Absence of a center of inversion in nematic liquid crystals: manifestation in second optical harmonic generation experiments

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Experiments on second optical harmonic generation in a nematic liquid crystal are described. The experimental data are carefully compared with the results of a calculation of the generation parameters of the second harmonic.

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1. INTRODUCTION

Recently there has been an intensive discussion of the symmetry of nematic liquid crystals (NLC) in the literature (see, for example, Refs. 1–3). Apparently, it can already be said that NLC molecules are closer in shape to a plane strip than to a rod, which suggests that they are optically biaxial (cf. Refs. 4–7). But this optical biaxiality of the molecules, being in fact fluctuational (cf. Ref. 8), may not manifest itself on a macroscopic scale the sample as a whole.

A more important question, of far-reaching consequence for the physics of liquid crystals (LC), is the question of the presence or absence of a center of symmetry in NLC. Liquid-crystal molecules themselves are, by their chemical structure, closer to being asymmetric (cf. Ref. 9), but they are in a state of continuous motion (rotation about their local axes), and the time-averaged orientation-probability density for the molecules may be centrosymmetric. In fact, the question is precisely whether this probability density, which should also be averaged over space (over the cross section of the probing beam in a specific optical experiment), possesses no center of inversion.

The question may be asked: To what experimental consequences should the absence of centrosymmetry in NLC lead? A number of experimental investigations have already been performed which can be interpreted from these positions. Here we should like to single out three points: first, the structural changes that occur in NCL in this case, in particular, the appearance of a spiral texture of the cholesteric type[10–15]; second, the direct observation of ferroelectricity (cf. Refs. 16 and 17); and, third, the observation of effects that are possible only in noncentrosymmetric media; optical activity and the linear electrooptical effect,[18–20] second-harmonic generation (SHG),[21] etc.[22]

But in the case of such a delicately equilibrated molecular structure as that possessed by LC, it is not always easy to given an unequivocal interpretation of the observed effects on the basis of only the symmetry of the molecules. In particular, the cited investigations do not admit of an unequivocal interpretation (these investigations are discussed in detail in our review paper[23]). Therefore, the question of the symmetry of NLC has thus far not been entirely elucidated, and the investigation of the symmetry of LC by the methods of nonlinear optics has assumed great importance. In particular, the investigation of the possibility of SHG in them, which, in the dipole approximation, is realizable only in noncentrosymmetric media, is in many cases is the most convenient method of finding out the symmetry of a medium.[24]

In the present paper we present new experimental data on SHG in the NLC N-p-methoxybdnzylidene-p-butylailine (MBBA). In our opinion, these data conclusively and unambiguously indicate the absence of a center of inversion in the oriented samples used.[21] The choice of such a well-known and relatively simple NLC was dictated by the wish to carry out to the end a comparison of the obtained experimental data with the calculated SHG parameters, although from the point of view of molecular structure MBBA is not very effective for SHG.

2. EXPERIMENT

SHG was experimentally observed in chemically pure samples of the nematic phase of MBBA, whose molecules were planarly oriented by rubbing the glass substrates with a diamond paste. The samples were tens of microns thick, and were prepared just before the experiment. The transition into the isotropic phase occurred roughly at 43 °C. As the pump, we used single-mode linearly-polarized radiation from a Q-switched LTIPCh-7 YAlG:Nd^{3+} laser ($\lambda = 1.06$ μm) with ~100-kW pulse peak power (the pulse duration was ~12 nsec) operating in a repeated regime (12.5 Hz). The laser radiation was focused onto the LC sample by a lens (f=8 cm). Two types of experiments were performed. In the first case the incident pumping radiation was perpendicular to the planes of the glass substrates (normal incidence), which could be rotated about the direction of the incident beam for the purpose of realizing different types of interaction during the SHG. In the second case oblique incidence was realized (the MBBA sample was rotated about axes perpendicular to the incident beam). In the latter case two hemispherical glass substrates were used. To separate the various types of interaction during the SHG (collinear geometry of the experiment), we used polarizing Nicol prisms (these prisms were also used to monitor the orientation of the LC samples).

The registration system consisted of two parts: a main and a backup channel. The optical radiation in each channel was registered by an (FEU-79) photomultiplier, whose electrical signal for each laser pulse was led out with the aid of an amplitude-conversion unit to a frequency meter (ChZ-38), and was recorded in a digital form. The results were averaged over 100 laser pulses. Gating was carried out in order to reduce the contribution of the background radiation to the registered power. Radiation from a quartz plate was recorded in the backup channel during the SHG. Light filters were used to separate out the SHG signal ($\lambda = 0.53\ \mu$m). Furthermore, the radiation in the main channel passed through a MDR-2 monochromator; lenses that collected all the power emerging from the sample during the SHG were used to effect matching with the monochromator.

