

Light-Induced Periodic Lattice of Defects in Smectic A and C Liquid Crystals: Structural and Dynamical Aspects

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Structural and dynamical studies of optically-induced effects in SmA and SmC* liquid crystals are presented. The smectic materials are doped with photosensitive molecules capable of trans-cis isomerization under light illumination. Laser irradiation leads to the formation of strongly scattering textures with periodical array of parabolic focal conic domains (PFCD's). What is most surprising is that the effect is caused by a low-power (<10 mW) He-Ne laser beam; its efficiency is highest in the visible part of the spectrum. The written information can be erased by another beam with shorter wavelength, such as from an Ar laser or a UV source. The PFCD's lattice can be stabilized by a polymeric network. The most plausible mechanism of the light-induced effect is compression/dilation of smectic layers caused by phototransformation of the molecules.

Keywords: Photoisomerization; trans-cis transformation; focal conic domains; undulations

1. INTRODUCTION

Optical fields can induce instabilities in liquid crystals in a variety of ways. In the most studied nematic (*N*) phase, light illumination changes the degree of molecular order or reorients the axis of molecular alignment [1,2]. The light-induced reorienting torque can be created either in the nematic

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bulk (light-induced Freedericksz transition [1,2]) or on the orienting photo-sensitive substrate [3–7]. Both bulk- and surface-driven optical effects observed in the *N* phase are rather hard to reproduce in the layered smectic *A* (SmA) phase since director reorientation is strongly limited by the layers' equidistance [8]. For example, field- or light-induced Freedericksz transitions which are easy to observe in the *N* phase, have never been reported for SmA. Furthermore, the layered SmA structure strongly limits the surface-driven effects: surface tilt breaks the layers, and the stabilizing "anchoring" energy turns out to be a few orders higher than its nematic counterpart [9].

In the effects reported so far in SmA, light is capable of producing structural transformations only if its intensity is sufficiently high to heat the sample substantially (~ 10 K), see the review [10]. In one instance, a laser beam melts the SmA phase into an isotropic or *N* phase [11–19]; subsequent cooling results in nucleation of ellipse-hyperbola focal conic domains. In another case, the heating stops at some temperature below the melting point; when the light intensity is abruptly reduced, the layers contract and undulate [20]. Finally, with 100 mW-beam, Zolot'ko and Kitaeva observed nucleation of ellipse-hyperbola domains apparently caused by surface reorienting torques [21]. Despite the drawback of high power consumption, all these thermo-optical effects remain promising for applications because of their high resolution and good response time [8,10].

In a recent publication [22] we call attention to an anomalously low-power opto-optical effect in a SmA doped with photosensitive molecules: An irradiation of a 1–10 mW He-Ne laser beam leads to undulations of layers and strongly scattering textures. The written information can be erased by another beam with different wavelength (e.g., by Ar laser).

In this paper we present results on structural and dynamical features of this opto-optical effect, extending our observations to SmA textures modified by polymeric network and to the SmC phase in which He-Ne laser illumination also causes parabolic focal conic domain (PFCD) textures similar to that described by Johnson and Saupe [23] for thermally-addressed SmC samples. Dynamic birefringence measurements and spectral studies indicate that the instability is caused by photo-isomerization of the dye molecules.

2. MATERIALS

An underlying idea of the work is that the thickness of smectic layers can be controlled by light if the liquid crystal contains molecules capable of photo-

isomerization. Molecular isomers possess different steric and electronic properties. Light-induced isomerization can substantially change the surrounding liquid crystal matrix. In the SmA and SmC phases, a natural response to phototransformations might be contraction or dilation of the layers. Once the smectic layers confined between two flat plates are contracted, the development of events is similar to what is already known for mechanically or thermo-induced effects [8, 10]: The contracted layers undulate to fill the space between the plates properly (the number of layers remaining constant until dislocations start to nucleate and restore an equilibrium flat configuration); Higher stresses result in the formation of strong ly light scattering textures of parabolic focal conic domains (PFCD's) [24].

