

The theory developed above can be applied to the intercalation compound $\text{TaS}_2(\text{Py})_{1/2}$, which displays superconducting properties at low temperatures. For $W < T_c$ and $d \sim \rho_0^{-1}$, which, apparently, is fulfilled for this compound, the critical field should not exceed 50–60 kOe. Measurements in a parallel field with such values have already been performed,⁹ but only the longitudinal resistivity was measured. It was discovered that at low temperatures it is equal to zero even in very strong fields $H \sim 150$ kOe. Unfortunately, it is not possible to detect the phase transition considered above by measuring the longitudinal conductivity. Measurements of the transverse conductivity might clarify the situation.

In conclusion the author thanks A. I. Larkin and P. B. Vigman for a discussion on the work.

- ¹L. N. Bulaevskii, Zh. Eksp. Teor. Fiz. **64**, 2241 (1973) [Sov. Phys. JETP **37**, 1133 (1973)].
- ²K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. **68**, 155 (1975) [Sov. Phys. JETP **41**, 76 (1975)].
- ³L. N. Bulaevskii, A. A. Guseinov, and A. I. Rusinov, Zh. Eksp. Teor. Fiz. **71**, 2356 (1976) [Sov. Phys. JETP **44**, 1243 (1976)].
- ⁴K. B. Efetov, Zh. Eksp. Teor. Fiz. **73**, 1944 (1977) [Sov. Phys. JETP **46**, 1020 (1977)].
- ⁵T. M. Rice, Phys. Rev. **140**, A1889 (1965).
- ⁶I. E. Dzyaloshinskii and E. I. Kats, Zh. Eksp. Teor. Fiz. **55**, 2373 (1968) [Sov. Phys. JETP **28**, 1259 (1969)].
- ⁷V. L. Berezinskii, Zh. Eksp. Teor. Fiz. **61**, 1144 (1971) [Sov. Phys. JETP **34**, 610 (1972)].
- ⁸P. G. de Gennes, Superconductivity of Metals and Alloys, Benjamin, N.Y., 1966 (Russ. transl., Mir, M., 1970).
- ⁹R. C. Morris and R. V. Coleman, Phys. Rev. **B7**, 991 (1973).

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Study of orientation-statistical properties of liquid crystals of the tolane class by optical methods

E. M. Aver'yanov, A. Vaitkyavichyus, A. Ya. Korets, R. Sirutkaĩtis, A. V. Sorokin, and V. F. Shabanov

Institute of Physics, Siberian Branch, Academy of Sciences, USSR
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The methods of Raman light scattering and optical probing are used to study the orientation-statistical properties of some new nematic liquid crystals of the tolane class: methoxy-amyltolane, ethoxy-hexyltolane, ethoxy-octyltolane. An improved method of Raman-scattering spectroscopy is proposed, which makes it possible to eliminate the effects of multiple scattering and to develop the spectroscopy of specimens with a thickness comparable with the scattered wavelength. On the basis of the experimental results, single-particle orientational distribution functions are constructed for the three crystals. It is shown that the negative order parameter observed experimentally is due to neglect of the anisotropy of the local field of the light wave. The effect of elongation of semiflexible segments of molecules and of increase of the mobility of their end groups on the orientation-statistical properties of a rigid molecular nucleus is explained. It is shown that the Maier-Saupe mean-field theory agrees satisfactorily with experiment far from the phase transition to an isotropic liquid, but that it does not give a satisfactory description of the orientational statistics of the mesophase in the pretransition temperature range.

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1. INTRODUCTION

The physical properties of nematic liquid crystals (NLC) are determined to a significant degree by the orientation-statistical properties of the structure of the mesophase. These in turn are connected with the character of the intermolecular interactions and depend on the chemical nature and conformational properties of the molecules. The orientation-statistical degree of order of molecules in a NLC is described by the single-particle orientational distribution function ${}^1F(\varphi, \theta, \psi)$, which gives the probability of finding the orientation of a molecule within a small solid angle $d\Omega$ close to the corresponding Euler angles φ, θ, ψ . The latter determine the orientation of the molecular system of coordinates with respect to the laboratory system (x, y, z) . The z axis coincides with the direction of the director \mathbf{r} , and the x and y axes lie in the plane perpendicular to it. On the basis of x-ray structural data it can be concluded^{2,3} that the directions \mathbf{r} and $-\mathbf{r}$ in a NLC are

equivalent and that the projections of the long molecular axes on the xy plane are randomly distributed.

The local uniaxiality of the nematic mesophase, the presence of rotation of the molecules about the long axes, and the closeness of their form to cylindrical permit us to regard a NLC as an ensemble of uniaxial structural units with an orientational distribution function $F(\theta)$. This function can be represented as a series of even Legendre polynomials $P_l(\cos\theta)$ ⁴:

$$F(\theta) = \sum_l \frac{2l+1}{2} \langle P_l(\cos\theta) \rangle P_l(\cos\theta), \quad (1)$$

where the coefficients of the series are determined by the expression

$$\langle P_l(\cos\theta) \rangle = \int_0^\pi P_l(\cos\theta) F(\theta) \sin\theta d\theta. \quad (2)$$

The first three coefficients have the form

$$\begin{aligned} \langle P_0 \rangle &= 1, & \langle P_2 \rangle &= \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \\ \langle P_4 \rangle &= \frac{1}{8} \langle 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \rangle. \end{aligned} \quad (3)$$

The function $F(\theta)$ satisfies the normalization condition

$$\int_0^\pi F(\theta) \sin \theta d\theta = 1. \quad (4)$$

Knowledge of the function $F(\theta)$ enables us to find the mean values $\langle M \rangle$ of physical quantities that depend on the orientational order of the NLC:

$$\langle M \rangle = \int_0^\pi M(\theta) F(\theta) \sin \theta d\theta. \quad (5)$$

On the basis of experimental data on Raman light scattering, one can determine the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and construct $F^{III}(\theta)$, the distribution function through the third term in the expression (1). Thus one establishes the correlation between the distribution function $F^{III}(\theta)$ and the molecular and physical properties of the mesophase.

