Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Second Harmonic Generation in Nematic Liquid Crystals: Effect of Molecular Symmetry, Nonlinear Susceptibility and Phase-Matching

S. M. Arakelyan [a], Yu. S. Chilingaryan [a], G. L. Grigoryan [a], G. A. Lyakhov [a], S. Ts. Nersisyan [a] & Yu. P. Svirko [a]
[a] Dept. of Physics, Yerevan State University, Yerevan, Armenia, USSR
Version of record first published: 20 Apr 2011.

To cite this article: S. M. Arakelyan , Yu. S. Chilingaryan , G. L. Grigoryan , G. A. Lyakhov , S. Ts. Nersisyan & Yu. P. Svirko (1981): Second Harmonic Generation in Nematic Liquid Crystals: Effect of Molecular Symmetry, Nonlinear Susceptibility and Phase-Matching, Molecular Crystals and Liquid Crystals, 71:1-2, 137-156

To link to this article: http://dx.doi.org/10.1080/00268948108072722

Mol. Cryst. Liq. Cryst., 1981, Vol. 71, pp. 137–156
0026-8941/81/7102-0137$06.50/0

Second Harmonic Generation in Nematic Liquid Crystals: Effect of Molecular Symmetry, Nonlinear Susceptibility and Phase-Matching

S. M. ARAKELYAN, Yu. S. CHILINGARYAN, G. L. GRIGORYAN, G. A. LYAKHOV, S. Ts. NERSISYAN and Yu. P. SVIRKO

Dept. of Physics, Yerevan State University, Yerevan, Armenia, USSR

(*Received August 21, 1978; in final form June 12, 1980*)

Second harmonic generation in the nematic liquid crystal MBBA was experimentally observed both for phase-matched and for non-phase-matched interactions. The nonlinear susceptibility tensor components values were measured for the first time.

The possible SHG mechanisms are discussed.

The obtained new physical information on liquid crystal structure is emphasized. The experimental results are thoroughly compared with calculations of second harmonic generation parameters. A physical interpretation of observable effects is given.

INTRODUCTION

Recently the symmetry of nematic liquid crystals (NLC) has been extensively discussed in the literature.[1-3]

To all appearance, it seems already possible to say that the shape of the NLC molecules is similar to a flat plank rather than to a rod, which is indicative of optical biaxiality of the molecules.[4-7] However, such an optical biaxiality, being essentially fluctuating, may just as well not manifest itself on a macroscopic scale in the whole sample.[8]

A more important question is the presence or absence of the symmetry center in NLC. The LC molecules themselves, due to their chemical structure, come close rather to asymmetric ones,[9] however, they rotate permanently round their local axes, and the time-averaged probability density of the molecule orientations may be centrosymmetrical. We actually mean the absence of the inversion center exactly in this probability density which is necessary to be

averaged also in space, i.e. in cross section of a sounding beam in a concrete optical experiment.

We actually mean here the physical difference between the "tails" of molecules in the NLC sample. This usually is reduced to the problem, whether the directions of directors (+n) and (−n) are equivalent or not. At present the opinion is adopted about a complete physical equivalence of these states.[10]

Physical difference of the (+n) and (−n) directions must bring in oriented LC to the presence of ferroelectrical properties[1,3,6,10-12] in the case when a molecule has a permanent dipole moment.

However, it should be noted that, first, arising of ferroelectrical properties of LC is directly connected with noncentrosymmetrical orientation of the sample molecules only for one-axial LC, in which case along with the quadrupole order [$<P_2(\cos 0)> \neq 0$] one should consider the dipole order [$<P_1(\cos 0)> \neq 0$] as well.[11] As to biaxial LC, the presence of the dipole moment perpendicular to a long molecule axis gives rise to the ferroelectricity without noncentrosymmetrical ordering of the molecules in the sample either in case the molecules do not rotate round their long axes, or if this rotation is somewhat complicated.[11]

Second, the noncentrosymmetry of the NLC samples must not necessarily bring to the difference of the (+n) and (−n) directions. In usual one-axial crystals their optical axis (director—for LC), as a rule, is not the polar vector, although they may be noncentrosymmetric. The important thing for LC is that the "tails" of molecules at ordering face the same direction, but what direction they face is of no importance. The situation resembles the Heisenberg ferromagnetic, where all the spins want to be parallel, but their energy is independent of the total moment direction.[10] Though, the sample orientation can lead in certain cases (for definite symmetry classes of crystals) to the optical nonequivalence of two mutally opposite directions of the crystal optical axis, which in this case actually becomes polar (the optic axis inversion effect).[13]

It is reasonable to inquire what are experimental effects caused by the NLC noncentrosymmetry. A number of works at present available may be considered in this respect. Here we should like to single out the following three points: first, structure changes that occur in NLC in this case, in particular, the appearance of helical texture of the cholesteric type;[14-19] second, direct observation of ferroelectricity[11,20,21]; and finally, observation of effects which are possible only in noncentrosymmetric media, i.e. the optical activity effect and the linear electrooptical effect,[22-24] second harmonic generation (SHG),[12,25] etc.[26]

SHG in LC's has already been discussed[28] but the dominant opinion following from the analysis of available results, is that three frequency nonlinear interactions in LC's are anomalously small due to the inversion symmetry of

their internal structure. We claim that such a conclusion for the mesomorphic state of a substance is not valid in general. For example, the noncentrosymmetricity of cholesteric LC's is well known.[10]

It is often stated that optical activity (as well as SHG) requires the absence of both inversion center and mirror plane.[29] (The terms responsible in the free energy for these effects are proportional to $\gamma_{ijj'}e_{jj'm}k_mE_i^*$ and $\chi_{ijj'}E_i^*E_jE_{j'}$ respectively). But this is not valid for oriented systems; the orientation significantly increases the number of optically active substances. These questions are discussed in detail in Ref. 30, a similar idea was expressed in Ref. 31. Therefore, in well oriented LC monocrystals SHG can be highly efficient.

However, it is not always easy to interpret unambiguously the effects of observation in such fine balanced molecular structure as LC is, when proceeding merely from the symmetry of molecules. By the way, the above cited works also give the ambiguous interpretation (explicit discussion is given in Ref. 12). Thus, there is no perfect clearness so far in the NLC symmetry problem.

The present paper is devoted to the experimental investigation of optical SHG in liquid crystals. The interest to such problems is related mainly to the fact that SHG (which for the dipole approach is possible only in noncentrosymmetric media) gives important information on both the local molecular ordering and the nature of intermolecular interaction in LC's. In many cases the SHG is the most convenient method to reveal the symmetry of the media. (Note, that X-ray structural analysis is not directly sensitive to the inversion center of the media). Here the essential point is the transition from the characteristics of an individual molecule to the nonlinear macroscopic susceptibility. Taking into account the extreme sensitivity of LC's to external fields, we can say that this transition is relatively simple in oriented LC's thin samples. Therefore, it appears possible to predict the efficiency of nonlinear transformations, proceeding from the molecular level, analysis where such a correlation can be explained best.[27] Furthermore, SHG allows one to look for potential applications of LC's in various thin layer devices, e.g. for frequency transformers.

We report here new experimental data on SHG in NLC p-methoxybenzyledene-n-p'butylaniline (MBBA), which, to our mind, convincingly and unambiguously confirm for the first time the noncentrosymmetry of the used oriented samples—a conclusion drawn for the first time in Ref. 25. Choice of such a well-known and comparatively simple NLC was motivated by a wish to carry out to end the comparison of the obtained experimental data with the calculations of the SHG parameters, although MBBA due to its molecular structure is low-effective for SHG.

