

Ordering mechanism in cholesteric liquid crystals

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(Submitted November 29, 1976)

Zh. Eksp. Teor. Fiz. 72, 2180-2188 (June 1977)

We measured, in a wide range, the variation of the pitch of the cholesteric helix in the Kano-Grandjean structure and the change in the width of the reflection band. It is shown that the average and extremal values of the pitch increase appreciably with decreasing layer thickness, as does also the width of the band. The balance of the Van de Waals and boundary-wall short-range interactions in the cholesteric structure is estimated, and a comparison is made with the theory. Information is obtained on the dependence of the deformation energy of the cholesteric helix on the pitch and on the thickness of the layer, and the limits of this deformation are determined. The genesis of the ordered structure is traced.

PACS numbers: 61.30.Eb

In a preceding paper^[1] we investigated the order in cholesteric liquid crystals (CLC) and have shown that their optical parameters vary nonlinearly with layer thickness. This nonlinearity, as shown by the theory,^[2] is typical even of an ideally ordered cholesteric planar structure; in the case when the order is incomplete, the dependence of the parameters on the layer thickness becomes even more complicated. It is obvious that an investigation of this dependence makes it possible to obtain a large volume of information on the mechanism of the ordering and consequently on the character of the intermolecular forces that act here.

In^[1,3,4] and in a number of other papers it was shown that at the customarily employed methods of orienting the CLC, the latter have a certain "polycrystalline" structure with different orientations of the layers in different regions, or else become gradually disordered with increasing distance from the orienting surface. In this paper an attempt is made to trace the properties of the layers that have the highest possible ordering attainable by the usual methods. This procedure makes it possible to draw qualitative conclusions, as well as to perform quantitative measurements.

EXPERIMENTAL TECHNIQUE

On the basis of special research it was established^[1] that the most ordered planar texture (which, as will be shown below, is comparable with the ideal one) is obtained in a wedge-like gap between bulky glass or quartz plates coated with a thin layer of SnO₂, by subsequent rubbing together the two surfaces making up the gap, and then drawing in the substance into the gap by capillary action in a form molten to the isotropic phase, and and—an important step, as shown in^[1]—by subsequently moving both plates relative to one another. All these operations should be done in a direction perpendicular to the thickness gradient.

If the surfaces are suitably purified beforehand, it is possible to obtain a well ordered structure extending over 5–8 cm along the wedge with sufficiently broad (1–2 mm) and distinct Grandjean layers.

The technique of the optical part of the experiment is described in^{[1,3,4]2)}. We investigated the selective reflection (SR), the dimension of the CLC film surface

subjected to spectrometry being 0.05×0.05 mm (the long side was parallel to the Grandjean layers). The aperture of the beam was ~3°. We measured also the transmission and the circular dichroism. We chose the following substances: 1) mixture of cholesteryl chloride + cholesteryl pelargonate + nematic liquid crystal ("mixture A"), 2) mixture of cholesteryl oleate + cholesteryl decanoate + cholesteryl benzoate + cholesteryl chloride ("mixture B"). For our purposes, the chemical composition is immaterial³⁾ and the choice of these mixtures was dictated only by convenience in the experiment—an important factor is the existence of a mesophase at room temperature and practical independence of the pitch of the helix of the temperature, so as to exclude the possibility of distortion of the structure by temperature gradients. It will be shown below that these distortions can be quite appreciable even if thermostatic control is used—by virtue of the "structural memory." We investigated also pure cholesteryl pelargonate.

