Conformation mobility of mesophase molecules by optical sounding

E. M. Aver'yanov, A. Ya. Korets, and V. F. Shabanov

Physics Institute, Siberian Division, USSR Academy of Sciences

(Submitted 7 December 1979)
Zh. Eksp. Teor. Fiz. **78**, 2374–2385 (June 1980)

Optical sounding has revealed a strong influence of conformation mobility of the molecules of a number of nematic liquid crystals of the tolane and cyanobiphenyl classes on the orientational ordering of impurity dye molecules. The effect manifests itself in a drastic decrease of the impurity order parameter S_{imp} relative to S_0 for rigid matrix molecules near the phase transition into an isotropic liquid, as well as in a strong decrease of S_{imp} relative to S_0 with increasing length of the flexible aliphatic chains in the matrix molecules. A theoretical interpretation of the observed phenomena is presented and used as a basis for a suggested new method of quantitatively determining the degree of conformational mobility of flexible chains of mesogenic molecules. The values of the conformational mobility parameters of alkyl and alkoxy chains in the investigated liquid crystals, obtained from the optical experiment, agree well with NMR measurement results. It is shown that conformational mobility of the molecules exerts a strong influence on the relations between the elastic constants of a nematic liquid crystal.

PACS numbers: 61.30. – v, 61.70.Rj, 36.20.Ey

1. INTRODUCTION

The needs of the theory and practice of liquid crystals (LC) have stimulated increased interest in the establishment of a correlation between the molecular characteristics and the macroscopic properties of the mesophase. One of the necessary conditions for the existence of the LC phase is the presence in the molecules of a relatively rigid core and flexible terminal segments—most frequently alkyl chains of different lengths.[1] Typical models of mesogenic molecules are shown in Fig. 1. Models 1 and 3 are typical of thermotropic LC of various types. Model 2 corresponds to lyotropic LC and to lipid molecules contained in cell membranes.[2] The published data on the role of flexible molecule chains and the orientational ordering of thermotropic and lyotropic LC structures are only qualitative, and experimental investigations of these questions are extremely scanty.

The presence of flexible chains leads to conformational instability of the molecules, to a change in the character of the interactions between the molecules, and to differences in the degree of orientational ordering

$$S_k = {}^1/_2\langle 3\cos^2\theta_k - 1\rangle \qquad (1)$$

for different segments of the molecule in the mesophase. Here θ_k is the angle between the axis of the k-th segment and the director of the sample, the brackets $\langle\cdots\rangle$ denote statistical averaging. The available experimental data on conformational mobility of molecules pertain to the parameters S_k determined by the *NMR* method for various sections of a flexible alkyl chain of nematogen molecules,[3,4] to the determination by the *EPR* method of the order parameter S_{imp} of the impurity molecules (spin marks in lipid bilayers[5]), the study of the effect of conformational mobility of flexible chains on the orientational properties of the rigid molecular core by the method of Raman scattering (RS) spectroscopy,[6,7] and the study of the mobility of luminescent probes in lypid bilayers. It was established in Refs. 3 and 4 that the values of S_k decrease with increasing distance between the *k-th* segment of the alkyl chain from the rigid molecular core. In lipid membranes, the luminescent-probe mobility was seen to increase both with increasing penetration into the bilayer at a fixed temperature, and with approach to the temperature T_f of the phase transition into the isotropic-liquid phase at a fixed depth of immersion of the probe.[2] This effect manifests itself most strongly near T_f. We have previously[6,7] observed that lengthening the flexible alkyl chain in nematogenic molecules of the tolane class leads to a negligible decrease of the order parameter $S_0 = \langle P_2\rangle$ of the rigid core of the molecule, but to a strong decrease of the parameter $\langle P_4\rangle$, particularly near T_f. In addition, a sharp decrease of the parameter S_{imp} of impurity dye molecules was observed in Ref. 7 following the lengthening of the chains of the matrix molecules.

