Light-induced reorientation of a smectic liquid crystal with memory

A. S. Zolot'ko and V. F. Kitaeva
P. N. Lebedev Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia

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Experiments reveal that linearly polarized light (at $\lambda = 6471$ Å) can convert the homeotropic texture of the smectic phase of the liquid crystal OCBP with an impurity of the azo compound methyl red into a stable confocal texture (this is a memory effect). In the latter texture, there is a predominant orientation of the confocal domains in the direction perpendicular to the electric field of the light wave.

The effective photoisomerization of azo compounds[1,2] makes it possible to observe some physical effects of scientific and practical interest in substances containing these compounds. For example, a reversible orientational photochroism[3,4] is observed in viscous solutions containing azo compounds when they interact with the light. A change in the orientation of the director of a nematic liquid crystal between surface layers containing azo compounds has been observed upon the application of UV light[5] and green light.[6] A reorientation of the director in a planar nematic liquid crystal has also been observed in the interaction of light with a crystal containing an impurity of an azo compound in its interior, rather than at its surface.[7]

In this letter we are reporting a study of the interaction of light with a smectic liquid crystal containing an azo-compound impurity.

Experimental procedure and results. The experimental apparatus consisted of a cw krypton ion laser ($\lambda = 6471$ Å), a double Fresnel rhomb for rotating the polarization plane of the incident light, a lens ($f \simeq 135$ mm) which focused the laser light into the homeotropically oriented crystal of octyl cyanobiphenyl (OCBP) containing a dye (methyl red) in a concentration $\sim 1\%$, a screen behind the crystal for observing changes which occurred in the beam, and a polarizer, in front of this screen, for analyzing the light transmitted through the crystal. The changes which occurred in the crystal were studied by photography with the help of a polarizing microscope. The thickness of the test crystal was $L \simeq 40$ μm.

The experimental results can be summarized as follows.

1. The light beam transmitted through the liquid crystal has changed in shape and polarization.

2. These changes occur not immediately after the crystal is illuminated but after a time T_{del}. This time depends on the beam power P and the crystal temperature t. Specifically, as t or P decreases, the time T_{del} increases: at $P \simeq 160$ mW and $t \simeq 23$ °C we find $T_{\text{del}} \simeq 3$ min, while at $t \simeq 24$ °C we find $T_{\text{del}} \simeq 1$ min.

3. After a time T_{del}, a "cross" appears on the screen in crossed polarizers; as time

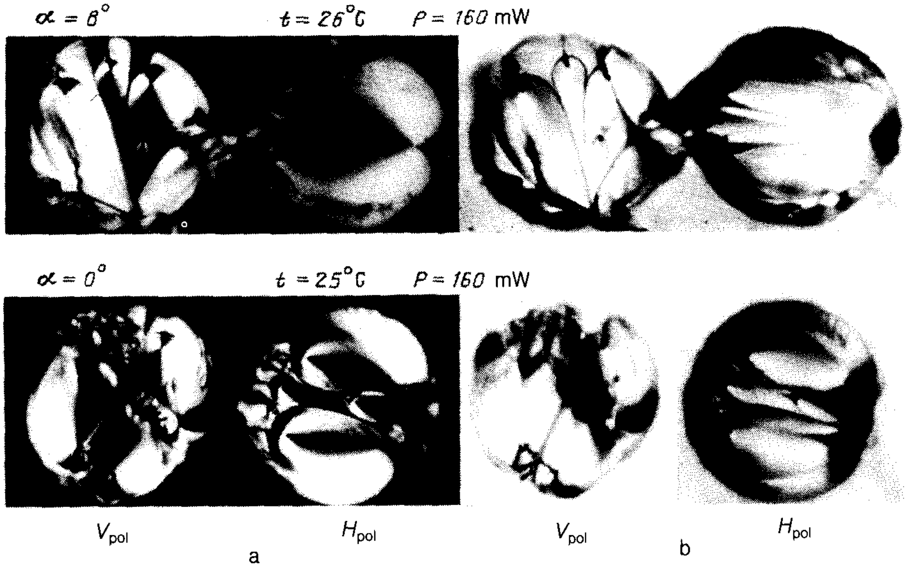

FIG. 1. Distortions of the director field caused by the laser light as a function of the polarization of this light. a—Crossed polarizers; b—parallel polarizers. V_{pol}) The incident light is polarized vertically; H_{pol}) horizontally in the plane of the cell, perpendicular to $\mathbf{k}$ (the wave vector) and $\mathbf{n}_0$ (the director).

elapses, this cross shrinks. Arcs appear around it. In the absence of the analyzer, we observe a spot, smaller than that at the beginning of the illumination, surrounded by rings. The number of rings corresponds to the number of arcs observed in crossed polarizers. A system of equidistant rings surrounding the cross with the arcs can frequently be observed.

