

Nonlinear optics of liquid crystals

S. M. Arakelyan, G. A. Lyakhov, and Yu. S. Chilingaryan

Erevan State University and M. V. Lomonosov Moscow State University
Usp. Fiz. Nauk 131, 3–44 (May 1980)

The results of theoretical and experimental studies of effects in the interaction of powerful laser radiation with liquid crystals (LC) are reviewed. Attention is drawn to two aspects of these studies: 1) use of LC materials in nonlinear optical devices (specifically, the nonlinear optics of LC); 2) the use of laser methods to study the LC state of matter (nonlinear spectroscopy of LC). Specific aspects of optical harmonic generation effects, induced Raman scattering, and the self-irradiation of powerful laser beams are discussed in detail. LC restructuring effects under the action of coherent radiation are described. The relation between the symmetry of the molecules forming the LC phase and the symmetry of macroscopic nonlinear susceptibilities is analyzed; a special role is reserved for the spatial dispersion of LC susceptibility, which has a bearing, in particular, on the possibility of generation of even optical harmonics and on the possibility of specific light self-action modes. Recent experiments on second-harmonic generation in nematic LC, on measurement of LC relaxation parameters in the pretransition range, and on the nonstationary self-focusing effect are described, as well as determination of higher elements of the orientation distribution function of LC molecules from induced-scattering characteristics.

PACS numbers: 78.20.Dj, 78.30.Cp, 42.65. – k, 42.60.He

CONTENTS

Introduction	245
1. Nonlinear optical susceptibilities of LC	247
a) Spatial dispersion of susceptibility	247
b) Symmetry of molecules and the macroscopic susceptibility of NLC	247
c) Second-harmonic generation and LC structure	248
d) The role of the statistics of the medium. Calculation of optical susceptibilities	250
e) Dependence of susceptibility on the structure of LC molecules. Comparison with molecular crystals	251
2. Linear and nonlinear optics of LC	252
a) Material equations	252
b) Wave interactions in media with periodic spiral structure	253
1) Linear optics of CLC	253
2) Third-harmonic generation and synchronism conditions in CLC	254
c) Third-harmonic generation in polycrystalline CLC specimens	255
d) Parametric interactions of light waves in LC	255
3. Nonlinear-optical methods for study of phase transitions. Measurement of higher distribution-function moments	256
a) Specifics of orientation effects in LC. The Kerr effect	256
b) Raman spectra and active Raman spectroscopy	258
1) Determination of distribution-function moments	258
2) Measurement of third-order nonlinear susceptibilities	259
c) Induced scattering	260
4. Self-action effects of strong radiation in LC	260
a) Self-focusing of light	261
1) Experimental observation. Stationary and nonstationary regimes	261
2) Self-focusing near a phase transition. Influence of SD of nonlinear susceptibility	262
b) Defocusing of light. The thermal-lens effect	262
c) Light-induced change in LC structure	263
1) Induction of line gratings in LC	263
2) Change in pitch of cholesteric structure in a traveling-wave field	263
3) Induction of cholesteric structure in NLC by the field of a spiral standing wave (SSW)	263
d) LC intraresonator nonlinear elements	264
Conclusion	265
References	266

INTRODUCTION

Nonlinear optical effects in liquid crystals (LC) are of interest for the physics of LC and for nonlinear optics. Use of nonlinear-optical methods to study these new materials yields important information on the structure of LC and on the nature of the intermolecular interaction that takes place in them, i. e., it allows us to

speak of the nonlinear spectroscopy of LC in the broadest sense. Further, the specifics of the nonlinear optical interactions in LC opens up opportunities for new LC applications in practical devices—frequency converters, tunable radiation generators, ultrasound generators. Here prospects are good for the creation of thin-film, low-power elements for control of laser radiation.

On the other hand, traditional nonlinear effects also present new features in LC, so that it is possible to establish the relation between the symmetry of the molecules and the macroscopic susceptibility of the medium in great detail and to begin a deliberate search, based on an analysis of matter at the molecular level,¹ for substances with record-high nonlinear susceptibilities among the LC.

The spatial dispersion (SD) of nonlinear susceptibility that is observed in LC^{2,3} becomes especially conspicuous in the phase-transition (PT) range; here also there are sharp changes in the relaxation times of orientational effects,^{2,4} so that it is possible to investigate the molecular aggregates that form.

Because of the extreme sensitivity of LC to the action of external fields, a powerful light wave changes the orientation of the molecules.¹⁾ Light-induced structural changes are reflected in all of the macroscopic properties of LC and are easily observed both in the mesophase^{5,6} and in the isotropic phase.⁷⁻¹⁰ However, the changes at optical frequencies are so fast that the LC molecule as a whole does not have time to respond to them¹⁴ (see also Refs. 11-13). Here the degree of alignment of the molecules is proportional not to the amplitude of the light-wave field, but to the intensity of the wave,¹⁰⁻¹³ i. e., already here we are dealing with a typically nonlinear optical effect.

In problems related to laser frequency conversion (harmonic generation, parametric processes), LC enable us to bring about synchronous interactions by methods that are not traditional for nonlinear optics—by compensating wave detuning with the reciprocal-lattice vector¹⁶; here it is possible for colliding as well as comoving waves to interact.¹⁷ Moreover, the very fact that nonlinear effects of various orders are observed (for example, second-harmonic generation) gives us valuable information on the symmetry of the LC molecules and their macroscopic susceptibility, which is manifested most simply precisely in nonlinear wave effects.^{15,16-19}

In the PT range, where the specifics of LC are most distinctly evident, nonlinear problems yield data on the higher moments of the orientation distribution function.²⁰⁻²¹

Active Raman scattering spectroscopy is especially effective in this area.²⁰⁻²³ We should also note the local nature of optical investigations in the PT range of the LC, i. e., the possibility of conducting an experiment with small volumes of matter, which, on the one hand, enables us to probe the nucleation processes of the new phase and, on the other, relaxes the homogeneity and temperature-stabilization requirements imposed on the medium and reduces the effects of extraneous factors (gravitational effects, etc.²⁴). This takes research of this kind out of the domain of the unique and makes it

much less time-consuming.

This review presents a generalization and critical analysis of studies published to date on the nonlinear optics of LC. Sections 1, 2, and 4 emphasize the novel aspects that LC bring into nonlinear optics. Section 3 [see also subsections (b) and (c) of Sec. 1] discusses a second aspect: use of the methods of nonlinear spectroscopy to obtain physical information on LC, especially on the PT range. For all practical purposes, the literature on linear LC optics does not figure here, and is brought in only in connection with problems of nonlinear optics (Sec. 2).

The range of problems discussed does not include those with a direct bearing on the generation of laser radiation in liquid-crystal matter, although already today we may speak of realistic prospects not only from the standpoint of miniaturization of these elements, but also from the standpoint of the purely physical possibilities that open up, such as lowering of the lasing threshold, broad tuning ranges, and variation of radiation parameters.^{25-27,2)} In Sec. 4 [subsection (d)] we shall discuss only intracavity LC nonlinear elements.

Before proceeding with the actual exposition of the material, let us briefly discuss the classification of LC.

LC are organic substances with long anisotropic molecules^{2,4,28-31}; on the transition from the solid to the liquid phase, they pass through an intermediate state—the mesophase, in which the molecules are disposed in a certain order and, consequently, the mechanical, optical and other properties are anisotropic. The molecules of LC are characterized by strong anisotropy of electron polarizability.

LC are divided into several groups on the basis of structural symmetry. The most thoroughly studied group is that of thermotropic LC: nematic (NLC), cholesteric (CLC), and smectic (SLC). NLC are characterized by long-range orientational order and full freedom of displacement of the centers of gravity of the individual molecules in space. CLC can be regarded as a variety of NLC: locally (at distances of the order of a molecular length), they have all the properties of NLC (orientational order is present and translational order absent). CLC are formed by substances with optically active molecules, whose asymmetry results in twisting of the LC's structure. The axis of preferred orientation of the molecules (the director) varies from point to point; in an ideal CLC, the director \mathbf{n} depends on only one coordinate: $n_x = \cos(qz + \varphi)$, $n_y = \sin(qz + \varphi)$, $n_z = 0$. Thus, the CLC has a spiral structure with a spatial period $p = 2\pi/q$ (if the directions $+\mathbf{n}$ and $-\mathbf{n}$ are physically equivalent); usually $p \sim 10^3 - 10^4$ Å, i. e., CLC can reflect visible radiation efficiently.

For SLC, one-dimensional translational order is characteristic in addition to orientational order. SLC are structurally most similar to solid crystals, so that in substances that are capable of forming NLC and SLC

¹⁾The effect in which LC are reoriented under exposure to laser radiation has been used, for example in Ref. 5, to obtain reversible records with high spatial resolution in the irradiated layer.

²⁾Compare also with Ref. 119.

the sequence of phase changes as the temperature decreases is as follows: IL-NLC-SLC-solid crystal.

Although they are the most widespread, the concepts outlined above concerning LC symmetry are quite crude and can serve only as a first approximation to the real structure of LC. Noncentral symmetry and optical biaxiality^{15,32-36} and the optical activity³⁷⁻³⁹ of NLC have recently been discussed. We shall also return to these problems below.

1. NONLINEAR OPTICAL SUSCEPTIBILITIES OF LC

The history of research on the nonlinear susceptibilities of LC at optical frequencies spans little more than a decade; much less is known concerning the nonlinear properties of LC than of the analogous properties in the gaseous, liquid, and solid states. The complexity of interpreting optical experiments with LC manifests itself in the fact that it is practically always necessary to take into account simultaneously inhomogeneity, statistics, spatial dispersion, and the uncertain symmetry of the medium, in contrast, say, to the case of solid crystals, in which isolation of any of these factors normally presents no difficulty. However, even the few results obtained thus far—and, in our view, this pertains in particular to results in second-harmonic generation in NLC—though they have not yet given us final answers to certain problems of LC physics, enable us in many cases to restate these problems in new formulations and more broadly.

a) Spatial dispersion of susceptibility

The ground state of LC is inhomogeneous: it is unstable with respect to breakdown into domains.⁴⁰ In this case, the Landau expansion for the free-energy density also contains derivatives of the order parameter with respect to the coordinates.^{2,3} This spatial inhomogeneity asserts itself in decisive fashion in the nonlinear optical properties of LC. Allowance for spatial dispersion (SD)—the nonlocal spatial coupling between polarization and field^{41,42}—for a homogeneous medium is essential if we are dealing with an inhomogeneous field; if the system consists of many particles, it is, generally speaking, necessary to consider the inhomogeneity of the field both within the particle and at lengths of the order of the distances between particles. In the former case, it is necessary to include higher multipoles along with the dipole moment of the particle. However, there are frequent situations in which the field inhomogeneity within a single molecule (the intramolecular SD) can be neglected and the dipole approximation can be used for the single molecule.⁴³ It is the “collective” SD effects which are nonvanishing in this case, that are important for LC.

