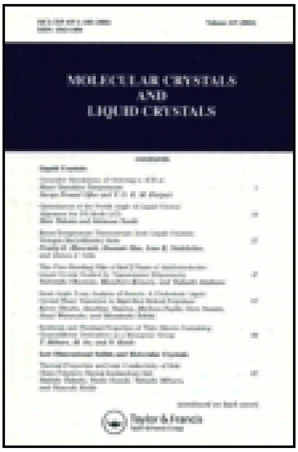

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ORIENTATIONALLY INDUCED SECOND ORDER SUSCEPTIBILITY IN NEMATICS

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Abstract Second-order susceptibility $\chi^{(2)}$ in homeotropically aligned nematic sample is discussed which is due to slight in centrosymmetrisity induced within the sample by orientational B-type grating, light-induced by origin. Such $\chi^{(2)}$ appears to be periodically space-inhomogenious and enables one to achieve phase-matching conditions for second harmonic generation for arbitrary pump polarization and incident angle.

INTRODUCTION

If a nematic liguid crystal's director field $\vec{n}(\vec{r})$ homogeunity is frustrated by some reason, the medium looses local centrosymmetrisity, which is provided by antiparallel aligument of neibouring molecules in case of nondisturbed orientation. Really, in case of disturbed reorientation we have one extra variable, namely

$\vec{\nabla} n_i$, which corresponds to a new local polar axis (see fig.1) in the medium (remember $\vec{n}$ and $-\vec{n}$ being equivalent). The simplest and well-known physical sequence of appearance of such polar axis is the direct flexoelectric effect (see, e.g.,[1]), i.e. the spontaneous polarization within the medium $\vec{P}_d = e_1 \vec{n} \cdot \mathrm{div}\,\vec{n} - e_3 \vec{n} \times \mathrm{rot}\,\vec{n}$.

Nevertheless, besides this polarization, defined as a matter of fact by the angular distribution function of molecules $f(\varphi)$ first momentum, its natural to expect other phenomena defined by odd momenta of $f(\varphi)$.

One of such phenomena, namely the second harmonic generation[2] in case of spatially periodic ("grating") director field perturbation will be discussed theoretically and experimentally in this report.

"FLEXOINDUCED" SECOND ORDER SUSCEPTIBILITY

Consider a homeotropic NLC sample, its director being slightly reoriented in a grating-like manner as shown in fig.1, $\Theta(z) = A(z) \sin qz$ $A(z)$ varying slow enough in q^{-1} scale for us to neglect $\partial A/\partial z$ in comparison with qA . Such

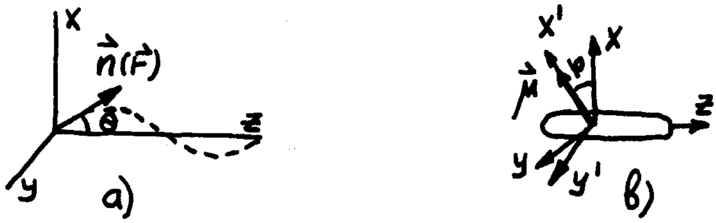

FIGURE 1

gratings are rather easily excited experimentally by co-propagating o- and e-waves, see[3], A being rather small ($A \sim 10^{-2}$rad). Let's consider the flexoelectric polarization $\vec{P}_d$ in such medium $\vec{P}_d \simeq \vec{e}_x P_d$ in terms of molecular dipoles' reorientation around their long axes (fig. 1b). In our approximation we consider molecules as long "cyllinders" having arbitrarily oriented dipole $\vec{\mu}_\Sigma = \vec{e}_{x'} \mu + \vec{e}_z \mu_{\parallel}$, their long axes being aligued along z (so we suggest order parameter $S = 1$ and neglect here a slight reorientation associated with the director deformation described above). Due to the general symmetry of the problem the antiparallel "package" of the molecules with respect to z axis is not destroged, so the dipole's z -components are compensated and we can consider the molecules having only the transverse dipole component $\mu \vec{e}_{x'}$. Being noncentrosymmetric, such molecules posess second-order hyperpolarizability aswell as permanent dipole. After taking into account "antiparallel package" wih respect to z axis, the effective molecular hyperpolarizability tensor γ_{ikl} , defined in x'y'z frame of referense, will have only 8 independent components, namely following:

$$\gamma_{111};\ \gamma_{122};\ \gamma_{221}=\gamma_{212};\ \gamma_{133};\ \gamma_{331}=\gamma_{313}; \tag{1}$$

$$\gamma_{123}=\gamma_{132};\quad \gamma_{321}=\gamma_{312};\quad \gamma_{213}=\gamma_{231}$$

Meanwhile all the rest components of effective γ_{ikl} are equal to zero independently of real molecular hyperpolarizability tensor. Within the framework of such approximation the flexopolarization can be only due to anisotropic modification of molecular dipoles' distribution function $f(\varphi)$.