The calibration of the recording system was carried out, using the second harmonic generated in a second standard quartz plate located in the main channel in place of the NCL cell. The signal power was determined during the SHG in the MBBA with the contribution of the background radiation (measured in the isotropic MBBA phase and in the empty cell) subtracted; as a rule, the background radiation was significantly weaker than the registered signal from the nematic phase.

The spectral width of the recorded radiation from the NLC cell corresponded to its typical values for signals recorded during the SHG in ordinary crystals: the signal power depended quadratically on the pump power, and the signal intensity depended significantly on the degree of orientation of the nematic MBBA phase in the cell, the time of preparation of the cell, and the duration of the irradiation. The power of the generated second harmonic decreased sharply when non-oriented samples were used, or when the generation occurred in cells used over a period of several days (especially in the case of the *oe-o* interaction). We also did observe SHG in the solid MBBA phase, but we did not carry out detailed measurements. We specifically checked the possibility of the appearance of a signal at the second-harmonic frequency upon the breakdown of the LC sample as a result of luminescence, etc.

3. RESULTS

1. SHG in the case of nonsynchronous interaction. Normal incidence

We carried out numerous series of nonsynchronous-SHG measurements (about 30) on planarly oriented nematic-MBBA layers of thickness 10 μm in the case of normal incidence of the pump radiation. Each series consisted of experiments in all the six geometries (see below). The different series corresponded to experiments on different samples, prepared just before the beginning of the measurements in a series; the LC material was taken each time from a hermetically sealed vial. Whenever we went over to a new series of measurements, we changed the order in which the SHG experiments were performed in the various geometries. Such a measurement procedure was made necessary by the fact that the generated-second-harmonic-signal power varied in time; the level and stability of the recorded signal depended on both the natural aging of the MBBA and the effect of the laser field. Detailed investigations of both of these factors are reported in Refs. 23 and 25, where the quantitative picture of SHG in NLC is made more precise.

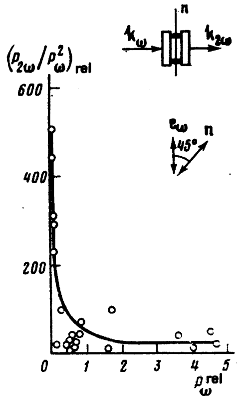

FIG. 1. Dependence of the power of the generated second-harmonic signal on the pump power in relative units. The cell with MBBA is shown at the top; the directions of the vector e_ω and n in the plane perpendicular to the vectors k_ω and $k_{2\omega}$ are shown directly on the graph.

The generated-second-harmonic-signal level was essentially determined by the pump-power value P_ω. In this case, for each geometry of the experiment on the various MBBA cells, a stable and reproducible SHG was observed only in sufficiently strong fields, i.e., in fields exceeding some threshold value $P_{\rm thr}$. For $P > P_{\rm thr}$ the second-harmonic power $P_{2\omega}$ was proportional to P_ω^2, as it should be for SHG.

Figure 1 shows the P_ω dependence of $P_{2\omega}$ obtained for one of the geometries of the experiment in the absence of the exit polarizer. The data presented in Fig. 1 are in relative units, and the $P_{2\omega}$ values are normalized to the same pump-power value with allowance for the dependence $P_{2\omega} \sim P_\omega^2$, therefore, the region of the plateau corresponds to the fulfillment of this dependence in the experiment. Notice that for this region the quantity $P_{2\omega}$ changed from one laser pulse to another (in a different manner for different geometries) immediately after the beginning of the irradiation of the oriented MBBA layer; these changes were especially irregular when a polarizer was located after the cell with the LC. But after some time—on the average, after roughly several minutes of irradiation (hundreds of laser pulses)—the $P_{2\omega}$ values stabilized. It is these relatively stable data that we recorded.

The value of $P_{\rm thr}$ can be estimated from the P_ω values at which the cited $P_{2\omega}$ dependence approaches a limiting value. For the dependence shown in Fig. 1, $P_{\rm thr}$ is estimated to be of the order of tens of kilowatts. A similar behavior has been obtained for the two other experimental geometries in which the polarization vector of the pump is parallel and perpendicular to the director. But in these cases the value of $P_{\rm thr}$ was roughly an order of magnitude higher.

Such a behavior should not be unexpected for NLC. The procedure for preparing the oriented LC samples is essentially equivalent to the growing of crystals in traditional—for nonlinear optics—media during the

SHG. In this last case the quality of the samples obtained and, hence, the SHG efficiency, can vary greatly from sample to sample. This should, to an even greater degree, be characteristic of such statistically inhomogeneous media as the LC, whose oriented layers are still very sensitive to external influences. This makes it difficult to obtain unambiguous information about SHG in NLC, and impairs the reproducibility of the data. But in principle all these effects can be controlled, and we can give a unique account of the experimental data.