To demonstrate the concept of a light-induced contraction of layers, we used a typical SmA compound octylcyanobiphenyl (8CB) and doped it with photosensitive *p,p'*-diheptylazobenzene (7AB). Azobenzene and its derivatives such as 7AB exist in two isomer forms, *trans* and *cis*, Figure 1. The *trans*-azobenzene form with linear shape is the ground state of the molecule. Upon UV illumination the molecules convert into a strongly bent *cis*-form. The latter can be returned into the *trans*-form thermally or by illumination with longer wavelength. The length of the *trans*-7AB molecule (determined by a CPK Precision Molecular Model as 29.0 Å) is close to the SmA layer spacing of 8CB (~ 31.5 [22]). Å The *cis*-7AB molecule is much shorter, about 17 Å for the configuration depicted in Figure 1.

Since 7AB has no substitutes with donor or acceptor properties, its spectral and photochemical features are practically identical to that of azobenzene. Indeed, the *UV*-visible absorption spectra of 7AB (Fig. 2, 3) are very close to the ones reported for azobenzene [25]. The *UV* ($\lambda = 366$ nm,

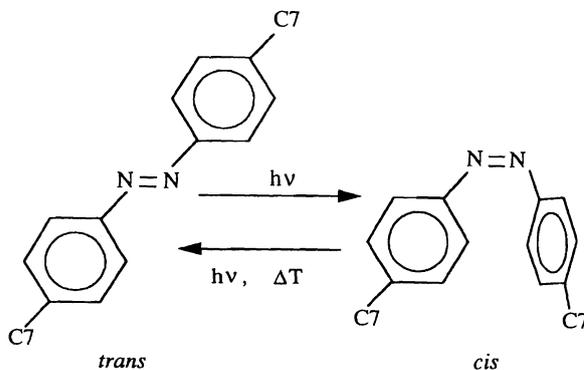


FIGURE 1 Trans and *cis* configurations of the 7AB molecule.

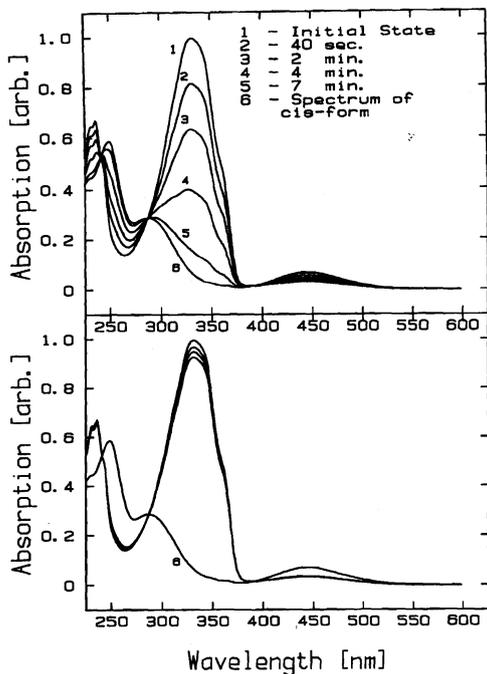


FIGURE 2 The absorption spectra of 7AB in octane. Initial states in are close to the pure transform; (a) transformation of the initial spectrum under *UV* irradiation by a 366 nm source; (b) transformation of the spectrum 1 under irradiation by a 437 nm source.

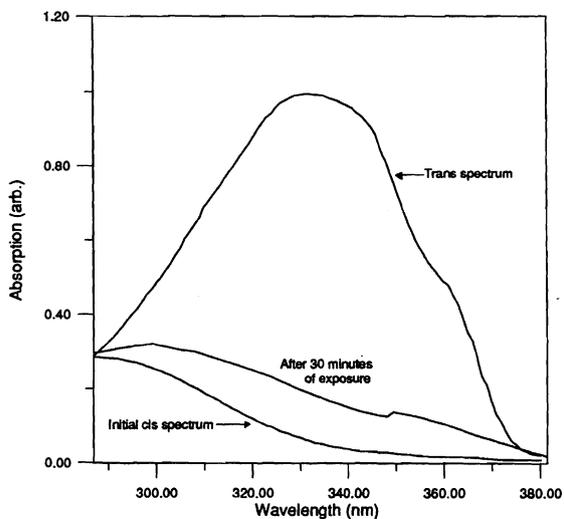


FIGURE 3 The absorption spectra of 7AB polymethylmetacrylate: relaxation of the initial spectrum of predominantly *cis*-7AB (*UV*-irradiated) under He-Ne irradiation at room temperature.

