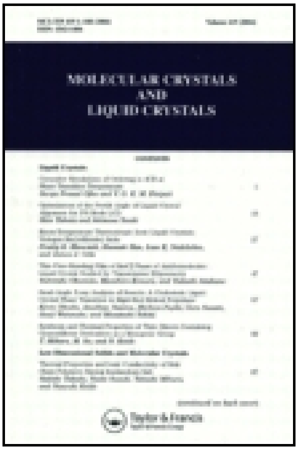

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Photorefractive Effect in Nematic Liquid Crystals: Ion-Diffusion Approach

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PHOTOREFRACTIVE EFFECT IN NEMATIC LIQUID CRYSTAL: ION-DIFFUSION APPROACH

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Abstract Results of first observation and theoretical treatment of photorefractive optical nonlinearity (PN) in nematics are discussed. Possible ways for further increase of PN are pointed out. Those lie in decreasing luminescence quantum efficiency of the dye used and increasing the mobilises' ratio of positive and negative ions induced by light. The influence of interface screening effects on PN is treated theoretically and the ways for obtaining exact results for bulk charge densities and fields are worked out.

INTRODUCTION

Photorefractive effect in nematic liquid crystal was observed and treated in [1,2]. In short words, it consists in light-induced creation of space-charge-field pattern in the medium via photogeneration of some ions and charge separation caused by diffusion of the latter. The proper space-charge field, coupled with homogeneous DC bias one, causes reorientation of LC director and correspondent modulation of refractive index. Sequence of these processes leads to very strong (three orders of higher than conventional orientational nonlinearity -ON) optial nonlinearity, photorefractive nonlinearity (PN) of LC.

The preliminary theoretical treatment of the phenomenon observed [2], although corresponding rather well in its results to experimental observations, uses only one of the possible schemes for carriers' photogeneration and a set of not fully justified assumptions. The aim of this paper is to analyse the ways for further increase of PN and a set of investigations to start with. So we'll at first give a short resume of the results obtained up to date [1,2].

FIRST OBSERVATION AND TREATMENT OF PN

Photoinduced conductivity and PN were observed in homeotropic 100-μm thick samples of 5CB doped by rhodamine 6G (R6G) its concentration being 0.1-1 mM. Electric conductivity σ, measured through observed DC resistance of the sample, revealed the increase of about a factor of ten under typical power density of argon-ion laser irradiation (λ=0.4880 μm) $I \leq 0.4 W/cm^2$,- in comparison with dark-state one $\sigma_d \cong 1.5*10^{-10}$Ohm/cm. The relaxation times of this conductivity (several seconds), as well as its dependence of R6G concentration (see Fig.1) showed the ion-drift, rather than, say, exchange type of conductivity (no percolation limit in concentration dependencies). The dependence of the conductivity upon I appeared to be a square- root one (see Figure 2), pointing out "bimolecular" type of carriers' recombination. Practically no non-reversible changes (degradation) of the mixture were observed under $I \leq 0.25 W/cm^2$, though some non-reversible absorption depletion was observed at higher intensities during the typical time scale of hours. One of the typical kinetic schemes [3] for such reversible changes was chosen for description of the phenomenon.

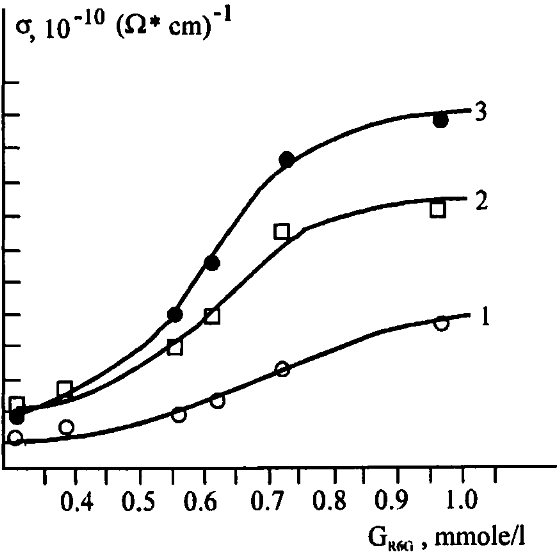

FIGURE 1 The electrical conductivity of the mixture as function of the R6G density: 1- I_0 =65 mW/cm², 2- I_0=165 mW/cm², 3- I_0 =225 mW/cm².

