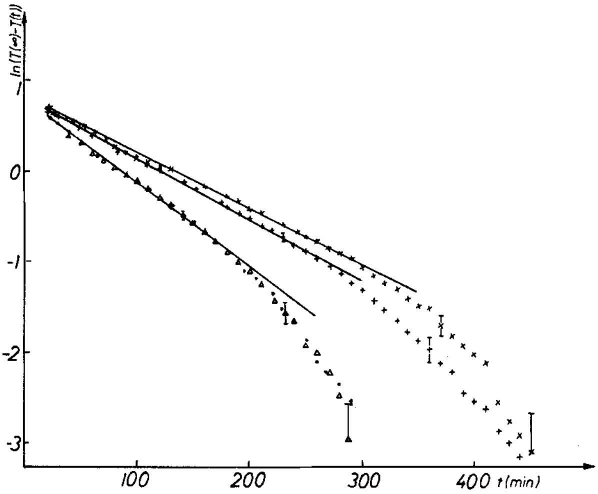

FIGURE 5 The $\ln(T(\infty) - T(t))$ vs $t$ dependence for NPOB. (+) = the sample was cooled from 357.1 K to 150 K and then maintained at the lower temperature for 23 h. Next, it was heated continuously to the transition: metastable phase → stable one temperature. (×) = the sample was cooled from 352.6 K to 150.8 K and then maintained at the lower temperature for 1 h, and next treated as above. (·) = the sample was cooled from 353.9 K to 104.5 K and then maintained at the lower temperature for 1 h and next treated as above. (Δ) = the sample was cooled from 349.5 K to 103.5 K and then maintained at the lower temperature for 23 h and next treated as above.

rate, even if the temperature increased by just about 0.1°. This is obvious if we take into account Equation (1). As we can see, at a given enthalpy of activation, the rate of transition depends on temperature. When the temperature increases, the rate of transition increases too, which was stated for the transition: a metastable phase → a stable one in all cases studied. In such investigations one could find a

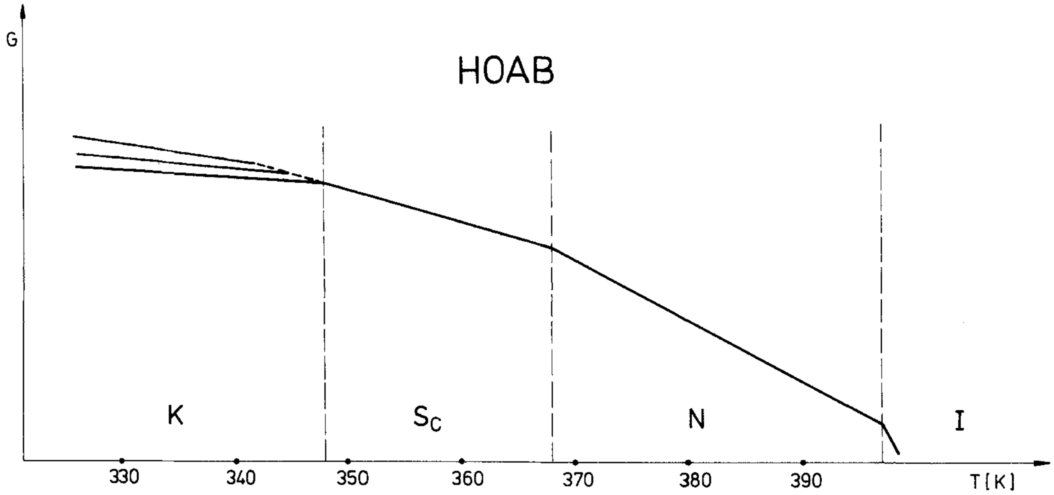

FIGURE 6 $G(T)$ dependence for HOAB. In this case none the metastable phases could be melted. This fact is marked by broken $G(T)$ lines.