The complete explanation of the experimental data is possible when taking into account the essentially new assumption of the symmetry and macroscopic

properties of NLC's. We have investigated both phase-matched and non-phase-matched SHG and have obtained the optimum thickness of NLC for the former case.

THE EXPERIMENT

Let's enumerate our results.[32] The SHG was experimentally observed in chemically-pure, prepared directly prior to the experiment samples of the MBBA nematic phase of thickness of the order of several ten microns, whose molecules were planarly oriented by abrasion. The temperature of transition to isotropic phase was about 43°C. As a pumping we used a single-mode (transverse) linearly polarized Q-switched YAIG: $Nd^{3+}(\lambda = 1.06\,\mu)$ with the on-peak power usually ~ 100 kw (pulse duration is 12 nsec) operated under frequency conditions. The laser beam was focussed on the LC sample by $f = 8$ cm lens.

Two types of experiments were performed. In the first one the pumping radiation was perpendicular to surfaces of the glass substrates (normal incidence). In the second one low incidence was performed. In the latter case two hemispheric glass substrates were used.

To separate different types of interactions for SHG we used Nicol prisms between which the MBBA cell was placed.

The registration system consisted of basic and supporting channels. The optic radiation registration in each of the channels was performed by a photomultiplier, then the signals were translated into a digital code for each laser pulse. In the supporting channel the radiation of SHG in a quartz plate was registered.

To extract the SHG signal ($\lambda = 0.533\,\mu$) we used light filters. Furthermore, in the basic channel the radiation passed through a monochromator, matching with whom was achieved by means of lenses that collected the whole power from the SHG sample.

The registration system calibration was performed by SHG from a second standard quartz plate placed in the basic channel instead of the NLC cell. The signal power of SHG in MBBA was determined after subtracting the background radiation (at measurements in the MBBA isotropic phase and in an empty cell without LC), which, as a rule, was much lower than a power registered from the nematic phase of MBBA.

The spectral width of the registered radiation from the MBBA cell corresponded to its typical values for the SHG signal in usual crystals, the signal power depended in quadratic fashion on the pumping power (see below). The possibilities of arising of the signal in the SHG frequency in case of breakdowns of the LC sample, luminescence etc., were specially controlled. The basic results obtained are reduced to the following.

As our measurements have shown, it is necessary to distinguish between the

"strong" $P_\omega > P_{\text{thresh}}$ and "weak" $P_\omega < P_{\text{thresh}}$ fields. The value of P_{thresh} can be estimated by the values of P_ω at which the given dependences for $P_{2\omega}$ fall onto the "plateau" (see Figure 1). For geometries (b) and (c) $P_{\text{thresh}} \sim 100$ kw, for the (a) case it is approximately one order less.

In Table I there are presented the obtained results for the power $P_{2\omega}$ in relative units (normalized to $P_{2\omega}$ in geometry I) for different types of non-phase-matched interaction at room temperature. The given data correspond to averaged results for each geometry of the experiment, but only in those cases when the type of interaction under question was the first in the run. The values of $P_{2\omega}$ at which SHG was registered corresponds to the region $P_\omega < P_{\text{thresh}}$ when the value of $P_{2\omega}$ is determined by the initial degree of orientation of the molecules in the LC sample (we neglected the laser beam influence in this case).

The SHG efficiency with respect to time was registered both at continuous laser operation (in frequency regime) and at its multiple successive swithing over a day. In the second case the obtained dependence for geometry 6 is presented in Figure 2.

The temperature dependences for $P_{2\omega}$ (normal incidence) which depended on the degree of orientation of the sample molecules were measured. For best monodomain samples they are shown in Figure 3.

In all the cases in the MBBA isotropic phase, just as in nonoriented samples, the SHG signal power decreased substantially and was at the limit of the registration system sensitivity.

In a nematic phase of MBBA we did not find any unmelted solids, which were the cause of arising the SHG in earlier experiments on mesophase centrosymmetry check.[28]

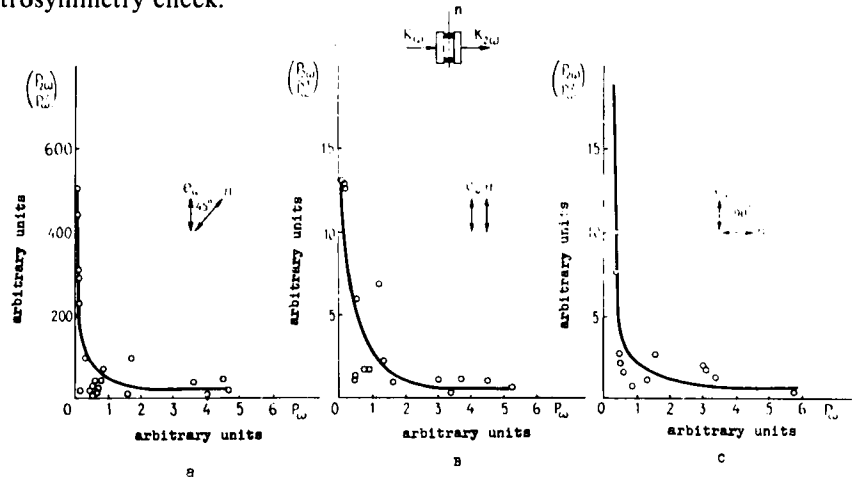

FIGURE 1 Dependence of the signal power in SHG on the pumping power in arbitrary units for three geometries of the experiment. The MBBA cell is shown at the top, the vectors l_ω and n are plotted in the plane perpendicular to vectors k_ω and $k_{2\omega}$.

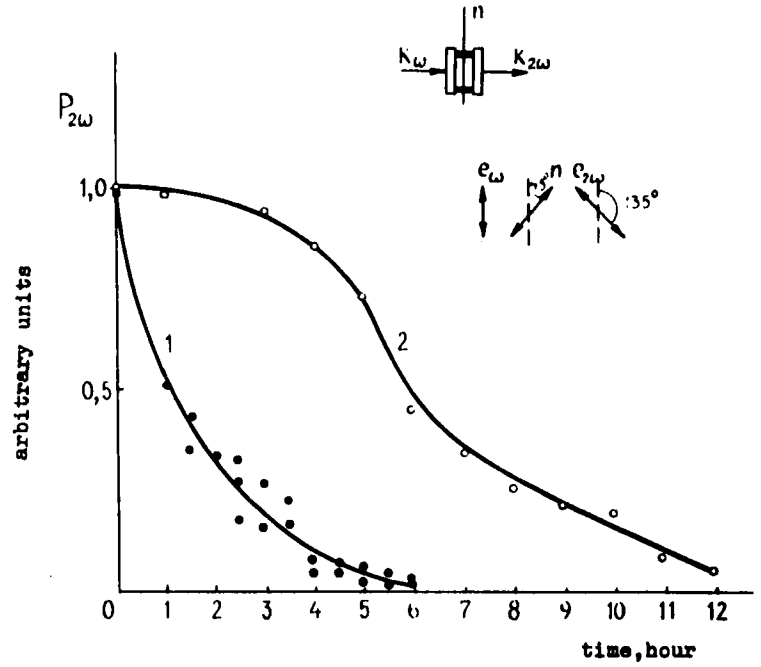

FIGURE 2 The value of $P_{2\omega}$ as a function of time in arbitrary units (at multiple successive switching of the laser) for the MBBA sample in the "plateau" region of Figure 1. The value of P_ω for curve 1 exceeds 5 times the value of P_ω for which curve 2 is obtained. The geometry is shown at the top.

