POLYMORPHISM OF LIQUID CRYSTALS INVESTIGATED BY RADIOTHERMOLUMINESCENCE AND DIFFERENTIAL SCANNING CALORIMETRY METHODS*

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The methods of radiothermoluminescence (RTL) and differential scanning calorimetry (DSC) are used for investigations of metastable phases and solid-crystal polymorphism in etoxybenzilidenbutylaniline, butyloxybenzilidenoctylaniline and Merk-389. It was found that fast freezing (with rates $\geqslant$ 500 deg/min) of different LC-phases down to 77 K allows their preservation at low temperatures. Temperature intervals for the existence of such recorded phases were determined. It is shown that a combined use of RTL and DSC methods allows one to identify phase transitions between metastable phases. The heating of irradiated LC-compounds is found to be accompanied by luminescent flares at the temperature of transitions between stable mesophases, as well as during the transition to the isotropic liquid.

1. Introduction

1.1. Metastable phases (MP) and solid-crystal (SC) polymorphism in liquid crystals (LC)

Much attention has been paid lately to the study of metastable phases of LC compounds, and to the possibility of their production [1–11]. It is known that some LC substances when cooled down below the melting point, can form different nonequilibrium metastable phases depending upon the temperature history of the sample [8–10]. If such nonequilibrium phases represent the supercooled LC-states with a corresponding space distribution of molecules, they would be characterized then by many LC-state properties. Thus, the temperature range of LC applications would be extended toward the low-temper-

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ature region. The method for establishing low-temperature MP is of great importance for the study of orientation, degree of molecular ordering and anisotropy of some properties typical of the corresponding stable LC-modifications. At low temperatures such properties will be manifested more vividly due to a sharp reduction in the molecular mobility.

The present paper investigates possible ways of MP formation in compounds having various LC-phases, and the conditions for the appearance of any MP depending upon the temperature history of the sample. For a series of compounds, the metastable phases have been identified. The temperature of phase transitions was determined, and the dynamic properties of MP investigated.

1.2. Objects and methods of investigation

In the temperature range from 77K to the isotropically liquid (IL)-phase temperature, by using the methods of radiothermoluminescence (RTL) and differential scanning calorimetry (DSC), three compounds of different LC-phases have been investigated, namely, etoxybenzilidenbutylaniline (EBBA), butyloxybenzilidenoctylaniline (BBOA), and Merk-389.

EBBA is one of the most typical and well studied representatives of nematic liquid crystals (NLC). The methods of calorimetry and Raman scattering spectroscopy have shown [5–7,10] that, depending upon temperature history, there can exist a few metastable phases of EBBA with essentially different properties. In Ref. [10] it has been found that as a result of rapid cooling of NLC-phase EBBA down to 77K, a metastable phase is formed, called by the authors a "glassy" NLC-phase, which is characterized by a stronger intermolecular interaction in comparison with a common NLC-phase. At 238K the "glassy" NLC-phase transforms to a metastable SC-phase, which at room temperature is transformed into a stable SC-modification. In Ref. [9] four SC-modifications of EBBA have been found to exist.

BBOA has a few LC-phases. Based on Mössbauer investigations, the existence of a "glassy" smectic LC-B (SLC-B) phase at low-temperature has been suggested [11].

An LC-compound Merk-389 represents a mixture of aromatic ethers and has an NLC-phase in a broad temperature interval. Such mixtures are disposed to supercooling, and to the formation of metastable states.

The radiothermoluminescence (RTL) method is based on the observation of thermoluminescence of substances exposed to irradiation by fast electrons or gamma-quanta at low temperature [12]. Thermoluminescent intensity is determined by the recombination rate of ions stabilized in the substance during its irradiation. As a result of smooth heating of irradiated substances, the RTL intensity sharply increases, and has its maxima at temperatures corresponding to the initial motion of the individual molecular segments, as well as the molecules, as a whole.

The shape of the luminescence curve (RTL intensity versus temperature) makes it possible to determine the presence and character of structural transitions, the degree of crystallinity of samples, and the homogeneity of two- and multicomponent mixtures. The registration of luminescent curves at different rates of defrostation allows one to estimate the activation energies of molecular motions.

So the RTL method proves to be rather promising when applied to a study of various aspects of the LC-state. But since this is a new approach to the problem [13], it is necessary to compare the results obtained via the RTL technique with the data of calorimetric investigations. A combined use of these two techniques makes it possible to obtain new information about pretransitional phenomena of unfreezing in molecular mobilities, relaxation processes in stable and metastable phases of LC-compounds.

