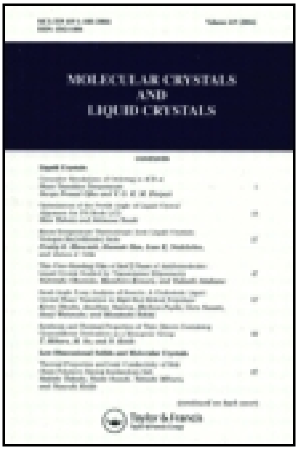

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Symmetry of Anisotropic Properties over a Temperature Range of LC-Phase

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Symmetry of Anisotropic Properties over a Temperature Range of LC-Phase

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The spatial model describing the changes of LC's anisoptropic characteristics in thermal fields has been considered. The model is based on symmetry of thermal vibrational motions of molecules relative to layer director. The method of approximate calculation of complete set of anisotropic physical quantities, which characterise liquid crystals properties within the mesophase interval, is proposed. The method of order parameter calculation is offered also.

Keywords: ordering degree; refraction index; nematic; smectic; phase trasition

INTRODUCTION

The present work is a natural continuation and generalization of the results described in ref.[1-4]. The majority of physical quantities connected with various characteristics of liquid crystals are described with the help of second rank tensors whose characteristic surface is generally represented by ellipsoid with three different principal axes. The thermal vibrations of molecules cause[1-4] a change of ellipsoid form, but there are some elements which remaun unchanged.

Theoretical Estimates

The various models are used in order to describe a degree of ordering in liquid crystals on microscopical level. Usually uniaxial ordering that is a characteristic of nematic phase is defined by the well-known expression that was proposed for the first time by V. N. Zvetkoff[5]:

$$S = 0.5(3\cos^2\Theta - 1) \qquad (1),$$

where Θ is the average angle between long molecular axes and layer director. In more general case the more comlicated models are employed. Particularly, the authors of [6,7] have discussed in details and employed in theirs works modified variant of Straley's model. That model is correct for not only uniaxial ordering but for biaxial one also and uses four order parameters (S,U,T and V).

In this model there are three Euiler angles transforming lab coordinate system which determines the orientation of layer director to the coordinate system where the molecular polarizability tensor has a diagonal form.

To connect micro- and macroparameters which characterise liquid crystals properties, such as molecular polarizabilities or effective molar refractions on the one hand and main refractive indices on the other hand, the models of Lorenz-Lorentz[8], Vuks[9], Neugebauer[10] are rather widely used. The works of Maier and Saupe[11], De Gennes[12] and Averianov[13] are devoted to the same problem.

Despite of various approaches to the problem the results of calculations that were made on the basis of cited works and presented in numerous articles concerning the properties of different synthesized LC are comparable in a first approximation.

In this work it is proposed to use the experimentally established fact, that average value of refractive index calculated with help of various models is always approximately equal to extraordinary wave refractive index, measured in the same direction relative to layer director[1-4]. This direction may be determined from expression (1) for order parameter, where S is equal to 0 if $\Theta_0 = \arccos\sqrt{1/3} = 54.7^0$.

If we use the ellipse equation (2) for characteristic surface of refractive index and substitute Θ_0 for Θ then we obtain independent equation which expresses $\mathbf{n}_{is}$ as function of main refractive indices more exactly

$$n_e(\Theta) = \frac{n_e n_o}{\sqrt{n_e^2 \sin^2\Theta + n_0^2 \cos^2\Theta}} \qquad (2)$$

$$n_{is} = \frac{n_e n_o \sqrt{3}}{\sqrt{2n_e^2 + n_o^2}} \qquad (3)$$

where $\sin\Theta = \sqrt{2/3}$, $\cos\Theta = \sqrt{1/3}$.

The obtained expression together with its known analogues Lorenz-Lorentz $(\bar{n}_{is} = \frac{n_e + 2n_o}{3})$ (4)

and Vuks $(\overline{n_{is}^2} = \frac{n_e^2 + 2n_o^2}{3})$ (5)

gives the relation between three quantities n_{is}, n_e, n_o.

In literature there are numerous data on measuring temperature dependencies of n_o and n_e for different materials. Comparison of the relations $n_e = f(n_o, n_{is})$ using three above mentioned expressions is presented in [4] for MBBA. The expression (3) gives more close agreement with experiment.