The most important condition for SHG in NLC is that the samples should have a single-domain character, which, on the one hand, depends on the preparation process itself and, on the other, is determined by the effect of the external field (in particular, the laser field) on the prepared oriented NLC layers. In the latter case, when self-action occurs, it is necessary, as our measurements showed, to distinguish between strong ($P_\omega > P_{thr}$) and weak ($P_\omega < P_{thr}$) fields. However, this subdivision is itself quite conditional, since the effectiveness of the action of the laser field on the orientation of the molecules in the LC cell depends on the state and thickness of the LC, on the external conditions, on the duration of the laser pulse, and on the duration of the irradiation. In particular, this effect of the pump field possesses memory (cf. Ref. 26), being a cumulative effect. In this sense, in the case of a prolonged irradiation any field can be considered to be equivalent in its action to a strong field. In Table I we present the data obtained in these two cases for the power $P_{2\omega}$ in relative units (normalized in the $P_{2\omega}$ value for strong fields in the geometry 1) for different types of nonsynchronous interaction (in the presence of an exit analyzer). The data cited correspond to averaged results obtained for roughly the same irradiation time in each experimental geometry, but only in those cases in which the type of interaction in question was the first in the series. The $P_{2\omega}$ values obtained in the same experimental geometry, but in different series did not differ from each other by more than a factor of two. The temperature of the MBBA cell was equal in this case to 25–26°C. The adjustment was always made at the maximum $P_{2\omega}$ value corresponding to the Maker fringes.[27]

We also observed that the $P_{2\omega}$ values depended on the order in which the experiments for the various geometries were performed. Although this variation often occurred in an irregular fashion (e.g., in poorly oriented cells of thicknesses of the order of tens of microns, the relative data for $P_{2\omega}$ in the geometries 1 and 2, as well as 3 and 4, could be the inverses of those presented in Fig. 1: inversion of $P_{2\omega}$ values), we can assert that the quantity $P_{2\omega}$ increases several-fold in the geometries 5 and 6 in the case in which the experiments in these geometries were performed immediately after the registration of the generated second harmonic in the geometries 1 and 2.

TABLE I.

Number of geometry of experiment	Geometry of experiment*)		$P_{2\omega}$		Number of geometry of experiment	Geometry of experiment*)		$P_{2\omega}$	
	n	$e_{2\omega}$	strong fields	weak fields		n	$e_{2\omega}$	strong fields	weak fields
1	0	0	1	14	4	90	90	4	40
2	0	90	2	7	5	45	45	3	18
3	90	0	20	11	6	45	135	344	3123

*)Here we give the angles (in degrees) that the vectors n and $e_{2\omega}$ form with the vector e_ω (e_ω and $e_{2\omega}$ are the unit polarization vectors of the pumping radiation and the generated second-harmonic signal; n is the direction of orientation of the NLC director).

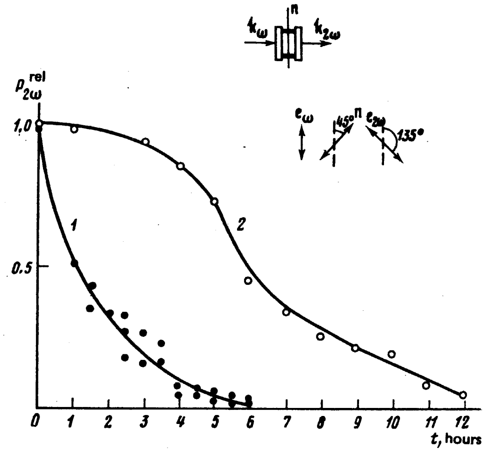

FIG. 2. Time dependence of the quantity $P_{2\omega}$ in relative units in the case of periodic irradiation of the MBBA sample in the region of the plateau in Fig. 1. The P_ω value for the curve 1 is five times higher than the P_ω value at which the curve 2 was obtained. The geometry of the experiment is shown at the top.

We carried out a separate investigation of the variation in time of the quantity $P_{2\omega}$ during a long period of time (~1 day). The SHG efficiency was measured as a function of the time during the irradiation of the same region of a freshly prepared cell with the LC by a laser beam, both in the case in which the laser operated continuously and in the case in which it was periodically switched on during the 24-hour period (in the case $P_\omega > P_{thr}$). The dependences obtained in the latter case with two P_ω values in the geometry 6 are shown in Fig. 2. The monotonic decrease in time of the quantity $P_{2\omega}$ is evident. Also evident is the fact that the decrease is faster in the case of the higher P_ω value. The same type of dependence was obtained when there was no exit polarizer. A similar result is obtained in the case of continuous sample irradiation. In both cases a tenfold decrease in the SHG efficiency occurred after the action on the MBBA sample of roughly 10^4–10^6 laser pulses (the number of pulses depended on the value of P_ω). In this case the $P_{2\omega}$ values in the geometries 5 and 6 approached each other in magnitude under the conditions of prolonged action of the laser field. When the pumping beam was shifted to a new place on the LC sample, the second-harmonic signal grew, and then began to decrease again. For the geometries 1, 2, and 3, 4 we did not observe such a significant decrease in the second-harmonic signal intensity over so short a time. The time dependence was not monotonic, especially for the geometries 3 and 4.