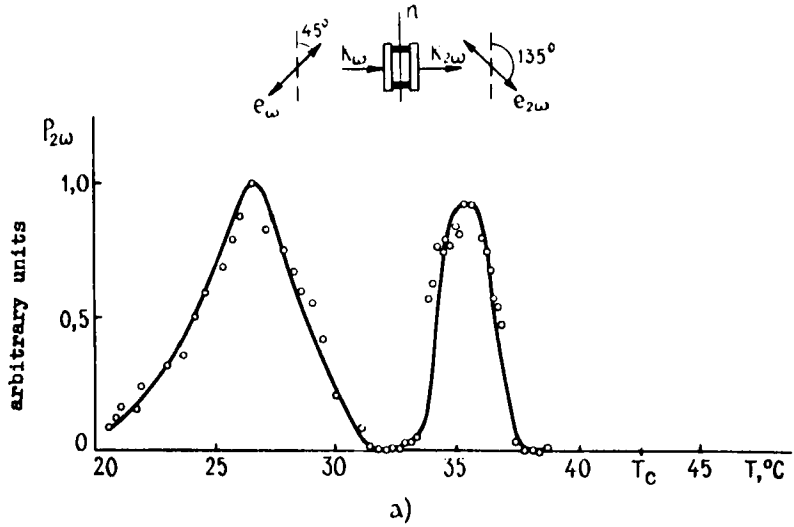

FIGURE 3 Characteristic curve for temperature dependence of the value of the SHG signal at normal incidence; T_c is temperature of phase transition to isotropic liquid for the used MBBA samples.

The angular dependences for $P_{2\omega}$ (low incidence) are shown in Figure 4 for different geometries, where θ is the observable angle between the wave pumping vector k_ω and director n of LC.

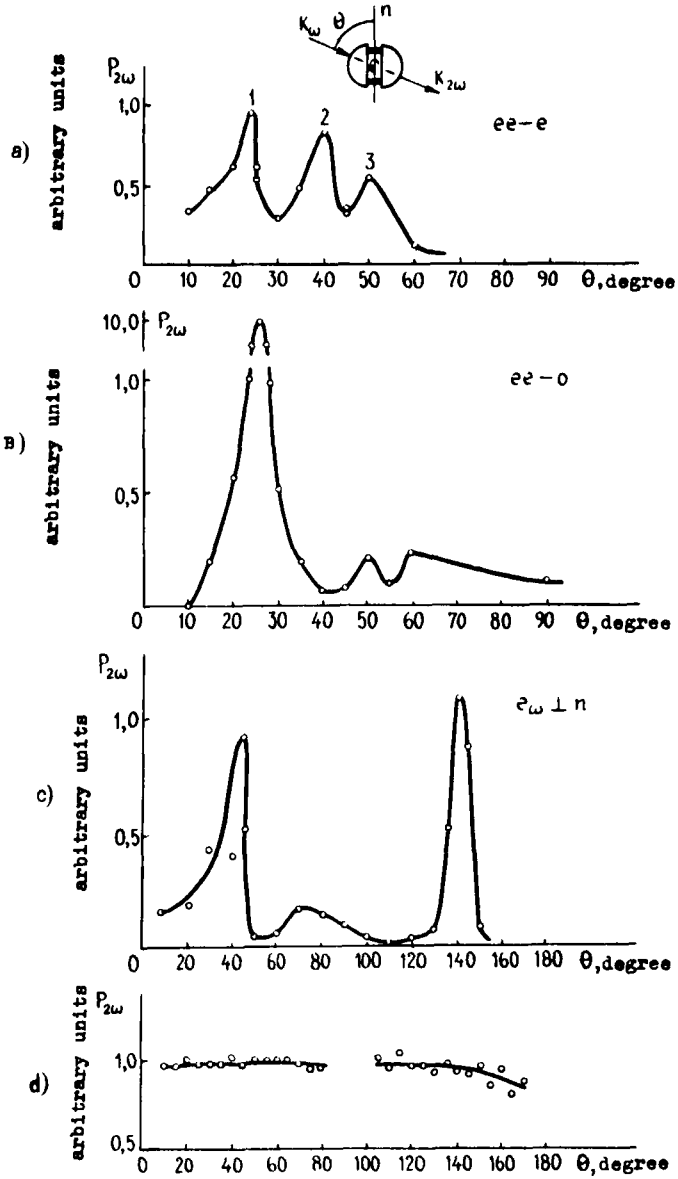

FIGURE 4 Angular dependences for $P_{2\omega}$ in different geometries of the experiment (a–c). Curve d) corresponds to the dependence for the registered signal at irradiation of the NLC cell with a second-harmonic light directly from a laser. Each of the curves is normalized in its intrinsic scale of arbitrary units.

The dependences $P_{2\omega}$ on the thickness of the MBBA layer are shown in Figure 5. With increasing thickness (deterioration of orientation of the MBBA molecules) the width of the curves of phase-matching increased (Figure 6).

The data on the absolute value of the SHG power in MBBA were obtained from the comparison with the SHG power in a standard quartz plate (the oo-o interaction) of thickness of 100 μ. The value of $P_{2\omega}$ in this case (at a maximum of the Maker oscillations) was equal to $3.7 \cdot 10^6$ in the same units as the data of Table I.

The components of the nonlinear susceptibility tensor $\chi^{(2)}_{iji'}$ measured in geometries 1-6 in the case of collinear wave interaction are shown in Columns II and III of Table II. They are calculated by the formulas of Ref. 33. It is assumed that in the NLC oriented samples the axis Z coincides with the director n; in a general case a possible macroscopic biaxiality of the oriented nematic is taken into account.

In Table III the calculated values at normal incidence for the coherent interaction lengths are given ($l_{coh} = \pi/\Delta k \equiv \lambda^{vac}/4(n_{2\omega} - n_{\omega})$, where $n_{2\omega,\omega}$ are the refraction indices at the harmonic and pumping frequences, respectively, $\lambda_{vac} = 1.064\,\mu$). The value of $n_{2\omega,\omega}$ are taken from References at $T = 25°C$[34] with recalculation with respect to our wavelengths by the Zeilmeyer formulas.