The sensitivity of the orientational properties of the impurity to the conformational mobility of the matrix molecules points to the feasibility of using impurity LC as model objects for the study of this mobility. The advantage of impurity systems lies in the fact that it is possible to vary the conformational properties of both the matrix and the impurity. One of the four possible combinations of these properties, when the matrix and impurity molecules are rigid, has by now been well investigated and found application in the solution of problems in technical electro-optics.[8] The ratio of the parameters S_{m} (for the matrix) and S_{imp} in such systems is determined by steric factors and depends on the ratio of the longitudinal matrix and impurity dimensions Λ_{m} and Λ_{imp}, respectively, if their transverse dimensions are close. The main relevant regularities were establ-

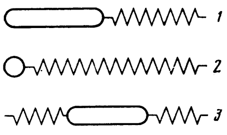

FIG. 1. Typical models of flexible molecules with flexible chains.

ished in Ref. 9, where a number of nematic LC were probed by dye molecules of varying lengths, and were later confirmed by subsequent studies.[10,11] The empirical data[9-11] on the ratio of S_m and S_{imp} can be approximated by the expression

$$\Delta S_{st}=S_m-S_{imp}=\varkappa(\Lambda_m-\Lambda_{imp})=\varkappa\Delta\Lambda, \qquad (2)$$

where the value of the coefficient $\varkappa$ depends on the nature of the matrix and of the impurity and on the order parameter S_m. The relation (2) is satisfied at $\Delta\Lambda<\Lambda_m$ and $\Delta\Lambda<\Lambda_{imp}$.

The question of the influence of the conformational mobility of the matrix molecules on the orientational properties of rigid impurity has not been investigated before. It is of practical importance both for the development of electro-opticla instruments, and for the use of impurity LC systems as laser media for the generation or radiation and for tuning its frequency.[8] On the other hand, a clarification of the quantitative aspects of the problem is useful for biology and is connected with prospects of using luminescent and spin probing in the research into the structure and properties of cell membranes.[5]

The purpose of the present paper is to demonstrate, with nematic LC of the tolane and cyanobiphenyl classes as examples, that a comprehensive use of the methods of(RS)and optical probing can yield quantitative information on the degree of conformational mobility of molecules in the mesophase and on its influence on the orientational-statistical properties of the matrix and impurity, as well as on the elastic properties of LC.

2. INVESTIGATED OBJECTS

For the investigation by the optical probing method we chose the nematic LC 4-amyloxy-4′ cyanobiphenyl (AOCB, nematic-phase existence interval 44-57 °C), 4-metoxy-4′-amyltolane (MOAT, 44–57 °C), 4-ethoxy-4′-hexyltolane (E06T, 48.5–75.8 °C), 4-ethoxy-4′-octyltolane (E08T, 47.5–73.5 °C), and the dye 4-dimethylaminc-4′ nitroazobenzene(DMANAB). These LC were thoroughly studied by the RS method in our earlier papers,[6,7,12] where their structural chemical formulas are given.

The choice of the objects was dictated by the following considerations. Among the LC indicated above, models 1 and 3 of mesogenic molecules are realized, and the variable length of their flexible chains is comparable with the lengths of the rigid molecular core. The electron structure of the dye is similar to the structure of the matrix molecules, and $\Lambda_{imp}\lesssim\Lambda_m$, a fact convenient for the estimate of the variation of ΔS_{st} by means of Eq. (2). The lowest electronic transition of the dye is polarized strictly along the long axis of the molecule.[9] The order parameters for the rigid nuclei of the AOCB and tolane molecules in the mesophase are markedly different,[6,7,12] an important factor in the explanation of the dependence of the effects of conformational mobility of the molecules on the degree of ordering of the sample. Finally, the LC considered here include both alkyl and alkoxy chains, the orientational ordering of whose individual segments was investigated earlier by the NMR method[3,4] in the nematic phase of the crystals 4-butoxybenzylidene-4′-octylaniline (BOBOA) and 4-cyanobenzylidene-4′octyloxyaniline (CBOOA), which are close in molecular structure to the tolanes and to AOCB.