2. The temperature dependence for the SHG. Normal incidence

We carried out numerous measurements of the quantity $P_{2\omega}$ as a function of temperature on a MBBA cell of thickness 5 μm in the geometry 6. The rate of variation (increase) of the temperature in these experiments was of the order of 0.1 deg/min. The results obtained depended on the degree of orientation of the molecules in the sample, and comprise three groups: in the first group, which corresponds to the best single-domain structure of the sample—virtually complete extinction of the light in crossed polarizers—the quantity $P_{2\omega}$ clearly exhibits peaks (sometimes one); in the second group $P_{2\omega}$ undergoes periodic oscillations (normally through three peaks) with a smoothly decreasing value as the temperature is varied; in the third group $P_{2\omega}$ varies little with temperature in the nematic phase (the quantity $P_{2\omega}$ itself is in this case small and close to the power of the background noise). The generated-second harmonic power $P_{2\omega}$ in this last case increases in the vicinity of the critical temperature T_{p}, of the transition of the NLC into the isotropic liquid phase. Figure 3 shows typical temperature dependences of $P_{2\omega}$ in relative units for the first two groups. The peaks in the graph a) are roughly 100 times higher than the signal represented by the curve 6).

In all the cases in which the isotropic MBBA phase was used, as in those in which non-oriented samples were used, the generated-second-harmonic-signal power was significantly lower, and was at the limit of the sensitivity of the recording system. We almost always observed in the immediate neighborhood of T_p (in the region of the heterogeneous state of the NLC[11]) a breakdown of the MBBA in the laser field, which was accompanied by a sharp increase in the registered signal intensity at the second-harmonic frequency (this increase is not shown in Fig. 3). After cooling from the isotropic phase in thise case, the SHG in the nematic phase was significantly less effective than before the breakdown; the orientation of the LC material at the breakdown point was also indeterminate. We did not observe in the nematic MBBA phase any of the unmelted solid NLC particles that were the cause of the SHG in the first experiments on the verification of the centrosymmetry of the mesophase (see the review of these investigations in Ref. 23).

3. The angular dependence for $P_{2\omega}$. Oblique incidence

The results obtained in numerous measurements were found to be relatively well reproducible in the measurements of the angular dependence of $P_{2\omega}$. Figure 4 shows this dependence (with a different scale of relative units for each curve) for the geometries 1 and 2 (the thickness of the NLC layer was 50 μm and the temperature was ~28 °C), where θ is the experimentally observed angle between the wave vector $\mathbf{k}_\omega$ of the pump and the director $\mathbf{n}$. For the geometry 3 we observed single peaks on both sides of the angle $\theta = 90°$, and the picture for the geometry 4 is close to the picture depicted in Fig. 4(a). The registration of a second-harmonic signal from an ordinary crystal, emerging directly from the laser and passing through the entire optical system, showed that the signal had a constant intensity, and did not depend on the rotation of the LC sample.

4. Dependence of $P_{2\omega}$ on the thickness of the MBBA layer

We measured the dependence of the signal power $P_{2\omega}$ on the thickness L of the MBBA layer in a cell. Here the experiments for the various L were performed with the same glass substrates, roughened once before the entire series of measurements. As the thickness of the NLC layer was increased, the degree of orientation of the molecules in the cell decreased (the brightening of the probing beam in crossed polarizers).

Figure 5 shows (on a relative scale) the dependence obtained at the peak of the synchronous SHG for the *ee-o* interaction. We can see the existence of an optimal MBBA-layer thickness $L_{opt} \sim 30$ μm, at which the SHG efficiency is highest. In this case the width of the

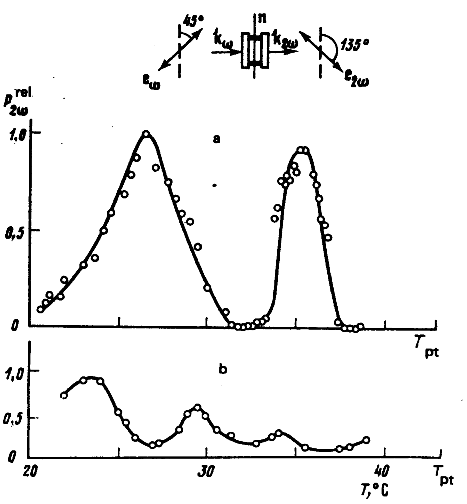

FIG. 3. Characteristic curves for the temperature dependence of the intensity of the generated second-harmonic signal in the case of normal incidence. Each curve is normalized to its own relative-unit scale.

