

# Spatially inhomogeneous quadratic susceptibility of nematics with light-induced orientational gratings

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A model of individual molecular hyperpolarizabilities is used to calculate the quadratic optical susceptibility tensor  $\chi_{ikl}^{(2)}$  of a nematic subjected to longitudinal bending. The linear relationship between the components of this tensor with the flex-polarization is formal rather than causal. In the case of a grating,  $B$  deformation of all six types of phase matching should be observed if a second harmonic is generated in such a nematic. A study is made of the characteristics of second harmonic generation under conditions of steady-state and transient excitation of  $B$ -deformation gratings.

If the spatial orientation of a nematic liquid crystal is for some reason disturbed, it follows from the symmetry considerations that the nematic medium loses its local inversion symmetry ensured in the unperturbed case by the anti-parallel packing of molecules. In fact (see Fig. 1) the medium acquires a preferred direction  $\nabla n_i$ , where  $\mathbf{n}$  is the director of the nematic (the directions  $\mathbf{n}$  and  $-\mathbf{n}$  are equivalent). A generally known physical manifestation of such "suppression" of a center of inversion is the direct flex (or flexoelectric) effect (see Ref. 1) involving the appearance—in an orientationally deformed nematic—of a spontaneous polarization

$$\mathbf{P}_d = e_1 \mathbf{n} (\text{div } \mathbf{n}) - e_3 [\mathbf{n} \text{ rot } \mathbf{n}].$$

However, in addition to this quantity—governed essentially by the first moment of the angular distribution function  $f(\theta, \varphi)$  of the polar molecular axes (Fig. 1)—we can naturally expect manifestation also of other phenomena due to the odd moments  $f(\theta, \varphi)$  in an orientationally deformed nematic. One of these phenomena is "flex-induced" second harmonic generation (SHG) in a nematic, first considered in Ref. 2 for the case of orientational deformations with the characteristic inhomogeneity scale of the order of the thickness of the sample. The resultant susceptibility  $\chi_{ikl}^{(2)}$ , phenomenologically proportional to  $\mathbf{P}_d$ , is interpreted in Ref. 2 as SHG in an "external field" due to a spatially inhomogeneous spontaneous polarization.

Our aim will be determination of the nature of the microscopic relationships between  $\hat{\chi}^{(2)}$  and  $\mathbf{P}_d$ , as well as investigation of the characteristics of the process of flex-induced SHG in the case of a spatially periodic (across the thickness of a sample) or grating-like deformation of the director of the investigated nematic.

## MODEL OF INDIVIDUAL MOLECULAR HYPERPOLARIZABILITIES

We must stress first that an analysis given below is limited to the case of a grating-like deformation caused by longitudinal bending ( $B$  deformation) of a nematic. This is the most interesting case because of the relative ease of inducing experimentally such deformations with a controlled wave vector  $\mathbf{q}$  (see Ref. 3). Another possible type of a grating-like deformation resulting in suppression of the inversion center is transverse bending ( $S$  deformation), but it is difficult to

realize experimentally and the mechanism of the appearance of the dipole susceptibility  $\chi_{ikl}^{(2)}$  in the  $S$ -deformation case is fully analogous to that in the  $B$ -deformation case, so that we shall ignore the  $S$  deformation.

We shall assume that a homeotropic sample of a nematic of thickness  $L$  (Fig. 1) exhibits a grating-like  $B$  deformation:

$$\theta(z) = A(z) \sin qz.$$

We shall regard the amplitude of the deformation to be "slow" on the scale of  $q^{-1}$  and small ( $A \lesssim 10^{-2}$  rad in the usual experimental situations), so that we can ignore small deviations of the long molecular axes from the preferred axis established by the deformation. For simplicity, we shall adopt an approximation with an order parameter  $S = 1$ , since allowance for the real distribution of the molecular axes in respect of the angle  $\theta$  does not change qualitatively the results, but simply complicates greatly the analysis. A nematic molecule is assumed, in accordance with the real structure of most nematics, to be completely asymmetric, i.e., it is assumed to have no symmetry axes or planes, and no center of inversion. The properties of such a molecule are described by its dipole moment

$$\boldsymbol{\mu} = \mu_{\parallel} \mathbf{e}_z + \mu_{\perp} \mathbf{e}_x.$$

The direction of the transverse component of the dipole moment of a nematic molecule is adopted to be the  $x'$  axis of an "intrinsic" coordinate (reference) system  $x'y'z$ , where  $\varphi$  is the angle between the  $x$  and  $x'$  axes. In this intrinsic coordi-

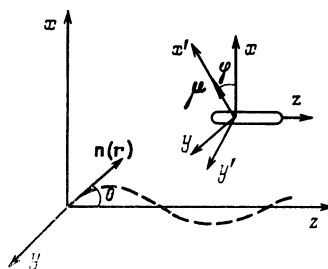


FIG. 1.

nate system we now define a quadratic hyperpolarizability tensor  $\gamma_{ikl}^{(0)}$  ( $2\omega = \omega + \omega$ ) for SHG-like processes and we assume that this tensor is independent of  $\varphi$ . We also assume that  $f(\varphi)$  is the distribution function of molecules in respect of  $\varphi$ , normalized to unity, and that it is isotropic in the case of an undeformed nematic, which corresponds to the absence of the spontaneous polarization  $\mathbf{P}_d$ :  $f^0 = 1/2\pi$ .

