Optically induced spatial charge separation in a nematic and the resultant orientational nonlinearity

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We have carried out a theoretical and experimental study of the photoinduced impurity electrical conductivity in a nematic. We have shown that in the case of nonuniform irradiation charge-density lattices appear in the medium as well as the corresponding static field lattices which are comparable with those occurring in solid photorefractive crystals. The reorientation of the directrix of the nematic produced by these fields gives rise to an optical nonlinearity which is larger by three orders of magnitude than the optical orientational nonlinearity of nematics.

1. INTRODUCTION

It is well known (see, e.g., Refs. 1 and 2) that liquid crystals, especially nematics, can easily be reoriented by external electric fields and that this, in conjunction with the large anisotropy of the refractive index, makes it possible to produce all kinds of electro-optical modulators (displays),[1] which in the case of a reorienting optical field leads to a very strong cubic nonlinearity of the medium—the so-called optical orientational nonlinearity of nematics (ON).[2]

On the other hand, in order to induce optically a reorientation of a nematic it is not necessary to achieve this just by the action of the wave itself. It is, for instance, sufficient to use radiation to exercise control of an external static or radiofrequency field, applied to a nematic layer such as that used in the so-called optically controlled liquid-crystal transparencies.[3] Another possibility consists using the radiation of a static field in the medium itself for the induction. Such fields are very widely known[4] in solid photosemiconductors (photorefractive crystals). The cause of their formation lies in the optically induced charge distribution in the case of spatially inhomogeneous illumination of photorefractive crystals. There are two basic mechanisms for such a distribution. The first of them is connected with the so-called photovoltaic effect which requires for its existence at least a medium without central symmetry. The second one is connected simply with the diffusion of minority carries which are produced when nonuniform radiation is present and can be realized fully even in an isotropic medium, in fact, in a medium of practically any symmetry. The only requirement for its existence is a photoconductivity with a sufficiently localized intensity-dependence of the carrier density (in order that the spatially inhomogeneous intensity produces a spatially inhomogeneous carrier density); moreover, the carrier density itself must be sufficient for the conductivity σ to be significantly larger than that of the dark current, $\sigma \gg \sigma_d$, while the Debye radius r_D for the screening of the carriers must be much smaller than the characteristic scale of the intensity variations (in actual cases—the period of the interference picture with wavenumber q: $qr_D \ll 1$); see Refs. 4 and 5.

It is well known that this static field can be several orders of magnitude larger than the amplitude of the field of the optical wave itself which excites it. It is thus reasonable to attempt to excite this kind of field in a nematic which must lead to an extraordinarily strong optical nonlinearity being several orders of magnitude larger than the ON. The present paper is devoted to a study of the possibility of such a process (we call it for the moment the photorefractive nonlinearity of a nematic).

2. ESTIMATES FOR THE POSSIBILITY OF PHOTOINDUCED CONDUCTIVITY (PC) IN A NEMATIC

Although photoinduced generation of charges in a liquid has recently been studied quite intensively, there are not many discussions (see, e.g., Refs 6 to 8) of photoinduced conductivity and photovoltages in nematics. On the whole the picture here is the following. Firstly, in a liquid, as in any translationally disordered system, ionization of the molecules by optical quanta is impossible (the corresponding ionization potentials are tens or hundreds times larger than the energy of an optical quantum). Apparently, as far as one can calculate things, the only feasible goal for realizing PC in a liquid is a selective heterolytic dissociation of molecules (or molecular complexes) from optically excited states accompanied by recombinations into the ground state. Clearly, for this process to be efficient it is desirable that this excited state have a long lifetime. Hence follows the proposal (which, in fact, was realized experimentally, see below) to use laser dyes as absorbing impurities in the nematic with a pumping wavelength corresponding to the radiation used (in the actual experiment rhodamine 6G (R6G) solutions in a 5CB nematic). It is well known (see, e.g., Ref. 9) that these dyes after excitation partially make a transition to long-lived ($\tau \approx 10^{-7}$ s) triplet states so that during the lifetime of a molecule excited in the triplet state it undergoes 10^3 to 10^5 collisions with the molecules of the solvent and can very well form a complex with them if this is thermodynamically stable. Moreover, it is well known[9] that in a number of cases

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(depending on the actual properties of the molecules of the dye A and the solvent S) a selective complex formation is possible in an excited state of a polar complex ($A^{\ominus}S^{\oplus}$) which is unstable in the ground state and which dissociates, sometimes heterolytically, after deactivation:

$$A \overset{h\omega}{\rightleftarrows} A^*;\quad A^* \to A_T^*;\quad A_T^* + S \to (A^{\ominus}S^{\oplus})^* \to A^{\ominus}S^{\oplus} + h\omega_f;$$

$$A^{\ominus}S^{\oplus}\ \begin{matrix} A+S \\ A^- + S^{+}. \end{matrix}$$

It is clear that a quantitative description of the kinetics of such processes is difficult and requires knowing a multitude of microscopic parameters for a given "solvent–dye" pair. The estimates given below must therefore be considered only as an indirect confirmation of the possibility of the PC observed by us (see next section), i.e., simply stated, as arguments in favor of this PC not being an artefact.