The possibility of phase-matched SHG in MBBA is shown in Column III; the values are given both for the phase-matched angle $\theta_{ph.m.}$ (between k_{ω} and n

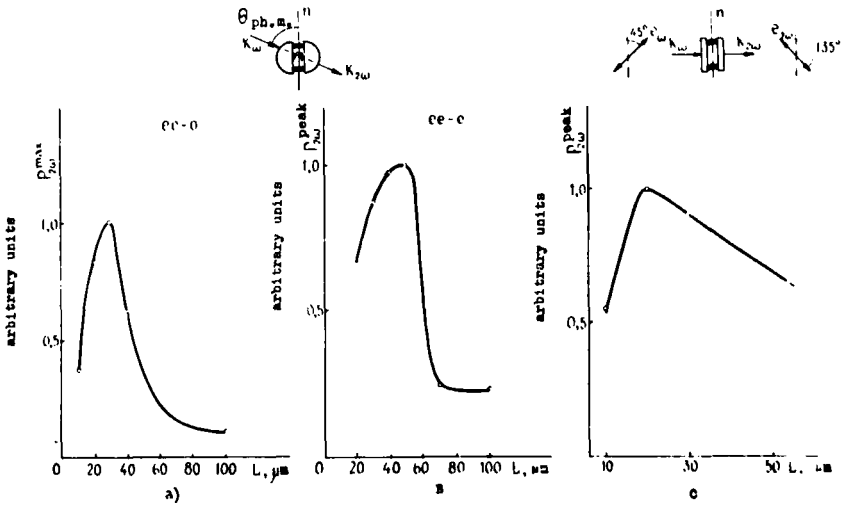

FIGURE 5 Dependence of $P_{2\omega}$ on the thickness of the MBBA layer for different geometries: a)-b)- at angular measurements. c)- at temperature measurements (normal incidence). Curve a) is obtained for the values of $P_{2\omega}$ at the maximum of phase-matched SHG, curves b), c) are obtained in peaks of Maker oscillations at non-phase-matched SHG. Each of the curves is normalized in its intrinsic scale of arbitrary units.

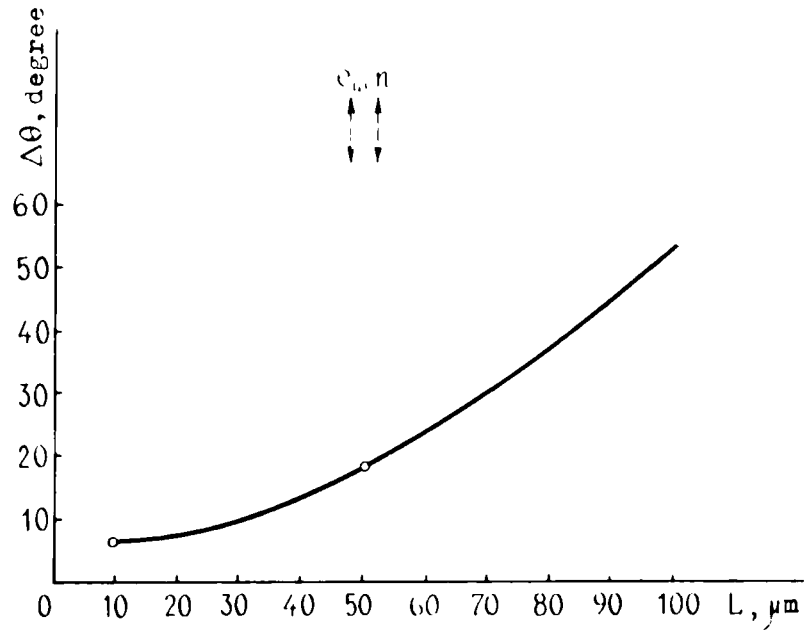

FIGURE 6 Dependence of the angular width of the SHG peaks on the cell thickness.

inside NLC) at 25°C and for $\Delta T_{\text{ph.m.}} = T_c - T_{\text{ph.m.}}$ ($T_{\text{ph.m.}}$ is the temperature of phase-matching at normal incidence, T_c is temperature of phase transition).

The estimates of the values of nonlinear susceptibilities $\chi^{(2)}$ in MBBA are shown in Column IV of Table III (the values are normalized to the value of $\chi^{(2)}$ for interaction I) and obtained from a general formula for $P_{2\omega}$ for the non-phase-matched SHG at the maximum of the Maker oscillation.[35] From the data for geometries 5 and 6 of Table I the recalculation from $P_{2\omega}$ to $\chi^{(2)}$ is done with respect to the components characterizing precisely the oe-e and oe-o interactions: $\chi^{(2)}_{332}$ and $\chi^{(2)}_{223}$, respectively, whose values are just given in the last two lines of Table III. As far as the sign of the components $\hat{\chi}^{(2)}$ is unknown, two possible values are given.

For the components $\chi^{(2)}_{331}$ and $\chi^{(2)}_{113}$ the values are the same, but with reverse signs for the sign "+" in the last two lines in Column III of Table II.

Reasoning from the data in Column IV of Table I, one can attempt as to reveal a crystallographic symmetry class which the oriented MBBA samples satisfy. The analysis shows that a most probable interpretation is possible within the three nonsentrosymmetric classes 1, m and 3. The first two classes describe biaxial crystals.

One can see from the obtained results that in the class m the SHG must be realized for the collinear wave interaction along the y axis (while at the inter-

TABLE I

I	II Geometry of experiment			III
	e_ω	n	$e_{2\omega}$	$P_{2\omega}$
1.				1.0
2.				0.5
3.				0.8
4.				2.9
5.				1.3
6.				223

Here e_ω, $e_{2\omega}$ are the unit vectors of the radiation polarization at SHG for pumping and signal, respectively; n is the NLC director orientation. In Column II the vectors $e_{\omega,2\omega}$ and n are given in the plane perpendicular to the vector k_ω.

TABLE II

I Type of geometry	II $\hat{\chi}^{(2)}$ Components for interaction along the x axis	III $\hat{\chi}^{(2)}$ Components for interaction along the y axis; "+" for $\varphi = \pi/2$ "−" for $\varphi = 3\pi/2$
1	(333)	(333)
2	(233)	(133)
3	(222)	(111)
4	(322)	(311)
5	$\frac{(322)}{2} + \frac{(333)}{2} - (332)$	$\frac{(311)}{2} + \frac{(333)}{2} \pm (331)$
6	$\frac{(222)}{2} + \frac{(233)}{2} - (223)$	$\frac{(111)}{2} + \frac{(133)}{2} \pm (113)$

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

TABLE III

	I Type of interaction	II l_{coh}, μ	III Possibility of phase-matching: With respect to angle θ ph.m.	III Possibility of phase-matching: With respect to temperature, ΔT ph.m., °C	IV $\chi^{(2)}_{exp} \equiv \chi^{(2)}_{(1)}$ $\chi^{(2)}_{(1)}$
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

Either upper or lower signs should be taken in Column IV for all interactions.

action along the x axis the SHG had to arise also in "forbidden" (zero) components of the tensor $\hat{\chi}^{(2)}$: $\chi^{(2)}_{233}$, $\chi^{(2)}_{222}$ and $\chi^{(2)}_{322}$). The SHG in "forbidden" $\chi^{(2)}_{133} \equiv \chi^{(2)}_{233}$ and $\chi^{(2)}_{331} = \chi^{(2)}_{322}$ had to be characteristic of the class 3 as well (see also next section point 3).

It makes sense to estimate the absolute value of $\chi^{(2)}$ for MBBA. For geometry 6 (the oe-o interaction) from the data of Table I (Column III) we obtain for $\chi^{(2)}$ (MBBA) $\simeq 0.06$: $\chi^{(2)}_{III}(SiO_2) \simeq 1 \cdot 10^{-10}$ CGSE (without corrections for scattering). The calculations showed that the curves of Figure 3, 4a, c correspond to Maker oscillations in case of non-phase-matched geometry, and Figure 4b—to those of phase-matched geometry of SHG. In inhomogeneously oriented samples the effective noncollinear SHG is possible due to strong scattering (the presence of the vector phase-matching). This may be typical of SHG even in comparatively good monodomain samples of NLC, particularly at the radiation focussing, and results in increasing both the angular and spectral curve widths for MBBA at SHG. In Figure 7 there are shown the calculated curves of vector phase-matching of SHG, both for the ee-o (a) and oe-o (b) interactions in MBBA.