Fig. 2a) and short-wave ($\lambda = 436$ nm, Fig. 2b) illumination of the initial trans-state causes predominantly trans-to-cis isomerization. Under UV illumination, the measured equilibrium concentration ratio of cis and trans isomers was found to be $c/t \sim 0.7$. For $\lambda = 436$ nm, the ratio is $c/t \sim 0.072$. In contrast, when the material is initially enriched with cis-isomers by UV irradiation and then is heated or exposed to He-Ne beam ($\lambda = 632.8$ nm, Fig. 3), the opposite cis-to-trans transformation is observed.

The data we report are collected for the mixture 8CB:7AB (molar ratio 90.4:9.6) with phase diagram ($< 24^\circ\text{C}$) Sm A (36°C) *N*. The SmA layer spacing weakly depends on the temperature with tendency to increase [22]. The light absorption coefficient is $\alpha = 255\text{ cm}^{-1}$ at $\lambda = 488$ nm (Ar laser) and $\alpha = 0.05\text{ cm}^{-1}$ at $\lambda = 632.8$ nm (He-Ne laser) [22].

To study the possibility of light-induced instability in the SmC* phase we also prepared a mixture of a ferroelectric SmC* material ZLI-3774 (EM Industries, phase diagram (< -30) SmC* (62) SmA (76°C) *N*) and 7AB (12% in weight).

3. EXPERIMENTAL RESULTS

3.1. Light-Induced Instability in SmA

All cells in our studies were composed of two glass plates covered with lecithin or dimethylchlorosilane to orient SmA layers parallel to the substrates. The thickness h of the SmA film varied from 10 to 200 μm . The radiation of a single transverse mode of He-Ne laser ($\lambda = 632.8$ nm, power 10 mW, beam divergency 1.2 mrad) was focused by a lens and directed normally to the cell. The intensity I_{in} of the incident light was controlled by two rotating polarizers. The spatial distribution of the radiation passed through the cell was observed in the focal plane of a wide aperture lens. The nonscattered (directly passing through the cell) light was cut off by a small screen.

Shortly after the beginning of He-Ne illumination, a ring pattern characteristic of a diffraction grating develops on a screen behind the sample (Fig. 4, insert). The silent time t_s decreases from ~ 100 sec at $I_{\text{in}} = 0.2\text{ W/cm}^2$ to ~ 1 sec at $I_{\text{in}} = 1.3\text{ W/cm}^2$ and follows the rule $t_s \sim 1/(I_{\text{in}} - I_{\text{in}}^{\text{thr}})$, where $I_{\text{in}}^{\text{thr}} = 0.1\text{ W/cm}^2$ is the threshold intensity. No instability is detected when $I_{\text{in}} < I_{\text{in}}^{\text{thr}}$.

Polarizing microscopy reveals that light scattering is caused by the PFCD lattice, Figures 4, 5. The periodicity P of the PFCD's increases with h , closely following the relation $P \sim \sqrt{h}$ [22]. We checked the equivalence