If, in addition, we let a light wave $\vec{E}_N$ with frequency ω propagate in the medium, the expressions for flexopolarization and double-frequency polarization $\vec{P}^{(2)}$ will be following:

$$\vec{P}_d = \vec{e}_x \mu N \int_0^{2\pi} \cos\varphi\, f(\varphi)\, d\varphi$$

$$P_j^{(2)} = L_{ji}(2\omega) L_{kt}(\omega) L_{eq}(\omega) N \int_0^{2\pi} \gamma'_{ikl}(\varphi) f(\varphi) E_{Nt}(\omega) E_{Nq}(\omega)\, d\varphi \tag{2}$$

Here N stauds for molecular concentration, $L_{ij} = (\varepsilon_{ij}+3)/2$ – local field tensor and γ'_{ikl} is γ_{ikl} tensor rewritten in xyz frame of reference and thus dependent on φ. For the case of orientationally nondisturbed NLC we consider $f(\varphi)$ being equal to $1/2\pi$, which immedialely provides $\vec{P}_d = \vec{P}^{(2)} = 0$ as they must be in centrosymmetric medium. If orientation is disturbed we assume $f(\varphi)$ being defined by some "molecular field" potential $U(\varphi)$, which is an even function of φ and after a Fourier series development gives following:

$$f(\varphi) = \frac{1}{2\pi}\exp\left(-\frac{U(\varphi)}{kT}\right) \approx \frac{1}{2\pi}\left(1-\frac{U(\varphi)}{kT}\right) = \frac{1}{2\pi}\left(1-\frac{h\mu\cos\varphi}{kT}\right) \quad (3)$$

Here we introduced the first Fourier coefficient az $h\mu$, h thus corresponding to some "molecular field" interacting with molecular dipole, and phenomenologically $\vec{h} \sim \vec{n}\times \mathrm{rot}\,\vec{n}$ for B-deformation. It should be noted that the nature of $\vec{h}$ is a great deal complicated, but fortunately we will manage to avoid presense of h in the resulting expression, so it is not nesessary to discuss it in detail here. Using (2) and (3) after some simple but rather extensive calculations one can obtain following result:

$$\vec{P}_d = \vec{e}_x \cdot \frac{\mu N}{2} \cdot \frac{\mu h}{kT} \qquad (3)$$

$$\chi^{(2)}_{jtq} = L_{ij}(2\omega) L_{kt}(\omega) L_{eq}(\omega) \frac{\mu h N}{2kT} \cdot \nu_{ik\ell}$$

Here the $\nu_{ik\ell}$ tensor has only 7 nontrivial (and 5 independent) components, namely following:

$$\nu_{xxx} = \frac{1}{4}(3\gamma_{111} + \gamma_{121} + 2\gamma_{221}); \ \nu_{xzz} = \gamma_{133}; \ \nu_{zzx} = \nu_{zxz} = \gamma_{331} \qquad (4)$$

$$\nu_{yxy} = \nu_{yyx} = \frac{1}{4}(2\gamma_{221} + \gamma_{111} - \gamma_{122}); \ \nu_{xyy} = \frac{1}{4}(3\gamma_{122} + \gamma_{111} - 2\gamma_{221})$$

Expression (3) immediately shows that $\chi^{(2)}_{jtq} \backsim P_d$, namely

$$\chi^{(2)}_{jtq} = L_{ij}(2\omega) L_{kt}(\omega) L_{eq}(\omega) \frac{P_d}{\mu} \nu_{ik\ell} \qquad (5)$$

