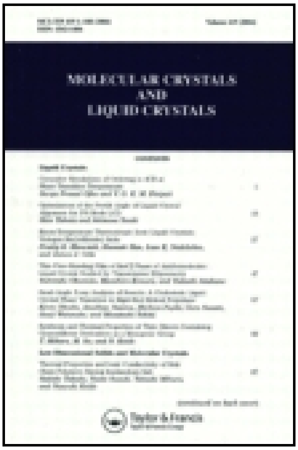

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Surface Screening Layers and Dynamics of Energy Transfer in Photosensitive Polymer-Liquid Crystal Structures

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Surface Screening Layers and Dynamics of Energy Transfer in Photosensitive Polymer-Liquid Crystal Structures

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The dynamics of energy transfer in photoconductive polymer liquid crystal structures can contain important information on interface effects and surface electric fields contributing to the strength of liquid crystal reorientation gratings. The characteristic, transient effects observed during switching on and off of incident light or electric field can be explained by the presence of surface screening layers. Screening layers play an important role in the reorientation of liquid crystal director in cells with different alignment layers. Strong screening of external DC field is present not only in cells with a photoconductive polymer (56 V), but in standard cells with thicker (0.3 μm) polyimide, aligning layers.

Keywords: nematic liquid crystals; photoconductive polymers; surface-charge field; two-beam coupling

INTRODUCTION

The process of asymmetric energy transfer via two-beam coupling was studied in different liquid crystal systems, but the most promising results were achieved in liquid crystals doped with dyes (or fullerenes) and in liquid crystal-photosensitive polymer structures. In particular, light amplification in hybrid, photorefractive material-liquid crystal

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systems can be used for optical addressing in light valves and spatial light modulators [1,2]. While achieving high gain is of considerable interest, the two-beam coupling process can also provide an important insight into the nature and mechanism involved in the reorientation of liquid crystal director under the influence of electric field and light.

I.C. Khoo and co-workers [3] reported very high gain in 5CB liquid crystal doped with C_{60}, which expressed in terms of exponential gain (also called gain coefficient or coupling coefficient) was of the order of 3000 cm^{-1}. Further experiments in similar systems by Zhang *et al.* showed [4] gain of 500 cm^{-1}, while those carried out by Mun and his group [5], gain of 90 cm^{-1}.

Dyes, such as Rhodamine 6 G or Methyl Red, dissolved in liquid crystals, such as 5CB, were also used to study nonlinear effects and two-beam coupling. Wiederrecht *et al.* [6] reported exponential gain of the order of 600 cm^{-1}. High nonlinearity and strong electric space-charge field is evidently present in dye doped systems – as demonstrated by, for example, high diffraction efficiencies [7] or large intensity dependent refractive index changes [8].

The other type of structure that was widely used for amplification of light via two-beam coupling is a hybrid liquid crystal-polymer system. It is, typically, based on a photorefractive polymer, poly-vinylcarbazole (PVK) doped with sensitisers such as TNF or C_{60} and used as alignment layer or as an intermediate layer, between an ITO electrode and aligning material. By doping PVK with sensitisers, its photoconductivity can be increased and shifted from the UV to the visible. High exponential gain was measured by Bartkiewicz and Kajzar in such systems [9,10], namely as high as 3700 cm^{-1}. In similar systems other groups also reported gain [5] of 220 cm^{-1} and 48 cm^{-1} – measured by Ono and his group [11].

In liquid crystals, the formation of a two-beam coupling grating relies on an electric field induced reorientation grating that leads to refractive index modulation. However, as the actual mechanism of the electric field build-up inside a liquid crystal-polymer cell is not clear, it is difficult to optimise the experimental conditions. This could be the reason for some differences in the data published so far on gain and diffraction efficiency. The groups that studied two-beam coupling in liquid crystal-PVK systems, also proposed different qualitative models of the mechanism involved in the formation of the electric space charge field.

Ono and co-workers [11] suggested that the space charge field is due to the generation of charges in a PVK layer. The trapping of charges takes place in an additional, insulating PVA layer, adjacent to the PVK layer. In the model suggested, PVA was essential for the formation of space-charge field. Mun and his group [5] explored this idea further and indicated that charge photogeneration occurs in the liquid crystal bulk. They proposed that charge trapping occurs at a PVK-liquid crystal interface, so PVA layers are, in fact, not essential. While these models of the space charge field formation were quite different, they shared a common assumption, namely they were all based on a standard model of charge generation, transport and trapping, as often used in bulk, solid-state photorefractive materials. Furthermore, in both models an externally applied DC field was assumed to cause a uniform reorientation of the liquid crystal director without illumination.