Before we calculate directly  $\mathbf{P}_d$  and the polarization at the doubled frequency  $\mathbf{P}^{(2)}$ , we must allow for the antiparallel packing of the molecules along the  $z$  axis, which should not be disturbed, as deduced from the macroscopic symmetry of the problem (with the polar axis  $x$ ). This can be allowed for by replacing the real molecules with some "new" molecules characterized by  $\boldsymbol{\mu} \equiv \boldsymbol{\mu}_\perp$  ( $\mu_\parallel = 0$ ), and redefining the hyperpolarizability as follows:

$$\gamma_{ikl}^{(4)} = \hat{B}^{-1} (\gamma_{ikl}^0 + B_{ip} B_{kr} B_{ls} \gamma_{prs}^0),$$

where  $\hat{B}$  is the matrix which transforms the coordinates on rotation by  $180^\circ$  about the  $x'$  axis. Therefore, without restricting in any way (in spite of the obvious symmetry in respect of  $kl$ ) the tensor  $\hat{\gamma}^0$ , we find that the tensor  $\hat{\gamma}^{(1)}$  has only eight independent components (which are in general complex variables):

$$\begin{aligned} \gamma_{x'x'x'}^{(1)} &= \gamma_{111}^0; & \gamma_{x'y'y'}^{(1)} &= \gamma_{122}^0; & \gamma_{y'x'y'}^{(1)} &= \gamma_{y'y'x'}^{(1)} = \gamma_{221}^0; \\ \gamma_{x'z'z'}^{(1)} &= \gamma_{133}^0; & \gamma_{z'z'x'}^{(1)} &= \gamma_{z'x'z'}^{(1)} = \gamma_{331}^0; & \gamma_{x'z'y'}^{(1)} &= \gamma_{x'y'z'}^{(1)} = \gamma_{123}^0; \\ \gamma_{y'z'z'}^{(1)} &= \gamma_{y'z'x'}^{(1)} = \gamma_{231}^0; & \gamma_{z'y'x'}^{(1)} &= \gamma_{z'x'y'}^{(1)} = \gamma_{312}^0. \end{aligned} \quad (1)$$

On the basis of this model the flex polarization observed along the  $x$  axis is described by an anisotropic modification of the function  $f(\varphi)$  in the  $B$ -deformation case and the expression for  $\mathbf{P}_d$  becomes

$$\mathbf{P}_d = e_x \mu N \int_0^{2\pi} \cos \varphi f(\varphi) d\varphi. \quad (2)$$

Here,  $N$  is the concentration of the molecules. We shall assume that an optical wave of frequency  $\omega$  propagates in the medium and then the approximation of individual (independently excited) molecular dipoles, at a frequency  $\omega$ , we find that the amplitude of nonlinear polarization at the doubled (second-harmonic) frequency  $P_j^{(2)}$  is given by

$$P_j^{(2)} = L_{ji}(2\omega) L_{ki}(\omega) L_{lq}(\omega) N \int_0^{2\pi} \gamma_{ikl}(\varphi) f(\varphi) E_i(\omega) E_q(\omega) d\varphi. \quad (3)$$

Here,  $\hat{\gamma}(\varphi)$  is the tensor  $\hat{\gamma}^{(1)}$  (for a molecule with the dipole moment  $\boldsymbol{\mu}$  oriented at an angle  $\varphi$  relative to the  $x$  axis), defined in the laboratory coordinate system  $xyz$ , whereas  $\hat{L}(\omega, 2\omega)$  is the tensor of a local field  $L_{ij} = (\epsilon_{ij} + 2)/3$ , where  $L/L_i(\omega, 2\omega)$  is the unperturbed permittivity tensor of the nematic, diagonal in the  $xyz$  system. The tensors  $\hat{\gamma}(\varphi)$  and  $\hat{\gamma}^{(1)}$  are related in the usual way:

$$\gamma_{ikl} = \hat{A}_{ip}(\varphi) \hat{A}_{kr}(\varphi) \hat{A}_{ls}(\varphi) \gamma_{prs}^{(1)},$$

where  $\hat{A}(\varphi)$  is the operator representing rotation of the coordinate system by an angle  $\varphi$  about the  $z$  axis. It should be pointed out that averaging of Eqs. (2) and (3) using an

isotropic distribution function  $f_0(\varphi) = 1/2\pi$  gives precision values for both quantities, which corresponds to the absence of the spontaneous polarization and dipole SHG in an undeformed nematic. In the case of a deformed nematic, it is natural to approximate  $f(\varphi)$  by the following expression:

$$\begin{aligned} f(\varphi) &= \frac{1}{2\pi} \exp\left(-\frac{U(\varphi)}{kT}\right) \approx \frac{1}{2\pi} \left(1 - \frac{U(\varphi)}{kT}\right) \\ &= \frac{1}{2\pi} \left(1 - \frac{h\mu \cos \varphi}{kT}\right). \end{aligned} \quad (4)$$

We have gone over here to thermodynamic perturbation theory [ $U(\varphi)/kT \ll 1$ ] and the energy of a molecule with a dipole  $\boldsymbol{\mu}$  oriented at an angle  $\varphi$  is represented by the energy of the interaction of this dipole with some effective "molecular field"  $\mathbf{h} \propto [\mathbf{n} \text{ curl } \mathbf{n}]$  directed in this case along the  $x$  axis. Such an interaction results in an orientation of the molecular dipoles along the  $+x$  axis, i.e., it ensures that  $\mathbf{P}_d \neq 0$ . The nature of the field  $\mathbf{h}$  is fairly complex (it is most likely to be of steric nature) and will not be discussed here. Calculating the polarization of Eq. (2) using this model function  $f(\varphi)$ , we obtain

$$\mathbf{P}_d = e_x \frac{\mu N}{2} \frac{\mu h}{kT}. \quad (5)$$

Calculation of the tensor expression for  $\chi_{jiq}^{(2)}$  on the basis of Eq. (3) requires extensive but basically simple calculations and gives the following result:

$$\chi_{jiq}^{(2)} = L_{ji}(2\omega) L_{ki}(\omega) L_{lq}(\omega) \frac{\mu h N}{2kT} v_{ikl}. \quad (6)$$