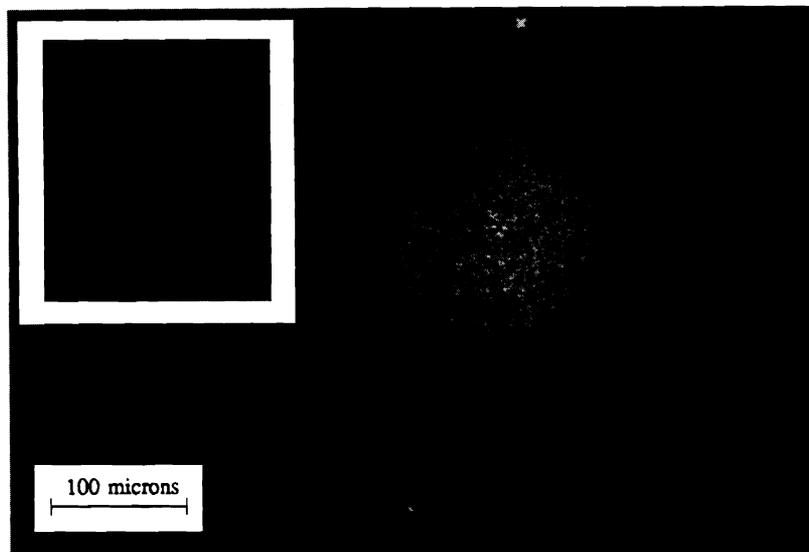


FIGURE 4 Microphotograph of a lattice of parabolic focal conic domains created in the area illuminated by a He-Ne laser beam; the insert shows a ring of light scattering at the defect lattice.

of the light-induced and mechanically-or thermally induced PFCD's instabilities described in detail in Refs.[23, 26, 27]. PFCD patterns created by the three methods, had practically identical textures and lattice periodicities. Note that the thermally-induced instability occurs only when the sample is cooled down; this is consistent with the fact that the layer spacing decreases under cooling [22].

After the He-Ne beam is cut off, the pattern gradually fades after $\sim 1-10$ min. The opto-optical effect becomes weak after several cycles of He-Ne laser switching on-off. The ability of the system to respond to He-Ne laser beam is restored by UV illumination which causes trans-cis transformations. An opposite effect occurs when the cell is held at a high temperature in the dark and the cis-isomers are converted into the stable trans-form. When the cell is cooled down to the room temperature to restore the homeotropic SmA texture, the He-Ne illumination causes no effect. No effect occurs in cells containing pure 8CB.

The efficiency of the instability in the mixture 8CB:7AB strongly depends on λ . First, the higher $\lambda = 710$ nm leads to a weaker effect with a threshold higher than that in the He-Ne case. For $\lambda = 750$ and $\lambda = 830$ nm, no instability is observed. The efficiency decreases also when λ changes in the

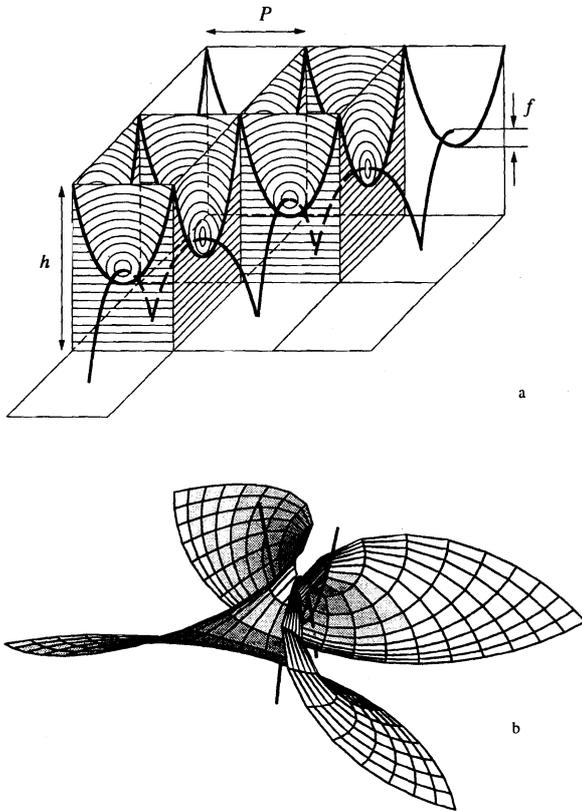


FIGURE 5 Layer and defect configuration in parabolic focal conic domains: (a) periodic lattice of domains corresponding to the texture of Figure 4; thick lines correspond to parabolic defects; thin lines are cross-sections of the smectic layers; (b) in the centre of the parabolic focal conic domain, the smectic layers are multiconnected and cross the vertical axis three times.