NLC of the tolane class are the best materials for solution of this problem. Molecules of the tolanes consist of a rigid nucleus and flexible lateral segments; the mobility of the end groups increases rapidly with increase of the length of the segments.⁵ Comparison of the results of experiment for several terms of a homologous series enables one to explain the effect of the conformation of the lateral segments on the orientation-statistical properties of the rigid nucleus, on the basis of a decisive majority of the physical characteristics of the mesophase (diamagnetic and optical anisotropy etc.).

It is interesting also to explain the influence of conformational instability of the molecules of a LC matrix on the degree of order of mixtures of molecules of a dye. This is especially timely in connection with the use of such systems for generation and frequency retuning of radiation.^{6,7} On the other hand, the molecular-statistical theory of Maier and Saupe⁸ and other theories that now exist⁹⁻¹¹ offer the possibility of calculating the distribution function $\rho(\theta)$:

$$\rho(\theta) = Z^{-1} \exp[-U(\cos \theta)/kT],$$

$$Z = \int_0^\pi \exp[-U(\cos \theta)/kT] d \cos \theta. \quad (6)$$

Here k is Boltzmann's constant, T is the absolute temperature, and $U(\cos \theta)$ is the potential of the mean field and is given by

$$U(\cos \theta) = -v \langle P_2 \rangle P_2(\cos \theta). \quad (7)$$

The value of v depends on the molecular properties. By use of the function $\rho(\theta)$ one can find the theoretical values of $\langle P_2 \rangle$, $\langle P_4 \rangle$, and $F^{III}(\theta)$ and compare them with the values found from experiment.

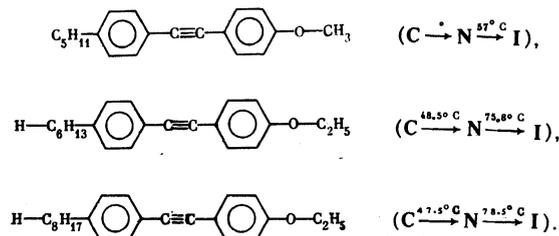
On the basis of mean-field theory^{8,11} one can explain satisfactorily many physical properties of NLC, in particular the temperature behavior of the order parameter $\langle P_2 \rangle$. But the first experiments on investigation of orientational order of NLC by the Raman light-scattering method showed an anomalous behavior of $\langle P_4 \rangle$ near the point T_f of phase transition between the nematic phase and an isotropic liquid. It was observed that in a doped crystal of methoxybenzylidene butylaniline (MBBA)⁴ and in pure pentylcyanobiphenyl (5CB)¹² the pa-

rameter $\langle P_4 \rangle$ has negative values in the pretransitional region. This contradicts the predictions of the theories^{8,11} and also experiments performed recently on spin probing¹³ of the nematic LC Merck Phase IV and on scattering of neutrons in para-azoxyanisole.¹⁴ In these experiments the values of $\langle P_4 \rangle$ obtained were in good agreement with the theoretical values.

The question of the correspondence of mean-field theory to experimental data remains short of final clarification for the following reasons. First, such data are at present vary scanty and contradict each other. Second, x-ray and neutron methods give information on the orientation of the whole molecule; and when the end groups have appreciable length, the information about the orientational properties of the rigid nucleus becomes less precise. The advantages of Raman-scattering (RS) spectroscopy in the study of the orientational statistics of liquid crystals lie in the possibility of determining $\langle P_2 \rangle$, $\langle P_4 \rangle$, and $F^{III}(\theta)$ for any structural elements of the molecule. A second problem of the present research is comparison of experimental data on $\langle P_2 \rangle$, $\langle P_4 \rangle$, and $F^{III}(\theta)$ for the rigid nucleus of molecules of a homologous series of tolanes with the predictions of molecular-statistical^{8,9} and continuum¹⁰ theories developed for description of the orientational statistics of rigid molecules.

2. EXPERIMENTAL METHODS AND RESULTS

In this work, we studied the nematic liquid crystals methoxyamyltolane (MOAT), ethoxy-hexyltolane (ÉO6T), and ethoxy-octyltolane (ÉO8T). The structural formulas of the molecules and the temperatures of the transitions between crystal (C) and nematic (N) and between nematic and isotropic liquid (I) are given below¹⁵:



The supercooled nematic mesophase was not investigated. Some details of the synthesis of these crystals are given in Ref. 16.