The process of liquid crystal director reorientation and two-beam coupling was also studied in liquid crystal cells with non-photoconducting polymer layers. The results of Pagliusi and co-workers [12] suggest that accumulation of charges on a liquid crystal interface is not limited to the case of photoconductive polymers.

Our own studies of liquid crystal-polymer systems [13] provided the evidence that, in fact, strong double charge layers form at the liquid crystal-photoconductive polymer interface and they are capable of screening high electric fields. In a qualitative model we proposed, the formation and discharge of a surface screening layer was key to for inducing reorientation gratings, rather than standard photorefractive processes taking place within a polymer, such as charge excitation, drift and trapping.

While the results of two-beam coupling gain do not provide any direct evidence for a particular mechanism involved in the formation of refractive index gratings, the difference in experimental results and qualitative explanations provided by different groups clearly indicate that more detailed studies of the role of charged dopants and surface effects are needed. Pursuing this idea, we focussed our work on two areas: first, on exploring in more detail the conditions and materials where surface charge screening is observed and secondly, on studying the dynamics of two-beam coupling process and its dependence on an applied electric field and light illumination.

EXPERIMENTAL SET-UP AND PROCEDURES

In a typical two beam coupling experiment the intensity of incident and transmitted beams, are measured. Figure 1a presents a schematic diagram of such experimental set-up. In our arrangement a liquid crystal cell was mounted on a rotation stage that could be precisely turned around the vertical axis (perpendicular to the plane containing the incident beams) at the point of intersection of the incident beams.

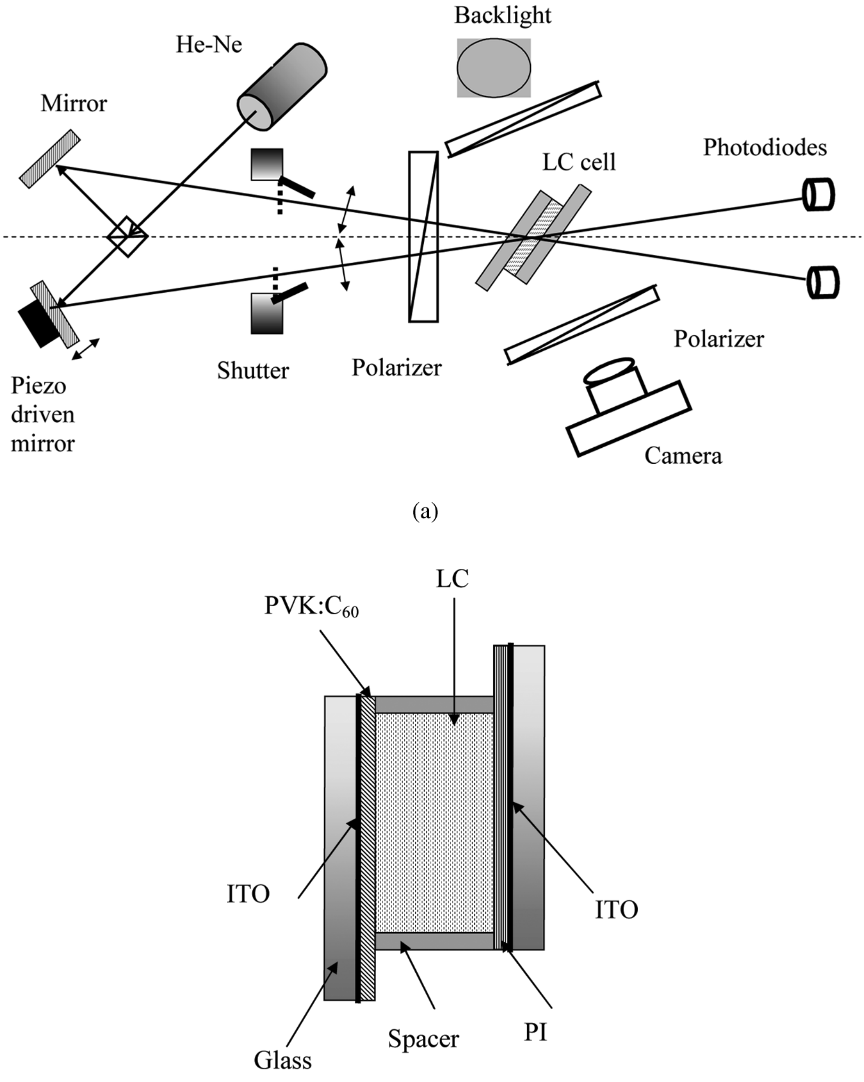

FIGURE 1 (a) Experimental set-up for measuring light induced reorientation and two-beam coupling gain; (b) Liquid crystal cell structure with one substrate covered with PVK:C_{60}.