opposite direction: $\lambda = 510, 488, 460,$ and 440 nm give no effect. Instead, the short-wavelength illumination causes either melting of the Sm A phase or indirectly produces the scattering textures when the beam is cut off and the sample cools down; this effect is caused by thermal contraction of the layers under cooling. Moreover, an Ar laser beam, $\lambda = 488$ nm (as well as UV light) suppresses the instability created by the He-Ne beam [22].

3.2. Light-Induced Instability in SmC*

The mixture of 7AB and ferroelectric SmC* material ZLI-3774 was placed between lecithin-treated plates separated by a distance $51.0 \mu\text{m}$. At tempera-

tures above 65°C the mixture is in the SmA phase. As in the case of the 8CB:7AB mixture, the He-Ne illumination creates PFCD texture. The instability occurs also at room temperature in the SmC* phase. However, the qualitative features of the SmC* instability are different from that of the SmA one: In SmC* there are two light-scattering rings rather than one. The larger outer ring appears first and corresponds to an undulation periodicity $P = 1.2 \pm 0.2 \mu\text{m}$. It gradually decays with time while a smaller ring is seen to develop. The smaller ring corresponds to a periodicity $P = 5.1 \pm 0.2 \mu\text{m}$, and its appearance on the screen is for all intents and purposes identical to light scattering patterns of PFCD's observed for the SmA phase. Microscopic observations reveal that the illuminated area has the textural characteristics of a PFCD lattice. This PFCD's lattice in SmC* is apparently preceded by a true undulation instability.

3.3. Dynamic Birefringence Measurements

There are three basic mechanisms by which light might cause changes of the refractive index of a liquid crystal: thermal [20], orientational [1,2] and conformational [28]. In this section we present dynamic birefringence measurements in the *N* phase of pure 7AB which further support the idea that the effect of He-Ne irradiation is conformational.

Molecular photo-transformations change the birefringence $\Delta n = n_e - n_o$ of the nematic phase (n_o and n_e are ordinary and extraordinary refractive indices, respectively) [28]. Kinetic dependencies of the phase retardation $\Delta\Phi = 2\pi\Delta nh/\lambda$ allows one to explore the relaxation of the photo-induced isomers.

When the He-Ne laser beam is turned off, the time relaxation of $\Delta\Phi$ and Δn is defined by the life-time τ_{iso} of the light-induced isomers and by the characteristic time τ_{dif} of their diffusion away from the illuminated area: $\Delta\Phi(t) = \Phi_0 \exp[-t/(\tau_{\text{iso}} + \tau_{\text{dif}})]$, where Φ_0 is the initial value of the phase retardation at $t = 0$; t is the time measured from the moment when the laser is turned off. Obviously, τ_{iso} is the intrinsic parameter of the material while τ_{dif} depends not only on the material parameters such as diffusion coefficient D but also on the characteristic size \mathfrak{R} of the illuminated areas: $\tau_{\text{dif}} = \mathfrak{R}^2 / 4\pi^2 D$.

The cell of thickness 234 μm was kept at 45.10°C in the *N* phase. The cell's plates provided a uniform planar orientation. The cell was placed between crossed polarizer and analyzer oriented at 45° with respect to the director. A neutral density filter was placed in front of the sample to sharply

reduce (by a factor 10^3) the intensity of the He-Ne illumination while still providing a signal passing through the cell to measure the relaxation kinetics.

