

Negative Photodielectric Effect in Structures Fullerene Film / Film of Ferroelectric Liquid Crystal

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This paper presents the research results of light influence on the dielectric properties of the structure fullerene film C60 / film of ferroelectric liquid crystal (FLC). It is experimentally shown that in the chiral smectic phase of FLC, unlike other phases, lighting of structures leads to a decrease in capacity (negative photodielectric effect). The mechanism of this effect is offered. On the basis of obtained data, the explanation of the positive photodielectric effect, which has been found in the work [1] for studying colloidal solution FLC + 43 wt. % mixture of fullerenes C60 + C70, is given.

Keywords: Ferroelectric liquid crystal, Fullerene, Dielectric permittivity.

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1. INTRODUCTION

We have shown in [1] that illumination by nonmonochromatic light of colloidal solution FLC + 43 wt. % mixture of fullerenes C60 + C70 leads to the decrease in the real component of the complex dielectric permittivity ε' in isotropic (*I*), cholesteric (*Chol*)- and smectic *A* (*SmA*) phases and increase of ε' in chiral smectic *C* (*SmC**) phase. This effect was called the positive photodielectric effect. We have also established that the ratio of the dielectric permittivity when illuminated to the dielectric permittivity in the dark $\varepsilon'_p/\varepsilon'_d$ was the maximum for the temperatures close to the *SmC** \rightarrow *SmA* phase transition temperature.

We should note that no features were found for these samples in the spectra of the imaginary component of the complex dielectric permittivity.

Another important factor is that the positive photodielectric effect was observed only for the frequencies of $f < 1$ Hz, namely, such frequencies at which almost all the voltage is applied to the near-electrode layers [2, 3].

Analysis of the recent publications on the properties of FLC shows that currently these materials are promising for use not only in display technologies but also in photonics [4, 5]. Therefore, it is important to establish the causes of manifestation of the positive photodielectric effect, since new practical applications of FLC can be connected just with this effect.

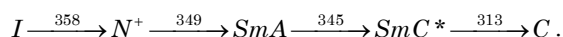
One can consider FLC and (C60 + C70) alternating layers as the simplest model of the investigated in [1] composite. Therefore, to establish the physical mechanism of the found effect it is necessary to have data on the properties of the FLC film/fullerene film structures. Just these investigations provide the study of the FLC/fullerene interface. This is also important, since, as it was noted above, the positive photodielectric effect was observed for those frequencies, at which electric field was applied to the near-electrode area.

Therefore, the aim of the present work is to investigate the influence of nonmonochromatic light on the dielectric properties of the FLC film/fullerene film struc-

tures and establishment based on the obtained data of the mechanism of the positive photodielectric effect revealed in [1] in the study of the colloidal solution FLC + 43 wt. % mixture of fullerenes C60 + C70.

2. MATERIALS AND METHODS

As in [1], for the study we have used the FLC which is an eutectic mixture (62.3 and 31.2 wt. %) of complex ethers 4-*n*-hexyloxyphenyl-4-*n*-oktyloxybenzoate in 4-*n*-hexyloxyphenyl-4-*n*-decyloxybenzoate. Luch-15 served as the chiral impurity [6]. Its concentration was equal to 6.5 wt. %. Such liquid-crystal mixture has the following states and temperatures of the phase transitions:



Chemically purified C60 (uncontrolled impurity concentration is less than 1 wt. %) was used to obtain the films. C60 layers were deposited on the glass substrate covered by the conductive and transparent in the visible spectral region ITO layer (mixture of indium and tin oxides) using thermal spraying at room temperature and pressure of 10^{-6} Torr. Film thickness was equal to 100 nm. FLC layer was deposited on the C60 film surface at the temperature of ≈ 363 - 368 K, and ITO electrode, which, as well as the bottom electrode, was deposited on the glass plate, was pressed by clamps. The sample capacity was controlled when approaching the electrodes. Electrodes approached each other until further approaching did not lead to the liquid crystal outflow. In this case, thickness of the FLC layer was specified by its viscosity and surface tension.

