Pretransition phenomena in cholesterics with a short helix pitch

V. A. Kizel' and S. I. Panin
Moscow Physicotechnical Institute

(Submitted April 9, 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 2, 74–77 (25 July 1986)

A method of circular dichroism has been used to study a cholesteric liquid crystal near the transition from the blue phase to an isotropic liquid and in the region in which this liquid is superheated. Pronounced fluctuations are observed within about 1 °C of the transition point. They contribute to a "structural" circular dichroism. Their spectrum and temperature dependence have been measured.

Most liquid crystals which exhibit a cholesteric phase with a short helix pitch produce so-called blue phases in the vicinity (~ 1–$2°$) of the transition to an isotropic liquid. In general, three thermodynamically stable phases can exist (Ch↔BPI↔BPII↔BPIII↔IL). The general features of the structures of BPI and BPII have been determined, while the structure of BPIII is not yet clear. It is also known that "pretransition phenomena" are observed near the BP↔IL transition; these phenomena are usually attributed to local fluctuations of the order parameter. Since the transition is nearly a second-order transition, these fluctuations can reach a considerable size.

In this letter we report a study of the course of events near the BPIII↔IL transition by means of measurements of the circular dichroism. The measurements are taken with a Jobin Yvon Mark III dichrograph; the techniques for preparing the samples and for maintaining a constant temperature are described in Ref. 2. We selected cholesterol nonanoate for this study. In the mesophase it forms a left-handed spiral, so that the "structural" circular dichroism is positive in the region of selective reflection. The peak of the selective reflection in the cholesteric phase (before the transition to the blue phase) is 360 nm. The nonanoate molecules exhibit a negative circular dichroism in their absorption region, according to measurements in a solution or melt. Near the nonanoate absorption band ($\lambda \lesssim 220$ nm), the negative molecular dichroism outweighs the structural dichroism, and one observes a characteristic bend on the curve (Figs. 1–3). Extensive preliminary measurements showed that the nature of the spectrum of the circular dichroism of BPIII varies only slightly as the thickness of the sample is varied from 9 to 100 μm (Fig. 2) and depends on neither the presence nor nature of an orienting coating. In these regards, this spectrum differs from those of the first two blue phases, whose orientation changes substantially depending on the coating. The circular dichroism in the isotropic liquid changes only in magnitude; the spectrum retains the same shape. Figure 1 shows spectra of the circular dichroism obtained for samples 100 μm thick without a coating. The spectra are labeled by the order of the measurements.

The BPIII that was obtained was cooled (curves 1 and 2) to the point at which nucleating regions of BPII appeared, as selective-reflection peaks (curve 3). The

