(1.1) except for the area bounded by Eq. (2.15). The permissible range of values  $h_1$  and  $\omega$  is shown shaded in Fig. 1. Thus, at a given pump field frequency  $\omega$ , the amplitude of the pump field has upper and lower bounds.

In the presence of damping, an important feature ensuring the retention of self-localized distributions of the magnetic moment (of the soliton type) is the possibility of a change of the sign of the derivative of the first integral (2.8), which is associated—according to Eq. (2.7)—with a change in the sign of the spatial derivative of the phase shift. The establishment of a constant phase shift in the homogeneous magnetization region, namely, the condition

$$\lim_{|z|\to\infty} \left(\frac{d\Phi}{dz}\right) = 0$$

corresponds to

$$\lim_{|s|\to\infty} \mathscr{H} = -\sin^2\theta_{\star} - 2\omega\cos\theta_{\star} + 2h_{\perp}\cos\Phi_{\star}\sin\theta_{\star}.$$

Consequently, a self-localized state of the magnetic moment should satisfy the condition

 $\int_{-\infty}^{\infty} dz \sin^2 \theta \frac{d\Phi}{dz} = 0.$ 

It should be noted that the above type of self-localized solution corresponds to the conservation of the projection of the total moment along the anisotropy axis:

 $\int dz (\cos \theta - \cos \theta_s) = \text{const.}$ 

We shall conclude by mentioning that the possibility of excitation of magnetic solitons by a traveling external magnetic field was considered by Akhiezer and Borovik.<sup>[5]</sup>

- <sup>1</sup>I. A. Akhiezer and A. E. Borovik, Zh. Eksp. Teor. Fiz. **52**, 508 (1967) [Sov. Phys. JETP **25**, 332 (1967)].
- <sup>2</sup>V. M. Eleonski<sup>1</sup>, N. N. Kirova, and N. E. Kulagin, Zh. Eksp. Teor. Fiz. **71**, 2349 (1976) [Sov. Phys. JETP **44**, 1239 (1976)].
- <sup>3</sup>B. A. Ivanov and A. M. Kosevich, Zh. Eksp. Teor. Fiz. 72, 2000 (1977) [Sov. Phys. JETP 45, 1050 (1977)].
- <sup>4</sup>L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred, Fizmatgiz, M., 1959 (Electrodynamics of Continuous Media, Pergamon Press, Oxford, 1960).
- <sup>5</sup>I. A. Akhiezer and A. E. Borovik, Fiz. Tverd. Tela (Leningrad) **10**, 1609 (1968) [Solid State Phys. **10**, 1275 (1968)].

Translated by A. Tybulewicz

## Optical properties and structural ordering of the planar texture of a cholesteric liquid crystal

A. V. Tolmachev, V. G. Tishchenko, and L. N. Lisetskii

All-Union Research Institute for Single Crytals, Scintillating Materials, and Highly Purified Chemical Substances (Submitted 23 February 1978) Zh. Eksp. Teor. Fiz. **75**, 663–672 (August 1978)

The experimental dependences of the circular dichroism are used to calculate the optical-anisotropy parameter and the number of turns of the helix of the planar texture of cholesteric liquid crystals (CLC) of the homologic series of cholesteryl alkanoates. The dependence of the orientational order of CLC on the temperature and structure of the mesogen molecule is investigated and it is shown that this order decreases regularly with increasing length of the alkyl chain of the ester. A section is found, not predicted by the theory, where the optical-anisotropy parameter drops jumpwise in the vicinity of the cholesteric-smectic-A phase transition. The temperature dependences of the relative change of the translational order of the CLC are obtained, the growth of the order being accompanied by untwisting of the cholesteric helix.