Thus, the rate W_T of generating molecules excited in the triplet state by radiation is

$$W_T(\mathrm{cm}^{-3}\,\mathrm{s}^{-1}) \approx (1-p)\frac{aI}{\hbar\omega}. \qquad (1)$$

Here p is the quantum luminescence efficiency, a (in cm^{-1}) is the absorption coefficient of the mixture, I (in $\mathrm{erg/cm^3 s}$) is the intensity of the radiation, and ω is its frequency. For our estimates we consider only the steady state of the process, so that we have $W_T = W_d$, with W_d the rate of generating deactivated unstable A^-S^+ complexes. We assume here additionally that all A_T^* form complexes, so that during their lifetime they undergo many collisions with S (see above). Furthermore, we have $W_d = W_A + W_{A^-}$, i.e., the rate of generating triplets is equal to the sum of the rates of the heterolytic and homolytic dissociation channels. Whereas the latter hardly involves activation, the first one is connected with overcoming a Coulomb barrier so that

$$W_{A^-}/W_A \approx \exp(-E_C/k_bT);\quad E_C \approx e^2/\varepsilon R.$$

Here R is the equilibrium distance between A^- and S^+ in the complex and ε is the dielectric permittivity of the medium. The rate at which charge carriers are generated is thus

$$W_C = 2W_{A^-} \approx 2\frac{\exp(-e^2/\varepsilon R k_b T)}{1+\exp(-e^2/\varepsilon R k_b T)}(1-p)\frac{aI}{h\omega} = 2\alpha I. \qquad (2)$$

The stationary carrier density is thus determined by equating the rate of the binary ion recombination W_r to the rate W_c at which they are generated:

$$W_r = \gamma n^+ n^-,\quad \gamma \simeq DR_S,\quad R_S \simeq e^2/\varepsilon k_b T. \qquad (3)$$

Here γ is the constant for the recombination which occurs in the liquid in the diffusive regime, estimated in the usual way where the radius R_S of the Smoluchowski sphere is estimated from considering the kinetic energy and their binary interaction potential energy of the ions to be equal; D is the diffusion coefficient; and $n^{\pm}$ are the positive and negative ion densities—in a spatially uniform case we have $n^+ = n^- = n$. The balance equation for the ions then has the form

$$\frac{\partial n^{\pm}}{\partial t} + \gamma n^+ n^- = \alpha I, \qquad (4)$$

and in steady state we have

$$n \approx \left\{ \frac{\exp(-e^2/\varepsilon R k_B T)}{[I+\exp(-e^2/\varepsilon R k_B T)]} \frac{\varepsilon k_b T}{De^2}(1-p)\frac{aI}{h\omega} \right\}^{1/2}. \qquad (5)$$

For our estimates we use the following set of parameters,[2,9] which are typical for a liquid crystal and R6G: $\varepsilon \approx 10$, $p \approx 0.95$, $D \approx 3\times10^{-6}\ \mathrm{cm^2/s}$, $a \approx 30\ \mathrm{cm}^{-1}$ (a 40% absorption in a 100 μm layer); and $R \approx 20$ Å. The diffusion coefficient was taken here for self-diffusion of nematics; the ionic one is, of course, smaller so that we get a lower bound for n; there is, of course, a large arbitrariness in R but in view of the large size of the R6G molecule its value is rather realistic.

Moreover, here and henceforth up to the calculation of the reorientation of the nematic we neglect the anisotropies in ε and D which would significantly complicate the calculations without, however, introducing any qualitatively new effects.

For the parameters given we get from Eq. (5):

$$n \approx (2\times10^{28} I\mathrm{W/cm^2})^{1/2} \approx 2\cdot10^{14}\ \mathrm{cm}^{-3}$$

$$\text{for } I \approx 200\ \mathrm{mW/cm^2},$$

which is close to the experimental values. The conductivity of the medium must here be of order

$$\sigma \approx 2en\mu = \frac{2D^{\pm}e^2 n}{k_B T} \approx 10^{-9}(\Omega\ \mathrm{cm}^{-1}). \qquad (6)$$

We have used here the familiar Einstein relation between $D^{\pm}$ and the mobility $\mu^{\pm}$ of the ions. Such values of σ are 10 to 100 times larger than σ_d of well purified nematics. As regards r_D for a given n it is equal to

$$r_D = \left(\frac{\varepsilon k_B T}{4\pi n e^2}\right)^{1/2} \approx 6\cdot10^{-5}\ \mathrm{cm}, \qquad (7)$$

i.e., permissible without saturating the space charge[4,5] of an interference pattern with a period of $\Lambda \geqslant 6\ \mu$m. The estimates (6) and (7) thus indicate the possibility of inducing in the medium the required PC by relatively weak light fluxes.

