

**Hidden surface photorefractive gratings in a nematic liquid
crystal cell in the absence of a deposited alignment layer**

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Abstract

We have carried out studies of photoinduced diffraction in a homeotropically aligned liquid crystal cell on indium tin oxide with no alignment layer deposited between the electrodes and liquid crystal. We have observed diffractive components from both persistent hidden gratings, and transient grating formed in the presence of a dc electric field and two coherent pump beams. Our experiments suggest that these persistent hidden gratings are due to a light induced modulation of the surface charge of adsorbed species that is hidden by diffusion of bulk charge to screen the surface charge in the absence of an applied field. The applied field removes the screening charge, revealing the hidden surface-bound charge modulation. This persistent hidden grating can be manipulated by the application of light and/or dc electric field. Dynamics and other properties are studied and described.

1. INTRODUCTION

Photorefraction in liquid crystals (LCs) has attracted significant attention since it is characterized by strong optical nonlinearities at low light intensities and voltage.¹⁻²² The photorefractive effect in a LC cell can be initiated by light induced charge generation both in the cell volume and in the LC orienting layer as well as in the LC-aligning layer interface. In *volume-mediated* photorefraction, the incident optical intensity grating generates photo-charges in the LC bulk, which migrate and diffuse within the LC to set up various *dc* space charge fields.¹⁻⁵ These space charge fields create a torque on the LC director, forcing its reorientation and hence changes of the orientation of the refractive index ellipsoid.

In *surface-mediated* photorefraction, the spatially modulated light field results in a modulation of the electric field either in the aligning layer itself^{7,10-12,20-22} or at the interface between the LC and the aligning layer.¹⁴⁻¹⁶ In the first case photoconductive aligning layers are applied. According to²⁰⁻²², in these experiments the photoexcited charges are trapped in the dark areas at the insulated polymer surfaces and the resulting space charge field reorients the LC in the cell. This increases the electric field in the LC bulk causing a spatially modulated reorientation of the director in the cell. This effect is reversible and the gratings disappear after termination of the incident light. In the second case, the photorefraction is controlled by the processes in the interface between LC and aligning surfaces, both of which can be nominally insensitive to light. Pagliusi and Cipparone¹⁵⁻¹⁶ observed surface-mediated photorefraction in planar oriented LC E7 in the cells which surfaces were covered by ITO electrodes and rubbed polymer layer of polyvinyl-alcohol (PVA) above. The observed phenomenon was attributed by accumulation of charges, initially presented in the LC, near the polymer surface due to external *dc*-field and following light-induced modulation of these charges. The modulation of the charge distribution was suggested to be due to photoinduced injection of carriers from the electrode through the aligning polymer to the LC and successive

recombination with ions accumulated on the opposite side of the interface".¹⁷ The resultant spatially modulated electric field induces a reorientation of the director in the bulk and the grating recording. The photorefractive gratings reported by Pagliusi and Cipparone^{15,16} occurred only during irradiation. If the origin of the photorefraction involves photoinduced injection of carriers from ITO, this effect should be rather universal and one that is especially effective in the cells made from two ITO electrodes with no deposited aligning layers.

Other characteristics of surface-mediated effect were found by Zhang *et al.* in homeotropic 5CB LC cells with nominally light insensitive aligning layers.¹⁴ It was observed that the recorded grating persists several hours and even days despite the disappearance of diffraction after switching the light and electric field off. This ‘hidden’ grating can be revealed by turning the *dc*-electric field on again. Zhang *et al.* suggested that this effect was due to a light-induced modulation of charges adsorbed on the aligning surface and their screening by free bulk charges. The possibility of recording of hidden grating should strongly depend on the strength of adsorption of charge on the aligning surface, which, seemingly, would be a specific property of the aligning material, for example, HTAB as used by Zhang *et al.*

The exact nature of the photoelectric processes occurring at the cell boundaries is still unclear. For example, it is not clear what the relative roles of the ITO/alignment layer and alignment layer/liquid crystal interfaces play in the observed processes. In this letter, we aim to begin to understand these processes by eliminating the alignment layer/liquid crystal interface. Here, we report on surface-mediated photorefractive effects in a cell with two ITO surfaces having no aligning layers deposited between the electrodes and the LC and using the homeotropically oriented LC 5CB. Surprisingly, it was found that an effective ‘hidden’ photorefractive grating was observed, even one recorded on gold electrodes. This suggests that surface-mediated photorefraction due to long-term light-induced modulation of the

surface potential is a rather general effect. As we will show, photo-induced adsorption is quite general as well, and can occur on the electrode as well as the alignment layer.