Namely, we guess that excited triplet states of R6G molecules A^*_t form polar complexes with the solvent S (5CB), those complexes becoming unstable after deactivation and their decay giving partially neutral components and partially ionised ones:

$$A + h\omega \leftrightarrow A^*;\; A^* \rightarrow A_T^*;\; A_T^* + S \rightarrow (A^\ominus S^\oplus)^* \rightarrow A^\ominus S^\oplus + h\omega_f;$$

$$A^\ominus S^\oplus \begin{array}{l} \rightarrow A + S \\ \rightarrow A^- + S^+ \end{array}$$

Rather crude evaluations, implying that all A^*_t form complexes (during its lifetime of about 10^{-7}s A^*_t undergoes about a thousand collisions with S), that the binary relaxation constant γ is diffusion-limited the Smolukhovsky sphere radius being about $R_s=e^2/\varepsilon k_b T$ (ε stands for dielectric permittivity), and that activation barrier of hetherolitic dissociation of the complex is purely Coulomb, the homolitic channel being non-activational, - gives following for σ (see [2] for detail):

$$\sigma \approx \frac{2De^2n}{k_bT} \cdot \left[\frac{\exp(-\frac{e^2}{\varepsilon Rk_bT})}{1+\exp(-\frac{e^2}{\varepsilon Rk_bT})} \cdot \frac{\varepsilon k_bT}{De^2} \cdot (1-p) \cdot \frac{aI}{h\omega} \right]^{1/2} \tag{1}$$

Here D is diffusion coefficient (guessed to be equal for positive and negative ions), a(cm^{-1}) - light absorption index; p- quantum efficiency of luminescence (typically about 0.95 for R6G); R - equilibrium distance between $A^\ominus_t$ and $S^\oplus$ charge density centres in the complex (unknown exactly but believed to be about 20A [3]). Such crude estimation gives unexpectedly good (within a factor of 2) coincidence with experimental results, and qualitatively confirms the square-root σ dependence of I.

But one extra point of experimental results shows that perhaps the picture is not so simple. Namely, all the results above deal with DC-"resistance" of the sample. Our attempts to measure the AC one failed due to efficient capacitance-type shunting of the sample even by 50-100 Hz frequencies. The proper evaluated "capacitance" (in brackets cause it's not so easy to define what namely this term means for such a system, see below) was extremely high, about 0.5-1 μF, which is quite strange but reveals mighty enough electrolytic screening at the electrode-LC interfaces. Since such screening appears, we are to state that true values for the field in the medium may be much lower than U/L (applied voltage over sample thickness), and hence true values for σ may be much higher than the measured, to provide experimentally observed currents. So to test more or less accurately any microscopic scheme of photoconductivity we first should find a way to measure and/or calculate charge distribution and density in surface layers and thus obtain more or less true values for σ in the bulk.

