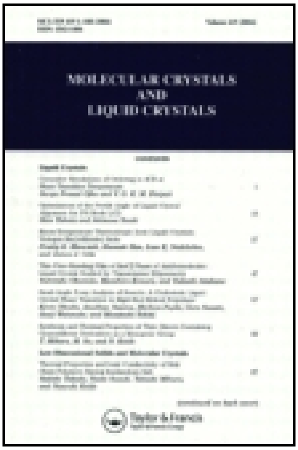

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Optical Second Harmonic Generation in Various Liquid Crystalline Phases†

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The zero-field and field-induced optical second harmonic generation (SHG) was investigated for the nematic and smectic A phases of various liquid crystals. The components of the cubic non-linear susceptibility tensor were measured for substances with different molecular structure. The phase-matched SHG was observed for all the compounds investigated. The directions of the phase synchronisms as well as the corresponding non-linear susceptibilities were determined for the ee-o and oe-o interactions. The zero-field phase-matched SHG was observed for the oe-o interaction. It was accounted for by a multipolar mechanism.

INTRODUCTION

Fifteen years have passed since the first observations of the optical second harmonic generation (SHG) from liquid crystals;[1] however, up to now, there is no final answer to the question concerning the nature of the effect. The problem is of fundamental importance because it is closely related to the symmetry properties of liquid crystals.

The first successful observations of SHG from cholesteryl carbonate were explained in terms of a lack of the inversion center in small liquid crystalline "swarms".[1] Later,[2,3] without any success, there has been carried out extensive search for the SHG in nematic, cholesteric and smectic (non-ferroelectric) liquid crystals, and the previous result was accounted for by the presence of solid crystals in the cholesteric phase.

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The second turn of the discussion around the nature of a SHG in nematic liquid crystals arised when the SHG was observed in oriented layers of 4-methoxybenzylidene-4′-butylaniline (MBBA).[4] The phenomenon has been explained by the lack of the symmetry center in the nematic phase. The zero-field SHG in MBBA was also investigated[5] but the nature of the effect was connected with the flexoelectric polarization of surface layers. Such a polarization has to remove the inversion center in surface liquid crystalline layers and to allow the SHG to be detectable. Another explanation of the zero-field SHG in terms of the electric quadrupolar interaction was suggested in.[6]

Recently there was also considerable activity in the investigations of the SHG in nematic and cholesteric phases induced by an external electric field.[7,8] Such experiments allow the high order molecular hyperpolarizabilities to be calculated.[9-11] The SHG was also observed in a ferroelectric (chiral smectic C*) liquid crystal.[12]

The aim of this paper is to investigate the optical SHG, both the zero-field and field induced in liquid crystals differing by their structure and molecular parameters (for example, by the value and direction of their permanent dipole moment).

In experiments with the field-induced SHG we always tried to obtain the phase-matched generation, having in mind to study the zero-field SHG in the same synchronism directions when the external field is switched off. The search for zero-field SHG in the phase-matched conditions increases markedly the sensitivity of an experimental set-up and allows the pump beam intensity to be lowered. The study of the field-induced SHG was also used for the calculation of the number of parameters of the liquid crystalline medium (a cubic non-linear susceptibility Γ_{ijkl}, a quadratic hyperpolarizability β_{ijk}[9-11] and the discussion of their connection with molecular structure. In contrast to isotropic liquids, the value of Γ_{ijkl} depends not only on molecular parameters but on the orientational order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ of liquid crystal as well. The latter opens the possibility to measure $\langle P_2\rangle$ and $\langle P_4\rangle$.

EXPERIMENTAL TECHNIQUE

Four liquid crystalline compounds were studied: 4-*n*-pentyl-4′-cyanobiphenyl (5CB), 4-*n*-octyl-4′-cyanobiphenyl (8CB), 4-*n*-hexyloxy-4′-*n*-pentyl-α-cyanostilbene (HOPCS) and MBBA. All the compounds have the nematic phase in convenient temperature range, and, in addition, 8CB has the smectic A phase. Both 5CB and 8CB have positive dielectric anisotropy ($\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp \approx +10$) while HOPCS and MBBA have the negative ε_a values ($\varepsilon_a = -5$ and -0.5, respectively). The difference in signs of ε_a is due to the different orientation of the dipolar cyano-group in the two cases, parallel with the long molecular axes for 5CB and 8CB and nearly perpendicular to them for HOPCS and MBBA.