3. PROCEDURE AND RESULTS OF OPTICAL PROBING

The optical-probing method is based on a comparison of the intensity of the impurity absorption of differently polarized components of the light beam incident on the oriented LC. In the case of planar orientation of the molecules and alignment of the dipole moment of the electronic transition of the impurity with the long molecular axis, the value of S_{imp} is determined from the expression[8]

$$S_{imp}=(Ng-1)/(Ng+2). \qquad (3)$$

Here the dichroism $N=D_\parallel/D_\perp$, and $D_{\parallel,\perp}$ are the integral optical densities of the sample in the impurity-absorption band for the components of the light incident on the crystal and polarized parallel and perpendicular to the sample axis; $D=\log(I_0/I)$, where I_0 and I are the respective intensities of the radiation incident on the crystal and passing through it. The correction factor

$$g=n_\parallel/n_\perp(f_\perp/f_\parallel)^2 \qquad (4)$$

depends on the refractive indices n_i of the matrix and on the components f_{ii} of the tensor of the local field in the impurity absorption band. In the director system, f is diagonal and its components are of the form

$$f_{ii}=1+L_{ii}(n_i^2-1), \qquad (5)$$

where L_{ii} are the components of the tensor Lorentz factor, which is diagonal in this system. The values of L_{ii} and their temperature dependence in the mesophase were obtained by the method proposed in Ref. 13 and were used earlier in the reduction of data obtained from measurements by the Raman spectroscopy method.[6,7,12] The temperature dependences of the refractive indices n_i at $\lambda=420$, 490, 560, and 736 nm were measured by a wedge procedure and are given in Ref. 12 for AOCB and in Ref. 14 for the tolanes.

Planar orientation of the LC in the sandwich cells was produced by texturing the internal surfaces by the Chatelain method.[8] The quality of the samples was gauged by the absence of disclinations, using an MIN-8 polarization microscope. The temperatures of the samples were stabilized in the experiments accurate to 0.2 °C. The impurity absorption spectra were measured with a VSU2-P spectrophotometer at the optimal sample thicknesses $d=20-40$ μm and dye concentration 0.1 – 0.3 wt.%. Tests have shown that this impurity concentration lowers the temperature T_f, but does not change the optical-anisotropy properties of the matrix in a reduced temperature scale $\Delta T=T_f-T$. The long-wave edge of the strong electronic absorption of the LC lies in the regions 380 nm for tolanes and 420 nm for AOCB. The absorption band of the dye has a maximum near 490 nm and lies in the transparency region of the matrices. Its short-wave edge, however, is markedly distorted by the absorption of the the matrix itself, especially in the case of AOCB. To prevent this, a

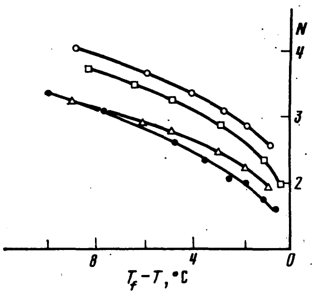

FIG. 2. Temperature dependence of the dichroism N of the impurity absorption of the dye DMANAB in the nematic phase of the crystals AOCB (●), MOAT (□), EO6T (○) and EO8T (△); T_f is the temperature of the transition from the nematic phase to an anisotropic liquid.

pure LC of the same thickness as the impurity LC was placed in the comparison arm of the optical system of the instrument, and the difference spectrum of the impurity absorption was recorded at equal values of the reduced temperatures of the pure and impurity samples was recorded. The temperature dependence of the dichroism N of the dye in the crystals MOAT, E06T, E08T, and AOCB is shown in Fig. 2. Using these data we obtained from formulas (3) – (5) the experimental values of $S_{\rm imp}$, which are shown in Figs. 3 and 4.

As seen from Fig. 3, the values of $S_{\rm imp}$ and S_0 in AOCB are in agreement for the rigid core of the molecules far from the phase-transition point. In the pre-transition region, the values of $S_{\rm imp}$ decrease rapidly as $\Delta T \to 0$. In tolane LC, the disparity between S_0 and $S_{\rm imp}$ increases markedly with increasing length of the flexible alkyl and alkoxy chains in the matrix molecules, especially on going from E06T to E08T, although the values of S_0 in these crystals differ little. It is also noted that in each tolane LC the difference $\Delta S = S_0 - S_{\rm imp}$ remains unchanged, within the experimental accuracy, when the mesophase temperature is changed. The effects noted here are obviously connected with the conformational mobility of the flexible chains in the matrix molecules and with the influence of this mobility on the orientational properties of the impurity dye molecules.