PACS numbers: 61.30.Eb, 78.20.Ek

## INTRODUCTION

One of the least investigated problems of liquidcrystal physics is the structural ordering of the molecules in the cholesteric mesophase. In particular, one cannot regard as finally settled so very important an aspect of the hypomolecular structure of cholesteric liquid crystals (CLC) as the quantitative characteristics of the orientational ordering, the onset of translational order near the cholesteric-smectic-Atransition, as well as the effect exerted on the structural ordering by macroscopic inhomogeneities of the planar structure. Orientational ordering in the cholesteric mesophase can be naturally described with the aid of the orientational-order parameter  $\eta = \langle P_2(\cos \theta) \rangle$ , where  $\theta$  is the angle between the long axis of the molecule and the axis of the predominant molecular orientation (director), and  $P_2$  is a Legendre polynomial. The presence of the helical twist makes it inconvenient to use for CLC most of the experimental methods employed to determine  $\eta$  in nematics. The theoretical  $\eta(T)$  temperature dependence was verified experimentally a number of times on nematic liquid crystals (NLC) (see, e.g., Refs. 1-3), and a connection was established between the subtle features of the structure of mesogenic molecules and the course of the  $\eta(T)$  dependence.<sup>[3,4]</sup> In this connection, the investigation of the influence of the structure of the molecules of cholesteric mesogens on the orientational ordering would be of considerable interest. However, in view of the difficulties noted above, the experimental data on  $\eta$  in CLC are extremely skimpy. An NMR method was used to obtain isolated results for nematic-cholesteric mixtures<sup>[5,6]</sup> and for cholesteryl chloride-cholesteryl oleate mixtures.<sup>[7]</sup> The cited studies were in fact demonstrations of the capabilities of the method and yielded no new information whatever on the structural ordering in CLC.

The temperature dependence of  $\eta$  in CLC was first obtained in Ref. 8 from measurements of the principal refractive indices of the planar structure of cholesteryl pelargonate. The obtained values  $\eta \leq 0.3$  are much lower than the theoretical ones; this might have been due, in particular, to the non-monodomain character of the texture, which manifested itself strongly in measurements with the Abbe refractometer. An  $\eta(T)$ relation close to the theoretical one was obtained in Ref. 9 by the NMR method for ortho- and parafluorobenzoates of cholesterine. The results enabled the authors, in particular, to conclude that the orientational-ordering mechanism and the intermolecularinteraction characteristics that govern this ordering in nematic and cholesteric liquid crystals are close to each other when account is taken of the spiral twisting of the hypomolecular structure of the cholesteric crystals.

An important feature of the structural ordering in CLC is also the onset of a translational order near the cholesteric-smectic-A phase transition, and the resultant untwisting of the cholesteric helix. Although these phenomena have been well investigated from the point of view of phase transitions,<sup>[10]</sup> the concrete mechanism of the ordering of the hypomolecular structure remains unclear, and in particular the role of the germs of the translationally ordered mesophase (the so-called smectic clusters<sup>[11]</sup>).

It seemed quite promising to investigate the structural ordering of CLC by optical methods, particularly to use the temperature dependence of selective optical characteristics of the planar structure. As shown by us in Refs. 12 and 13, these characteristics are highly sensitive to changes of the structural ordering in the mesophase.

The purpose of the present paper is to determine the macroscopic parameters of the structural ordering of



FIG. 1. Circular dichroism of planar texture of cholesteryl laurate (10  $\mu$ m thick) at temperatures (K): 1-353.10, 2-353.38, 3-353.80, 4-354.03, 5-354.10, 6-354.57, 7-355.60, 8-356.92, 9-358.00, 10-359.28, 11-359.75. CLC, viz., the optical anisotropy and the number of turns of the helix, to determine the connection between the structure of the mesogenic molecules and the parameters of the structural ordering, as well as the influence exerted on these parameters by the pre-transition phenomena at the boundaries of the interval in which the cholesteric mesophase exists. Isolated preliminary results were reported by us earlier in Ref. 14.

## 2. DETERMINATION AND ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE MACROSCOPIC PARAMETERS OF THE PLANAR STRUCTURE

We chose for the investigation esthers of the cholesteryl alkanoate series, namely caprinate, laurate, myristate, and palmitate. These substances form a cholesteric as well as a smectic-A mesophase, so that both the orientational and the translational orders can be studied. In addition, comparison of the data for various homologs yields information on the effect of the length of the hydrocarbon radical on the investigated structural-ordering parameters.