The measurements of the intensity of the light passing have revealed that the characteristic decay time (defined as the time required for the signal to reach $1/e$ of its initial value) was $t_d = (3.0 \pm 0.6) \times 10^3$ sec for a beam with $\mathcal{R} = 1$ mm. This t_d value is much larger than the characteristic times of both thermal ($t_{th} \sim (0.1 - 1)$ for our experimental conditions) and director re-orientation effects ($t_{or} \sim 1$ sec) [28,29]. To find an estimate of the lower limit of τ_{iso} , we measured the relaxation time for two beams with different width \mathcal{R} : a narrow beam with $\mathcal{R} = 250$ μm and a broad beam with $\mathcal{R} = 1$ mm. The ratio of the measured relaxation times $t_{d,narrow}/t_{d,broad} \approx 1/20$ for these two beams is close to the ratio of the illuminated areas, $(\mathcal{R}_{narrow}/\mathcal{R}_{broad})^2 = 1/16$. Since τ_{iso} should not be \mathcal{R} -dependent, the result means that the predominant relaxation factor is the diffusion of the photo-induced isomers from the illuminated region rather than their finite life-time. The lower-limit estimate of τ_{iso} is, therefore, $t_d = (3.0 \pm 0.6) \times 10^3$ sec. Experimental results lead also to the estimate of the diffusion coefficient, $D \sim 10^{-7}$ cm^2/s , in good agreement with other measurements [29].

3.4. Dynamics of Relaxation in the Polymer-Modified SmA Structure

In recent years there has been a great deal of interest in the use of polymer networks as stabilizing agents in liquid crystal devices, see, e.g., [30]. The light-induced PFCD's structures have a finite decay time. This decay time ($\sim 10^2 - 10^3$ sec) is smaller than the life-time of the photo-induced isomers, estimated to be at least $\sim 3 \times 10^3$ sec in the nematic phase. Therefore, structural reconstructions such as motion of dislocation might be the dominant mechanism of the decay of PFCD's lattice. In fact, the observed decay time is in good agreement with a characteristic time required for edge dislocations to move across a stressed SmA area of size $\sim 0.5 - 1$ mm [26]. This observation suggests that a polymer network can be used for pinning of defects to prolonge the life-time of the PFCD lattice.

The polymer-stabilized SmA mixtures were prepared by using 70% (by weight) of 8CB, 10% of 7AB, 16.5% of the monomer 4,4'-bis-acryloyl-biphenyl (BAB), and 3.5% of a photo-initiating material benzoin methyl ether (BME). The homeotropic SmA sample was irradiated for twenty minutes with ultraviolet light to cure the monomer and to create the crosslinked polymer network.

The light induced PFCD's were created in samples with polymer network; the decay of the scattering pattern was measured with a weak testing beam. The typical size of the illuminated area was 0.5 – 1 mm. The scan was compared with samples that do not contain the polymeric network. The results shown in Figure 6 clearly indicate that the polymeric network significantly enhances the stability of the light-induced scattering pattern. The lifetime of the PFCD pattern increases from approximately 80 sec for a sample without the polymeric network to 10^3 sec and more with the polymeric network in place.

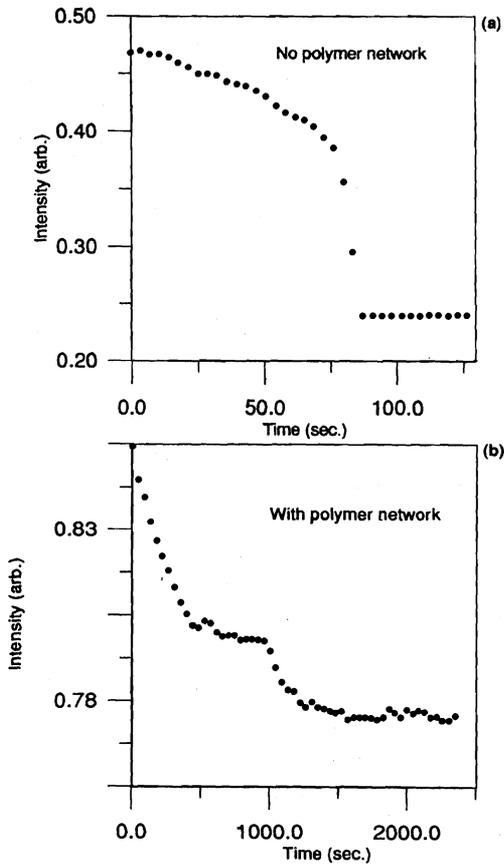


FIGURE 6 Decay of the PFCD instability manifested through the decrease in the intensity of scattered light for pure 8CB:7AB mixture (a) and for the 8CB:7AB mixture with the polymeric network (b).