Electric shutters, that blocked or unblocked the beams, as well as application of electric field, were controlled by a computer. The intensity grating, created by the interference of two, horizontally polarized, beams (543 nm) had a spacing of either 3 or 60 μm. This experimental set-up was also used to measure the light and DC field thresholds for reorientation of liquid crystals with single beam illumination.

The structure and appearance of an illuminated spot on a sample was simultaneously monitored through second pair of polarisers and backlight and then recorded on a CCD camera. Monitoring of the illuminated area of the cell enabled us to record the dynamics and uniformity of light and electric field driven reorientation.

The liquid crystal-polymer cell structure is shown on Figure 1b. PVK doped with photosensitiser (C_{60}) was deposited as a thin and uniform layer onto ITO covered glass substrates. Both C_{60} and PVK were dissolved in chlorobenzene. Doping of PVK with C_{60} was achieved by adding a saturated concentration of C_{60} solution to the PVK solution with concentration of approximately 14.9% by weight. Polymer films were then spincoated onto clean ITO covered glass and dried at high temperature.

The substrates were unidirectionaly rubbed and uniform planar alignment was achieved. Doped PVK layer was deposited only on one substrate, while the other was covered with standard polyimide (PI) as an alignment layer. All the cells were 30 μm thick and filled with pure (undoped) E7 liquid crystal mixture. A DC bias applied to the cell ITO electrodes had a negative contact applied to the PVK covered substrate.

For the study of surface charge screening, we also prepared cells with polyimide on both substrates, without any photosensitive layers. The cells had either thin, less than 0.05 μm, or thick, approximately 0.3 μm, layers of polyimide.

The experimental procedure for precise detection and measurement of two-beam coupling consisted of several steps where the incident beams were either blocked or unblocked. The value of applied DC field varied from 0 to 56 V. There are several stages of the measurement all controlled by a computer. In step one and two, the shutters were closed and then opened to let both beams through simultaneously. Then, just one beam (pump) was present, followed by a step where both beams were again illuminating a cell. Further, the shutter for the pump beam was closed and for the probe opened. Finally, both beams were let through and then both blocked. In this way, time dependence of beam intensities could be recorded and monitored and the response of the system to transient changes in incident light and applied DC field could be recorded.

For measuring the steady-state gain magnitude, the measurements were taken when steady-state values of transmitted intensities were reached and the final, returned value of intensity was taken as an average of 600 data points. This sequence of steps could be repeated for different values of DC field, increasing from zero. The complete experimental procedure allowed us to measure gain and, at the same time, monitor the total change in beam intensities.

Using this experimental methodology two-beam coupling gain could be measured in two different ways. In the first experiment, transient beam intensities and gain was measured to observe the dynamic response of the system to fast changes of parameters, such as incident light intensity (or a DC field). In the second experiment, the steady-state values of beam intensities were recorded after relaxation of the system to a quasi-equilibrium state.

RESULTS AND DISCUSSION

Surface charge layers that form at the liquid crystal and polymer (or other aligning material) interface can strongly influence the magnitude of a DC electric field penetrating the liquid crystal bulk. In cells with PVK:C_{60} layers, we observed that the bulk of liquid crystal could be completely screened [13] from the external electric field. In this case, strong surface charge field could completely block the external electric field, so no Freedericksz transition was observed up to 56 V (1.9 V/μm) of applied DC field. However, this threshold could be significantly reduced if the cell was illuminated by visible light. The incident beam could have low intensity, namely as low as μW/cm^2, to induce the transition provided its wavelength was within the visible range of spectrum, where PVK:C_{60} is photoconductive. Figure 2 presents how the threshold voltage decreases with increasing incident light intensity up to saturation of photoconductivity. As sensitised PVK becomes highly conductive in illuminated areas, the applied electric field can reach liquid crystal bulk. The higher the incident intensity is, the more efficiently surface charge layers can be selectively annihilated and liquid crystal reoriented. Low dark conductivity of PVK – either sensitised or not – also means that patterns and gratings with resolution down to 3 μm could be written and high resolution, reorientation and refractive index patterns created in the liquid crystal. As expected, when an AC field was applied, the usual Freedericksz transition occurred with a threshold of approximately 2 V.