DISCUSSION

It follows from the foregoing that the presence of SHG in the used oriented samples of the NLC MBBA is subject to no doubt. Moreover, such a noncentrosymmetry is not the result of only surface effects (the non-phase-matched SHG), but characterizes a volumetric state of LC (the presence of phase-matched interactions). Thus, one can confirm the noncentrosymmetry of oriented (planarly) textures of MBBA. This fact should be taken into account for the high-order nonlinear interactions in LC's when the cascade processes can play an important role.[36]

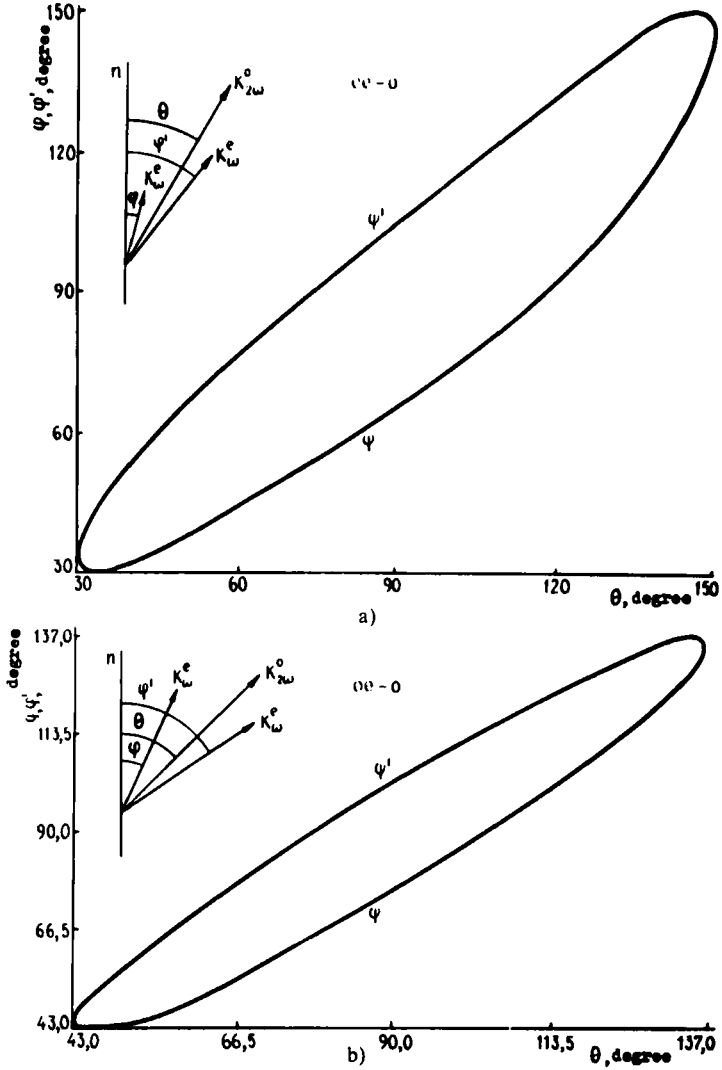

FIGURE 7 Calculation dependences for noncollinear SHG in MBBA for the ee-o (a) and oe-o (b) interactions.

Let's discuss the possible mechanisms, responsible for SHG in our experiment.

1) *The SHG should be directly related on symmetry of LC molecules.* Many NLC's consist of molecules with the symmetry "m" (optical biaxiality† and no center of inversion);[22-24] we may say that the shape of these molecules is rather a flat plank, than a rod. The z-axis is chosen to be parallel to the long axis of the molecules and the y-axis is perpendicular to the mirror plane (we consider the monocrystalline sample of LC). As in (Ref. 22, 24) we assume that in the oriented LC the mirror plane of molecule is perpendicular to the glass plates of LC's cell. In the case of ideal homogen, "freezed," orientation of LC's sample, the symmetry of molecule is transferred on the whole sample.[30] The absence of the inversion center in such systems is not connected with beforehead given conformation of the molecule, but is connected with the ordering of molecules during their interaction with each other and with other fields (ef. "pseudoscalar" LC's[31]).

2) *The laser field orientational effect* in itself usually cannot lead to a separate (polar) direction in LC, but affects the degree of orientation of the molecules along the direction if the latter exists.[12,51]

Such an effect is much more efficient for the nematic phase provided the following two conditions are fulfilled: the extraordinary polarization of the pumping wave and its oblique incidence relative to the director.[39] The both conditions can be fulfilled in our experiment even for the normal incidence (particularly for geometries 1–2, 5–6) owing to a possible orientation of the molecules at some angle to glass surfaces in a real sample of MBBA. In this case in geometry 1–2 the laser field will improve the degree of the NLC orientation (self-adjustment of nonoriented regions), while in the geometry 5–6 the laser field will deteriorate it.

The light-induced phenomena in the laser field are reduced not only to production of regions with different orientation due to the self-influence effects, but also to decomposition of the mesophase, in particular, the effects of the LC material polimerization are also possible. In this case complex irregular textures can be produced. Such factors must affect to a greater degree at long irradiation. One should take into account the influence of more slower processes of "natural ageing" of LC, for example, due to the hydrolysis of MBBA to its amin and aldehyde components,[40] the gumming effects. In this case T_c is also displaced.

Our results obtained for the SHG efficiency (Figures 1, 2) indicate exactly to a local reorientation of the MBBA molecules under the action of the laser field, and not to the formation of nonoriented regions or destruction of meso-

† Note, that the spontaneous Raman spectroscopy is not sensitive to LC's molecular optical biaxiality.[18]

phase. In geometry 6, which is most effective for SHG, the laser field leads to formation of intermediate orientation, therefore the value of $P_{2\omega}$ decreases. The pumping beam being displaced to a new place in LC, the signal must increase again, just as was observed. Sounding by low-powered continuous radiation the region which produced SHG, we really observed the reorientation of the LC molecules on the drop of the curve of Figure 2. On this account the appearance of the phase-matching peaks for the oo-o interaction, which approaches the ee-o one as a result of the molecule reorientation, is possible.

It is necessary also to take into account the possible effective rotation of the linear polarization of the produced radiation of SHG at its propagation in an anisotropic, moreover, statistically inhomogeneous medium due to the presence of a component of a field with orthogonal linear polarization. For the pumping wave the effects of nonlinear rotation of polarization take place, which we observed in independent experiments. This can provoke the relatively distinctless reproductivity of the results in different cells. At the absence of the output polarizer the variation of the value of $P_{2\omega}$ for this reason must not take place.†

The situation is complicated also by the processes connected with the LC material "natural ageing" which greatly increases in the presence of radiation and goes on even after switching off the radiation.

3) *Influence of medium inhomogeneities, both microscopic and macroscopic.* While in ideal homogeneous media for phased-matched SHG $P_{2\omega} \sim L^2$, where L is the thickness of a nonlinear material layer, in the case of inhomogeneous samples $P_{2\omega} \sim L$.[41] The dependence $P_{2\omega} \sim L^2$ may occur in statistically inhomogeneous media as well, but only for very small thicknesses ($L \leq \lambda / 2\pi n_{2\omega}$).[42] In non-phase-matched interactions the value of $P_{2\omega}$ is determined by the coherent length. In phase-matched SHG gathering of N molecules in groups with fixed orientation results in $P_{2\omega}$ increasing $N(\lambda / 2\pi)^3$ times at recalculation per one molecule. (For inhomogeneity sizes $l_{\text{inhom}} \leq \lambda / 2\pi\Delta n$ this is fulfilled for non-phase-matched SHG, too.[42] This increase is saturated at $l_{\text{inhom}} \sim \lambda / 2\pi$.

