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G. L. Nekrasov [a]

[a] Institute of Electronics, Belarus Academy of Sciences, Logoiski trakt, 22, 220090, Minsk

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THREE-DIMENSIONAL MODEL OF ANISOTROPIC PROPERTIES OF LIQUID CRYSTALS IN THERMAL FIELDS.

G.L. NEKRASOV
Institute of Electronics, Belarus Academy of Sciences
220090 Minsk, Logoiski trakt, 22

Abstract. A simple three-dimensional model is proposed which is based on characteristic surface the second rank tensor - three-axial ellipsoid. It is shown that due to symmetry of molecular oscillations in a liquid crystal (LC) it is possible to calculate its basic anisotropic characteristics by using oscillation magnitudes in isotropic state as a reference. It has been found that in ellipsoid sections there are directions, corresponding to an angle $\Theta_0 = \arccos\sqrt{1/3}$ relative to major semiaxes of ellipsoid sections, with respect to which thermal properties of anisotropic physical quantities remain invariant. It is shown that ordinary wave refractive index n_0 has different values for light beams propagating along and normal to the oriented nematic director.

INTRODUCTION

The present work is a natural continuation and generalization of the results described in refs. [1-3]

The majority of physical quantities connected with optical characteristics of crystals are described with the help of second rank tensors whose characteristic surface is generally represented by an ellipsoid with three different principal axes. For example, consider an ellipsoid of refractive indices in cartesian coordinates whose axes N_x, N_y and N_z are oriented along X,Y and Z directions.

Let $N_x > N_y > N_z$:

$$\frac{x^2}{N_x^2} + \frac{y^2}{N_y^2} + \frac{z^2}{N_z^2} = 1 \tag{1}$$

If all semimajor axes are different, we have either a solid crystal or smectic LC where three-dimensional long-range order is still retained. In case of slow uniform heating, increase in temperature will cause amplification of molecular oscillatory movements. In mesogenic crystals at first faster oscillations are amplified more intensity, i.e. those around long molecular axes. (This fact is indicated by mesophase changing order).

As it is known, molecular ordering in LC's can be described by the order parameter:

$$\rho = 0.5 \cdot (3 \cdot \overline{\cos^2 \Theta} - 1) \quad (2)$$

where Θ is the average angle of deviation of oscillating molecules from their main orientation direction (the director).

It follows from this expression that when the average angle Θ reaches the value $\Theta_0 = \arccos\sqrt{1/3} \approx 54{,}74^{\circ}$, the order parameter changes to zero. It is obvious that, physically, this corresponds to transition from oscillatory movement of molecules to their rotational movement; in any case, the situation becomes similar to such transition.

It has been shown in refs.[1-3] that if **E**-vector of a polarized light wave makes an angle Θ_0 with the director a number of physical quantities characterizing anisotropic properties of LC-material (such as extraordinary wave refractive index (n_e), absorption coefficient $k_{||}$, optical density $D_{||}$, and others) undergo no changes with changing layer temperature. Let us consider this situation in a greater detail.

THEORETICAL ESTIMATES

Since oscillations of molecules around long and lateral molecular axes differ in frequency by several orders of magnitude and are shifted in amplitude to different sections of mesophase temperature interval, we shall assign each of them a specific order parameter: S_1 - to lateral oscillations, and S_2 - to longitudinal oscillations. In case of longitudinal oscillations, we shall reckon the angle Θ from the y-axis. Here, it will be more pertinent to consider the main section of ellipsoid (1) passing through yoz-plane

$$\frac{y^2}{N_y^2} + \frac{z^2}{N_z^2} = 1 \quad (3)$$

In polar coordinates, we can write

$$n_y = \frac{N_y \cdot N_z}{\sqrt{N_y^2 \cdot \sin^2 \Theta + N_z^2 \cdot \cos^2 \Theta}}, \quad (4)$$

where n_y is the magnitude of the radius-vector of the ellipse, Θ is the angle measured from its long axis (N_y).

As noted above, the wave refractive index corresponding to Θ_0-direction will remain unchanged, while N_y and N_z will change with temperature, thus causing changing of the ellipse size. However, all ellipses associated with different temperatures will have common points corresponding to Θ_0 -direction up to their degeneration to a circle. In this case, the magnitude of radius-vector $R_2 = n_y(\Theta_0)$ shared by these points will be

$$R_2 = \frac{N_y \cdot N_z \cdot \sqrt{3}}{\sqrt{2 \cdot N_y^2 + N_z^2}} \quad (5)$$

and remain constant down to nematic phase transition where the crystal becomes optically uniaxial and the ellipsoid (1) becomes ellipsoid of revolution, and $N_y=N_z=N_o$ whereas $N_x=N_e$.