The tensor  $v_{ikl}$  is determined completely by the molecular hyperpolarizability  $\hat{\gamma}^0$  and its seven nonzero components (of which five are independent) are described by

$$\begin{aligned} v_{xxx} &= \frac{1}{4} (3\gamma_{111}^0 + \gamma_{121}^0 + 2\gamma_{221}^0); & v_{xyy} &= \frac{1}{4} (3\gamma_{122}^0 + \gamma_{111}^0 - 2\gamma_{221}^0); \\ v_{yyx} &= v_{yxx} = \frac{1}{4} (2\gamma_{221}^0 + \gamma_{111}^0 - \gamma_{122}^0); & & \\ v_{zzz} &= \gamma_{133}^0; & v_{zzx} &= v_{zzx} = \gamma_{331}^0. \end{aligned} \quad (7)$$

In the special case (Fig. 2) when the molecule can be represented by an ensemble of independent, arbitrarily oriented relative to  $x'y'z$ , anharmonic linear oscillators,<sup>4</sup> the expression (6) simplifies and the tensor  $\chi_{jiq}^{(2)}$  has just three (out of a total of seven nonzero) components:

$$\begin{aligned} \chi_{jiq}^{(2)} &= L_{ji}(2\omega) L_{ki}(\omega) L_{lq}(\omega) \frac{\mu h N}{4kT} \left\{ \left( \sum_{\alpha} \gamma_{\alpha} \cos^3 \theta_{\alpha} \cos \beta_{\alpha} \right) a_{ikl} \right. \\ &\quad \left. + \left( \sum_{\alpha} \gamma_{\alpha} \sin^2 \theta_{\alpha} \cos \theta_{\alpha} \cos \beta_{\alpha} \right) b_{ikl} \right\}, \end{aligned} \quad (8)$$

where the nonzero components  $a_{ikl}$  and  $b_{ikl}$  are as follows:

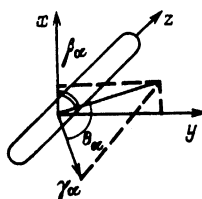


FIG. 2.

$$a_{xxx}=3; \quad a_{yyx}=a_{xyy}=a_{xyx}=1; \quad b_{zzx}=b_{xzx}=b_{xzz}=2.$$

Comparing Eqs. (5) and (6), we readily obtain the traditional relationship between  $\hat{\chi}^{(2)}$  and  $\mathbf{P}_d$ :

$$\chi_{j_iq}^{(2)} = L_{j_i}(2\omega)L_{k_l}(\omega)L_{l_q}(\omega)\frac{P_d}{\mu}v_{ikh}. \quad (9)$$

However, in this case the relationship between  $\chi^{(2)}$  and  $\mathbf{P}_d$  can be expressed explicitly in terms of the properties of the nematic molecules:  $\mu$  and  $\hat{\gamma}^0$ , and also the local Lorentz field tensor. It should be pointed out that a phenomenological linear dependence of  $\hat{\chi}^{(2)}$  on the spontaneous flex polarization frequently creates an incorrect impression that  $\hat{\chi}^{(2)}$  is due to orientation of the molecules (more exactly, the dipole is  $\mu$ ) in a field due to the polarization  $\mathbf{P}_d$ . In fact, such a static field  $\mathcal{E}_0$  does exist in our medium and in the case of a grating-like  $B$  deformation we readily find from  $\text{div}\mathbf{D} = 0$  that

$$\varepsilon_{0\perp}\mathcal{E}_{0x} = -4\pi P_{dx} = -4\pi e_3 q A \cos qz. \quad (10)$$

Here,  $\varepsilon_{0\perp}$  is the component of the permittivity tensor at zero frequency; differentiation is carried out ignoring a small derivative with respect to  $A$ . We shall estimate the quadratic polarizability induced in such a medium by the field in question employing the general relationship (see Ref. 5)

$$\chi_{j_iq}^{(2)}(\vec{\mathcal{E}})$$

$$= L_{j_i}(2\omega)L_{k_l}(\omega)L_{l_q}(\omega)N\left(\langle\beta_{iklm}^{(4)}\rangle_\varphi + \frac{1}{kT}\langle\gamma_{ikh}^{(4)}\mu_m\rangle_\varphi\right)\mathcal{E}_{0m}. \quad (11)$$

Here,  $\beta_{iklm}^{(4)}$  is the cubic hyperpolarizability tensor derived allowing for the antiparallel packing of the molecules along  $z$  and the angular brackets denote averaging over to  $\varphi$  using the function  $f_0(\varphi)$ . The first term in the parentheses is present, since the field  $\vec{\mathcal{E}}_0$  is the true electric field, in contrast to the "molecular field"  $h$  and can create  $\hat{\chi}^{(2)}$  not only by the reorientation of the molecules, but also by the polarization of the molecular orbitals. In our estimates we shall take typical values of  $\beta$ ,  $\gamma$ , and  $\mu$  from Ref. 6:  $\beta \approx 10^{-37}$  cgs esu,  $\gamma \approx 10^{-30}$  cgs esu,  $\mu \approx 10^{-19}$  cgs esu (these are the data for the nematic called 5CB, which is pentyl cyanobiphenyl). It follows from these values that at  $T \approx 300$  K we can ignore the first deformation-induced term in Eq. (11) and then the answer reproduces completely Eq. (6) apart from the replacement of  $h$  with  $\mathcal{E}_0$ . We thus have

$$\hat{\chi}^{(2)}(\vec{\mathcal{E}}_0) = \frac{\mathcal{E}_0}{h}\hat{\chi}^{(2)}.$$

Using Eqs. (5) and (10), we readily obtain the following estimate of the coefficient in the above relationship:

$$\frac{\mathcal{E}_0}{h} = \frac{4\pi\mu^2 N}{2\varepsilon_{0\perp}kT} \approx 10^{-4}.$$

Hence, we can see that  $\hat{\chi}^{(2)}(\vec{\mathcal{E}}_0)$  is negligible compared with  $\hat{\chi}^{(2)}$ .

