

Local-Field Anisotropy in Cholesteric Liquid Crystals

E. M. Aver'yanov

*Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia*

e mail: aver@iph.krasn.ru

Received February 24, 2009

The first experimental values of the Lorentz tensor components L_j for the cholesteric and smectic A phases of derivatives of cholesterol have been obtained using the dispersion of the refractive indices in the visible range. The temperature dependence of the components L_j has been determined; it is invariant with respect to the cholesteric–smectic A phase transition. The effect of the isotropization of the Lorentz and local field tensors with decreasing anisotropy of the molecular polarizability has been revealed.

PACS numbers: 42.70.Df, 61.30.Cz, 64.70.Md, 78.20.-e

DOI: 10.1134/S0021364009070030

1. The helical structure of cholesteric liquid crystals is typical of self-organized ensembles of optically active anisotropic molecules [1]. This circumstance stimulates an active interest in the methods for investigating cholesteric liquid crystals that provide information on their short- and long-range order structures, as well as on the molecular properties (polarizability, electronic structure, and conformation), which determine the chemical and biological activity of the molecules. The optical properties of cholesteric liquid crystals, which are associated with the presence of a helical structure and its change under external actions, have been investigated in detail [2]. Optical and spectral investigations of the molecular properties of cholesteric liquid crystals are very scarce [3] because of the necessity of the inclusion of the local field effects and the absence of information on the components $f_j = 1 + L_j(\varepsilon_j - 1)$ of the local field tensor in the quasi-nematic layer of cholesteric liquid crystals for light waves polarized along ($j = \parallel$) and across ($j = \perp$) the director \mathbf{n} . Here, $\varepsilon_j = n_j^2$, n_j are the refractive indices of the quasi-nematic layer, and L_j are the Lorentz tensor components ($\text{Tr} L = 1$).

Since information on the parameters L_j and f_j for cholesteric liquid crystals is absent, model representations have been developed under arbitrary assumptions on the tensors L and f and molecular polarizability γ (see, e.g., [4, 5]). The degree of justification of these models is unclear and the use of these models led to nonphysical consequences from optical measurements [6].

In this work, a method free of model representations and a priori assumptions on unobservable molecular parameters is proposed for experimentally determining the components L_j for cholesteric liquid crystals. It is based on the use of the dispersion of the

refractive indices $n_j(\lambda)$ in the visible range. The relations of these refractive indices to the refractive indices $n_{j, \text{Ch}}(\lambda)$ of the planar texture of cholesteric liquid crystals measured on a refractometer with a high accuracy are known [7].

2. For the planar texture of a cholesteric liquid crystal with a helical axis (optical axis) specified by the unit vector \mathbf{q} , the local symmetry of the quasi-nematic layer with the director $\mathbf{n} \perp \mathbf{q}$ is characterized by point symmetry group D_2 with three C_2 symmetry axes along the $X \parallel \mathbf{n}$, $Y \parallel [\mathbf{q} \times \mathbf{n}]$, and $Z \parallel \mathbf{q}$ axes. The presence of two separated directions \mathbf{n} and \mathbf{q} and the \mathbf{nq} plane causes the local biaxiality of the cholesteric liquid crystal, which is manifested in the difference between the refractive indices n_Z and n_Y , but the difference $n_Z - n_Y$ for known thermotropic cholesteric liquid crystals has not yet been measured owing to its smallness and does not affect the optical properties of cholesteric liquid crystals [2, 7]. Under the conditions of total internal reflection for a light wave with the wave vector \mathbf{k} that is incident on the planar texture of a cholesteric liquid crystal and is polarized in the plane of incidence \mathbf{kq} , the refractive index $n_{\perp, \text{Ch}} = n_Z$ [7] is measured; the following refractive index is measured for a wave polarized in the quasi-nematic layer plane [7]:

$$n_{\perp, \text{Ch}} = \varepsilon^{1/2} \left\{ 1 + \frac{\alpha^2 \varepsilon_Y P^2}{32\lambda^2} + \frac{1}{\varepsilon} o[\alpha^4] \right\}^{1/2}. \quad (1)$$