For the planar texture of each substance we determined the temperature dependence obtained for the optical circular dichroism by direct measurements of the transmission coefficients of linearly polarized light, using the procedure described in Ref. 13. A typical form of the experimental curves is shown in Fig. 1 for cholesteryl laurate. The amplitude of the circular dichroism increases jumpwise in the vicinity of the point  $T_c$  of the cholesteric-smectic (translational) phase transition and subsequently decreases smoothly as the temperature rises to the bleaching point  $T_b$  (towards the orientation phase transition).

The search for the macroscopic parameters of the planar texture (optical anisotropy  $\delta$  and the number L of turns of the spiral for a known ratio (1.47/1.49) of the refractive indices of the quartz glasses and of the investigated CLC) was carried out with a computer by least squares, with the experimental curve  $D_{eff}(\gamma, T)$ =const) fitted by trial and error to the nearest theoretical curve  $D_{\text{theor}}(\lambda, \delta, L)$ .<sup>1)</sup> The fitting was terminated by yielding the macroscopic parameters and the relative value of the mean squared deviation  $\varepsilon^*$ , Fig. 2. The algorithm for the reduction of the experimental data ensured uniqueness of the search of  $\delta$  and L in two stages. The assumed value of L, specified at each temperature point by dividing the absolute thickness of the liquid-crystal layer (10  $\mu$ m) by the pitch of the planar-texture helix, was first fixed, followed by fitting to the parameter L for the obtained value of  $\hat{o}$ . The preliminary checkout of the program was with the aid of the theoretical circular-dichroism curves for known  $\delta$  and L. The mean squared deviations amounted in this case to  $\sim 10^{-4} - 10^{-5}$ . From the methodological point of view, the search for the macroscopic parameters must be admitted to be correct, since the relative deviation  $\varepsilon^*$  exceed the mean squared error in the measurement of the transmission coefficient of the linearly polarized light ( $\sim 1\%$ ).



FIG. 2. a) Optical-anisotropy parameter of planar texture of cholesteryl alkanoates, b) temperature dependence of the number of periods of the helical structure of cholesteryl alkanoates in a 10  $\mu$ m layer, and c) relative mean squared deviations of spectral dependences of circular dichroism on the experimental ones: 1—pelargonate, 2—caprinate, 3—laurate, 4—myristate, 5—palmitate.

For each homolog at the temperature point of the maximum amplitude of the function D(T), corresponding to the minimal  $\varepsilon^*$ , the experimental circular-dichroism curve is similar to the envelope of the  $D_{\text{theor}}$  curve, i.e., to the curve drawn through the points of the side and central maxima of the theoretical curve-Fig. 3. The abscissas are the values of the reduced wavelength  $\lambda = \lambda_{max} / \varepsilon^{1/2} p$ , where  $\lambda_{max}$  is the wavelength corresponding to the amplitude  $D_{max}$  of the spectral circular-dichroism curve, 1/2 is the refractive index of the ordinary ray for CLC, and p is the pitch of the helix. The proximity of the  $D_{\text{theor}}$  and  $D_{\text{exp}}$  curves at the points  $\varepsilon^*_{min}$  attests to a predominantly equal and sufficiently high degree of orientation of the homogeneous planar-texture regions demarcated by greasy strips and producing no regular Grandjean stratification. When the temperature changes and the amplitudes  $D_{exp}$  decrease, the accuracy of the sorting decreases, owing to the following singularities of the CLC structure: the thermal fluctuations near the phase transition into an isotropic liquid, and formation of germs of the smectic mesophase in the vicinity of the translational phase transition.

The optical anisotropy parameter makes it possible, in principle, to calculate the absolute value of the orientation order in the form  $\eta = \delta/\delta_0$  (after determining the anisotropy  $\delta_0$  of a fully oriented liquid crystal and introducing an internal field that takes into account the connection of the permittivity of the liquid crystal not only with the angular distribution of the long axes of the molecules, but also with the relative distance between them<sup>[11]</sup>). A direct solution of this problem is as yet difficult, but the information of interest to us can



FIG. 3. Theoretical (1) and experimental (2) curves of circular dichroism of planar texture of cholesteryl pelargonate: T-346.40 K,  $\varepsilon^*=1.9\%$ , L=33.0,  $\delta=0.0267$ ,  $\lambda_{max}=448$  nm  $(\overline{\epsilon})^{1/2}=1.49$ .