2. EXPERIMENTS AND DISCUSSION

We studied optically written gratings in 20- μm thick LC cells. Our glass substrates were coated with ITO (surface resistivity 80 Ohm/\square) without any aligning layers. Substrates were washed by ethyl-alcohol and distilled water and then were dried in a nitrogen flow at room temperature. The cells were filled with LC 5CB (K15 from EM Industries) in the isotropic phase at $T = 40^\circ\text{C}$. Observation in a polarizing microscope showed high quality homeotropic alignment of the LC in the cell. Placing the cell between crossed polarizers did not change the transmittance of the system; the optical field remained completely dark, and rotation of the cell around the optical axis did not result in a change of the transmittance. At the same time, inclination of the cell with respect to the optical axis caused the appearance of light in the optical field of the microscope.

The experimental set-up was a standard two-beam coupling arrangement.¹⁴ Two polarized beams from a continuous *He-Cd*-laser ($\lambda = 0.44 \mu\text{m}$) of equal intensities, $I_{1,2} \approx 100 \text{ mW}/\text{cm}^2$ crossed in the cell, producing an interference pattern with a period of 15 - 20 μm . The polarisation of the incident beams was in the plane of wave-vectors of the recording beams and normal to the cell (*p*-polarisation). The sample was set perpendicular to the plane of the beam intersection and could be rotated in the plane of incidence. A dc voltage, U , in the range $\pm 10 \text{ V}$ was applied to the cells.

Irradiation of the cells resulted in the recording of dynamic Raman-Nath diffraction gratings. Photodiodes detected the intensities of zero diffraction orders, $I_{1,2,(0)}$, and (-1)-order self-diffraction beams, $I_{1,2,(-1)}$. The grating was also probed by a weak *He-Ne*-laser beam.

Recording of the grating simultaneous with the application of a dc-field at oblique incidence leads to a monotonic increase of diffraction toward a quasi-stationary diffraction efficiency, $\eta \sim 10 - 20\%$ in about 100 s. The diffraction does not disappear as the pump and dc-field remain for extended periods of time. The maximum diffraction efficiency was observed when the angle ψ between the normal to the cell and bisector of the recording beams was about 45° . Decreasing ψ resulted in a corresponding decrease of the diffraction toward zero at normal incidence. The analogous dependence was observed for diffraction of the probe beam on the angle between the probe beam and the normal to the cell. We also found that the probe-diffraction strongly depended on the polarization of the probe beam; maximum diffraction was observed at *p*-polarization of the probe, while there was no diffraction of *s*-polarization of the probe beam. Rotation of the cell around the bisector of the recording beams did not change the diffraction and self-diffraction.

We observed efficient coupling between the recording beams. The measured exponential gain coefficient was, $\Gamma \approx 1000 \text{ cm}^{-1}$, which is typical for photorefraction in LC systems, although we note that, in the Raman-Nath regime, this characteristic gain would not necessarily be descriptive as a figure of merit for applications. The direction of energy transfer between the beams was determined by the sign of the dc-field and by the direction of the beam tilt with respect to the normal to the cell.

Switching off the recording beams and dc-field resulted in disappearance of the diffraction of the probe beam after few minutes. If we turned the dc-field off keeping the beams on, a sharp spike in the diffraction efficiency was observed followed by the slow disappearance of diffraction after about 100s. However, if the cell was again subjected to a step-like dc-field, strong diffraction of the probe beam reappeared. This indicates that a “hidden grating” remained in the cell, which can be “developed” by repeated application of the dc-field. The hidden grating could be recovered after several hours, and in some samples,

for several days following recording. The time of the recording of the hidden grating was several tens of seconds and the maximum efficiency of the hidden grating varies from cell to cell in range 0.1-0.2.

We found that the grating recording strongly depended on the previous charge state of the cell. If a dc-field has never been applied to the sample with all of the light beams applied, either no diffraction or very weak, short-lived self-diffraction and probe beam diffraction was observed (efficiency, $\eta \sim 10^{-3}$) at oblique incidence. If observed at all, the first-order self-diffraction and probe-diffraction disappeared after approximately 1 min exposure. Later application of a step-like dc-field did not result in diffraction, i.e. a hidden grating was not recorded.

Prior application of a dc-field to the cell changed the situation drastically leading to recording of both a visible grating and a hidden grating. The recording dynamics of the grating when a dc-field was applied depended on the duration of the application of the dc-field prior to the pumps (Fig.1). One observes a peak and subsequent decay of the diffraction intensity under irradiation to a steady non-zero value. The amplitude of this transient peak increases with the duration of the previous application of voltage, but the persistent diffraction intensity does not. This suggests that the observed processes are reversible.