TABLE I

The characteristic parameters for the metastable phase → stable phase transition in HOAB

| Transition | Average Temperature of Transition [K] | $\tau$ [min] |
|---|---|---|
| Metastable phase I → metastable phase II | 339.5 | 232 ± 25 |
| Metastable phase II → stable phase | 343.7 | 670 ± 65 |
| Metastable phase I → metastable phase II | 335.8 | 594 ± 34 |

TABLE II

The characteristic parameters for the metastable phase II → stable phase transition in HOAB

| Transition | Average Temperature of Transition [K] | $\tau$ [min] |
|---|---|---|
| Metastable phase II → stable phase | 344.4 | 5192 ± 1144 |

temperature (lying just above the first registered temperature of transition: a metastable phase → a stable one) at which no heat emission is observed because the transition took place earlier. A slightly more complicated situation occurs, for example, in HOAB case. It was found here that after the transition at 337 K is over and the sample has been heated, when measuring specific heat vs temperature, another selfheating of the sample can, be observed this time at 344 K. After finishing the last heating the pure stable phase is received. The earlier stage of selfheating at 337 K resulted in obtaining the phase depicted by specific heat curve that lies between two curves i.e. specific heat curve for metastable phase, and stable one.

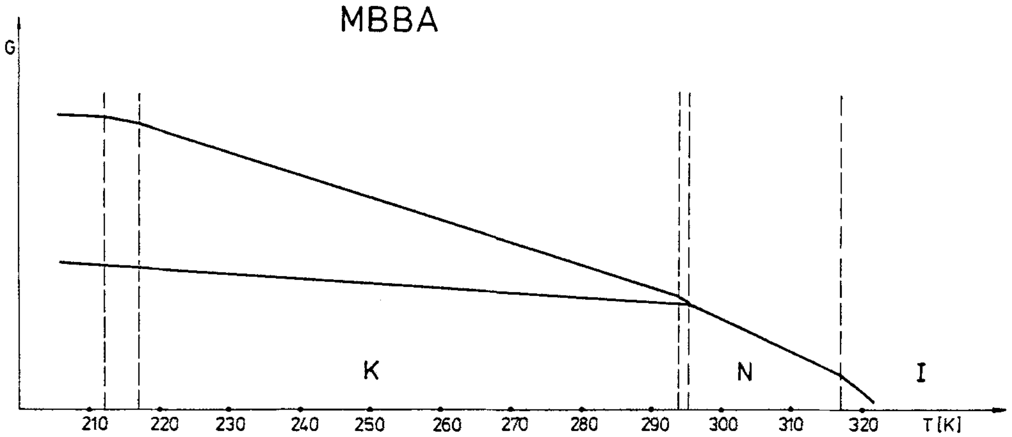

FIGURE 7 $G(T)$ dependence for MBBA. In this case a metastable phase could be melted. This fact is marked by the solid $G(T)$ line in the region of melting.

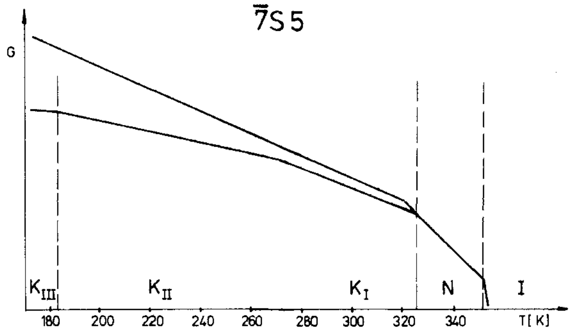

FIGURE 8 $G(T)$ dependence for 7̄S5. A metastable phase could not be melted. The fact is marked by broken $G(T)$ line.

If we come back to the transition at about 344 K, we should stress the fact that although the temperature is higher than before, the time constant $\tau$ is here about 2 times longer. This is so because in this case $\tau$ characterises the other transition (metastable phase II → stable phase) which is different from that previously quoted (i.e. metastable phase I → metastable phase II) (see Figure 6). This influence of temperature on the rate of transition can be taken into account considering a specific transition, for example metastable phase I → metastable phase II or metastable phase II → stable phase, both of which are observed at various temperatures. Since the two transitions concern two different processes, they can not be compared as regards $\tau$, as clearly seen from Table I.