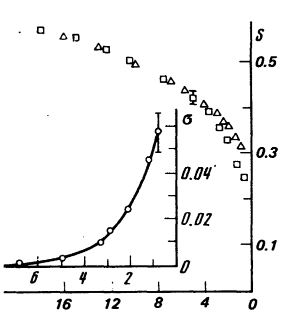

FIG. 3. Temperature dependences: △—of the order parameter S_k of rigid cores of the molecules of the AOCB matrix (Raman spectroscopy data[12]); □—of the order parameter $S_{\rm imp}$ of the impurity dye molecules (optical probing). Inset-temperature dependence of the conformation-mobility parameter σ of the alkoxy chain of AOCB molecules, calculated from Eq. (8).

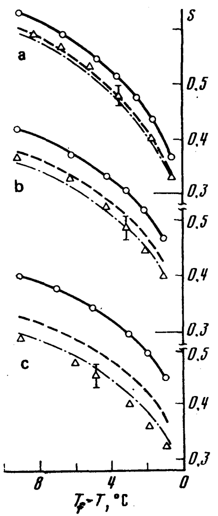

FIG. 4. Temperature dependence of the order parameter in the nematic phase of the crystals MOAT (a), EO6T (b), and EO8T (c); ○—S_0, Raman-spectroscopy data; 6, 7 △—$S_{\rm imp}$, optical probing. The dashed lines correspond to the variation of $\bar{S}$ with allowance for the conformational-mobility effect in accord with Eq. (12); dash-dot lines—change of $\bar{S}$ with allowance for the conformational and steric effects.

4. INTERPRETATION OF EXPERIMENTAL RESULTS AND SOME CONSEQUENCES

In the mesophase, the conformation and mobility of individual sections of alkyl chains of molecules are intermediate between those of the gas phase in a solid crystal. The spectroscopic and thermal data[15] obtained in the investigation of the vapors, and electron-diffraction investigations[16] of chain compound crystals show that in these phases the energywise favored configuration of the alkyl chains constitute a flat zigzag of the carbon atoms. The C–H bonds of the methyl groups lie in planes that pass through the carbon atoms perpendicular to the chain axis.

Thermal motion in the mesophase leads to mobility gradients of the individual groups of an alkyl chain whose one end is connected to the rigid core of the molecule. NMR experiments[3,4] on deuterated methylene groups have shown that at a fixed mesophase temperature the gradient of the chain flexibility manifests itself in a lowering of the order parameter S_{C-D} of the C–D bonds as their distance to the rigid molecular core increases, and this dependence is close to linear. Therefore the dependence of the order parameter S_k of the k-th chain segment parallel to the chain axis will be approximated by the expression

$$S_k = S_0 - \sigma k, \qquad (6)$$

where σ = const characterizes the average conformational mobility of the chain at a given mesophase temperature. Taking into account the fact that $S_k = 2S_{C-D}(k)$ we can determine the values of δ_a for the alkyl chain and σ_{a0} for the alkoxy chain in the meatic phase of the crystals BOBOA and CBOOA at T = 0.7 °C, namely $\sigma_a = 0.032$ and $\sigma_{a0} = 0.051$. In the pre-transition temperature region the mobility of the alkoxy-chain is higher than that of the alkyl chain. At T = 15 °C, however, we can obtain from the data of Refs. 3 and 4 the inverse relation $\sigma_a = 1.43\sigma_{a0}$, i.e., the temperature dependence of σ depends on the character of the molecular interactions in the mesophase and is determined in this case by the difference between the properties of the remaining segments of the BOBOA and CBOOA molecules. Inasmuch with respect to the chemical structure of the individual molecular structure the crystals BOBOA and CBOOA are similar to those investigated by us, we use the parameters σ_a and σ_{a0} obtained above to interpret the experiment.

At $\sigma = 0$ the value of S_{imp} would be determined by Eq. (2). If, however, $\Lambda_m \approx \Lambda_{\text{imp}}$ and $\sigma \neq 0$, and the matrix molecules produce no associates with one another or with the impurity molecules, the value of S_{imp} represents the average orientational order of the different segments of the matrix molecules:

$$S_{\text{imp}} = \bar{S} = \sum_k S_k l_k \Big/ \sum_k l_k. \tag{7}$$

Here S_k is the order parameter of the *k-th* segment of the molecule, and l_k is the length of the segment. In the case of the alkyl chain $l_k \equiv l = l_{c-c} \sin 56°$, where l_{c-c} is the length of the $C-C$ bond. Since the orientational order of the mesophase is determined to a considerable degree by the steric repulsion forces, Eq. (7) can be used if the transverse dimensions of the individual segments are close, as is the case in the object considered here.