With allowance for SD, the susceptibility of the medium depends on the wave vector \mathbf{k} of the light wave: $\hat{\chi} = \hat{\chi}(\mathbf{k}, \omega)$. This relation is important when $|\mathbf{k}|L_{or} \gtrsim 1$, where L_{or} is the characteristic scale of the particle interaction (orientation length). In NLC, it can be assumed that L_{or} is of the order of the dimensions of the regions of spontaneous molecular orientation or the dimensions of the domains, which may greatly exceed

k^{-1} for the visible region.

In harmonic generation and parametric processes, allowance for SD lets $\chi_{ijk}^{(2)}, \chi_{ijk}^{(3)}, \dots$ remain as tensors of third, fourth, etc., rank, but the vectors $\mathbf{k}_1, \mathbf{k}_2, \dots$ are “external” parameters with respect to the crystals (like the external applied fields), so that symmetry transformations of the crystal do not affect them.⁴³ The result is that the symmetry properties of $\chi_{ijk}^{(2)}, \chi_{ijk}^{(3)}$ are quite different when SD is considered. For weak SD, $\chi_{ijk}^{(2)}$ can be expanded in series in \mathbf{k} :

$$\chi_{ijk}(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2) = \chi_{ijk}^{(0)}(\omega_1, \omega_2) + \chi_{ijkl}^{(1)}(\omega_1, \omega_2)k_l + \chi_{ijkl}^{(2)}(\omega_1, \omega_2)k_l k_m + \dots$$

Even in the presence of an inversion center, this tensor may be nonzero: in this case $\chi_{ijk}^{(0)} = 0$ but $\chi_{ijkl}^{(1,2)} \neq 0$ and the latter do not depend on the external parameters \mathbf{k} , E , and H and their properties are determined by the symmetry of the crystal.

Structural periodicity must also be taken into account in CLC. For crystals characterized by a system of reciprocal-lattice vectors \mathbf{q} , the susceptibility (for example, of second order) may be represented in the form⁴³

$$\chi_{ijk}^{(2)}(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \omega_1, \omega_2) = \sum \chi_{ijk}^{(2)}(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2) \delta(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2 - \mathbf{q}).$$

Generally speaking, the terms $\chi_{ijk}^{(2)}(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2)$ with $\mathbf{q} \neq 0$ are not small compared to $\chi_{ijk}^{(0)}(\mathbf{k}_1, \omega_1, \mathbf{k}_2, \omega_2)$. For CLC, $q = 2\pi/p$, where p is the pitch of the spiral, which is easily varied over a wide range, so that it is necessary here to take the inhomogeneity of the specimen's structure into account.

b) Symmetry of molecules and the macroscopic susceptibility of NLC

Without touching upon the general properties of LC symmetry space groups (see, for example, Ref. 44), we shall confine ourselves to important particular cases that must be taken into account in specific nonlinear transformations.

Here the main problem is the relation between the macroscopic susceptibilities and the symmetry of the LC's molecules. This relation is, of course, determined by the orientation of the LC molecules and must be described statistically; this approach will be examined in subsection 4. Here, however, we shall discuss certain qualitative results on the assumption that the LC is an ideally oriented system (a single LC).

The nonlinear susceptibility can be presented as the sum of symmetric and antisymmetric tensor components (see, for example, Ref. 18). In a square-law medium, the antisymmetric part describes the difference, usually small, between the effects of the fields $E_1(\omega_1)$ and $E_2(\omega_2)$ on the medium as compared to that of the fields $E_1(\omega_2)$ and $E_2(\omega_1)$, and the antisymmetric susceptibility $A_{ijk}^{(2)}$ is much smaller than the symmetric one $S_{ijk}^{(2)}$. But in an isotropic medium, where $S_{ijk}^{(2)} \equiv 0$, the antisymmetric part of the tensor may prove to be the principal source of nonlinear effects.^{1,45} An example of such a medium is an isotropic solution of optically

active³⁾ molecules, in which it is possible to obtain sum and difference frequencies.⁴⁵

Further, the antisymmetric part of the nonlinear susceptibility may become nonzero (in a solution of molecules without an inversion center) when there is absorption at one of the interacting frequencies; in this case the well-known symmetry relations for the tensor components of the susceptibilities are not satisfied.¹⁶ This LC problem is of independent interest in connection with the generation of tunable laser radiation using dyes in LC matrices.²⁵⁻²⁷

Thus, three-frequency nonlinear interactions are made possible by the tensor $A_{i\mu}^{(2)}$ even in the isotropic phase of LC formed from optically active (OA) molecules. However, studies in the mesophase are of the greatest interest, and it is these that we shall discuss now.

The problem of the symmetry of NLC molecules has recently been under intensive discussion in the literature. It now seems to have been established that NLC molecules have shapes closer to a flat strip than to a rod, an indication that they are optically biaxial.^{34-36,46} However, the question as to the presence or absence of an inversion center in these molecules is more important. Here we are actually concerned with whether the ends of the molecules can be distinguished physically: are the directions (+n) and (-n) of the director equivalent or not in the LC?

There are several experimental results on the behavior of NLC in constant magnetic fields (magneto-optical) activity and the linear electrooptical effect; in the latter case $F \sim \chi_{ij\mu}^{(2)} E_i^* E_j E_\mu^0$ where E_μ^0 is the constant field) that point to the conclusion that there is no inversion center in the NLC molecule [in particular, in the case of *p*-azoxyanisole (PAA)³²]. Good agreement is obtained here between theory and experiment if it is assumed that the PAA molecule has symmetry *m* (one reflection plane)³³ (Fig. 1a). Apparently, many liquid crystals consist of molecules with this symmetry or the higher symmetry *mm2*.³³ All such molecules lack an inversion center, but each has one (*m*) or two (*mm2*) reflection planes; these molecules are nonenantiomorphic, i. e., their specular reflections can be superposed.

Molecules with this symmetry do not exhibit OA in isotropic liquids, but it has long been known⁴⁷ that OA may appear in crystals of *m* or *mm2* symmetry. A generally erroneous statement often encountered in the literature has it that the appearance of OA requires that neither a center of symmetry nor a reflection plane be present. A good illustrative example of OA for the molecule of water H₂O is given in Ref. 48. The H₂O molecule (symmetry *mm2*) (Fig. 1b) can be viewed along a certain direction k_1 as part of a spiral, say a left-handed spiral (the direction k_1 lies in none of the

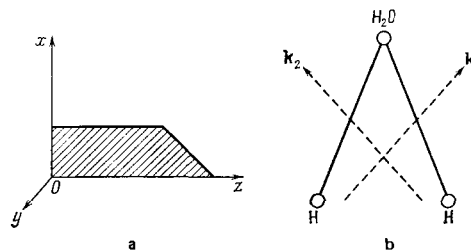


FIG. 1. a) Schematic representation of molecule of symmetry class *m* (the *z* axis corresponds to the long axis of the molecule);³³ schematic representation of H₂O molecule (symmetry class *mm2*).

planes of symmetry). There obviously exists another direction k_2 for which this molecule looks like part of a right-handed spiral, so that OA can, in principle, appear in a system with oriented water molecules. Although this example of OA is highly artificial, it illustrates the situation nicely for LC in which OA and the linear electrooptical effect in a PAA specimen oriented by a constant magnetic field were both observed experimentally³² and explained theoretically.³³ We stress once again the role of orientation: OA in these substances is determined not simply by the disposition of the atoms in the molecule, but basically by the ordering of the molecules as they interact with one another and with external fields.³⁸

Physical differentiability of the director directions (+n) and (-n) when the molecule has a constant dipole moment should result in the appearance of ferroelectric properties in an oriented LC.^{36,44,49,54,4)}

In a system as subtly balanced as the LC, it is not always possible to give a straightforward interpretation of observed effects solely on the basis of molecular symmetry: other significant factors are defects and grains, especially at the boundary of the specimen, static distortions and strains in single crystals (the flexoelectric effect, for example, may result in the appearance of a polar axis), and various dynamic properties of the LC, as well as the purity of the specimens studied.^{2,4,50,51} It is for these reasons that the question of LC symmetry is not yet fully resolved. Studies of LC symmetry by the methods of nonlinear optics become highly important in this context; in particular, the possibility of second-harmonic generation (SHG), which can be brought about in the dipole approximation only in noncentrally-symmetric media, yields important information on local molecular ordering and on the nature of the molecular interaction in LC, and is in many cases the most convenient method of establishing symmetry.¹⁹

c) Second-harmonic generation and LC structure

Cholesteryl-2-(2-ethoxy)-ethyl carbonate was investigated in the first experimental study to observe SHG

³⁾The coincidence of the conditions for optical activity and for nonlinear effects on quadratic susceptibility can also be traced in the corresponding terms of the free energy $F: \gamma_{ij\mu}^{(2)} E_i^* E_j k_\mu$ and $\chi_{ij\mu}^{(2)} E_i^* E_j E_\mu$.

⁴⁾In this case, we may expect the LC to develop a helicoidal structure of the cholesteric type, which has apparently been observed in *N-p*-methoxybenzylidene)-*p*-butylaniline (MBBA).^{37,39} (See Refs. 128,129 for generation of harmonics in ferroelectric LC.)