be obtained in first-order approximation from the  $\delta(T)$ temperature dependence. The parameter  $\delta = (\varepsilon_1 - \varepsilon_2)/$  $(\varepsilon_1 + \varepsilon_2)$  characterizes the difference between the permittivities in two mutually perpendicular directions relative to the director orientation in the plane of a quasinematic layer, so that the  $\delta(T)$  dependence should correspond to the relative change of the orientationalorder parameter. The method of quantitatively estimating  $\eta$ , based on this assumption and proposed by us in Ref. 14, yields quite acceptable values on the order of 0.4 - 0.6, which are close both to the NMR results<sup>[9]</sup> and to the results of the reduction of the birefringence indices with allowance for the anisotropy of the internal field and for the effective molecular polarizability.<sup>[16]</sup> Thus, the character of the change and the magnitude of the optical-anisotropy parameter are regarded in the present paper as a measure of the structural ordering in the temperature interval of the cholesteric mesophase.

The temperature dependence of  $\delta(T)$  (Fig. 2a) in the low-temperature region is characterized by the presence of essential anomalies, obviously due to the proximity to  $T_c$ . This will be discussed in greater detail in Sec. 3. The values of the temperature  $T_{\text{choi}}$ corresponding for each homolog to the start of the smooth decrease with temperature, can be regarded as a sort of boundary between the cholesteric state proper and the region where the translational order sets in. Thus, for pelargonate and caprinate, in which the cholesteric-mesophase interval  $(10 - 12^{\circ}C)$  is 1.5 - 2times broader than that for laurate, myristate, and palmitate, the value of  $T_{chol}$  coincides exactly with the start of the smooth change of the pitch of the planar structure. Thus, the optical-anisotropy parameter of the planar structure of a CLC that does not form a smectic should not change jumpwise when the temperature is lowered. A similar result was obtained by us in investigations of the optical activity of the planar texture of cholesteryl valerate.[12]

A comparison of the parameters of the optical anisotropy in the series of investigated cholesteryl alkanoates leads to the conclusion that the orientational ordering of the planar structure decreases regularly with increasing number of the homolog, i.e., with increasing number of carbon atoms in the alkyl chain of the ester, from 8 for pelargonate to 16 for palmitate. The deviations of the experimental  $\eta(T)$  from the theoretical one, determined in the molecular-statistical Maier-Saupe theory with the aid of the self-consistency equation, are known for nematic liquid crystals.<sup>[11]</sup> The undervalued  $\eta$  are attributed in Refs. 4 and 5 to the decrease of the coefficients of the higher-order terms in the expansion of the angular dependence of the potential energy of the molecule in a medium field in Legendre polynomials. The physical cause of this fact is the action of additional disordering forces, which in our opinion, as applied to CLC, can be represented in the following manner:

We shall consider the molecules of cholesterine esters, consisting of a basal plane (rigid steriod core) and a semiflexible end group. If the minimum of the interaction energy of the rigid rods is reached when they are oriented in parallel (or at a certain angle  $\theta_0$ between the long axes of the molecules if the latter are chiral), then when account is taken of the conformation energy of the lateral chain, the minimum of the total energy, as shown by us in Ref. 17, is reached at a certain angle  $\theta_0 \pm \Delta \theta$  between the long axes of the molecules, with  $\Delta \theta$  increasing with increasing length of the alkyl radical, owing to the decreased rigidity of the molecule. This smears out the maximum of the angular distribution function of the molecules and lowers correspondingly the degree of orientational order. The fact that the molecules are energywise hindered from assuming a mutual arrangement corresponding to maximum anisotropy oc the macroscopic properties can prevent formation of the mesophase.