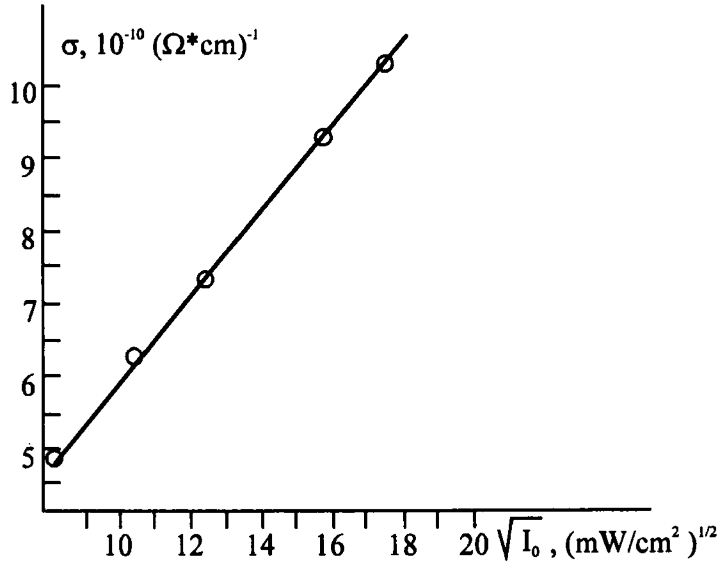

FIGURE 2 The electrical conductivity as function of the radiation intensity. The R6G density is $C = 0.63$ mmole/l.

Such space-charge field is (interference pattern) due to diffusion of carriers from "hot" fringes of the pattern to "cold" ones. Having mentioned this, let's proceed with experimental results [1,2]. When two oblique e-waves of laser radiation, intersecting in the plain containing their polarisations and wave vectors $\underline{\mathbf{k}}_{a,b}$, see Fig.3, propagate through our 100μm-thick homeotropic sample, a rather strong Raman-Natt self-diffraction occurs (its diffraction efficiency for ±1 orders $\underline{\mathbf{k}}_{\pm1}$ up to $\eta \cong 0.2$) provided an external bias DC voltage of about 0.1-2V is applied along the non-perturbed director $\underline{\mathbf{n}}^0$ (see Fig.3). The effect appears to be due to grating-type reorientation θ of the director (see [1,2] for detail), the proper effective third-order susceptibility being three orders of magnitude higher than for ON. We interpret this grating reorientation as being induced by superposition of bias field $\underline{\mathbf{E}}_0$ and space-charge field $\underline{\mathbf{E}}$ (see Fig.3), arising in the medium since the illumination is non-uniform just in common with that in photorefractive crystals with bipolar (electron-hole) photoconductivity, see e.g. [4], the proper expression for space-charge field is [2]:

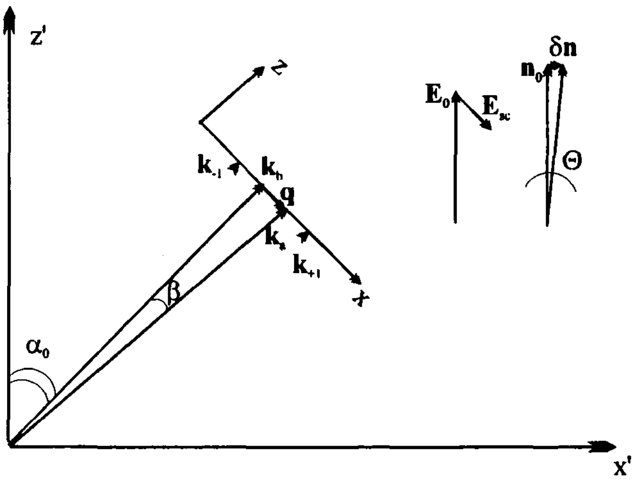

FIGURE 3 Geometry for observing the PC in a nematic.

$$E=\frac{mk_bT}{2e}\cdot q\nu\cdot\frac{\sigma-\sigma_d}{\sigma}\cdot\cos(qx);\quad \nu=\frac{D^+-D^-}{D^++D^-};\tag{2}$$

Here m is the depth of interference pattern modulation, $I=I_0(1+\sin(qx))$, q being the pattern wave number; $D^{\pm}$ - diffusion coefficients for positive/negative ions. Up to this point we've neglected anisotropy of the medium, cause it introduces nothing new but technical complications. Having solved the quite routine problem of reorientation and refractive index modulation (see, e.g. [5]) by the static field **E** + **E₀**, one can readily obtain following expression for diffraction efficiency [2]:

$$\eta\approx\left[\frac{\varepsilon_a\varepsilon_{aL}\cdot\sin\alpha_0\cdot\cos\alpha_0\cdot E_0}{1+\dfrac{\varepsilon_aE_0^2}{2\pi Kq^2}}\cdot\frac{L}{\lambda\sqrt{\varepsilon_0}}\cdot\frac{mk_bT}{eKq}\cdot\nu\frac{\sigma-\sigma_d}{\sigma}\right]^2\tag{3}$$