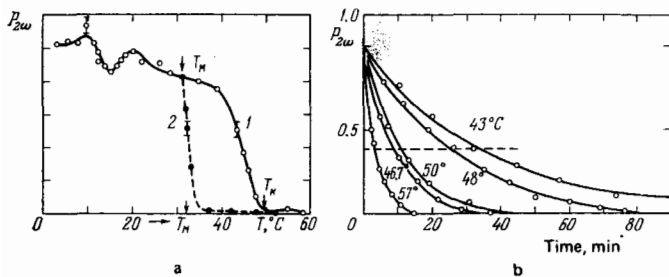


FIG. 2. a) SHG power vs. temperature for the CLC 2-(2-ethoxy) ethyl carbonate⁵³ (1—for one specimen in the case of fast temperature change; 2—for other specimens with temperature stabilized over 18 hours; T_K is the temperature of the "cholesteric phase-isotropic phase" transition; T_M is the melting point); b) $P_{2\omega}$ as a function of time for various specimens at fixed temperatures (the level e^{-1} corresponds to the melting time of small crystals of the solid CLC phase).

in LC.⁵² Observation of the second harmonic in two other LC—cholesteryl-2-(methoxyethoxy)-ethyl carbonate and cholesteryl-2-(2-butoxyethoxy)ethyl carbonate—was also reported in the same paper. The signal at the doubled frequency was recorded both in thick cells and in oriented LC films; the effect was related in Ref. 52 to orientation of the molecules within randomly disposed "swarms," which eliminates the inversion center.

It was concluded in later studies⁵³ that the second-harmonic signal is absent in the LC mesophase. In an analysis of the experiment of Ref. 52, it was concluded that the second-harmonic signal was the result of generation in minute crystals of solid-phase matter suspended in the interior of the specimen; it was also concluded that the orientation of the LC does not influence SHG.

The double-frequency signal vanished when the temperature was raised above T_K ^{52,53} (Fig. 2); however, when the specimen was cooled it did not reappear even at $T < T_K$, although it is known that the transition of an LC to an isotropic liquid is reversible; nor was SHG observed in other LC substances, specifically nematic PAA oriented by rubbing the backing or by a 1.5 kV electric field. It was concluded on this basis in Ref. 53 that the central symmetry of the mesomorphic LC phase is compensated as in ordinary liquids.

Similar conclusions were drawn in Refs. 16 and 72, which report studies of various LC mixtures.

Thus, the most widely held opinion is that three-frequency nonlinear interactions in the mesomorphic phases of nematic LC are anomalously small, since their internal structure is inversely symmetric. It follows from the results of subsection (b) of Sec. 1, however, that second-order nonlinear susceptibility may be quite high in well-oriented single LC. The moderate conversion efficiency in LC SHG that was observed in the studies cited, and the absence of confirmed reports of SHG, can be explained on the one hand by the use of unoriented LC layers and, on the other, by the absence of synchronous wave interaction in the single specimens, which would, of course, require special adjustment of the experimental geometry, and, finally, by the fact that the small thickness of these cells ($\leq 100 \mu\text{m}$) means a very low signal level, which requires a sensitive registration system. Furthermore, analysis

of the molecular compositions of the LC that have been studied thus far shows that actually "random" LC were investigated, which would have to be inefficient in nonlinear optics. The situation here recalls the early stages in the development of the nonlinear optics of ordinary crystals: the first SHG experiments were performed in a quartz crystal, and quartz is far from the most suitable material for SHG (lack of synchronism and inadequate conversion efficiency).¹⁸

Let us now turn to recent experimental data on SHG in an MBBA NLC,¹⁵ which yielded the first estimates of the second-order nonlinear susceptibility tensor components.

SHG was obtained in homogeneous (chemically pure) MBBA NLC cells about $10 \mu\text{m}$ thick for nonsynchronous interaction and several tens of microns thick for synchronous interaction (the specimens were oriented by rubbing the glass backing) in the field of single-mode Q-switched YA1G:Nd³⁺ laser ($\lambda = 1.06 \mu\text{m}$); the power density of the radiation in the cell was several GW/cm^2 . A recording system based on a photomultiplier (PM) ensured a sensitivity threshold at the single-photoelectron level at $\lambda = 0.53 \mu\text{m}$. Temperature synchronism at 90° was found to be possible for synchronous SHG (the temperature in the thermostat was stabilized to within 0.1°C).

The angular and spectral widths of the signal recorded from the cell with the NLC (after subtraction of the background) was typical for SHG. A collinear SHG geometry was realized in the experiment; the tensor components $\chi_{ijk}^{(2)}$ measured in the process appear in Table I. The absolute value of $\chi_{333}^{(2)}$ for MBBA was obtained from measurements referred to the susceptibility of quartz $\chi_{333}^{(2)} = 2 \cdot 10^{-10}$ cgs esu.

The signal power $P_{2\omega}$ at the doubled frequency dropped off significantly in the unoriented MBBA specimen and in its isotropic phase, to values at the limit of detection of the instruments. In the solid phase, the value is comparable to the $P_{2\omega}$ for synchronous generation in the nematic phase; no detailed studies were made here.

Thus, the level of the recorded signal in Ref. 15 depended strongly on the degree of orientation of the NLC molecules: higher efficiency would be expected for orientation by a constant magnetic field. Noticeable SHG is also possible in the unoriented NLC if the dimensions

TABLE I. Second-harmonic generation in an MBBA nematic liquid crystal.¹⁵

Type of interaction	Components of $\hat{\chi}^{(2)}$ for interaction along x axis	Components for interaction along y axis: "+" for $\varphi = \pi/2$, "-" for $\varphi = \pi - 3/2$	Experimental values of $\chi_{ijk}^{(2)}$ μm	$\chi_{ijk}^{(2)}$ μm	Synchronism possibility: Angle Temperature	Nonvanishing components in class <i>m</i>		
						Interaction along x axis	Interaction along y axis: "+" for $\varphi = \pi/2$, "-" for $\varphi = \pi - 3/2$	
ee-e	(333)	(333)	1	0.9	-	-	(333)	(333)
ee-o	(233)	(133)	0	1.6	+	+	0	(133)
oo-e	(322)	(311)	0.05	0.5	-	-	(322)	(311)
oo-o	(222)	(111)	0	2.5	-	-	0	(111)
oe-e	$\frac{(322) + (333)}{2}$	$\frac{(311) + (333)}{2}$	0	0.6	-	-	$\frac{(322) + (333)}{2}$	$\frac{(311) + (333)}{2}$
	- (332)	\pm (331)						\pm (331)
oe-o	$\frac{(223) - (222)}{2}$	$\frac{(111) + (133)}{2}$	0.22	7.5	+	+	(223)	$\frac{(111) + (133)}{2}$
	- (233)	\pm (131)						\pm (131)

of the spontaneous-orientation regions are comparable to the wavelength. This must be taken into account in analyzing higher-order interactions, when cascade processes may become important. The presence of synchronism indicates that the generation is of bulk nature, which makes a flexoelectric effect improbable.^{2,4} When the thickness *l* of the NLC layer was increased (or the temperature was raised), in which case the degree of homogeneous orientation of the molecules dropped (an effect of the statistics of the medium),⁵ P_2 decreased; this explains the comparatively small gain as compared to nonsynchronous generation and implies an optimum thickness of the cell with the NLC ($l_{\text{opt}} \sim 18 \mu\text{m}$ in Ref. 15) (Fig. 3). There was practically no change in signal level on further purification of the LC, so that impurities would appear to play no insignificant role.

In Ref. 15, SHG due to electric quadrupole interaction ($P_i^{\text{nl}} \sim \chi_{ijkl}^{(3)} E_j \nabla_k E_l$) was prohibited by the geometry of the experiment. However, a possible inclination of the molecules to the backing surfaces in oriented LC specimens⁴ must be borne in mind.⁶ But also in this case the quadrupole SHG mechanism is still weak in NLC: even though they may exhibit optical activity, it is due not to a large intramolecular spatial dispersion (the isotropic phase of an NLC is optically inactive), but to ordering of the molecules resulting from their interaction with the external fields or with each other in the nematic phase (in a calcite crystal, for example, $\hat{\chi}^{(3)}(2\omega) \sim 10^{-17} - 10^{-18}$ cgs esu).⁷⁵

In addition, a change in the structure of the LC (either at the molecular level or in macroscopic regions) in the laser field (Kerr effect, light pressure, heat effects) may play a certain role in SHG. These processes may influence the degree of orientation of the molecules along some distinguished polar direction in the LC. However, light-induced effects are evidently incapable of creating a polar direction in an LC. The only vector

in the light field that could be responsible for this effect would be the vector $\mathbf{E} \times \mathbf{H}$ (compare with Refs. 56, 15), but a simple phenomenological analysis within the framework of the mechanisms generally accepted for the interaction of electromagnetic fields with LC (see also Ref. 83) indicates that it need not be considered in SHG analysis.

The above discussion suggests that the SHG of Ref. 15 was directly related to the symmetry of the oriented NLC's molecules, many of which, as we noted above, can be assigned symmetry class *m*. The nonzero susceptibility components for this class are also given in Table I.

Further hypotheses are required to explain the results fully (last two lines of Table I). In particular, it is necessary to assume for the interaction along the *x* axis (second column) that Kleinmann's symmetry rule¹⁸ for the components $\chi_{ijk}^{(2)}$ is violated; then $\chi_{332}^{(2)} \neq 0$.

We note in conclusion that inferences as to the symmetry of NLC molecules that follow from SHG can also be applied to other types of LC. The extension to the case of CLC is obvious (the CLC can be represented as a system of layers of an oriented nematic with the directors in each layer rotated with respect to one another²), and SHG should be possible in SLC because their ferroelectric properties are well known.^{44,49,51,54,7)}

d) The role of the statistics of the medium. Calculation of optical susceptibilities

It was assumed for purposes of the above discussion that the LC were ideally oriented, i. e., that the properties of the medium as a whole were identical to the properties of the single molecule ("frozen" LC). In reality, however, the coupling of these properties is of statistical nature. To find the average values of the nonlinear parameters, it is necessary to average over the various orientations of the molecules.

In principle, this procedure should be analogous to

⁵⁾This results in additional scattering of the light.

⁶⁾The experimental values of $\chi_{ijk}^{(2)}$ given in Table I should then correspond to certain effective values of the nonlinear susceptibility.

⁷⁾A recently published paper¹²⁰ reported measurements of the temperature dependence of SHG in the ferroelectric "C"-smectic DOBAMBTs placed in a constant electric field.