4. When the crystal is illuminated for a time $T_{ill} > 1$–3 min, distortions of the director field which arise in the zone of the light beam and which are retained in the memory of the crystal can be observed under a microscope.

5. The shape of these distortions depends on the laser power P, the crystal temperature t, the polarization of the incident light, and the duration of the illumination, T_{ill} (Figs. 1–3). The homeotropic orientation of the director is usually disrupted in regions 60–200 μm in diameter (depending on T_{ill}), in which a confocal texture appears instead of a homeotropic texture. The confocal texture is characterized by a special direction (the axis of the confocal domains). This direction is governed by the polarization of the incident light: It is always perpendicular to the electric vector of the light wave.

6. The axis of the confocal domains is usually in the plane parallel to the walls of the cell and perpendicular to the vector $\mathbf{n}_0$, which specifies the original orientation of the director (Fig. 1). Less frequently we observe domains with axis parallel to $\mathbf{n}_0$, i.e., perpendicular to the cell walls. On occasion, the pattern observed under the micro-

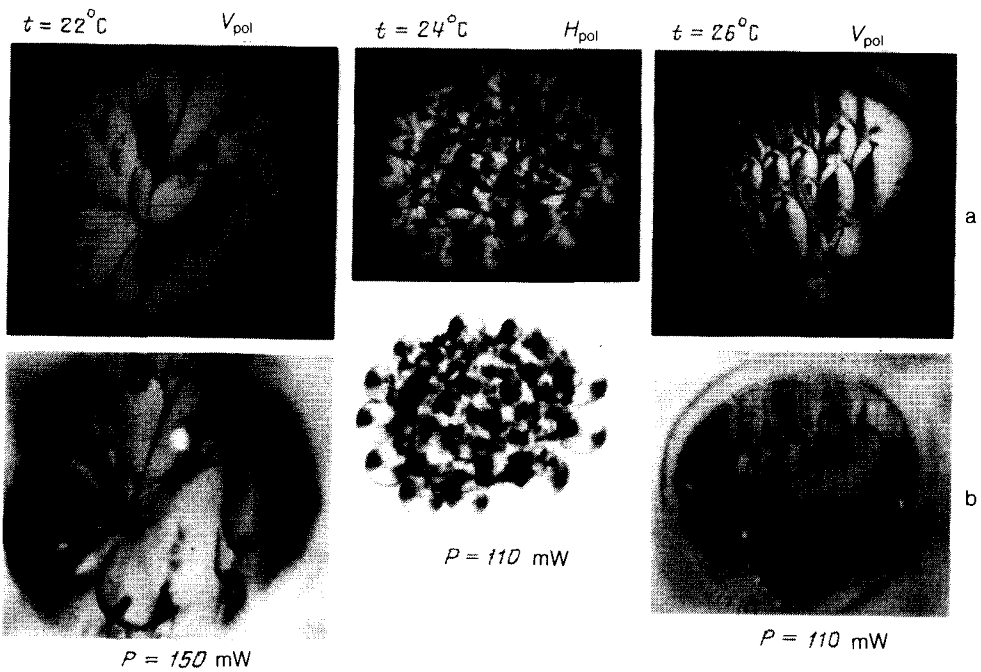

FIG. 2. Distortions of the director field caused by the laser light versus the crystal temperature. a—Crossed polarizers; b—parallel polarizers.

scope is reminiscent of that which arises in the course of a Parodi transition[8] (Fig. 2b, $t=24\,^\circ\mathrm{C}$).

7. Heating the crystal to $t>t_{N-I}$ (where t_{N-I} is the temperature of the phase transition from a nematic liquid crystal to an isotropic liquid) does not change the position of the axis of the confocal domains in the first of the three cases outlined in paragraph 6, but the domains themselves become larger. In the two other cases, the confocal texture undergoes some substantial restructuring: The domains "lie" in the plane parallel to the cell walls. The axis of the domains is now perpendicular to the electric field of the light wave in this plane.