Such proportionality was mentioned phenomenologically in[2], but it was considered in such manner that $\hat{\chi}^{(2)}$ is by origin a dc-field induced one, the dc field $\vec{\mathcal{E}}_0$ in turn being produced by spatially inhomogenious $\vec{P}d$. It can be shown (see[4]) that such "field-induced" $\hat{\chi}^{(2)}(\vec{\mathcal{E}}_0)$ will be

$$\hat{\chi}^{(2)}(\vec{\mathcal{E}}_0) = \frac{\mathcal{E}_0}{h} \hat{\chi}^{(2)}; \quad \frac{\mathcal{E}_0}{h} = \frac{2\pi \mu^2 N}{\varepsilon_a kT} \approx 10^{-4}$$

and thus negligibly small compared to expression (5). It's thus obvious that the linear dependence of $\hat{\chi}^{(2)}$ upon $\vec{P}_d$ is rather formal than intrinsic, both magnitudes in fact being independent consequenses of the same origin-anisotropic modification of $f(\varphi)$. Now using the phenomenological expression for $\vec{P}_d$ we can simply derive the final expression for $\hat{\chi}^{(2)}$:

$$\chi^{(2)}_{jtq} = L_{ji}(\omega) L_{kt}(\omega) L_{eq}(\omega) \frac{e_3 A(z) q}{2M} V_{ikl} \{ \exp(iqz) + c.c. \} \quad (6)$$

So the second order susceptibility appears to be a spatiallyalternating grating. Varying $\vec{q}$ one can obtain phase-matched SHG for arbitrary polarization type of interacting waves and their propagating directions. Let's consider those phaze-matching conditions in more detail.

SHG IN NLC WITH B-GRATING OF ORIENTATION

It can be seen from (6) that as fur as SHG is considered the medium behaves as biaxial crystal, the $\hat{\chi}^{(2)}$ tensor having polar axis x and generally non-equivalent axes y and z. Meanwhile the <u>linear</u> permittivity tensor is uniaxial (to say nothing of slight perturbations due to $\theta(z)$, z being its' optical axis. Heuse the SHG properties are different in cases of xz and yz planes of incidense (correspondent effective susceptibilities are different). Nevertheless the wave vectors' geometry is defined by linear properties and is quite the same for both planes (see fig.2).

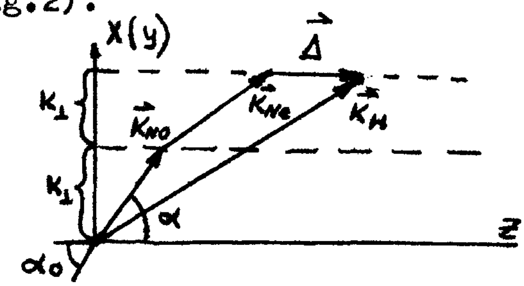

FIGURE 2. SHG wave vectors' geometry.

Let a plane wave, having in general both o- and e- components be incident upon a homeotropic sample by incident angle α_0 . According to the traditional boundary conditions the "wave vector mismatching" $\vec{\Delta}$ will be directed along z, as well as q, and the shortened equation for SH wave magnitude E_H can be written as follows

$$\frac{\partial E_H}{\partial z} = i\, g_n^{\beta} E_{N1} E_{N2}\, q\, A(z) \left\{ \exp(i\Delta_+ z) + \exp(i\Delta_- z) \right\} \quad (7)$$

Here summation by n is not suggested, subscript n corresponding to the number of interaction polarization type in the Table 1, and β superscript denotes the plane of incidense (β =x,y). Explicit expressions for g_n^{β} are a great deal sophysticated (see[4]), the order of magnitude for them bejng $g \approx 40\frac{\gamma e_3}{\mu\lambda^3} \approx 10^{-10}$ CGS where γ is some "typical value" for γ_{ikl} component ($\sim 10^{-30}$CGS), $\lambda \sim 10^{-4}$cm is the $\vec{E}_n$ wavelength, and $\Delta_\pm = \pm q - \Delta = \pm q - (\vec{K}_H(\alpha_0) - \vec{K}_{N1}(\alpha_0) - \vec{K}_{N2}(\alpha_0))_z$ Qualitative data for g_n^β (whether its' zero or not) is presented in Table1.

TABLE1.

n	Type	Possibility of interaction β =x	β =y
1	oo → o	1	0
2	oo → e	0	1
3	oe → o	1	0
4	oe → e	0	1
5	ee → o	0	1
6	ee → e	1	0

In typical experiment only a very small portion of $\vec{E}_N$ wave (about $10^2 \div 10^4$ photons per pulse) is transmitted into E_H, it is natural to cosider $E_{N1,2}(z)$=const, eq.7thus having simple solution:

$$E_H(L) = i g_n^\beta E_{N1} E_{N2} q \int_0^L A(z) \{ \exp(i\Delta_+ z) + \exp(i\Delta_- z) \} dz \quad (8)$$