The sketch of the experimental set-up is shown in Figure 1. A Q-switched Nd-YAG laser, operating at 1.06 μm and a pulse repetition 2–12.5 Hz was used to provide the fundamental (pump) beam. The peak power was 200–300 kW. The beam was focused with a 43 cm lens so that the power density on the sample placed in a thermostate was about 100–200 MW$\cdot$cm.$^{-2}$ For investigation the field-induced SHG, short pulses (t_p = 20 μs) of high voltage (U_p = 4kV) were provided by an electrical generator. The pulse duration was chosen from the condition $\tau < t_p < T$, where τ is the relaxation time for dipolar (Debye) polarization, and T is the director reorientation time. Under such a condition, molecular dipoles are oriented by the field but the Fredericks transition does not take place. The sensitivity of our set-up was about 30 photons of the optical second harmonic per single laser pulse. The cell temperature was stabilized with an accuracy of 0.1° K.

In experiments, there were measured the intensities of the second harmonic $I_{2\omega}^{\parallel,\perp}$ and the coherence length of $l_{\parallel,\perp}$ in the liquid crystalline phases and the corresponding parameters $I_{2\omega}^{ISO}$, l_{iso} for the isotropic phase. From these

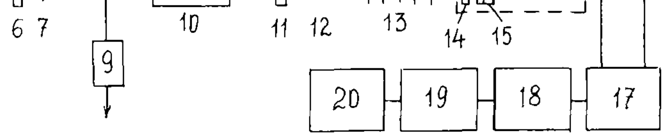

FIGURE 1 Experimental set-up: 1. Q-switch Nd-YAG laser; 2. laser controlling unit; 3. device for synchronization laser pulses with voltage pulses driving a liquid crystal cell; 4. high voltage pulse generator; 5. strobe-pulse generator (pulse duration 0.7 μs); 6. optical filter for fundamental beam; 7. long-focus lens; 8. beam splitter; 9. photocell for measuring the power of the fundamental beam; 10. thermostate with a liquid crystal cell; 11., 14 optical attenuators for fundamental beam; 12. analyzer; 13. neutral filters; 15. interference filter for the optical second harmonic (532 nm); 16. photomultiplier; 17. analog switch with a preamplifier; 18. amplifier and oscilloscope; 19. integrator; 20. digital voltmeter.

values the cubic susceptibilities $\Gamma_{\|,\perp}$ and Γ_{iso} were calculated. The coherence lengths and second harmonic intensities in maxima of Maker's oscillations were measured using wedge-form cells, Figure 2a. For the z-axis being oriented along the director of a liquid crystal, and the subscripts $\|$ and $\perp$ referring to the z-direction we have $\Gamma_{\|} \equiv \Gamma_{zzzz}$ and $\Gamma_{\perp} \equiv \Gamma_{xxxx}$. The values $l_{\|}$, $I^{\|}_{2\omega}$ and $\Gamma_{\|}$ were determined from experiments with homogeneously oriented layers when the directions of the dc field, and the optical fields of the first and second harmonics were all parallel with the director. The value $l_{\perp}$, $I^{\perp}_{2\omega}$ and $\Gamma_{\perp}$ were measured using homeotropically oriented layers when the directions of all the fields were collinear and perpendicular to the director.

To obtain the homogeneous orientation of a liquid crystal glass plates were covered by a film of polyvinyl alcohol and rubbed with cotton or other tissue. For the homeotropic orientation a film of chromium stearylchloride was used. The quality of orientation was periodically checked using a polarization microscope. The inner angle of wedge-form cells was measured by means of a goniometer. The accuracy of measurements of the coherence length and second harmonic intensities was 3% and 10%, respectively. The absolute values of susceptibilities Γ were calculated using the d_{11}-component of crystalline quartz as a reference ($d_{11} = 8 \cdot 10^{-10}$ CGSU).

The rectangular prisms, Figure 2b, were used for the investigation of SHG under the phase-matched conditions. One of the acute angles of the prisms was chosen to be equal to either 30° or 45° respectively for homeotropically and homogeneously oriented layers. The synchroneous angles Θ_s were measured and the corresponding (synchroneous) non-linear susceptibilities Γ_s and χ_s were calculated.

