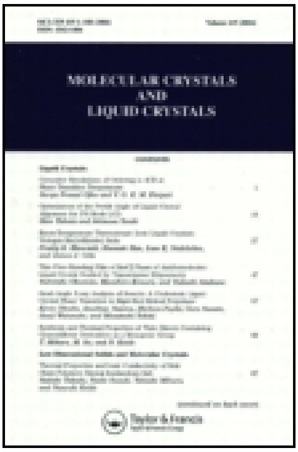

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LOW-POWER LASER INDUCED INSTABILITIES IN SMECTIC A LIQUID CRYSTALS

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Abstract A low power He-Ne laser beam is shown to induce layer instabilities in a smectic A liquid crystal cell possessing initial homeotropic orientation. The effect occurs when the smectic A phase is doped with a photosensitive azo-compound. The most plausible mechanism for the instability is phototransformation of the guest molecules (e.g. trans-cis isomerization), and a subsequent decrease in the smectic layer spacing.

INTRODUCTION

When a homeotropically aligned smectic A (SmA) cell is subjected to a mechanical strain, the system finds it energetically more favorable for the layers to undulate rather than dilate continuously to fill the excess space. This is the so called Helfrich-Hurault instability [1]. At a higher strain the layer undulations transform into a network of parabolic focal conic domains (PFCD's) [2,3]. Here we report on a new mechanism for creating the instability using a low power He-Ne laser (< 10 mW).

The experiment is based on the idea of light-induced phototransformation of SmA molecules. Let us imagine a SmA phase doped with photosensitive molecules that undergo trans-to-cis transformation under light irradiation. The initial guest molecules have a trans-conformation; their transformation to the cis-form would mean an effective decrease in the SmA layer spacing: $d_{mixture} = \sum_{i=1}^{N} c_i d_i$ in the first approximation [4,5], where

c_i and d_i are molar fractions, and molecular lengths of the components respectively; N is the number of components. Since the cell thickness remains constant, the decrease in layer spacing should result in undulations to provide a proper filling of the space. The effect is thus similar to the well-known Kahn thermo-optical effect, in which the laser beam is used to change the temperature of the system and, as a result, change the effective smectic layer spacing [1,6,7]. Square lattices of distorted layers have been recently produced under conditions similar to the Kahn experiment by Zolot'ko et al. [8]. In the effect that we describe below however, the thermal behavior of the system most likely opposes the instability caused by the phototransformed molecules. Other experiments employing direct laser control with photosensitive nematic and cholesteric compounds have been reported elsewhere in the literature [9,10].

MATERIALS, EXPERIMENTAL TECHNIQUES, AND RESULTS

We use a binary mixture of 4-octyl-4'-cyanobiphenyl [8CB] (Cry 21.5 SmA 33.5 N 40.5 °C I), and p,p'-diheptylazobenzene [7AB] (Cry 41.0 N 48.6 °C I). The 7AB molecule possesses a double nitrogen bond which is susceptible to trans-cis photo-isomerization [11,12-14]. A partial phase diagram for our system is shown in figure 1. All molar concentrations from 0-14% 7AB in 8CB possess the smectic A and nematic phases. For simplicity all measurements discussed in this article were done on a mixture of 9.6 mol% 7AB in 8CB.

The maximum extended length of the 8CB, and 7AB molecules were determined by using a precision molecular model kit [15] to be 22.1, and 29.0 Å respectively. We also estimated with models the longitudinal length of the cis-form of the 7AB molecule to be in the range of 18 to 24 Å. X-ray measurements done to characterize the layer spacing d of pure 8CB, and the mixture are shown in figures (2a,b). In the temperature range