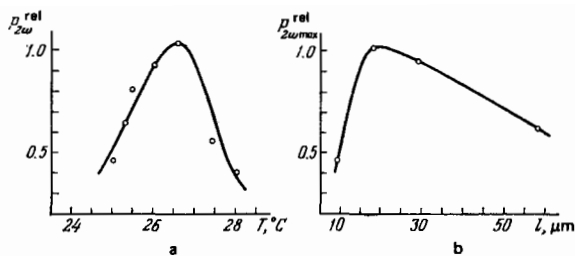


FIG. 3. Curve of temperature synchronism for SHG in MBBA NLC (cell thickness $l=18 \mu\text{m}$) (a) and dependence of power $P_{2\omega}^{\text{rel}}$ on l at synchronism maximum (b) for $oe-o$ interaction.¹⁵

that used in nonlinear optics.⁵⁵ However, the problem is more complex for LC, since the orientation-order parameter is a tensor quantity. To find the average values, it is necessary to derive equations connecting the anisotropic macroscopic parameters of a system of structural elements with the microscopic parameters of the individual elements and with the structure parameters.²¹ The structure of the mesophase is given concrete form by the statistical distributions of the centers of gravity and orientations of the molecules; the result of averaging depends on the hypotheses as to the symmetry of the molecular interaction. The assumptions made above concerning the symmetry of NLC molecules have far-reaching implications: the presence of an intrinsic dipole moment of the molecules changes the statistical distribution functions in the mesophase.⁴⁴ If the medium as a whole has an inversion center (unoriented LC or their isotropic phase), this does not necessarily mean the absence of nonlinear effects due to quadratic susceptibility (and to even susceptibilities in general). In this case $\langle \chi_{ijk}^{(2)} \rangle = 0$, but the intensity of nonlinear scattering is proportional to the two-point susceptibility correlator $\langle \chi_{i\mu}^{(2)}(1) \chi_{i\mu}^{(2)}(2) \rangle$,^{52,55} which is nonzero in NLC at distances of the order of the domain size or at least at distances of the order of the effective range of the intermolecular forces; near a PT, it may be comparable to an optical wavelength. In the latter case (microscopically inhomogeneous medium), study of SGH yields information on the nonlinearity of individual molecules or ensembles of molecules. But if the size of the spontaneous-orientation region is greater than the optical wavelength, the medium becomes macroscopically inhomogeneous, and the solution of this problem is similar to the analysis of nonlinear effects in crystalline powders.⁵⁵

In the presence of constant fields, it is also necessary to consider orientational in addition to electron nonlinearity, since its contribution is especially large in organic molecules with large dipole moments.⁵⁷ Here the analysis can retrace the procedure used in analysis of SHG in gases, liquids, and centrally symmetric crystals in external fields.⁵⁷ The anisotropy of the internal field must also be taken into account for LC.²¹

e) Dependence of susceptibility on the structure of LC molecules. Comparison with molecular crystals

It is now usually assumed that dispersion (van der Waals) attractive forces between molecules and steric repulsive forces play a decisive role in the formation

of the LC state,⁴ and for this reason that nonlinear effects in LC should be attributed to covalent rather than to ionic crystals (compare with Refs. 1, 19). The presence of a conjugation chain (alternation of single and double chemical bonds) along the molecule increases the longitudinal component of molecular polarizability, but the shape of the terminal groups of the molecule is essential: lengthening of the terminal group lowers the polarizability anisotropy. Further, the dipole moment of a conjugated molecule is associated with its electron-donor and electron-acceptor substituents, so that the presence and optimum positioning of the latter is among the important criteria in the search for substances with high nonlinear susceptibility.

For all practical purposes, no deliberate search for LC with high nonlinearity has as yet been mounted. There is hope in the situation that obtains in organic systems with conjugate bonds, e.g., in molecular crystals, which come closest in their structure to LC. Comparison with these crystals indicates the direction in which the search for effective materials for nonlinear optics among LC should proceed. Below we shall for the most part follow the ideas developed in Refs. 1, 19, and 58.

The high nonlinear susceptibility $\hat{\chi}$ of molecular crystals does not result solely from their high linear polarizability, as is the case for inorganic crystals, i.e., Miller's rule is not satisfied for them.⁵⁹ It is determined basically by an excited state of the molecule with intramolecular charge transfer (ICT) along a conjugate-bond system. A known condition for the existence of ICT is the presence of a conjugate-bond system and acceptor substituents (ICT is strongest when donors are present in addition to acceptors).

The compounds listed in Table II can be divided into two classes. $P_2 \geq 10$ for the first and $P_2 \leq 5$ for the second. All compounds belonging to the first class have acceptor groups associated with a conjugate-bond system, i.e., they possess ICT. Compounds 12 and 13, which do not have an extended system of π bonds do have donors and acceptors, are exceptions. ICT is impossible in compounds of the second class, in com-

TABLE II. Second-harmonic power of neodymium laser in molecular-crystal powders.¹

Chemical compound	$P_{2\omega}^{\text{rel}}$	Acceptors (conjugated)	Chemical compound	$P_{2\omega}^{\text{rel}}$	Acceptors (conjugated)
1. <i>m</i> -Nitroaniline	50	-NO ₂	14. <i>m</i> -Aminophenol	0.5	--
2. Anesthesin	30	-COOH	15. Trihydroxybenzene (symmetric)	0.5	--
3. <i>m</i> -Nitrobenzaldehyde	35	{ -HCO -NO ₂	16. <i>o</i> -Nitrobenzaldehyde	3	--
4. <i>p</i> -Nitrobenzaldehyde	40	{ -HCO -NO ₂	17. Picric acid	5	--
5. <i>m</i> -Aminobenzoic acid	10	-COOH	18. Amino acids	1	--
6. Phthalic anhydride	15	>CO	19. Hippuric acid	3	--
7. 5-Nitouracil	100	-NO ₂	20. Tartaric acid	1	--
8. 5-Iodouracil	20	>CO	21. 1,8-Dinitronaphthalene	0.5	--
9. Barbitol sodium	25	>CO	22. Triphenylbenzene (symmetric)	0.5	--
10. 5-Nitrophenol	15	-NO ₂	23. Veronal	1-2	--
11. <i>p</i> -Hydroxybenzoic acid methyl ester	10	-CO ₂ (CH ₃)	24. <i>N-p</i> -methylbenzoylacetylacetamide	1	--
12. Urea (carbamide)	10-15	--	25. 3-Aminoquinoline	2-5	--
13. Nitroguanidine	20	--	26. Acetamide	2.5	--
			27. Purine	1-2	--

pounds 14, 15, 22–24, and 27, because of the absence of acceptor groups; the $\hat{\chi}^{(2)}$ of these substances may nevertheless be quite high owing to the presence of a strong donor. In compounds 18–20 and 26, which do not have an extensive conjugate-bond system, $\hat{\chi}^{(2)}$ is determined by packing and may be large in the event of an accidentally favorable disposition of the bonds if the molecules are small. Finally, ICT is weakened by the steric factor in compounds 16, 17, and 21, which have conjugate bonds and acceptor substituents.

It can be stated from general considerations¹ that $\hat{\chi}^{(3)}$ should increase with an increase in $\hat{\chi}^{(2)}$ due to the ICT contribution. Then $\hat{\chi}^{(3)}$ depends strongly on the number of bonds in the system⁶⁰; the contribution of system length to $\hat{\chi}^{(3)}$ can be investigated by observing induced Raman scattering of light⁶¹ in LC.

It can be assumed also for LC that the nonlinear susceptibility is determined by electrons weakly bound to the core, e.g., electrons on extended π orbitals. These delocalized electrons are responsible for specific properties of the conjugated molecules: high reactivity, strong dimagnetism, and such unusual optical properties as high polarizability and strong absorption in the visible region.

The susceptibility $\hat{\chi}^{(2)}$ (tensor of odd rank) will be large given sufficient asymmetry of these orbitals, but for large values of the components of the even-rank tensor $\hat{\chi}^{(3)}$ the presence of extended filled π orbitals is sufficient. However, it must be remembered that the substance may lose its ability to form a mesophase in the presence of strong donor-acceptor substituents.

Turning from the properties of an individual molecule to the medium as a whole, the orientation (packing) of the molecules plays an important role in determination of optical properties even if the van der Waals bond between molecules is weak. Packing is determined by the type of LC and by the orientation of its molecules in the specimen under the action of external fields. This situation is characteristic for systems with disturbed rotational symmetry and resembles a Heisenberg ferromagnetic, in which all spins tend to line up parallel but the energy does not depend on the direction of the total angular momentum.² The spatial structures of most LC in the solid phase are now known; at best, only the symmetry class can be stated. It would therefore be worthwhile to find methods for determination of the possible molecular packing in LC from the symmetry of the molecules, at least approximately; one of these methods is the close-packing method.⁶²

Yet another factor that determines the conversion efficiency is the proximity of the absorption band to the frequency of the generated radiation. The resonant contribution to nonlinear susceptibility is appreciably larger than the nonresonant contribution already at the edge of the absorption band.⁶³

Thus, experiments to generate the second harmonic in NLC indicate that the symmetry of the LC may be lower than is usually assumed; this should give impetus to the design of new experiments oriented to broadening the range of compounds studied by the procedures

developed for molecular crystals, to broadening the frequency range all the way to the ultraviolet, and finding nonlinear-interaction geometries that are optimal for various generation mechanisms.

2. LINEAR AND NONLINEAR OPTICS OF LC

To study the behavior of LC under the action of electromagnetic fields, it is, generally speaking, necessary to solve the equation of motion of the director, the dynamic equations, and the Maxwell equations simultaneously.^{2,64} But if $\tau \gg \omega^{-1}$ (τ is the relaxation time of the LC molecules and ω is the field frequency) the problem reduces to minimization of the time-averaged free energy of the LC and the field in the medium and solution of the Maxwell equation in a medium with an average distribution of the director. Solution of the nonlinear problem makes sense when the energy of the light wave is comparable to the characteristic elastic energies of the LC; but at low intensities (linear process), we can speak only of passage of light through an LC with a given function $\varepsilon(x, y, z)$. Here we shall discuss a general approach to the optical properties of LC based on an analysis of a traceless orientation tensor whose components are the internal thermodynamic parameters of the LC. These problems were also discussed qualitatively above, but here we shall concentrate our attention on a mathematical formalism that enables us to describe the interaction of a strong light wave with an LC.

a) Material equations

A general scheme for calculation of NLC susceptibilities was developed in Ref. 3 (see also Ref. 65). The LC is described by the orientation tensor S_{ij} , whose components are functions of the coordinates and time. It possesses a certain symmetry and a zero trace (five independent components) and has the significance of an average:

$$S_{ij} = \langle v_i^{(\alpha)} v_j^{(\alpha)} \rangle - \frac{1}{3} \delta_{ij}, \quad (1)$$

where $v_i^{(\alpha)}$ is the unit vector along the long axis of the α th molecule. In accordance with the relations

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + N \varepsilon_a S_{ij}, \quad \mu_{ij} = \mu_0 \delta_{ij} + N \mu_a S_{ij}, \quad (2)$$

the orientation tensor determines the permittivity and permeability tensors; here N is the number of molecules per unit volume.