The thickness of the planar texture, determined by the product of the calculated number L of the helix turn by the size of the pitch, is 4-5% smaller than the total layer thickness, which is set by the liner (10  $\mu$ m). Since the mean squared deviation in the fitting of the macroscopic parameters is determined mainly by the accuracy with which  $\delta$  is determined, the thickness difference can be regarded as an objective estimate of the degree of distortion of the equilibrium cholesteric helix by the pinning of the molecules to the walls, i.e., to the difference between the pitch near the walls and that in the interior of the sample. In order of magnitude (~0.5  $\mu$ m) this value agrees both with the theoretical estimate<sup>[18]</sup> and with the data obtained by investigating the structure of CLC in a wedge.[19] The presence near  $T_b$  of a section where L(T) increases noticeably (Fig. 2b) is due to the decrease of the pitch of the helix when the orientational order is decreased because of the increase of the amplitude of the anharmonic rotational vibrations of the chiral molecules. A similar phenomenon was noted by us earlier for substituted cholesteryl benzoates.[20]

Thus, the noted singularities in the change of the macroscopic parameters of the planar texture of cholesteryl alkanoates agrees well enough with the known theoretical premises and with the model-dependent representations of the CLC structure. In addition, for CLC with minimal distortions of the structural ordering (Fig. 2c, curves 1-3), the relative mean squared deviation  $\varepsilon^*$  of the theoretical circular-

336 Sov. Phys. JETP 48(2), Aug. 1978

dichroism curve from the experimental one is only ~2%. This allows us to conclude that the real cholesterics are adequately represented by the CLC structure used in the present paper, in the form of a helix with a dielectric tensor that describes the rotation of the axis of preferred molecular orientation on going from one plane perpendicular to the optical axis to another.<sup>[1]</sup>

An alternate model was proposed in Refs. 21 and 22, where the CLC was represented in the form of an aggregate of linear helix chains with arbitrary phases in the planes perpendicular to the axes of the helices. This model, however, does not agree with the molecular-statistical theory, for it would be impossible to speak of a long-range orientational order that gives rise to the existence of the mesophase-if there were no correlation of the indicated phases within the limits of the macroscopic section of the plane perpendicular to the helix axis. With respect to liquid crystals, including cholesteric ones, only a partial scatter of the orientations of the long axes of adjacent molecules is permissible. The presence of two inversion points on the experimental curves of the dispersion of the optical activity of the planar structure in Ref. 22 was considered by the authors as a confirmation of the theoretical consequences of the model of linear chains, from which follows the presence of a reversal of the sign of the optical activity both at  $\lambda_1 = \overline{\epsilon}^{1/2} p$  and at  $\lambda_2$ =  $0.5\overline{\epsilon}^{1/2}p$ . These results cannot serve as experimental confirmation of the cited model, since the second inversion point in such systems is due to the intrinsic absorption of one of the mixture components whose molecules are oriented along a helix in a planar structure. The observation of two inversion points in the investigated mixtures is possible, since one of the components was cholesteryl benzoate with intrinsic absorption in the near ultraviolet region (~300 nm). The optical activity of the planar texture of aromatic derivatives of cholesterine, with account taken of the intrinsic absorption, was investigated in detail in Ref. 23. A similar effect can be obtained by introducing dye molecules into the cholesteric matrix.<sup>[24]</sup> The positions of the inversion points of the optical activity is determined in this case by the pitch of the helix of the cholesteric matrix and by the absorption wavelength of the dye molecules oriented by this matrix, which can be either smaller or larger than the wavelength of the selective reflection; the relation  $\lambda_2$  $\approx 0.5\lambda_1$  for real planar texture is accidental.

## 3. SINGULARITIES OF SUPERMOLECULAR STRUCTURE OF CLC NEAR THE PHASE TRANSITION INTO THE SMECTIC-A MESOPHASE

We consider now the singularities of the  $\delta(T)$  curves (Fig. 2a), due to the influence of the translational ordering. The available x-ray structure analysis data (see, e.g., Refs. 11 and 25) attest to formation in the pre-transition region, above  $T_c$ , of germs of a translationally ordered mesophase (smectic clusters) that contain about 100-500 molecules. Being a locallyspatial inhomogeneity with respect to the oreintational ordering proper, the smectic clusters cause a corresponding perturbation of the director N. To investigate the influence of the translational order on the pitch of the cholesteric spiral, we examine the expression for the free energy of a CLC, in which account is taken of the growth of the elastic torsion modulus  $K_{22}$  near the temperature  $T_c$  (Ref. 26):