4. DISCUSSION

4.1. Geometry of Parabolic Focal Conic Domain and an Estimate of Layers Contraction

Undulation and PFCD patterns in SmA cells with fixed thickness occur when the SmA layers are contracted [8,23,24,26,27]. The critical fraction Δd of the layer spacing d sufficient to produce an undulations is $\Delta d = 2\pi d\lambda/h$, where $\lambda = \sqrt{K/B} \sim d$, K is the splay elastic constant, and B is the compressibility modulus. The PFCD instability occurs at slightly higher threshold (factor 1.7) [27]. Each PFCD is formed by layers folded around two singular parabolae, Figure 5.

The physical reason of the appearance of the PFCD as a response to contracted layers is multiconnectivity of smectic layers in PFCD's. To demonstrate this, let us consider the function $u(x, y, z_0)$ introduced by Rosenblatt *et al.* [24] to describe the displacement of layers along the vertical axis z . Each point (x, y) that belongs to a layer originally forming a plane $z = z_0$, shifts by a distance u along z when the PFCD forms. The axis z is normal to the initial layers; $z = 0$ is located in the center of the cell. At points $(x = 0, y = 0)$ all layers remain normal to the z -axis, and $u(0, 0, z_0)$ shows where the layer crosses the z -axis. The equation for $u(x, y, z_0)$ reduces to $(u + f)^3 - (u + f)^2(3f - 2z_0) + 2f(u + f)(f - 2z_0) = 0$, with f being the focal length of parabolae. The last cubic equation has three real roots ($z_1 = f + z_0$; $z_2 = -z_0$; $z_3 = -f + z_0$) when $-f/2 < z_0 < f/2$ and one real root when $-h/2 < z_0 < -f/2$ or $f/2 < z_0 < h/2$. Thus each layer located initially between the points $(-f/2, f/2)$, transforms into a triple-connected layer when the PFCD forms. Such a layer crosses the z -axis three times; its effective "thickness" is $3d$. It explains why the PFCD's occur when the layers are contracted: multiply connected layers allow the system to fill the fixed space between the glass plates by thinner layers without changing the total number N of these layers; i.e. without nucleation and propagation of dislocations.

Using the idea that the total number of layers remains constant, $N = h/d = (h - 2f)/(d + \Delta d) = \text{const}$, one finds that the formation of PFCD's accomodates the change in the thickness of each smectic layer by $\Delta d = -2fd/h$. Taking into account that the distance P between the ends of the parabolae measured at the cell's surface is defined by f and h as $P = 2\sqrt{2fh}$, one gets an estimate of the layer's contraction through parameters P and h which are easy to determine experimentally: $-\Delta d/d = P^2/4h^2$. With typical experimental values of P and h , $P/h \sim 0.1$, one

finds that the photo-induced contraction of each layer is of the order of 0.1\AA .

4.2. Possible Mechanisms of the Light-Induced Instability

Generally, there are at least three possible mechanisms of the layer's contraction under the light illumination: (1) reorientation torque caused by dielectric coupling between the medium and the electric field of the beam; (2) direct heating because of the finite absorption; (3) photo-transformations of molecules.

In dye-doped nematic materials Jánossi *et al.* [31, 32] observed an anomalously low optical Freedericksz threshold which is two order of magnitude lower as in the pure host. The mechanism of this instability is still debated. However in any event, it is unlikely that the observed effect in SmA phase is related to the Freedericksz mechanism and simple dielectric reorientation torque: as already indicated, the equidistance of smectic layers makes the Freedericksz effect practically impossible [8]. In practice, even if the external electric field is high enough, one would expect nucleation of focal conic domains in the form of elliptical-hyperbolic pairs prior the Freedericksz transition [33]. The geometry of the field-driven elliptical-hyperbolic domains is quite different from the PFCD's driven by layers contractions.