We note once again that these estimates by themselves are more than approximate, they use only one of the possible scenarios of the process, and also a number of not fully justified assumptions. Their usefulness would be close to zero, except that there are experimental results which agree rather well with them. We turn to a consideration of those.

3. EXPERIMENTAL OBSERVATION OF PC IN A NEMATIC

In the experiment we used samples of thickness $L = 100\ \mu$m of a solution of R6G in the 5CB nematic with densities of 0 to 10^{-3} mole/1. The glass surfaces of the cell were covered by standard transparent SnO_2 electrodes on which we reached a homotropic orientation of the nematic without any additional processing of the surface. The resistivity of the sample was measured by an E6-13A teraohmmeter. The sample was illuminated by the radiation from an argon laser ($\lambda = 0.4880\ \mu m$) with an intensity which was uniform throughout the sample. Teflon separators between the surfaces guaranteed a resistivity of the unfilled cell of more than 2 GΩ. The intensity of the radiation varied in the range from 10 to 400 W/cm^2.

Qualitatively one can reduce the results of the experiment to the following. We recorded an increase in the conductivity of the sample for the above parameters of more than a factor 10 as compared to the dark conductivity, $\sigma_d = 1.5 \times 10^{-10}\ (\Omega\ cm)^{-1}$. These changes were attained for samples with R6G densities producing an absorbed energy fraction of order 40%.

In order to check whether these changes were the consequence of the heating of the sample through absorption we placed the sample in a thermostat and removed the temperature dependence of its resistivity down to the transition to the isotropic phase in the absence of illumination. The result showed that to within 5% σ_d was independent of the temperature.

There is a discussion in Ref. 5 of an observation under experimental conditions similar to ours of very large (up to a fraction of a volt) photoinduced voltages in cells with nematic mixtures, in particular, homologs of 5CB. Although those results are rather odd (where a polar signal comes in a centrally symmetric medium with symmetric boundary conditions, the identical electrodes in Ref. 5, is a mystery), nonetheless the presence of such signals could significantly distort our measurement of σ. We therefore carried out a separate check of the presence of such voltages when our samples were illuminated and we established that they were not present, to an accuracy of $\leqslant 1\ \mu V$. It is clear that, if we take into account that the measuring voltage applied to the cell was on the order of 0.5 V, there is no such error in our measurements.

We carried out measurements of the dependence of the conductivity of the mixture on the R6G density C for a given intensity of the radiation. The results are given in Fig. 1. It is clear that we observed a monotonic increase in $\sigma(C)$ up to densities corresponding to a concentration quenching of the luminescence of R6G.[9] This form of function in conjunction with the long times (on the order of one to tens of seconds) needed to establish σ indicate the ionic-drift (rather than, say, exchange) nature of the conductivity, the more so since in the case of exchange conductivity σ there should be a percolation limit for small C which is not observed experimentally.

We show the function $\sigma(\sqrt{I})$ for given C in Fig. 2. It is clear that it is linear within experimental accuracy, while the absolute values of σ are completely satisfactorily in agreement with the estimate (6) so that, apparently, notwithstanding the roughness of these estimates they are close to the true values.

One should especially note that the measurements of σ were carried out for a direct current. Attempts to repeat the measurement with alternating current failed because of the anomalously large ($\approx 1\ \mu F$) capacitance of the illuminated cell which shunted its active resistivity even for frequencies on the order of 50 to 100 Hz. Such values of the capacitance for a cell area of 1 cm^2 are an additional indication of the electrolytic nature of the PC. Preliminary estimates show that they are theoretically possible for the R6G densities used when the ionic recombination constants at the surface of the electrodes are very low (of order 10^{-8} cm/s).

Thus we apparently have PC with a completely sufficient carrier density when the conditions $\sigma \gg \sigma_d$ and $qr_D \ll 1$ are satisfied. We still need to elucidate whether the localizability of this PC for a spatial charge distribution under the action of radiation with a spatially inhomogeneous intensity distribution (interference pattern of two waves) is sufficient.

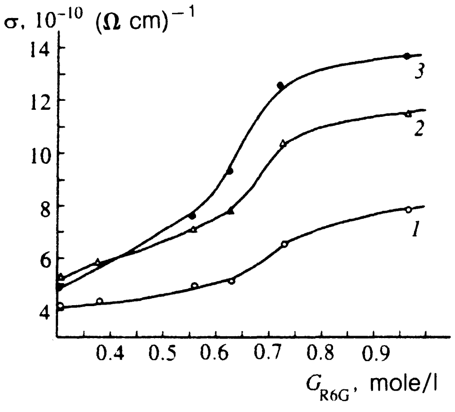

FIG. 1. The electrical conductivity of the mixture as function of the R6G density: *1*—$I_0 = 65$ mW/cm^2, *2*—$I_0 = 165$ mW/cm^2, *3*—$I_0 = 225$ mW/cm^2.