This corresponds to the fact that  $h$  (estimated from Eq. (5) using the phenomenological expression for  $P_d$  and assuming  $e_3 \approx 10^{-4}$ ,  $A \approx 10^{-2}$ , and  $q \approx 10^4$  typical of the optically induced orientational deformations) amounts to  $h \approx 8$  kV/cm, i.e., it is comparable with the external field needed for SHG,<sup>6</sup> whereas under the same conditions we have

$\mathcal{E}_0 \approx 50$  V/cm, which is clearly insufficient.

It therefore follows that the linear relationship between  $\hat{\chi}^{(2)}$  and  $\mathbf{P}_d$  cannot be regarded as causal. In fact,  $\hat{\chi}^{(2)}$  and  $\mathbf{P}_d$  are two independent consequences of the general cause: an anisotropic modification of  $f(\varphi)$  in a deformed nematic [representing respectively the third and first moments of  $f(\hat{\varphi})$ ].

We can describe SHG processes in a  $B$ -deformed nematic representing conveniently  $P_d$  in Eq. (9) with the aid of the following phenomenological expression:

$$\chi_{j_iq}^{(2)} = L_{j_i}(2\omega)L_{k_l}(\omega)L_{l_q}(\omega)\frac{e_3 A(z)q}{2\mu}v_{ikh} \times \{\exp(iqz) + \exp(-iqz)\}. \quad (12)$$

Therefore, it follows that an alternating-sign grating of the quadratic polarizability with a wave vector  $\mathbf{q}$  is established in the investigated medium. It is clear that variation of  $\mathbf{q}$  can, in principle, ensure phase-matched SHG for any variations of the polarizations of the interacting waves along the direction of their propagation.<sup>7</sup> We shall now consider the phase matching in greater detail.

#### GENERATION OF THE SECOND OPTICAL HARMONIC IN A $B$ -DEFORMED NEMATIC

It is obvious from Eq. (12) that from the point of view of SHG a deformed nematic represents a biaxial medium since the tensor  $\hat{\chi}^{(2)}$  has a preferred axis  $x$  and generally inequivalent axes  $y$  and  $z$ . On the other hand, the linear permittivity tensor is uniaxial (apart from small perturbations caused by the  $B$  deformation) and has a preferred axis  $z$ . Therefore, the properties of the SHG process are not the same in the cases when the planes of incidence are  $xz$  and  $yz$  (because the effective nonlinear susceptibilities are different). However, the geometry of the wave vectors, governed solely by the linear properties of the medium, is the same for both planes and it is shown in Fig. 3.

We shall consider a homeotropic nematic of thickness  $L$  with a  $B$  deformation of the kind described above and assume that it is illuminated at an angle  $\alpha$  in one of the planes mentioned above with light of frequency  $\omega$ , which generally contains both the ordinary ( $o$ ) and extraordinary ( $e$ ) component (Fig. 3). Then, in the interior of the sample two waves are excited,  $\mathbf{E}_{Ne} \exp(i\mathbf{k}_{Ne}\mathbf{r})$ , and  $\mathbf{E}_{No} \exp(i\mathbf{k}_{No}\mathbf{r})$ , and the  $x$  and  $y$  components of their wave vectors are equal to the corresponding components of the wave vector of the incident wave. The boundary conditions on the exit face of the sample ( $z = L$ ) ensure that the SHG process produces a

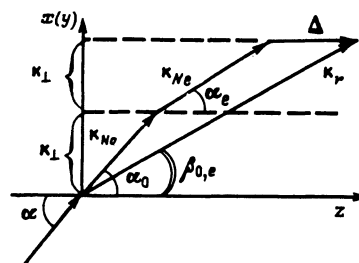


FIG. 3.

wave  $\mathbf{E}_r$ ,  $\exp(i\mathbf{k}_r \cdot \mathbf{r})$ , with the  $x$  and  $y$  components of the wave vector equal to the corresponding components of the wave vector of the nonlinear polarization of the nematic medium, i.e., to the doubled component of the wave vector of the incident wave, which represents the case of collinearity of the second-harmonic wave and the pump wave  $\mathbf{E}_N$  outside the sample (see, for example, Ref. 8). Therefore, the wave vector of the "mismatch"  $\Delta$  has only the  $z$  component and the reduced Helmholtz equation for the wave  $\mathbf{E}_r$  is

$$2ik_{rz} \frac{\partial E_{ri}}{\partial z} = -\frac{2\pi\omega^2}{c^2} \Pi_{ij} \chi_{jij}^{(2)}(z) E_{N1} E_{N2} q \exp(-i\Delta z). \quad (13)$$