Here, $\varepsilon = (\varepsilon_X + \varepsilon_Y)/2$, $\alpha = (\varepsilon_X - \varepsilon_Y)/(\varepsilon_X + \varepsilon_Y)$, P is the helical pitch, and λ is the light wavelength. The applicability condition $\lambda^2 > P^2 \varepsilon/8$ for Eq. (1) is certainly satisfied for the parameters $\lambda \approx P$, $\varepsilon \approx \varepsilon_Y \approx 2$, $\varepsilon_X - \varepsilon_Y \approx 0.2$, and $\alpha \approx 0.1$ typical of cholesteric liquid crystals [2], and the correction to $\varepsilon^{1/2}$ is 0.0004 and corresponds to the best accuracy of the measurement of

$n_{\perp, \text{Ch}}$ on the refractometer [8]. This validates the neglect of the correction to $\varepsilon^{1/2}$ and the use of the local uniaxiality approximation for the quasi-nematic layer with $n_{\parallel} = (2n_{\perp, \text{Ch}}^2 - n_{\parallel, \text{Ch}}^2)^{1/2}$ and $n_{\perp} = n_{\parallel, \text{Ch}}$.

The parameters $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ and $Q = (\varepsilon_{\parallel} - \varepsilon_{\perp})/(\bar{\varepsilon} - 1)$ determine the following quantities for a cholesteric liquid crystal with N molecules per unit volume and the mean molecular polarizability $\bar{\gamma}$:

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0, \quad (2)$$

$$b_1 = \frac{2r_0Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2.$$

The desired L_{\perp} value is given by the expression [9]

$$L_{\perp} = L_{\perp k} - \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)} \quad (3)$$

$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}],$$

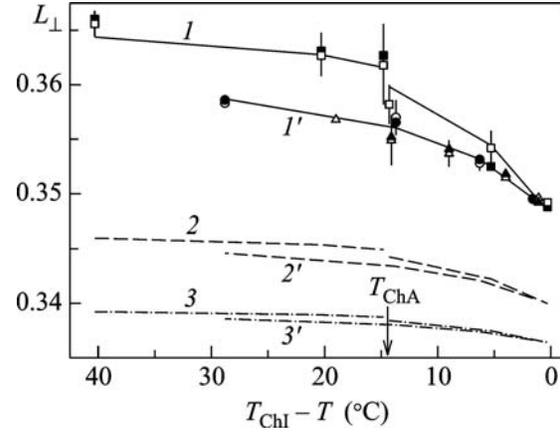
where $L_{\perp k} = (3 + 2Q)/3(3 + Q)$. The function $b(\lambda, T)$ depends on the unknown quantity $\bar{\gamma}$. For nematic liquid crystals with the $L_{\perp}(T)$ values known from experiment [10], the function $b(\lambda)$ obtained from Eq. (3) at a fixed L_{\perp} value varies slightly in the visible range and is well approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \dots + a_r(T)\lambda^r \quad (4)$$

with $r \leq 2$ [11].

The method proposed for determining the component $L_{\perp}(T)$ at a fixed temperature of the liquid crystal is as follows. With known $n_j(\lambda, T)$ values for a discrete set of values λ_j ($i = 1, 2, \dots, p$) in the visible range, the function $b(\lambda, T)$ in the interval $\lambda_1 - \lambda_p$ is approximated by polynomial (4). Since $L_{\perp} \neq L_{\perp}(\lambda)$, each temperature of the liquid crystal corresponds to a set of $r + 2$ unknowns ($L_{\perp}^{(r)}, a_0, a_1, \dots, a_r$). They are obtained from the system of $r + 2 = p$ equations (3), each corresponding to one of the values λ_j . Thus, the degree r of polynomial (4) is determined by the number p of the values λ_j . The use of a higher approximation in Eq. (4) implies a higher accuracy of the experimental values $n_j(\lambda, T)$; otherwise, the system of equations for ($L_{\perp}^{(r)}, a_0, a_1, \dots, a_r$) can have no physical solutions or lead to an irregular $L_{\perp}^{(r)}(T)$ dependence. This procedure used for nematic liquid crystals of various chemical classes with L_{\perp} values known from spectral measurements [3, 10] provides $L_{\perp}^{(r)}(T)$ values that coincide with L_{\perp} , but are much more accurate [11].