The photodielectric properties of the sample were analyzed by the changes in the capacity and resistance induced by illumination. The values of *C* and *R* were measured in the range of 10^{-3} - 10^6 Hz by the oscilloscope method [3, 7]. Illumination of the samples was performed using both nonmonochromatic light of halogen incandescent lamp and interference filter with the transmission peak for the wavelength of 485 nm (this wavelength corresponds to the maximum absorption of

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fullerene molecules). The light intensity was equal to 50 mW/cm² in the case of the monochromatic light and 0.5 mW/cm² for the wavelength of 485 nm. Temperature in the range of 310-370 K was maintained to within 0.2 K using a specially developed thermostat with the low level of electromagnetic disturbances.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Since, in contrast to the colloidal solution studied in [1], the sample was composed of two materials different in the properties, it was impossible to describe its dielectric properties in terms of the components of the complex dielectric permittivity. Under these circumstances, capacity and resistance, whose values were determined directly using the oscilloscope method, were chosen to be the main parameters for the analysis.

Photodielectric properties of the C60 film/FLC film structures were analyzed by the frequency dependences of the capacity C_p/C_d and resistance R_d/R_p ratios. Here index d corresponds to the measurements without illumination and index p – under illumination. Frequency dependences of C_p/C_d (a) and R_d/R_p (b) which correspond to the *I* (curves 1) and *SmC** (curves 2) FLC phases are illustrated in Fig. 1.

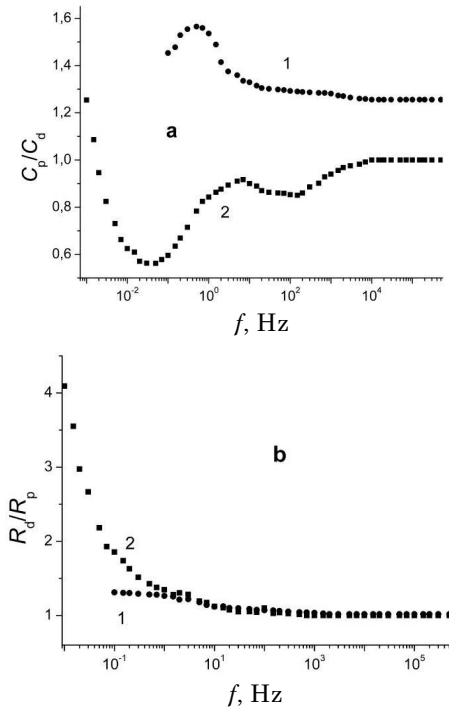


Fig. 1 – Frequency dependences of the capacity C_p/C_d (a) and resistance R_d/R_p (b) ratios corresponding to the *I* (curves 1) and *SmC** (curves 2) FLC phases

As it follows from Fig. 1b, illumination of the samples leads to the decrease in the resistance at the temperatures corresponding to both *I* (curve 1) and *SmC** (curve 2) FLC phases. It is important to note that frequency dependences of R_d/R_p for the *I*- and *SmC**-phases are almost identical. For the frequencies of $f > 10^3$ Hz the R_d/R_p ratio is equal to 1, i.e. illumination does not influence the properties of the samples. This result gives reasons to state that, as well as in the case of the col-

loidal solution, light influences the parameters of the near-electrode layer.

In Fig. 1a we present the frequency dependences of C_p/C_d . It is seen that, unlike the resistance, frequency dependence of C_p/C_d in the *I*-phase (curve 1) differs significantly from the frequency dependence of $C_p/C_d(f)$ in the *SmC**-phase (curve 2). Firstly, $C_p/C_d > 1$ in the *I*-phase (capacity of the sample increases under illumination for all the frequencies), while for the *SmC**-phase of the C60 film/FLC film structures this dependence is only observed for $f < 2 \cdot 10^{-3}$ Hz. Secondly, only one maximum at $f \approx 1$ Hz is observed on the frequency dependence of C_p/C_d in the *I*-phase, while several extremes are observed on the frequency dependence of C_p/C_d in the *SmC*-phase.