So thephase-matched SHG takes place if Δ_+ =0 or Δ_- =0 (neglecting small shifts due to slow A(z) phase drift). Here one can see qualitative differenses for various polarization types of interaction, namely for the types <u>which do not exhibit phase matching</u> by spatially homogenious $\hat{\chi}^{(2)}$ (say, external field-induced one[5]), i.e. oo→o, oo→e, oe→e and ee→e, situation is following. If $q < \min\{|\Delta(\alpha)|\}$ or $q > \max\{|\Delta(\alpha)|\}$ n o phase matching takes place. By $\min\{|\Delta(\alpha)|\} < q < \max\{|\Delta(\alpha)|\}$ <u>one</u> phase-matching peakarrives in $\vec{E}_H(\alpha)$ dependense (due to $\Delta_+=0$ or $\Delta_-=0$, while the rest "mismatching" never equals zero as sign $\Delta(\alpha)$=const).

For interactions <u>exhibiting phase matching by $\hat{\chi}^{(2)}(\vec{r})$=const</u>, i.e. ee→o and oe→o, the situation is quite different. Namely, for $q > \max\{|\Delta(\alpha)|\}$ phase matching is absent. For $\min\{|\Delta(\alpha)|\} < q < \max\{|\Delta(\alpha)|\}$ <u>one</u> phase matching peak takes place. At last for low values of q: $q < \min\{|\Delta(\alpha)|\}$ the "homogenious" phase-matching peak <u>is "doubled"</u>. Explicit expressions for phase-matching angles'calculation are obvious but very huge, so we won't present them here.

Now we are to say some words about the means of orientatioonal B-gratings excitation, and hence the explicit expression for A(z). As far sa we know, the only such means up to date is the light-induced reorientation[6,7] under the influence of co-propagating o- and e-waves (see fig.4). Some explanations should be made here. Up to now we assumed that $\vec{E}_N$ does not influence the director orientation. Its true for typical experiment $\vec{E}_N$ being a Q-switched laser pulse, powerful enough to excite SHG, but of too little energy density to create observable reorientation. So one needs an extra wave $\vec{E}_R$ (millisecond pulse in our experiment) to excite the grating.

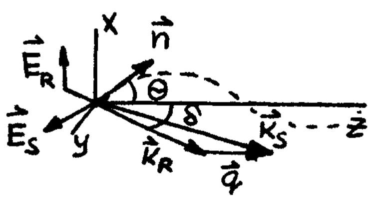

FIGURE 3. Orientational SS geometry.

Let an ordinary wave penetrate the sample by the incident angle δ_0 in yz-plane, it will cause orientational stimulated scattering (SS) into $\vec{E}_S$ e--wave[6,7]. In transient regime, which was our experimental case, SS is discribed by the following equations[7]

$$\frac{\partial A}{\partial \xi} = S\,; \quad \frac{\partial S}{\partial z} = i\gamma A\,; \quad S(0,\xi) = \varepsilon\,; \quad A(z,0) = 0 \qquad (9)$$

Here $S = \frac{\varepsilon_{aR}\sin\delta}{8\pi\eta}\,\frac{E_S}{E_R}$, $\xi = \int_0^t |E_R|^2 dt'$, ε corrsponds to spontaneous scattering cross section. It should be noted that one can easily manage the value of q varying δ_0. As to σ , it equals $\sigma = \varepsilon_{aR}^2 \sin^2\delta\, \omega_R / 32\pi\eta\, n_s\, c \cos\delta$, η being orientational viscosity, ε_{aR} - permittivity anisotropy for ω_R frequency, n_S - the $\vec{E}_S$ refraction index, c - light velosity. Using the second eq.(9) we can rewrite (8):

$$E_H(L) = \frac{g_n^{\beta} E_{N1} E_{N2}\, q}{\sigma} \int_0^L \left\{ \frac{\partial S}{\partial z} \exp(i\Delta_+ z) + \frac{\partial S^*}{\partial z} \exp(i\Delta_- z) \right\} dz \qquad (10)$$

Since $S(z,\zeta) = I_0(2\sqrt{i\sigma z \zeta})$ is a rather complicated function, analitical integration in (10) fails but in the case of phase-matched SHG(Δ_+ or Δ_-=0). In such case

$$|E_H(L)|^2 \simeq \frac{|g_n^{\beta}|^2 |E_{N1}|^2 |E_{N2}|^2 q^2}{\sigma^2} |S(L)|^2 \qquad (11)$$

Physical meaning of thes expression is quite obvious: the SHG signal must be proprotional to current value of SS power efficiency by $\vec{E}_N$=const.

