Critical case of the onset of smectic order in the cholesteric metaphase

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A new phenomenon was observed in certain cholesteric crystals, namely a nonmonotonic variation of the pitch P of the helical structure when the crystal is cooled at a rate exceeding a certain critical value: the function $P(T)$ has a maximum near the lower temperature limit of the cholesteric mesophase, whereas under ordinary conditions (in slow cooling) there is no maximum. The phenomenon is analyzed within the framework of the existing theoretical models. It is shown that it can be due to the appearance of critically small smectic fluctuations when a temperature gradient is produced. A quantitative estimate is obtained of the change of the characteristic-lengths ratio needed to observe the phenomenon in the liquid crystal. The possibility of practical use of this phenomenon is noted.

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For liquid-crystal (LC) substances that are capable of formation of both cholesteric and smectic mesophases, characteristic pre-transition phenomena are observed in the vicinity of the cholesteric—smectic phase transition. In particular, a strong increase of the pitch P of the helical structure (untwisting of the helix) is observed when the phase-transition temperature T^* is approached. This effect was investigated in a number of studies,[1–5] whose results make it possible to obtain a general idea of the phenomenon from the point of view of the order of the macrostructure.

According to contemporary concepts,[1,4,5] the physical gist of this phenomenon is that the local fluctuating regions with ordering of the smectic type, which appear at temperatures close to the phase transition, interact with the field of the director and lead to the appearance of an additional contribution to the free energy of the liquid crystal. The quantity $\alpha(T)=2\pi/P$, which minimizes the free energy, tends in this case to zero, i.e., $P\to\infty$. To analyze the change of the pitch P of the structure, the theory makes use of the analogy between the smectic A phase and a superconductor.[4,5]

In the cited papers, the phenomenon has been investigated for smectogenic cholesterics under thermodynamic-equilibrium conditions. As noted by us previously,[6] under nonequilibrium conditions the picture becomes more complicated—an increase in the cooling rate increases noticeably the range of variation of the pitch of the structure of the smectogenic cholesteric. If at the same time the smectic fluctuations are critically small, the phenomenon acquires qualitatively new features, and it is these which are the subject of the present paper.

EXPERIMENT

The pitch P of the structure is determined from the spectra of the selective transmission with the aid of the known relation $\lambda_{\max}=P\bar{n}$ ($\bar{n}=1.5$), where $\lambda_{\max}$ is the wavelength of the peak of the selective curve. A selective-transmission spectra were plotted with an SF-8 spectrophotometer at normal incidence of the light, using a unified procedure whose details were described earlier[6,7].1) Orientation by shear was effected at temperatures several degrees lower than the isotropic transition. The sample in a flat cell, with a real planar texture that is controllable under the microscope, had a LC layer thickness 12 μm.

For all the curves given below, with the exception of the one plotted in fast cooling, measurements of the selective transmission were carried out in isolated temperature points within the limits of the mesophase. The accuracy of the temperature stabilization was ±0.03 °C. Before the measurement, the sample was maintained at each temperature point for 15–20 minutes to attain thermal equilibrium.

RESULTS AND DISCUSSION

Figures 1 and 2 show plots of $\lambda_{\max}(T)$ for the members of the homologic series of 4-n-alcoxybenzoates of cholesterine. The higher homologs, starting with the seventh, are smectogenic, as is well seen on the plot of $\lambda_{\max}(T)$ by the sharp increase of $\lambda_{\max}$—untwisting of the helix—in the region of the phase transition, in analogy with the results of Refs. 1–5. For these homologs, at zero cooling rate, the maximum fixed value of the pitch P was proportional to this rate. A qualitatively new phenomenon was observed for homolog No. 6 (4-n-hexyloxybenzoate) of cholesterine, a fast twisting of the helical structure after its ordinary untwisting in monotonic cooling at a rate higher than a certain critical value (Fig. 3). The maximum value of $\lambda_{\max}$, as is seen, reaches 615 nm, compared with 480 nm when cooling with near-zero rate, and in the subsequent twisting it decreases to 556 nm, after which crystallization takes place.

For curve 2 of Fig. 3, the rate of cooling is ~6.5 deg/min in the region of the peak of the curve. The critical cooling rate at which the derivative $d\lambda_{\max}/dT$ reverses sign is 5–6 deg/min, and at lower rates, as usual, $d\lambda_{\max}/dT<0$, and the largest $\lambda_{\max}$ reaches in this case, in proportion to the cooling rate, values intermediate between 615 and 480 nm.