Solution of the equations determining S_{ij} in the presence of an external electric field enables us to find the coefficients in the expansion

$$S_{ij} = \alpha_{ij} + \alpha_{ijk} E_k + \alpha_{ijkl} E_k E_l \quad (3)$$

(we retain only terms that are linear and quadratic in the field).

We find the electric displacement by differentiating the the free-energy density:

$$F = F(E=0) - \frac{1}{8\pi} \varepsilon_{ij} E_i E_j, \\ D_i = -4\pi \frac{\partial F}{\partial E_i} = \varepsilon_0 E_i + \varepsilon_a N S_{ij} E_j. \quad (4)$$

This gives the quadratic and cubic (static) susceptibili-

ties of the medium:

$$D_i = \epsilon_{ij} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l.$$

The dynamic susceptibilities are evaluated similarly taking into account both temporal and spatial dispersion.

An expression for the free energy of the LC can be obtained by the average-field method from the Hamiltonian proposed by Maier and Saupe⁶⁶ (it is assumed that the molecules do not have intrinsic dipole moments).⁶⁷

For the nematic phase (δS_{ij} is the deviation from the equilibrium value),

$$F = \frac{1}{2} \int \left[A (n_{ij}^0 \delta S_{ij})^2 + J (\nabla S_{ij})^2 - \frac{\epsilon_a}{4\pi} N S_{ij} E_i E_j \right] dV \quad (5)$$

(integration is carried out over the volume of the specimen), where $n_{ij}^0 = \sqrt{3/2} [n_i^0 n_j^0 - (\delta_{ij}/3)]$, n^0 is the director, J is the intermolecular interaction constant, and A depends on the temperature, the number density of the particles, and the entropy density (and its derivatives with respect to $S = S_{ij} S_{ij}$).³

For a cholesteric phase, expression (5) is generalized by addition of terms of the type $e_{ijk} S_{ij} \partial_k S_{ij}$ and by introduction of a periodic dependence of n^0 on the coordinate.

The equation of motion for S_{ij} has the form

$$m_{ijkl} \ddot{S}_{kl} + \eta_{ijkl} \dot{S}_{kl} = - \frac{\delta F}{\delta S_{ij}} + \partial_k \frac{\delta F}{\delta (\partial_k S_{ij})}, \quad (6)$$

where \hat{m} and $\hat{\eta}$ are the mass and viscosity tensors, which possess the properties $m_{ijkl} = m_{ijlk} = 0$, $m_{ijkl} = m_{klij}$ (and similarly for $\hat{\eta}$), which follow from the reciprocity relations. The terms on the right-hand side of (6) describe the forces acting on S_{ij} . It is a joint analysis of (6) and (4) that gives us expressions for the nonlinear susceptibilities (for details see Ref. 3).

The scheme outlined above uses the Maier-Saupe internal field tensor model, which relates the average values of the macroscopic and microscopic characteristics. Use of this model for an analysis of the anisotropic properties of the system is justified only in the immediate vicinity of the PT range, when the anisotropy of the internal field is small. For optical measurements in the mesophase it is necessary to consider the difference between the local field of the light wave and the macroscopic field; a procedure for derivation of equations linking the birefringence of the NLC as an ensemble of oriented molecules to the anisotropy properties of effective molecular polarizability was developed in Ref. 21.

b) Wave interactions in media with periodic spiral structure

1) Linear optics of CLC. General problems of the propagation of light waves in CLC can be analyzed in the same way as in subsection (a) of Sec. 2 (see also

Refs. 70 and 122). Here, however, we shall briefly discuss certain peculiarities of CLC linear optics (without taking the statistics of the medium into account) that are necessary for interpretation of experiments in nonlinear wave interaction.

CLC exhibit OA in the isotropic phase. Generally, all types of interactions contribute to OA:² electric dipole-electric dipole (d, d), electric dipole-magnetic dipole (d, m), electric dipole-electric quadrupole (d, q), and so forth. It is found on summation of the contributions from individual molecules that only the (d, m) tensor makes a nonzero contribution if all orientations are equiprobable; if, however, the medium is ordered, other terms also become nonzero, with the result that the OA increases.

OA reaches high values ($10^4 - 10^5$ deg/mm) in the cholesteric phase; this is explained specifically by the spiral structure of the CLC.

The linear optical properties of a spiral medium have been studied in detail⁶⁷ on a model in which the medium is treated as a birefringent crystal twisted around one of the principal axes z in the form of a spiral with pitch p .

The dielectric-permittivity tensor then takes the form

$$\epsilon_{ij}(z) = \begin{pmatrix} \epsilon_0 + \epsilon_a \cos 2\theta & \epsilon_a \sin 2\theta & 0 \\ \epsilon_a \sin 2\theta & \epsilon_0 - \epsilon_a \cos 2\theta & 0 \\ 0 & 0 & \epsilon_{||} \end{pmatrix}, \quad (7)$$

where $\theta = qz$ ($q = 2\pi/p$). In normal incidence of the light wave on the CLC (incidence along the axis of the cholesteric spiral), the propagation of the circularly polarized components $E_{\pm} = E_x \pm iE_y$ is described by the equations

$$\left(\frac{d^2}{dz^2} + \frac{\omega^2 \epsilon_0}{c^2} \right) E_{\pm} + \frac{\omega^2 \epsilon_a}{2c^2} E_{\mp} e^{\pm 2i\theta} = 0. \quad (8)$$

The solution of (8) is a superposition of four circularly polarized waves (right-handed and left-handed spirals; forward and backward waves):

$$E_{\pm} = A_{\pm} e^{i(q \pm \beta)z},$$

where

$$\beta^2 = k^2 + q^2 \pm k \sqrt{4q^2 + k^2 \frac{\epsilon_a}{\epsilon_0}}, \quad k^2 = \frac{\omega^2 \epsilon_0}{c^2}. \quad (9)$$

Analysis of the solutions gives the following results⁶⁸: (a) if $|k - q| < q\epsilon_a/2$ holds, one of the circular components is reflected from the CLC; (b) if $|k - q| \gg q\epsilon_a/2$ holds, the principal effect is rotation of the polarization plane of the linearly polarized wave; the rotation per unit length is $\Delta k = k^4/4q(q^2 - k^2)$ (c) if $|k - q| \geq q\epsilon_a/2$, a standing wave is set up in the CLC; (d) if $k^2 - q^2 \geq q^2$ holds, two plane-polarized waves propagate with the polarization vector of each undergoing rotation with pitch qz . The resonant-reflection condition has the form $(2\pi/q) \cos \alpha = m\lambda$, where m is an integer (the order of reflection) and α is the angle of incidence. For oblique incidence, the appearance of higher orders of reflection is characteristic (they are forbidden in the case of normal incidence^{2,64,69}). In thick CLC specimens, in which multiple scattering is significant, three characteristic cases are possible for arbitrary angles of incidence of the light onto the crystal, depending on the deviation from the Bragg condition⁶⁴:

⁶⁸ Consistent analysis of nonlinear susceptibilities, especially of even order, requires retention in this Hamiltonian of the terms describing the interaction of higher multipoles.

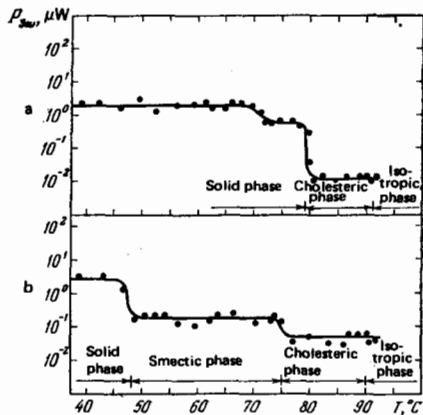


FIG. 4. THG power $P_{3\omega}$ vs. temperature during heating (a) and cooling (b) of cholesteryl nanoate CLC specimen $25 \mu\text{m}$ thick.²²

(a) weak diffraction reflection; (b) total reflection of the light with a certain elliptical polarization; (c) total reflection of the light with arbitrary polarization.

Interesting peculiarities appear in the diffraction-reflection range if absorption occurs in the CLC. Suppression of absorption is possible here for a certain deviation from the Bragg condition.⁶⁹ This effect is highly sensitive to the degree of molecular ordering of the CLC and can be used for a direct determination of the CLC's order parameter.⁶⁴

All the above pertains to unbounded media and gives only a qualitative idea of the optical properties of the real LC cells being investigated. Accurate quantitative estimates require that the presence of dielectric boundaries should be taken into account.^{64,71,9)}

2) Third-harmonic generation and synchronism conditions in CLC. It is convenient to use the one-dimensional¹⁰⁾ wave equation for the field amplitude $E_z(z, 3\omega)$ in a rotating coordinate system to analyze third-harmonic generation (THG) in CLC ($\hat{\sigma}$ is the rotation operator)¹⁶:

$$\left[\frac{\partial^2}{\partial z^2} - \left(\frac{2\pi}{p} \right)^2 + \frac{4\pi}{p} \hat{\sigma} \frac{\partial}{\partial z} + \left(\frac{3\omega}{c} \right)^2 \varepsilon_T^l \right] E_T(z, 3\omega) = -4\pi \left(\frac{3\omega}{c} \right)^2 P_T^nl(z, 3\omega). \quad (10)$$

THG has been investigated for many LC.⁷² The power of the third harmonic in cholesteryl nanoate undergoes substantial variations near temperature PT (Fig. 4). The intensity of the third harmonic in the solid phase (specimen $25 \mu\text{m}$ thick) is nearly 100 times higher than that in the isotropic phase; in thick specimens, its power decreases owing to large scattering losses. The intensities of the harmonic are comparable in $25\text{-}\mu\text{m}$ -thick specimens of the cholesteric and isotropic phases.