Here $\varepsilon_a,\varepsilon_{aL}$ are dielectric constant anisotropies for static and optical fields correspondingly, K - Frank's constant (single-constant approximation is used), λ - vacuum wavelength of radiation, ε_0 - nonperturbed effective dielectric constant for e-waves propagating at α_0 angle to the director. So the qualitative dependencies of η upon I, E_0 and q (corresponding to intersection angle β: $q=2\pi\beta/\lambda$) are following: $\eta\propto I$ at low intensities and independent at high ones ($\sigma >> \sigma_d$); $\eta \propto E_0^2$ under the fields lower than the Fredericksz transition one (about 2.5 volts bias experimentally); $\eta \propto \beta^{-2}$. Experimentally obtained dependencies of η upon I, β, U (Figs. 4,5,6 respectively) confirm those

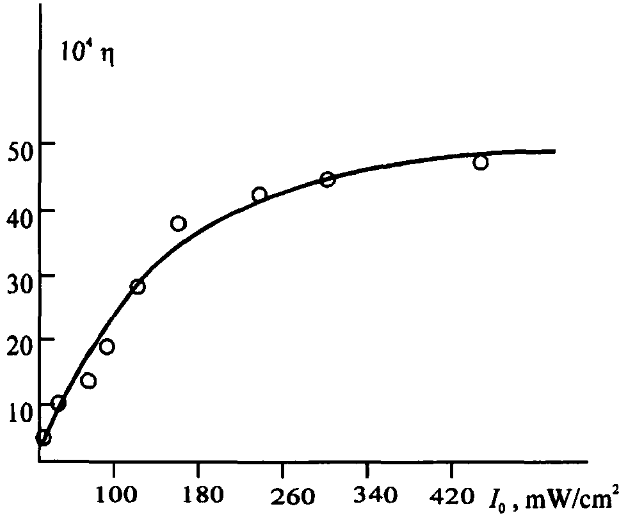

FIGURE 4 Diffraction efficiency as function of the total wave intensity. $U_0 = 1.75$ V; $\beta = 1.9*10^{-2}$ rad.

statements and quantitative comparison of η with (3) gives a rather low value for $\nu \cong 0.04$, which means $D^+/D^- \cong 0.92\text{-}1,08$.

DISCUSSION OF THE RESULTS OBTAINED

The results obtained ensures one that this a good deal complicated phenomenon of PN, including at least three stages: hetherolitic photodissociation, ionic charge transfer and director reorientation,- really exists and leads to extremely high values of third-order non-linear optical susceptibilities. On the other hand, it is quite obvious that neither the kinetics of dissociation, nor charge separation processes are clear enough up to date. The situation has much in common with the first observation of optical second harmonic generation, which was carried out using the quarz crystal nowadays known as early not the worst one for the purpose. There are at least two obvious ways for further increase of PN. The first one is (if only our kinetic scheme is really valid) to use "bad" laser dyes