For longitudinal inhomogeneities (along L), which are particularly important in orientation of NLC by abrasion of glass substrates, there is the optimal thickness for SHG $l_{\text{opt}} \approx (3\lambda / 2^{\partial\Delta n} / \partial L)$.[43] For the oriented layer L of MBBA a rough estimate of the value of l_{opt} leads to the values of $l_{\text{opt}} \sim 14 - 40\ \mu$.

The mentioned dependences of $P_{2\omega}$ on the thickness agree qualitatively with those obtained in our experiment for MBBA.

However, the nonhomogeneity of the NLC samples must affect the value of $\hat{\chi}^{(2)}$ itself, which, besides, decreases as the orientation degree becomes worse

† An analogous effect may be exerted by flowing and the presence of impurities in LC.

(at heating of the sample or increasing of its thickness; this leads also to additional scattering of light).

Analyzing the influence of this important factor, it is possible to obtain the following. First, the angular distributions in SHG substantially change (appearance of modified conditions of phase-matching and increase of widths of the latter,[41,44] influence of superficial effects-see also Ref. 42; in particular, phase-matched SHG is possible in the types of interaction for which it is impossible in a homogeneous sample. Second, the SHG is possible in "forbidden" components of nonlinear susceptibility tensor with a comparable by value intensity.[45]

Finally, an optimal width of the NLC layer l_{opt} for SHG must exist.[46] The influence of all these factors, which manifest themselves differently in different samples of NLC, can account for the complex picture of angular and temperature dependences we obtained.

Note also, that a possibility of formation in NLC of biaxial regions (statical) which are of particular importance in a local laser experiment on SHG also varies angular and temperature characteristics of SHG in NLC.

4) *SHG stimulated by quadrupole electrical interaction* on the nonlinear susceptibility of a higher order ($P_i^{NL} \sim \chi^{(3)}_{ijj'e}(2\omega)$. $E_j \nabla_{j'} E_e$ is the account of internal molecular spatial dispersion.[35] For the "freezed" model of NLC (when the oriented LC layer symmetry elements similar to those of the individual molecule) the realized experimental geometry for the symmetry class "m" does not allow to separate those two mechanisms of SHG without additional discussion. That's why the research of quadrupole interaction for LC is of a special interest. In the second order (on field) of the peturbation theory, the polarization at the double frequency accounting the spatial dispersion is equal to:

$$P_i(2\omega,z) = L^2(\omega)L(2\omega)N[k_1^e i <\alpha_{ijj'e}> E_1^j E_1^{j'} \exp(-2ik_1 z) + ik_2^e <\alpha_{ijj'e}> E_2^j E_2^{j'} \exp(-2ik_2 z) + i(k_1^e + k_2^e) <\alpha_{ijj'e}> E_1^j E_2^{j'} + i(k_1^e - k_2^e) <\sigma_{ijj'e}> E_1^j E_2^{j'} \exp(-i(k_1 + k_2)z)] \quad (1)$$

Here $k_{1,2}$ and $E_{1,2}$ wave vectors and the amplitudes of two pumping waves, $L(\omega)$ is the acting field's factor. The hyperpolarizability molecular tensors $\hat{\alpha}$ and $\hat{\sigma}$ are valid to the equalities of symmetry, if they are out of the absorbing area:

$$\alpha_{ijj'e} + \alpha_{jij'e} + \alpha_{jj'ie} = 0,\ \sigma_{ijj'e} = -\sigma_{ij'je},\ \alpha_{ijj'e} = \alpha_{ij'je} \quad (2)$$

$< \ldots >$—is the orientational average. At the averaging according to Mayer-Saupe's famous distribution, 18 components of susceptibility tensor differ from zero†;[12]

---

† The systematic analysis of nonlinear susceptibilities require the conservation of terms in Mayer-Saupe's Hamiltonyan which describe the interaction of the following multipoles.

$$\chi^{(3)}_{iji'e}(2\omega) = \mathrm{N}L^2(\omega)L(2\omega)\langle\alpha_{iji'e}\rangle;$$

$$\chi_{1122} = \chi_{2211} = \chi_{1212} = \chi_{2121} = -\tfrac{1}{2}\chi_{2112} = -\tfrac{1}{2}\chi_{1221}$$
$$= \frac{N}{4}L^2(\omega)L(2\omega)[2(\alpha_{1122} + \alpha_{2211})\langle\cos^2\theta\rangle + (\alpha_{1133} + \alpha_{3311} + \alpha_{2233} + \alpha_{3322})\langle\sin^2\theta\rangle];$$

$$\chi_{1133} = \chi_{2233} = \chi_{1313} = \chi_{2323} = -\tfrac{1}{2}\chi_{3113} = -\tfrac{1}{2}\chi_{3223}$$
$$= \frac{N}{4}L^2(\omega)L(2\omega)[2(\alpha_{1133} + \alpha_{2233})\langle\cos^2\theta\rangle + (\alpha_{1122} + \alpha_{2211} + \alpha_{3311} + \alpha_{3322})\langle\sin^2\theta\rangle];$$

$$\chi_{3311} = \chi_{3322} = \chi_{3131} = \chi_{3232} = -\tfrac{1}{2}\chi_{1331} = -\tfrac{1}{2}\chi_{2332}$$
$$= \frac{N}{4}L^2(\omega)L(2\omega)[2(\alpha_{3311} + \alpha_{3322})\langle\cos^2\theta\rangle + (\alpha_{1122} + \alpha_{2211} + \alpha_{1133} + \alpha_{3311})\langle\sin^2\theta\rangle] \quad (3)$$

The fact, that some components of $\hat{\chi}^{(3)}(2\omega)$ are nonzero does not yet provide the possibility of high-frequency SHC (transverse) wave. This possibility cannot be realized in the isotropic phase; as to the nematic phase, its monoaxiality is the direct reason of the SHG. In collinear geometry ($k_\omega \| k_{2\omega}$) for example, it can be shown,[12] that the intensity of SHG $I_{2\omega}$ is proportional to the second power of the order parameter. For the phase-matched interaction (e.g. oe-o):

$$I_{2\omega} = \left[\frac{4\pi\omega}{c}\cdot\frac{k^o(\omega) + k^e(\omega)}{n^o(2\omega)}\right]^2 |\tilde{\chi}|^2 S^2 l^2 I_\omega^2 \quad (4)$$

where S is the order parameter of NLC, $\tilde{\chi} = N/2(\alpha_{1122} + \alpha_{2211} - \alpha_{1133} - \alpha_{2233})\sin\psi\cos\psi$ (ψ is the angle between Z-axis of NLC and $k_{2\omega}$). In our experiment $\psi = 90°$, therefore, the table's data of SHG cannot be explained by this mechanism.

5) *Note we assumed*, that the ideal planar LC's molecular orientation is (along the axis Z) parallel to the surface of the glass plates. But in real sample they can be oriented at a certain angle to the plate.[10] In this case the components combinations, which results in the SHG of the given experiment's geometry, (see the Table II), must be changed. Then the experimental data given in the Table III for $\hat{\chi}^{(2)}$ correspond to certain effective meanings of nonlinear susceptibility.