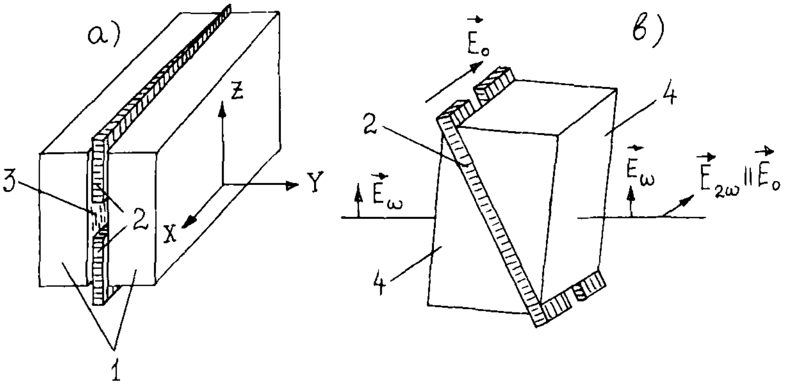

FIGURE 2 Cells for measuring coherence lengths $l_{\|,\perp}$ and non-linear susceptibilities (a): cells for observation of phase-matching (b): 1. glass plates; 2. electrodes; 3. liquid crystal; 4. glass rectangular prisms; y-axis coincides with beam direction.

It should be noted that 5CB was chosen from the methodical point of view as a reference because it has been investigated previously. Our results on 5CB agree well with those from Ref. 7.

RESULTS AND DISCUSSION

A. Field-induced SHG

The measured values of coherence lengths $l_{\parallel}$, $l_{\perp}$, l_{iso} and the corresponding cubic non-linear susceptibilities $\Gamma_{\parallel}$, $\Gamma_{\perp}$, Γ_{iso} for all the compounds investigated are shown in Table. The effective cubic polarizabilities $\gamma_{\parallel}^{*}$, $\gamma_{\perp}^{*}$, γ_{s}^{*} and γ_{iso} were calculated using the isotropic (Vuks)[13] form for the local electric field. The value of β_{μ} (the projection of the vectorial part of the quadratic hyperpolarizability β_{ijk} on the direction of the molecular dipole moment $\vec{\mu}$) was calculated from the formula[14]

$$\gamma_{iso} = \frac{1}{5}\gamma_{iijj} + \frac{1}{5\mathrm{kT}} g\mu_i\beta_{ijj} = \frac{1}{5}\gamma_{iijj} + \frac{1}{5\mathrm{kT}}\mu^{*}\beta_{\mu}, \tag{1}$$

where $\mu^{*} = g\mu$ is an effective molecular dipole moment, g is the Kirkwood factor.

Let us discuss data from Table I and begin with the isotropic phase. It is seen that the quadratic hyperpolarizabilities are almost equal for all the substances despite the pronounced difference in molecular structure. By the way, the values are approximately two times more than that for nitrobenzene. Probably, the main contribution to the β_{μ} value results from the benzene rings of molecules containing conjugated chains of π-bonds. The value of the cubic polarizability γ_{iso} depends linearly on the permanent dipole moment of molecules (the molecular dipole moments of 5CB, 8CB and HOPCS are nearly equal and markedly higher than that for MBBA). The latter result is consistent with increasing degree of the field orientation of the molecules which is proportional to the product μE.

The situation is more complicated for liquid crystalline phases. Nonlinear parameters for different liquid crystals vary to a larger extent. For all the substances investigated $\Gamma_{\parallel}$-values are higher than $\Gamma_{\perp}$. It is quite natural since, on measuring $\Gamma_{\parallel}$, the electric field of the fundamental beam, thanks to the nematic order, effectively interacts with the longitudinal component of a quadratic molecular polarizability which is larger than the transverse component for all the compounds studied. When measuring $\Gamma_{\perp}$, on the contrary, the transverse (small) components of the polarizability are responsible for SHG. Thus, even for equal degree of the field-induced molecular