The second thermal mechanism should also be rejected since, first, the layer spacing tends to increase with temperature, second, the direct heating of the cells never produces an instability and finally, the temperature changes caused by He-Ne laser are quite small. To show this, let us calculate a maximum temperature increase ΔT in the spot of area S illuminated by He-Ne laser. Since $\alpha h \ll 1$, the change in the intensity of light passed through the cell is $\sim \alpha h I_{\text{in}}$. The energy absorbed by the smectic material during time t is $\Delta Q = \alpha h I_{\text{in}} S t$. Thus $\Delta T = \Delta Q / c p h S = \alpha I_{\text{in}} t / c \rho$, where c is the heat capacity and ρ is the density of Sm A. With typical $c = 2.5 \times 10^3 \text{ J} / (\text{K kg})$ [30], $I_{\text{in}} t = 10^5 \text{ J} / \text{m}^2$, $\rho = 10^3 \text{ kg} / \text{m}^3$, and measured $\alpha \approx 0.05 \text{ cm}^{-1}$ at $\lambda = 632.8 \text{ nm}$ one gets only a small temperature change $\Delta T \approx 0.2 \text{ K}$.

The remaining mechanism of the observed effect is the phototransformation of 7AB molecules. The photoresponse of the system to different λ is the most interesting part of the phenomenon. At first sight, since the cis-form is shorter than the linear trans-form, the layers should contract when the light provokes trans-cis isomerization. Our results indicate that just the opposite takes place: neither UV ("cis-producing" light) nor Ar laser are capable of creating the undulations while He-Ne or other long-wave "trans-producing"

illuminations easily cause the effect. Note here that the direction of photo-transformations depends not only on λ but also on the initial state of the system. At a given temperature and λ , there is always some finite quantity of trans- and cis isomers. The results presented above indicate that the undulation instability appears most probably because the He-Ne irradiation transforms cis-molecules of 7AB into the trans-form. The conclusion is consistent not only with the spectral data, Figures 2,3, but also with the observations that (1) after several cycles of He-Ne irradiation (when presumably most of the molecules are already in the trans-form) the instability ceases to appear, and (2) UV -irradiation that restores significant fraction of cis-isomers is also restoring the ability of "dead" cells to create PFCD's textures under He-Ne illumination.

The most intriguing question is *how* the cis-to-trans transformations cause layers' contraction. One interesting possibility is that the cis-form is located in between the Sm layers rather than inside the layers. Really, it is hard to imagine that a strongly bent cis-molecule can incorporate itself into well-ordered rows of 8CB dimers forming smectic layers; the interlayer regions with reduced density and order seem to be more appropriate place for it. In fact, a "transverse" interlayer order was predicted by R. van Roij *et al.* [34]: computer simulations demonstrated that in a SmA system of identical hard rods there was always a finite fraction of particles trapped in between the layers and oriented normally to the director. If one assumes that 7AB molecules change their location from interlayer regions (while in cis-form) to in-layer regions (while in trans-form), then the layers' contraction under the He-Ne irradiation is natural. Further work needs to be done to confirm this possibility rigorously or to deny it.

5. SUMMARY

We described structural and dynamical aspects of the optical effect in SmA and SmC liquid crystals. The effect consists of the appearance of a periodic lattice of parabolic focal conic domains under low-power He-Ne laser illumination. The instability occurs in liquid crystals doped with photosensitive molecules capable of trans-cis isomerization. With dopant diheptylazobenzene the effect is pronounced in the region $600 < \lambda < 750$ nm. Illumination with shorter wavelength suppresses the defect lattice. The spectroscopic data suggest that the defect lattice is caused by cis-to-trans transformations. Dynamic birefringence measurements confirm that He-Ne

irradiation leads to formation of stable isomers with long life-time. Finally, we demonstrated that the light-induced lattice of parabolic focal conic domains can be stabilized by a polymeric network in the smectic bulk.

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