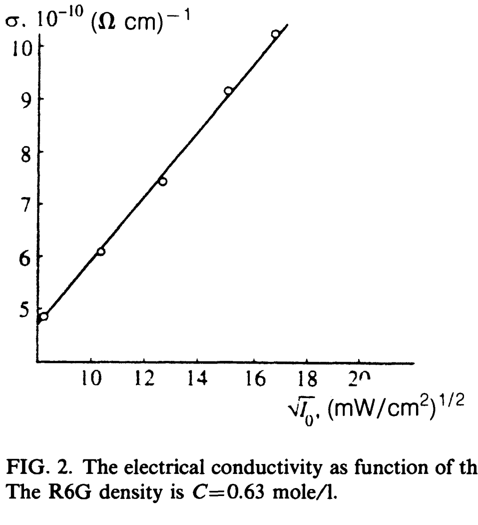

FIG. 2. The electrical conductivity as function of the radiation intensity. The R6G density is $C = 0.63$ mole/l.

4. CALCULATION OF THE FIELD OF THE SPATIAL CHARGE IN A NEMATIC

Therefore, let the intensity of the radiation in the medium be inhomogeneous:

$$I = I_0[1 + m\sin(qx)].$$

So far the direction of the x axis is arbitrary, so that at this stage we do not take into account the anisotropy of the nematic and also neglect edge effects, assuming the medium to be infinite. In reality we have $qL \gg 1$, so that the inhomogeneity in the density along the thickness of the sample is appreciably less important than across the lines of the interference pattern. Generally speaking, under such conditions Eq. (4) must be modified by taking into account possible diffusion and drift fluxes:

$$\frac{\partial n^\pm}{\partial t} + \gamma n^+ n^- + D^\pm \frac{\partial^2 n^\pm}{\partial x^2} \pm E\mu^\pm \frac{\partial n^\pm}{\partial x} = \alpha I(x). \tag{8}$$

The expression for the current density j in the medium has the form:

$$\frac{j}{e} = D^+\partial_x n^+ - D^-\partial_x n^- + E(\mu^+ n^+ + \mu^- n^-) + \frac{\sigma_d}{e}E. \tag{9}$$

In (8) and (9) E is the assumed field of the spatial charge directed along the lattice wavevector, i.e., along x. Moreover, one must take into account that the medium is electrically neutral on average:

$$\int_x^{x+\Lambda} (n^+ + n^-)dx' = 0. \tag{10}$$

Equations (8)–(10) are nonlinear even in the time-independent case and cannot be solved explicitly, so that we must simplify them using some assumptions. We start with an estimate of the relative magnitude of the terms on the left-hand side of (8). Using Eq. (3) we have

$$\begin{gathered} W_r \approx \frac{De^2}{\varepsilon k_B T} n^2, \quad W_{dr} \approx W_d \approx mDq^2 n, \\ \frac{W_r}{W_d} \approx \frac{e^2 n}{m\varepsilon k_B T q^2} \approx \frac{1}{m}(qr_D)^{-2} \gg 1. \end{gathered} \tag{11}$$

We assumed here that the diffusion and drift currents are approximately equal which follows from (9) in the stationary case ($j=0$) if we neglect the dark-current conductivity. Equation (8) can thus be simplified to its original form (4) which also means that the I-dependence of $n^\pm$ is local as discussed above, and in the stationary case we have the following set of equations:

$$\begin{gathered} \gamma n^+ n^- = \alpha I_0[1 + m\sin(qx)], \\ D^+\partial_x n^+ - D^-\partial_x n^- + E(\mu^+ n^+ + \mu^- n^-) + \frac{\sigma_d}{e}E = 0, \\ \partial_x E = \frac{4\pi e}{\varepsilon}(n^+ - n^-), \quad \int_x^{x+\Lambda}(n^+ - n^-)dx' = 0. \end{gathered} \tag{12}$$

We have added here the Poisson equation for $\partial_x E$. The set (12) is again nonlinear and one finds its solution using perturbation theory in the small parameter $\zeta = W_d/W_r$. In fact, we put $n^\pm = n_0^\pm n_1^\pm$, where $n_1 = O(\zeta)$. At the same time we have $D^\pm q \sim E\mu^\pm \sim O(\zeta)$.