The absolute error in the determination of the position of the maximum of the reflection is ~40 Å, and the flatness of the plates, i.e., the deviation of the thickness scales from linearity, is not worse than 0.1 μm.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the wavelength at the maximum of the reflection λ_m on the local thickness d of the wedge-shaped gap, and the same dependence for the spectral half width $\Delta\lambda$ of the reflection band. It is seen that over one Grandjean layer the value of λ_m changes quite noticeably—by 20–30%; this means an equivalent change in the pitch of the helix. The peaks on the $\Delta\lambda$ curve are due to the fact that in the course of the spectrometry of the boundary between the layers, sections of two adjacent layers with different λ , as well as the Kano disclination region fall in the field of view of the instrument; thus, the curve should be considered without these points. Insofar as can be judged, at this measurement accuracy, $\Delta\lambda$ changes little within the limits of one layer; however, the general tendency of $\Delta\lambda$ to decrease with increasing d is clearly noticeable, as well as the decrease of the average and extremal values of λ . The quite regular variation of $\lambda(d)$ inside the band, which is shown in the figure, is by itself evidence of a rather high^[6] degree of order. Figures 2,

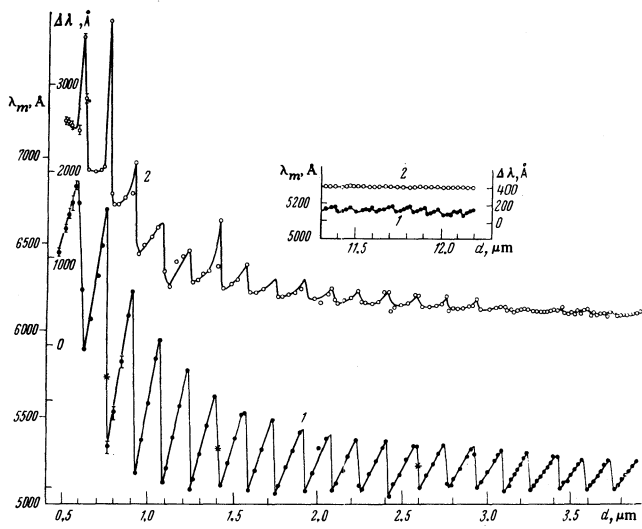


FIG. 1. Dependence of the wavelength of the maximum selective reflection λ_m (1) and of the half-width $\Delta\lambda$ of the reflection band (2) on the local width of the gap in the wedge. Mixture A, measurement temperature $T=20^\circ\text{C}$, incidence and reflection angles $\varphi_i = \varphi_r = 20^\circ$.

3c, 4b, and 4c show the variation of the optical parameters of the objects, which is quite close to the theoretical ones calculated under the assumption of complete order.^[7-10] The curves obtained without the SnO_2 layer have a much larger scatter of the points, i.e., the structure is less ordered in this case or has many defects and disclinations. The reproducibility of the structures of type Fig. 1 is adequate.

We note that the origin of the thickness scale, i.e., the absolute thickness, is determined with accuracy $\sim 0.3 \mu\text{m}$.

As a certain control on the quality of the structure, measurements of the circular dichroism (see Fig. 2) for different Grandjean bands, every time for the center of the band, are quite illustrative. The results are sufficiently close to those calculated theoretically assuming an ideal structure.^[8,10] Experimental curves of this type were obtained in measurements in^[11] for a planar texture produced within parallel plates. Our results differ from those of^[11] in a certain shift of λ_m for dif-

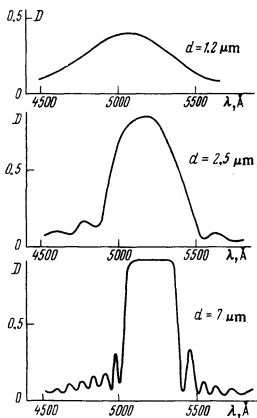


FIG. 2. Circular dichroism at different points of a wedge-shaped gap. Mixture A, $T=20^\circ\text{C}$, normal incidence.

