Quasiperiodic structures in multicomponent mixtures of nematic liquid crystals in the region of the nematic liquid crystal–isotropic liquid phase transition

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We have observed the appearance of quasiperiodic structures in multicomponent nematic liquid crystals in the region of the nematic liquid crystal–isotropic liquid phase transition. © *1995 American Institute of Physics.*

A unique property of oriented liquid crystals, which determines whether a series of effects can be observed in them (for example, nonlinear optical effects), is the collective nature of the response to an external force. Specifically, the periodic distortions of the director field (square lattices) in oriented liquid crystals[1,2] and some features of a phase transition in homeotropically oriented OCB crystals[3] are determined by the collective aspect of the response to external forces.

In addition to one-component liquid crystals, investigators are also interested in multicomponent mixtures of liquid crystals,[1] which are essentially liquid-crystalline substances with new properties. The collectiveness of the response to external actions in mixtures can play a special role in structural changes occurring in them and, primarily, near a phase transition, which for mixtures is well known to be diffuse; i.e., it occurs in a certain temperature interval.

In the present study we observed spatial quasiperiodic structures in multicomponent mixtures near the nematic liquid crystal–isotropic liquid phase transition. The collective nature of the response of a homeotropically oriented crystal plays a definite role in the formation of such structures.

Experimental conditions and experimental results. We investigated homeotropically oriented ZHKM-1277 nematic liquid crystals (produced by the Main Scientific Center of the Russian Federation, Scientific-Research Institute of Organic Intermediate Products and Dyes; the phase transition is a nematic crystal–isotropic liquid transition near ~60°C) and E-63 liquid crystals (produced by the Merck Company, phase transition near ~80°C), which are multicomponent mixtures (specifically, ZHKM-1277 is a mixture of five components, 80% of the mixture consisting of cyanobiphenyl). The main part of the investigations was conducted with the ZHKM-1277 crystal. The thickness L of the experimental samples was equal to 40 μm or 100 μm. The cell with the crystal was placed in a temperature-controlled chamber. The crystal was illuminated with a beam of polarized light from a cw argon-krypton laser with low power P (approximately several mW) and a wavelength of 6471 or 5145 Å. A film analyzer was placed in the path of the

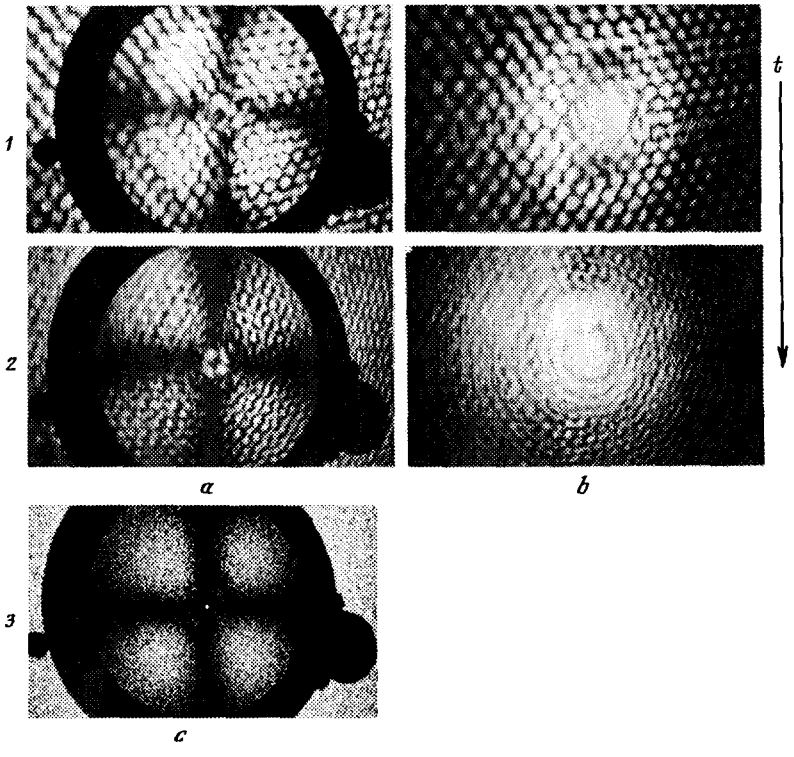

FIG. 1. Diffraction pattern as a function of $\Delta t = t - t_0$: *1* — $\Delta t = 1.5°$, *2*, *3* — $\Delta t = 2°$, *1*, *2* — narrow light beam, *3* — wide light beam; a, c — in crossed polarizers, b — no analyzer.

beam behind the crystal, and a screen, on which the changes occurring in the beam transmitted through the crystal were observed, was placed behind the analyzer. The changes occurring in the crystal itself could be observed on the screen with a microscope which gave a magnification of ~400.