We consider the model 1 of the mesogenic molecule in Fig. 1. For this case we have from (6) and (7)

$$\bar{S} = S_0 - \frac{\sigma l n(n+1)}{2(l_0 + nl)}, \tag{8}$$

where n is the number of carbon atoms in the chain, and l_0 is the length of the rigid molecular core. It follows from (8) that the increase of the number of CH_2 groups of the alkyl chain of the matrix molecules should lead to an increasing difference between S_0 and S_{imp}. At constant σ and fixed n, the difference $\Delta S = S_0 - \bar{S}$ does not depend on the temperature of the mesophase. Obviously, formula (8) can be used for an experimental determination of the constant σ in different mesophase temperature intervals. The inset of Fig. 3 shows the temperature dependence of σ in AOCB, calculated from the experimental values of ΔS. At $\Delta T = 0.7$ °C the value $\sigma_{ao} \approx 0.058$ for AOCB agrees well with the value 0.051 obtained for CBOOA from NMR measurements.[4] Far from the phase transition, the value $\sigma_{ao} \approx \sigma_a/1.43 \approx 0.022$ yields $\Delta S \approx 0.02$, which is also within the limits of the accuracy of optial experiments. Within the framework of the Maier-Saupe theory, the question of the influence of the conformational properties of the alkoxychain on the order parameter of a nematic at $T = T_f$ was considered in Ref. 17 in connection with an explanation of the even-odd effect. From the results of this paper it is possible to obtain at the phase transition point a theoretical value $\sigma_{ao} \approx 0.018$, which deviates greatly from the experimental value (Fig. 3, inset).

We consider now several limiting cases that depend on the ratio of the lengths of the flexible and rigid parts of the molecule, $\xi = nl/l_0$:

$$\xi \ll 1, \quad \Delta S = \xi\sigma(n+1)/2; \tag{9}$$

$$\xi = 1, \quad \Delta S = \sigma(n+1)/4; \tag{10}$$

$$\xi \gg 1, \quad \Delta S = \sigma(n+1)/2. \tag{11}$$

The case (9) corresponds to rigid mesogenic molecules and predicts, in accord with experiment,[9-11] a small difference between the values of S of the matrix and the impurity at $\Lambda_m \approx \Lambda_{\text{imp}}$. Case (10) is most typical of mesogenic molecules with one flexible chain. Case (11) is typical of lipids (model 2, Fig. 1) contained in cell membranes. The structure of the latter includes a lipid bilayer with polar groups of lipids located on the surface, and alkyl chains of fatty acids occupying the central part of the membrane and oriented on the average normal to the surface.[2] Since the polar part of the lipid is rigidly fixed on the surface of the bilayer, we can put $S_0 = 1$. Then at $n = 14-22$ and $\sigma = 0.032$ formula (11) yields $\bar{S} = 0.76-0.63$. This estimate agrees well with the value $S_{\text{imp}} = 0.67$ obtained at the same values of n by an EPR method using a spin probe in a number of lipid membranes.[5]

For the model 3 (Fig. 1) of a molecule contain alkoxy and alkyl chains of different length, it follows from (6) and (7) that

$$\Delta S = \frac{l[\sigma_{ao} n_1(n_1+1) + \sigma_a n_2(n_2+1)]}{2[l_0 + (n_1+n_2)l]}. \tag{12}$$

At $\sigma_{ao} = 0.022$, $\sigma_a = 0.032$ and the structural-chemical data of Ref. 18 the values of ΔS were calculated for MOAT, E06T, and E08T using Eq. (12). The temperature dependences of $\bar{S}$ are shown for these crystals in Fig. 4. The calculation and experimental results agree MOAT and E06T, but for E08T the agreement of the results is less satisfactory. The reason may be failure to take into account the steric effect,[9] inasmuch the value of $\Delta\Lambda$ in (2) increases with increasing length of the flexible chains of the matrix molecules.