Several factors explain the interesting fact that the intensity of the harmonic values strongly near the PT in cholesteryl nanoate.⁷² First of all, the symmetry of the medium is lowered with the transition from

the disorganized isotropic liquid through the mesomorphic state with its higher degree of molecular ordering to the crystalline solid phase. As a result, a large number of nonlinear-susceptibility tensor components contribute to THG; this is demonstrated by the experimentally observed changes of the third-harmonic polarization vector in the PT range. Secondly, there is a relation between the coherence length, which depends on the dispersion and birefringence of the medium, and the effective "grain" size of the polycrystalline phase; the increase of THG power in the solid phase of cholesteryl nanoate as compared to cholesteryl myristate and palmitate may be due to large "grain" sizes after crystallization into the solid phase. Thirdly, a certain contribution to increased nonlinear susceptibility may be expected from molecular-interaction effects in ordered phases.

The possibility of wave synchronism is an important question bearing on nonlinear conversions.¹⁸ Satisfaction of the synchronism condition in CLC depends on the one-dimensional property periodicity inherent in their structure: synchronism of the interacting waves is ensured by transfer of part of the photon's momentum to the lattice of the medium.

In Refs. 16 and 73, the synchronism conditions were satisfied at the outset by compensating the mismatch $\Delta k = k^{3\omega} - 3k^\omega$ with a reciprocal-lattice vector of length $q = 2\pi/p$ (optical transfer properties). The lattice constant of the CLC can be changed quite easily, and through a broad range, by adjusting the temperature or concentration of the solution²; over a certain range of temperatures and concentrations it falls in the range of optical wavelengths. This means that the possible synchronous interactions also include interactions of colliding waves, which, as we know, have a number of important peculiarities (for a frequency-nondegenerate interaction, for example, there is the possibility of cavityless generation⁷⁴).

In collinear interaction (along the z axis of the CLC spiral), there are various possibilities for phase synchronism¹⁶:

$$\pm |k_\pm^{3\omega}| = \pm |k_\pm^\omega| \pm |k_\pm^\omega| \pm |k_\pm^\omega|, \quad (11)$$

where $(+|k|)$ corresponds to the forward wave and $(-|k|)$ to the backward wave. The signs \pm , which appear as subscripts on the wave vector, indicate opposite circular polarizations of the waves. Twelve variants (Table III; \bar{k} corresponds to the backward wave) of collinear synchronous interaction in a CLC consisting of a mixture of cholesteryl chloride and cholesteryl myristate (proportions by weight 1.75:1) $130 \mu\text{m}$ thick were investigated in Ref. 16 with a phase-locked neodymium-laser pump ($\lambda = 1.06 \mu\text{m}$). Phase synchronism was obtained by adjusting the spiral to an appropriate pitch—either by varying the temperature of the specimen or by varying the concentration composition of the CLC studied. Figure 5 shows the temperature-synchronism peaks for the $3k_\pm^\omega = k_\pm^{3\omega}$ interaction, in which the highest conversion efficiency was obtained: 10^{-14} of the energy of the incident radiation. The efficiency was increased by a factor of 400 when the radiation was focused into a beam 0.1 mm in diameter.

⁹⁾ See Ref. 130 for detailed numerical calculations.

¹⁰⁾ The pump and third harmonic in CLC are easily synchronized in collinear geometry (see below), use of which maximizes the interaction region.

TABLE III. Third-harmonic generation in a mixture of cholesteryl chloride and cholesteryl myristate.¹⁶

Synchronism conditions	Spiral pitch p (μm) for synchronous THG	Calculated temperature for synchronous interaction, $^{\circ}\text{C}$	$d\eta/dT$, $\text{nm}/^{\circ}\text{C}$	Observed synchronism temperature, $^{\circ}\text{C}$	Relative intensities in THG	
$k_+^{\omega} + 2k_-^{\omega} = \bar{k}_+^{3\omega}$ $3k_-^{\omega} = \bar{k}_+^{3\omega}$	$3k_0^{\omega} = \bar{k}_0^{3\omega} + q$	0.24	38 \pm 3	0.7	39.5	$2 \cdot 10^{-4}$
		0.24				
$\bar{k}_+^{\omega} + 2k_+^{\omega} = \bar{k}_+^{3\omega}$ $k_+^{\omega} + \bar{k}_+^{\omega} + k_-^{\omega} = \bar{k}_+^{3\omega}$	$2k_0^{\omega} + \bar{k}_0^{\omega} = \bar{k}_0^{3\omega} + q$	0.35	32 \pm 2	1.3	30.5	$1 \cdot 10^{-2}$
		0.35				
$2k_+^{\omega} + k_-^{\omega} = \bar{k}_+^{3\omega}$	$3k_0^{\omega} = \bar{k}_0^{3\omega} + 2q$	0.47	38.2 \pm 1	3.6	38.1	$1 \cdot 10^{-4}$
$2k_+^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$	$2k_0^{\omega} + \bar{k}_0^{\omega} = k_0^{3\omega} - q$	0.69	30.1 \pm 0.6	8.5	29.9	$3 \cdot 10^{-1}$
$k_+^{\omega} + k_-^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$		0.69				
$2k_+^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$	$2k_0^{\omega} + \bar{k}_0^{\omega} = \bar{k}_0^{3\omega} + 2q$	0.70	31.1 \pm 0.6	8.5	31.2	$3 \cdot 10^{-2}$
$2k_+^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$		1.4				
$2k_+^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$	$2k_0^{\omega} + \bar{k}_0^{\omega} = k_0^{3\omega} - 2q$	49.4 \pm 0.2	6400	49.3	49.3	1
$2k_+^{\omega} + \bar{k}_+^{\omega} = k_+^{3\omega}$		54.2 \pm 0.2				
$3k_+^{\omega} = k_+^{3\omega}$	$3k_0^{\omega} = k_0^{3\omega} - q$	17	54.1	54.1	54.1	1

$k_{\pm} = k_0 \pm 2\pi/p$, $k_0^{\omega} = \omega \sqrt{\epsilon_0/c}$, $\epsilon_0 = (\epsilon + \epsilon_-)/2$.

c) Third-harmonic generation in polycrystalline CLC specimens

The above discussion implies that the efficiency of THG in CLC depends on the degree of circular polarization of the pump radiation and on the quality of preparation of the CL single crystal, i. e., on the homogeneity of the CLC's texture in the test cell. The first condition is trivial: it is easy to produce a circularly polarized wave accurate to no worse than one percent. Here it is essential that THG is impossible in isotropic media with circular polarization of the incident wave,⁷⁵ so that the problem of excluding background radiation (generation in the backings, in the air, etc.) does not arise.

The second condition calls for a separate discussion. This is because preparation of a single CLC of comparatively large thickness (of the order of several hundred microns) is no simple matter.^{2,4} It is not possible to produce a uniform spiral in thick CLC layers; here the texture of the CLC consists of randomly oriented spiral segments which lowers conversion efficiency in THG. On the other hand, the power in the harmonic increases, other conditions remaining the same, with increasing specimen thickness, so that it is worthwhile to find the CLC layer thickness that is the optimum with respect

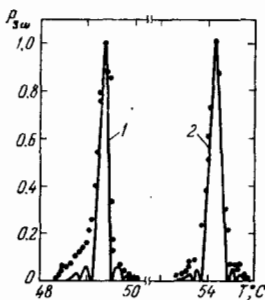


FIG. 5. THG power $P_{3\omega}$ (relative units) as a function of temperature in a CLC mixture.¹⁶ Cell thickness 130 μm ; curve 1 corresponds to a left-handed spiral, curve 2 to a right-handed spiral.

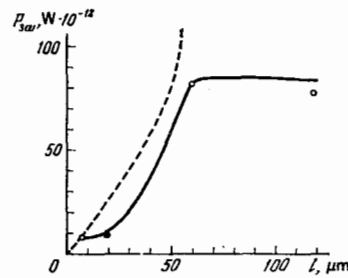


FIG. 6. Third-harmonic power $P_{3\omega}$ in CLC as a function of layer thickness l .²³ The dashed curve indicates the $P_{3\omega} \sim l^2$ relation.

to converted power.

This problem was investigated experimentally in Ref. 73, which reports observation of a synchronous temperature interaction $3k_+^{\omega} = k_+^{3\omega}$ in a mixture of the same composition as in Ref. 16. THG was obtained in cells with CLC 130, 60, 20, and 8 μm thick (which were placed in a thermostat). The temperature stabilization was no worse than 0.01 $^{\circ}$. The single-mode radiation of a Q-switched YA1G laser ($\lambda = 1.06 \mu\text{m}$) was used as pump (pulse energy $7 \cdot 10^{-4}$ J).

The complex dependence (Fig. 6) of $P_{3\omega}$ on $l^{11)}$ can be explained by variation of the tightness of the CLC spiral with layer thickness (the spiral becomes nonuniform); the width of the synchronism temperature curve increases with increasing l .

The most uniform CLC was obtained at $l = 8 \mu\text{m}$. The quality of the spiral generally deteriorates in thicker layers, remaining almost unchanged at $l = 20$ and 60 μm . In a cell with $l = 130 \mu\text{m}$, deterioration of CLC spiral uniformity begins to result in an appreciable decrease in the power radiated in the harmonic. Thus, conversion is most efficient in THG in CLC layers on the order of ten microns thick; the texture of CLC is least critical to thickness variation in cells several tens of microns in thickness. In the layer with $l = 8 \mu\text{m}$, the (energy) coefficient of conversion to radiation in the harmonic was $1.4 \cdot 10^{-9}$; the corresponding effective nonlinear susceptibility was $\chi_{\text{eff}}^{(3)} = 3.3 \cdot 10^{-15}$ cgs esu.

In a theoretical analysis of wave interactions in polydomain LC, it is necessary to remember that both the pitch of the spiral and the direction of its axis are random variables. The corresponding calculations are given in Ref. 70 for CLC nonlinear optics. It can be shown that the randomness of the pitch distribution at small l ($l < \Delta p$, where Δp is the spiral-pitch dispersion) has no significant influence, and that $P_{3\omega} \sim l^2$ ($\sim p$ in very thin cells, so that boundary effects must be considered). For thick cells, $P_{3\omega} \sim l$ (compare with Ref. 55) at a constant Δp ; but the saturation (and possibly even the drop) of the $P_{3\omega}(l)$ curve is explained by an increase of Δp with increasing l .

d) Parametric interactions of light waves in LC

Frequency-degenerate interactions in LC have not yet been investigated experimentally or subjected to detailed

¹¹⁾ $P_{3\omega} \sim l^2$ should hold in an ideal single-crystal specimen.¹⁸

theoretical analysis; at the same time, such studies are obviously promising, primarily in light of the often discussed^{76-78,17} possibility of obtaining synchronous conversion of colliding waves.