OBSERVATION OF SHG DISCUSSED ABOVE

Experimental observation of SHG enhancement by grating B-deformation and phase-matched SHG oo→→o was carried out in a hometropic 5CB sample of 70μm thickness. Grating was excited by orientational SS of o-polarized free-running ruby laser pulse of about 0.5J total energy and beam diameter within the sample of FWHM=1.5mm. SHG was excited by a Q-switched single mode and frequency Nd laser pulse of total energy of about 10mJ, which was slightly focused upto FWHM=0.5mm within the sample, its divergense being about o.3^o. Following parameters were measured: total energy of $\vec{E}_N$,$\vec{E}_H$ pulses (the SH registration threshold being 50 photons per pulse), temporal envelopes of $\vec{E}_{R,S}$ pulses and $Q_R(t) \propto \xi$ (by integrating circuit) and $\vec{E}_H$ polarization (with the help of Glan prism). $\vec{E}_N$ wave propagated along z axis being polarized along x (see fig.1), $\vec{E}_H$ appeared to be x-polarized as well.

Qualitatively, the results were following. In the absense of $\vec{E}_R$ wave a very weak (perhaps, quadrupole) SHG occured, SH signal revealing traditional square dependense of $\vec{E}_N$energy Q_N and yielding Maker's oscillations by slightly varied E_N incidence angle - thus ensuring its volume origin. In the prsense of $\vec{E}_R$ wave Q_H enhanced drastically (more than 50 times) with the increase of Q_R (see fig.4), Q_N and δ_o being constant

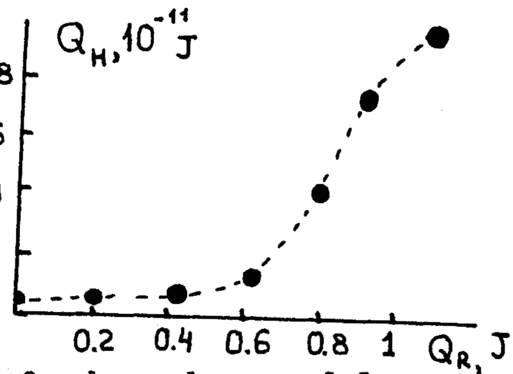

FIGURE 4. Q_H dependense of Q_R.

In order to verify the grating character of induced $\hat{\chi}^{(2)}$ the dependense of Q_H of δ_o was investigated (see fig.5), Q_N and Q_R being maintained constant. The dependense reveals a typical phase-matching peak by incidense angle δ_o =38.5°, which corresponds to refraction angle δ =25.16° - coinsiding with the calculated value for phase-matching (δ_c =25.4o°) within the $\vec{E}_N$ beam divergense.

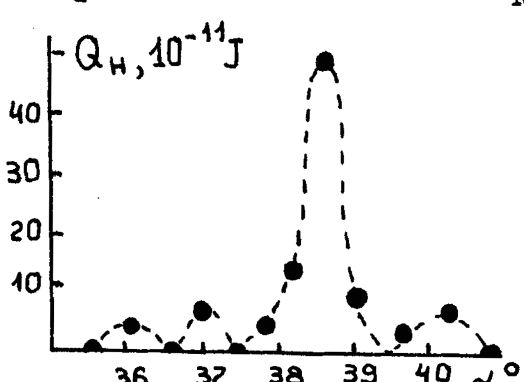

FIGURE 5. Angular dependense of SHG sinal.

Maintaining now the phase-matching value for δ_o , we measured the dependense of Q_H upon $|S|^2$ (see eq.11) keeping Q_N constant. The results presented in in fig.6 reveal linear dependense $Q_H(|S|^2)$, thus confirming eq.11. The coefficient of this dependense appeared to be 10 times greater than that calculated from (11), which is quite satisfactory remembering incertainity of material parameters used. The absolute value of SHG efficiency achieved $R=Q_H/Q_N=5.10^{-12}$ i.e. quite comparable to external dc-field induced SHG (see[5]).

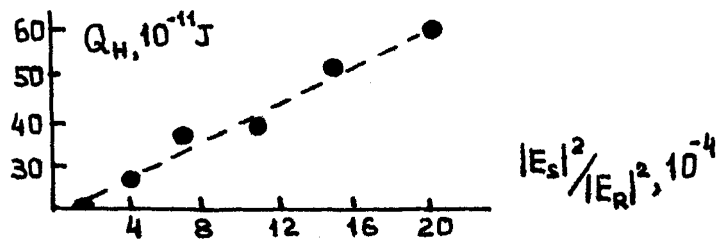

FIGURE 6. SH signal dependense of SS efficiency

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