2. Experimental procedure

The curves of RTL luminescence were taken on a thermoluminograph TLG-68 [14]. The samples were irradiated at 77K with a ^{60}Co-source, the irradiation dose being 1 Mrad. The irradiation rates for RTL curves were of 5 and 10 Mrad/min. It should be noted that irradiation reaching 1 Mrad changes the phase transition temperatures by a few tenths of a degree (due to the effect of impurities produced during radiolysis [15, 16]). Hence, the data obtained by the RTL technique can be attributed to the initial, that is, nonirradiated sample.

Calorimetric investigations have been performed with the use of a differential diathermic calorimeter [17]. The response of the device is 10^{-5} cal/sec, time constant, 100 sec, the range of working temperatures, 100–400 K, and the rate of temperature scanning, 0.2–3.0 deg/min.

According to the specification data, the EBBA has the following temperatures for phase transitions:

$$\mathrm{SC} \xrightarrow{305\,\mathrm{K}} \mathrm{NLC} \xrightarrow{356\,\mathrm{K}} \mathrm{IL}.$$

The mixture Merk-389 was obtained from the Merk Company (Darmstadt, BRD). Specification data for this mixture are:

$$\mathrm{SC} \xrightarrow{253\,\mathrm{K}} \mathrm{NLC} \xrightarrow{333\,\mathrm{K}} \mathrm{IL}.$$

TABLE I

Substance	Conditions for preparation / Sample No.	Temperature of thermostatic control and the phase	Rate of cooling down to 77 K (deg/min)	Note
Merk-389	Sample A1	293 K, NLC	500	Studied by DSC method
	Sample A1′	293 K, NLC	1500	RTL method
EBBA	Sample B1	293 K, SC	500	DSC method
	Sample B2	318 K, NLC	500	DSC method
	Sample B1′	293 K, SC	1500	RTL method
	Sample B2′	318 K, NLC	1500	RTL method
BBOA	Sample C1	293 K, SC	500	DSC method
	Sample C2	318 K, SLC-B	500	DSC method
	Sample C1′	293 K, SC	1500	RTL method
	Sample C2′	318 K, SLC-B	1500	RTL method

BBOA was kindly donated by Dr. D. Uhrich (Kent State University, USA), and upon cooling undergoes the following scheme of transitions [18]:

$$\text{SC} \xrightarrow{315\,\text{K}} \text{SLC–B} \xrightarrow{321\,\text{K}} \text{SLC–A} \xrightarrow{336\,\text{K}} \text{NCL} \xrightarrow{352\,\text{K}} \text{IL}.$$

In our experiments none of the substances was subjected to preliminary purification.

In this paper we studied EBBA, Merk-389 and BBOA samples prepared by means of heating the substances up to temperatures corresponding to different LC-phases, maintaining that temperature, and a subsequent rapid cooling down to 77 K. The regimes for the preparation of samples are listed in Table I.

3. Experimental results and discussion

3.1. Merk-389

Figure 1a shows a curve of RTL luminescence for an A1′ sample. A low-temperature peak 1 observed at 133K is due to a recombination resulting from a combination of local relaxation processes. During a further heating of the sample, one can observe at 205 K

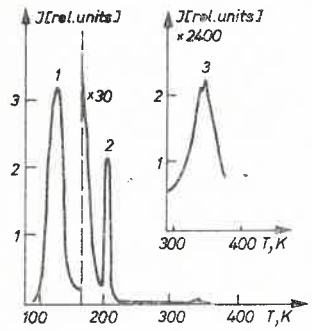

Fig. 1. RTL curve for A1′ sample Merk-389

a symmetric, rather narrow RTL maximum (peak 2). After that the thermoluminescent intensity sharply decreases almost down to zero. Note that the A1′ luminescence curve in the low-temperature region (the temperature range 77–300 K) is very similar to a typical luminescence curve for an amorphous low-molecular organic substance. During a gradual heating of the irradiated amorphous substance one can observe the appearance of a narrow maximum of luminescence at T_v (vitrification temperatures), after which the luminescence ceases. One can therefore assume that below 200 K the sample A1′ is in the pseudoamorphous state (called the "glassy" LC-state by the authors of [10, 11]). The RTL-registered transition at 200–215 K is caused by a softening of the pseudoamorphous phase in the sample (i.e. the transition of the "glassy LC" → "supercooled LC" phase, according to the authors' terminology [10, 11]). Temperature increase above 215 K, and a corresponding increase in the mobility of LC molecules, results in the recombination of almost all the ions

produced from sample irradiation. A characteristic frequency of molecular vibrations corresponding to the peak 2, is from 0.1 to 1 Hz [12].