A. Optical probing

The method of optical probing is based on comparison of the intensity of the impurity absorption of differently polarized components of the light beam incident on the NLC, and it can be applied to the study of the structural order of NLC.¹⁷ If the dipole moment of the electron transition of the impurity is polarized along the long molecular axis and if the absorption band of the impurity lies in the transparency range of the liquid crystal, the value of $\langle P_2 \rangle$ for the impurity can be determined from the expression¹⁷

$$\langle P_2 \rangle = (Ng-1)/(Ng+2). \quad (8)$$

Here $N = D_{\parallel}/D_{\perp}$ is the dichroism; D_{\parallel} and D_{\perp} are the integral optical densities of the specimen in the absorption

band of the impurity for components of the light beam incident on the crystal that are polarized parallel and perpendicular to the optic axis of the specimen. $D = \log(J_0/J)$, where J_0 and J are intensities of the incident and transmitted radiation, respectively.

The correction factor

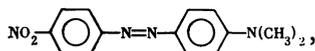
$$g = \frac{n_{\parallel}}{n_{\perp}} \left(\frac{f_{\perp}}{f_{\parallel}} \right)^2 \quad (9)$$

depends on the refractive indices n_{\parallel} and n_{\perp} of the matrix and on the components of the local-field tensor f . The indices of refraction n_{\parallel} and n_{\perp} for the nematic phase of EO6T and EO8T have been measured by the wedge method over the spectral range 420 to 740 nm and are given in our paper Ref. 18. The values of n_i for the MOAT crystal were taken from the paper of Labrunie and Bresse.¹⁹ The tensor f relates the amplitude \mathbf{E} of the macroscopic field of the light wave in the liquid crystal to the amplitude \mathbf{E}^l of the local field that acts on the molecule: $E^l = f_{ij} E_j$. In the laboratory coordinate system defined above, the tensor f is diagonal, and its components have the form

$$f_{ii} = 1 + L_{ii}(n_i^2 - 1), \quad (10)$$

where L_{ii} are the components of the Lorentz-factor tensor, which is diagonal in this system.

The properties of the tensor f in uniaxial liquid crystals have been treated in detail in Refs. 20 and 21. The values of n_i and f_{ii} in (9) are taken at the wavelength λ_i that corresponds to the maximum of the impurity absorption band in the i th component of the spectrum. A suitable material for application of the method of optical probing in tolanes is the dye



which has dimensions, a shape, and an electronic structure of the molecule that are close to the liquid crystals being studied, especially to MOAT. The lowest electronic transition of the dye is polarized along the long molecular axis. The absorption band of the dye has a maximum in the neighborhood of 490 nm in a LC matrix and lies in the transparency range of the matrix. The long-wavelength edge of the lowest electronic absorption band of the tolanes is in the neighborhood of

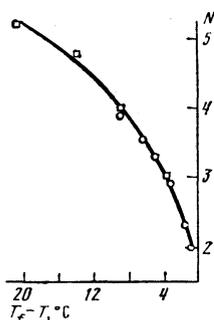


FIG. 1. Temperature variation of the dichroism N of impurity absorption of a dye in the nematic phase of crystals MOAT (○) and EO6T (□). T_f is the temperature of transition between the nematic phase and an isotropic liquid.

380 nm. The procedure for preparation and control of the specimens was described in detail earlier.²² The impurity absorption spectra were obtained on a VSU-2P spectrometer, with optimal values of specimen thickness $d = 20$ to $40 \mu\text{m}$ and of impurity concentration 0.1 to 0.3 wt%. The temperature variation of the dichroism N of the dye in MOAT and EO6T crystals is shown in Fig. 1. By use of the data of the figure, values of $\langle P_2 \rangle$ were calculated by formulas (8)–(10) for the impurity in the LC matrix; they are shown in Fig. 3 (see below). The components L_{ii} and their temperature variation were determined by the method described in Refs. 16 and 20. Figures 3a and 3b show also the values of $\langle P_2 \rangle$ corresponding to the approximation of an isotropic local field, $f_{\parallel} = f_{\perp}$.

B. Raman light scattering

In this work we used the LC cell mount shown in Fig. 2a. The beam that excites the RS spectrum is directed along the Z axis and polarized along the X axis of the system of coordinates of the apparatus. The two components of the light scattered in the Y direction, polarized along X and Z , are analyzed. The intensities J_{XX} and J_{XZ} of these components are measured for two orientations of the director \mathbf{r} of the crystal: $\mathbf{r} \perp \mathbf{X}$ (a) and $\mathbf{r} \parallel \mathbf{X}$ (b). To these specimen orientations correspond the experimental values of the degree of depolarization of the chosen spectral line

$$\rho_1 = J_{XZ}(\text{a})/J_{XX}(\text{a}),$$

$$\rho_2 = J_{XZ}(\text{b})/J_{XX}(\text{b}).$$

An important fact is that the spectrum was obtained under conditions close to total internal reflection of the exciting beam. This was achieved by choosing a cell material with an index of refraction n satisfying the condition $n_{\perp} < n < n_{\parallel}$ and an angle ϵ of inclination of the cell to the Z axis that was small, $\epsilon \leq 5$ to 7° . Here the values of n_{\parallel} and n_{\perp} correspond to the wavelength of the exciting beam. Under such experimental conditions, the fraction of the molecules that take part in the scattering is significantly increased, and the effect of multiple scattering, which leads to a strong dependence of the values of