The results can be summarized as follows. 1. The structure of the light beam transmitted through the crystal starts to change as the temperature t of the NLC increases and approaches the region of the phase transition: At some temperature $t_0 \sim 60°$C a diffraction patterns appears on the screen behind the crystal. A diffraction pattern is observed in the temperature range $\Delta t = t - t_0 = 1.5 - 2°$; the photographs in Fig. 1 illustrate it. The photographs in Fig. 1 (curves *1* and *2*) correspond to a narrow light beam (diameter ~100 μm) and the photograph in Fig. 1 (curve *3*) corresponds to a wide light beam (diameter ~2000 μm). The appearance of a diffraction pattern indicates that the crystal produces anisotropic formations which diffract the light beam that passes through the crystal. The difference of the diffraction patterns observed in the narrow and wide light beams indicates that the anisotropic formations are not distributed in the crystal randomly but rather quasiperiodically.

2. The diffraction pattern at constant temperature t of the crystal depends on the irradiation time T. This dependence is different (see Fig. 2) for thick and thin crystals

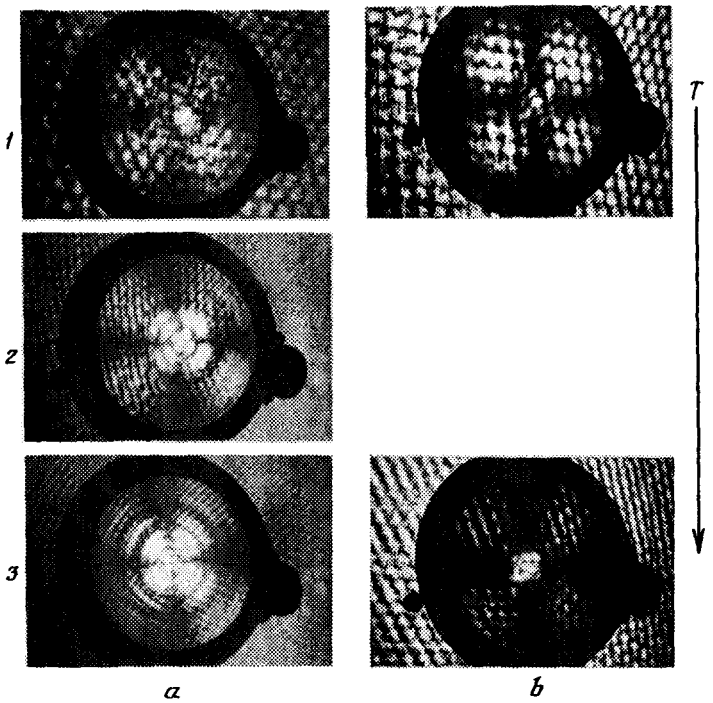

FIG. 2. Diffraction pattern as a function of the irradiation time T for thick ($L=100$ μm, $P=5$ mW) (a) and thin ($L=40$ μm, $P=10$ mW) (b) crystals at constant temperature in the region of the phase transition. Crossed polarizers. *1* — $T=30$ s, *2* — $T=2$ min, *3* — $T=10$ min.

(this is seen especially clearly in crossed polarizers). At $T\leqslant 30$ s the diffraction patterns for the thick ($L=100$ μm) and thin ($L=40$ μm) crystals are virtually identical. But for $T>30$ s a large difference is observed. This difference increases with increasing T: An additional bright cross with arcs appears against a background cross and a diffraction grating with $L=100$ μm. The intensity of the cross with a grating decreases rapidly as T increases.

Estimates of the dimensions of the anisotropic formation, used to scatter the light beam, which can lead to the appearance of a cross with arcs, from the angular dimensions of the cross with the arcs give a value of ~ 0.5 times the diameter of the light beam in the zone of the crystal.

3. The texture of the crystal observed under a microscope is shown in Fig. 3. As the temperature of the crystal increases, there appears a system of spots (in the crossed polarizers — crosses consisting of spots), the distance between which is characterized by some quasiperiod. The time dependence of the texture of the crystal at constant temperature is similar to the temperature dependence: The total number of anisotropic formations which arise decreases and their dimensions increase.

4. The quasiperiod of the distortions of the director field depends on the temperature t of the crystal, and for constant t it also depends on the time T. The increase in t