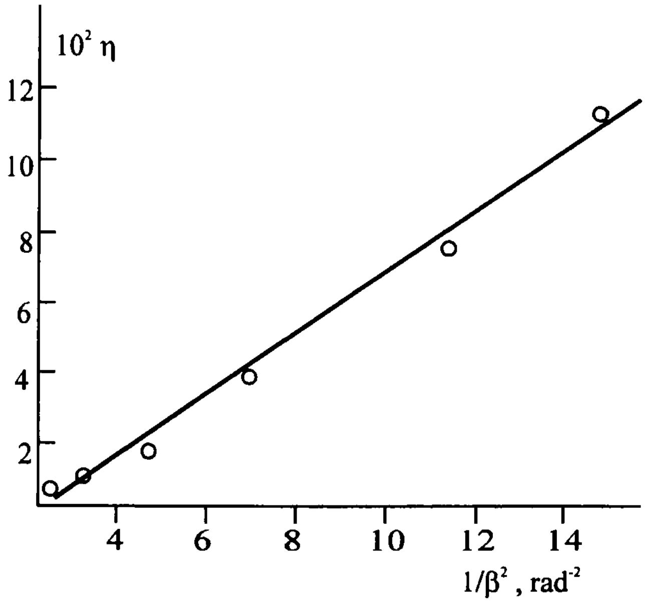

FIGURE 5 Diffraction efficiency as function of the intersection angle of the waves in the sample. $I_0 = 200$ mW/cm^2, $U_0 = 1.41$ V.

with low luminescence quantum efficiency. This allows one to produce more triplet states, provided, of cause, the latter tend to form proper polar complexes with the solvent. The second one is to choose the **A-S** pairs producing ions with much more different mobilises than ν=0.04.

Here we should note one more difficulty: in the end of previous section ν was evaluated using E_0=U/L which may not be valid again due to screening mentioned in the same section.

It is obvious that both ways require more or less detailed knowledge of photodissociation kinetics, that implies testing a set of possible kinetic schemes for giving a proper value of ions' density. This, in turn, requires exact data for bulk values of the latter, i.e.

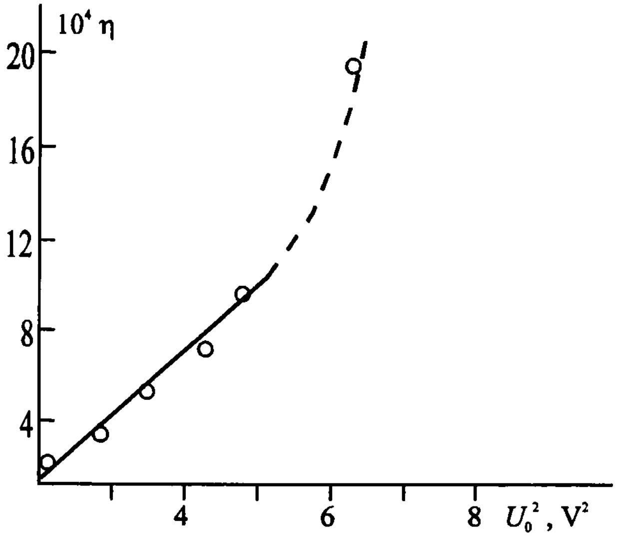

FIGURE 6 Diffraction efficiency as function of the voltage applied to the cell; $I_0 = 180$ mW/cm^2; $\beta = 1.9*10^{-2}$ rad.

true bulk conductivity. So we must conclude that the problem of the surface screening is early not the main for further investigations of PN.

PROBLEM OF SCREENING -PHENOMENOLOGY

Let's at first state the proper problem for homogeneous illumination. Let the medium occupy the space $-L \le z \le L$, $z = -L$ plane being positive and $z = L$ - negative electrode. Dynamics of charge and fields separation and relaxation is described by the following system of equations:

$$\begin{aligned} &\frac{\partial n_+}{\partial t} + \gamma n_+ n_- + \frac{\partial}{\partial z}\left(-D^+ \cdot \frac{\partial n_+}{\partial z} + E_0 \mu^+ n^+\right) = \alpha I; \\ &\frac{\partial n_-}{\partial t} + \gamma n_+ n_- + \frac{\partial}{\partial z}\left(-D^- \cdot \frac{\partial n_-}{\partial z} - E_0 \mu^- n^-\right) = \alpha I; \\ &\frac{\partial E_0}{\partial z} = 4\pi e(n_+ - n_-) / \varepsilon; \end{aligned} \tag{4}$$