 0021-3640/86/140093-04$01.00

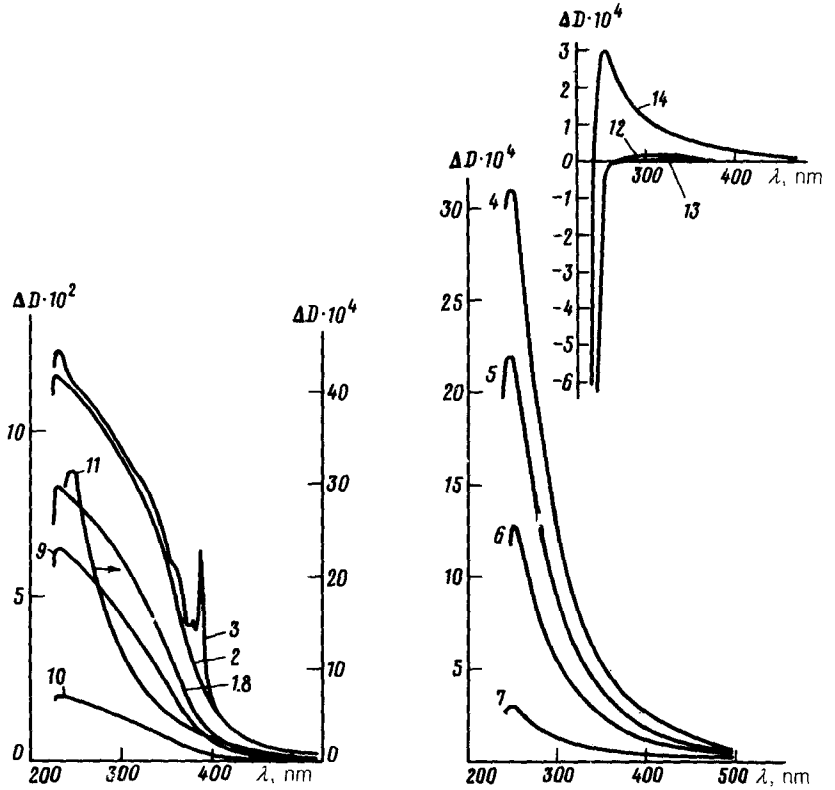

FIG. 1. Circular dichroism of a cholesterol nonanoate sample 100 μm thick. The temperature of the transition to the isotropic phase is $T_c = 90.85 \pm 0.005$. 1—90.820 (BPIII); 2—90.800 (BPIII); 3—90.785 (BPIII + BPII); 4—90.855 (IL); 5—90.890 (IL); 6—91.000 (IL); 7—91.730 (IL); 8—90.820 (BPIII); 9—90.835 (BPIII); 10—90.845 (BPIII); 11—90.855 (IL); 12—123.3 (IL); 13—94.06 (IL); 14—92.0 (IL).

BPIII was then melted to an isotropic liquid and heated (curves 4–7). A subsequent cooling to BPIII (curve 8; 1 and 8 are slightly different) and a reheating to the isotropic liquid (curves 9–11) show that the form of the circular dichroism, which is typical of BPIII and the isotropic liquid, does not depend on the thermal history of the sample (at the accuracy with which the temperatures are reproduced). A further heating (curves 12–14) erases the structural circular dichroism, and in the region 3–30° we are left with only molecular circular dichroism. There is no change in the shape of the curves (12, 13). The spectra of BPIII and the isotropic liquid are quite different.

We thus see that the region of very large fluctuations which contribute the "structural" circular dichroism is small: on the order of 1° from the melting point. Hornreich and Shtrikman[3] have examined the possibility of describing BPIII as highly developed pretransition fluctuations. The present study has shown that there is a fundamental difference between BPIII and fluctuations in the isotropic liquid. The spectrum in the isotropic liquid and the orders of magnitude of the circular dichroism correlate with

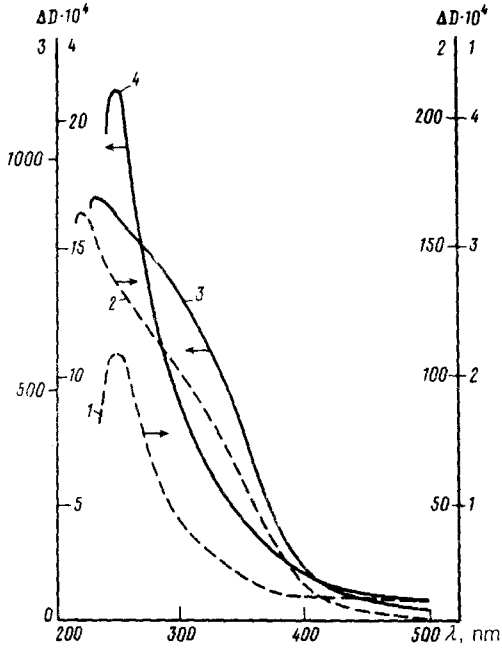

FIG. 2. Circular dichroism of cholesterol nonanoate, for samples 100 μm thick (solid lines) and 9 μm thick (dashed lines), for BPIII (2, 3) and the isotropic liquid (1, 4). The labels on the ordinate scales match the curve labels.