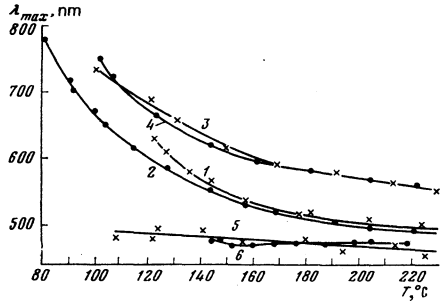

FIG. 1. Plot of $\lambda_{max}(T)$ for 4-*n*-alcoxybenzoates: homologs Nos. 1–6: $H_{2x+1}C_xO{-}C_6H_4{-}COO{-}Hol$ ($x=1{-}6$, Hol is the cholesterine core). The high-temperature parts of curves 1–4 are not shown.

A similar phenomenon was observed by us (at higher cooling rates) for the nonsmectogenic 2-chlorbenzoate of cholesterine, for which the maximum value of λ_{max} reached ~600 nm as against ~380 nm in slow cooling, with a return to ~570 nm.

That the observed phenomenon is connected with the onset of smectic order is indicated by a number of data. Homolog No. 6 does not form a smectic phase, but this does not exclude the possibility of its containing small smectic fluctuations in view of the proximity of the molecular structure to the structure of homolog No. 7, which forms this phase. For homolog No. 6, the smectic phase can be monotropic. In the literature there are certain qualitative indications that the produced structures depend on the rate of melting or crystallization. In Ref. 8 (see also Ref. 9) it was noted that for substances, which under ordinary conditions do not have a mesophase, symptoms of a cholesteric mesophase appear in very slow cooling or very fast cooling followed by melting, i.e., the cholesteric phase in these substances is monotropic. It seems that in our case we are faced with monotropy of the smectic phase. In the homolog No. 6 a weak growth of λ_{max} is observed near the crystallization temperature (compare curve 6 of Fig. 1 with curve 5), and in analogy with the three higher homolog, smectogens, it has under ordinary conditions no noticeable supercooling ($T_{melt}=146$ °C), whereas the three closest lower homologs become supercooled by more than 10 degrees below the melting point. This favors the presence of small fluctuations in the homolog No. 6.

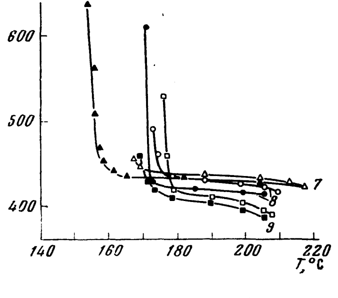

FIG. 2. Plot of $\lambda_{max}(T)$ for 4-*n*-alcoxybenzoates: homologs Nos. 7–9: $H_{2x+1}C_xO{-}C_6H_4{-}COO{-}Hol$ ($x=7{-}9$, Hol is the cholesterine core). Contour points—heating, solid—cooling.

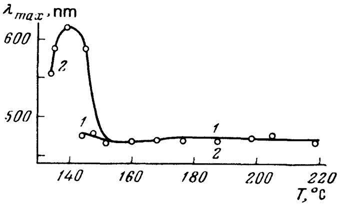

FIG. 3. Dependence of $\lambda_{max}(T)$ for 4-*n*-hexyloxybenzoate of cholesterine (homolog No. 6) at various (average) rates of cooling of the mesophase: 1—≤0.2 deg/min (corresponds to curve 6 of Fig. 1), 2—~6.5 deg/min.

Taking this into account, the described phenomenon can be interpreted within the framework of the existing theoretical model of Vigman and Filev.[5] They have shown[5] that the behavior of cholesteric liquid crystals near a phase transition is determined by three characteristic lengths—the correlation length $1/\xi$ in the *xy* plane perpendicular to the helix axis z, the depth ω of penetration of the twist deformations, and a length connected with the spatial inhomogeneity of $1/\xi$ along the z direction (or the homogeneity length ξ, for example, $1/\xi=0$ for nematics). An estimate of the change δP of the pitch under the influence of the smectic fluctuations gives the ratio[5]

$$\delta P/P_0=(P-P_0)/P_0>8\text{Gi}\,\beta, \qquad (1)$$

where P_0 is the pitch of the helix in the absence of fluctuations, $\beta=\omega/\xi$, and Gi is the Ginzburg parameter, a small quantity ($\leqslant 0.1$) defined as the ratio of the singular part of the heat content of the cholesteric phase to the heat content of the smectic phase calculated by the Landau theory. As indicated above, the smectic phase can be regarded as monotropic, a fact that justifies the formal introduction of the parameter Gi in this case. In Ref. 5 they used the self-consistent-field approximation and have shown that the corresponding smallness of the parameter Gi makes it possible to regard the fluctuations as small and to take them into account by using perturbation theory.