But unlike non-liquidcrystalline amorphous substances, a further heating of A1′ sample gives rise to the appearance of a set of peaks 3 at temperatures of the stable NLC--phase. The intensity of these peaks is a few orders lower than that of the low-temperature peaks 1 and 2. Interpretation of RTL peaks in the region of a stable mesophase, and the nature of sample luminescence in that temperature range will be considered below.

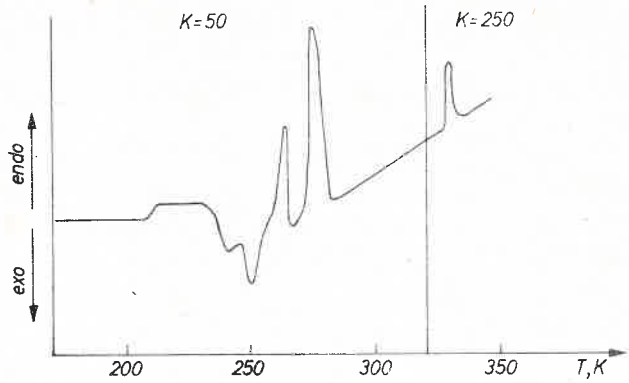

Fig. 2. Calorimetric curve of A1 unfreezing (Merk-389)

Figure 2 shows a calorimetric curve of A1 sample unfreezing (differing from the A1′ sample by the freezing rate only, see Table I). With an increase in sample temperature in the range 200–215K one can observe an uneven increase in the heat capacity. Such a change in heat capacity is typical of various relaxational transitions. The transition glass → supercooled liquid in amorphous substances [17] characterized by a sharp increase in the molecular mobility, and a decrease in the viscosity, is one of the examples. It should be noted that the space structure symmetry of this transition remains invariant. With further heating of the A1 sample, the calorimetric curve shows two exothermic peaks at 239 and 254 K, and three endothermic peaks at 262, 270 and 349 K.

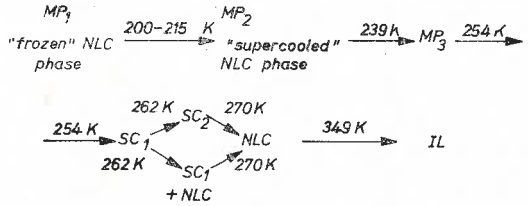

Fig. 3. Scheme of phase transitions Merk-389

By analyzing the curves for RTL luminescence and calorimetric unfreezing of Merk-389 samples produced by a fast cooling from the NLC-phase, one can assume that using this procedure of sample preparation it is possible to observe the metastable NLC-state at 77 K. In the temperature range from 77 to 200 K the metastable "frozen" NLC-phase

(MP_1) is characterized by low molecular mobility comparable to the solid-state mobility, but probably the same space distribution of molecules as in the stable NLC-phase. At 200–215 K there occurs a sharp increase in the molecular LC mobility (revealed by the uneven increase in heat capacity, and the presence of RTL maximum), and a transition to another metastable state, i.e. supercooled NLC-phase (MP_2)[1]. At 239 K the MP_2 probably turns into the metastable SC-phase (MP_3), which in comparison with MP_2 has a higher order, and at 254 K, into the stable SC-modification. The calorimetric curve has an exothermal peak at 262 K, which can be indicative of the transition to another SC-modification. Then at 270 K the sample would turn into the NLC-phase. However, during the aging of the Merk-389 mixture there probably occurs the formation of a heterogeneous system. Then the transition to NLC-phase can take place step-by-step at 262 and 270 K. At 349K the sample A1 changes to the IL-phase.

The attempts to crystallize Merk-389 samples during their cooling were unsuccessful. The RTL curves for Merk-389 taken after a gradual cooling of the samples from the NLC-phase down to 268 K, and the thermostatic control of samples at room temperature for five hours, did not differ in fact from similar curves for A1'.

One can thus propose a scheme of phase transitions of Merk-389 mixture on the basis of data resulting from DSC and RTL analysis (Fig. 3).