That's why SHG's possibility in our experiments, caused by internal molecular spatial dispersion, requires the additional discussion. However, the quadrupole electrical interaction appears small in NLC. Though they can be optically active[22,23] but the activity is not connected with the great value of internal molecular spatial dispersion,† as is aforementioned but with the ordering of

† In isotropic phase NLC's are not optically active.

molecules, which aren't enantiomorph. (e.g. in the calcite crystal, $\chi^{(3)}_{iii'e}(2\omega) \sim 10^{-17} \div 10^{-18}$ CGSE.[37]

6) *The influence of different defects*, static distortion and deformation in LC on SHG. In particular, the polar axis in NLC may be caused by the flexcelectric effect.[10] The fact, that the phase-matched SHG (it characterizes the volume interaction) was observed, makes this mechanism scarcely probable.

7) *"Natural ageing" of MBBA*, mentioned above, induced by chemical reasons, must affect equally all the types of interactions. Here we should like to emphasize the relaxation mechanism of "ageing," which also can account for the decrease in time of the SHG signal. In point of fact we mean the well-known effect for heavy-viscous microinhomogeneous media.[47]

For these liquids, described by the nonlocal relaxation theory, variation of properties can be observed, for example, immediately after their vacuum distillation and condensation on the substrates; returning of the properties of these liquids to equilibrium values is performed gradually and takes a certain period of time (a few days).[47] Similar processes must be characteristic of the NLC as well, especially in thin oriented layers immediately after their making (it is interesting that usually LC is purified precisely by means of distillation).

Note, that these processes are not equivalent to formation and resolution of disclinations in LC, since the disclinations cannot be even superficial;[10] in our case the volumetric SHG is meant. An analogous conclusion can be made also on the defects of the 180°-wall type in LC. The more so, as such textures are easily observable by means of usual optical methods. Such kinds of inhomogeneities in MBBA were really observed by us, but only near the phase transition in a heterogeneous region.

8) *The signal value of SHG is practically unchangeable at the additional purification* of the MBBA according to preliminary data. It shows the small contribution of impurities to SHG in our case. But this question is not a simple one. Let's discuss it in short.

The calculation of the values of LC's sample's macroscopic susceptibility $\hat{\chi}$ must be done by the equation $\hat{\chi} = N < \hat{\beta} >$, where N-is the number of molecules, and β-is molecular susceptibility. It can be shown (by analogy with 4) that if there is the absorption of one of the interaction waves, then the nonlinear polarization of the frequency 2ω is not zero.[38] This is connected with Kleinman's symmetry breaking law for the components $\beta^{(2)}_{ijj}$ in this case. For the oriented, e.g. along z, NLC the non-zero components are:

$$\chi^{(2)}_{xyz} = -\chi^{(2)}_{yxz} = \frac{N}{2} < P_2(\cos\theta) > (\beta^{(2)}_{xyz} - \beta^{(2)}_{yxz}) \tag{5}$$

Then we may have for the phase-matching interaction, an equation similar to (4). That's why in this case $I_{2\omega}$ will be zero in isotropic phase ($S = 0$), too.

CONCLUSIONS

The discussion given above indicates that regardless of the available several factors which can bring SHG in NLC, our experimental results yet indicate to the fact that the registered SHG in MBBA really is connected with non-zero nonlinear susceptibility of the second order $\chi^{(2)}$.

Although the registered value of $P_{2\omega}$ itself strongly depends on specific conditions of the experiment still the influence of different factors (which are nontrivial and need separate consideration) is quite controllable. The marked "instability" of the results is characteristic of such fine equilibrium systems as liquid crystals are.

The conclusions on noncentrosymmetry of oriented samples MBBA must be true, in general, for all NLC.

Arising of noncentrosymmetrical blocks may be characteristic of NLC which transmit different distortions, e.g. from alien molecules onto macroscopic regions whose sizes exceed substantially their intrinsic sizes.[10]

At availability of internal intensities in the NLC sample the mechanism of their formation may be of flexoelectrical nature, but this must give rise to the superficial SHG only.

The noncentrosymmetry must be characteristic of the other types of LC. Of most interest in this respect are smectical LC, particularly, hyral "C" smectics, since their ferroelectrical properties are known well. It was actually reported in Ref. 45 about studying of the temperature dependence $P_{2\omega}$ for LC DOBAMBC using the external constant electric field E^{0}. However, in this case the SHC must be mainly determined by the nonlinear polarization term proportional to $P_i^{NL} \sim \chi^{(3)}_{iil'e} E_i^{\omega} E_{i'}^{\omega} E_e^{0}$. Such a mechanism of SHG was recently observed in Ref. 52 for the nematic phase of LC 5CB, where for $\chi^{(3)}$ a value of the order of 10^{-12} CGSE was obtained.

The noncentrosymmetry of MBBA we demonstrated in our experiments makes it possible to explain the known smallness (whose reason is unknown so far) of the coefficient B in the Landau expansion for the thermodynamic potential in the region of phase transfer to isotropic liquid:[8] noncentrosymmetry of the medium must automatically tend the value of B to zero.[48] Moreover, at availability of local regions in MBBA with correlation of the NLC molecules, both in orientation and in the center-of-gravity position, and also at optical biaxiality of the samples (note, that the presence of biaxiality is quite enough even for local regions, most important for SHG), the coefficients A and C must be small.[49] Thus, a simple explanation is given for the recently discussed tricritical character of phase transition to NLC, in paticular, to MBBA.[50]

Acknowledgments

The authors are grateful to S. A. Akhmanov for support and valuable discussions, to B. Ya. Zeldovich and M. A. Nshanyan for useful discussion and to L. M. Dorozhkin assistance in obtaining some test results.