Within the framework of this model, the described phenomenon can be due to enhancement of the action of the small fluctuations on the pitch of the helix because of the appearance of a temperature gradient that leads to a change in the ratio of the characteristic lengths. Rapid cooling of a flat cell undoubtedly leads to the appearance of a noticeable temperature gradient along the z axis (perpendicular to the cover glasses), and this produces gradients in the density, in the pitch P, and apparently also dynamic deformations. The homogeneity length ξ therefore decreases rapidly along the z axis, whereas there are no grounds for assuming that the lengths ξ and ω change considerably. Then δP increases, as does also the quantity $\beta=\omega/\xi$ in accordance with relation (1). In the cooling process, the gradient of T decreases gradually because of equalization of the temperatures in view of the difference between the masses of the thin liquid crystal film and the cell. Then β begins to decrease and the change of P is reversed.

Such a situation can occur only if the fluctuations are so small that under ordinary conditions—in slow cooling—they produce no increase, or hardly any increase, of P (i.e., the fluctuations are weaker than those considered in Ref. 5). Such a picture can hardly be observed in smectogenic cholesterics, inasmuch as for these substances the enhancement of the smectic fluctuations near the phase-transition temperature is a natural pre-transition process[1-5]—under these conditions the contributions of other factors are of the same order of or larger than the contribution of the gradient of T, so that for these substances only an increase of the range of variation of P is increased. The absence in this case of a reversal of the variation of P is possibly due also to the dimensions of the region of absolute instability of the cholesteric state near T.[5] Since homolog No. 6 does not form an enantropic smectic phase, the parameters of its region are different.

From Fig. 3, using relation (1), we can estimate the change of β corresponding to change of P in the experimental situation. For curve 1 we have $\delta P/P_0 \approx 10$ nm /470 nm $= 0.02$; for curve 2 we have $\delta P_{\text{crit}}/P_0 \approx 135$ nm /480 nm $= 0.28$. Using the estimate of Ref. 5 for the Ginzburg parameter ($\text{Gi} \approx 0.1$), we have

$$\beta_{\text{crit}} \approx 14\,\beta, \tag{2}$$

i.e., the described phenomenon is observed when the ratio ω/ξ of the two characteristic lengths changes by approximately one order of magnitude compared with the ordinary conditions.

The estimate (2) must be regarded as approximate in view of a certain uncertainty in the value of the parameter Gi under nonequilibrium conditions. In addition, it is doubtful whether it is possible to use here the self-consistent field approximation, within the framework of which relation (1) was obtained. It is shown in Ref. 5 that the analysis there is valid in the region $T - T_{\text{crit}} > 0.4$ °C. Recognizing that in our case the fluctuations are much weaker, and T^* and T_{crit}, because of the monotropy, are shifted towards lower temperatures, it can be assumed that this approach is valid for the greater part of the peak of curve 2 of Fig. 3. For a more accurate estimate, of course, it is necessary to take into account the nonequilibrium fluctuations, the singularities of the kinetics of the growth of the smectic formations,[10] and other factors. It should be noted that the possibility of a nonmonotonic dependence of the helix pitch on the temperature for cholesteric liquid crystals was predicted by the theory[11] on the basis of an analysis of the forms of the anharmonicity of the potential curves of the intermolecular forces, and the question of the equivalence of this analysis to that given by us above should be considered separately.

It is important to note in conclusion that the observed effect can be not only of scientific interest—in the sense of studying the physics of phase transitions—but also of practical interest, especially when it comes to producing nonequilibrium states by applying electric or magnetic fields, pressure, or laser radiation (the so called recording with laser thermal addressing). In the latter case, since the principal role is played here not by the value of the temperature but by the gradient, the rate of recording can be increased.

1) The same reference gives data on the purity of the substances, on methods of purification, and on elimination of extraneous phenomena connected with the impurities.

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