Here,  $\Pi_{ij}$  is an operator projecting nonlinear polarization onto a plane perpendicular to  $\mathbf{k}_r$ ; on the right hand side we have  $E_{N1} E_{N2}$  instead of  $E_N^2$  to ensure that Eq. (13) is suitable for the description of the polarization interaction. Using Eq. (12), we find very time-consuming but basically simple transformations reduce Eq. (13) to the following form, which applies to any of the six possible polarizations:

$$\frac{\partial E_r}{\partial z} = ig_n^\beta E_{N1} E_{N2} q A(z) \{ \exp(i\Delta_{n+} z) + \exp(i\Delta_{n-} z) \}. \quad (14)$$

There is no summation over  $n$  in the above equation and the index itself represents the number of the type of interaction in Table I. The index  $\beta$  identifies the plane which is only the plane of incidence ( $\beta = x, y$ ). The quantity  $g_n^\beta$  depends weakly on the angle of incidence  $\alpha$  and its order of magnitude is

$$g \sim 40 \frac{\gamma e_3}{\mu \lambda}.$$

Here,  $\gamma$  is some "typical" value of the component  $\hat{\gamma}^0$  ( $\sim 10^{-30}$  cgs esu is given in Ref. 6) and  $\lambda \sim 10^{-4}$  cm is the wavelength of the incident light (pump radiation), i.e.,  $g \approx 10^{-10}$  cgs esu. Explicit expressions for  $g_n^\beta$  are very cumbersome and they are calculated in the Appendix, where the explicit form of the expression for  $\Delta_{n\pm}$  is also given. Moreover, the values of  $\Delta_{\pm}(\alpha)$  are described by

$$\Delta_{\pm}(\alpha) = \pm q - \Delta(\alpha) = \pm q - (k_+(\alpha) - k_{N1}(\alpha) - k_{N2}(\alpha))_z.$$

Qualitative information on the possibility of realization of one particular type of interaction in one of the planes (absence or vanishing of  $g_n^\beta$ ) is given in Table I. It is interesting to note that the interactions possible in the  $xz$  plane are impossible in the  $yz$  plane and vice versa.

Since we are discussing a very "weak" SHG process ( $10^2$ – $10^4$  photons per pulse in the experiments reported in Refs. 6, 9, and 4), then we can naturally assume that the pump wave is inexhaustible, i.e., that  $E_{N1,2}(z) = \text{const}$ . In this case Eq. (14) has the very simple solution

TABLE I.

№	Type of interaction	Possible realization	
		in $xz$ planes	in $yz$ planes
1	$oo \rightarrow o$	0	1
2	$oo \rightarrow e$	1	0
3	$oe \rightarrow o$	1	0
4	$oe \rightarrow e$	0	1
5	$ee \rightarrow o$	0	1
6	$ee \rightarrow e$	1	0

$$E_r(L) = ig_n^\beta E_{N1} E_{N2} q \int_0^L A(z) \{ \exp(i\Delta_{n+} z) + \exp(i\Delta_{n-} z) \} dz \quad (15)$$

for given values of  $A(z)$  and we shall consider the explicit form of the latter in the next section. Clearly, phase-matched SHG can occur only [this is accurate to within small corrections due to the phases of the slow functions  $A(z)$ ] if  $\Delta_+ = 0$  or  $\Delta_- = 0$ . There are important differences between the various types of interactions. In fact, in the case of the interactions for which the phase matching is impossible ( $oo \rightarrow o$ ,  $oo \rightarrow e$ ,  $oe \rightarrow o$ ,  $ee \rightarrow e$ ) for a spatially homogeneous  $\chi^{(2)}$ , which is true of an SHG process in an external field, the situation is as follows. If  $q < \min\{|\Delta(\alpha)|\}$  or  $q > \max\{|\Delta(\alpha)|\}$ , there is no phase matching for any value of  $\alpha$ . If  $\min\{|\Delta(\alpha)|\} < q < \max\{|\Delta(\alpha)|\}$  there is only one phase-matching peak in the angular dependence of the second harmonic signal [since  $\Delta_+(\alpha) = 0$  or  $\Delta_-(\alpha) = 0$  the second "mismatch" does not vanish because of the alternating-sign nature of  $\Delta(\alpha)$ ].

However, in the case of the interactions which are phase-matched when  $\hat{\chi}^{(2)}(\mathbf{r}) = \text{const}$  (these are the processes  $ee \rightarrow o$ ,  $oe \rightarrow o$  discussed in Ref. 6) we find that  $\Delta(\alpha)$  is monotonic and has a variable sign. Therefore, if  $q > \max\{|\Delta(\alpha)|\}$  there is no phase matching. If  $\min\{|\Delta(\alpha)|\} \leq q \leq \max\{|\Delta(\alpha)|\}$ , the phase matching has just one peak. If  $q < \min\{|\Delta(\alpha)|\}$ , there are two phase-matching peaks in the angular dependence, which are due to vanishing of  $\Delta_+(\alpha)$  and  $\Delta_-(\alpha)$  in turn. Explicit expressions for the calculation of the relevant phase-matching angles are given in the Appendix.

We shall conclude this section by noting that experimental determination of all six nonzero values of  $g_n^\beta$  makes it possible to find, for known values of  $e_3$  and  $\mu$ , the five independent components of the tensor  $\hat{\gamma}^0$  out of a total of fifteen, which provides extensive information on the properties of nematic molecules.