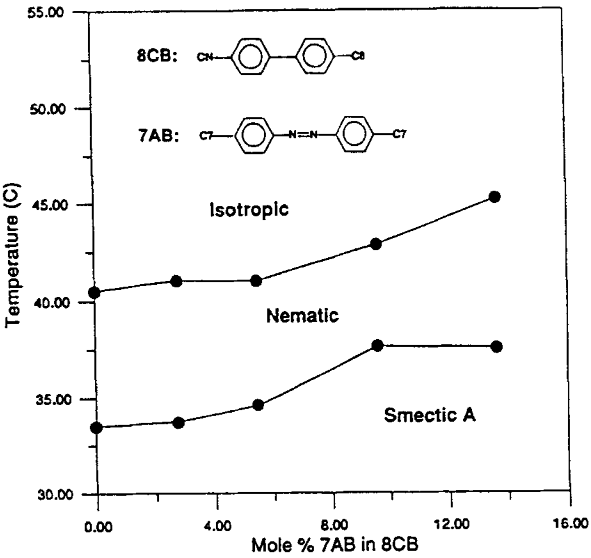

FIGURE 1 Phase diagram of the binary mixture 7AB in 8CB.

measured (24 to 37.5 °C), the mixture is in the smectic A_2 phase [16,17]. For example, at T=24.0 °C there is a large peak at 2θ=2.8° which corresponds to a layer spacing of 31.6 Å, and a smaller peak occurring at 2θ=1.4°, that most probably corresponds to a second periodicity in the system of 63 Å.

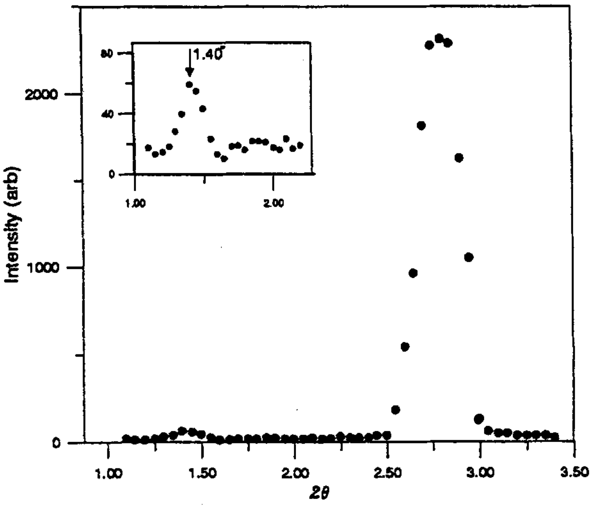

FIGURE 2a Typical x-ray scan of the 9.6 mol% mixture shows two peaks. One at 31.6 Å, and another at 63Å.

Temperature behavior of layer spacing for both pure 8CB, and the mixture is shown in figure 2b.