Further increase in temperature will result in amplification of lateral molecular oscillations, and here we should consider section of ellipsoid (1) in the xoy-plane:

$$\frac{x^2}{N_e^2} + \frac{y^2}{N_o^2} = 1 \quad (6)$$

Having analyzed numerous experimental literature data concerning measurements of temperature dependence of various anisotropic characteristics of nematics (including refractive indices), we have found that the above-described regularities are recurring, and intersection points of all ellipses will correspond to the magnitude of the radius-vector

$$R_1 = \frac{N_{ei} \cdot N_{oi} \cdot \sqrt{3}}{\sqrt{2 \cdot N_{ei}^2 + N_{oi}^2}} \quad (7)$$

where N_{ei} and N_{oi} are main refractive indices of nematic taken at different temperatures. T_i. R_1 corresponds to refractive index of isotropic state near phase transition.

EXPERIMENTAL RESULTS

Figure 1 illustrates intersection of basic ellipses for two sections of an ellipsoid with corresponding circles of radii R_1 and R_2.

Experimental data for solid-crystalline and nematic phases have been taken from ref. [4]

Based on the above arguments, a fairly simple graphic (or numerical) method can be employed to obtain a family of ellipses. Such method will make it possible to characterize main refractive indices of a liquid crystal in a wide temperature range. To do this it will be sufficient to have a circle of radius R_1 equal in value to the refractive index of mesogen in isotropic state near its phase transition, designate two coordinate axes, plot an angle $\Theta_0 = 54.74^\circ$ relative to one of them, and obtain points of intersection of a given direction with the circle. By using equation (7), pairs N_{ei} and N_{oi} matching in temperature can be obtained at any interval, and by using equation (6) we can have a variety of ellipses (see Fig. 2). In the case under consideration, the initial value $R_1=1.602$ for MBBA has been taken from ref.[5] together with experimental

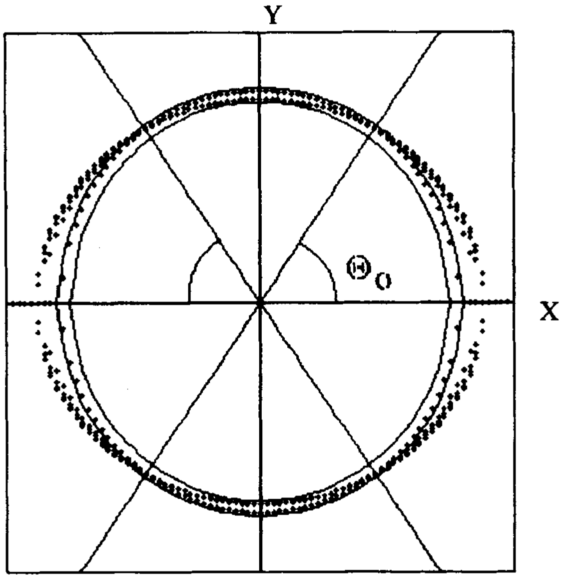

FIGURE 1 Principal sections of ellipsoid $N_xN_yN_z$ by XOY plane for various temperatures, and circles of radii R_1 and R_2 for $N_x = 1.465$, $N_y = 1.514$, $N_z = 1.891$.

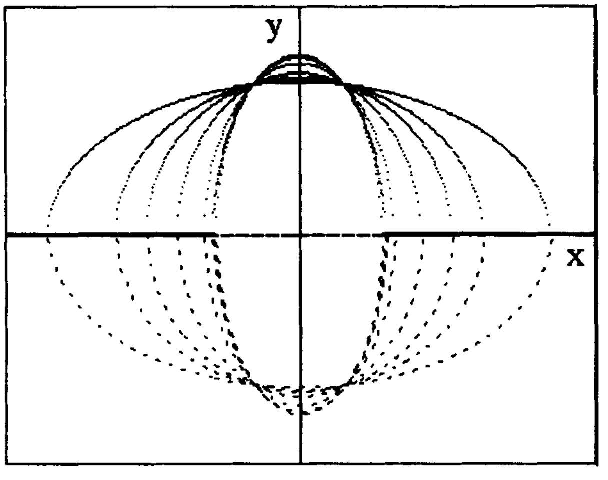

FIGURE 2 A family of ellipses with axes N_{oi}, N_{ei} calculated by using expressions (6) and (10) for MBBA.

results of the authors. Comparison of these results with calculated data is made in Table 1.