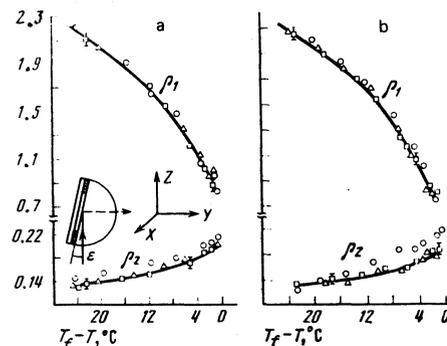


FIG. 2. Temperature variation of the degrees of depolarization ρ_1 and ρ_2 of crystals EO6T (a) and EO8T (b), at various specimen thicknesses d : ○, $60 \mu\text{m}$; △, $35 \mu\text{m}$; □, $5 \mu\text{m}$. Figure 2a shows also a schematic diagram of the liquid-crystal cell mount and of its position with respect to the coordinate system (X , Y , Z) of the apparatus. In case b, the first three divisions correspond to the values 0.16, 0.18, and 0.24; the rest are as in case a.

ρ_i on the specimen thickness,⁴ is eliminated. As experiment shows, the intensity of the lines is approximately the same for crystal thicknesses from 60 to 5 μm . The scattering wavelength is $\lambda = 0.736 \approx 1 \mu\text{m}$.

The method described here makes it possible to develop RS spectroscopy on thin specimens, $d = 5 \mu\text{m} \approx \lambda$, with low-power lasers and with good experimental accuracy. The RS spectrum was excited by a laser with generation wavelength $\lambda_0 = 632.8 \text{ nm}$ and power 30 mW. The radiation scattered from the active part of the crystal within a solid angle $\Omega = 0.2$ steradians was collected. The method of exciting and recording the spectrum was similar to that described earlier.²² We analyzed the intensity of the RS spectrum at the nondipolar valence oscillation ($\nu = 2220 \text{ cm}^{-1}$) of the $C \equiv C$ bond, which coincides with the long molecular axis 3. The RS tensor for this oscillation in the characteristic coordinate system has the form

$$a_{ij} = a\delta_{ij} + (b-a)\delta_{i3}\delta_{j3},$$

where δ_{ij} is the Kronecker symbol. From the degree of depolarization ρ of the chosen spectral line of the isotropic phase, by the formula

$$\rho = (1-R)^2 / (8R^2 + 4R + 3)$$

we found $R = a/b = 0.045 \pm 0.007$ for all three tolanes. The experimental values of ρ_i in the nematic phase of crystals $\dot{E}O6T$ and $\dot{E}O8T$, for various specimen thicknesses, are shown in Fig. 2.

The degrees of depolarization for MOAT were measured by us earlier.²² As is seen from the figure, the ρ_i are practically independent of specimen thickness; that is, the effect of multiple scattering has been eliminated. The very slight variation of ρ_2 with thickness at $d = 60 \mu\text{m}$ is explained by the fact that the measurement of ρ_2 is made with $n < n_{\parallel}$, which does not satisfy the condition for total internal reflection of the exciting beam. The degrees of depolarization ρ_i depend on the mean values $\langle s^2 \rangle = \langle \sin^2 \theta \rangle$ and $\langle s^4 \rangle = \langle \sin^4 \theta \rangle$. With allowance for the effects of reflection and refraction of the scattered radiation at the LC-glass boundary, and also for the anisotropy of the local light field in the LC, we have

$$\rho_1 = \frac{f_{\parallel}^2(n_{\perp} + n)^2[A\langle s^4 \rangle + B\langle s^2 \rangle]}{f_{\perp}^2(n_{\parallel} + n)^2[C\langle s^4 \rangle + D\langle s^2 \rangle + E]} \quad (11)$$

$$\rho_2 = \frac{f_{\perp}^2(n_{\parallel} + n)^2[\langle s^2 \rangle - \langle s^4 \rangle]}{f_{\parallel}^2(n_{\perp} + n)^2[2\langle s^4 \rangle - F\langle s^2 \rangle + G]} \quad (12)$$

In (11) and (12), the coefficients A , B , C , D , E , F , and G depend on the geometry of the experiment and on the value of R and are given in Ref. 22. The refractive indices n_{\parallel} and n_{\perp} , here and in formula (10), correspond to the wavelength of the scattered light. From the experimental values of ρ_i one can determine the values of $\langle s^2 \rangle$ and $\langle s^4 \rangle$ and the coefficients $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the series expansion (1) of the function $F(\theta)$: $\langle P_2 \rangle = 1 - \frac{3}{2}\langle s^2 \rangle$, $\langle P_4 \rangle = \frac{35}{8}\langle s^4 \rangle - 5\langle s^2 \rangle + 1$. The temperature behavior of the quantities $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for the tolanes investigated here is shown in Fig. 3, in the isotropic and anisotropic local-field approximation.