The set for HOAB from Table I should be completed by the following set (Table II). We can see that although the average temperature of that transition is practically the same as in the former set (Table I), the time constant $\tau$ here is many times greater. This behaviour can be related to the fact that the thermal histories were different. In the former set the sample was cooled from the isotropic phase to 88K

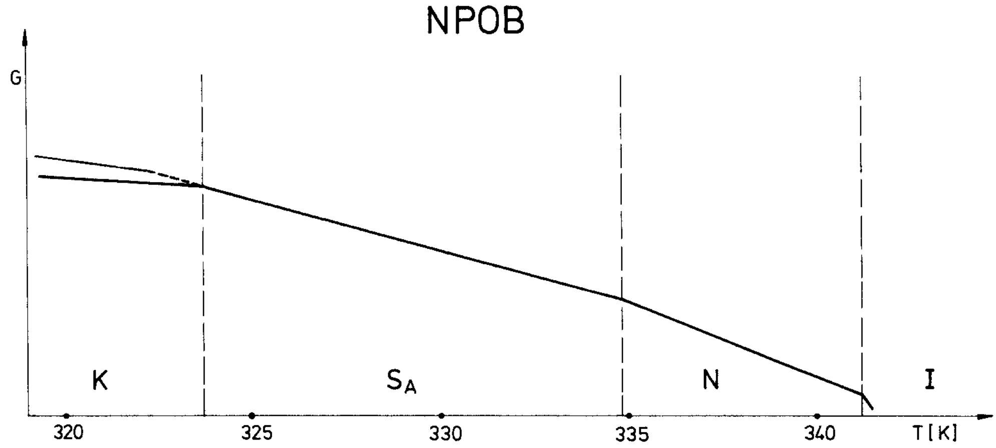

FIGURE 9 $G(T)$ dependence for NPOB. A metastable phase could not be melted. It is marked by broken $G(T)$ line.

TABLE III

The dependence of $\tau$ on the thermal history of NPOB

| Experiment Number | Temperature Down to Which the Sample was Cooled [K] | Time of Storage of Sample at Given Temperature [h] | Average Temperature of Transition [K] | $\tau$ [min] |
|---|---|---|---|---|
| 1 | 150 | 23 | 295.2 | 149 ± 16 |
| 2 | 150.8 | 1 | 295.2 | 160 ± 27 |
| 3 | 104.5 | 1 | 295.2 | 96 ± 18 |
| 4 | 103.5 | 23 | 295.1 | 96 ± 18 |

and heated stepwise to about 333 K (when the observation of the first phase transition was started) while simultaneously, measuring the specific heat. In the second set of experimental data the sample was cooled from the isotropic phase to 333 K only. No pure metastable phase was observed in that case. What we obtain is a so-called intermediate phase (i.e. metastable phase II) which passed to the pure stable phase about 343 K. The behaviour observed for HOAB was also observed in other the liquid crystal substances: MBBA and $\bar{7}$S5. The observation can be summarized as follows: cooling of any liquid crystal phase or of an isotropic one only several dozen degrees lower than the temperature of melting, caused the creation of a metastable phase which was much more stable than the one obtained, when the sample was greatly cooled well below the transition temperatures. In the case of MBBA the metastable phase obtained in that way was so stable that, it could be melt (see Figure 7). In the case of $\bar{7}$S5 the temperature region of its metastable phase was extended from about 294 K at which usually the transition: metastable phase → stable one was observed, to high temperatures that is about 324 K (see Figure 8). In the case of HOAB, however, only a significant slowing of the transition: metastable → stable phase could be observed.