Frequency dependences of C_p/C_d in the *Chol*- and *SmA*-phases were similar to the same type of dependences in the case of the *I*-phase if FLC. It follows therefrom that decrease in the capacity of the samples under illumination is typical only for the FLC *SmC**-phase. We called this effect the “negative photodielectric effect”; and its detection and analysis can be considered the main scientific achievement of the given work.

For a more comprehensive analysis of the behavior of the negative photodielectric effect, we will consider the temperature dependence of the C_p/C_d and R_d/R_p ratios. It is seen from Fig. 1a (curve 1) that the maximum value of the C_p/C_d ratio is observed for the frequency of $f = 1$ Hz. Therefore, C_p/C_d and R_d/R_p ratios from Fig. 2 are given just for this frequency.

As seen from Fig. 2, the maximum change in resistance under the action of light ($R_d/R_p = 1.6$) is observed at the temperature corresponding to the *SmA*-phase of FLC. The obtained temperature dependence of R_d/R_p differs slightly from the results obtained for the colloidal solutions in [1]. As it was shown in [1], maximum of the temperature dependence of $\epsilon''_p/\epsilon''_d$ was not observed. The value of $\epsilon''_p/\epsilon''_d$ monotonously increased with increasing temperature.

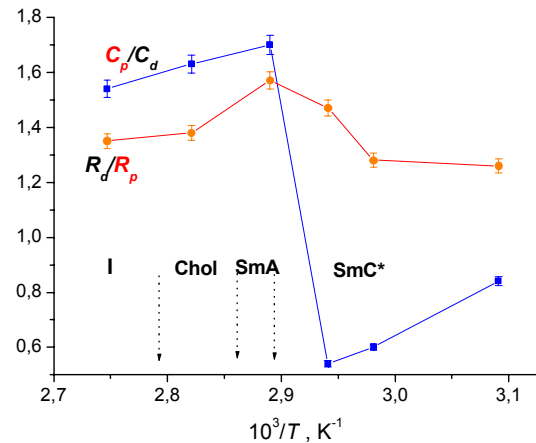


Fig. 2 – Temperature dependence of the C_p/C_d (curve 1) and R_d/R_p (curve 2) ratios of the C60 film/FLC film two-layer structure for the frequency of $f = 1$ Hz

In Fig. 2 (curve 1) we illustrate the temperature dependence of the C_p/C_d ratio. It is seen that $C_p/C_d > 1$ at the temperatures of $T > 345$ K (*I*-, *Chol*- and *SmA*-phases of FLC). The maximum value of C_p/C_d (≈ 1.7) was obtained in the *SmA*-phase of FLC. In going from the *SmA*

to the SmC^* -phase, C_p/C_d ratio becomes less than 1. It is important to note that decrease in the samples capacity under illumination is typical for all temperatures of the SmC^* -phase existence. Another important factor is that C_p/C_d ratio differs most from 1 near the $SmC^* \rightarrow SmA$ phase transition temperature.

It is logical to compare the temperature dependence of C_p/C_d with the temperature dependence of $\varepsilon_p/\varepsilon_d$ of the composite [1]. It was shown in [1] that $\varepsilon_p/\varepsilon_d > 1$ in the SmC^* -phase and $\varepsilon_p/\varepsilon_d < 1$ in the I -, $Chol$ - and SmA -phases of FLC. Moreover, maximum change in $\varepsilon_p/\varepsilon_d$ is also observed in the $SmC^* \rightarrow SmA$ phase transition region. Hence, we can conclude that temperature dependence of C_p/C_d (Fig. 2) is inversely proportional to the data obtained in [1]. The reason of these differences will be analyzed after the establishment of the negative photodielectric effect nature.