$$F = \frac{1}{2} \int_{\mathbf{v}} dV \left[ K_{22} \left( \operatorname{N} \operatorname{rot} \mathbf{N} + \frac{2\pi}{p_0} \right)^2 - A \left( \operatorname{\sigma q} \mathbf{N} \right)^2 \right], \tag{1}$$

where **q** is a vector perpendicular to the plane of the smectic layers and equal in absolute magnitude to the reciprocal distance 1/d between the layers;  $0 \le \sigma \le 1$  is a parameter of the translational (smectic) order, defined in general form for small volumes located at various points of the radius vector **r** (Ref. 27) as

$$\sigma = \frac{1}{V} \int \sigma(\mathbf{r}) \, dV.$$

For the smectic-A mesophase we have  $\sigma = \langle \cos(2\pi x/d) \rangle$ (Ref. 28) in a small vicinity of **r** if the x-component of the radius vector coincides with the direction of **q**.

It is easily noted that the representation of the free energy in the form (1) is similar to that used in the Meier-de Gennes theory<sup>[1]</sup> for the free energy of a cholesteric liquid crystal in an external (electric or magnetic) field perpendicular to the z axis of the helix twist. The factor  $\sigma q$ , with allowance for this fact, can be treated as a certain "smectic" field that orients the molecules contained in the cholesteric mesophase relative to the aggregate of molecules that have already become clustered.<sup>[29]</sup> Assuming the long axes of the molecules to remain in a plane perpendicular to z, and separating in explicit form the temperature dependences of the elastic modulus of the torsion and of the pitch, we have

$$F = \frac{1}{2} \int K_{22}(T) \left[ N(z) \operatorname{rot} N(z) + \frac{2\pi}{p(T)} \right]^2 dz.$$
 (2)

Each value of the "smectic" field corresponds to a value p(T) that minimizes F and determines the change of the director N. In analogy with the Meier-de Gennes theory, the change of the pitch in the pre-transition region will be written in the form

$$\frac{p}{p_0} = \frac{4}{\pi^2} K(k) E(k),$$
(3)

where K(k) and E(k) are complete elliptic integrals of the first and second kind, and

$$\frac{k}{E(k)} = \frac{\sigma q}{(\sigma q)_o} = \frac{\sigma}{\sigma_o},$$
(4)

where  $(\sigma \mathbf{q})_0$  is the critical "smectic" field that transforms completely the cholesteric spiral into a state with  $p \to \infty$ .

Starting from the experimental p(T) relations,<sup>[12]</sup> we calculated in accord with (3) and (4) the temperature dependences of the relative change of the translational ordering of cholesteryl alkanoates. For each homolog, the values of  $p_0$  were taken to be those determined near  $T_{b}$ . The obtained relations are plotted in Fig. 4.

The obtained  $\sigma/\sigma_0 = f(T)$  curves exhibit a nonmonotonic temperature dependence of  $d\sigma/dT$ , which manifests itself distinctly for substances with a sufficiently broad region of pre-transition phenomena (curves 1-3). We note that McMillan's results of direct x-ray structure investigations<sup>[28]</sup> of cholestryl pelargonate also attest to the presence of a section where the growth of the translational order slows down in this temperature interval. The disturbance of the smoothness of the  $\sigma/\sigma_0 = f(T)$  curves occurs at the temperature when a noticeable change begins in the pitch of the planar texture (see Ref. 12). It is therefore natural to treat the noted singularity as a consequence of the growth of the clusters at a rate exceeding the transition of the molecules from the cholesteric to the smectic phase. This can be connected, in particular, with the start of an intense coalescence of the clusters.

The obtained  $\delta(T)$  dependences, which are sensitive to the change of the ordering of a liquid crystal in the vicinity of phase transitions, take into account by the same token that part of the orientational distribution function of the molecules in the mesophase for which the CLC structure can no longer be represented by an undistorted helix. The observed anomalies near  $T_c$  are typical of cholesteric liquid crystals, since the degree of ordering of the hypomolecular structure of the cholesteric is determined not only by the short-range orientational order but also by the macroscopic inhomogeneities of the helix. For this reason one should therefore probably observe also a stronger decrease of the absolute value of the order parameter, obtained from optical measurements when the texture becomes thermally disordered near  $T_b$ .