We have then to zeroth order:

$$\begin{gathered} \gamma n_0^- n_0^+ = \alpha I_0[1 + m\sin(qx)], \\ \int_x^{x+\Lambda}(n_0^+ - n_0^-)dx' = 0 \end{gathered} \tag{13}$$

and to first order:

$$\begin{gathered} D^+\partial_x n_0^+ - D^-\partial_x n_0^- + E(\mu^+ n_0^+ + \mu^- n_0^-) + \frac{\sigma_d}{e}E = 0, \\ \partial_x E = \frac{4\pi e}{\varepsilon}(n_1^+ - n_1^-). \end{gathered} \tag{14}$$

As zeroth approximation we choose $n_0^+ = n_0^- = (\alpha I(x)/\gamma)^{1/2}$. The validity of such a choice will be justified by the answer, i.e., it can be retained in the case where the $n_1^\pm$ turn out to be merely insignificant corrections to the spatially inhomogeneous part $n_0^\pm$. We then get directly from (14):

$$\begin{gathered} E = \frac{mk_B T}{2e} qv \frac{\sigma - \sigma_d}{\sigma}\cos(qx), \quad v = \frac{D^+ - D^-}{D^+ + D^-}, \\ \sigma - \sigma_d = e(\mu^+ + \mu^-)\sqrt{\alpha I_0[1 + m\sin(qx)]/\gamma}. \end{gathered} \tag{15}$$

We must also verify whether indeed $n_1^+ - n_1^-$ is appreciably less than the variable part $n_0^\pm$. From the second Eq. (14) we obtain in the most interesting case $\sigma \gg \sigma_d$:

$$\Delta n = n_1^+ - n_1^- = \frac{mk_B T\varepsilon}{2\pi e^2} q^2 v\sin(qx)$$

and the ratio of this difference to the spatially inhomogeneous part $n_0^\pm$ is:

$$\frac{\Delta n}{n_v} \approx \frac{\varepsilon k_B T q^2 v}{4\pi e^2 n_0} = v(qr_d)^2 \ll 1. \tag{16}$$

The estimate (16) confirms the admissability of our zeroth approximation and thereby the validity of Eq. (15) for the space-charge field. We now turn to a consideration of the reorientation of the nematic under the action of this field.

5. REORIENTATION BY THE SPACE CHARGE FIELD AND THE WAVE SELF-DIFFRACTION CAUSED BY IT

Before we start immediately to a calculation of the angles θ of the reorientation of the directrix **n** of the nematic and of the changes caused by this reorientation in the optical dielectric permittivity ε_s for its excited waves we must make a few remarks.

Firstly, in contrast to FRC, there occurs in nematics a quadratic (albeit very strong) electrooptic orientational effect, $\delta\varepsilon_s \propto E^2$, rather than a linear one. Therefore, if we use for the reorientation only the spatial charge field we are most likely to obtain a dielectric permittivity lattice with a doubled wavenumber with respect to the interference pattern, which is undesirable. The natural way out is to apply to the cell an external uniform static field E_0 such that

$$\delta\varepsilon_s \propto E_0 E = E_0 E_s \cos(qx),$$

where

$$E_s = \frac{mk_B T}{2e} qv \frac{\sigma - \sigma_d}{\sigma}.$$

Moreover, this gives an additional amplification of the expected reorientation. Indeed, if the external potential applied to the cell is comparable to the threshold for the Fréderiksz transition,[1] i.e.,

$$E_0 \approx (4\pi^3 K/\varepsilon_a)^{1/2},$$

where K is the Frank constant (we shall use a single-constant approximation for the elastic energy; see Ref. 1) and ε_a the anisotropy in the static dielectric permittivity, we have

$$\frac{E_s}{E_0} \approx \frac{mk_B T}{2e} \nu(\varepsilon_a/4\pi^3 K)^{1/2}(qL). \tag{17}$$

Note that we probably have $\nu \leqslant 1$, so that we can hardly expect that the ionic diffusion coefficients will differ by more than 20 to 30%, and for typical values of $\varepsilon_a \approx 5$ we can put $K \approx 10^{-6}$ dyne. Equation (17) gives $E_s/E_0 \approx 5 \times 10^{-4}(qL) \leqslant 0.05$ up to $\Lambda = 6\ \mu$m, which is the maximum from the point of view of r_d. The magnification effect by a uniform external field is thus clear.

It is true, one should estimate whether the presence of an external field E_0 does not lead to an appreciable outflow of carriers from the interaction region which might affect the results of the preceding calculations. We must thus estimate the ratio of W_r to W_{dr} in the field E_0:

$$W_r/W_{dr} = \frac{en_0 L^2}{U_0} \simeq \frac{600}{U_0(B)} \gg 1. \tag{18}$$

In the estimate (18) U_0 is the constant potential U_0 applied to the nematic layer which is at most equal to U_F, the threshold potential for the Fréderiksz transition, which is of the order of a few volts.[1] The apprehension about the effect of E_0 on $n^{\pm}$ is thus not justified and the results of the calculations of E remain in force.