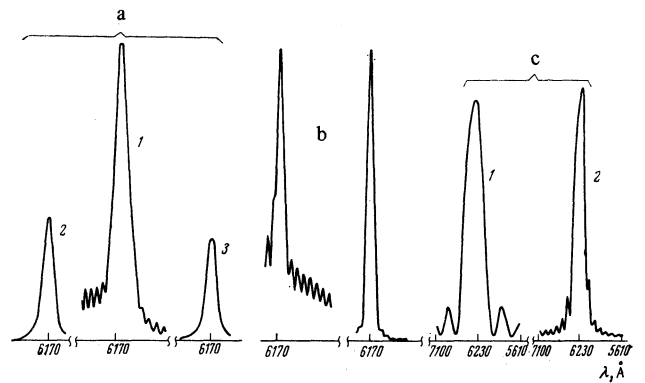


FIG. 3. Spectrograms of reflection from a plane-parallel cell ($d=12 \mu\text{m}$): a) after moving the front wall at the measurement temperature (curves 1— $\varphi_i = \varphi_r = 20^\circ$, 2— $\varphi_i = 40^\circ$, $\varphi_r = 0$, 3— $\varphi_i = 0$, $\varphi_r = 40^\circ$); b) after moving at the transition temperature (70°C) followed by cooling (two sections of the compound, $\varphi_i = \varphi_r = 20^\circ$); c) spectrograms for wedge-shaped gaps (shift at measurement temperature, different points of the wedge: 1) $d=6 \mu\text{m}$, 2) $d=12 \mu\text{m}$). The ordinate scales are different—the intensity increases from a to c. Mixture B, measurement temperature 20° .

ferent thicknesses, and this shift is obviously also the cause of the shift of the inversion point of the dispersion curves of the optical rotation, which was noted in^[1]. Thus, the sensitivity to changes of the structure is quite high in our method of orientation.

The mechanism of orientation of CLC in the course of the shift was considered in^[1]. In the present experiment, in contrast to^[1], both plates move, as a result of which the effect of the shift increases. The rubbing of the plates seems to produce on the surfaces microscopic grooves that add to the stability of the orientation of the nearest layer of molecules, both via purely mechanical action and by the force of cohesion of the groove walls. It is usually assumed that the molecules closest

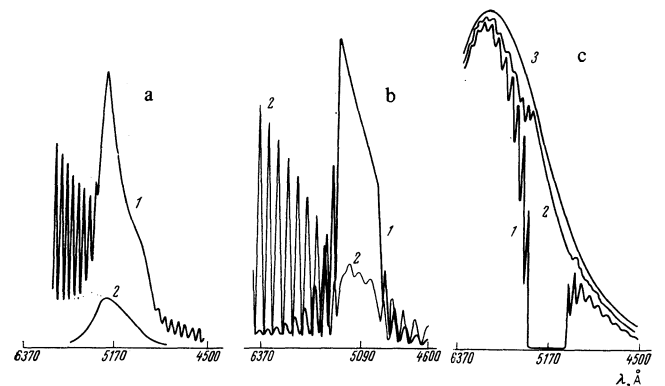


FIG. 4. Spectrograms of reflection: a) from plane-parallel cell ($d=10 \mu\text{m}$) after single advance at the measurement temperature (curves 1— $\varphi_i = \varphi_r = 20^\circ$, 2— $\varphi_i = 10^\circ$, $\varphi_r = 30^\circ$); b) for wedge shaped gap, complete ordering, $d=10 \mu\text{m}$, $\varphi_i = \varphi_r = 20^\circ$ (curve 1—left-circular polarized light I_- , 2—right circular polarized light I_+ , the scale of I_+ is increased 20 times); c) transmission spectrogram for the preceding objects (1—left-circular polarization, 2—right-circular polarization, 3—without sample). Mixture A, measurement temperature 20° .

TABLE I.

Number of band (number of half- turns)	$\Delta_m \lambda / \lambda$	
	Experiment	Calculation
4-5	0.22	0.23
8-9	0.12	0.11
15-16	0.063	0.050

to the wall attach themselves on the wall under the influence of the short-range forces in such a way that their directors are oriented along the direction of the rubbing and the shear.