We estimate now the maximum decrease of ΔS_{st} on account of the steric factor in the LC considered here, assuming that the alkyl chains of the molecules are rigid, $\sigma = 0$. From the results of Ref. 2 it follows that for the nematic LC BEHA (4-butoxyphenyl ester of 4′-hexylbenzoic acid), which is closest in molecular dimensions and the value of S_0 to the tolanes investigated here, and dyes similar to DMANAB, we obtain $\varkappa = 5 \times 10^{-3}$. The calculated values of $\bar{S}$ for MOAT(Λ_m = 19.3Å), E06T(21.9Å), and E08T (24.4Å) are shown in Fig. 4. It is seen from the figure that when account is taken of the two effects it is possible to attain complete agreement between the results of the calculation and of the experiment. The principal role is played here by the allowance for the conformational mobility of the matrix molecules.

The manifestation of the conformational mobility in the decrease $\bar{S}$ differs substantially in models 1 and 3 of the molecules (Fig. 1) at equal total length of the flexible alkyl chains. Since in model 1 each chain contains $2n$ carbon atoms and in model 3 only n, it follows from (8) and (12) that

$$\Delta S_1 = \frac{\sigma\xi(2n+1)}{1+2\xi}, \qquad \Delta S_3 = \frac{\sigma\xi(n+1)}{1+2\xi}, \qquad \frac{\Delta S_1}{\Delta S_3} \approx 2. \tag{13}$$

This is seen also from the experiment (Fig. 4): the addition of two carbon atoms to one alkyl chain on going from E06T to E08T leads to a greater lowering of S_{imp} than the addition of one carbon atom to each of the chains on going from MOAT to E06T. The reason for this difference is apparently that in model 1 the conformational mobility of the flexible chain makes probable a banana-like shape of the molecule in the mesophase. In model 3, the cis- and transorientations of the flexible chains relative to the rigid core are equally probable, and on the average the molecule can have higher values of $\overline{S}$.

At $\xi \lesssim 1$, the values of S obtained from diamagnetic and refractometric measurements characterize to a greater degree the orientational properties of the rigid molecular core that makes the main contribution to the diamgantic and optical anisotropy of the molecules. These methods when combined with optical probing can also be used to investigate the conformational properties of the LC-matrix molecules.

The conformational mobility of flexible chains influences greatly the orientational-statistical properties of the rigid molecular core.[6,7] This can alter noticeably the macroscopic properties of the sample and in particular the ratio of the elastic constants.

5. CONFORMATIONAL MOBILITY OF THE MOLECULES AND "ANOMALOUS" CHANGE OF THE ELASTIC CONSTANTS OF LC

It is known that the elastic properties of a nematic LC can be described by three elastic constants corresponding to transverse flexure (K_1), torstion (K_2), and longitudinal flexure (K_3).[1] For practical purposes it is important to establish the correlation between elastic constants and the molecular properties, and in particular with the dimensions of the molecules. The recently performed first systematic investigations have shown[19] that in the case rigid nematogen molecules the ratio K_3/K_1 increases with increasing ratio $R = \Lambda/d$ of the longitudinal (Λ) and transverse (d) dimensions of the molecule in accord with with the prediction of the theory. In molecules of type 1 (Fig. 1), however, an anomalous decrease of the ratio K_3/K_1 with increasing R as a result of the lengthening of the flex-alkyl chain was observed.[20] This fact could not be explain-within the framework of the Maier-Saupe theory, which was developed for the description of the orientational statistics of rigid molecules and does not take into account their conformation properties.

This behavior of K_3/K_1 can be explained when account is taken of the influence of the conformational mobility of the flexible segments on the orientational-statistical properties of the rigid nucleus and on the shape of the molecules themselves. At $\xi \lesssim 1$ a definite contribution to the total intermolecular-interaction energy is made by the interaction of the rigid cores.[21] Therefore, the behavior of the elastic constants is determined mainly by the orientational properties of the rigid core. According to Ref. 22, for spheroidal molecules

$$\frac{K_3}{K_1}=\frac{1+\Delta+4\Delta'(\langle P_4\rangle/\langle P_2\rangle)}{1+\Delta-3\Delta'(\langle P_4\rangle/\langle P_2\rangle)}, \tag{14}$$

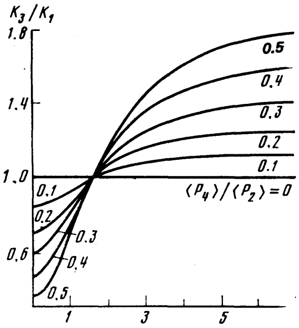

FIG. 5. Dependence of K_3/K_1 on R calculated from (14) and (15) for various values of the ratio $\langle P_4\rangle/\langle P_2\rangle$.