First two of those are material ones for positive and negative ions' densities $n^{\pm}$, $\mu^{\pm}$ being their mobilises, γ - recombination constant, αI - light-induced source of ions, uniform over the sample bulk. The last equation (4) is the Poisson one for the field inside the medium. Introducing dimentionless concentrations $n^+ = n^0 c$; $n^- = n^0 d$, $n^0 = (\alpha I/\gamma)^{1/2}$; coordinate $z = \xi L$, and assuming for sake of simplicity that $\nu = 1$, one can readily obtain:

$$\begin{aligned} &\frac{\partial c}{\partial \tau} + cd + A\frac{\partial}{\partial \xi}\left(-\frac{\partial c}{\partial \xi} - c\frac{\partial \Phi}{\partial \xi}\right) = 1; \\ &\frac{\partial d}{\partial \tau} + cd + A\frac{\partial}{\partial \xi}\left(-\frac{\partial d}{\partial \xi} + d\frac{\partial \Phi}{\partial \xi}\right) = 1; \\ &B \cdot \frac{\partial^2 \Phi}{\partial \xi^2} = d - c; \end{aligned} \tag{5}$$

Here $\tau = \gamma n^0 t$, $\Phi(\xi) = eV(z)/k_bT$ - dimentionless potential ($E_0 = -\partial V/\partial z$); $A = D/\gamma n^0 L^2$; $B = (r_d/L)^2$, $r_d = (\varepsilon k_b T/4\pi e^2 n^0)^{1/2}$ - Debye radius for the ions. Note that for diffusional evaluation of γ used in the first section, $A \equiv B$, which assumption we'll use further for the sake of simplicity.

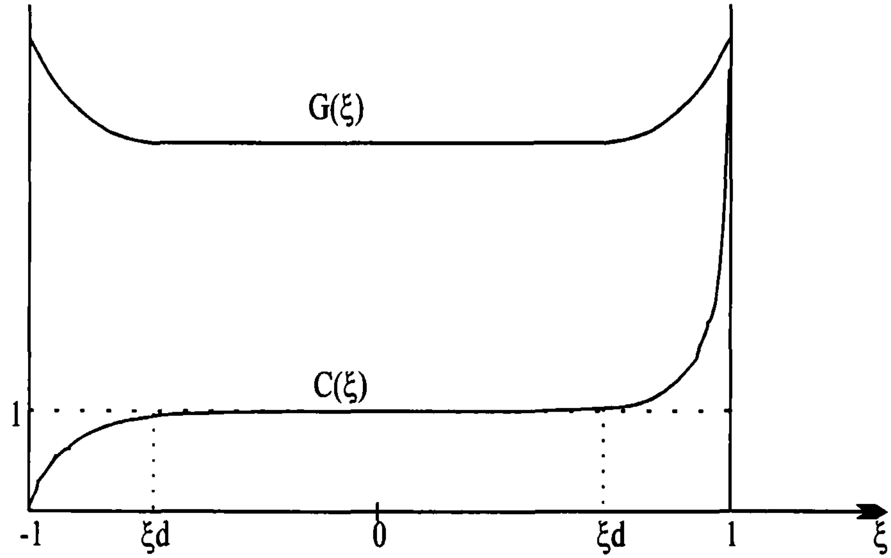

FIGURE 7

Now let's turn to boarder conditions. The straightforward and really effective way is to write some kinetic equations for the processes of ions' discharge at the electrode surface. But the matter is that correspondent electrode processes may include several channels (straight trapping of ion, electron injection etc., see, e.g., [6]) no one of which is studied in detail, particularly for our SnO_2 electrode + unknown ion pair. So we prefer purely phenomenological approach, consisting in fixing current at the electrode to experimental value and attributing it to the flow of the proper sign ions inside the medium (naturally, only in steady-state regime, when the charge distribution is stable). The flow of "incorrect" sign ions is to be put equal to zero at the electrode in such case. The expression for dimentionless current is

$$i = \frac{J}{SBe\gamma n_0^2 L} = -d\cdot\frac{\partial\Phi}{\partial\xi} + \frac{\partial d}{\partial\xi} - c\cdot\frac{\partial\Phi}{\partial\xi} - \frac{\partial c}{\partial\xi}; \tag{6}$$