The usual treatment of the Kano-Grandjean structure consists usually of the assumption that these forces exceed, within certain limits, the forces produced when the cholesteric helix is twisted or untwisted relative to the equilibrium configuration for the given temperature. As a result, the number of rotations (turns) of the helix in a wedge-shaped gap remains unchanged within the indicated limits, at the expense of the change of the pitch, i. e., the pitch increases with increasing gap thickness in one Grandjean layer with m half-turns, until the energy of the forced untwisting of the helix becomes equal to the energy of the forced twisting of a helix with $m+1$ half-turns. Further untwisting becomes energywise unprofitable, and a jumplike rotation of the boundary molecules through 180° takes place (or 360° , if the direction of the director in the anisotropic surrounding does matter), and another Grandjean layer with $m+1$ half-turns in the helix is produced. This is precisely the picture corresponding to Fig. 1. We note that the interval of variation of the quantity λ_m within the limits of one layer (20-30%) is close to that obtained under artificial tension and compression by Adams and Nelson^[12], in the same interval, lie the values of the pitch of the helix, which can be obtained by twisting the nematic structure by rotating one of the walls.

It is seen furthermore that over the extent of one band the value of λ_m changes almost linearly with d . One can therefore draw the following obviously primitive calculation. Assuming that within the limits of one band, corresponding to m half-turns, the pitch p varies like

$$p = p_0 + x/m, \quad -p_0/2 \leq x \leq p_0/2, \quad (1)$$

we can easily calculate that the relative jump in the pitch at the boundary between bands with m and $m+1$ half-turns is equal to

$$\frac{\Delta_m p}{p_0} = \frac{\Delta_m \lambda}{\lambda_0} = \frac{2m+1}{2m(m+1)}, \quad (2)$$

where λ_0 is the average value of λ for the given bands, and $\Delta_m \lambda$ is its jump on the boundary of the neighboring bands. Table I lists the values of $\Delta_m \lambda / \lambda$, calculated from formula (2) and obtained experimentally for the boundaries marked by the asterisks in Fig. 1. It is seen that the qualitative picture of the phenomena agrees with experiment in the first rough approximation.

If we assume the foregoing premise that within the

limits of one band the number of half-turns (between disclinations) remains unchanged, then the linearity of the variation of λ_m is dictated by the linearity of the wedge. We note the statements made repeatedly in^[1] that if there are no devices for "bilateral" orientation, the ratio p/d is apparently not an integer, since the variation of p with temperature in ordinary cells takes place, according to the data of all workers, smoothly and continuously, i. e., the ends of the helix are less rigidly fixed.

The change in the angles of the forced twisting of the entire helix in all the disclinations is the same and is equal to 180° . The change, per half-turn of a helix having m half-turns, is equal to $180^\circ/m$. Therefore when d (or m) is increased, the amplitudes of the crests on the curves decrease asymptotically, and the pitch tends to an equilibrium value p_0 of the free helix at the given temperature, as seen from Fig. 1.

To our knowledge, there are no rigorous theoretical calculations for the Kano-Grandjean structure. In^[5,13] are given, by way of a first-order approximation, schematic dependences of the pitch on the wedge thickness; they were based on additional assumptions that the value of p_0 does not change with thickness and that this value is obtained at the center of the interval between the disclinations ($p_0 = p_{av}$). The first assumption excludes the influence of the walls, according to which the dependence of the deformation energy U on p is symmetrical with respect to p_0 ($U \approx [(\Delta p)^2]^{1/2}$). These schemes agree, within the limits of the initial premises, with our results. The real situation, evidently, is more complicated.