3. In this work, homologs of a series of cholesterol esters (ECh m) [8] are investigated:



Temperature dependences of (open points) $\langle L_{\perp}^{(2)} \rangle$ and (closed points) $L_{\perp}^{(3)}$ for homologs ECh m with $m =$ (○, ●) 2, (△, ▲) 5, and (□, ■) 8. Lines 1 (1'), 2 (2'), and 3 (3') correspond to relation (5) for $L_{\perp} = \langle L_{\perp}^{(2)} \rangle$ and $L_{\perp k}(\Delta T)$ and $L_{\perp}^{(H)}(\Delta T)$ dependences, respectively, for (1–3) ECh8 and (1'–3') (ECh2) at $\lambda = 0.5893 \mu\text{m}$. The arrow marks the cholesteric–smectic A transition temperature for ECh8.

with $m = 2, 5$, and 8. The homologs with $m = 2, 5$ (8) have a cholesteric (cholesteric and smectic A) phase. The refractive indices $n_{j, \text{Ch}}$ and n_j for the planar texture of cholesteric liquid crystals and the smectic phase of these objects are measured on a refractometer and are tabulated in [8] for $\lambda_1 = 0.4358 \mu\text{m}$, $\lambda_2 = 0.5086 \mu\text{m}$, $\lambda_3 = 0.5461 \mu\text{m}$, $\lambda_4 = 0.5893 \mu\text{m}$, and $\lambda_5 = 0.6438 \mu\text{m}$. Owing to this circumstance, the $L_{\perp}^{(3)}$ value and the average $\langle L_{\perp}^{(2)} \rangle$ over five $L_{\perp}^{(2)}$ values, which correspond to possible combinations of four λ_j values from the λ_{1-5} set, can be determined at each temperature of the liquid crystal.

The parameters $\langle L_{\perp}^{(2)} \rangle$ and $L_{\perp}^{(3)}$ are shown in the figure as functions of $\Delta T = T_{\text{ChI}} - T$, where T_{ChI} is the cholesteric–isotropic liquid (Ch–I) transition temperature. The $L_{\perp}^{(2)}$ values have a noticeable dispersion only near the temperature T_{ChA} of the cholesteric–smectic A (Ch–SmA) phase transition, where it is very difficult to obtain a uniform orientation of the smectic phase and, particularly, the planar texture of the cholesteric liquid crystal and, hence, the accuracy of refractometry is low. As a result, the system of equations (3) for the unknowns ($L_{\perp}^{(3)}, a_0, a_1, a_2, a_3$) for the planar texture of ECh8 near T_{ChA} has no physical solutions. Beyond this region, the dispersion of the $L_{\perp}^{(2)}$

values is negligibly small and the $L_{\perp}^{(3)}$ values coincide with $\langle L_{\perp}^{(2)} \rangle$.

In the absence of the smectic phase, the $L_{\perp}^{(r)}$ values for ECh2 and ECh5 are independent of the ordinal number of a homolog and the length of the alkyl chain. The presence of the smectic phase for ECh8 leads to a small increase in $L_{\perp}^{(r)}$ in the cholesteric phase near the point T_{ChA} , a stepwise increase in $L_{\perp}^{(r)}$ at this point, and a small change in the smectic phase. For the same ΔT values, the values $L_{\perp} = 0.35\text{--}0.36$ for ECh m in the cholesteric phase are intermediate between the values $L_{\perp} = 0.37\text{--}0.40$ for nematic liquid crystals with a larger birefringence value $\Delta n = n_{\parallel} - n_{\perp}$ [3, 10] and the values $L_{\perp} = 0.34\text{--}0.35$ for a nematic liquid crystal with a smaller Δn value [12]. The ECh m molecule has no aromatic fragments and is characterized by a small polarizability anisotropy $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}$ [3], where γ_{\parallel} and γ_{\perp} are the longitudinal and transverse components of the tensor γ , respectively. Thus, the quasi-nematic layer of cholesteric liquid crystals, as well as for nematic liquid crystals, is characterized both by the $L_j(\Delta\gamma)$ dependence for a fixed ΔT value and by the isotropization of the tensors L and f with a simultaneous decrease in $\Delta\gamma$ and Δn .