In standard liquid crystal cells with non-photoconducting polymer layers, the DC field threshold of reorientation was approximately ten times smaller than the one observed in our experiments. For example, cells with alignment layers made of PVA (polyvinyl alcohol) and liquid crystal E7 had the reorientation threshold [12] of 5 V.

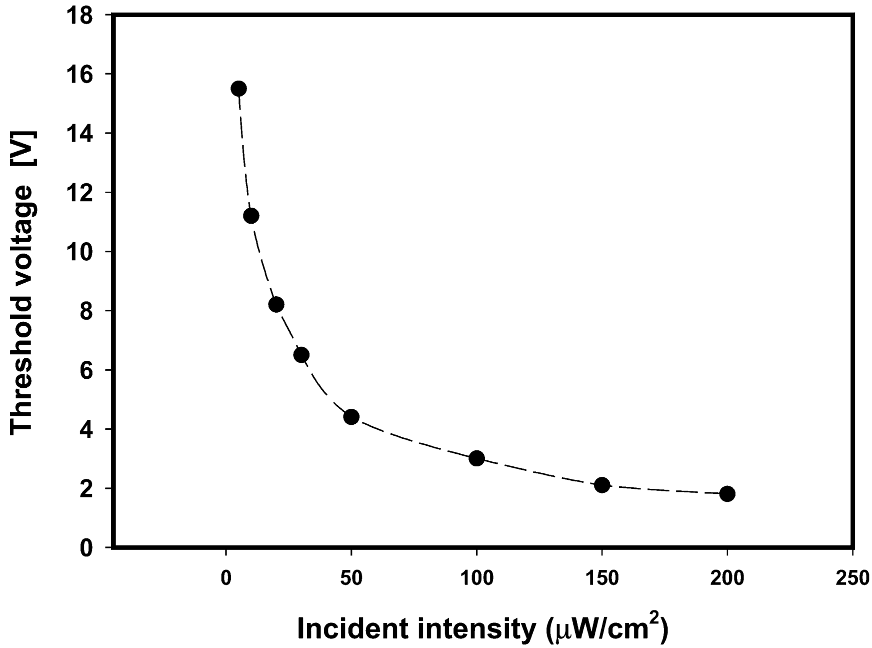

FIGURE 2 Threshold voltage of Freedericksz transition and its dependence on the incident light intensity.

While surface charge layers are particularly strong in the case of PVK, they can also develop in other types of cells. We investigated this effect in cells with polyimide aligning layers and found the evidence of strong screening. For cells with thin, less than 0.05 μm polyimide layers the reorientation threshold was between 2 to 3 V, as expected. However, when a thicker layer of polyimide was deposited, approximately 0.3 μm, the reorientation threshold increased significantly reaching the levels of 20 V.

Further, detailed analysis of charge generation and transport between electrodes, aligning layers and liquid crystal as well as theoretical modelling is needed to optimise and to understand more fully the nature of interface effects. However, as a first step, we studied in more detail the transient response of the liquid crystal-PVK:C_{60} system to applied light and DC field.

In particular, we compared the time evolution of both amplified and depleted beam for the two ways in which a two-beam coupling grating can be written. In the first one, both beams were unblocked and illuminated the cell at the same time (with a DC field present) and

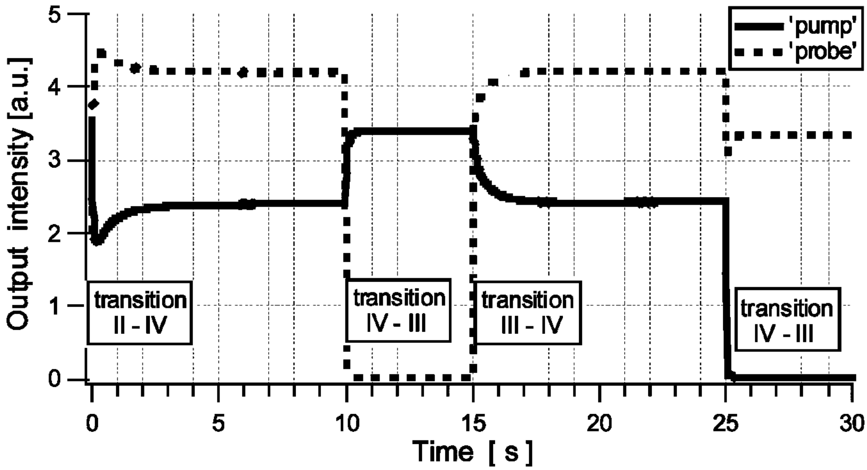

FIGURE 3 Dynamics of two-beam coupling under different illumination and applied electric field conditions.