Surprisingly, prior application of dc-field allowed us to record a hidden grating even without application of dc-field during application of the light beams. Later application of a step-like dc-field did result in strong diffraction of the probe beam; an initial spike in the diffraction is followed after few seconds by much slower dynamics where the diffraction attains a maximum and then slowly disappears over several minutes (Fig.2).

The observed recording of a long-lived hidden grating coupled with the necessity of a dc-field to visualize the grating suggests that the irradiation pattern modulates the surface chemistry. This surface modification is made visible by bulk diffraction arising from the

modulated director when an electric field is applied. Chemical modification could involve the modulation of either free or bound charges near the ITO surfaces. However, in the absence of an applied field, free charges native to the LC bulk diffuse to the surface and screen the surface-bound charge (and the resulting potential modulation) which hides the grating. Application of the field normal to the surfaces, $E = E_z$, withdraws the mobile screening charges from the surface and a strong spatial modulation of the surface charges occurs. Charge modulation leads to a concomitant modulation of the surface potential: $\Phi(z = 0, x) = -\phi_1 / 2 + \phi_0 \cos qx$, $\Phi(z = L, x) = \phi_1 / 2 + \phi_0 \cos(qx + \delta)$ (phase shift is given by non-normal incidence of the recording beams) and the appearance of a spatially modulated electric field. This field distorts the homeotropic orientation of the director through a torque proportional to the product $E_x E_z$ (x in plane; z perpendicular to plane) adjacent to the surface²⁰. This torque reorients the director leading to a diffraction spike just after application of the dc-field. The characteristic time of this reorientation, is determined by the elastic-viscosity properties of LC $\tau_{orient} \approx \frac{\gamma \Lambda^2}{\pi^2 K} \approx 0.4$ s ($\Lambda = 20$ μm , $\gamma = 1$ Pas, $K = 10^{-11}$ N). After that an additional director reorientation occurs, due to bulk carriers drifting in the external field with a much longer time constant, τ_{bulk} , due to low carrier mobility. After a couple of minutes, diffusion of charges in the plane (x) decreases the spatial modulation of the reorientation torque $\sim E_x E_z$ resulting in the disappearance of diffraction.

The described model explains not only peculiarities of hidden grating recording but also the dynamics of recording under a dc-field (Fig.1). The appearance of an intensity peak following the application of the dc voltage is explained by the accumulation of bulk carriers near the electrodes. The increased concentration of charge near the electrode enriches the surface charge layer increasing diffraction when the grating is recorder later. Following this, the free charges redistribute along x -axis to screen this modulation, and the efficiency of the

grating decreases to its steady-state value. As was noted above, extinguishing the dc-field with the pump beams applied, resulted in a spike in the diffraction efficiency followed by slow disappearance of the diffraction. To understand the appearance of the spike, we need to remember that the total field in the bulk of the cell is determined by a difference between the external field and the field which is produced by the double electric layer near the surfaces. Just after the external field is switched off, the total field abruptly increases causing a sharp increase in the diffraction efficiency. Then the surface charges are compensated by charges of the opposite sign accumulating from the LC bulk. This charge compensation results in the subsequent slow disappearance of the diffraction and screening the grating.

The crucial role of surface charges in the grating recording is well illustrated by the decreased “writability” of the grating with illumination and rejuvenation of the “writability” by application of dc-field (Fig.3). In the first part of the plot, the dynamics of the recording under simultaneous action of two crossed beams and a *dc*-field is depicted. After quasi-stationary diffraction is attained, the *dc*-field and one of the beams was blocked, but the other beam was kept on for 10 min. It resulted in erasure of the diffraction grating (Part-2 of the plot). When the *dc*-field and the other beam were unblocked again, only weak diffraction was observed over the same time scale (Part-3 of the plot). However, the sensitivity of the cell was restored by prior application of a *dc*-field again (Parts-4;5 of the plot), since this field restores the original surface charge layer.

3. CONCLUSIONS

Summarizing our results, we can say that even in the simplest LC system, containing bare ITO electrodes and the ostensibly light insensitive nematic compound 5CB, a variety of different surface-mediated photorefractive mechanisms occurs. At present, we know that the surface photorefractive is governed by carriers fixed on the electrode surfaces and by the bulk mobile carriers. Surface-fixed carriers may be either adsorbed ions of 5CB or adsorbed

charged residuals of the chemical synthesis. The observed enhancement of the diffraction following prior *dc*-field application is explained by enrichment of the electrode surface charge by the adsorbed ions due to their drift to the electrode. Alternatively, a layer of bound charge induced by interaction of the CN-group of 5CB with high electron affinity ITO surface may contribute. Illumination alters the surface-fixed charge on the ITO surface, presumably due to photoinduced injection of carriers from the electrode, resulting in a spatially-modulated distribution of the charges or dipole moment. In the absence of an applied field, the bulk free charge screens this modulation, depressing the diffraction. Application of the *dc*-field unscreens the modulation and produces the reorientation torque leading to strong diffraction. Besides, prior application of the *dc*-field sensitizes the surface. Simultaneous action of the electric field and light results in an additional modulation of the double charged layer and additional diffraction.