the estimates in Ref. 3. The spectrum in the isotropic liquid can be described extremely well by a power law $\Delta D = A(T)/\lambda^{\alpha}$ with an exponent $\alpha = 5.4 \pm 0.2$ at all temperatures. In order to compare this spectrum with the theoretical spectrum, it will be necessary to take into account the dispersion of the refractive index and of the anisotropy for x-nonanoate in this region. Nevertheless, we can interpret the temperature

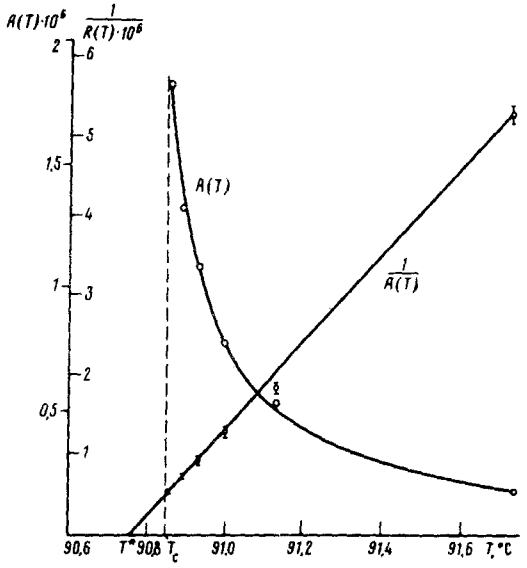

FIG. 3. Temperature dependence of the coefficient $A(T)$ and of its reciprocal, $1/A(T)$. The transition temperature is $T_c = 90.85 \pm 0.005$, $T^* = 90.76 \pm 0.01$.

dependence. The temperature dependence $A(T)$ shown in Fig. 3 can be approximated well by the expression.

$$A(T) = \frac{A_0}{T - T^*} ,$$

where $T^* = 90.76\,^\circ\text{C} \pm 0.01$ and $T_c = 90.85\,^\circ\text{C} \pm 0.01$ (the point of the transition to the isotropic liquid); i.e., we have $T_c - T^* = 0.09 \pm 0.01$.

The theoretical descriptions of pretransition phenomena[4] deal primarily with fluctuations in the mode of a conical spiral, and they assume a square-root dependence of the rotation of the polarization plane of the light or of the circular dichroism on the distance from the transition temperature $[\sim (T - T^*)^{-1/2}]$, with $T_c - T^* \simeq 1^\circ$. A dependence of this sort has been observed experimentally in measurements of the rotation[5] at distances from the transition up to tens of degrees (cf. also Ref. 6).

The phenomenon described in the present letter apparently operates by some other mechanism.

We wish to thank V. A. Belyakov and V. E. Dmitrienko for useful discussions.

[1]V. A. Belyakov and V. E. Dmitrienko, Usp. Fiz. Nauk **146**, 369 (1985) [Sov. Phys. Usp. **28**, 535 (1985)].
[2]V. A. Kizel' and V. V. Prokhorov, Zh. Eksp. Teor. Fiz. **87**, 450 (1984) [Sov. Phys. JETP **60**, 257 (1984)].
[3]R. M. Hornreich and S. Shtrikman, Phys. Rev. A **28**, 1791 (1983).
[4]S. Cheng and R. B. Meyer, Phys. Rev. A **9**, 2744 (1974); D. Bensimon, E. Domany, and S. Shtrikman, Phys. Rev. A **28**, 427 (1983); V. M. Filev, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 625 (1978) [JETP Lett. **27**, 591 (1978)].
[5]V. K. Dolganov *et al.*, Zh. Eksp. Teor. Fiz. **78**, 2343 (1980) [Sov. Phys. JETP **51**, 1177 (1980)]; Pis'ma Zh. Eksp. Teor. Fiz. **38**, 368 (1983) [JETP Lett. **38**, 445 (1983)].
[6]V. P. Romanov and A. N. Shalaginov, Opt. Spektrosk. **59**, 386 (1985) [Opt. Spectrosc. **59**, 231 (1985)].

Translated by Dave Parsons