in the second option, the two beams were unblocked in series, one after another, also with a DC field already applied to the cell. Let's call the first option "dark-to-grating" transition and the second as "bright-to-grating" transition. We systematically considered possible states of grating formation and transitions during for each option of running the two-beam coupling experiment.

We observed different dynamics of the grating build up for the two cases: in the first case, the build up is much faster with a characteristic, transient peak in amplified probe beam (and a corresponding dip in the depleted probe) followed by decay to a steady-state level. In the second case, the build up is slower, without a transient peak, as shown on Figure 3. However, the final equilibrium state and the value of gain reached in both cases was the same.

This steady-state value of gain was high, reaching approximately $500\,cm^{-1}$. Its magnitude was found to depend on several parameters such as the DC field – its bias, direction and value; the direction of the cell tilt with respect to the bisector between the incident beams, intensity and ratio of beam intensities, as well as the quality of the sample.

The possible equilibrium states of our system (sample) relative to ambient conditions could be identified and compared with the data on the measured intensities of beams in the two-beam coupling experiment. Those states can be labelled I to IV for clarity (as shown on Fig. 3). In the first stage (I) a sample is in a steady-state with some equilibrium distribution of the director set by the original alignment conditions and without any externally applied field, either electrical or optical. As the sample is not illuminated, no intensities are measured. In the second stage (II) the sample remains unilluminated, but since a DC field is applied, screening charge layers develop. However, the director distribution remains as in state I. This was confirmed by investigating cell between crossed polarisers with very weak backlight and also by illuminating the cell with light of wavelength beyond the photoconductivity band of PVK:C_{60}. It is important to note that equilibrium screening charge is always supported or supplied by an external DC field and discharged via the dark conductivity of PVK. As in the previous stage, the sample is not illuminated, so beam intensities are not be measured. Further (state III), the sample is as state II but is now illuminated by one laser beam and the director reorients in illuminated areas. This state III is present only in illuminated part of the sample, unilluminated part of the sample remains in state II. Transmitted beam intensities can be measured and this state corresponds to intervals between 13–15 and 27–30 seconds on Figure 3. An alternative state (state IV) is for the sample, starting from state II, to be illuminated by two laser beams, so the director is reoriented in bright fringes. This state (state IV) corresponds to intervals 8–10 and 23–25 seconds on Figure 3. State IV is also present only in the part of the sample illuminated with intensity pattern and, with certain approximation, is a combination of states II and III (dark and bright fringes, correspondingly).

The transitions from one state to another and the behaviour of coupled beams could be explained qualitatively using the model of surface charge layers and their selective annihilation. Let us consider the sample in state I, namely without illumination. According to our model, after applying an external DC bias, surface screening charges accumulate near the PVK:C_{60} surface and that reduces the potential applied to the liquid crystal layer to the level below the Freedericksz transition.

If the cell is now illuminated, then in bright areas, screening field is reduced or discharged completely. This causes the reorientation of the liquid crystal director by the superposition of an external DC field and the remaining screening field. After some transition period, state III is reached.

Now let's consider the two possible transitions leading to state IV. The first way is "dark-to-grating" transition, corresponding to state II to state IV transition, and the second way is "bright-to-grating" transition, equivalent to state III to IV transition.

As indicated above, there is a clear difference in evolution of amplified and depleted beams for the two cases and we propose a qualitative explanation for this effect. For the case of state II to IV transition, the sample in state II is illuminated by the interference pattern produced by two laser beams, so the surface charge is discharged in bright fringes and the director is reoriented, following the pattern of bright and dark fringes. There are two important parameters contributing to the speed and strength of reorientation and refractive index gratings. These parameters are the relaxation time of photoconductivity of PVK:C_{60} and the response time of liquid crystal. The peak and strong maximum in the amplified signal could be explained by the fast discharge of surface layers and subsequent sudden application of the DC field, sensed by the liquid crystal bulk. Strong, but transient gain suggests more pronounced, initial director reorientation followed by its relaxation towards the original state. The contribution from additional, transient current going through the cell at the moment of discharge could also contribute to this peak in amplification. This transition corresponds to interval 0 to 5 seconds (Fig. 3).