TABLE 1

T_i	23	20	17	14	11	8	6	4	2
N_{oi}	1.543	1.544	1.545	1.546	1.548	1.551	1.554	1.558	1.564
N_{ei}	1.754	1.749	1.742	1.735	1.727	1.717	1.71	1.701	1.687
R_{1i}	1.605	1.604	1.603	1.602	1.601	1.601	1.601	1.602	1.602
Θ_i	34.434	34.584	34.912	35.271	35.5	35.699	35.607	35.448	35.283

To calculate average refractive index value one may use well-known relationships from Lorentz-Lorenz model:

$$n_i = (1/3)\cdot(n_e + 2\cdot n_o) \tag{8}$$

or Vuks model:

$$n_i = \sqrt{(1/3)\cdot(n_e^2 + 2\cdot n_o^2)} \tag{9}$$

Values obtained by using these relationships are fairly close to those obtained by means of the proposed elliptical model. Fig. 3 shows dependences $N_{ei}(N_{oi})$ calculated by using these expressions (curve 2,3) and based on expression (7) (curve 1). Experimental points (MBBA [5]) are designated with x's.

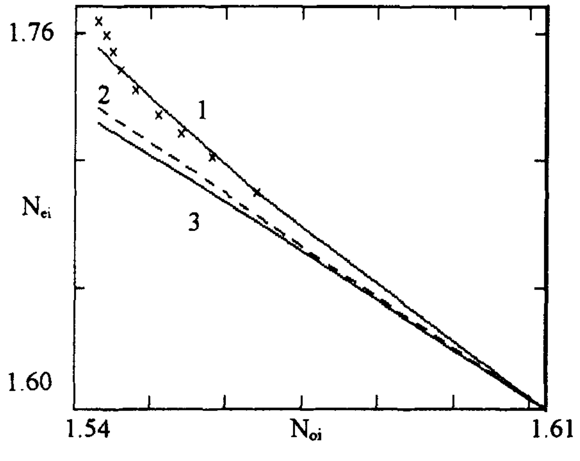

FIGURE 3. $N_{ei}(N_{oi})$ dependences calculated on the basis of different models

As seen from the figure, curve 1 is characterized by a good agreement between calculated and experimental values, where N_{ei} follows from (7)

$$N_{ei} = \frac{R_1 \cdot N_{oi}}{\sqrt{3 \cdot N_{oi}^2 - 2 \cdot R_1^2}} \qquad (10)$$

A thorough examination of Fig. 2 shows that the range of N_o values is limited by the interval from R_1 to the shortest ellipse axis for all the family, which cannot be less than $R_1\sin(\Theta_0)$, i.e. $R_1 \cdot \sqrt{2/3} < N_{oi} \leq R_1$.

In accordance with equation (10), for $N_{oi}^2 = 2/3 \cdot R_1^2$ Nei tends to infinity. Therefore, to calculate the whole family of ellipses or a full set of N_{ei} and N_{oi} values corresponding to nematic phase, we should confine ourselves to considering a linear portion of curve 1. It is worth noting that expressions (8) and (9) offer no restrictions.

Analysis of available experimental data based on the elliptical model suggests that since along the axis (or layer director) the refractive index of ordinary wave is equal to that of extraordinary wave (the two waves are indistinguishable in the given geometry), we, in fact, deal with temperature dependence of $N_e(0^o)$. As the oscillation amplitude is enhanced the average angle of molecular deviation from the director increases up to Θ_0, and the effective value of $N_e(0^o)$ is no longer equal to $N_e(0^o)$ becoming a function of that angle just because n_e depends on the light wave propagation angle. It is a well-established experimental fact that in this geometry n_e and n_o are indistinguishable. Hence, in this geometry N_{oi} is also a function of the average molecular oscillation angle. If as a starting or reference point we take ellipse of refractive indices constructed on the basis of N_o and N_e values at the moment of nematic formation from solid or smectic phase, we find that $N_e(0^o)$ passes through all $n_e(\Theta)$ values corresponding to Θ-angle ranging from 0^o to 35.26^o (counting from ellipse minor axis), whereas $N_e(90^o)$ passes through all $n_e(\Theta)$ values corresponding to Θ changing from 90^o to 35.26^0 (the same angle count direction).