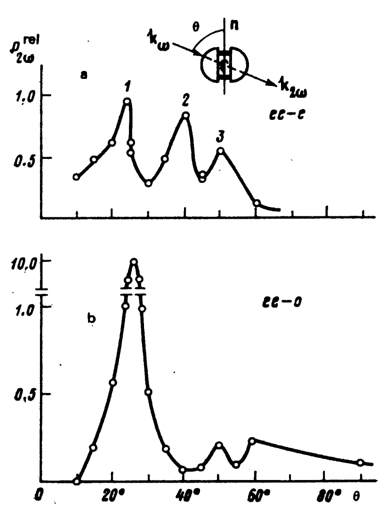

FIG. 4. Angular dependences for $P_{2\omega}$ in two geometries of the experiment. Each curve is normalized to its own relative-unit scale.

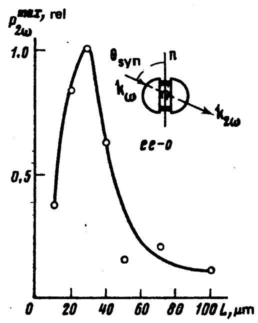

FIG. 5. Dependence of $P_{2\omega}$ on the thickness of the MBBA layer for the $P_{2\omega}$ values at the peak of the synchronous SHG.

synchronism curves increased with increasing thickness. Similar qualitative dependences are obtained at the peaks of the Maker fringes for the nonsynchronous SHG in the angular and temperature measurements. In these cases $L_{opt} \sim 20-40\ \mu m$.

5. Comparison with the SHG in quartz

The data on the absolute value of the power of the second harmonic generated in MBBA were obtained from a comparison with the power of the second harmonic generated in a quartz plate of thickness 100 μm for the *oo-o* interaction. The $P_{2\omega}$ value, normalized in this case to the same pump power to which the data in Table I are normalized, was equal to 5.3×10^7 in the same relative units. (For the *oo-e* interaction in quartz, the recorded $P_{2\omega}$ value was almost 10^5 times smaller, and was due to various spurious noises generated at the second-harmonic frequency.)

4. DISCUSSION

1. The parameters characterizing the SHG in MBBA

1. The nonlinear-susceptibility-tensor components $\chi^{(2)}_{ijj'}$ measured in the geometries 1–6 (see Table I) for the collinear interaction of the waves are presented in Table II. They were computed from Okoda and Takizawa's formulas.[36] Here the z axis in the oriented NLC samples is assumed to coincide with the director direction **n** (the index j' corresponds to the coordinate z; the index i, to x; and the index j, to y); the possible macroscopic biaxiality of the oriented nematic material is taken into consideration in the general case. In Table III we give the computed values for normal incidence and the coherence interaction length

$$l_{coh}=\pi/\Delta k=\lambda_{vac}/4(n_{2\omega}-n_{\omega}),$$

where $n_{2\omega,\omega}$ are the refractive indices at the second-

TABLE II.

Number of geometry of experiment	$\chi^{(2)}$ components	
	for interaction along x axis	for interaction along y axis; "+" for $\varphi=\pi/2$, "–" for $\varphi=3\pi/2$.
1	(333)	(333)
2	(233)	(133)
3	(222)	(111)
4	(322)	(311)
5	$^1/_2$(322) + $^1/_2$(333) – (332)	$^1/_2$(311) + $^1/_2$(333) ± (331)
6	$^1/_2$(222) + $^1/_2$(233) – (223)	$^1/_2$(111) + $^1/_2$(133) ± (113)

Footnote: Here $\chi_{ijj'}=\chi_{ij'j}$.

TABLE III.

Number of geometry of experiment	Type of interaction	l_{coh}, μm	Possibility of synchronism		χ exp $\equiv\chi^{(2)}_{(i)}/\chi^{(2)}_{(1)}$
			with respect to θ_{syn}, deg	with respect to ΔT_{syn}, °C	
1	*ee – e* *	+2.7	–	–	±1,0 **
2	*ee – o*	–2.1	30	0	±0.9
3	*oo – o*	+7.1	–	–	±0.3
4	*oo – e*	+1.0	–	–	±4,1
5	*oe – e*	+1.5	–	–	±3.1; ∓0.8
6	*oe – o*	–5.9	43	0,6	±6,3; ∓5.9

*Here *o* and *e* are respectively the ordinary and extraordinary rays; the first and second letters pertain to the pumping wave, while the third pertains to the generated second-harmonic wave.

**In this column it is necessary to take for all the interactions either only the upper, or only the lower, signs.

harmonic and pump frequencies and $\lambda_{vac}=1.064\ \mu m$. Here the n_ω and $n_{2\omega}$ values were taken from the published data for 25 °C (Ref. 29), and recalculated to correspond to the wavelengths used in our experiment with the aid of the Sellmeier formulas.