Secondly, it is well known from the theory of the ON of nematics[2] that there are a multitude of different geometries for an orientational interaction of waves with nematics, depending on the orientation of the directrix (planar or homotropic), the polarizations, and the angles of wave incidence on the sample. The proposed PC also admits a multitude of such variants, but an enumeration of all of them is not part of the problem of the present paper. We therefore restrict ourselves to merely describing our experimental geometry, which is similar to the geometry for the observation of orientational self-focussing in a nematic.[10]

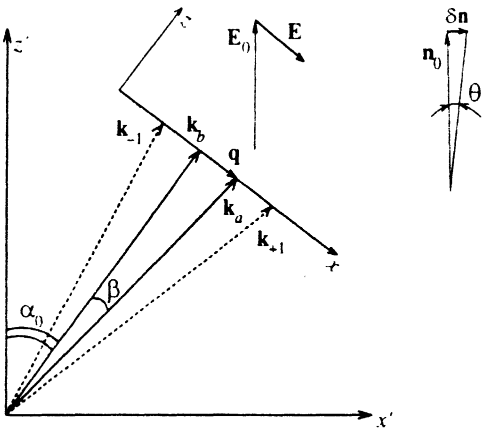

FIG. 3. Geometry for observing the PC in a nematic.

The interaction geometry is shown in Fig. 3. Two e-type waves $E_{a,b}$ propagate in a homotropic sample at an angle to the unperturbed directrix $\mathbf{n}^0$ at the refractive angle φ (the angle between the two, β, is much smaller than φ). The difference between their wavevectors, $\mathbf{q}$ (the wavevector of the lattice), has x and z components as has the space charge field $\mathbf{E}$ which is directed along $\mathbf{q}$. The external field $\mathbf{E}_0$ is directed along z.

The calculation of the reorientation is carried out in the single-constant approximation for the Frank energy:[1]

$$F_{Fr} = K\partial_\alpha n_\beta \partial_\alpha n_\beta/2$$

by standard variational methods (see Ref. 2) and leads in the steady case to the following equation for the reorientation angle θ of the directrix:

$$\frac{\partial^2\theta}{\partial z^2} + \frac{\partial^2\theta}{\partial x^2} - \frac{\varepsilon_a}{2\pi K} E_0^{2*}\theta = -\frac{\varepsilon_a}{2\pi K} E_0 E_s \cos(\varphi)\cos(\mathbf{qr}). \tag{19}$$

Here we have neglected the term $E^2\theta$ in comparison with $E_0^2\theta$ and also $E^2 \cos\varphi \sin\varphi$ in comparison with $E_0 E \cos\varphi$.

Moreover, for simplicity we have neglected the boundary conditions $\theta(0,x) = \theta(L,x) = 0$, since they make a contribution which is small in the parameter $(qL)^{-2}$. Restricting ourselves thus to a particular solution of (19) we get

$$\theta = \theta_0 \cos(\mathbf{qr}), \quad \theta_0 = \frac{\varepsilon_a E_0 E_s \cos(\varphi)}{2\pi K q^2(1 + \varepsilon_a E_0^2/2\pi K q^2)}. \tag{20}$$

This reorientation lattice leads to a modulation of the optical dielectric permittivity for the waves excited by it (see Fig. 3):

$$\begin{gathered} \varepsilon_L = \varepsilon_{0L} + \varepsilon_1 \cos(q_x x + q_z z), \\ \varepsilon_1 = \delta\varepsilon_{Lx'x'} = 2\varepsilon_{aL} n_{0x'} \delta n_{x'} = 2\varepsilon_{aL}\theta_0 \sin(\varphi)\cos(\varphi). \end{gathered} \tag{21}$$

Here ε_{0L} is the dielectric permittivity for the e-waves propagating at an angle φ to the axis and ε_{aL} is the anisotropy in the dielectric permittivity at the light frequency. Note that here, following Ref. 10, we have neglected the fact that the waves $E_{a,b}$ are slightly nontransverse.

By virtue of the rather small thickness of the sample, for small β the waves will undergo Raman–Natto self-diffraction in the ±1,2,... orders. We assume that the amplitude of the lattice is sufficiently small that we can neglect second-order diffraction (as was the case experimentally), i.e., the waves $E^{\pm}$ (see Fig. 3) are the result of diffraction to first order of the wave E_a and to first order of the wave E_b, respectively. The calculation of the diffraction efficiency η for such first-order self-diffraction is completely standard (see, e.g., Ref. 11) and we shall therefore not give it her but merely state the result. In the Born approximation we have

$$\eta = \frac{|E_-|^2}{|E_a|^2} = \left(\frac{\pi L \varepsilon_1}{\lambda \varepsilon_0^{1/2}}\right)^2 \left[\frac{\sin(\Delta L/2)}{(\Delta L/2)}\right]^2 . \tag{22}$$

Here $\Delta = (k_a + q - k_-)_z \approx \omega\beta^2/c$ is the wave mismatch—in the first-order diffraction with respect to the spatial component of the polarization of the medium excited by it—which is found, as usual, from the condition $(k_a + q - k_-)_x \equiv 0$. Estimates show that for $L \approx 100$ μm, $\lambda \approx 0.5$ μm the factor $(\sin a/a)^2$ is unimportant (of order unity) up to $\beta \approx 6 \times 10^{-2}$ rad; this was the range of angles used in the experiment. We can therefore finally rewrite (22) without that factor:

$$\eta = \left[\frac{\varepsilon_a \varepsilon_{aL} \sin(\varphi)\cos(\varphi) E_0}{1 + \varepsilon_a E_0^2/2\pi K q^2} \frac{L}{\lambda\sqrt{\varepsilon_0}} \frac{m k_B T \nu}{eKq} \frac{\sigma - \sigma_d}{\sigma}\right]^2 . \tag{23}$$