Optical investigations yield information that supplements the results of NMR investigations of the CLC close-range order due to mutual correlations of neighboring molecules. Thus, for example, the formation of smectic clusters will not affect the form of the NMR spectrum, inasmuch as a certain increase of the oreintational order inside the clusters has practically no effect on the  $\langle p_2(\cos\theta) \rangle$  averaging, in view of the small volume of the cluster relative to the volume of the entire sample. As to the optical method, it is sensitive to the presence, in the planar structure of macroscopic defects of the helix, which are fixed at distances on the order of the incident-light wavelength.

Thus, measurement of the selective optical characteristics makes it possible to take into account the larger-scale factors of the structural ordering. This becomes particularly significant if it is recognized that, in contrast to the pure orientational ordering in the mesophase, most aspects of the supermolecular structure of CLC have remained practically uninvestigated.

We note in conclusion that the initial structural model



FIG. 4. Temperature dependence of translational ordering of cholesteryl alkanoates: 1—perlargonate, 2—caprinate, 3—laurate, 4—myristate, 5—palmitate. of a cholesteric crystal does not make it possible to trace separately the changes of the translational and rotational orders, although in our opinion a rigorous separation of the two types of ordering in real CLC is quite arbitrary. The theoretically postulated helical structure, although represented in the form of an aggregate of quasinematic layers, admits of correlation of the gravity centers of the molecules. The form of the dielectric tensor that governs the character of the propagation of the electromagnetic waves in the medium remains unchanged in this case. Therefore the presence of extremal points on the temperature dependence of the optical-anisotropy parameter (Fig. 2a) can be interpreted as an additional organization of the structure of the liquid crystal, due to the ordering of the long axes of the molecules on account of their more rigid interaction with the lateral directions. When the temperature drops to the phase-transition point, growth and spontaneous coalescence of the clusters takes place in a narrow interval (one or two tenths of a degree), as a result of which, the orientational order decreases with untwisting of the helix, and this is accompanied by a decrease of the amplitude and of the half-width of the optical characteristics of the planar textures.

The authors are grateful to V. A. Belyakov for a number of valuable remarks and to P. Adamski (Poland) for a useful discussion.

- <sup>1)</sup>The theoretical dependence of the optical characteristics of a CLC layer on or L was analyzed by us in Ref. 15.
- <sup>1</sup>P. G. de Gennes, The Physics of Liquid Crystals, Oxford U. Press, 1974.
- <sup>2</sup>R. L. Humphries, P. G. James, and G. R. Luckhurst, J.
- Chem. Soc., Faraday Trans. II, 1031 (1972).
- <sup>3</sup>E. B. Priestley, RCA Rev. 35, 144 (1974).
- <sup>4</sup>S. Jen, N. A. Clark, and P. S. Pershan, Phys. Rev. Lett. **31**, 1552 (1973).
- <sup>5</sup>C. E. Tarr, M. E. Field, L. R. Whalley, and K. R. Brownstein, Mol. Cryst. Liq. Cryst. **35**, 231 (1976).
- <sup>6</sup>P. J. Collins, S. I. Goss, and J. R. McColl, Phys. Rev. A 11, 684 (1975).
- <sup>1</sup>V. A. Andreev, N. I. Lebovka, Yu. A. Marazuev, and G. Yu. Shimanskaya, Zh. Eksp. Teor. Fiz. 72, 1926 (1977) [Sov. Phys. JETP 45, 1012 (1977)].