Let us add right now that it is not only thermal history of the sample that can

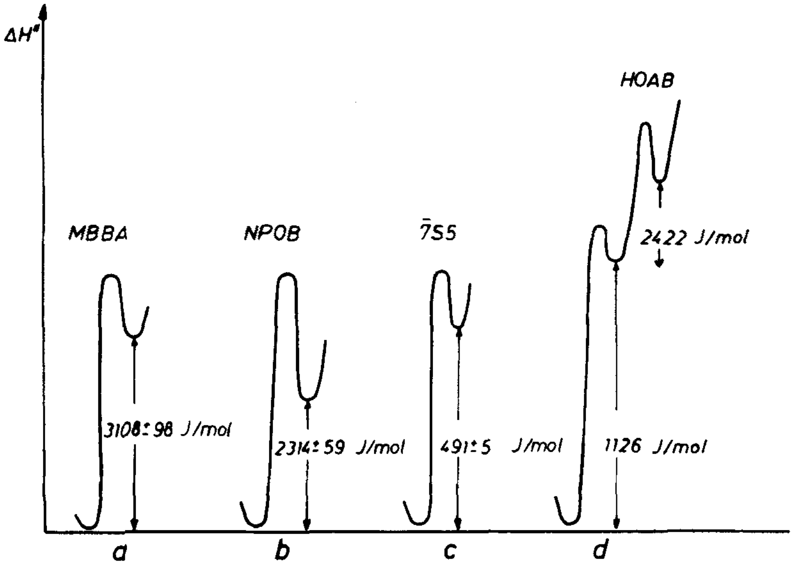

FIGURE 10 Energy diagram for substances studied. We can see the small error of $\Delta H''$ for $\bar{7}$S5. The reason is small statistic of the measurement runs, we need. In the case of HOAB error of $\Delta H''$ was not estimated, because specific heat values in the region of transition: metastable phase → stable one were not measured.

influence the kind of the newly created phase and determine its stability, the size and shape of the sample are factors that also play an important role here. As good examples compare the results of Reference 7 in comparison with those received in Reference 8.

In Reference 7 the transition: the metastable phase → the stable one in MBBA was observed by using of Raman spectroscopy. The transition was observed at 286 K. Its rate was much slower than the one for the sample studied by IR spectroscopy[8] at 276 K. This observation contradicts the previous remarks concerning an influence of temperature on the rate of transition. It could be explained in the following way. Staying in contact with surface, the free energy for appearance of critical nucleation sites is lower in IR than the energy needed for the creation of nucleation sites within the phase (in R) in capillary. The nucleation rate increases in the direction in which the energy is falling, which means that the rate of transition a metastable phase → a stable one, also increases because the kinetics of the process depends on the phenomenon of nucleation.

The properly arranged experiment (in the case of NPOB, see Figure 9) gives us additional information about $\tau$. The characterization of the experiment is showed in Table III.

I should explain that errors in $\tau$ shown in Table I–III are estimated with an assumption of one relaxation process responsible for the transition: metastable → stable phase.

It is seen that $\tau$ values for experiments 1,2 and 3,4 are the same. Therefore the temperature to which the sample was cooled has a great influence on the $\tau$ values.

We remember that the transition is described by (1). In Table III we can see that the average temperature of transition is practically the same in all experiments. Similarily, $\Delta H'$ should also be constant, because it is the activation energy for the same transition of a given substance. Because the $\tau$ values for two groups of experiments 1,2 and 3,4 are different, values $k$ (factors of transition rate) differ. Therefore the constants $A$ describing the transition must also be different.

An influence of the thermal history of the sample on the $k$ value was also stated for another liquid crystal substances studied in this work i.e. for MBBA. MBBA is difficult for investigating because of its poor chemical stability. As long as we get a good repetition of experimental runs for the substance we consider the results reliable.

The observation of the $\tau$ values in this described group of experiments reveals the correspondence of their behaviour to the previously presented experimental data. Thus the higher the temperature to which the sample was cooled, the more stable the metastable phase received. The $\tau$ value is larger in such a case. In other words, the metastable phase passes into the stable phase less eagerly. Bearing all that in mind, we can say that constant $A$ is the constant for a given thermal history of the sample—the history which preceded the formation of a metastable phase of the investigated substance.

Therefore we can see that the degree of stability of metastable phase can change significantly. Among chemical substances diamond is in one extreme, although it happens that diamonds change into graphite.

In a given system the metastability degree can in some region be changed, for example, rubbing a sample is an effective way to transform a metastable crystal into a stable one.

On the basis of the calorimetric data obtained, the energy diagram of the investigated phases was calculated and is presented in Figure 10. The increase in temperature during the self-heating process was not greater than 2 K. The $\Delta H''$ were obtained from multiplying $\Delta T$ (the increase of temperature) by average value of heat capacity (in the region of thermal increase). This value was divided by the mass of the sample.

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