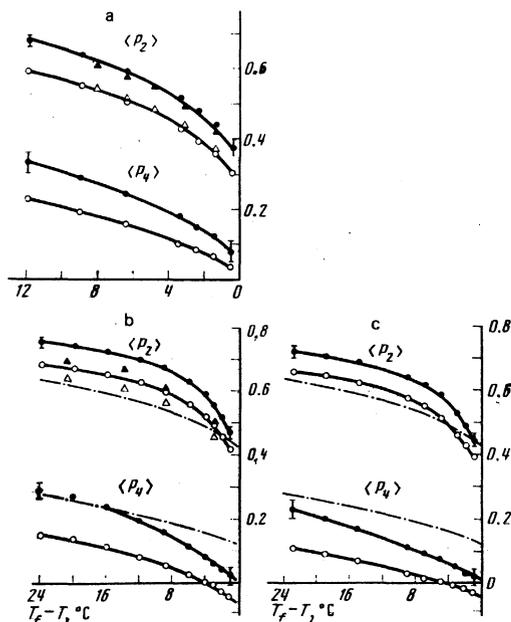


FIG. 3. Temperature variation of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ in the liquid crystals MOAT (a), EO6T (b), and EO8T (c), according to the results of various methods: \circ and \bullet , RS spectroscopy; \triangle and \blacktriangle , optical probing. The symbols \circ and \triangle correspond to the approximation of an isotropic local-field tensor f , \bullet and \blacktriangle to allowance for the anisotropy of the tensor f . The dash-dot curves in Figs. 3b and c correspond to a calculation of the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ by the Maier-Saupe theory.⁸

3. DISCUSSION

Comparison of the data on RS in Fig. 3 shows agreement, within the limits of experimental accuracy, of the values of $\langle P_2 \rangle$ for the three crystals. At the same time, the values of $\langle P_4 \rangle$ decrease sharply as we go from the more rigid molecule of MOAT to the molecules of $\dot{E}O6T$ and $\dot{E}O8T$, especially in the pretransition range of temperature. Thus the value of $\langle P_4 \rangle$ is very sensitive to the conformational properties of the molecules in the mesophase. Without allowance for the anisotropy of the local field, the values of $\langle P_4 \rangle$ for $\dot{E}O6T$ and $\dot{E}O8T$ in the pretransition range become negative. A quantitatively and qualitatively similar variation of $\langle P_4 \rangle$ was observed in PCB,¹² where the approximation of an isotropic local field was used. We emphasize that the results presented here show the effect of anisotropy of the local field on $\langle P_4 \rangle$ in a pure form, since they relate to the orientational properties of the rigid nucleus of the molecule. The experiments of Ref. 4 were performed on $C \equiv N$ end groups, whose mobility and orientation with respect to the long molecular axis are not known with certainty. Furthermore, the strongly polar oscillation of the $C \equiv N$ bond is very sensitive to intermolecular interactions,²³ and this may lead to a difference in the orientational statistics of the end group from that of the rigid nucleus of the molecule in the mesophase. Therefore the comparison made in a number of papers^{4,9} between the experimental results⁴ and the predictions of mean-field theory is not entirely correct.

As is evident from Fig. 3a, in the NLC MOAT the values of $\langle P_2 \rangle$ for the dye impurity coincide with those for the crystal matrix. The increase of the length and

mobility of the end groups in the EO6T molecule leads to a lowering of the value of $\langle P_2 \rangle$ of the impurity. Hence it is clear that the method of optical probing can give correct information about the structural order of the crystal matrix when the impurity molecule has dimensions and shape close to those of the molecules of the liquid-crystal matrix.

Also shown in Figs. 3b and 3c are the temperature variations of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ predicted by the Maier-Saupe theory.⁸ In this theory, the primary role in the establishment of orientational order of the mesophase is assigned to anisotropic dispersion forces of attraction with the potential (7). The theory uses the mean-field approximation, in which short-range correlations in the orientations of the particles are neglected. The Maier-Saupe theory predicts a universal dependence of the parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ on T/T_f for all NLC. As is seen from Fig. 3, the absolute values of $\langle P_2 \rangle$ far from the phase transition are higher in experiment than in theory. This is apparently due to neglect of the forces of intermolecular repulsion in the establishment of orientational order. In the pretransition range, the experimental values of $\langle P_2 \rangle$ are satisfactorily described by the theory. But the value of $\langle P_4 \rangle$ agrees better with theory in the low-temperature range near the phase transition; this may be due to neglect, in the Maier-Saupe theory, of the conformational properties of the molecules and of their variation in the mesophase. As another test of the correctness of the theory, we may compare the predicted relation between $\langle P_4 \rangle$ and $\langle P_2 \rangle$ with experiment. In order to bring out the most important differences between the theories of the liquid-crystal state that exist at present, we have selected for comparison with experiment the theories of Maier and Saupe, of Luckhurst and Yeates,⁹ and of Faber.¹⁰

In the Luckhurst-Yeates theory, it is assumed that the mesophase consists of cylindrically symmetrical molecules, between which there are interaction forces of purely repulsive nature. The repulsive pseudopotential is chosen in the form

$$\begin{aligned} U(\theta) &= 0, & \theta < \theta_0, \\ U(\theta) &= \infty, & \theta > \theta_0. \end{aligned} \quad (13)$$

From the expressions (2), (6), and (13) one can derive

$$\begin{aligned} \langle P_2 \rangle &= \cos \theta_0 (\cos \theta_0 + 1) / 2, \\ \langle P_4 \rangle &= \cos \theta_0 (\cos \theta_0 + 1) (7 \cos^2 \theta_0 - 3) / 8. \end{aligned} \quad (14)$$

Because there are no obvious physical considerations to determine the choice of the angle θ_0 in (13) and its relation to thermal molecular properties, it is impossible to calculate absolute values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for the tolanes studied. But from (14) one can plot the variation of $\langle P_4 \rangle$ with $\langle P_2 \rangle$. This variation is shown in Fig. 4, together with the variation given by the Maier-Saupe theory. We note that the Luckhurst-Yeates theory predicts negative values of $\langle P_4 \rangle$ for values of $\langle P_2 \rangle$ less than 0.54. In Faber's continuum theory,¹⁰ the reason for incompleteness of the orientational order is assumed to be the existence of normal elastic orientational waves in the liquid-crystal continuum; their amplitude depends on the temperature and on the elastic constants of the medium.