3.2. EBBA

Figure 4 shows calorimetric curves of B1 and B2 sample unfreezing. For the sample B1 endothermic peaks corresponding to transitions between the stable phases of EBBA are observed. For the sample B2 at 183–203 K an increase in the heat capacity is observed

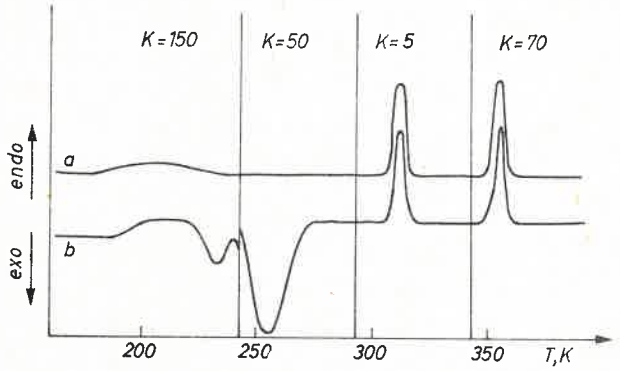

Fig. 4. Calorimetric unfreezing curves of EBBA samples: a) sample B1, b) sample B2

(similar to the sample A1), as well as some additional exothermic peaks (in comparison with B1) having maxima at 233 and 253 K. Hence, unlike B1 (being in SC-phase at 77 K), the sample B2 is at 77 K in the metastable state, having a more disordered distribution of molecules, in comparison with the SC-phase. The metastable state seems to correspond

[1] To determine accurately the space structure of metastable phases of Merk-389, it is necessary to perform additional investigations, e.g. an X-ray structural study.

to the "frozen" NLC-phase EBBA (MP_1), which at 183–203 K turns into the "supercooled" NLC-state (MP_2). According to the DSC data, for the sample B2 there is observed another low-temperature metastable phase MP_3 (with the transition temperature about 233 K), and the transition to the SC-phase is observed at 253 K. The samples B1 and B2 are transformed to the stable NLC-phase at 305 K, the IL-phase, at 356 K.

The RTL curves for B1′ and B2′ samples differing from B1 and B2 only by the rate of cooling (see Table I) are shown in Fig. 5. The difference in the curves confirms a previous conclusion that the sample B2′, and respectively, B2 are at 77K in the metastable state.

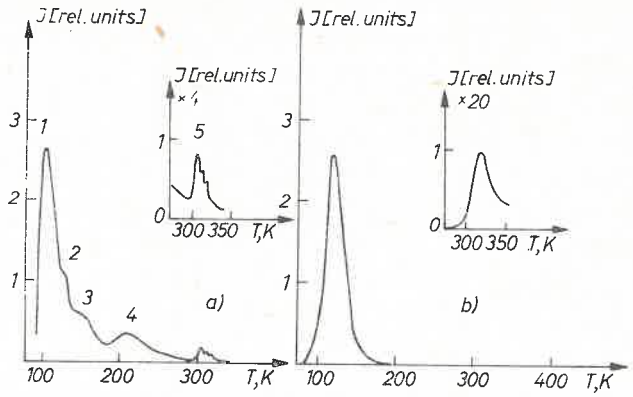

Fig. 5. RTL curves for EBBA sample: a) sample B1′, b) sample B2′

The thermoluminescent intensity of the sample B2′ is reduced almost to zero by 200 K. It should be noted that unlike Merk-389, the B2′ samples do not show a narrow RTL maximum corresponding to a sharp increase in the molecular mobility of the sample. In the low-temperature region the shape of the RTL curve for B2′ is characteristic of inhomogeneous amorphous structures with a high spread of transition temperatures T_r. For such systems the softening envelopes a wide temperature region, which results in a monotonous decay in thermoluminescence intensity. Peak 1 in the luminescence curve for B2′

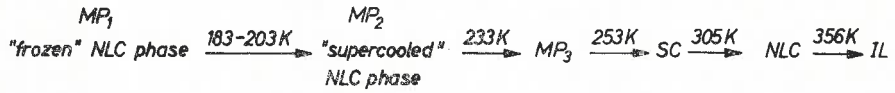

Fig. 6. Scheme of phase transitions EBBA

is likely to be caused by recombinative luminescence resulting from the local processes of molecular relaxation, as well as by the "unfreezing" of molecular mobility being highly relaxed by temperature

The RTL curve for the B1′ sample frozen from the SC-phase EBBA (Fig. 5) is characterized by the peak 1 (at 106 K), which is shifted, unlike a similar peak for B2′, toward the lower-temperature region, and has the peaks 2, 3 and 4 (131, 158, and 210 K, respectively). All these peaks are likely to be attributed to the "unfreezing" of mobilities of some EBBA parts (e.g. to the oscillations or rotations of some molecular fragments).