where $\langle P_i\rangle$ are the orientational order parameters of the molecule, and the quantities Δ and Δ' depend on R:

$$\Delta=\frac{2R^2+2}{7R^2+20},\quad \Delta'=\frac{27(R^2/16-1/6)}{7R^2+20}. \tag{15}$$

The plots of $K_3/K_1(R)$ calculated from (14) and (15) are shown in Fig. 5. As seen from the figure, and the typical values $R > 2$ of mesogenic molecules the ratio K_3/K_1, at close values of R, decreases rapidly with decreasing ratio $\langle P_4\rangle/\langle P_2\rangle$. The drastic decrease of $\langle P_4\rangle$ following a negligible change of $\langle P_2\rangle$ was in fact observed in our studies[6,7] on going from MOAT to homologs of E06T and E08T with longer alkyl chains.

At $\Delta T = 15$ °C an increase of the number of segments of the flexible chain of nematogenic homologs anisilidene-p-aminophenylacetate (APAPA) from four to seven has led in Ref. 20 to a decrease of the ratio K_3/K_1 by a factor 1.29 at $R \approx 3$. In our experiments[7] a transition from MOAT to E08T at the same values of R lowered the ratio $\langle P_4\rangle/\langle P_2\rangle$ from 0.52 to 0.2. According to Fig. 5 this corresponds to a decrease of K_3/K_1 by a factor 1.26, which is close to the experimental data of Ref. 20.

In the presence of conformational mobility of the chain, the banana shape of the molecules of type 1 (Fig. 1) can also lower K_3/K_1, as noted in Ref. 23. In accord with the remarks made concerning the formulas in (13), the experiments[24] on molecules of type 3 (Fig. 1) revealed a less explicit tendency of K_3/K_1 to decrease with lengthening of the flexible chain in the mesogenic molecules of one homologic series.

In conclusion, we thank P. B. Adomenas (Vilnius State University) and V.G. Rumyantsev (Research Inst. for Organic Intermediate Products and Dyes) for supplying the liquid crystal and the dye, and L. M. Blinov for calling our attention to Refs. 19 and 20.

[1] P. G. de Gennes, The Physics of Liquid Crystals, Oxford, 1974.

[2] J. B. Robinson, transl. in: Biologicheskie membrany, (Biological Membranes), B. P. Skulacher, transl. ed., Atomizdat, 1978, Chap. 2, 5.

[3] B. Deloche, J. Charvolin, L. Leibert, and L. Strzelecki, J. Phys. (Paris) **36**, C1-21 (1975).

[4] B. Deloche and J. Charvolin, J. Phys. (Paris) **37**, 1497 (1976).

[5] M. L. Hubbel and H. M. McConnel, J. Am. Chem. Soc. **93**, 314

(1971).

[6] E. M. Aver'yanov, P. V. Adomenas, A. V. Sorokin, and V. F. Shabanov, Fiz. Tverd. Tela (Leningrad) **21**, 2209 (1979) [Sov. Phys. Solid State **21**, 1271 (1979)].

[7] E. M. Aver'yanov, A. Vaitkyavichyus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin, and V. F. Shabanov, Zh. Eksp. Teor. Fiz. **76**, 1791 (1979) [Sov. Phys. JETP **49**, 910 (1979)].

[8] L. M. Blinov, Elektro- i magnitooptika zhidkikh kristallov (Electro- and Magneto-Optics of Liquid Crystals), Nauka, 1978.

[9] L. M. Blinov, V. A. Kizel', V. G. Rumyantsev, and V. V. Titov, Kristallografiya **20**, 1245 (1975) [Sov. Phys. Crystallogr. **20**, 750 (1975)].

[10] A. Bloom, P. L. K. Hung, and D. Meyerhofer, Mol. Cryst. Liq. Cryst. Lett. **41**, 1 (1977).

[11] J. Constant, E. P. Raues, I. A. Shanks, D. Coates, G. W. Gray, and D. J. McDonnell, J. Phys. D: Appl. Phys. **11**, 479 (1978).

[12] E. M. Aver'yanov, Yu. Denite, A. Ya. Korets, A. V. Sorokin, and V. F. Shabanov, Kristallografiya **25**, 319 (1980) [Sov. Phys. Crystallogr. **25**, 184 (1980)].