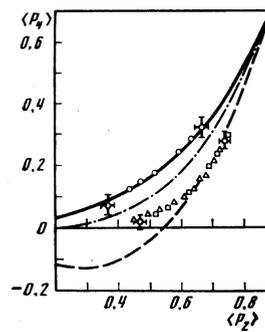


FIG. 4. Relation between the order parameters $\langle P_4 \rangle$ and $\langle P_2 \rangle$ for the nematic phase of the crystals MOAT (\circ), EO6T (\square), and EO8T (\triangle), according to the results of RS spectroscopy with allowance for the anisotropy of the local-field tensor. The solid curve corresponds to the theory of Maier and Saupe,⁸ the dashed curve to the theory of Luckhurst and Yeates,⁹ the dash-dot curve to the theory of Faber.¹⁰

The theory gives an expression for the coefficients of the series (1) in the form

$$\ln \left(\frac{1}{\langle P_l \rangle} \right) = \frac{1}{4} l(l+1) \frac{kT}{\pi^2 K} \left(\frac{6\pi^2 N}{V} \right)^{1/2} \quad (15)$$

where K is a reduced elastic constant of the NLC, N is the number of molecules in the specimen, and V is the volume of the specimen. From (15) we get the relation between $\langle P_2 \rangle$ and $\langle P_4 \rangle$ predicted by Faber's theory:

$$\ln \langle P_4 \rangle = 10/3 \ln \langle P_2 \rangle. \quad (16)$$

The relation calculated from (16) is shown in Fig. 4. It follows from (15) that in the continuum theory, negative values of $\langle P_4 \rangle$ are impossible.

As is seen from Fig. 4, the greatest difference between the predicted values of $\langle P_4 \rangle$ at a given $\langle P_2 \rangle$ occurs near the phase-transition point; that is, in the range of values $\langle P_2 \rangle = 0.4$ to 0.5 . These differences decrease in the high-order region. The Maier-Saupe theory describes the $\langle P_4 \rangle$ vs $\langle P_2 \rangle$ relation well for the stiffer and shorter molecules of MOAT. The Faber theory also gives a relation close to the experimental one. Increase of the length of the semiflexible tails, as well as thermal elastic orientational oscillations of the molecule, is an additional mechanism for the lowering of $\langle P_4 \rangle$ that is not taken into account in the continuum theory. For the longer molecules of EO6T and EO8T, the experimental $\langle P_4 \rangle$ vs $\langle P_2 \rangle$ relation is well described by the Luckhurst-Yeates theory in the region of high orientational order.

The important role of the forces of intermolecular repulsion in the region of high orientational order of the mesophase is also indicated by the results of molecular-dynamic computer experiments.²⁴ With approach to the phase-transition point, the experimental $\langle P_4 \rangle$ vs $\langle P_2 \rangle$ relation deviates from that predicted by the repulsion theory of Ref. 9. Therefore in the pretransition range, the role of repulsive forces becomes less important and that of intermolecular attractive forces more important. This is corroborated also by the agreement of the experimental values of $\langle P_2 \rangle$ and the values predicted by the Maier-Saupe attraction theory in the pretransition range. Here one can trace an analogy with the lattice dynamics of a molecular crystal. It is known²⁵ that the frequencies of orientational oscillation of the

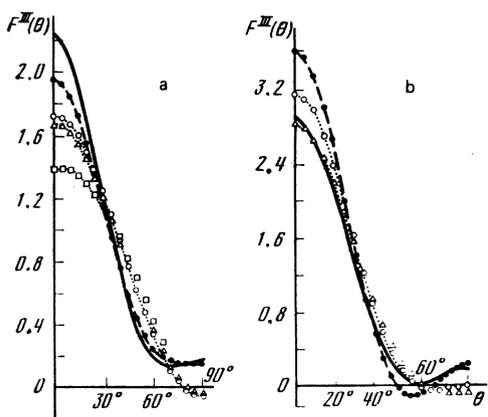


FIG. 5. Single-particle molecular orientational distribution function $F^{\text{III}}(\theta)$ of the nematic phase of crystals MOAT (\bullet), EO6T (\circ), and EO8T (Δ), for $\Delta T = T_f - T = 1^\circ \text{C}$ (a) and 12°C (b). The symbol (\square) in Fig. 5a corresponds to crystal EO6T in the approximation of an isotropic tensor f . Solid curve, calculation by the Maier-Saupe theory.⁸

molecules are primarily determined by the forces of intermolecular repulsion, while the sublimation energy of the crystal depends on the forces of intermolecular attraction. Obviously the relation between the forces of repulsion and of attraction in the intermolecular interaction depends on the structure of the electronic shell and on the shape and conformation of the molecules, and this must be taken into account in comparison of theory with experiment on other NLC.