Since the dependence of the helix deformation energy on its pitch p is undoubtedly strongly anharmonic, one should expect p_{max} and p_{min} (and respectively λ_{max} and λ_{min}) to be asymmetrically located relative to the equilibrium p_0 (λ_{eq}). It is seen from the figure, however, that when the layer thickness is decreased, the pitches—both the average and the extremal—increase. This shows that the very form of the dependence of the deformation energy and of the twisting torque on the pitch change with decreasing d . It appears that this is due to the increase of the relative role of the wall layers, i. e., to the difference between the pitch near the walls and at the center, since the wall forces are short-range; at small thicknesses, the contribution of the wall layers is relatively larger. This balance is considered in^[14] for a nematic crystal, and it is shown that indeed there exists a certain critical thickness, at which the action of the wall forces exceed the Van der Waals forces. The picture proposed above for the phenomena agrees with this conclusion. For thin layers, an estimate of the order of the critical thickness yields $\sim 0.5 \mu\text{m}$. In our case, an appreciable deviation of p_{av} from p_0 begins at $\sim 1.5-2 \mu\text{m}$ (i. e., four or five helix pitches), which agrees in order of magnitude with the estimate of Kats^[14] and with our results.^[1] It is difficult to carry out quantitative calculations, inasmuch as Kats^[14] considered nematic crystals and since the character of the orientation of the director in the plane of the wall, in the presence of rubbing and formation of a microrelief,

which plays an important role, lends itself with difficulty to mathematical formulation.

The increase of $\Delta\lambda$ for small d follows also from the theory for an ideal structure without wall effects (see, e.g.,^[10] where the theoretical curve agrees well with the data of our Fig. 2). The existing theories, however, start out from constancy of the pitch, and therefore for the region $d < 1.5\text{--}2\ \mu\text{m}$ of interest to us their direct utilization is difficult. It is probable that, besides the indicated factor, the increase of $\Delta\lambda$ is connected also with the appearance of a certain gradient of the pitch along the helix, inasmuch as the wall forces are short-range. This behavior of $\Delta\lambda$ in the presence of a pitch gradient was obtained in^[15]. A relatively larger broadening for thin layers was observed also in the case of mechanical motion.^[16]

We note incidentally that the theory of Helfrich and Hurault^[17] describes the deformation of the structure of CLC under the influence of an electric field; the period l of the deformation, in first-order approximation, also depends linearly on d within the limits of a single band:

$$l = ({}^{3/2}K_{11}/K_{22})^{1/2} (2/m)^{1/2} d, \quad (3)$$

where K_{11} and K_{12} are the elastic moduli for twisting and longitudinal bending, respectively. It is assumed in^[5] that these moduli change in thin layers, in agreement with our results.

GENESIS OF STRUCTURE

For a better understanding of the processes that occur in the investigated layers, it is necessary to trace the genesis of this structure; it is illustrated in Figs. 3 and 4.

When mixture B is molten in a plane-parallel cell to the isotropic phase, and subsequently cooled for 24 hours⁴⁾ without any orienting procedures, when a con-focal structure is produced, the selective reflecting is exceedingly weak and depends little on the incidence angle, thus indicating that the structure is disordered. Figure 3a shows reflection from the same compound after a displacement of the cover glass; the produced structure is still "polycrystalline," as can be seen from the character of the nonspecular reflection. The maxima of the SR at $\varphi_i = 0^\circ$ and $\varphi_r = 40^\circ$, according to the formula of Ferguson^[18] corresponds to an inclination of the layers relative to the wall by approximately $13\text{--}14^\circ$. The intensity of the SR increases by one and a half or two orders of magnitude.

This shift is produced here at the measurement temperature $T = 20^\circ\text{C}$ (approximately the midpoint of the mesophase interval). If the shift is made at the temperature of the transition to the mesophase (i.e., practically during the time of this transition) and the substance is then slowly cooled to the measurement temperature, then the SR band becomes noticeably narrower and more intense—the shift generates a more ordered structure in the course of the transition, Fig. 3b.

If we change to a wedge-shaped gap with all the indicated orienting procedures, then we obtain a highly or-

dered structure—Fig. 3c; the intensity of the central maximum is higher here by approximately one order than on Fig. 3b, and the intensity of the nonspecular reflection decreases below the sensitivity limit of the instrument.