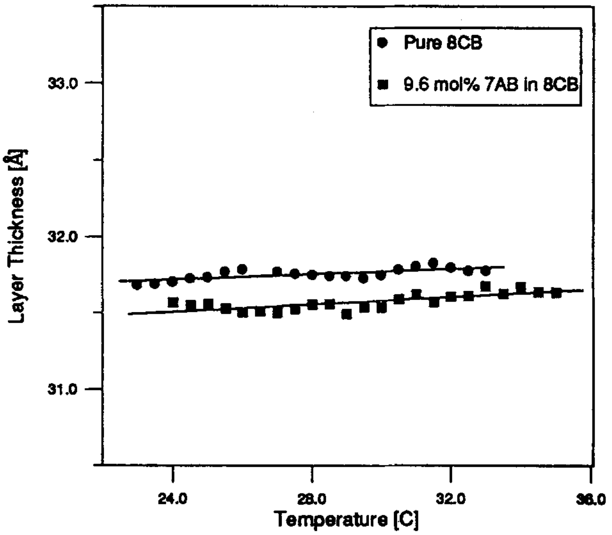

FIGURE 2b Comparison of layer spacing of pure 8CB, and the mixture upon heating

In our experiment light from a He-Ne laser (λ=632.8 nm, P=10 mW) is focused by a lens (F_1=10, 15, or 20 cm) onto a homeotropically oriented SmA cell of this mixture, (the direction of propagation of light is parallel to the long axis of the molecules). After a few seconds a ring pattern characteristic of a diffraction grating is seen to develop on a screen placed behind the sample. Microscopy reveals a circular pattern with a diameter of ≅200 μm at the point of illumination. The pattern possesses a polydomain texture of square lattices characteristic of PFCD's [2,3]. We observe that the periodicity *P* of the pattern decreases as one moves radially outward from the center of the spot. This fact was an important clue that *P* depends on the incident light intensity, since the laser beam has a gaussian profile with maximum intensity at its center. The induced pattern is permanent under constant illumination. However, we noted that sudden fluctuations such as changes in temperature, or light intensity could cause it to disappear. After the laser beam is removed the pattern fades after several minutes. Light from the microscope could speed up this process presumably by heating the sample. Filters were used in some cases for microscopic observation to remove the component of the spectrum that is strongly absorbed by the sample. Similar cells containing pure 8CB have been tested, and reveal no layer instability under the heating, or illumination of the cells.

To characterize the instability quantitatively, a goniometer setup was built utilizing a computer controlled stepper motor, and a photodiode to scan the diffraction ring scattering off of the light-induced lattice, as a function of scattering angle. The periodicity P of the defect lattice could then be determined by using the simple equation [18] $P = \lambda / \sin[\tan^{-1}(R / F_2)]$, for scattering from a diffraction grating in the Fraunhofer geometry. As a check, P was also measured by microscopy techniques. Figures 3-5 show results for three separate experiments to study P as a function of cell thickness, incident light intensity, and temperature respectively.

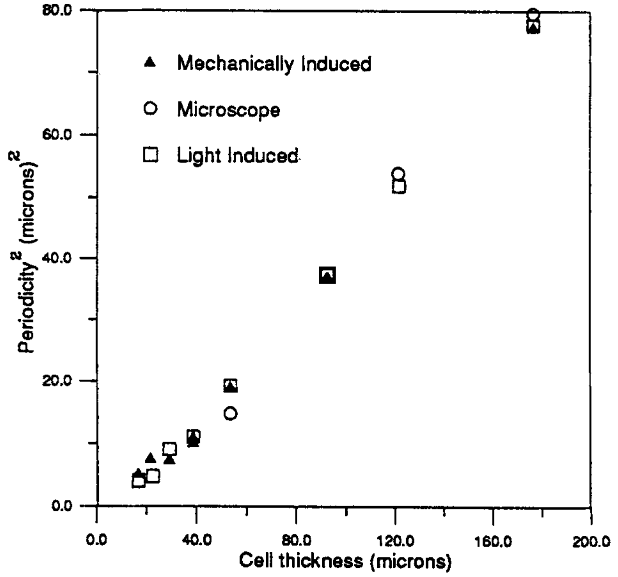

FIGURE 3 Thickness dependence of lattice periodicity. 9.6 mol% 7AB in 8CB at room temperature.

Figure 3 shows the lattice periodicity dependence on cell thickness. Cells ranging from 10 to 130 microns were studied. To check the equivalence of the light-induced and mechanically induced instabilities, defect patterns created by mechanical stresses were also studied. The light and mechanically-induced instabilities revealed similar textures, and lattice periodicity's that practically coincide. This curve can be roughly described by the relation $P\alpha\sqrt{h}$, which follows from the theory of Helfrich-Hurault instabilities, PFCD lattices, and experiments done on mechanically induced instabilities [4,19,20].