For the temperatures corresponding to transitions between SC-NLC- and IL-phases, the RTL curves of EBBA samples also reveal a set of luminescence peaks, that is, 5 peaks for B1′ (Fig. 5c), and 2 for B2′ (Fig. 5d). The character of peaks will be considered below.

The scheme of phase transitions EBBA proposed on the basis of data obtained by DSC and RTL techniques is shown in Fig. 6.

3.3. BBOA

Figure 7 shows calorimetric curves of unfreezing for C1 and C2 samples (see Table I). In the case of C1 only endothermic peaks in the temperature region of transitions between different mesophases are observed, in accordance with the data of D. Uhrich.

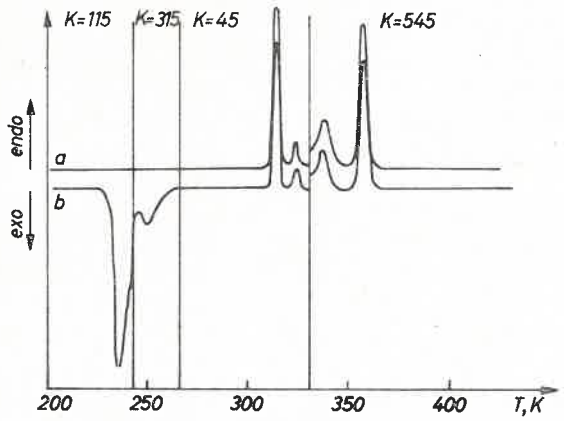

Fig. 7. Calorimetric unfreezing curves for BBOA samples: a) sample C1, b) sample C2

In comparison with the sample C1, the sample C2 shows two additional exothermic peaks with maxima at 230 and 253 K. So, the sample C2, as well as A1 and B2, are at 77 K in the metastable state (MP_1). According to DSC data, at 230 K the sample C2 turns into another metastable phase (MP_2), and at 253 K, into SC-phase (Fig. 7b). Figure 8 shows RTL curves for C1′ and C2′ samples. The curve for C2′ differs from that for the

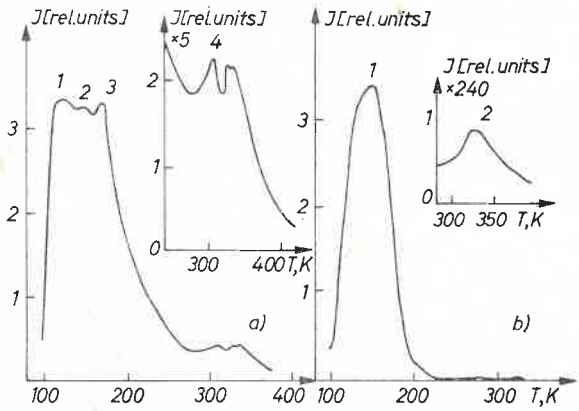

Fig. 8. RTL curves for BBOA samples, a) sample C1′, b) sample C2′

C1′ sample at 77 K in the stable SC-modification, which is also indicative of the possible appearance of a metastable state at 77 K for C2′. The character and origin of the RTL peak 1 for C2′ (149 K, Fig. 8) are similar to the peak 1 for B2′. The DSC curve shows no evident stepwise increase in the heat capacity, neither does the RTL curve have a sharp peak (as peak 2 on RTL curve for A1′). Therefore, one cannot make any definite conclusion about the existence of a "frozen" LC-phase for C2′ at 77 K. Nevertheless, the space structure of LC-molecules in C2′ at 77K may correspond to the "frozen" SLC-phase.

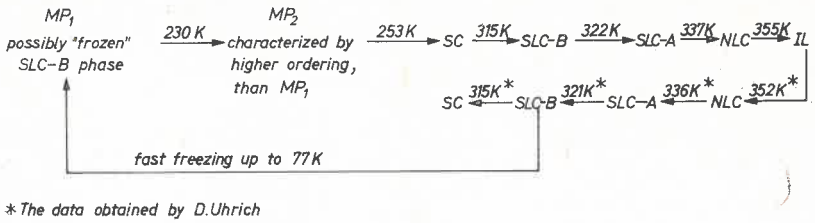

Fig. 9. Scheme of phase transitions BBOA

The RTL peak 1 for C1′ is also shifted (in respect to peak 2 for C2′) toward lower temperatures. Moreover, the RTL curve for C1′ has the peaks 2 and 3 (at 155 and 176 K, see Fig. 8 b, d) associated with the unfreezing of mobilities of some parts in BBOA molecule.