Figure 4a shows the same characteristics as in Fig. 3a, but for different substances, while Fig. 4b shows the SR from a section of the wedge with planar structure for cylindrically polarized components. The picture is quite close to that obtained theoretically by Tur^[7] under the assumption of an ideal structure. The lateral interference maxima of the reflecting component I_r are weak in this case, and those of the transmitted component I_t are relatively more intense, inasmuch as the latter is influenced by a component due to reflection from the real wall (which in practice does not occur for I_r), while the component reflected by the CLC itself is of low intensity (none of the shown spectrograms have been corrected for the spectral composition of the source and for the dispersion in the case of the single-beam scheme). Figure 4c shows the phenomena in the volume.

For substances in which λ_m depends strongly on the temperature, it is much more difficult to obtain a homogeneous planar texture. Thus, for example, for cholesteryl pelargonate in a plane-parallel cell, when the compound is obtained from the isotropic melt by slow (6–8 hours) linear cooling in a thermostat ($\pm 0.05^\circ$), a single shift of the cover glass (inside the thermostat at the measurement temperature) usually results in an inhomogeneous picture: SR bands with λ_m ranging from ~ 6700 to $\sim 4700\ \text{\AA}$ are obtained in different sections. Since λ_m at given incidence angles and reflection angles depends only on the pitch, this means that the pitch of the helix is different in different regions. When thermostatically controlled, such pictures remain unchanged for 24 hours and more. In a thick layer, even in the same location in the cell, a broad band is obtained with several maxima that occupy approximately the same interval, i.e., a superposition of pictures obtained from regions of different depths takes place.

One cannot assume the presence of the temperature gradients, amounting to several degrees ($\sim 8\text{--}10$), which are needed for such changes. The mechanism whereby regions with different pitches are produced under conditions of thermostatic control and such a slow variation of the temperature consist apparently in the fact that the transition to the mesophase is not simultaneous at different points of the cell, be it only because of the random distribution of the nuclei (and the fact that CLC have an extended transition region), etc. Local release or absorption of the heat of the transition takes place in this case (Armitage and Price^[19] have shown that the heat capacity of cholesteryl pelargonate in the mesophase exceeds the heat capacity in other phases and varies with temperature). This in turn leads to a local change of the pitch (since, as shown, the action occurring in the transition region are "remembered" best of all). This phenomenon is particularly noticeable for pelargonate, where the dependence of the pitch on T is very strong.^[3,4] After a certain time, owing to the thermostatic control and the heat transfer (which are

slow in CLC), the temperatures and the heat fluxes become, naturally, completely equalized. It appears, however, that residual stresses and strains in various sections, similar to the stresses after quenching, do remain; to these must be added the local tensions produced in the course of orientation. The values of these tensions were estimated from the differences in the pitch; as seen from the figures, these differences are of the same order as in the Grandjean layers, i. e., the helices are compressed and are stretched here in the same limits, meaning the same balance between the wall and volume forces.

From all the foregoing we can conclude the following:

1. Our measurements show, with Kano-Grandjean structures and other structures as examples, that the influence of the method of orientation, primarily, and also the influence the shape of the cell and of the thermal prior history, change the pitch of the cholesteric helix at a given stable temperature within the limits up to 30–40% in some cases.
2. The degree of deformation of the cholesteric helix, at which the torque produced in it becomes equal to the forces of adhesion to the wall, can reach 25–30% of the pitch.
3. The pitch of the helix and the width of the reflection band at large thicknesses of the layer approach the equilibrium value, while at small thicknesses they increase substantially in comparison with the equilibrium value, i. e., the helix is "stretched" by the wall. The value of the critical thickness at which the stretching begins agrees with the theoretical estimate in order of magnitude.
4. The course of the stretching shows that the dependence of the deformation energy—twisting or untwisting of the cholesteric helix (and of the elastic of modulus for twisting)—on the pitch of the helix is essentially anharmonic and that probably the very form of the dependence changes as a function of the balance of the wall forces and the van der Waals interactions in the volume.