8. The confocal textures persist in the crystal for a time which increases with $T_{\rm ill}$. At $T_{\rm ill}>3$ min, and at sufficiently large values of t and P ($t\simeq 23\,^\circ\mathrm{C}$ and $P\simeq 200$ mW; $t\simeq 24\,^\circ\mathrm{C}$ and $P\simeq 160$ mW), we observe no changes in the texture in the course of a week. At $T_{\rm ill}>5$–7 min, repeated heating of the crystal to $t>t_{N-I}$ does not erase the light-induced deformation of the director field, but the texture does change (Fig. 3).

It follows from these results that the laser light causes a reorientation of the director field in the smectic phase of the liquid crystal OCBP containing an impurity of the azo compound methyl red, and this reorientation is memorized by the crystal. A confocal texture with a clearly defined orientation arises in the process.

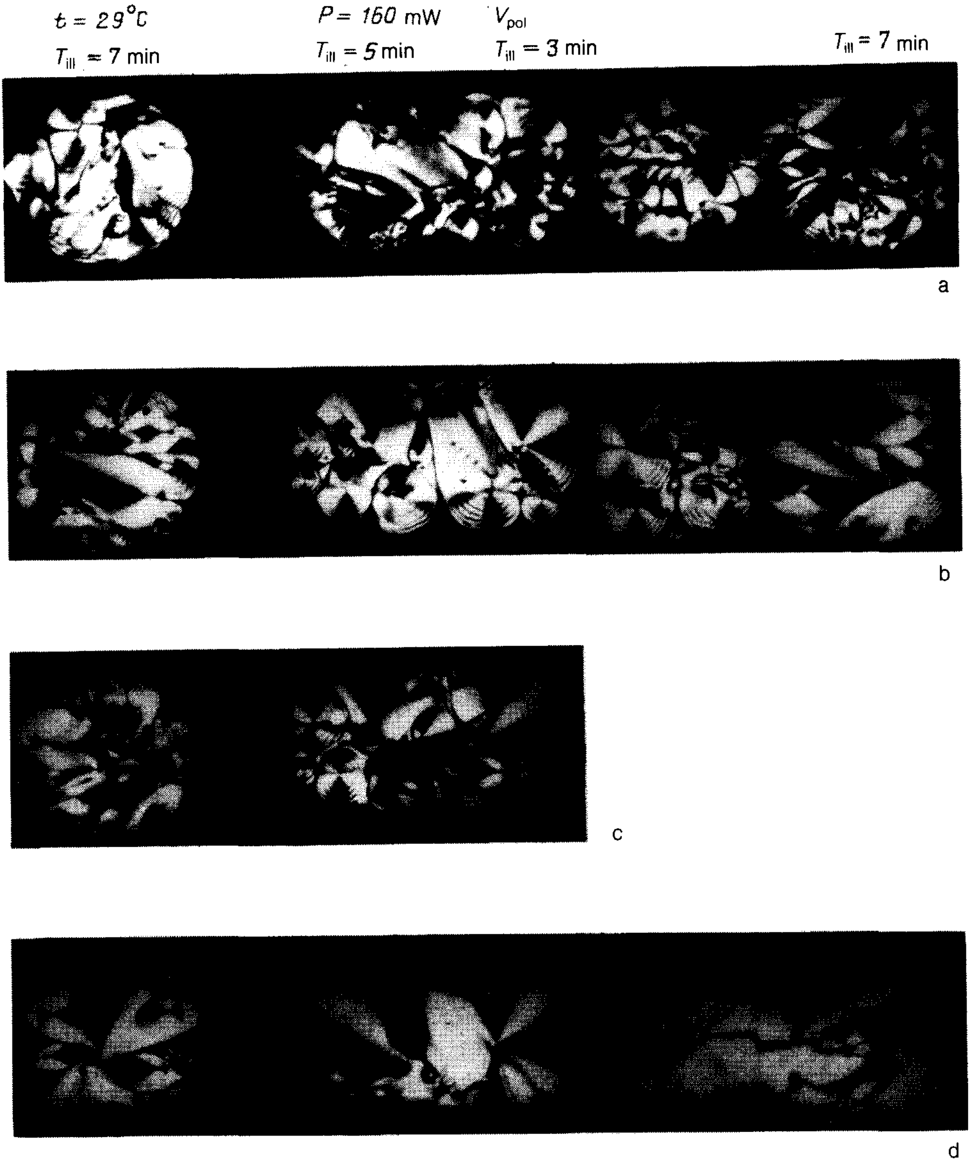

FIG. 3. a: Effect of the laser light versus the duration of the application of the light to the crystal. b–d: Effect of heating from $t > t_{N-I}$ on the distortions of the director field formed in the laser beam zone in the crystal. b—First heating of the crystal to $t > t_{N-I}$; c—second heating to $t > t_{N-I}$; d—third heating to $t > t_{N-I}$.