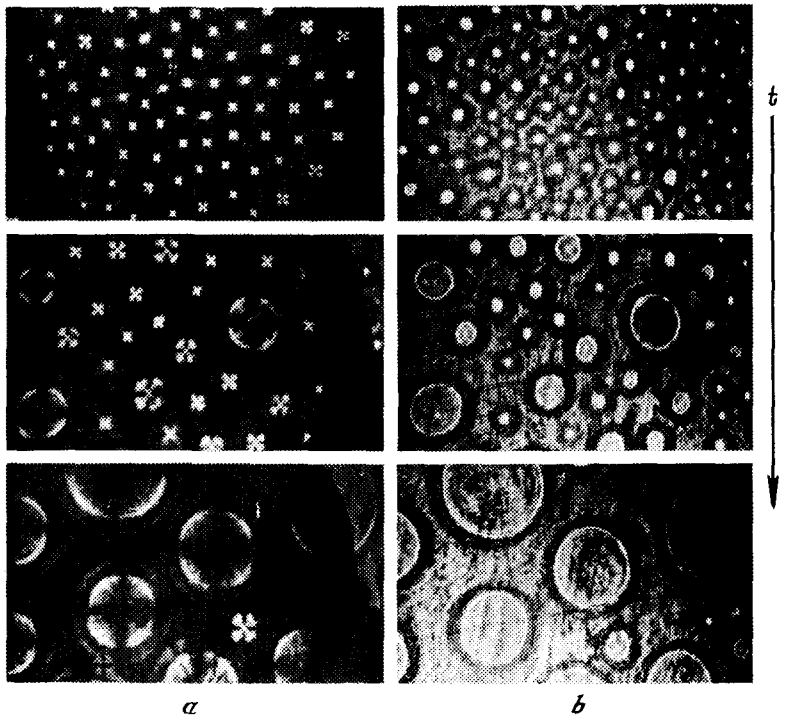

FIG. 3. Crystal texture as a function of temperature in the region of the nematic liquid crystal–isotropic liquid phase transition. a — Crossed analyzers, b — no analyzer.

increases the length of the quasiperiod. The quasiperiod falls in the range 30–100 μm, depending on t. These same values are also obtained from the diffraction pattern. At a constant temperature the quasiperiod increases with increasing T (minutes, tens of minutes, depending on t).

5. The rate of decrease of the quasiperiod with increasing time T at a constant temperature of the crystal depends strongly on the thickness L of the crystal. For a thick crystal ($L=100$ μm) it is much larger (~ 10 times) than for a thin crystal ($L=40$ μm).

6. The dynamics of the anisotropic formations, which the microscopic system allows one to study, reduces at constant temperature t to a slow (minutes) increase of their size and decrease of their total number. As the temperature increases, this process proceeds at virtually the same rate as the rate of heating of the cell.

7. The results obtained with the E-63 crystal are similar to the results obtained with the five-component mixture ZHKM–1277.

Discussion of the results. It is well known that phase separation is possible with a diffuse phase transition.[4] Analyzing the results obtained, it is natural to assume that drops of an isotropic liquid appear in the crystal when the temperature of the crystal is higher than the temperature at the lower limit of the temperature interval of the diffuse phase

transition in the crystal (phase separation occurs). Under the influence of the forces acting on the nematic liquid crystal–isotropic liquid interface, the initial homeotropic orientation of the director near a drop becomes distorted, and elastic moments, which attempt to restore the initial distribution, arise. Ultimately, there appears in the crystal a new equilibrium distribution of the director field with a transition from a homeotropic orientation of the nematic phase, with a degree of ordering of the molecules close to one, to regions of an isotropic phase with a zero degree of ordering. The deformations of the director field in the vicinity of each drop are axisymmetric, and for this reason crosses are observed in the crossed polarizers in the microscope.

We now discuss the quasiperiodicity in the spatial arrangement of the drops. Ordering in their distribution can be produced by the forces acting between the drops in the director field deformed by them (the existence of forces of this nature was pointed out in Ref. 5). For an ideal crystal, it should be expected that a periodic distribution of the drops will be energetically favored. According to the experimental data, for a real crystal it is quasiperiodic.

The time over which a new equilibrium distribution of the director field is established as a result of the collective nature of the process of reorientation of the molecules in the vicinity of the drops should be quite long. The results obtained (tens of seconds, minutes) support this assertion. The new distribution of the director field under the conditions of the experiment (instability of the crystal temperature, presence of defects in real crystals, and others) is a quasiequilibrium distribution. The drops increase in size, though slowly (minutes).

Many (~ 10) orders of diffraction of approximately equal intensity are observed in the diffraction pattern of a narrow light beam diffractted by a quasilattice whose period is 1–3 times smaller than the diameter of the beam. This can be attributed to the fact that the periodically deformed director field modulates the phase of the light field. The intensities of the higher diffraction orders charactristically decrease more slowly for phase gratings than for amplitude gratings.[6]

The dependence of the temporal evolution of the diffraction pattern on the thickness of the crystal indicates that the quasiperiodic structures are more stable with respect to the action of a light beam in a thin crystal. This stability is evidently associated with the stabilizing orientational effect of the walls, which is more efficient in a thin crystal. In a thick crystal, even a weak optical radiation gives rise not only to blurring of the quasiperiodic diffraction pattern, but also to the appearance of a bright cross with arcs in the scattering. This indicates that an additional anisotropic axisymmetric structure is formed in a thick crystal.

In summary, in the present work we discovered the appearance of spatial quasiperiodic structures in multicomponent mixtures of nematic liquid crystals in the region of the nematic crystal–isotropic liquid phase transition.

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