Optically induced deviation from central symmetry; lattices of quadratic nonlinear susceptibility in a nematic liquid crystal

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An increase in the efficiency of second-harmonic generation by a factor of more than 300 has been observed in the nematic liquid crystal 5CB during excitation of a spatially periodic B deformation in it by the light from a free-running ruby laser. Synchronous second-harmonic generation can be achieved for the oo→o interaction by varying the spatial period of the deformation. The effect is attributed to a local elimination of the inversion center, as in the flex effect.

Orientational deformations of the S or B type of nematic liquid crystals locally eliminate the inversion center of the medium.[1] One manifestation of this effect is the appearance of a spontaneous polarization $\mathbf{P}_d = e_1\mathbf{n}(div\ \mathbf{n}) + e_3(\text{curl}\ \mathbf{n}\times\mathbf{n})$: the "flex effect." However, one would naturally expect that the flex effect would also accompany other effects (including nonlinear effects) which are determined by odd moments of the angular distribution of the molecular dipoles. In particular, a dipole quadratic nonlinear susceptibility $\chi^{(2)}_{ikl}$ might appear in a medium, as was first pointed out in Ref. 2. Our purpose in the present study was to directly observe such a dipole susceptibility $\chi^{(2)}$ experimentally in the case of a spatially periodic ("lattice"), optically induced B deformation of the director $\mathbf{n}$.

We consider a homeotropic sample of a nematic liquid crystal with a slight lattice B deformation in the xy plane (Fig. 1): $\theta(z) = A(z)\cos qz$. An intense pump wave E_N is propagating along the unperturbed direction $\mathbf{n}^0 \equiv \mathbf{e}_z$ (in a real experimental situation, this would be a nonosecond pulse from a neodymium laser with a high power but

with an energy too small to cause the director to reverse its orientation, which requires surpassing a threshold). A quadratic susceptibility of a medium due to a B deformation can be described fairly simply in the following model.

The liquid-crystal molecule is a cylinder whose axis runs along the local direction of **n** (see the inset in Fig. 1). This cylinder has a polar side branch which itself has a dipole moment μ, oriented perpendicular to **n**, and a quadratic hyperpolarizability $\beta^{(2)}$ (a one-dimensional anharmonic oscillator in the direction of μ). This model is a very close approximation of the actual structure of many mesogenic molecules. The longitudinal dipole moment $\mu_{\|}$ and also $\beta_{\|}^{(2)}$ will be ignored here, since symmetry considerations rule out a disruption of an antiparallel packing in the z direction. The deviation from central symmetry which is induced corresponds to a modification of the originally isotropic distribution of molecular dipoles with respect to azimuthal angle, $f(\varphi)$. We assume that this distribution has been normalized to the density of molecules N. The spontaneous polarization of the medium and the quadratic nonlinear polarization are then described by

$$P_d^i = \delta_{ix}\mu \langle \cos\varphi f(\varphi)\rangle ; \qquad P_2^i = \delta_{ix} R_w R_w R_{2w} E_N^2 \beta \langle \cos^3\varphi f(\varphi)\rangle . \tag{1}$$

The angle brackets here mean an average over φ, and R_w is the local-field factor at the frequency w (more precisely, in the geometry of Fig. 1 it is the principal value of the local-field tensor $R_{w\perp}$). Expressions (1) make it possible to relate P_2^x to P_d^x, with the help of a phenomenological expression for $\mathbf{P}_d$ and the linear relationship between the first and third moments of the function $f(\varphi)$. These moments can be approximated

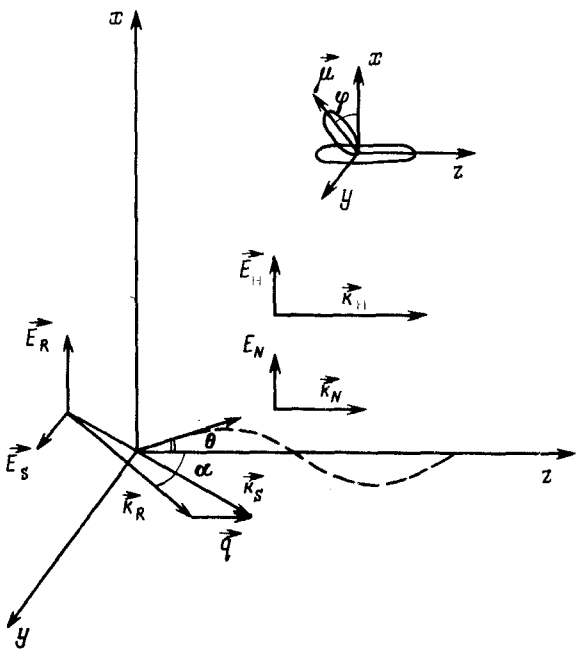

FIG. 1.

by the following expression on the basis of thermodynamic perturbation theory:[3]

$$f(\varphi) \approx \frac{1}{2\pi}\left(1 - \frac{U(\varphi)}{k_B T}\right); \quad U = h\mu\cos\varphi \Rightarrow \langle \cos\varphi f(\varphi)\rangle = 2\langle \cos^3\varphi f(\varphi)\rangle . \tag{2}$$