The orientation-statistical properties of a NLC are described by the distribution function $F(\theta)$. From formula (1) and the experimental results shown in Fig. 3, F^{III} as a function of θ was calculated for various temperatures of the mesophase. The curves are shown in Fig. 5. A check showed that the normalization (4) of the experimental function $F^{\text{III}}(\theta)$ is satisfied with an accuracy no worse than 0.003. The function $F^{\text{III}}(\theta)$ according to the Maier-Saupe theory is also shown in the figures.

It is near the transition point that the conformational characteristics of the molecule are most clearly manifested in the determination of the distribution function. As is seen from Fig. 5a, the lengthening of the semi-flexible tails of the molecule leads to smearing out and lowering of the maximum of the distribution function. In the approximation of an isotropic local field, the maximum of $F^{\text{III}}(\theta)$ is still further lowered and is shifted from $\theta = 0^\circ$ to the region $\theta^* = 5$ to 10° . This result has been interpreted^{4,26} as a manifestation of additional disordering forces of unknown nature, which tend to align the molecules at an angle θ^* to the director near the phase-transition point. In the materials considered here, the shift of the maximum of $F^{\text{III}}(\theta)$ is removed by allowance for the anisotropy of the local light field in the processing of the experiment. In the pretransition range of temperatures, the theoretical function $F^{\text{III}}(\theta)$ differs substantially from experiment, especially for the materials EO6T and EO8T.

At $\Delta T = 12^\circ \text{C}$ the theoretical function $F^{\text{III}}(\theta)$ already agrees better with the experimental, and at $\Delta T = 24^\circ \text{C}$ complete agreement of theory and experiment is ob-

tained.¹⁸ At the same time, it is in this temperature range that the difference between the theoretical and experimental values of $\langle P_2 \rangle$ is greatest. Comparison of graphs a and b in Fig. 5 shows the important role of the quantity $\langle P_4 \rangle$ in the determination of the distribution function $F^{\text{III}}(\theta)$ of a NLC both far from the phase transition to isotropic liquid, and also in the pretransition region. The negative values of $F^{\text{III}}(\theta)$ at large values of the angle θ are due to neglect of later terms of the series (1). As is seen from comparison of Figs. 5a and 5b, allowance for these terms is more important far from the phase transition, and also for the MOAT crystal with more rigid molecules.

The experimental material presented above shows the necessity for developing the theory of the nematic mesophase with allowance for the forces of intermolecular attraction and repulsion, and also for the conformational properties of the molecules.

In conclusion, the authors consider it their pleasant duty to thank V. L. Pokrovskii and E. I. Kats for discussion of the research. As has been remarked by them, these experimental results may be useful for discussion of the energy characteristics of the mesophase. In this case it is advantageous to use an expansion of the logarithm of the distribution function as a series of Legendre polynomials.

- ¹P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford, 1974 (Russ. transl., Mir, 1977).
- ²B. K. Vainshtein and I. G. Chistyakov, *Problemy sovremennoy kristallografii* (Problems of Modern Crystallography), Nauka, 1975, pp. 12-26.
- ³I. Chistyakov, in: *Advances in Liquid Crystals*, Vol. 1, Academic Press, N. Y., 1975, p. 143.
- ⁴S. Jen, N. A. Clark, and P. S. Pershan, *J. Chem. Phys.* **66**, 4635 (1977).
- ⁵J. W. Emsley, J. C. Lindon, and G. R. Luckhurst, *Mol. Phys.* **30**, 1913, (1975).
- ⁶I. P. Il'chishin, E. A. Tikhonov, M. T. Shpak, and A. I. Dorozhkin, *Pis'ma Zh. Eksp. Teor. Fiz.* **24**, 336 (1976) [*JETP Lett.* **24**, 303 (1976)].
- ⁷P. S. Akopyan, G. A. Lyakov, Yu. P. Svirko, and Yu. S. Chilingaryan, *Summaries of reports of All-Union Scientific-Technical Conference on Interaction of Laser Radiation with Liquid Crystals*, Izd. ErGU, 1978, p. 27.
- ⁸W. Maier and A. Saupe, *Z. Naturforsch. A* **13**, 564 (1958); **14**, 882 (1959); **15**, 287 (1960).
- ⁹G. R. Luckhurst and R. N. Yeates, *Mol. Cryst. Liq. Cryst. (Letters)* **34**, 57 (1976).
- ¹⁰T. E. Faber, *Proc. R. Soc. A* **353**, 247 (1977).
- ¹¹R. L. Humphries, P. G. James, and G. R. Luckhurst, *J. Chem. Soc. Faraday Trans. II* **68**, 1031 (1972).
- ¹²K. Miyano, *Phys. Lett.* **A63**, 37 (1977).
- ¹³G. R. Luckhurst and R. Poupko, *Chem. Phys. Lett.* **29**, 191 (1974).
- ¹⁴M. Kohli, K. Otnes, R. Pynn, and T. Riste, *Z. Phys.* **B24**, 147 (1976).
- ¹⁵R. Sirutkaitis, L. Mazhelis, and A. Vaitkyavichyus, *Data of IV All-Union Conference on Liquid Crystals*, IvGU, Ivanovo, 1977, p. 104.
- ¹⁶V. F. Shabanov, E. M. Aver'yanov, P. V. Adomenas, and V. P. Spiridonov, *Preprint Institute of Physics, Siberian Branch, Academy of Sciences, USSR, No. 79F, Krasnoyarsk*, 1978.