We draw attention to the fact that the factor $(1 + \varepsilon_a E_0^2/2\pi K q^2)$ in the denominator in (23), which for $\varepsilon_a < 0$ formally may give resonant amplification of the diffraction efficiency for well defined E_0, q, in actual fact does not do so. Indeed, for $\varepsilon_a < 0$ external fields for which we have $E_0 \leqslant U_F/L$ are allowed and for larger external fields a Fréderiksz transition occurs which is azimuthally degenerate, as it always is in the $\varepsilon_a < 0$ case,[1] so that the uniformity of the orientation is broken. We then have

$$\frac{\varepsilon_a E_0}{2\pi K q^2} \leqslant \frac{2\pi^2}{(qL)^2} = \frac{1}{2}\left(\frac{\Lambda}{L}\right)^2 .$$

In the $qL \gg 1$ case discussed above this factor is always of order unity.

If, on the other hand, we decrease q, maintaining $E_0 L \leqslant U_F$. For $\Lambda \ll L$ we must take into account the effect of the zero boundary conditions in z which were omitted above when we calculated the reorientation; this causes Kq^2 in the above solution to be replaced by $K(\pi/L)^2$ (lowest reorientation mode, sinusoidal in z; see Ref. 10) In that case $\varepsilon_a E_0^2/2\pi K(\pi/\lambda)^2$ again does not reach an absolute magnitude of unity. Therefore, if this "resonant" denominator has to lead to some observable result, it can be only in a deviation of the function $\eta(E_0)$ from being quadratic for $\Lambda \approx L$, i.e., for small β, about equal to 5×10^{-3} rad.

In Table I we give the main functional dependences of the diffraction efficiency on I, E_0, and q. For a comparison we give there also the same for self-diffraction in the usual orientational nonlinearity which can also occur for the geometry of Fig. 3, although it is true for higher (by two or three orders of magnitude) radiation intensities, as we shall now show.

TABLE I. Dependence of the diffraction efficiency on the experimental parameters for the photorefractive and orientational nonlinearities.

	Nonlinearity	
Parameter	photorefractive	orientational
I_0	$\left(\frac{\sqrt{I_0}}{\sqrt{I_0 + a}}\right)^{1/2}$	I_0^2
E_0	E_0^2	practically no dependence for $E_0 L \leqslant U_F$
q	q^{-2}	q^{-4}

Note: $a = \sigma_d/(\mu^+ + \mu^-)e\sqrt{\alpha/\gamma}$.

Indeed, the ratio of the diffraction efficiencies for the two mechanisms is [see Eq. (20) and also Ref. 10]:

$$\xi = \frac{\eta_{FN}}{\eta_{ON}} = \left(\frac{\theta_{0FN}}{\theta_{0ON}}\right)^2 \approx \frac{\varepsilon_a E_0 E_s}{\varepsilon_{aL} E_a E_b^* \sin(\varphi)\cos\varphi} . \tag{24}$$

Using $c\sqrt{\varepsilon_0} E_a E_b^*/4\pi = mI_0$, $\sin\varphi\cos\varphi \leqslant 1/2$ and also Eq. (15) for E_s we get (in the case when we have $\sigma \gg \sigma_d$, $E_0 L \simeq U_{\mathrm{F}}$):

$$\xi = \left(\frac{\sqrt{\varepsilon_a} k_B T q \nu \sqrt{\pi K}}{\varepsilon_{aL} I_0 e L}\right)^2 . \tag{25}$$

The estimate (25) gives $\xi \approx 10^{-6}$ for the value we used, $I_0 \approx 200$ mW/cm^2, so that to observe the self-diffraction in the ON the radiation intensity was three orders of magnitude too low.

We now turn to a description of the experimental observation of the effects described above.

6. EXPERIMENTAL OBSERVATION OF SELF-DIFFRACTION

For the observation of self-diffraction in a homotropic sample of thickness $L = 100$ μm of an R6G-5CB mixture with a concentration of 7×10^{-4} mole/1, corresponding to a maximum σ for a given I_0, we intersected two beams of an argon laser ($\lambda = 0.4880$ μm) at a small angle $\beta \leqslant 6 \times 10^{-2}$ rad with a total power density which reached 300 mW/cm^2. The incident angle of the radiation on the sample was varied from 0 to 60° in the geometry of Fig. 3, i.e., $0 \leqslant \varphi \leqslant 35°$. We applied a voltage of up to ~3 V (U_F for the given mixture) to the transparent electrodes of the cell. We studied the angular spectrum of the radiation passing through the sample. One can reduce the main qualitative results to the following.