Here we have introduced an effective "potential energy" U for the interaction of the polar radical with an orienting "molecular field" $\mathbf{h} = h\mathbf{e}_x \sim (\mathbf{n}\times\operatorname{curl}\mathbf{n})$. This field is rather complex (primarily of a steric nature), and we will not discuss it here. For a B deformation we then have

$$P_2^x = \frac{R_{2w}R_w^2 E_N^2 \beta}{2\mu} P_d^x = \frac{R_{2w}R_w^2 E_N^2 \beta e_3}{2\mu}(\operatorname{curl}\mathbf{n}\times\mathbf{n})_x \approx \frac{R_{2w}R_w^2 E_N^2 \beta e_3 A(z) q}{2\mu}\sin qz \tag{3}$$

$$\chi_{xxx}^{(2)} = -\frac{R_w^2 R_{2w}\beta e_3 q A(z)}{2\mu}\sin qz.$$

In differentiating here, we have ignored the derivative of the slow amplitude $A(z)$; $R_{2w} = R_{2w\perp}$ are components of the local-field tensor for the second-harmonic wave $\mathbf{E}_H$. Note that a linear relationship between $\chi_{xxx}^{(2)}$ and $\mathbf{P}_d$ cannot be regarded as causal. The static fields associated with $\mathbf{P}_d$ (~ 150 V/cm according to Ref. 2) are too weak for $\chi^{(2)}$ to be induced through a polarization of molecular orbitals (the fields required are ~ 10 kV/cm; Ref. 3). Consequently, the flexoelectricity and the dipole susceptibility $\chi^{(2)}$ should be regarded as *accompanying* effects which have a common cause: an anisotropy of $f(\varphi)$ induced by a longitudinal curvature of the director. The spatial evolution of wave $\mathbf{E}_H$ is described by the equation

$$\frac{\partial E_H}{\partial z} = bA(z)E_N^2\{\exp(2ik_N + iq - ik_H)z + \exp(2ik_N - iq - ik_H)z\}; \tag{4}$$

$$b = \frac{\pi^2 R_{2w}R_w^2 e_3 q\beta}{4\lambda_N \mu n_{\perp H}} .$$

Here λ_N is the wavelength of E_N in vacuum, and $n_{\perp H}$ is the refractive index of the o-polarized second harmonic. By virtue of the normal dispersion of the medium, we would have $k_H > 2k_N$ in the geometry of Fig. 1, so the second term on the right side of (4) could not contribute a synchronous second harmonic. We will thus omit it. The lattice B deformation which was required was excited through a time-varying stimulated orientational scattering of the o wave $\mathbf{E}_R$ (the pulse from a free-running ruby laser in the experiments) into an e-polarized wave $\mathbf{E}_s$ (Ref. 5). Here $q = q(\alpha)$ is determined by the usual Fresnel equation for n_e and n_0 (Ref. 6). By varying α, we can satisfy the condition $q(\alpha_0) = k_H - 2k_N$. Second-harmonic generation of this type in a medium with a spatially periodic $\chi^{(2)}$ was discussed in Ref. 7.

The time-varying stimulated orientational scattering[4] is described by the following equation for the parameter $s(z,t) = E_s(z,t)/E_L(t)$

$$\frac{\partial s}{\partial z} = i\sigma, \quad \frac{\partial \sigma}{\partial y} = gs, \text{ where } \sigma = \frac{\pi\epsilon_a}{\lambda_R(n_e n_0)^{1/2}}A; \quad g = \frac{\epsilon_a^2 \sin\alpha\epsilon_\perp}{16\pi\epsilon_\parallel \eta (n_0 n_e)^{1/2}\lambda_R}. \tag{5}$$

Here $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ is the anisotropy of the dielectric constant, λ_R is the wavelength of the ruby laser, the refractive indices n_o and $n_e(\alpha)$ correspond to this wavelength, η is the orientation viscosity, and $y = \int_0^t |E_R|^2 dt'$ is the energy exposure of the pulse $\mathbf{E}_R$ up to the time t. In the particular case $\alpha = \alpha_o$ (synchronous second-harmonic generation), a functional dependence of $E_H(z = L)$ on $s(L)$ (L is the thickness of the sample), which can be tested easily in experiments, follows from Eqs. (4) and (5):

$$\frac{\partial E_r}{\partial z} = ibA(z)E_N^2 = iv|\mathbf{E}_N|^2 \frac{\partial s}{\partial z};$$

$$v = \frac{\lambda_R (n_e n_0)^{1/2}}{\pi \epsilon_a} b \Rightarrow |\mathbf{E}_r(L)|^2 = v^2 |\mathbf{E}_N|^4 |s(L)|^2. \tag{6}$$