The use of selected direction Θ_o gives possibility of easy-to-grasp geometrical interpretation of construction of all ellipses as a selections of characteristic surfaces of second rank tensors, that describe various anisoptropic characteristics of liquid crystals in thermal fields. In order to do this it is sufficient to take the circumference of radius n_{is} near the clearing point, draw two diameters at angle Θ_o with respect to randomly selected axis x, that must be passed through centre. All of ellipses having the main axes equal to experimental values n_o and n_e at different temperatures pass through the crossing points of those diameters with circle. It is shown in Fig.1 for MBBA, where for clarity both the experimental and calculated data are presented.

It will be of interest to run down the changes of refractive indices of mesogens at transition of them from solid phase into nematic one. In [14] the refractive indexes for the set of nematics at different temperatures are presented, among them the data of measurement of three refractive indices in solid phase are presented too.

When the temperature is raised in solid phase the vibrations of molecules around long molecular axis are amplified from the first. At this time the crystal has still some biaxiality. Then vibrational motion proceeds to rotational one. This is accompanied by phase transition into uniaxial nematic phase (sometimes through smectic phase).

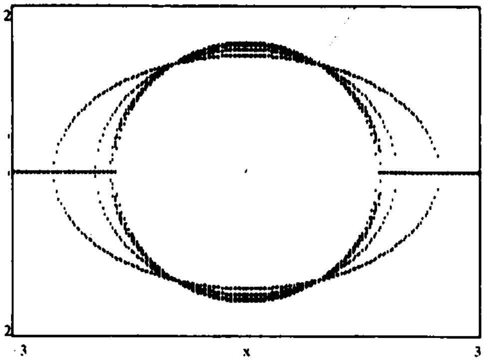

FIGURE 1.

Assuming the described above pattern in vibrations of molecules around long molecular axis let us try to run down the changes of refractive indices from solid phase to liquid one. The refractive indices of 4(4'-etoxyphenylazo-phenylundecylenate) may serve as initial data. Those data are presented in [14] and they have next values in solid phase: $N_1=1.891$; $N_2=1.514$; $N_3=1.465$. Refractive indices of nematic phase are presented in Table 1.

TABLE 1.

ΔT	n_e	n_o	n_{is}
1	1.562	1.562	1.562
-10	1.699	1.502	1.560
-24	1.738	1.496	1.565
-35	1.758	1.495	1.569
-40	1.767	1.495	1.571

Here values of n_{is} are calculated in accordance with expression (3). By analogy with (3) for the vibrations around long axis

$$N_{23}=\frac{N_1N_3\sqrt{3}}{\sqrt{2N_2^2+N_1^2}}, \qquad N_{23}=1.481 \tag{6}$$

Supposing that at the transition into nematic phase N_{23} becomes n_o and N_1 becomes n_e, in accordance with (3) we have

$$n_{is} = \frac{N_1 N_{23}\sqrt{3}}{\sqrt{N_{23}^2 + 2N_1^2}} \qquad (7)$$

Substituting the value of N_{23} from (6) it is possible to connect n_{is} with three main refractive indexes:

$$n_{is} = \frac{3}{\sqrt{\frac{3}{N_1^2} + \frac{2}{N_2^2} + \frac{4}{N_3^2}}}, \qquad n_{is}=1.581 \qquad (8)$$

A discrepancy between the calculated value and experimentally measured one for isotropic phase may be minimised by taking into account long molecular axes vibrations.

Let's evaluate how the three refractive indices are changing as we approach the nematic phase. We take into account the weak vibrations of the long molecular axis around short ones. In accordance with above-mentioned N_{13} is equal

$$N_{13} = \frac{N_1 N_3\sqrt{3}}{\sqrt{2N_1^2 + N_3^2}}, \qquad N_{13} = 1.574 \qquad (9)$$

Let there N_{3i} will be an independent variable and we will change it with step of 10^{-3} (here i = 1,2,3... 16). Then from expressions (6) and (9) we will obtain : (see Table 2)

$$N_{2i} = N_{3i} = \frac{N_{23}}{\sqrt{3N_{3i}^2 - 2N_{23}^2}}; \qquad N_{1i} = N_{3i} = \frac{N_{13}}{\sqrt{3N_{3i}^2 - 2N_{13}^2}}.$$

Taking from Table 2 the last values of refractive indices (i=16) we obtain $N_{2i} = N_{3i} = n_o = 1.481$, $N_{1i} = n_e = 1.827$.

Then for isotropic phase in agreement with (2) : n_{is} = 1.574, that is rather close to value of n_{is} calculated from experimental data for nematic phase (see Table 1). The error is in the range 0,2-0,3 %.