In Table III it is noted the possibility of synchronous SHG in MBBA ($l_{coh}=\infty$); we give values for both the angle of synchronism θ_{syn} (between $\mathbf{k}_{\omega,2\omega}$ and **n** inside the NLC) at 25 °C and $\Delta T_{syn}=T_{pt}-T_{syn}$ (T_{syn} is the temperature at which synchronous SHG occurs) at normal incidence. As can be seen from these data, the attainment of temperature-governed synchronous interaction for SHG in single-domain MBBA samples (90-degree or noncritical synchronism) is in principle possible, but only in the immediate neighborhood of T_{pt}, which is difficult to attain in experiment.

Let us estimate the $\chi^{(2)}$ values for MBBA on the basis of the data given in Table I for $P_{2\omega}$ in the case of weak fields. These values are given in Table III (they are normalized to the $\chi^{(2)}$ value for the *ee-e* interaction), and were computed from the standard formula for $P_{2\omega}$ for nonsynchronous SHG at a Maker-fringe peak.[27] Here, using the data for the geometries 5 and 6 in Table I, we made the $P_{2\omega}\to\chi^{(2)}$ conversion to the components characterizing precisely the *oe-e* and *oe-o* interactions: $\chi^{(2)}_{332}$ and $\chi^{(2)}_{223}$ respectively; the values of these components are given in the last rows of Table III. Two possible values are shown, since a quadratic equation had to be solved, and the signs of the $\chi^{(2)}$ components are unknown. The same values are obtained for the components $\chi^{(2)}_{331}$ and $\chi^{(2)}_{113}$, but for the + sign in the last two rows of the third column of Table II they are obtained with opposite signs.

Analysis of the obtained data shows that the SHG in the geometry 6 is largely determined by the *oe-e* interaction. In the geometry 5, however, comparable contributions to the quantity $P_{2\omega}$ are made by all three types of inteaction.

We can attempt to establish the crystallographic symmetry class to which the oriented MBBA samples belong. Analysis shows (see Tables II and III) that the most probable interpretation is possible within the framework of three noncentrosymmetric classes: 1, *m*, and 3. The first two classes describe biaxial crystals (the class 1 does not have symmetry elements at all). It can be seen from the obtained results that, in the class m, the SHG should be realized for the collinear interaction of the waves along the y axis; and in the case of interaction along the x axis SHG should also occur at the forbidden (zero) $\chi^{(2)}$-tensor components: $\chi^{(2)}_{233}$, $\chi^{(2)}_{222}$, and $\chi^{(2)}_{332}$. The occurrence of SHG at the forbidden components $\chi^{(2)}_{133} \equiv \chi^{(2)}_{233}$ and $\chi^{(2)}_{331} = \chi^{(2)}_{332}$ should also be admissible for the class 3. Let us note that by itself the fact that SHG is admissible at the forbidden components may be a characteristic of NLC.[30] But the $\chi^{(2)}$ values given in Table III are, in fact, estimates. The nonuniform orientation of the NCL in the sample and the action of the laser field itself in the NLC and its natural aging lead in different experiments, as noted in Subsec. 1 of Sec. 3, to $\chi^{(2)}$ values that differ from each other (cf. the data for $P_{2\omega}$ in Table I).

Nevertheless it makes sense to estimate the absolute value of $\chi^{(2)}$ for MBBA. This can be done through a comparison with SHG in quartz (see Subsec. 5 of Sec. 3); from the data for the geometry 6 in Table I (the last column) we obtain the value $\chi^{(2)}(\text{MBBA}) \approx 0.06\, \chi^{(2)}_{111}(\text{SiO}_2)$. But $\chi^{(2)}_{111}(\text{SiO}_2) \approx 0.85 \times 10^{-2}$ cgs esu,[27] and therefore $\chi^{(2)}(\text{MBBA}) \approx 1 \times 10^{-10}$ cgs esu. Notice that the cited numerical data correspond to data directly obtained from experiment without corrections for scattering.

2. Let us discuss the angular dependences. The experimental curves obtained indeed pertain to SHG in MBBA, and characterize precisely the angular dependence of the generated second harmonic. They are not due to different geometric factors arising during the rotation of the plane-parallel sample, a fact which, as has already been noted, was specifically verified by us.

For nonsynchronous SHG in the general case of oblique incidence of the waves, we can easily derive the following expression for the period Δx of the Maker fringes (the distance between neighboring peaks):

$$\Delta x = \frac{\pi L}{2 l_{\text{coh}}} \left\{ \left[\frac{\Delta(\Delta n)}{\Delta n} + \frac{\Delta L}{L} \right] \cos \vartheta_t - \Delta\vartheta_t \sin \vartheta_t \right\},$$

where L is the sample thickness; ϑ_t is the refraction angle (for the pump wave); l_{coh} is the coherence length for normal incidence during the SHG; $\Delta(\Delta n)$, ΔL, and $\Delta\vartheta_t$ are the differences between the corresponding parameters for neighboring peaks during the rotation of the sample ($\Delta n = n_{2\omega} - n_\omega$, L, and ϑ_t are their average values). The Δx_e values thus obtained from the experimental data should be compared with the distances Δx_t between the neighboring peaks of the function $(\sin x)^2/x^2$, which should describe the angular dependence of $P_{2\omega}$ for nonsynchronous SHG.