As seen from Fig. 1, the most significant changes of the structures capacity under the action of light are observed at those frequencies where, as it is shown in [1], the near-electrode phenomena play an essential role. For these frequencies, small values of the capacities and resistances of C60 and FLC can be ignored.

Since negative photodielectric effect is observed only in the SmC^* -phase of FLC, this allows to assume that the dipole polarization processes in the near-electrode layer can play a significant role in its manifestation. For this FLC phase, dipole polarization can occur due to the oscillations of the dipole moments of molecules. In the SmC^* -phase of FLC, these oscillations can occur when molecules turn (and, therefore their dipoles) around the helicoid axis. Such oscillations, even within the angles corresponding to the fluctuations of the order parameter, can be much easier to perform in the chiral smectic phase than in other FLC phases.

As shown in [5, 6], existence of a sufficiently thin near-electrode layer (that is equivalent to a large near-electrode capacity) in dielectric liquids is conditioned by a more complex, than in electrolytes, process. The main reason that prevents the charge exchange at the electrode/dielectric liquid interface is the presence on ions of a solvation shell of neutral molecules.

Charge exchange at the interface electrode (which C60 film is in our case) and FLC because of the electron transfer at the C60/FLC interface is carried out in all phases of a liquid crystal. However, charge transfer on account of the oscillations of the dipole moments around the helicoid axis can be an alternative to such mechanism only in the SmC^* -phase. As it was shown in [7, 8], such molecular vibrations occur in thin near-electrode layer, to which almost all the voltage is applied. Thickness of such layer exceeds more than one order of magnitude the thickness of the layer in which electron exchange takes place.

Under illumination of the structures C60 film/FLC film, conduction of the C60 films increases. To provide the additional charge transfer only in the SmC^* -phase of FLC, the other charge transfer channel is involved due to the oscillations of the FLC molecule dipoles. The larger angle, at which molecules will turn in the oscillations around the helicoid axis, is, the larger current will be transferred in this case. Therefore, it is necessary when illuminated that electric field was applied to

a larger in thickness of the near-electrode region of FLC. And this leads to the decrease in the capacity (Fig. 1) relatively to the capacity when measurements are performed without illumination.

Proposed mechanism of the negative photodielectric effect explains the causes of the decrease in the capacity of the FLC/C60 structures under illumination for the frequencies of $2 \cdot 10^{-3} < f < 10^4$ Hz. As follows from Fig. 1, for $f < 2 \cdot 10^{-3}$ Hz capacity of the FLC/C60 structures increases under illumination. The reason of this effect is that electric field is applied to a very thin near-electrode layer at sufficiently low frequencies (we have shown in [8-10] that the lower frequency of the measured electric field is, the smaller area of the electric field application is). For rather small thicknesses of the near-electrode layer the charge transfer mechanism due to the oscillations of molecule dipoles becomes ineffective because of the very small angles of rotation.

As shown in [3, 8], charge exchange on account of the electron transfer can be described as the dynamical process with certain relaxation time. Therefore, in the case when the alternating electric field period is of the same order or more than this time, then efficiency of the charge exchange should considerably increase.

In order to confirm the made assumption concerning the reasons of the increase in the capacity under illumination ($f < 2 \cdot 10^{-3}$ Hz) it is necessary to estimate the relaxation time. As it was shown in [3, 8], dispersion of the components of the complex dielectric permittivity during the electron exchange at the electrode/dielectric liquid interface can be described by the Debye equation modified by Cole-Cole

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}, \quad (3.1)$$

where ε_s and ε_∞ are the dielectric permittivities for the frequencies of $f = \infty$ and $f = 0$; τ is the dielectric relaxation time; α is the Cole-Cole parameter ($0 < \alpha < 1$).