[13] E. M. Aver'yanov and V. F. Shabanov, Kristallografiya **23**, 320 (1978) [Sov. Phys. Crystallogr. **23**, 177 (1978)].

[14] E. M. Aver'yanov, A. Vaitkyavichyus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin, and V. F. Shabanov, Preprint No. 88F, Phys. Inst. Sib. Div. USSR Acad. Sci. Krasnoyarsk, 1978.

[15] W. J. Taylor, J. Chem. Phys. **16**, 257 (1948).

[16] B. K. Vaĭnshtein and Z. G. Pinsker, Dokl. Akad. Nauk SSSR **72**, 53 (1950).

[17] S. Marcelja, J. Chem. Phys. **60**, 3599 (1974).

[18] A. I. Kitaigorodskiĭ, Organicheskaya kristallokhimiya (Organic Crystal Chemistry), Izd-vo Akad. Nauk SSSR, 1955.

[19] F. Leenhouts, A. J. Dekker, and W. H. de Jeu, Phys. Lett. **72A**, 155 (1979).

[20] F. Leenhouts, H. J. Roebers, A. J. Dekker, and J. J. Jonker, J. Phys. Colloq. C3 **40**, C3-291 (1979).

[21] D. A. Pink, J. Chem. Phys. **63**, 2533 (1975).

[22] R. G. Priest, Phys. Rev. A **7**, 720 (1973).

[23] H. Gruler, J. Chem. Phys. **61**, 5408 (1974).

[24] H. Gruler, Z. Naturforsch. Part C **28A**, 474 (1973).

Translated by J. G. Adashko

Effect of fluctuations in the critical range in a second-order phase transition on a nonequilibrium phase transition

Yu. L. Klimontovich

M. V. Lomonosov Moscow State University

(Submitted 11 December 1979)
Zh. Eksp. Teor. Fiz. **78**, 2384–2391 (June 1980)

The effect of fluctuations in the critical range, during phase transitions in ferroelectric materials and liquid crystals, on a nonequilibrium phase transition is considered in concrete cases, generation of light at impurity atoms and molecules. Two different mechanisms for this effect are considered. The first determines the effect of fluctuations of the phonon subsystem in ferroelectrics in the critical range on the threshold for generation at impurity atoms (ions). It is shown that, depending on the detuning of the generation frequency from the frequency of transition between the operating levels of the impurity atoms, the generation threshold may either increase (small detuning) or decrease (large detuning). It is the first case that has practical significance. The second mechanism determines the effect of fluctuations of orientation of the molecules of nematic liquid crystals, in the critical range, on the threshold for generation at impurity molecues and on the wavelength of the generated radiation. It is shown that the generation threshold drops on approach to the critical point. The wavelength also decreases. The pertinent temperature dependencies are found. The results are in qualitative agreement with experimental data [S. Kuroda and K. Kubota, Appl. Phys. Lett. **29**, 737 (1976); S. A. Akopyan, G. A. Bardanyan, G. A. Lyakhov, and Yu. S. Chilingaryan, Sov. Tech. Phys. Lett. **5**, 217 (1979)].

PACS numbers: 64.70.Kb, 64.70.Ew, 77.80. – e, 61.30. – v

1. INTRODUCTION

Substances are known in which there are second-order phase transitions kind and which, at the same time, can be used as operating media, for example in lasers. For such substances it is of interest to investigate the mutual influence of equilibrium and nonequilibrium phase transitions. An example is a transition through a generation threshold.

Examples of such substances are laser ferroelectrics, in which the generation occurs at the impurity-ion levels,[1,2] and also solutions of dye molecules in liquid crystals.[3,4] Experimental investigations are known in which the effect of fluctuations on the generation process was observed in the critical range during a phase transition in nematic liquid crystals. Thus a dependence of the generation threshold on the degree of proximity to the phase-transition point has been observed.[3,4] It was observed that on approach to the critical point (either from above or from below) the generation threshold decreased. A decrease of the wavelength of the generated radiation was also observed.

The present paper considers two possible mechanisms for the effect of fluctuations in the critical range on the process of generation of optical radiation. The first mechanism may manifest itself in ferroelectrics. In this case, the generation parameters change on ap-