References

1. S. A. Pikin and V. L. Indenbom, *Usp. Fiz. Nauk*, **125,** 251 (1978).
2. Y. Chandrasekher, *Rep. Progr. Phys.*, **39,** 613 (1976).
3. A. N. Golubyatnikov, *Dokl. Akad. Nauk SSSR*, **240,** 293 (1978).
4. R. Alben, J. R. McColl and S. Shin, *Solid State Comm.*, **11,** 1081 (1972).
5. G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Mol. Phys.*, **30,** 1345 (1975); P. S. Flory and J. Leonard, *Am. Chem. Soc.*, **87,** 2102 (1965); A. Wulf and A. G. De Rocco, *Chem. Phys.*, **55,** 12 (1971).
6. P. I. Bos, P. Uklya, I. W. Doani and M. E. Neubert, *Mol. Cryst. Liq. Cryst.*, **40,** 773 (1977).
7. S. P. Straley, *Phys. Rev.*, **10A,** 1881, 1974.
8. V. L. Pokrovsky and E. I. Kats, *Zh. Eksp. Teor. Fiz.*, **73,** 774 (1977).
9. J. C. Parsons, *J. Chem. Phys.*, **67,** 5585 (1977); *Phys. Rev. Lett.*, **41,** 877 (1978).
10. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974.
11. R. Blinc and B. Zeks, *Soft modes in ferroelectrics and antiferroelectrics*, North-Holland Publishing Company, Amsterdam. Oxford American Eisevier Publishing Company, Inc. New York, 1974.
12. S. M. Arakelyan, G. A. Lyakhov and Yu. S. Chilingaryan, *Usp. Fiz. Nauk*, **131,** 3 (1980), Nonlinear Optics of liquid Crystals, Preprint KO-79-02 Erevan State University.
13. F. I. Fyodorov, *Optika i spektr.*, **6,** 377 (1969); E. L. Ivchenko, S. A. Permogorov and A. V. Celkin, *Pis'ma v JETF*, **28,** 649 (1978); **27,** 27 (1978); 573 (1978).
14. A. G. Khachaturyan, *Phys. Lett.*, **51A,** 103 (1975); *J. Phys. and Chem. Sol.*, **36,** 1055 (1975).
15. S. M. Arakelyan, L. E. Arushanyan, M. A. Nshanyan and Yu. S. Chilingaryan, *Fiz. Tverd. Tela*, **20,** 3131 (1978).
16. Faettis and B. Fronzoni, *Solid St. Comm.*, **25,** 1087 (1978).
17. J. D. Parsons, *Phys. Rev. Lett.*, **41,** 877 (1978).
18. Jen Shen, N. A. Clark, P. C. Pershan and E. B. Priestley, *Phys. Rev. Lett.*, **34,** 1552 (1973); *J. Chem Phys.*, **66,** 4635 (1977); *Mol. Cryst. Liq. Cryst.*, **23,** 369 (1973).
19. F. Volino, A. J. Dianoux and H. Hervet, *Mol. Cryst. Liqu. Cryst.*, **38,** 125 (1977).
20. J. P. Marterou and S. Prost, *Phys. Lett.*, **A66,** 218 (1978).
21. S. G. Dmitriev, *Zh. Eksp. Teor. Fiz.*, **61,** 2049 (1971); A. S. Vasilevskaya and A. S. Sonin, *Fiz. Tverd. Tela*, **21,** 196, 1979; A. N. Chuvirov and O. A. Skaldin, *Pis'ma Zh. Tekh. Fiz.*, **4,** 1314 (1978).
22. R. Williams, *Phys. Rev. Lett.*, **21,** 342 (1968); *J. Chem. Phys.*, **50,** 1324 (1969).
23. D. Meyerhofer, A. Sussman and R. Williams, *Appl. Phys.*, **43,** 3685 (1972).
24. H. J. Kimura, *Phys. Soc. of Japan*, **30,** 1273 (1971).
25. S. M. Arakelyan, G. L. Grigoryan, S. Ts. Nersisyan, M. A. Nshanyan and Yu. S. Chilingaryan, *Pis'ma Zh. Eksp. Teor. Fiz.*, **28,** 202 (1978).
26. A. N. Lachinov, A. N. Chuvirov and N. Kh. Gilmanova, *Zh. Tekh. Fiz.*, **50,** 189 (1980); *Kristallografiya*, **25,** 326 (1980).
27. L. G. Koreneva, V. F. Zolin and B. L. Davidov, *Molekularnie crystalli v nelineynoj optike*, Nauka; Moskva, 1975; J. Ducuing. *Proceedings of the international school of Physics "Enrico Fermi" course LXIV* ed. N. Bloembergen. Nonlinear Spectroscopy. Societa Italiana di Fisica, Bologna-Italy, 1977, p. 276.
28. J. Freund and P. M. Rentzepis, *Phys. Rev. Lett.*, **18,** 393 (1967); *Bull, Amer. Phys. Soc.*, **12,** 81 (1967); G. Durand and C. H. Lee, *C. R. Acad. Sci., Paris*, **B.264,** 1397 (1967). *Mol. Cryst.* **5,** 171 (1968); L. S. Goldenberg and S. H. Schur, *Appl. Phys. Lett.*, **14,** 306 (1969); *Radio Electr. Engin.*, **39,** 279 (1970); J. W. Shelton and Y. R. Shen, *Phys. Rev. Lett.*, **25,** 23 (1970): *Phys. Rev.* **A-5,** 1867 (1972).
29. M. V. Volkenstein, *Molekulyarnaya Optika*, Gostechizdat, Moskva, 1951.
30. L. D. Barron, *Nature*, **238,** 17 (1972).
31. Ya. B. Zeldovich, *JETP*, (*Journal eksperimentalnoy e teoreticheskoy Fiziki*), **67,** 2357 (1974). V. I. Makarov, *Pis'ma v JETP*, **26,** 169 (1977).
32. S. M. Arakelyan and Yu. S. Chilingaryan, *Interaction of Laser Radiation with Liquid Crystals*, Yerevan State University, Yerevan, 1980.
33. M. Okada and K. Takizawa, *Jap. J. Appl. Phys.*, **16,** 55 (1977).
34. M. Brunet-Germain, *C. R. Acad. Sci.*, **B271,** 1075 (1970).
35. F. Zernike and J. E. Midwinter, *Applied Nonlinear Optics*, New York-Sydney-Toronto-London, 1973.

36. S. A. Akhmanov, A. N. Dubovik, S. H. Saltiel, T. V. Tomov and V. G. Tunkin, *Pis'ma v JETP*, **20**, 264 (1974).
37. R. W. Terhune, P. D. Maker and S. M. Savage, *Phys. Rev. Lett.*, **8**, 404 (1962).
38. Y. Giordmaine, *Phys. Rev.*, **138**, A 1599 (1965).
39. B. Ya. Zeldovich, N. F. Pilipetskij, A. V. Sukhov and N. V. Tabiryan, *Pis'ma Zh. Eksp. Teor. Fiz.*, **31**, 287 (1980).
40. T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **25**, 509 (1970).
41. S. A. Akhmanov and A. S. Chirkin, *Statistical Phenomena in Nonlinear Optics, Izd.*, Moscow State University, M., 1971.
42. N. B. Baranova and B. Ya. Zeldovich, *Zh. Eksp. Teor. Fiz.*, **71**, 727 (1976); Preprint No 31, FIAN SSSR, M., 1976.
43. L. P. Malnik, N. N. Filonenko and A. I. Kholodnikh, *Kvantovaya Elektronika*, **6**, 25 (1979); *Izv. VUZov, Radiofizika*, **22**, 542 (1979).
44. A. A. Mayer, A. P. Sukhorukov and R. N. Kuz'min, *Pis'ma Zh. Eksp. Teor. Fiz.*, **29**, 30 (1979).
45. A. N. Vturin, V. P. Ermakov, B. I. Ostrovskij and V. F. Shabanov, Preprint IFSO-104F, Krasnoyarsk, 1979.
46. S. A. Akopyan, S. M. Arakelyan, R. V. Kochikyan, S. Ts. Nersisyan, and Yu. S. Chilingaryan, *Kvantovaya Elektronika*, **4**, 1441 (1977).
47. M. A. Isakovich, *Usp. Fiz. Nauk*, **129**, 531 (1979).
48. L. D. Landau, *Zh. Eksp. Teor. Fiz.*, **7**, 627 (1937).
49. Francis Hardou in, *The'se doct sci.*, Univ., Bordeaux, 1978.
50. P. H. Keys, *Phys. Lett.*, **67 A**, 132 (1978); *Phys. Rev. Lett.*, **42**, 722 (1979); M. A. Anisimov, V. M. Zaprudsky, V. M. Mamnitsky and E. L. Sorokin, *Pis'ma Zh. Eksp. Teor. Fiz.*, **30**, 523 (1979).
51. S. M. Arakelyan, N. V. Tabiryan and Yu. S. Chilingaryan, *Zh. Tekh. Fiz.*, **50**, 1328 (1980).
52. S. K. Saha and G. K. Wong, *Appl. Phys. Lett.*, **34**, 171, 423 (1979).