## SECOND HARMONIC GENERATION DUE TO OPTICAL EXCITATION OF AN ORIENTATIONAL $B$ GRATING

At present the only way of inducing the required volume  $B$ -deformation grating is light-induced reorientation of the director under the influence of interfering ordinary ( $o$ ) and extraordinary ( $e$ ) waves (see Refs. 3, 10, 11). Some refinements are necessary at this stage. Up to now we have implicitly assumed that the pump wave  $\mathbf{E}_N$  does not influence the orientation of the director. This implies that the wave  $\mathbf{E}_N$  (usually a nanosecond pulse from a solid-state laser—see for example, Ref. 4) is quite powerful, but the pulse is too short so that its energy is insufficient for reorientation of the director. Therefore, in a typical experimental situation we require an additional wave  $\mathbf{E}_R$  (usually of different frequency  $\omega_R$ ) for reorientation of the director. This may be continuous-wave radiation (for the steady-state excitation of a grating) or a millisecond pulse (for transient excitation—see Ref. 11). It is this last variant that was observed experimentally<sup>4</sup> and it represented the phase-matched  $oo \rightarrow o$  SHG.

We shall now assume that a high-power  $o$ -type wave

$$\mathbf{E}_R \exp(i\mathbf{k}_R \cdot \mathbf{r} - i\omega t)$$

and a weak (possibly frequency-shifted toward the Stokes region)  $e$ -type wave

$$\mathbf{E}_S \exp (i\mathbf{k}_S \mathbf{r} - i\omega t + i\Omega t)$$

propagate in a homeotropic nematic at some angle  $\delta$  relative to the director (Fig. 4), but outside the nematic the two waves are collinear. In this geometry (see Refs. 3 and 10) the required  $B$  deformation in the  $xz$  plane is excited in the nematic medium.

The equations describing the reorientation amplitude and the spatial evolution of  $\mathbf{E}_S$  are of the form<sup>3</sup>

$$\begin{cases} \frac{\partial A}{\partial t} + \frac{A}{\tau_\alpha} = \frac{\varepsilon_{aR} \sin \delta}{8\pi\eta} \mathbf{E}_R \cdot \mathbf{E}_S, \\ \frac{\partial \mathbf{E}_S}{\partial z} = \frac{i\omega_R \varepsilon_{aR} \sin \delta}{4n_s c \cos \delta} A \mathbf{E}_R, \\ A(z, 0) = 0, \quad \mathbf{E}_S(0, t) = s_0 \mathbf{E}_R(0, t). \end{cases} \quad (16)$$

Here,  $\varepsilon_{aR}$  is the permittivity anisotropy at a frequency  $\omega_R$ ;  $\tau_\alpha^{-1} = K_3 q^2 \eta^{-1} + i\Omega$ ;  $\mathbf{K}_3$  and  $\eta$  are, respectively, the Frank elastic constant and the orientational viscosity of the nematic;  $q = q(\delta)$ . It should be noted that in the first two sections we ignored the dependence  $A(t)$ , which is justified from the point of view of SHG, because a pump pulse  $\mathbf{E}_N$  is very short and throughout this pulse the change in  $A(t)$  is insignificant. For example,  $A$  in Eq. (16) is precisely the same as in Eq. (15) and having calculated it, we can obtain the final answer for  $\mathbf{E}_r(L)$ .

It is convenient to do this in three different cases.

a) Waves unshifted along the frequency scale and  $A$  sufficiently small so that in the first equation of the system (16) we can assume that  $\mathbf{E}_s \approx \text{const}$  (Born approximation—see Ref. 10). Then, under steady-state conditions, we have

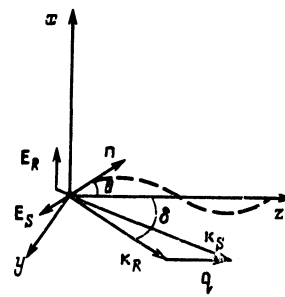


FIG. 4.

$$A = \frac{\varepsilon_{aR} \sin \delta}{8\pi K_3 q^2} s_0 |E_R|^2. \quad (17)$$

It therefore follows that the grating amplitude is constant in space and we can deduce directly from Eq. (15) that the conditions for phase-matched SHG correspond exactly to  $\Delta_{n\pm} = 0$ , and we also have  $|E_r(L)|^2 \propto |E_R|^4$ , i.e., the second harmonic signal is proportional to the square of the power of the wave  $\mathbf{E}_R$ .

b) A wave  $\mathbf{E}_S$  is frequency shifted and it experiences orientational steady-state stimulated scattering in the forward direction (see Ref. 3). In this case if  $\Omega = \Omega_{\text{opt}} = K_3 q^2 \eta^{-1}$ , we quite readily obtain the following expression:

$$A = \frac{\eta s_0}{\sqrt{2} K_3 q^2} |E_R|^2 \exp \left\{ (i+1) \frac{G |E_R|^2}{2} z \right\} \exp(i\pi/4),$$

$$G = \frac{\omega_R \varepsilon_{aR}^2 \sin^2 \delta}{32\pi n_s c \cos \delta K_3 q^2}. \quad (18)$$

Substituting this expression in Eq. (15), we obtain

$$|E_r(L)|^2 = b_m^\beta \sum_{+,-} \frac{\exp(G |E_R|^2 L) - 2 \exp(G |E_R|^2 L/2) \cos(G |E_R|^2 L/2 + \Delta_{m\pm}) L + 1}{(G |E_R|^2/2)^2 + (\Delta_{m\pm} + G |E_R|^2/2)^2}, \quad (19)$$

$$b_m^\beta = 1/2 |g_m^\beta E_{N1} E_{N2} \tau_0 s_0| |E_R|^2.$$

Here,  $\Sigma_{+,-}$  denotes summation of two identical expressions, one of which is characterized by  $\Delta_+$  and the other by  $\Delta_-$ . An interesting feature of Eq. (19) is the fact that it has a maximum as a function of  $\alpha$  (phase matching peak) not at  $\Delta_{m\pm} = 0$ , but at  $\Delta_{m\pm} + G |E_R|^2/2 = 0$ , i.e., the phase-matching angle depends on the wave intensity  $E_R$ . True, this correction is slight compared with  $q$ :

$$q \sim \frac{\Delta n \omega_R}{c} \gtrsim 10^4 \text{ cm}^{-1},$$

whereas in the case of orientational stimulated scattering a characteristic value is  $G |E_R|^2 L \approx 6$ , where  $G |E_R|^2/2 \approx 5 \cdot 10^2 \text{ cm}^{-1}$ , but nevertheless it is fully detectable and can be observed experimentally.