For the case of state III to IV transition, the illumination conditions only change from a uniform (Gaussian beam) to an interference field of two laser beams. The situation is different – the uniformly illuminated area with discharged surface screening layers is replaced by a modulated pattern of dark and bright fringes. As a result, the process of recharging in dark fringes takes place and the director reorientation follows the changes in the modulated electric field profile. In this case, the intensities of both amplified and depleted beams change smoothly with time, exponentially approaching the equilibrium, steady-state value reached in state III. This process is much slower than the first transition and there are two processes that could be responsible. First, the formation of the surface charge layers requires time to develop; a process that is limited by the conductivity of liquid crystal, substrates as well as by the presence of impurities or ions in the liquid crystal bulk. Secondly, when a uniform illuminated spot is replaced by an interference pattern, it takes time for photoconductivity to decay in the dark fringes. Limited value of photoconductivity means that surface charge will not be discharged instantly. This transition corresponds to the time interval 15–20 seconds (Fig. 3). The reverse transition from the state IV to III takes place when one of the two beams is closed and the grating decays to the uniformly reoriented state due to discharge of the screening layers in the previously dark places. This case corresponds to time intervals 10–13 and 25–27 seconds (Fig. 3).

Figure 4 presents a photograph of most relevant states of the sample (I–IV). In order to illustrate better the lack of reorientation with a DC field applied, but without illumination, a 200 μm wire was placed

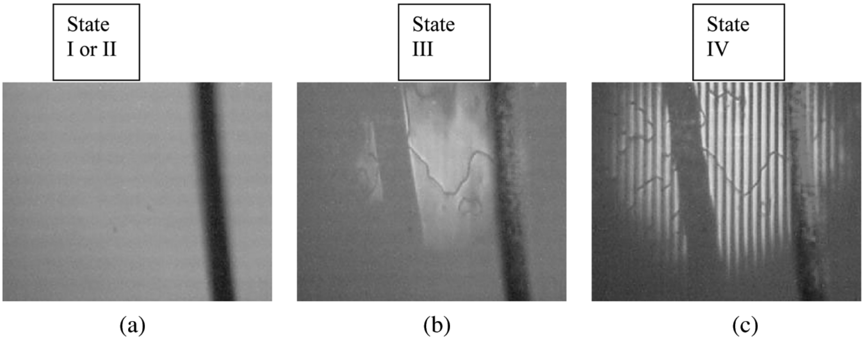

FIGURE 4 Demonstration of selective reorientation of liquid crystals in a cell with an applied DC field. A 200 μm wire is placed in front of the cell to help to illustrate the effect. (a) without illumination no reorientation occurs; (b) illumination by a single beam-liquid crystals get reoriented except in the area where light is blocked by the wire illuminated by one beam; (c) an interference pattern is incident on the cell and high resolution, 50 μm, reorientation grating is recorded, apart from the region that is behind the wire. (See COLOR PLATE XVI)

in front of the cell (Fig. 4a). Figure 4b shows the case of uniformly reoriented area, where a single beam was incident on a cell, except in the area behind the wire. For the case of incident interference pattern (Fig. 4c) with 50 μm spacing, high contrast reoriented grating is clearly visible.

CONCLUSIONS

In conclusion, we reported and analysed the characteristic features and dynamics of light and electric field induced two-beam coupling process in cells with alignment layers made of PVK doped with fullerene (C_{60}) as a photosensitiser. The time evolution of amplified and depleted beams for the different DC field and illumination conditions support the idea that selective discharge of strong, surface charge layers plays an important role in efficient reorientation gratings in the bulk of the liquid crystal.

There is a strong dependence of Freedericksz transition threshold on the incident light intensity. The Freedericksz transition threshold (without illumination) is very high (56 V) for cells with PVK:C_{60}. However, liquid crystal cells with non-photoconductive, but thicker polyimide layers, this threshold can reach 20 V. Surface screening layers can clearly be present in a wide variety of different cell design and materials. They can be regarded as "command" layers and allow a flexible control of diffraction and energy transfer in liquid crystal cells.

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