- <sup>8</sup>P. Adamski and A. Dylik-Gromiec, Mol. Cryst. Liq. Cryst. 35, 337 (1976).
- <sup>9</sup>P. J. Collins, T. J. McKee, and J. R. McColl., J. Chem. Phys. 65, 3520 (1976).
- <sup>10</sup>P. B. Vigman and V. M. Filev, Zh. Eksp. Teor. Fiz. 69, 1466 (1975) [Sov. Phys. JETP 42, 747 (1975)].
- <sup>11</sup>J. Voss, U. Würz, and E. Sackmann, Ber. Bunsenges. Phys. Chem. 78, 874 (1974).
- <sup>12</sup>A. S. Sonin, A. V. Tolmachev, V. G. Tishchenko, and V. G. Rak, Zh. Eksp. Teor. Fiz. 68, 1951 (1975) [Sov. Phys. JETP 41, 977 (1965)].
- <sup>13</sup>A. S. Sonin, A. V. Tolmachev, and V. G. Tishchenko, Kristallografiya 21, 1164 (1976) [Sov. Phys. Crystallogr. 21, 673 (1976)].
- <sup>14</sup>A. V. Tolmachev, V. G. Tishchenko, and L. N. Lisetskii, Fiz. Tverd. Tela (Leningrad) **19**, 1886 (1977) [Sov. Phys. Solid State **19**, 1105 (1977)].
- <sup>15</sup>A. V. Tolmachev and A. S. Sonin, Fiz. Tverd. Tela (Leningrad) **17**, 3096 (1975) [Sov. Phys. Solid State **17**, 2052 (1975)]; Kristallografiya **21**, 794 (1976) [Sov. Phys. Crystallogr. **21**, 450 (1976)].
- <sup>16</sup>E. M. Aver'yanov and V. F. Shabanov, Preprint IFCO-65F, Krasnoyarsk, 1977.
- <sup>17</sup>V. G. Tishchenko, M. M. Fetisova, R. M. Cherkashina, and L. N. Lisetskii, in: Fizika i khimiya kristallov (Physics and Chemistry of Crystals), Khar'kov, VNII Monokristallov, 1977, p. 110.
- <sup>18</sup>E. I. Kats, Zh. Eksp. Teor. Fiz. 70, 1394 (1976) [Sov. Phys. JETP 43, 726 (1976)].
- <sup>19</sup>V. A. Kizel' and S. I. Kudashev, Zh. Eksp. Teor. Fiz. 72, 2180 (1977) [Sov. Phys. JETP 45, 1145 (1977)].
- <sup>20</sup>L. N. Lisetskii, A. V. Tolmachev, and V. G. Tishchenko, Pis'ma Zh. Eksp. Teor. Fiz. 27, 205 (1978) [JETP Lett. 27, 191 (1978)].
- <sup>21</sup>E. K. Galanov, Opt. Spektrosk. **41**, 440 (1976) [Opt. Spectrosc. (USSR) **41**, 253 (1976)].
- <sup>22</sup>E. K. Galanov, R. I. Mel'nik, M. V. Mukhina, and G. K. Kostyuk, Zh. Strukt. Khim. **17**, 696 (1976); Opt. Spektrosk. **40**, 1006 (1976) [Opt. Spektrosc. (USSR) **40**, 577 (1976)]; Kristallografiya **22**, 880 (1977) [Sov. Phys. Crystallogr. **22**, 504 (1977)]
- <sup>23</sup>Yu. V. Denisov, V. A. Kizel', and E. P. Sukhenko, Kristallografiya 22, 339 (1977) [Sov. Phys. Crystallogr. 22, 192 (1977)].
- <sup>24</sup>K. J. Mainusch and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. 78, 927 (1974).
- <sup>25</sup>J. Voss and E. Sackmann, Z. Naturforsch. Teil A 28, 1496 (1973).
- <sup>26</sup>R. Alben, Mol. Cryst. Liq. Cryst. 20, 231 (1973).
- <sup>27</sup>L. N. Lisetskii and V. G. Tishchenko, Fiz. Tverd. Tela (Leningrad) 18, 3674 (1976) [Sov. Phys. Solid State 18, 2139 (1976)].
- <sup>28</sup>W. L. McMillan, Phys. Rev. A 4, 1238 (1971); 6, 936 (1972).
- <sup>29</sup>L. N. Lisetskii and V. G. Tishchenko, in: Kholestericheskie zhidkie kristally (Cholesteric Liquid Crystals), Sib. Div. USSR Acad. Sci., Novosibirsk, 1976, pp. 14, 24.

Translated by J. G. Adashko