Based upon the results of a DSC and RTL analysis one can propose a scheme of BBOA phase transitions given in Fig. 9.

3.4. RTL luminescence in the region of stable-state SC-phases

As noted above, for all the LC samples studied by the RTL technique, the luminescence at temperatures corresponding to the existence of stable-state mesophases has been observed (see Figs. 1, 5, 8).

It should be noted that the luminescence has a rather low intensity, but does not disappear when the LC-samples turn into IL-phase. The nature of that luminescence has been studied by us in [13]. The luminescence was suggested to be caused by chemoluminescence (in particular, the luminescence, which accompanies the recombination of peroxide radicals partially produced during irradiation of samples containing the doped oxygen atoms). But a fine structure of luminescent peaks at high temperature can correlate with the temperatures of transitions in the LC region. Actually, the phase transitions accompanied by a sharp change of such properties of the substance as viscosity, mobility of molecules, etc. can affect significantly the rate constants of chemical reactions, and as a result, the intensity of resultant luminescence.

4. Conclusions

1. By using RTL and DSC methods the metastable phases of some LC were studied.

2. It was found that a fast freezing (with rates $\geqslant$ 500 deg/min) of different LC-phases down to 77 K allows their preservation at low temperatures. Temperature intervals for the existence of such recorded phases were determined.

3. It is shown that a combined use of RTL and DSC methods allows one to identify phase transitions between metastable phases.

4. The heating of irradiated LC-compounds is found to be accompanied by luminescent flares at temperature of transitions between stable mesophases, as well as during transition to the isotropic liquid.

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REFERENCES

[1] I. D. Bernal, D. Crowfoot, *Trans Faraday Soc.* **29**, 1032 (1933).
[2] R. C. Robinder, J. C. Poiriez, *J. Am. Chem. Soc.* **90**, 4769 (1968).
[3] G. Mayer, T. Waluga, J. A. Janik, *Phys. Lett.* **41A**, 102 (1972).
[4] J. O. Kessler, J. E. Lydon, *Liquid Cryst. and Order, Fluids*, Vol. 2, New York-London 1974, pp. 331–339.
[5] E. Sciesinska, J. Sciesinski, J. Twardowski, J. A. Janik, *Mol. Cryst. Liq. Cryst.* **27**, 125 (1974).
[6] J. H. Schuur, M. Haas, W. Z. Adair, *Phys. Lett.* **41A**, 326 (1972).
[7] E. M. Barrall, K. E. Bredfelt, M. J. Vogel, Fourth International Liquid Crystal Conference, Kent State University, Kent, Ohio, August 21–25, 1973, paper 158.
[8] K. Deniz, V. R. K. Usha Rao, A. I. Mehta, A. S. Paraujpe, P. S. Parvathanthan, *Mol. Cryst. Liq. Cryst.* **42**, 127 (1977).
[9] K. S. Kunihisa, M. Gotoh, *Mol. Cryst. Liq. Cryst.* **42**, 97 (1977).
[10] F. Cavatori, M. P. Fountana, N. Kirov, *Mol. Cryst. Liq. Cryst. Lett.* **34**, 241 (1977).
[11] D. L. Uhrich, V. O. Aimiuwi, P. V. Ktorides, W. J. La Price, *Phys. Rev.* **A12**, 211 (1975).
[12] V. Nikolskii, *Radiothermoluminescence*, Soviet Science Review, March 1972, p. 77.
[13] V. Ya. Rochev, O. P. Kevdin, A. M. Kaplan, V. G. Nikolskii, N. M. Styrikovich, P. Detjen, Martin-Lüther-Universität, Halle-Wittenberg, DDR, Wissenschaftliche Beitrage, **21**, 21 (1978).
[14] N. Mironov, V. G. Nikolskii, *Zav. Lab.* **39**, 1272 (1972).
[15] A. M. Kaplan, Candidate thesis, Inst. Chem. Phys., Moscow 1976.
[16] A. P. Kushelevskii, L. Feldman, Z. B. Alfassi, *Mol. Cryst. Liq. Cryst.* **35**, 353 (1976).
[17] Z. B. Alfassi, L. Feldman, A. P. Kushelevskii, *Int. J. Appl. Radiat. Isot.* **27**, 722 (1976).
[18] D. Uhrich, private communication.