Self-diffraction, i.e., the $E^{\pm}$ waves, were observed only when the e-waves were obliquely incident upon the sample and only when there was a voltage U_0 applied to the sample. The diffractive efficiency η reached 20% for small intersection angles ($\beta \approx 2 \times 10^{-2}$ rad) of the waves.

To reach such values of η through the ON or the thermal nonlinearity of the nematic one needs two to three orders of magnitude larger radiation power densities.

The fact that self-diffraction is observed only for oblique incidence unambigously indicates the orientational mechanism for tracing the ε_L lattice, since it means that the principal values of the tensor ε_L are unchanged (in the opposite case self-diffraction would occur also for normal

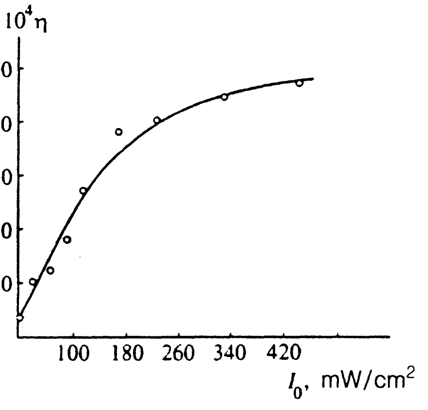

FIG. 4. Diffraction efficiency as function of the total wave intensity. $U_0 = 1.75$ V; $\beta = 1.9 \times 10^{-2}$ rad.

incidence). Therefore the possibility of self-diffraction due to a very strong conformational nonlinearity of nematics[12] also drops out.

The necessity of an external U_0 for self-diffraction in conjunction with the orientational nature of the tracing of the lattice leads to the conclusion that the reorientation occurs just due the action of a static (probably spatially inhomogeneous) field (see Table I) and not of an optical field.

The qualitative results indicate thus that we are apparently dealing with the PC of nematics which we described above. For a quantitative comparison with the theoretical predictions we studied the dependence of η on the parameters given in Table I.

We show the function $\eta(I_0)$ in Fig. 4. It is clear that it is linear for small I_0, while for $I_0 \simeq 450$ mW/cm^2 it approaches a constant value corresponding to $\sigma \gg \sigma_d$ (see Fig. 2). Both of these confirms Eq. (23).

The results of studying the dependence of η on the wavenumber of the lattice are given in Fig. 5 in through $\eta(\beta^{-2})$. It is clear that in accordance with (23) and the additional remarks about the "resonant" denominator this function is linear (it is removed for $U_0 < 0.5 U_F$). In Fig. 6 we give the function $\eta(U_0^2)$. In accordance with (23) it is linear up to values $U_0 \approx U_F$ and deviates from linearity by becoming larger when U_0 approaches U_F.

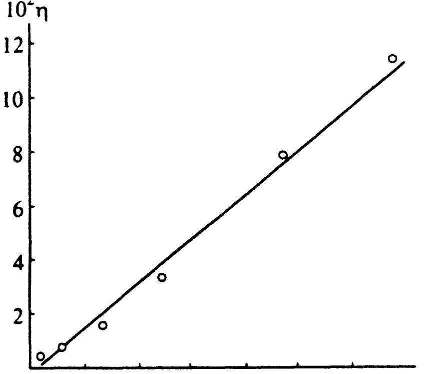

FIG. 5. Diffraction efficiency as function of the intersection angle of the waves in the sample. $I_0 = 200$ mW/cm^2; $U_0 = 1.41$ V.

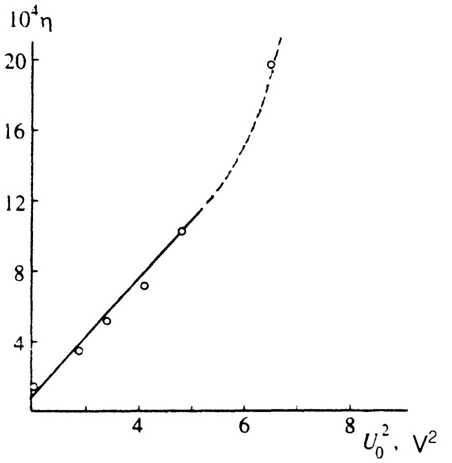

FIG. 6. Diffraction efficiency as function of the voltage applied to the cell; $I_0 = 180$ mW/cm^2; $\beta = 1.9 \times 10^{-2}$ rad.

Finally, we note that we estimated from the experimental data a value of ν for the given mixture: $|\nu| \approx 4 \times 10^{-2}$ which corresponds to the ratio of the mobilities of the positive and negative ions (or vice versa; in the given experimental set-up it is impossible to establish this) which is equal to 0.92.

7. CONCLUSION

There is therefore every justification to state that we have predicted and observed a new mechanism for a cubic nonlinearity of nematics, which is larger by three orders of magnitude than those known earlier. We note especially that this nonlinearity can be further enhanced by the choice of an optimal composition and concentration of the mixture (by approximately an order of magnitude due to ν and by much more due to α through using dyes with smaller luminescence quantum yields).

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