¹⁾We are most grateful to S. I. Belyaev and L. M. Blinov for reporting to us the details of the orientation technique developed by them (see also ^{5, 6}).

- ²⁾There is a misprint in^[1]. The wavelength scale in Fig. 4 should be shifted to the left by one division downward and by one and a half divisions upward.
- ³⁾The exact prescription of mixture A is given in ^[5], while the parameters of mixture B are given in ^[1, 4] (under its trade name "Liocrystal").
- ⁴⁾For the purpose of stabilization, the crystals were preconditioned in all cases by repeated remelting to the isotropic phase.

- ¹⁾Yu. V. Denisov, V. A. Kizel', and E. P. Sukhenko, Zh. Eksp. Teor. Fiz. 71, 679 (1976) [Sov. Phys. JETP 44, 357 (1976)].
- ²⁾E. I. Kats, Zh. Eksp. Teor. Fiz. 59, 1854 (1970) [Sov. Phys. JETP 32, 1004 (1971)].
- ³⁾Yu. V. Denisov, V. A. Kizel', E. P. Sukhenko, and V. G. Tishchenko, Tr. MFTI Fizika, No. 6, 193 (1975).
- ⁴⁾Yu. V. Denisov, V. A. Kizel', and E. P. Sukhenko, Kristallografiya 21, 991 (1976); 22, 339 (1977) [Sov. Phys. Crystallogr. 21, 568 (1976); 22, 192 (1977)].
- ⁵⁾S. I. Belyaev and L. M. Blinov, Zh. Eksp. Teor. Fiz. 70, 184 (1976) [Sov. Phys. JETP 43, 96 (1976)].
- ⁶⁾D. Berreman and T. Scheffer, Mol. Cryst. Liq. Cryst. 13, 223 (1972).
- ⁷⁾M. Tur, Mol. Cryst. Liq. Cryst. 29, 345 (1975).
- ⁸⁾S. Chandrasekhar and J. Shashidhara Prasad., Mol. Cryst. Liq. Cryst. 14, 115 (1971).
- ⁹⁾A. V. Tolmachev and A. S. Sonin, Fiz. Tverd. Tela (Leninograd) 17, 3090 (1975) [Sov. Phys. Solid State 17, 2048 (1975)]; Kristallografiya 21, 794 (1976) [Sov. Phys. Crystallogr. 21, 450 (1976)].
- ¹⁰⁾V. A. Belyakov, D. E. Dmitrienko, and V. P. Orlov, in: Kholestericheskie zhidkie kristally (Cholesteric Liquid Crystals), izd. SO Akad. Nauk SSSR, Novosibirsk, 1976, p. 35.
- ¹¹⁾J. Shashidhara Prasad, J. Phys. (Paris) 36, C1, 289 (1975).
- ¹²⁾J. Adams and K. Nelson, Mol. Cryst. Liq. Cryst. 31, 319 (1975).
- ¹³⁾C. Gerritsma, W. Goossens, and A. Nussen, Phys. Lett. A34, 354 (1971).
- ¹⁴⁾E. I. Kats, Zh. Eksp. Teor. Fiz. 70, 1394 (1976) [Sov. Phys. JETP 43, 726 (1976)].
- ¹⁵⁾S. Mazkedian, S. Melone, and F. Rusticelli, J. Phys. (Paris) 36, C1, 283 (1975); 37, 731 (1976).
- ¹⁶⁾D. Ciliberti, G. Dixon, and L. Scala, Mol. Cryst. Liq. Cryst. 20, 27 (1973).
- ¹⁷⁾J. Hurault, J. Chem. Phys. 59, 2068 (1973).
- ¹⁸⁾J. Ferguson, Mol. Cryst. Liq. Cryst. 1, 293 (1966).
- ¹⁹⁾D. Armitage and F. Price, J. Phys. (Paris) 36: C1, 133 (1975).

Translated by J. G. Adashko