Here both drift and diffusion components are taken into account, J is experimental current value for given $U = (\Phi(-1) - \Phi(1))k_bT/e$; S is the sample area. So the boarder conditions will be following:

$$\begin{aligned} &c\frac{\partial\Phi}{\partial\xi} + \frac{\partial c}{\partial\xi}\Big|_{-1} = 0; \quad && d\frac{\partial\Phi}{\partial\xi} - \frac{\partial d}{\partial\xi}\Big|_{-1} = -i; \\ &c\frac{\partial\Phi}{\partial\xi} + \frac{\partial c}{\partial\xi}\Big|_{1} = -i; \quad && d\frac{\partial\Phi}{\partial\xi} - \frac{\partial d}{\partial\xi}\Big|_{1} = 0; \end{aligned} \tag{7}$$

The last two ones are obvious conditions of fixed potentials of the electrodes.

So we have the sixth order system with six boundary conditions and one unknown parameter B. The latter depends only upon the light intensity (through n^0) and material constants. Evaluations of B from results above, neglecting the interface screening, gives for typical values of I $B \approx 10^{-4}$-10^{-5}.

The system (5) as well as boundary conditions (7) are non-linear and can't be solved analytically in general case, so we'll start with some qualitative reasons. In fact we've no reason to wait for any appreciable gradients of ion densities and field $G = -\partial\Phi/\partial\xi$ within the bulk but for thin layers (of about $\sqrt{B}$ thickness) at the electrodes. Moreover, we put the problem quite symmetrically for positive and negative ions, i.e. $d(-\xi) = c(\xi)$. The proper typical curves we should obtain for c, $G(\xi)$ are presented in Fig.7.

In the bulk $c \approx d \approx 1$, $\frac{\partial c}{\partial\xi} = -\frac{\partial d}{\partial\xi}(0)$, so $G(0) \approx i/2$ (from (6)). The first obvious attempt of analysis is to try to linearize (5,7) considering c,d perturbation in the screening layers as small compared to 1.

LINEAR ANALYSIS

So we guess c=1+c'; d=1+d' and in steady-state immediately obtain from (5) the following:

$$\begin{aligned}&c'+d'-B\cdot\frac{\partial^2 c'}{\partial\xi^2}-B\frac{\partial c'}{\partial\xi}\cdot\frac{\partial\Phi}{\partial\xi}-B\cdot(c'+1)\cdot\frac{\partial^2\Phi}{\partial\xi^2}=0\\&c'+d'-B\cdot\frac{\partial^2 d'}{\partial\xi^2}+B\frac{\partial d'}{\partial\xi}\cdot\frac{\partial\Phi}{\partial\xi}-B\cdot(d'+1)\cdot\frac{\partial^2\Phi}{\partial\xi^2}=0\\&B\cdot\frac{\partial^2\Phi}{\partial\xi^2}=d'-c'\end{aligned}\tag{8}$$

(8) is not yet linear. To linearize it one should require at least $\partial\Phi/\partial\xi=o(1)$. But it is obvious that the screening layers $|\partial\Phi/\partial\xi|=G\geq\Phi_0/2$ (see Fig.7), thus we must require $\Phi_0<<1$. This is rather unpleasant requirement cause in real PN experiment $\Phi_0\approx 30\text{-}40$. So the only way is following. We may hope to obtain real B(I) dependence from linearized model, which will require additional set of low-voltage measurements of J(I) dependencies under fixed U. Knowing those, we may solve numerically the non-linear system for real PN voltages thus obtaining charge distributions and bulk fields for real PN conditions. So let's guess $\Phi_0<<1$. Then we immediately obtain:

$$\begin{aligned}&B\cdot\frac{\partial^2 c'}{\partial\xi^2}-2c'=0;\\&B\cdot\frac{\partial^2\Phi}{\partial\xi^2}=c'-d';\end{aligned}\qquad\begin{aligned}&\frac{\partial\Phi}{\partial\xi}+\frac{\partial c}{\partial\xi}\Big|_{-1}=0;\\&\frac{\partial\Phi}{\partial\xi}+\frac{\partial c}{\partial\xi}\Big|_{1}=-i;\\&\Phi(\pm1)=\pm\Phi_0/2;\end{aligned}\tag{9}$$