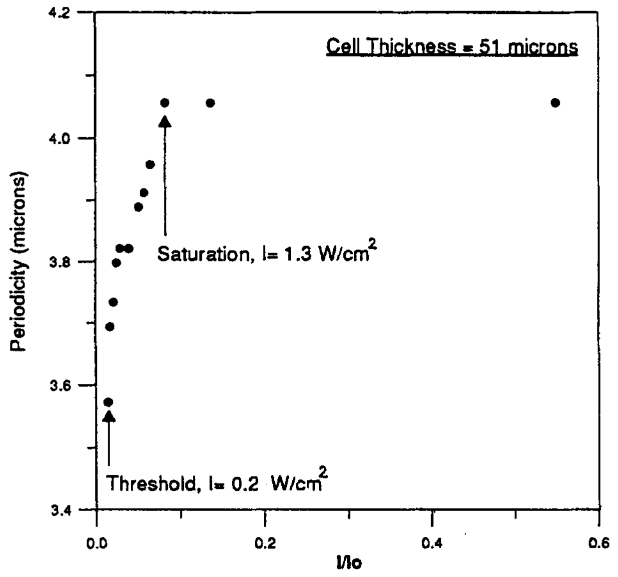

FIGURE 4 Intensity dependence of lattice periodicity. $I_0 \cong 15$ W/cm^2.

Figure 4 shows the intensity dependence of lattice periodicity. Two adjustable polarizers were used to control light intensity in accordance with the relation $I = I_0 \sin^4(\Delta\theta)$. In this experiment we adiabatically increase the incident light intensity at a given spot, allowing the sample to equilibrate before doing a scan. Experiments of this type allow us to study quasi-static nucleation of the defect pattern. The pattern develops at a threshold intensity of ~0.2 W/cm^2, and then increases monotonically until saturation at ~1.3 W/cm^2. For each position on the graph the pattern was stable indefinitely. It shows that between threshold and saturation the periodicity of the lattice can be increased continuously.

The temperature dependence of lattice periodicity is depicted in figure 5. P increases sharply when the SmA-N transition is approached. The fit shows that the dependence can be described by a power law $P(T) = A_o(T - T_c)^{-\alpha}$, where the fitting parameter T_c=310.5 K is close to the SmA-N transition temperature determined by DSC techniques (T_{AN}=310.7 K), and α=(0.06±0.01).

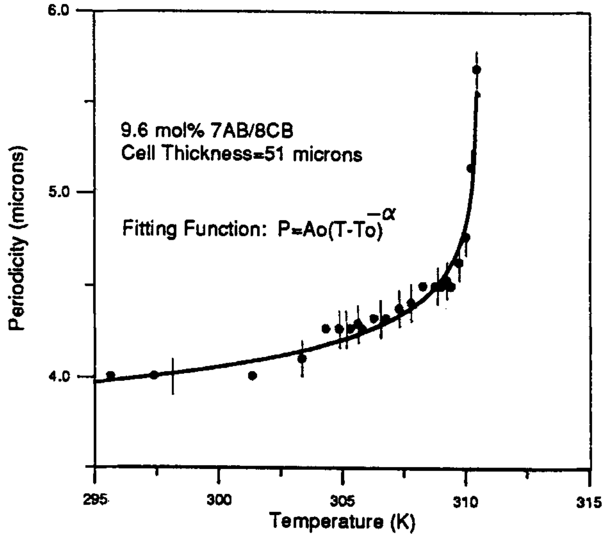

FIGURE 5 Temperature dependence of lattice periodicity.

The width of the scattering ring is approximately constant in the entire temperature region except near the SmA-N phase transition, where it increases drastically. Close to that temperature, (within 0.2 K) the scattering pattern becomes diffuse, and the scattering ring disappears.

To study the dynamics of pattern formation, the goniometer setup was replaced by a short focal length lens which focused the scattered light onto a photodiode. The direct beam was blocked by a small screen. One key feature found was that there exists a 'silent time' after the start of illumination before scattered light is detected. By fitting the curve in figure 6 to the expression $t_s = t_s^{sat} / (I_{exc} - I_{exc}^{thresh})$ we find that $I_{exc}^{thresh} = 0.1 W / cm^2$, and $t_s^{sat} = 1 \sec$ is the silent time at the saturation intensity. The presence of a silent time indicates that the smectic layers must absorb a threshold number of quanta in order for the instability to occur. This is consistent with the basic theory of mechanically induced instabilities in smectics, which dictates that the strain exerted on the smectic layers must exceed some threshold value before the undulations develop [1,20].