TABLE I

	Liquid crystalline phase				
	Nematic phase				Smectic A phase
Parameters	HOPCS (23°C)	MBBA (23°C)	5CB (23°C)	8CB (33°C)	8CB (23°C)
$l_\parallel$, μm	3.4	3.3	4.8	5.85	5.4
$l_\perp$, μm	8.95	8.65	9.88	11.65	12.2
θ_c(ee-o), degree	27.7	26.7	26.1	—	24.5
θ_c(oe-o), degree	38.9	38.0	34.5	—	33.0
$\Gamma_\parallel \cdot 10^{14}$, ESU	118	109	260	205	196
$\Gamma_\parallel \cdot 10^{14}$, ESU	42	22	41	31	21
$r_s \cdot 10^{14}$, ESU	24	12	23	—	21
$\chi_s \cdot 10^{12}$, ESU	1.6	1.5	0.7	—	0.95
$\gamma_\parallel^* \cdot 10^{36}$, ESU	119	83	158	156	149
$\gamma_\perp^* \cdot 10^{36}$, ESU	42.5	16.7	25	23.5	16
$\gamma_c^* \cdot 10^{36}$, ESU	24.3	9.1	14	—	16
$\Gamma_\parallel/\Gamma_\perp$	2.8	4.95	6.35	6.6	9.3
		Isotropic phase			
l_{iso}, μm		5.9	5.6	7.4	8.6
$\Gamma_{iso} \cdot 10^{14}$, ESU		69	49	106	83
$\gamma_{iso} \cdot 10^{36}$, ESU		70	37.2	64.5	63
$\beta_\mu \cdot 10^{31}$, ESU		42	39	40.5	39.5

orientation along and across the director, the effective quadratic susceptibility parallel to the director is higher than that for the perpendicular direction.

Moreover, it is evident, that for equal quadratic polarizabilities a higher value of $\Gamma_\parallel$ should correspond to the molecules with bigger dipole moments as, in this case, the degree of the field orientation (the field polarization of the medium) is higher. In addition, the orientation of the dipole relative to the molecular axis is of importance. So, the cubic susceptibility $\Gamma_\parallel$ for both 5CB and 8CB (dipole moment $\mu \approx 5$D is parallel to the long molecular axis) is markedly higher than that for HOPCS and MBBA (dipole moments $\mu \approx 4$ and 2D, respectively, are directed at an angle $\theta \approx 60°$ to the long axis). The susceptibility $\Gamma_\perp$ is maximum for HOPCS whose molecules have maximum transverse component of the dipole moment. Relatively high values $\Gamma_\perp$ for 5CB and 8CB may be accounted for by an essential contribution from big longitudinal dipole moments due to the non-ideality of the nematic order, $S < 1$. It is seen from Table I that the anisotropy of the cubic susceptibility $\Gamma_\parallel/\Gamma_\perp$ increases when one follows from liquid crystals with negative dielectric anisotropy to those with positive one. Thus the values and the directions of dipolar groups play a crucial role in the magnitude of components of the cubic susceptibility tensor.

To study the SHG peculiarities for the smectic A phase, there was investigated the temperature behavior of the coherence lengths $L_\parallel$ and $L_\perp$ in 8CB (Figure 3), as well as the intensities of the second harmonic $I^\parallel_{2\omega}$ and $I^\perp_{2\omega}$. There exist simple relationships between the coherence lengths in the nematic ($l_\parallel, l_\perp$) and isotropic (l_{iso}) phases[7]

$$\frac{1}{l_\parallel} - \frac{1}{l_{iso}} = K\langle P_2\rangle; \qquad \frac{1}{l_{iso}} - \frac{1}{l_\perp} = \frac{K}{2}\langle P_2\rangle, \tag{2}$$

where $\langle P_2\rangle$ is an orientational order parameter. We can calculate the order parameter as a function of temperature using experimental data on $l_{\parallel,\perp}$. The coefficient K was determined from the condition $\langle P_2\rangle = 0.64$ at $t - t_{iso} = -17$ °K.[15] The calculated curve is given in Figure 4, where, for comparison, the temperature dependence $\langle P_2\rangle$ from the refractive index measurements[13] is also shown. Both results qualitatively agree.