The feasibility of bringing about interactions of colliding waves in LC results from the previously discussed compensation of the wave detuning with the reciprocal-lattice vector of the LC structure, i. e., by using distributed feedback (DFB)⁷⁶ of waves of mismatched frequencies. DFB in quantum generators makes it possible to get by without a mirror resonator and, if smooth variation of the parameters is possible, to tune the frequency within the amplification loop. A generator with DFB provided by parametric interaction of waves using a pump wave at the sum or difference frequency can work even without laser amplification.⁷⁶ The main problem encountered in building one consists of meeting the phase-synchronism condition. For a three-photon interaction $\omega_1 + \omega_2 = \omega_p$ (the pump wave ω_p and the idler wave ω_1 propagate in the direction opposite that of the signal wave ω_2), this condition takes the form $\omega_2/\omega_p = (n_1 - n_p)/(n_1 + n_p)$, where $n_{1,2,p}$ are the refractive indexes at the respective frequencies; for four-photon interaction, $2\omega_p = \omega_1 + \omega_2$ and $\omega_2/2\omega_p = (n_1 - n_p)/(n_1 + n_p)$. These conditions are satisfied only if $n_1 > n_p$; consequently, the three-photon interaction is possible in media with anomalous dispersion or in birefringent media (the four-photon interaction is also possible in the normal-dispersion range). In isotropic media, the difference $n_1 - n_p$ can be increased by injecting impurities, but the ratio ω_2/ω_p then becomes small. Use of media that are periodically inhomogeneous in space to provide phase synchronism (in particular, CLC) makes it possible to avoid rigid frequency limitations. If q is the reciprocal-lattice vector of this medium and α is the angle between q and the pump wave vector k_p , the synchronism condition assumes the form

$$\omega_2 = n_1 \omega_1 - \sqrt{n_p^2 \omega_p^2 + c^2 q^2 - 2n_p \omega_p c q \cos \alpha} \frac{1}{n_1 + n_p}; \quad (12)$$

for the three-photon interaction (for the four-photon interaction, ω_p is replaced by $2\omega_p$) and the inequalities $\omega_2 \ll \omega_p$ and $n_1 > n_p$ become superfluous. Another way to meet the synchronism conditions is to use waveguide films⁷⁹; the use of NLC is natural in this case.

Together with such advantages as the absence of the mirror resonator and the possibility of retuning the output frequency when the pump frequency is changed or on a change in synchronism conditions (by varying α or $n_1 - n_2$ by adding impurities, changing the temperature, or rotating the cell with the LC), the generator scheme described above makes it possible to use a broad-band pump with significant narrowing of the spectrum of the signal (backward) wave (ω_2).⁷⁷

Additional possibilities result from the use of nonlinear media in which amplification conditions are created at the idler or signal frequency (population inversion at the appropriate levels). Such media can be made by injecting various laser dyes into CLC. As compared to the series amplification and parametric conversion scheme, laser amplification and parametric interaction in the same medium⁷⁹ (superheterodyne amplification)

reduces the influence of amplification saturation effects.⁸⁰ In addition, the former scheme does not permit efficient utilization of a broad-band pump.

Use of the superheterodyne amplification principle was analyzed theoretically in Refs. 79, 80, and 17. It was shown that the creation of an inversion at the signal or idler frequency: (1) lowers the generation threshold; (2) makes it possible to obtain the practical quantum-yield limit at lower pump levels; and (3) permits generation with upward frequency conversion.

Considering the comparative simplicity of changing the pitch of the CLC spiral and the already demonstrated efficiency of dye lasers²⁵⁻²⁷ in liquid-crystal matrices, we may conclude that the described principle is attractive for the design of tunable parametric generators with broadband pumps and tunable mirrorless lasers controlled by parametric pumps; these energy-efficient systems are of special interest for integrated optics.

3. NONLINEAR-OPTICAL METHODS FOR STUDY OF PHASE TRANSITIONS. MEASUREMENT OF HIGHER DISTRIBUTION-FUNCTION MOMENTS

Let us now discuss a second aspect of LC nonlinear optics—use of the methods of nonlinear spectroscopy to obtain new information on the structure of LC. In the PT range, nonlinear optical conversions make it possible to measure higher moments of the distribution functions of LC molecules. Inferences as to the symmetries of LC obtained from SHG measurements were already discussed in Sec. 1. Here we shall concern ourselves with effects based on the third-order nonlinear optical susceptibility.

a) Specifics of orientation effects in LC. The Kerr effect

The optical Kerr effect has been used to investigate pretransition phenomena in NLC at the PT from isotropic to nematic.^{6-10,14,87} Similar studies were reported in Ref. 81 for plastic crystals. The interaction of light with LC must be brought about by a high-frequency Kerr-effect-type mechanism, since the heavy molecules of the crystals cannot keep up with the optical-frequency perturbation. Intermolecular interaction forces governing the orientation order in the NLS make it difficult for the molecules to rotate about their short axis,⁴ and nematic packing may improve conditions for rotation of the molecules around their long axes as compared to the isotropic phase; this actually reduces the relaxation time of the transverse dielectric permittivity component.⁸² Rotation around the long axes may also be made difficult in the presence of appreciable optical biaxiality of the LC molecules, as discussed earlier; this is especially important in experiments with oriented LC cells.

Various group moments of the molecules (methoxy-group and azoxy-bridge dipoles¹¹⁻¹³) may contribute to orientational polarization. For example, the relaxation time characterizing the rotation of the methoxy group in the PAA NLC is $3 \cdot 10^{-12}$ sec,¹²³ and these molecules have a noticeable response even to short laser

pulses; in NLC, therefore, many features of the low-frequency Kerr effect can also be manifested in the optical region. Moreover, interpretation of orientation effects becomes more difficult for LC with ferroelectric^{36,44,51,54} and paramagnetic¹¹ (see also Ref. 83) properties.

Let us consider aspects of the Kerr effect in the pre-transition range of the isotropic phase of an NLC.^{2,4,12)} At temperatures significantly above the temperature T_K of the PT to the isotropic phase, compounds that form LC exhibit the ordinary Kerr effect in electric fields. With the approach to T_K , the Kerr constants of LC substances change sign in some cases⁸⁴ and increase sharply in others,⁸⁵ reaching values 200 times greater than the Kerr constant of nitrobenzene. These anomalies are explained by the presence of nuclei of the LC phase in the isotropic liquid-molecular aggregates with close-range orientational order that simultaneously lower the Kerr-effect response speed to $10^{-7} - 10^{-8}$ sec (Ref. 4; see also Ref. 86).

The order parameter S for the Kerr effect can be determined from the relation (below we follow the results of Ref. 10, 14, 87)

$$\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} = S\Delta\epsilon, \quad (13)$$

where ϵ_{\parallel} and ϵ_{\perp} are the optical-susceptibility components parallel and perpendicular, respectively, to the applied linearly polarized field E and $\Delta\epsilon$ is the anisotropy at complete alignment of the molecules.

Minimization of the free energy density with respect to S yields the following expression for the refractive index anisotropy δn induced by molecular ordering:

$$\delta n = \frac{\pi(\Delta\epsilon)^2 |E|^2}{3\alpha n(T - T_K)}, \quad (14)$$

where α is a constant.

The dynamic properties of light-induced anisotropy are described by the relation

$$S(t) = \int_{-\infty}^t \frac{\Delta\epsilon |E|^2}{6\eta} \exp\left(-\frac{t-t'}{\tau}\right) dt', \quad (15)$$

where $\tau = \eta/A = \eta/a(T - T_K)$ is the order parameter relaxation time (η is the viscosity).

If the duration of the light pulse is shorter than τ , the order parameter S and, consequently, the induced optical anisotropy δn decrease exponentially with a time constant τ , with the relaxation time varying in accordance with the law $(T - T_K)^{-1}$ as $T \rightarrow T_K$. This is an analogy to the well-known critical inhibition of induced magnetization in a paramagnetic crystal near the paramagnetic-ferromagnetic transition point.

By measuring the nonstationary response $\delta n(t)$ induced by a pulse $|E|^2$ of specified shape, we can find τ and the third-order nonlinear susceptibility:

$$\chi_S^{(3)} = \frac{(\Delta\epsilon)^3}{6a(T - T_K)}. \quad (16)$$

A result of their critical divergence ($T \rightarrow T_K$) is that the

¹²⁾The Kerr effect is masked in the nematic phase by other, stronger orientation effects.^{2,4}

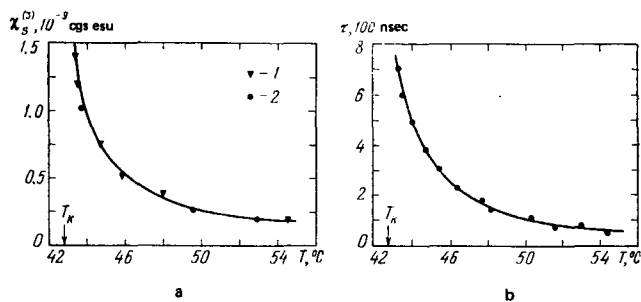


FIG. 7. a) Third-order nonlinear susceptibility in MBBA vs. temperature [1) experimental data from measurements of optical Kerr effect; 2) from measurements of polarization-ellipse rotation. The solid curve represents theory]; b) relaxation time τ as a function of temperature of MBBA (the solid curve represents theory, the plotted points the experimental data).⁸⁻¹⁰

values of the anisotropy δn and of the time to establish it in the isotropic phase of the LC compound are much larger, especially near the PT point, than in an ordinary liquid. These relationships were investigated experimentally in Refs. 10, 14, and 87. A strong laser pulse is used to induce optical anisotropy ($S \neq 0$); on the other hand, a weak continuous laser beam is used to probe the induced optical anisotropy. Since $\tau \geq 10^{-8}$ sec for LC, the laser-pulse parameters needed for the experiment are obtained either by Q-switching or by weakly-coupled-mode operation. Experiments of this kind have been performed with a large number of nematic compounds. The curves in Fig. 7 clearly demonstrate the critical divergence of $\chi_S^{(3)}$ and τ for an MBBA NLC; the values of $\chi_S^{(3)}$ and τ shown in Fig. 7 are far larger than the corresponding values for ordinary liquids. At $T - T_K = 5^\circ\text{C}$, $\chi_S^{(3)}(\text{MBBA}) = 2.7 \cdot 10^{-10}$ cgs esu—a value nearly 100 times the cubic susceptibility of the well-known Kerr liquid CS_2 at room temperature, and $\tau(\text{MBBA}) \approx 100$ nsec— $5 \cdot 10^4$ times greater than $\tau(\text{CS}_2)$. Such large values of $\chi_S^{(3)}$ and τ appear to be characteristic for LC (Table IV and Fig. 8). Because of the high values of the optical Kerr constants and the relaxation constants, LC in the isotropic phase are ideal systems for investigating the self-focusing of light.