It follows from Figs. 1–3 that the sharpness of the orientation of the confocal texture depends primarily on the original temperature of the smectic phase. At 29 °C, which is closest to the temperature of the smectic–nematic phase transition, t_{S-N}, a clearly reoriented confocal texture arises only in certain places in the crystal

(Fig. 3a). Even when the crystal is repeatedly heated into the isotropic phase and then cooled, however, the original homeotropic orientation of the crystal is not restored. The preferential orientation of the confocal texture is retained.

Discussion of experimental results

1. The changes which occur in the intensity distribution in the beam transmitted through the crystal indicate changes in the properties of the crystal.

The cross and the changes in time associated with this cross are evidence, as in Ref. 9, that the original direction of the optical axis is not conserved and that a spatial nonuniformity arises in the beam zone (there is a deformation of the smectic layers).

The light beam which creates this spatial optical inhomogeneity is diffracted by it, with the result that arcs appear on the screen (in crossed polarizers), along with equidistant rings.

The length scale of the nonuniformity was estimated from the diffraction pattern. It was found to correspond to the dimensions of the regions of the confocal pattern memorized by the crystal.

2. The fact that the distortions of the homeotropic orientation of the smectic phase, with a predominant direction for the orientation of the defects, are retained after the crystal is heated into the isotropic phase and then cooled clearly indicates that the light causes stable changes in the properties of the surfaces orienting the crystal. This effect could result from only the presence of the small impurity of the azo compound methyl red in the OCBP crystal, since in the pure OCBP crystal the "memorizable" change in texture does not occur, even at substantially higher power levels of the light beam (at $\lambda = 6471$ Å), according to our experiments.

It is natural to suggest that the methyl red molecules in the homeotropically oriented OCBP at the cell walls are also initially oriented predominantly perpendicular to the walls. During illumination, conformational changes occur in the azo-compound molecules: a transition from the equilibrium *trans*-state to the excited *cis*-state, followed by a relaxation. In the course of the conformational restructuring of the molecules of the azo compound, they undergo a rotation,[3,4,10,11] which entrains the OCBP molecules. The molecules of the azo compound tend to become aligned perpendicular to the electric field of the light wave in the process. The light-altered orientation of the molecules may be fixed at the cell walls because of surface forces and may cause a change in the original homeotropic orientation of the director even in the interior of the crystal.

Why does the orientation of the texture that arises depend on the polarization of the light? We first note that the probability for the absorption of a photon (and thus for a rotation) depends strongly on the relative orientation of the long axis of the methyl red molecule and the polarization vector of the light (this probability is at a maximum when the two are parallel). As was mentioned above, the molecules are initially oriented perpendicular to the walls (and parallel to the vector $\mathbf{n}_0$). If, as a result of the rotation, a molecule is no longer in the Σ plane, perpendicular to the vector $\mathbf{E}$, then the probability for subsequent rotation is higher for this molecule than for a molecule which is in the Σ plane. In other words, the orientation of the molecules in the Σ plane is the stablest.

The onset of various textures at different crystal temperatures and for different parameters of the applied light apparently results from different relations between the surface forces which reorient the director and the elastic forces which oppose this reorientation. The latter forces also depend on the crystal temperature and the parameters of the applied light. The orienting surface forces are most effective during the cooling of the crystal from the isotropic phase. In this case, well-oriented confocal domains always arise.

The fairly long times $T_{\rm ill}$ required for memorization of the effect of the light are apparently due primarily to the lifetime of the methyl red molecule in the excited *cis*-state. In general, this time is a strong function of the particular material in which these molecules are dissolved. For the liquid crystal MBBA, this time is[12] 64 s. This time agrees in order of magnitude with the time the OCBP crystal containing the methyl red impurity must be illuminated in order to obtain an orienting effect.

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