The temperature behavior of non-linear susceptibilities $\Gamma_\parallel$, $\Gamma_\perp$ normalized to the value Γ_{iso} is illustrated in Figure 5. The values $\Gamma_\parallel$ and $\Gamma_\perp$ depend upon molecular parameters and the order parameter of a mesophase.[7] If the order parameter is described only by the value $\langle P_2\rangle$ then, neglecting the temperature dependence of density, we have

$$R_\parallel = \frac{\Gamma_\parallel}{\Gamma_{iso}} = \frac{F_\parallel}{F_{iso}}\left(\frac{T_{iso}}{T} + \frac{2}{7}\frac{\alpha}{\gamma_{iso}}\langle P_2\rangle\right) \tag{3}$$

$$R_\perp = \frac{\Gamma_\perp}{\Gamma_{iso}} = \frac{F_\perp}{F_{iso}}\left(\frac{T_{iso}}{T} - \frac{1}{7}\frac{\alpha}{\gamma_{iso}}\langle P_2\rangle\right) \tag{4}$$

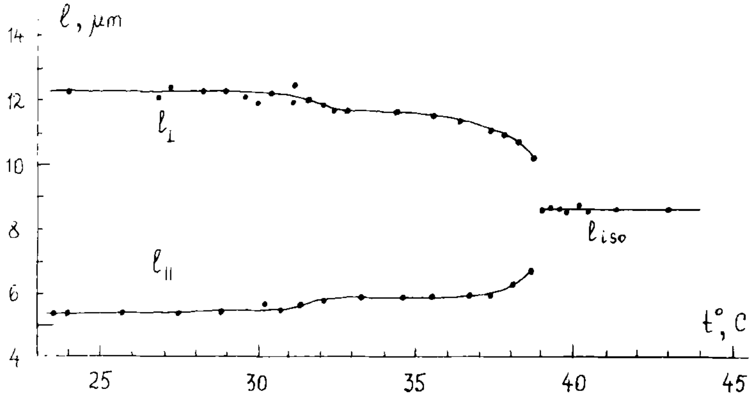

FIGURE 3 Coherence lengths of 8CB as functions of temperature.

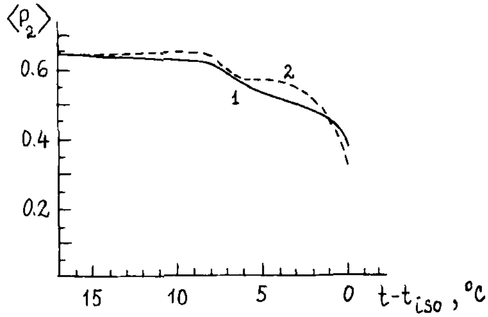

FIGURE 4 Temperature behavior of the order parameter for 8CB. 1. results of the paper;[13] 2. values calculated from formula.[1]

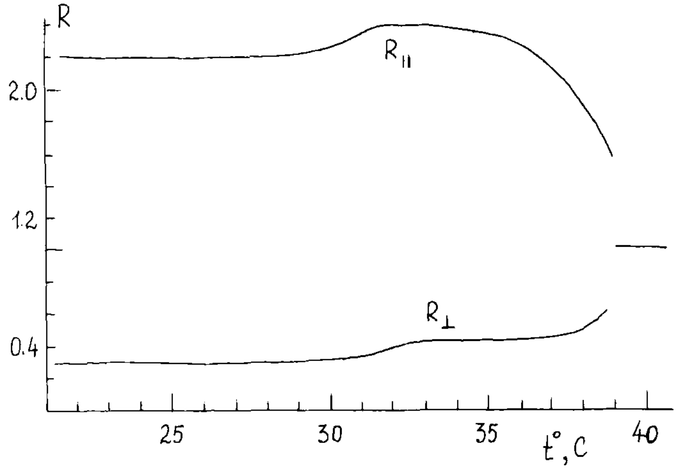

FIGURE 5 Temperature behavior of cubic non-linear susceptibilities for 8CB. Absolute value $\Gamma_{iso} = 8.3 \cdot 10^{-13}$ CGSU.