c) The duration of a pulse of the wave  $\mathbf{E}_R$  is much less than  $\tau_0$ . In this case the frequency shift is not so important (see Ref. 11) and the system (16) reduces to

$$\frac{\partial A}{\partial y} = s, \quad s(0, y) = s_0 \frac{\varepsilon_{aR} \sin \delta}{8\pi\eta},$$

$$\frac{\partial s}{\partial z} = i\sigma A, \quad A(z, 0) = 0. \quad (20)$$

Here,

$$s = \frac{\varepsilon_{aR} \sin \delta}{8\pi\eta} \frac{E_S}{E_R}, \quad y = \int_0^t |E_R|^2 dt'$$

is the running value of the exposure to a pulse of  $\mathbf{E}_R$  and

$$\sigma = \frac{\varepsilon_{aR}^2 \sin^2 \delta \omega_R}{32\pi\eta n_s c \cos \delta}.$$

Using the second equation in the system (20) to find  $A$  and substituting it into Eq. (15), we obtain

$$E_r(L) = \frac{g_m^\beta E_{N1} E_{N2}}{\sigma} q \int_0^L \left\{ \frac{\partial s}{\partial z} \exp(i\Delta_{n+} z) + \frac{\partial s^*}{\partial z} \exp(i\Delta_{n-} z) \right\} dz. \quad (21)$$

Since  $s(z)$  is a fairly complex function

$$s \propto I_0(2(i\sigma z)^{1/2}),$$

the integral in Eq. (21) cannot be calculated analytically. All we can do is to assume, by analogy with steady-state stimulated scattering, that the experimentally observed phase matching can be described accurately by the condition  $\Delta_{n_{\pm}} = 0$ . In this specific case, we have,

$$|E_r(L)|^2 = \frac{g_m^{\beta} |E_{N1}|^2 |E_{N2}|^2}{\sigma^2} q^2 |s(L)|^2. \quad (22)$$

The expression (22) is readily checked experimentally: the second harmonic signal should be proportional to the coefficient representing the efficiency of  $\mathbf{E}_R \rightarrow \mathbf{E}_S$  conversion in stimulated scattering. The results<sup>4</sup> confirm satisfactorily the relationship (22) for phase-matched SHG in the  $oo \rightarrow o$  process.

## CONCLUSIONS

We shall now summarize briefly the main qualitative results of the present study.

Firstly, the dipole susceptibility  $\hat{\chi}^{(2)}$  in the orientationally deformed nematics (known as the flex-induced susceptibility  $\hat{\chi}^{(2)}$ ) is not due to the electric field resulting from the flex polarization, but due to the ordering of the polar axes of the molecules associated with such polarization, so that the linear relationship between  $\hat{\chi}^{(2)}$  and  $\mathbf{P}_d$  is purely-formal.

Secondly, a  $B$ -deformed nematic is biaxial from the point of view of SHG, so that a given polarization interaction cannot be realized simultaneously in both  $xz$  and  $yz$  planes (Fig. 1).

Thirdly, when a grating-like  $B$  deformation is induced in a nematic medium, phase-matched SHG is then possible for all six types of the polarization interaction and in the case of "phase-mismatched" processes ( $oo \rightarrow o$ ,  $ee \rightarrow e$ ,  $oe \rightarrow e$ ,  $oo \rightarrow e$ ) there is no more than one phase-matching angle in the dependence  $E_r(\alpha)$ , whereas in the case of the "phase-matched" ( $ee \rightarrow o$ ,  $oe \rightarrow o$ ) processes there can be two peaks of the same dependence.

Finally and fourthly, when a  $B$ -deformation grating is excited under the conditions of an orientational stimulated scattering the phase-matching direction for SHG depends on the intensity of the pump wave involved in stimulated scattering and the phase-matched SHG signal is proportional to the coefficient representing the efficiency of the  $\mathbf{E}_R \rightarrow \mathbf{E}_S$  conversion process. This last property can be converted in terms of multifrequency holography.<sup>12</sup>

## APPENDIX

We shall now give explicit expressions of  $g_n^{\beta}$  if we determine first the quantities which occur in these expressions:  $n_{e1,2}$  are the refractive indices of the extraordinary wave at the frequencies of the first and second harmonics;  $n_{o1,2}$  are the corresponding quantities for the ordinary waves;  $L_{\parallel,\perp}(\omega, 2\omega)$  are the principal values of the local field tensor  $L_{ij} = (\epsilon_{ij} + 2)/3$  at the frequencies of  $\omega$  and  $2\omega$ , respectively;  $\alpha_{o,e}$  is the refractive index for the  $o$  and  $e$  polarizations at the frequency  $\omega$ ;  $\beta_{o,e}$  apply to the  $o$ - and  $e$ -polarized second harmonic signals.