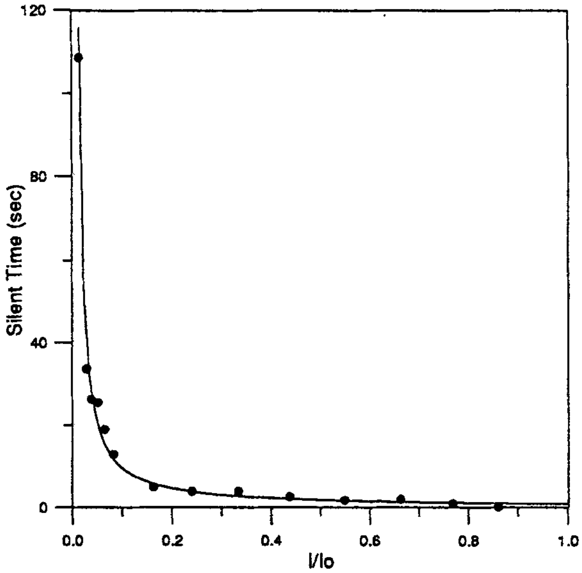

FIGURE 6 Incident light intensity dependence of 'silent time'. Note the behavior at low intensities.

DISCUSSION

As it follows from the results described above, the likely mechanism of the observed instability is light-induced transformations of the 7AB molecules that dope the 8CB matrix. The illumination of pure 8CB reveals no sign of instabilities. The most plausible type of phototransformation seems to be trans-cis isomerization, since 7AB belongs to the class of azobenzenes with a double nitrogen bond that are shown to undergo light-induced trans-cis isomerization [8,9,10]. The consequence of isomerization in the context of the present study is a difference in effective lengths of the initial, and phototransformed species of 7AB molecules. Within the scope of the simplest approximation, the layer spacing of the mixture of 8CB and initial 7AB molecules is $d_{mixture,o} = c_{8CB} d_{8CB} + c_{7AB} d^{o}_{7AB}$, where d_{8CB} is the length of 8CB dimers, and d^{o}_{7AB} is the length of the 7AB trans-isomer. Photo-transformation results in the appearance of the shorter cis-form with some non-zero fraction of the origional trans-isomers, $x(0<x<1)$ and molecular length d^{photo}_{7AB}. The difference $d^{o}_{7AB} - d^{photo}_{7AB}$ may reach a few angstroms in the case of trans-cis isomerization (up to 10 Å in the limit of the free molecular model, see above). Therefore, the light irradiation reduces the effective layer spacing of the smectic mixture, if $d^{photo}_{7AB} < d^{o}_{7AB}$: $\Delta d = d^{photo}_{mixture} - d_{mixture,o} = c_{7AB} x(d^{photo}_{7AB} - d^{o}_{7AB}) < 0$. The undulation instability threshold is defined as an effective decrease of the total SmA cell thickness by $\sim 2\pi d_{7AB}$ [1,20]. For a typical cell of thickness 100 μm, $d \approx 30$ Å, and $c_{7AB} \sim 0.1$, one finds that the instability would occur when $x(d^{o}_{7AB} - d^{photo}_{7AB}) \sim 0.2$ Å. In other words, even for a modest $(d^{o}_{7AB} - d^{photo}_{7AB}) \sim 1$ Å, the instability might occur when only 20% of the initial 7AB molecules are transformed.

An alternative mechanism of the instability is a temperature-driven decrease of the layer spacing under the illumination. Results of layer spacing temperature dependence shown in figure 2b for pure 8CB are similar to those reported by Ouchi et al.[21]. Results for the mixture are also shown. They indicate that the layer spacing changes little with temperature, but the overall trend is positive. Unfortunately, the resolution of our machine is only ±0.5 Å. Consequently, confirmation of an increasing layer spacing (which would definitely prove the impossibility of the thermal mechanism) with temperature is tentative. Further work using high resolution x-ray techniques could substantiate a positive $d(d_{mixture})/dT$. However, the hypothesis that $d(d_{mixture})/dT > 0$ is consistent with other independent observations. Namely, by cooling the cell we observe that PFCD's develop. Also, we observe the Kahn effect in homeotropic cells filled with the mixture when they are irradiated by light from an argon laser (λ=488 nm): A spot on a homeotropic cell of the sample