Here, $F_{\parallel}$, $F_{\perp}$ and F_{iso} are local field factors, α is a molecular parameter including the dipole moment, second order and third order hyperpolarizabilities. Under condition $F_{\parallel} = F_{\perp} = F_{iso}$ the formula[3] does not agree with the experiment for 8CB. Indeed, it follows that $\Gamma_{\parallel}$ should increase at the transition from the nematic to smectic A phase according to the increase in $\langle P_2 \rangle$.[3] However, in the experiment, $\Gamma_{\parallel}$ markedly decreases. The similar temperature behavior was earlier observed for dielectric permittivity $\varepsilon_{\parallel}$ of 8CB.[16] In the latter case the decrease in $\varepsilon_{\parallel}$ is due to the antiparallel correlation of molecular dipoles in the smectic A phase,[17] which results in a decrease in the effective dipole moment μ.* Thus, the decrease in $\Gamma^{\parallel}$ may be ascribed to the decreasing parameter α including μ^* and the hyperpolarizability β_{ijk}. It is also possible that the dipolar correlation influences the β_{ijk}-value, too. Indeed, it is difficult to ascribe quantitatively all the changes in $\Gamma_{\parallel}$ only to the decrease in μ^* calculated from the temperature dependence of $\varepsilon_{\parallel}$.

For all the substances investigated we managed to observe the phase-matched SHG of the ee-o and oe-o types. The corresponding directions, characterized by an angle Θ_s between the liquid crystal director and the wave vector of the fundamental beam, are also shown in the table. The values for the non-linear (synchroneous) susceptibility Γ_s for the ee-o interaction is presented, too. The curve of the phase synchronism for the smectic A phase of 8CB is shown in Figure 6.

B. Zero-field SHG

Figure 7 shows the intensities for the phase-matched SHG in MBBA measured for both ee-o and oe-o types of the synchronism. It shows that the ee-o synchronism is observed only for the field-induced SHG, while the oe-o type is observed in both the field-induced and zero-field cases. It

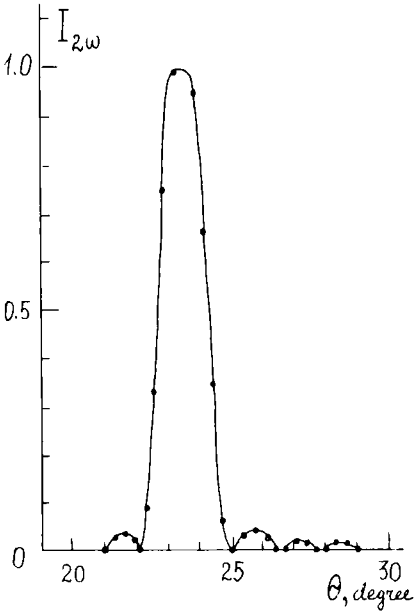

FIGURE 6 The intensity of the second harmonic $I_{2\omega}$ as a function of the angle Θ between the director and wave vector of the fundamental beam for 8CB (t = 23°C).

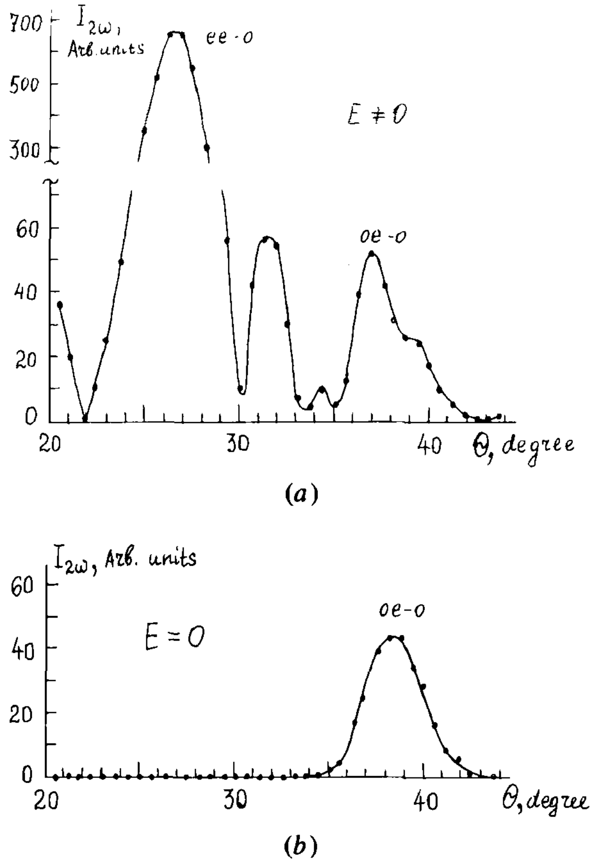

FIGURE 7 The intensity of the second harmonic on angle Θ for homeotropically oriented MBBA: (a) the induced field is switched on (E = 14 kV · cm^{-1}); (b) zero-field SHG. Cell thickness 50 μm, t = 23.5°C.