As seen in the figure, for homologs ECh2 and ECh8 in the cholesteric and smectic phases at a fixed ΔT value, the correlation of L_{\perp} values is similar to the correlation of $L_{\perp k}$ values. This indicates the relation

$$L_{\perp}(\Delta T) = A(\lambda)L_{\perp k}(\Delta T, \lambda) + B(\lambda), \quad (5)$$

which is well satisfied for the liquid crystals under investigation and is invariant with respect to the Ch–SmA transition. The coefficients of Eq. (5) are related as $B = (1 - A)/3$ with a high accuracy. In particular, for ECh2 (ECh8), $B = -0.4160$ (-0.554) and $(1 - A)/3 = -0.4162$ (-0.552). This means the validity of the relation

$$A = (L_{\perp} - 1/3)/(L_{\perp k} - 1/3) = \text{const}, \quad (6)$$

which is previously predicted for the $L_{\perp}(\Delta T)$ dependence in nematic liquid crystals [3].

The inequalities $L_{\perp} > L_{\perp k}$, $b < 0$, and $\Delta f = f_{\parallel} - f_{\perp} < 0$ are valid for the compounds under discussion. In view of Eqs. (2) for b and $r_0 < 1$, these inequalities provide the following constraints for $\bar{\gamma}$ in cholesteric liquid crystals:

$$\bar{\gamma} > \frac{3(\bar{\epsilon} - 1)}{4\pi r_0 N(\bar{\epsilon} + 2)} > \frac{3(\bar{\epsilon} - 1)}{4\pi N(\bar{\epsilon} + 2)}. \quad (7)$$

They demonstrate the incorrectness of the formula

$$\bar{\gamma} = \frac{3(\bar{\epsilon} - 1)}{4\pi N(\bar{\epsilon} + 2)}, \quad (8)$$

which was used in [4, 6] and numerous other works on the optics of cholesteric liquid crystals. In the isotropic approximation $\Delta f = b = 0$, the left inequality in (7) becomes an equality, whereas the right inequality holds. Formula (8) corresponds to the values $b = b_H = 1 - r_0 > 0$, $L_{\perp}^{(H)} < L_{\perp k}$, and $\Delta f > 0$, which contradict the experimental data. The $L_{\perp}^{(H)}(\Delta T)$ dependences shown in the figure also satisfy relation (5) with a high accuracy.

The Lorentz tensor L_{Ch} , whose components are determined from the relations $L_{\parallel, \text{Ch}} = L_{\perp}$ and $\text{Tr} L_{\text{Ch}} = 1$, is introduced for the planar texture of cholesteric liquid crystals in [5]. Analysis shows that the condition $\text{Tr} L_{\text{Ch}} = 1$ can be satisfied at $L_{\perp} = L_{\perp}^{(S)} = A_S(L_{\perp k} - 1/3) + 1/3$, where

$$A_S = \frac{27(3 + Q)(4 + Q)}{2(3 - Q)(3 + 2Q)(6 + Q)(\bar{\epsilon} - 1)} \times \left\{ \left[1 + \frac{8(3 - Q)(3 + 2Q)(6 + Q)(\bar{\epsilon} - 1)}{81(4 + Q)^2} \right]^{1/2} - 1 \right\}.$$

Therefore, $A_S < 1$ and $L_{\perp}^{(S)} < L_{\perp k}$. The values $L_{\perp}^{(S)} < L_{\perp}^{(H)}$ are very close to each other. Thus, all known assumptions on the values $\bar{\gamma}$ and $\text{Tr} L_{\text{Ch}}$ [4–6] for cholesteric liquid crystals are equivalent to the values $L_{\perp} < L_{\perp k}$ and $\Delta f > 0$ inconsistent with the experimental data.