The expressions for  $n_{e1,2}(\alpha_e, \beta_e)$  occurring in the above

equations should be calculated employing the Fresnel equation;

$$\begin{aligned} \alpha_o &= \arcsin\left(\frac{\sin \alpha}{\epsilon_{\perp 1}^{1/2}}\right), \\ \alpha_e &= \arcsin\left[\frac{\sin \alpha}{\epsilon_{\perp 1}^{1/2}} \left(1 + \sin^2 \alpha \frac{\epsilon_{a1}}{\epsilon_{\perp 1} \epsilon_{\parallel 1}}\right)^{-1/2}\right], \\ \beta_o &= \arcsin\left(\frac{\sin \alpha}{\epsilon_{\perp 2}^{1/2}}\right), \\ \beta_e &= \arcsin\left[\frac{\sin \alpha}{\epsilon_{\perp 2}^{1/2}} \left(1 + \sin^2 \alpha \frac{\epsilon_{a2}}{\epsilon_{\perp 2} \epsilon_{\parallel 2}}\right)^{-1/2}\right]. \end{aligned} \quad (A1)$$

The corrections for the  $e$ -polarized waves, which are in parentheses in Eq. (A1), do not exceed 2%. Moreover, the dispersion between the frequencies  $\omega$  and  $2\omega$  is weak. Therefore, in practical calculations of  $g_n^{\beta}$  (but not in calculations of the phase-matching angles!) we can assume that  $\alpha_o = \alpha_e = \beta_o = \beta_e$ . The expressions for  $g_n^{\beta}$  obtained in this way are as follows (the types of interaction are labeled in accordance with Table I):

$$\begin{aligned} g_1^x &= 0; \quad g_1^y = \frac{\pi \omega \epsilon_3 L_{\perp}^2(\omega) L_{\perp}(2\omega)}{16 c \epsilon_{\perp 2}^{1/2} \cos \beta_o \mu} (3\gamma_{111}^0 + \gamma_{121}^0 + 2\gamma_{221}^0); \\ g_2^x &= \frac{\pi \omega \epsilon_3}{16 n_{e2}(\beta_e) c \mu} L_{\perp}^2(\omega) L_{\perp}(2\omega) (3\gamma_{122}^0 + \gamma_{111}^0 - 2\gamma_{221}^0); \\ g_2^y &= 0; \\ g_3^x &= \frac{\pi \omega \epsilon_3 \cos \alpha_e}{8 \epsilon_{\perp 2}^{1/2} \cos \beta_o \mu c} L_{\perp}^2(\omega) L_{\perp}(2\omega) (2\gamma_{221}^0 + \gamma_{111}^0 - \gamma_{122}^0); \\ g_3^y &= 0; \\ g_4^x &= 0; \\ g_4^y &= \frac{\pi \omega \epsilon_3}{2 n_{e2}(\beta_e) c \mu \cos \beta_e} \left\{ \frac{\cos \beta_e \cos \alpha_e}{4} L_{\perp}^2(\omega) L_{\perp}(2\omega) \right. \\ &\quad \times (2\gamma_{221}^0 + \gamma_{111}^0 - \gamma_{122}^0) + \sin \beta_e \sin \alpha_e L_{\parallel}(2\omega) L_{\parallel}(\omega) L_{\perp}(\omega) \gamma_{331}^0 \left. \right\}; \\ g_5^x &= 0; \\ g_5^y &= \frac{\pi \omega \epsilon_3}{4 \epsilon_{\perp 2}^{1/2} c \mu \cos \beta_o} \\ &\quad \times \left\{ \frac{\cos^2 \alpha_e}{4} L_{\perp}^2(\omega) L_{\parallel}(2\omega) (3\gamma_{122}^0 + \gamma_{111}^0 - 2\gamma_{221}^0) \right. \\ &\quad \left. + \sin^2 \alpha_e L_{\perp}(2\omega) L_{\parallel}^2(\omega) \gamma_{133}^0 \right\}; \\ g_6^x &= \frac{\pi \omega \epsilon_3}{4 n_{2e}(\beta_e) c \mu \cos \beta_e} \\ &\quad \times \left\{ \frac{\cos \beta_e \cos^2 \alpha_e}{4} L_{\perp}^2(\omega) L_{\perp}(2\omega) (3\gamma_{111}^0 + \gamma_{121}^0 + 2\gamma_{221}^0) \right. \\ &\quad \left. + \cos \beta_e \sin^2 \alpha_e L_{\parallel}^2(\omega) L_{\perp}(2\omega) \gamma_{133}^0 \right. \\ &\quad \left. + \sin \beta_e \sin 2\alpha_e L_{\parallel}(\omega) L_{\perp}(\omega) L_{\parallel}(2\omega) \gamma_{331}^0 \right\}; \\ g_6^y &= 0. \end{aligned} \quad (A2)$$

It should be pointed out that in practical calculations we can also ignore the  $n_e(\alpha, \beta)$  dependence in the expressions in the system (A2).

We shall conclude by giving the explicit form of the

equation for the phase-matching angle in different geometries:

$\Delta_{m\pm} =$

$$\pm q - \frac{\omega}{c} [2(n_r^2(\alpha) - \sin^2 \alpha)^{1/2} - (n_{N1}^2(\alpha) - \sin^2 \alpha)^{1/2} - (n_{N2}^2(\alpha) - \sin^2 \alpha)^{1/2}] = 0. \quad (\text{A3})$$

Here,  $n_r(\alpha)$ ,  $n_{N1}(\alpha)$  and  $n_{N2}(\alpha)$  should be the refractive indices of the appropriate waves in accordance with the type of interaction labeled by the number  $m$  in Table I. Equation (A3) is quite complex and for most of the interactions it would require a numerical solution.

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