It will be of interest to run down how the tilt of circle sections of three-axis ellipsoid in relation to small axis will change as we approach the transition point of solid phase into nematic one.

$$tg\psi = \sqrt{\frac{N_3^2 - N_2^2}{N_2^2 - N_1^2}} \qquad (10)$$

Calculated values of ψ_i are presented in Table 2.

TABLE 2.

N_{3i}	N_{2i}	N_{1i}	ψ^0	n_{ei}	$S(n_{ei})$
1.465	1.514	1.891	23.534	1.891	1
1.466	1.512	1.887	22.845	1.871	0.949
1.467	1.510	1.882	22.127	1.851	0.896
1.468	1.507	1.878	21.375	1.831	0.841
1.469	1.505	1.874	20.586	1.811	0.785
1.470	1.503	1.870	19.756	1.791	0.727
1.471	1.501	1.866	18.878	1.771	0.667
1.472	1.499	1.862	17.945	1.751	0.604
1.473	1.497	1.858	16.649	1.731	0.540
1.474	1.495	1.854	15.876	1.711	0.473
1.475	1.493	1.850	14.710	1.691	0.404
1.476	1.491	1.846	13.426	1.671	0.332
1.477	1.488	1.842	11.985	1.651	0.285
1.478	1.486	1.838	10.325	1.631	0.181
1.479	1.484	1.834	8.305	1.611	0.101
1.480	1.482	1.830	5.558	1.591	0.018
1.481	1.481	1.827	0.193	1.587	0

It must be noted that these expressions are not connected to the temperature. This problem is solved in different works by a various manner. So far the analytical expressions which connect an order parameter and refraction indices to a temperature have empirical nature. Constants in those expressions are adjusted for each material individually.

In our case for solid phase this question is more complicated since transition SC-NLC is the phase transition of the first order. This circumstance can markedly narrow the temperature interval in which refractive indices from Table 2 should be located. Unfortunately, as to the author knowledges, there are no experimental works in which the temperature dependencies of refractive indices of solid mesogens can be revealed.

One of the methods to relate order parameter S to the temperature is extrapolation of linear regions of curve SΔR as a function of logarithm ($\ln(\Delta T/T_{is})$) to 0° K, where $S=1$. This procedure gives the possibility to determine the maximum anisotropy. If to determine $n_e=N_e$ and $n_o=N_o$ at S=1 by extrapolation and to exclude Θ from expression (1), (2) and (3), it is possible to relate the order parameter to quantities n_e or n_o, which are experimentally measured at a given temperature of nematic phase

$$S(n_e) = 0.5\left(3\frac{\left(n_e^2 - N_o^2\right)N_e^2}{\left(N_e^2 - N_o^2\right)n_e^2} - 1\right) \tag{11}$$

If N_o and N_e are taken as main axes of initial ellipsoid in equations (2), the value of Θ can be considered equal to average angle of deviation of long molecular axes in expression (1). This conclusion is based on the fact that all values of $N_e(T)$ and $N_o(T)$ run the corresponding values of $n_e(\Theta)$ from (2) at increasing the temperature of the layer. At that, while changing from perfect order (S=1) to disorder (S=0) the value $n_e(\Theta)=n_e$ in equation (11) decreases from N_e to $n_i=n_e$ ($\Theta_o=54.7°$). At the same time $n_o(T)$ increases from N_o to n_i in line with the values of $n_e(\Theta)$ in the range from $\Theta=90°$ to $\Theta=54.7°$. These reasons give the possibility to express S as a function of n_o if to take in account relations between n_o to n_e in equation (3) (see [4] in more details).

The values of order parameter S which are calculated in accordance with expression (11) for quantities n_{ei} assuming N_e =1.891, N_o=1.481 are presented in Table 2.

CONCLUSIONS

Unconditionally the proposed model cannot be considered as universal one. One can bring out the experimental results that shows a discrepancy more than a fraction of the percent. Wide experimental verification is hindered since most of temperature dependencies of the physical quantities in literature are presented in graphical form but not in tabulated one. The attempt to use this model for biaxial phase instead of Straley model is warranted by its simplicity and by convenience to use it for the evaluations.

In addition one must take into account, that the contribution of order parameters (U,T and V) additional to S in Straley model do not exceed of a few percent in comparison with S. It can be explained at first by the reason that vibrations of molecules around long and short axes take place at different temperature intervals (by phase change sequence). At second, they differ in frequency by about three orders of magnitude, that decreases significantly their mutual influence.

It would be interesting to examine the presented model more thoroughly on polymerised liquid crystals and for Kerr-effect in isotropic phase as well as to do it for another tensor characteristics. This is supposed will be done in the future works.

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