- ¹⁷L. M. Blinov, V. A. Kizel', V. G. Rumyantsev, and V. V. Titov, *Kristallografiya* **20**, 1245 (1975) [*Sov. Phys. Crystallogr.* **20**, 750 (1975)].
- ¹⁸E. M. Aver'yanov, A. Vait'kyavichyus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin, and V. F. Shabanov, Preprint Institute of Physics, Siberian Branch, Academy of Sciences, USSR, No. 88F, Krasnoyarsk, 1978.
- ¹⁹G. Labrunie and M. Bresse, *C. R. Acad. Sci. B* **276**, 647 (1973).
- ²⁰E. M. Aver'yanov and V. F. Shabanov, *Kristallografiya* **23**, 320 (1978) [*Sov. Phys. Crystallogr.* **23**, 177 (1978)].
- ²¹E. M. Aver'yanov, K. S. Aleksandrov, and V. F. Shabanov, *Dokl. Acad. Nauk SSSR* **242**, 84 (1978) [*Sov. Phys. Doklady* **23**, 665 (1978)].
- ²²V. F. Shabanov, E. M. Aver'yanov, P. V. Adomenas, and V. P. Spiridonov, *Zh. Eksp. Teor. Fiz.* **75**, 1926 (1978) [*Sov. Phys. JETP* **48**, 970 (1978)].
- ²³E. Sackmann, P. Krebs, H. U. Rega, J. Voss, and H. Mõhwald, *Mol. Cryst. Liq. Cryst.* **24**, 283 (1973).
- ²⁴A. L. Tsykalo and A. D. Bagmet, *Fiz. Tverd. Tela* **20**, 1326 (1978) [*Sov. Phys. Solid State* **20**, 762 (1978)].
- ²⁵V. G. Podoprigora and V. F. Shabanov, *Kristallografiya* **20**, 1109 (1975) [*Sov. Phys. Crystallogr.* **20**, 677 (1975)].
- ²⁶F. Volino, A. J. Dianoux, and H. Hervet, *Mol. Cryst. Liq. Cryst.* **38**, 125 (1977).

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High-efficiency electronic accomodation in the interaction of atomic hydrogen with single-crystal germanium

A. E. Kabanskii and V. V. Styrov

Tomsk Institute of Automatic Control Systems and Radio Electronics
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We describe an original experimental procedure for determining the probability of electronic excitation of a crystal η_e , with formation of dissociated electron-hole pairs, and of the coefficient β_e of electronic accomodation in the acts of chemical excitation of atomic hydrogen with the (111) surface of single-crystal germanium. The results $\eta_e = 0.6 \pm 0.1$ and $\beta_e > 0.10 \pm 0.02$ attest to effective conversion of chemical energy into energy of electronic excitation of the crystal. The surface quasimolecule approximation is used to construct a theoretical model that describes the production and transport of electronic excitation in a crystal in the elementary chemical act. It is concluded that the electron accomodation must be taken into account in addition to the phonon accomodation in processes of chemical energy relaxation on a surface.

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1. INTRODUCTION

Interest has increased lately in the problem of energy exchange on the interface between a gas and a solid, in connection with the study of the possible use of lasers for selective activation of adsorption and catalytic processes¹⁻³ and adsorption isotope separation.^{4,5} This is a vital problem from many points of view, inasmuch as energy dissipation processes play an important role in many heterogeneous processes (plasma etching of semiconductors, crystal growth, formation of molecular coatings and layers, two-dimensional phase transitions, and others).

Energy exchange between solids and gas molecules (atoms) that have in the general case translational, rotational, and vibrational energies, are usually treated in terms of Knudsen thermal accomodation coefficients (see Ref. 6). Wood, Mills, and Wise⁷ introduced the concept of the accomodation coefficient for a chemically reacting gas consisting of free atoms (radicals). Since the main contribution to energy exchange is made in this case by chemical energy, compared with which the energy of thermal motion can be neglected, we take the accomodation coefficient β to mean that part of the released chemical energy which is transferred in the mean to the solid in the elementary reaction act: $\beta = Q/q$ (Q is the energy transferred to the body and q is the

thermal effect of the reaction event). It is assumed here that the accomodating energy is received by the solid in the form of vibrational energy, and just as in the case of Knudsen accomodation, it leads in final analysis only to thermal effects.

It has been recognized of late, however, that the accomodation of chemical energy in heterogeneous reactions can lead to substantial disruption of the equilibrium in the electronic system of the crystal, and is accompanied by crystal luminescence, by electron emission,⁸ and by other nonequilibrium effects⁹⁻¹¹ that are the surface analogs of the corresponding effects in optical excitation. Thus, besides the vibrational mechanism one can speak of an electronic accomodation mechanism, i.e.,

$$\beta = \beta_e + \beta_v = \eta_e E_e / q + \eta_v E_v / q. \quad (1)$$

Here η_e and η_v are the probabilities of the electronic (e) and vibrational (v) excitations of the surface of the solid in the course of the reaction ($\eta_e + \eta_v = 1$), E_e is the energy of the excited electronic state, E_v is the energy transferred to the vibrational degrees of freedom ($E_e + E_v = Q$), β_e and β_v are the partial accomodation coefficients in the electronic and vibrational mechanisms.

If we imagine a gas + solid system in which $\eta_e \approx 1 > \eta_v$ and $E_e \gg E_v$, such that the electronic excitations relax