(9.6 mol% 7AB in 8CB) is illuminated with the Ar laser, the beam intensity is then sharply reduced by insertion of a neutral density filter. A transient scattering ring is observed on a screen placed behind the sample. The ring pattern disappears after a brief time (~1 sec) when the system comes back into thermal equilibrium. At this wavelength the mixture strongly absorbs light. The absorption coefficient, α, at λ=488 nm is α=255 cm^{-1}. On the other hand, if layer spacing decreased with temperature this would not be observed. At the wavelength of the He-Ne laser, where the instability is observed, the absorption coefficient, α is quite small: α=0.05 cm^{-1} at λ=632.8nm. So heating is negligible due to the He-Ne laser, and we can infer that direct heating of the sample is apparently not the agent responsible for the observed instability.

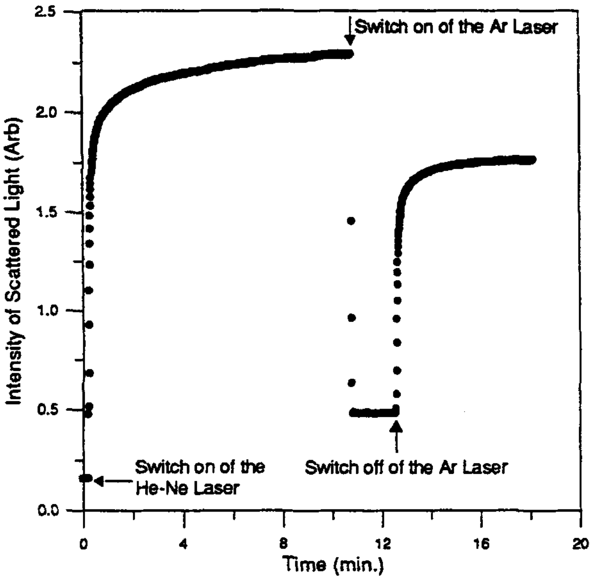

FIGURE 7 Suppression of the light-induced PFCD pattern by the Argon laser.

In order to test our hypothesis that the He-Ne laser is prompting a decrease in layer spacing, an additional experiment was performed, where first the PFCD lattice was induced in the cell by the He-Ne laser. An Argon laser (λ=488 nm) was situated on the opposite side of the cell, and aligned so that the beam would strike the sample in the same spot. A 50% mirror was used to reflect the signal passing through the cell from the He-Ne laser, passed through a line filter, and then focused onto a photodiode using a short focus lens. After the pattern was created the Ar laser was switched on. The effect was to suppress the ring pattern, see figure 7. The information written by the He-Ne laser can be erased by an Argon laser, or by sample heating. The characteristic time of erasure of the He-Ne induced pattern becomes shorter when the argon laser beam intensity increases. This supports the idea that the main result of Ar irradiation is heating (and consequent expansion of the layers) while the He-Ne laser contracts the layers (most probably by trans-cis isomerization).

CONCLUSION

We have observed a pronounced effect of low-power He-Ne laser illumination on the structure of a SmA phase: An initially homeotropic structure with layers parallel to the cell plates undergoes a transition to the spatially modulated pattern when the light intensity exceeds some threshold value. The effect is detected by two techniques: light scattering and polarizing microscopy. The most plausible mechanism of the instability is a decrease in the effective SmA layer spacing caused by transformations of photosensitive molecules. The mechanism proposed here is connected neither with thermal effects, nor with the light induced SmA-nematic or SmA-isotropic phase transitions observed earlier, see e.g. [7,22,23]. Since the instability and light scattering textures occur for anomalously low-power irradiation, the phenomenon observed might find some practical applications. Further studies are in progress.

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