Fig. 4 shows Θ-dependences of $N_e(0^o)$ and $N_e(90^o)$ in the indicated range of angles which are plotted to the same scale (the first range is slightly extended) to allow us to establish correlation between $N_{ei}(0^o)$ and $N_{ei}(90^o)$. Experimental points given for the same temperature values are designated with x's (MBBA[5]).

Taking into account different geometries of measuring $n_o(90^o)$ and $n_o(0^o)$, it is obvious that temperature dependences of these quantities, just as those of refractive index values measured along and normal to the optical axis, will be different. Experimental data taken from a number of papers concerned with $n_o(90^o)$ measurement exhibit a weaker temperature dependence, and the curve $n_o(0^o)$ is almost parallel to the temperature coordinate, changing its direction only in the immediate vicinity of phase transition (This data are absent in present work). This dependence differs slightly from that obtained on the basis of the proposed elliptical model because in the latter case $n_o(0^o) = n_e(0^o)$.

DISCUSSION

The regularities described in this paper pertain not only to refractive indices. They are also observed in analyzing experimental temperature dependences of dielectric permittivities at non-optical frequencies. The behaviour of optical density, molecular polarizability and other anisotropic characteristics also fits into this pattern. In this study, there is no relation to temperature. Empirical dependences available in literature are still linked to specific materials and, clearly, require a more generalized approach.

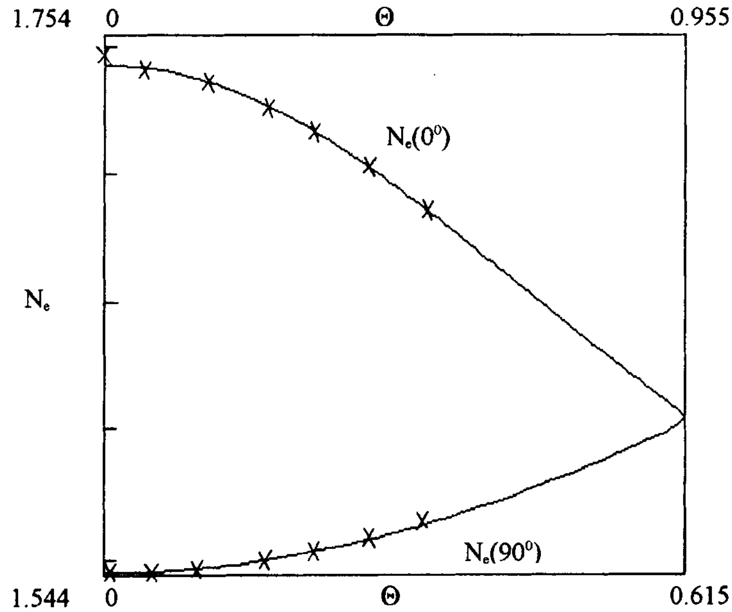

FIGURE 4. Θ-dependences of $N_e(0°)$ and $N_e(90°)$ obtained in equation (4)

From our viewpoint based on conclusions of this study, most interesting are the results presented in ref.[6], where three different refractive indices have been measured in nematic state and the authors assume that they deal with biaxial nematic.

Obviously, their interesting findings deserve further investigation and discussion, but they illustrate well our reasoning. Below (Fig. 5), we present a figure from that paper which shows temperature dependences of $n_o(T)$ measured for parallel and normal propagation directions of light beam with respect to substrate polishing direction.

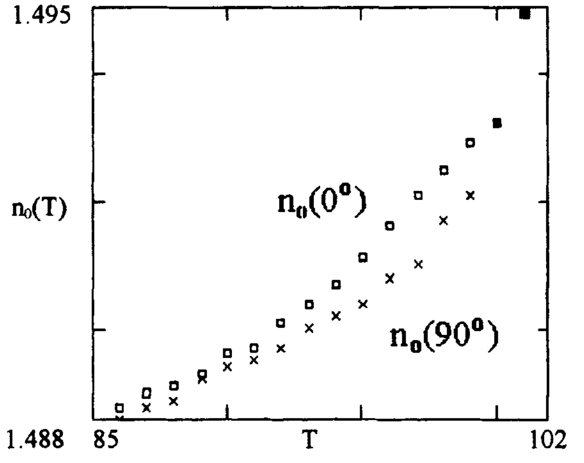

FIGURE 5. $n_o(0^o)$ and $n_o(90^o)$ values obtained in ref.[6]

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