For the *ee-e* interaction [see Fig. 4(a)] the experimental values for the distances between the first and second, and second and third, peaks of the fringes are $\Delta x_e = 1.48\pi$ and 0.87π. In this case $x = \pi L/2 l'_{\text{coh}} \gtrsim 5.10\pi$, where $l'_{\text{coh}} = l_{\text{coh}}/\cos \vartheta_t$. Therefore, $\Delta x_t \approx 1.0\pi$. The obtained agreement between Δx_t and Δx_e can be considered to be satisfactory if we allow for the fact that the geometry of the experiment is significantly different for e waves, and that the refractive indices for MBBA were taken from the literature; the inhomogeneity of the sample and the inevitable errors in the determination of the quantities L, ϑ_t, etc. should also give rise to differences between Δx_t and Δx_e. A definite influence is also exerted by the laser field itself[25]: its action causes the term $\Delta L/L$ in the above cited expression for Δx to play a relatively greater role.

Thus, the curve in Fig. 4(a) corresponds to the Maker fringes for nonsynchronour SHG in MBBA.

At the same time, similar arguments for the *ee-o* interaction [Fig. 4(b)] show that the peak found in the angular dependence of $P_{2\omega}$ should correspond to synchronous SHG, and the difference between the exmental value for the angle of synchronism (recomputed to correspond to an angle inside the LC: $\theta^e_{\text{syn}} \approx 35°$) and θ^t_{syn} can similarly be explained.

The *oo-o* interaction does not admit of synchronous SHG, but possesses a large l_{coh} value; therefore, to record the Maker fringes, we must rotate the NLC sample through appreciable angles in order to attain a sufficient change in the layer thickness. Estimates show that it is not possible under our conditions to record two neighboring peaks for the nonsynchronous SHG. Therefore, the above-noted $P_{2\omega}$ dependence for the *oo-o* interaction corresponds to one Maker-fringe peak on each side of the angle $\theta = 90°$. In the case of the *oo-e* interaction, which also does not admit of synchronous SHG, but which possesses a significantly smaller l_{coh} value, we observed, as discussed in Subsec. 3 of Sec. 3, Maker-fringe peaks of the type of the dependence shown in Fig. 4(a), which satisfactorily agree with the theoretical estimates.

In nonuniformly oriented samples, because of scattering, effective noncollinear SHG (vector synchronism), in which two wave vectors $\mathbf{k}_\omega$ of the pump are directed at the angle to $\mathbf{k}_{2\omega}$, is possible. This should be characteristic of NLC, and leads to the broadening of the synchronism curves (the quantity l_{coh} also changes). The angles necessary for the closure of the triangle of wave vectors ($\mathbf{k}_\omega + \mathbf{k}_\omega = \mathbf{k}_{2\omega}$) are not so large, and can arise even in relatively good single-domain NLC samples, especially under conditions of focusing and small diameters of the laser beams in the LC. As an example,

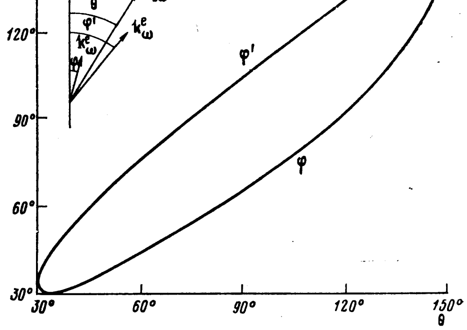

FIG. 6. Computed dependence for the noncollinear SHG in MBBA for the *ee–o* interaction.

we show in Fig. 6 the computed vector-synchronism curve for SHG under conditions of the *ee-o* interaction in MBBA. It can be seen that under conditions of normal incidence the width of the angular synchronism curve can attain a value of the order of tens of degrees.

3. Let us turn to the temperature dependences. For the curve in Fig. 3(a), $\Delta x_e = 1.0\pi$; allowing for the fact that here $x = 3.7\pi$, we see an excellent agreement with the value $\Delta x_t \approx 1.01\pi$ [in the formula for Δx in the case under consideration $\Delta(\Delta n)$ and ΔL are the changes occurring in the parameters as the temperature is varied; the magnitude of the coefficient of thermal expansion of MBBA ~10^{-3} deg^{-1} (Ref. 10)]. Thus, the curve 3(a) corresponds to the temperature Maker fringes.

Since the temperature interval between the peaks of these fringes is relatively large (~10°)—the quantity $l_{\rm coh}$ is large and the existence domain for the nematic phase ~20°—it is understandable why only one $P_{2\omega}$ peak is sometimes observed in experiment.