should be noted that SHG is detectable for both homogeneously and homeotropically oriented layers. To decide whether the zero-field SHG has volume or surface nature the $I_{2\omega}$ for the oe-o synchronism was measured as a function of layer thickness (L) using a wedge-form cell and scanning a laser beam along cell. At small thicknesses, the SHG intensity $I_{2\omega}$ is proportional to L^2 (Figure 8). Such a dependence is observed up to the values $L \approx 50$ μm, and then the slope of the curve decreases. For the sake of comparison, in the same Figure curve $I_{2\omega}(L)$ is also shown for the field-induced SHG of the ee-o type. In the latter case, the dependence $I_{2\omega} \sim L^2$ is observed up to thicknesses ~100 μm. This difference in critical

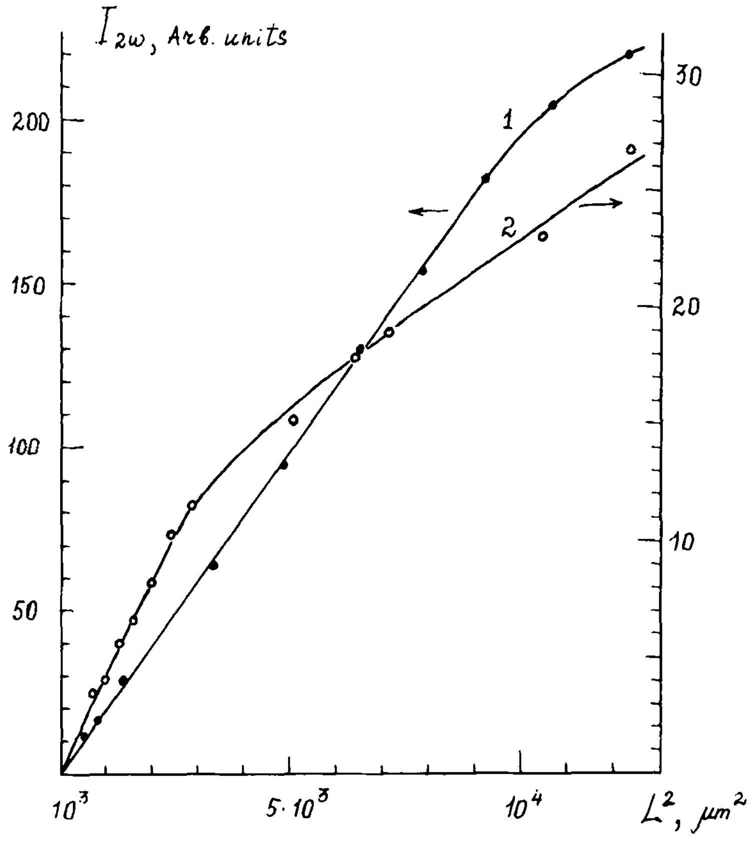

FIGURE 8 The second harmonic intensity as a function of the thickness for a homeotropically oriented layer of MBBA. 1. field-induced SHG for ee-o interaction, 2. zero-field SHG for oe-o interaction.

thicknesses appears to be due to a different character of light scattering for the two wave interaction types. Both the thickness dependence and the coincidence of observed and calculated angles for the phase-matched SHG allow us to conclude that the zero-field as well as the field-induced SHG are of volume nature and cannot be referred to the surface phenomena.

The zero-field oe-o type SHG, in our opinion, may be accounted for by a multipolar (the quadrupolar) mechanism known for the solid crystals.[18] The effective second-order susceptibilities χ_s calculated from the experimental data on the oe-o synchronism are shown in the Table. Their order of magnitude is typical of the quadrupolar SHG mechanism. So, the phenomenon of the zero-field second harmonic generation in nematic and smectic A liquid crystals can be understood from the traditional point of view on these substances as center-symmetrical media. Such an interpretation is completely consistent with the theoretical approach developed in Ref. 19.

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