Here we omit the equation for d', since $d'(\xi)=c'(-\xi)$. Remembering that $\Phi(\xi)$ is an odd function and $\partial\Phi/\partial\xi(0)=-i/2$ one can readily obtain:

$$\begin{aligned}&\Phi=\frac{i-\Phi_0}{2}\cdot\frac{sh(\lambda_d\xi)}{sh\lambda_d}-i\xi/2;\\&\rho=\frac{\Phi_0-i}{2}\cdot\frac{sh(\lambda_d\xi)}{sh\lambda_d};\end{aligned}\tag{10}$$

Here $\lambda_d=(2/B)^{1/2}$, $\rho=c'-d'$ is dimentionless charge density in the screening layer. Yet expressions (10) are valid for any given B, J and U and we need one more condition to define B from given J and U. This condition may be obtained if we utilise the experimental "capacities" (i.e. charge relaxation) data. Really, total charge of screening layer is:

$$Q(esu) = en_0 S\int_0^{1} \rho d\xi \cong \frac{W}{\sqrt{8B}}(\Phi_0 - \frac{JL}{WB})(\tanh\sqrt{\frac{2}{B}})^{-1}$$
$$\mathbf{W} = \frac{\varepsilon k_b TS}{4\pi e L^2}; \qquad (11)$$

For given Q, Φ_0 and J one can readily obtain true value for B, solving transcendent equation (11) numerically. The only problem is to obtain experimental value for Q. There is at least one, though a little bit crude, way to evaluate Q. Guess that after measuring J(U) dependence we instantly re-switch the sample from voltage supply source to input resistance of oscilloscope and measure the charge relaxation time. In some more or less crude approximation [6] the sample may be described by equivalent circuit Fig.8,

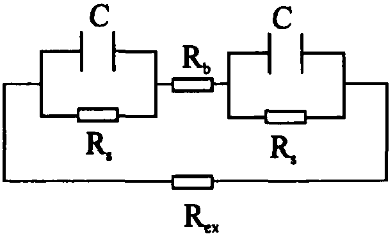

FIGURE 8

where C denotes screening layer capacitance, R_s - its resistance, R_b - resistance of the bulk, R_{ex} - input resistance of oscilloscope. The signal registered in such circuit U(t) is:

$$U(t) = R_{ex} Q(\frac{1}{cR_s} + 1/\tau)\exp(-t/\tau);$$
$$\tau^{-1} = \frac{1}{C}(\frac{1}{R_b + R_s} + 1/R_{ex}); \qquad (12)$$

Here τ is the experimentally measured exponential relaxation time of the order of a few seconds. Varying R_{ex}, one can easily obtain all the necessary parameters from the $\tau(R_{ex})$ dependence and thus calculate Q for given J, U and I.

So we hope that the procedure delivered in this section allows one to obtain the true B(I) dependence, although it requires a lot of experimental effort. The proper measurements are now carried out and the preliminary results show that he bulk density of carriers is at least about thrice higher (and the proper field lower) then those calculated neglecting surface screening.

CONCLUSIONS

So we've discussed the results of first observation and theoretical treatment of PN and found out that further improvement of the phenomenon parameters requires exact knowledge of surface screening effects. The phenomenological model above enables one to study those effects in detail (it must be noted that numeric integration for given B of non-linear system (5,7) makes no problem) and thus obtain the dependencies of bulk carriers density and bulk bias field of light intensity and applied bias voltage. Those are quite necessary for further studies of photodissociation kinetics and charge separation in photorefractive gratings.

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