There is a great difference between Δx_e and Δx_t for insufficiently well oriented MBBA samples. For example, for the curve in Fig. 3b, Δx_e is of the order of 0.4π and 0.6π (for x equal to 4.2π and 3.7π) for the distances between the first and second, and the second and third, peaks, while Δx_t is equal to 1.01π, i.e., more closely spaced fringes (with a shorter period) are observed. This may be due to the inhomogeneity of the sample, and leads to additional phase difference between the pumping and second-harmonic waves.

The above-noted increase of the quantity $P_{2\omega}$ near the phase transition temperature $T_{\rm pt}$ can also be related to the inhomogeneities, which manifest themselves especially strongly in the vicinity of $T_{\rm pt}$. Besides the formation here in the NLC of complex noncentrosymmetric structures[11] (which can lead to efficient SHG) and the prebreakdown state of the sample, we must have in mind the fact that the conditions for synchronous SHG can be fulfilled because of the large changes that occur in the values of the refractive indices at the boundaries of the inhomogeneities.[31,32]

Let us also note that, when the NLC is heated, the quantity $P_{2\omega}$ may, on the one hand, decrease because of the decrease of the degree of orientation in the sample, and, on the other, increase because of the increase of the quantity $l_{\rm coh}$. The variation in time of the $T_{\rm pt}$ value in MBBA also has a definite effect on the reproducibility of the results.

Thus, as follows from the foregoing, the occurrence of SHG in the oriented MBBA NLC samples used has been firmly established. Furthermore, this absence of a center of inversion is not a consequence of purely surface effects (nonsynchronous SHG), but characterizes the volume state of the LC (the presence of synchronous interactions), i.e., we can say that (planarly) oriented MBBA textures do not form a centrosymmetric structure. Consideration of the possible mechanisms responsible for SHG in NLC[23] shows that the SHG observed in our experiments in MBBA is indeed due to the fact that the second-order nonlinear susceptibility $\chi^{(2)}_{ijj'}$ is nonzero, i.e., we can say that the investigated oriented MBBA samples are macroscopically noncentrosymmetric.

2. Physical consequences

The absence of a center of inversion in the oriented samples should in general be characteristic of all NLC, and may be a local property: in this respect a LC is close to a crystal with an incommensurable superstructure.[28] In the presence of internal stresses in the NLC sample, the mechanism underlying the formation of the noncentrosymmetric structures may also have a flexoelectric character, but this should lead to only surface SHG (see also Ref. 33). Furthermore, the conversion of the LC into the isotropic phase with subsequent cooling should remove these stresses.

Of greatest interest in connection with SHG are the smectic LC especially the C^*-type smectic materials, since their ferroelectric properties are well known. Indeed, Vtyurin *et al.*[30] have reported the study of the temperature dependence of $P_{2\omega}$ for DOBAMBS in an external constant electric field E^0. But in this case the SHG should be due largely to the term in the nonlinear polarization proportional to

$$P_i^{NL} \sim \chi^{(3)}_{ijj'l} E_j^* E_{j'}^* E_l^0.$$

Such an SHG mechanism was recently observed by Saha and Wong[34] in the nematic phase of 5CB, in which $\chi^{(3)}_{ijj'l}$ has a value of the order of 10^{-12} cgs esu.

The fact, proved in our experiments, that MBBA is noncentrosymmetric may explain the well-known smallness of the coefficient B in the Landau expansion for the thermodynamic potential in the region of the phase transition into the isotropic liquid, the cause of which is thought to be unclear[8,35]: the absence of a center of inversion in the medium should automatically lead to the closeness of the quantity B to zero. Furthermore, the coefficients A and B in this expansion should be small when the NLC contains local regions where the NLC molecules are correlated with respect to both their orientations and the positions of their centers of gravity. Thus, we also have a simple explanation for the tricritical character, which has for some time past been the subject of discussions, of the phase transition in MBBA.[35] A discussion on this theme will be published by us separately together with the results of independent experiments on the nonlinear scattering of light in the phase transition region. Here we only note that the closeness of B to zero should give rise to optical biaxiality of the MBBA samples,[8] at least in local regions; the data obtained by us on SHG admit of an interpretation within the framework of a biaxial noncentrosymmetric class of symmetry m.

In conclusion, let us note that, although the SHG efficiency obtained by us is low, this is due not to the general properties of LC, but rather to the fact that MBBA is essentially an "accidental" medium for SHG, and no purposeful search for the most effective LC for SHG was made.[1)] Meanwhile, the synthesis of such materials is possible. We are convinced of this by the situation that obtains in the field of molecular crystals, where a record number—for nonlinear optics—of materials have been produced. Therefore, the direction in which the search for effective materials for the nonlinear conversion of the LC medium should be made is clear.[23]

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[1]The situation is reminiscent of the initial stages of the development of nonlinear optics, when the first SHG was realized in quartz crystals, which are quite an unsuitable medium for SHG.

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