4. The basic conclusions of the work are as follows. The method proposed for determining the components L_j for cholesteric liquid crystals is free of a priori assumptions on unobservable molecular properties ($\bar{\gamma}$ value [4, 5], oscillator strengths of molecular transitions [3, 10, 12]), which are used in theoretical and experimental [3, 10, 12] methods for determining these parameters in liquid crystals. This is important for obtaining objective information on the properties of molecules in liquid crystals and their change in the process of molecular self-organization. In particular, constraint (7) on the $\bar{\gamma}$ value follows from anisotropy $\Delta f < 0$ found here for cholesteric liquid crystals. At the same time, model theories based on a priori assumptions on the $\bar{\gamma}$ value [4, 5] or $\text{Tr} L_{\text{Ch}} = 1$ [5, 6] give values $\Delta f > 0$. The revealed $L_j(\Delta\gamma)$ dependence at a fixed ΔT value, which is common for cholesteric and nematic liquid crystals [3], has not yet been explained in the modern molecular statistical theory of the local field.

The use of spectral methods [3] for cholesteric liquid crystals is complicated by the unremovable depolarizing effect of director fluctuations on the polarization spectral measurements and diffraction effects. The refractometry of cholesteric liquid crystals is free of the effect of director fluctuations and the diffraction corrections to $n_{\perp, \text{Ch}}$ are taken into account by Eq. (1).

As a result, the accuracy of the refractometric method for determining L_j is much higher than the accuracy of the spectral methods [3]. This circumstance made it possible to confirm that dependence (5) predicted for nematic liquid crystals is valid for the cholesteric liquid crystals investigated here. New possibilities of refractometry demonstrated here for investigating cholesteric liquid crystals can stimulate the development of refractometry in the direction of increasing the accuracy and expanding the spectral range.

This work was supported by the Presidium of the Russian Academy of Sciences (Basic Research Program, project no. 27.1) and by the Siberian Branch, Russian Academy of Sciences (Interdisciplinary Basic Research Program, project no. 5).

REFERENCES

1. Y. Bouligand, in *Liquid Crystalline Order in Polymers*, Ed. by A. Blumstein (Academic, New York, 1978), Ch. 8, p. 276.
2. V. A. Belyakov and A. S. Sonin, *Optics of Cholesteric Liquid Crystals* (Nauka, Moscow, 1982) [in Russian].
3. E. M. Aver'yanov, *Effects of Local Field in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999) [in Russian].
4. D. Krishnamurti and H. S. Subramhanyam, *Mol. Cryst. Liq. Cryst.* **31**, 153 (1975).
5. H. S. Subramhanyam, *Indian J. Phys. A* **57**, 268 (1983).
6. R. Manohar and J. P. Shukla, *J. Phys. Chem. Solids* **65**, 1643 (2004).
7. R. Dreher, G. Meier, and A. Saupe, *Mol. Cryst. Liq. Cryst.* **13**, 17 (1971).
8. G. Pelzl and H. Sackmann, *Z. Phys. Chem. (Leipzig)* **254**, 354 (1973).
9. E. M. Aver'yanov, *Zh. Eksp. Teor. Fiz.* **135**, 194 (2009) [*JETP* **108**, 176 (2009)].
10. E. M. Aver'yanov, V. A. Zhuikov, V. Ya. Zyryanov, and V. F. Shabanov, *Zh. Eksp. Teor. Fiz.* **86**, 2111 (1984) [*Sov. Phys. JETP* **59**, 1227 (1984)].
11. E. M. Aver'yanov, *Zhidk. Krist. Ikh Ispolz.*, No. **4**, 26 (2008).
12. E. M. Aver'yanov, V. G. Rumyantsev, and V. M. Muratov, *Zh. Eksp. Teor. Fiz.* **88**, 810 (1985) [*Sov. Phys. JETP* **61**, 476 (1985)].

Translated by R. Tyapaev