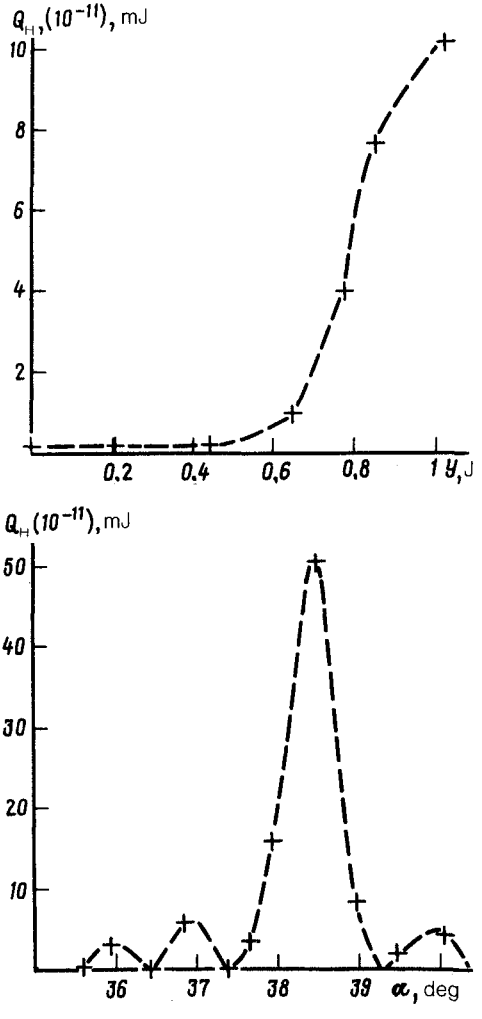

FIG. 2.

In the experiments, we observed an increase in the efficiency of the second-harmonic generation in the presence of a lattice B deformation and a synchronous oo→o second-harmonic generation in a homeotropic sample of 5CB with a thickness of 70 μm in the geometry of Fig. 1. The orientational lattice was induced by an o-polarized pulse from a free-running ruby laser with an energy ~ 0.5 J. The beam diameter in the same was $FWHM_p = 1.5$ mm. The second-harmonic generation was excited by a weakly focused beam from a neodymium laser with an energy ~ 10 mJ and a beam diameter $FWHM_p \approx 0.5$ mm in the sample. The angular divergence of the wave E_N was $\approx 0.3°$. In the course of the experiments we monitored the following: the pulse energies E_N and E_H (the sensitivity of the detection system in terms of the second harmonic was ~ 50 photons per pulse), the temporal envelopes of the $\mathbf{E}_R$ and $\mathbf{E}_s$ pulses, the exposure $y(t)$, and the polarization of the wave $\mathbf{E}_H$ (with the help of a Glan prism).

The experimental results can be summarized qualitatively as follows. The polarization of the second-harmonic signal agrees with that of $\mathbf{E}_N$ (the o wave). For a weak (probably quadrupole) second-harmonic signal in the absence of the wave $\mathbf{E}_R$, we observed a normal quadratic dependence on the energy Q_N and also Meĭkerov oscillations, which are evidence that the second harmonic is of a bulk nature. In the presence of the pulse $\mathbf{E}_R$, the second-harmonic signal increased sharply (by a factor of more than 50) with increasing y at fixed values of $\mathbf{E}_N$ and α [Fig. 2(a)]. To see whether $\chi^{(2)}$ was of a "lattice"nature, we measured the energy of the second harmonic, Q_H, as a function of α at fixed values of Q_N and y [Fig. 2(b)]. When the wave $\mathbf{E}_R$ was incident at an angle $\alpha_B = 38.5°$, which corresponded to $\alpha = \alpha_c = 25.16°$, the energy Q_H increased by a factor of more than 10 (the width of the peak was 1°). This result was evidence of a synchronous second-harmonic generation. The calculated value of α_o is $\alpha_o = 25.40°$, which agrees with the experimental value within the angular divergence of the wave $\mathbf{E}_N$. For comparison with the model outlined above, we measured Q_H as a

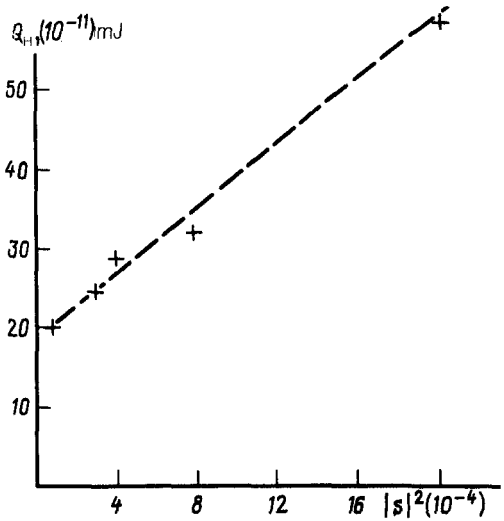

FIG. 3.

function of $|s|^2$ at $\alpha = \alpha_c$. The results in Fig. 3 demonstrate a good linear dependence of Q_H on $|s|^2$. The coefficient here is about 10 times the estimate found from (6). This agreement is completely satisfactory within the error of the estimate. We also note that the absolute values of the coefficient of second-harmonic conversion reached $R = Q_H/Q_N \approx 5 \times 10^{-12}$.

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