It is impossible to analyze the relaxation process for the C60/FLC structures in terms of the dielectric permittivity. Therefore, as well as in the work [11], we have analyzed the frequency dependence of C and R taking C and $(\omega R)^{-1}$ as the analogues of ε' and ε'' , respectively. Thus, dependence $(\omega R)^{-1}(C)$ will be the Cole-Cole diagram for the investigated structures. Analysis of this dependence has shown that it can be approximated with small error by an arc (this corresponds to the Cole-Cole relaxation process). It was found that relaxation time is equal to 103 ± 10 s. This value corresponds to the frequency of 10^{-2} Hz and agrees well with the region on which C_p/C_d ratio becomes more than 1 (capacity of the samples under illumination increases).

Based on the proposed model of the negative photodielectric effect one can explain another important experimental fact, namely, the maximum change in the C_p/C_d value in the vicinity of the $SmC^* \rightarrow SmA$ phase transition. As known [12], rotational dynamics of the FLC dipoles under the electric field action in the SmC^* -phase can be described by the following relation:

$$\eta_r \sin^2 \Theta \frac{d\phi}{dt} = K \sin^2 \Theta \frac{d^2\phi}{dz^2} - P_s E \sin \phi, \quad (3.2)$$

where φ is the azimuth rotation angle of the FLC molecules around the helicoid axis; Θ is the polar rotation angle in the helicoid axis plane (in the plane which is perpendicular to the smectic layer).

Rotational viscosity depends most on the temperature among the parameters characterizing the FLC dynamical properties. Just the decrease in the value of η_r with increasing temperature is the main reason that the maximum decrease in the capacity under illumination is observed just near the $SmC^* \rightarrow SmA$ transition.

Now we consider how based on the proposed in this work model of the negative photodielectric effect one can explain the positive photodielectric effect in composites FLC – (C60 + C70).

The main difference between the composite and two-layer structure is that conduction in it using the charge transfer through the fullerene and FLC can occur along the parallel (independent from each other) channels. Initiation of the electron (or hole) conduction channels through the fullerene under illumination (and, so, decrease in the effective area of the electrodes) can be explained by the decrease in the capacity under illumination of the FLC – (C60 + C70) composite in the *I*-, *Chol*- and *SmA*-phases of FLC. Here, it is necessary to take into account the electron transfer between fullerene molecules through the near-electrode region of the sample.

Only in the *SmC**-phase charge transfer through the near-electrode region also occurs on account of the oscillations of the bound charges (FLC molecule dipoles). Just this charge transfer process becomes more effective under illumination. Such that, decrease in the number of conduction channels through the fullerene molecules takes place. Thus, this leads to the increase in the ef-

fective area of the electrode, and, as a consequence, to the increase in the capacity of the near-electrode region of the sample.

Comparison of the photosensitivity of the fullerene film/C60 film structures and the glycerol film/C60 film structures shows that the studied in this work structures have much less photosensitivity than the samples investigated in [11]. According to the conclusions done in the work [11], the reason of this is not only a small FLC conduction, but also, in a greater degree, non-optimal (for obtaining the maximum photosensitivity) fitting of the organic film/liquid crystal pair. As it was shown in [11], the maximum photosensitivity is realized when the Maxwell-Wagner mode is provided between the near-electrode regions of the contact bodies. Assurance of this mode for the studied samples is a technological and not a scientific problem.

4. CONCLUSIONS

It is experimentally shown that illumination of the C60 film/FLC film structures leads to the increase of the capacity in the *I*-, *Chol*-, *SmA*-phases of FLC and to the decrease of the capacity in the *SmC**-phase (the negative photodielectric effect). Increase in the rotation angle during oscillations of the FLC molecules in the near-electrode region of the sample in order to provide the photocurrent transfer, appearing under illumination, is the possible mechanism of this effect.

Increase in the effective area of the near-electrode region, in which charge transfer occurs due to the oscillations of the molecule dipoles around the helicoid axis, is the possible mechanism of the positive photodielectric effect of the colloidal solution revealed in [1].

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