Even though these results are explained phenomenologically by our model, the chemical nature of the fixed-charges on the ITO-surface and the mechanism of their control by light remains are not yet understood. It is likely that the CN-groups of 5CB play an important role. We can speculate that this group may donate charge toward the ITO-surface forming a bound layer of adsorbed 5CB molecules on the ITO surface whose characteristics can be controlled by light-induced adsorption and desorption from the electrode material. This idea is supported by the fact that these hidden gratings were not observed when 5CB was replaced by LC mixture, ZLI 4801, which do not contain CN-moieties.

Preliminary experiments carried out on 5CB-cells containing gold electrodes yielded similar results: we also observed a hidden grating and stationary diffraction in a *dc*-field. Since hidden gratings were also observed on ITO electrodes covered by HTAB,¹⁴ these effects may be quite general. It is clear, though, that by eliminating the alignment layer, we are able to demonstrate the adsorption of charged species is quite general and can occur on

the electrode as well as the alignment layer. Future work will be aimed at elucidating more clearly the relative role of the electrode/alignment layer and alignment layer/liquid crystal interfaces in the process, since this work has demonstrated the importance of adsorption from the liquid crystal bulk in mechanisms of photorefractive in liquid crystals.

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Figure 3. Dynamics of the grating recording and relaxation. The intensities of the beams are $I_1 = I_2 \approx 50$ mW cm⁻². The dependence of the voltage applied to the cell on time is depicted in the top plot. Regions 1, 3, 5 have two laser beams applied; region 2 has one beam applied; region 4 has no light applied.

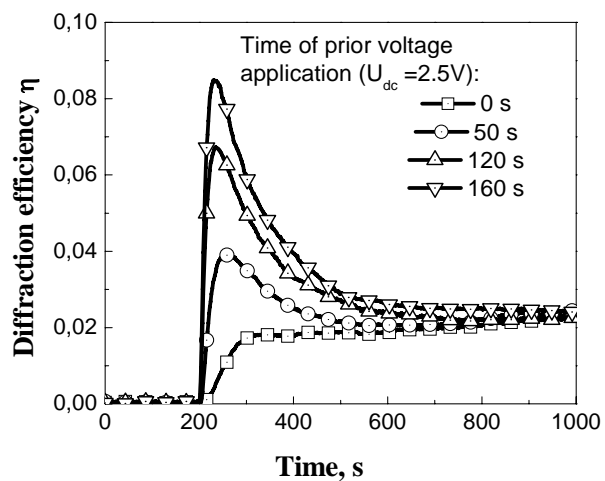


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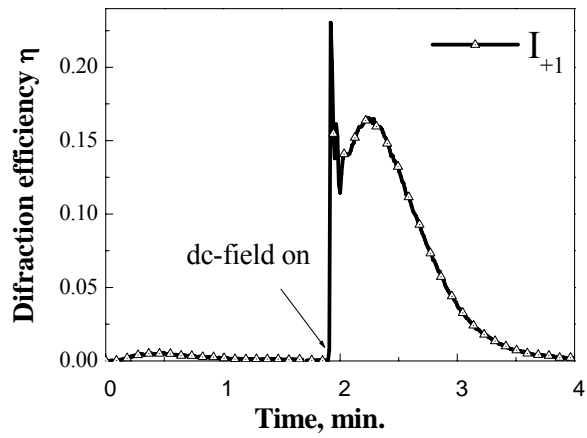


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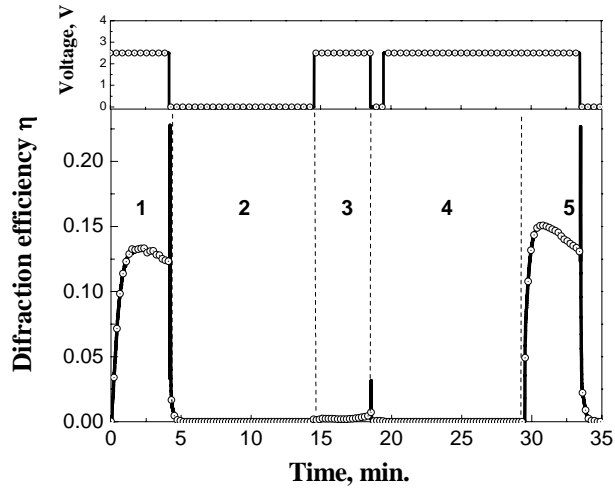


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