The constant-field Kerr effect is characterized by a temperature dependence different from $(T - T_K)^{-1}$.^{84,85} It was shown in Ref. 87, a study of a homologous series of LC with different numbers of methylene groups, that this results from the local-field correction; the temperature dependence of the Kerr effect enables us to separate the contributions of constant and induced dipoles to the Kerr constant.

TABLE IV. Parameters of Kerr effect in nematic liquid crystals.¹⁰

Compound	R	$T_K, ^\circ\text{C}$	$\tau(T - T_K), 10^{-9}, \text{sec} \cdot \text{K}$	$\chi_S^{(3)}(T - T_K), 10^{-10} \text{ cgs esu} \cdot \text{K}$
$\text{C}_6\text{H}_5 - (\text{C}_6\text{H}_4) - \text{CH} : \text{N} - (\text{C}_6\text{H}_4) - \text{R}$	CH_3	41.7	67	13.2
	C_2H_5	67.6	21	7.8
$\text{RO} - (\text{C}_6\text{H}_4) - \text{N}_2\text{O} - (\text{C}_6\text{H}_4) - \text{OR}$	CH_3	130.7	8.5	15
	C_2H_5	161.0	7.5	10.2
	C_2H_{11}	115.0	25	5.6
	C_2H_{13}	128.0	15	4.7
	C_7H_{15}	121.3	15	5.4

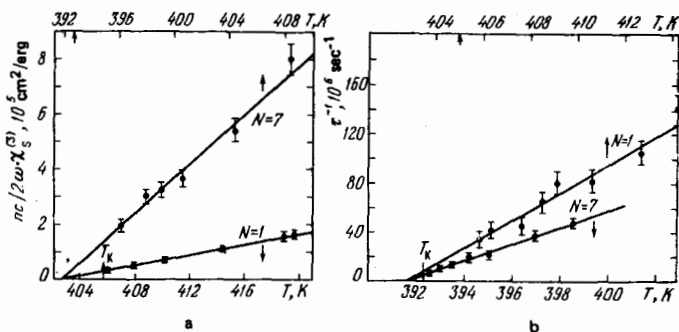


FIG. 8. Experimental plots of $\chi_S^{(3)}$ (a) and τ (b) against temperature for the homologous series $C_N H_{2N+1} - O - C_4 H_6 - N_2 O - C_6 H_4 - OC_N H_{2N+1}$ with $N=1$ and $N=7$. The solid lines represent theory.

An interesting result was obtained in Ref. 10: addition of CH_2 groups to the alkyl chain in a homologous series of NLC increases the average polarizability much more than the polarizability anisotropy.

Nonlinear optical measurement enable us to make quantitative estimates not only of the nonlinear susceptibilities, but also of other parameters of the medium; in addition to the order parameter and the refractive-index anisotropy, it is possible to obtain the values of T^* , the fictitious temperature of the second-order PT; the viscosity η ; and a , b , and d , the coefficients of the Landau expansion for the free energy. These parameters were measured in Ref. 8 for a homogeneous series of LC; the remaining parameters in Table V were calculated from measurements of the PT temperature T_K , the macroscopic order parameter S_K at $T = T_K$, the refractive-index anisotropy δn , and the transition latent heat ΔH_{exp} . The variation of the Landau parameter in the mixtures suggests that the average-field theory is not a good approximation for description of the "isotropic liquid-nematic" transition in these mixtures. We note also that the latent heat ΔH calculated from the formula $\Delta H = 3aT_K S_K^2/4$ differs appreciably from the experimental values, especially in the higher members of the homologous series.

b) Raman spectra and active Raman spectroscopy

Raman and active Raman spectroscopy (ARS), which have developed rapidly in recent years,⁸⁸ offer a convenient method for quantitative analysis of the rotation-

TABLE V. Parameters characterizing phase transition for homologous NLC series⁸ with structure $CH_3 - (CH_2)_{N-1} - O - (C_6 H_4) - N_2 O - (C_6 H_4) - O - (CH_2)_{N-1} - (CH_3)$.

N	1	2	3	4	5	6	7
$T_K, ^\circ C$	132.7	163.1	149.95	129.9	118.6	123.9	119.3
S_K	0.400	0.571	0.395	0.475	0.358	0.437	0.431
δn	108.9	97.1	87.2	79.0	74.9	64.5	60.9
$\Delta H_{exp} 10^6 \text{ erg/cm}^3$	25.4	52.5	22.8	31.4	19.9	26.2	23.5
$T_K - T^*, K$	3.0	3.8	2.75	4.9	4.4	0.9	0.7
$\tau \Delta T, 10^{-9} \text{ sec} \cdot K$	90	80	180	155	240	150	140
$B \Delta T, 10^{-3} \text{ cgs esu}^*$	10.5	9.2	9.0	8.9	6.4	3.9	2.2
$\eta, 10^{-3} \text{ P}$	62.6	52.1	95.9	68.9	135.4	105.1	151.3
$a, 10^6 \text{ erg/cm}^3 \cdot K$	6.69	6.52	5.33	4.45	5.57	7.00	10.81
$b, 10^7 \text{ erg/cm}^3$	21.0	19.4	15.0	17.9	24.1	4.4	6.0
$d, 10^7 \text{ erg/cm}^3$	41.1	27.3	29.7	29.1	49.4	6.9	10.1
$\Delta H_{theor} 10^6 \text{ erg/cm}^3$	33.9	56.9	24.6	30.3	20.9	39.8	59.0

*) The constant $B = 2\omega\chi_S^{(3)}/nc$.

al and other kinetic properties of molecules, as well as the vibrational dynamics of substances in the mesophase.^{20-23,89} They make it possible to find higher moments of the LC's distribution function for any valence bond in the molecule, including those for terminal groups. The latter is important for establishment of the part played by individual molecule groups in formation of the mesophase.

Moreover, study of the Raman spectra and their temperature dependence enables us to follow structural changes in LC at PT.⁹⁰ The ARS method can be used to probe local new-phase nucleation processes at PT and, in rather simple fashion, to measure third-order resonant and nonresonant susceptibilities²²⁻²³; polarization measurements are especially valuable here.⁸⁹ The structural changes and ordering that occur at PT are reflected primarily in the low-frequency spectrum and less strongly in the high-frequency spectrum.⁹⁰⁻⁹¹

1) Determination of distribution-function moments. Since NLC molecules are treated as rigid rods in the simplest model, the orientational ordering of the molecules is described by a function $f(\theta)$ that depends on the angle θ between the axis of the molecule and the director n .^{2,4} The average values of $S_{2m} \sim \langle P_{2m}(\cos\theta) \rangle$ which, being nonzero only in an anisotropic system, can be regarded as orientational order parameters of the LC,² figure as coefficients in the expansion of $f(\theta)$ in Legendre polynomials $P_{2m} \cos\theta$. Several remarks are in order here. First of all, the expansion of $f(\theta)$ in even Legendre polynomials only is equivalent to the assumption that the directions (+n) and (-n) in the LC are indistinguishable. This makes it necessary to modify it for LC that exhibit ferroelectric properties (the intermolecular-interaction mechanism is modified here).

Secondly, the assumption that the molecules of the LC are axially symmetric rigid rods is a rather crude one. Generally, the angular distribution function of the molecules must depend on the three Euler angles $f(\varphi, \theta, \psi)$ (biaxiality of the LC). This leads to the appearance of additional terms in the expression for the order parameter.^{20,46} However, the biaxiality is still small and should be manifested only in special cases: NMR,³⁴⁻³⁶ OA and the linear electrooptical effect,³²⁻³³ and SHG.¹⁵ On the other hand, polarization Raman scattering studies of LC orientational order are fairly insensitive to such local biaxiality.²⁰

Thirdly, quantitative agreement between theory and experiment requires correction of calculations made under the Maier-Saupe theory to take into account the local-field anisotropy of the light wave in the LC and the influence of close-range ordering, which determines the correlation of the oriented pairs.²⁰⁻²¹

Fourthly and finally, it must be remembered that typical LC molecules have a rigid central part with mobile terminal groups (usually hydrocarboxyl), whose presence may change the relaxation times of various orientational effects.¹¹⁻¹³

To clarify the physics of LC, therefore, it will be necessary to investigate the higher moments of the orientation distribution functions of their molecules.

References 20-21 and 89 were the first experimental studies devoted to this problem. Polarization measurements of spontaneous RS in oriented NLC and SLC specimens were made in Ref. 20. The depolarization coefficients (ratios of the corresponding scattered-light intensities, $R_1 = I_{xy}/I_{zz}$; $R_2 = I_{xy}/I_{yy}$, $R_3 = I_{yx}/I_{xx}$) were measured in various experimental geometries for homeotropic and homogeneous orientation of the specimen, together with R_1 , the isotropic-phase depolarization coefficient. Calculation relates the four measured quantities to the order parameters S_2 and S_4 and to the spontaneous-RS tensor components of the vibration being studied.

An MBBA-BBCA (*N*-(*p*'-butoxybenzylidene)-*p*-cyanoaniline) mixture was investigated in the experiment. The BBCA test molecule (up to 20% in the mixture) is structurally similar to MBBA and has a terminal CN group with its axis parallel to the principal axis of the molecule. The group has a strong narrow anisotropic Raman band at around 2225 cm⁻¹, which is spectrally isolated from the other BBCA and MBBA bands. The orientation of the BBCA molecules presumably follows that of the MBBA molecules ("host-guest" effect),⁴ so that studies of the BBCA vibrations yielded information on the order parameter of the MBBA. Quantitative orientation-statistics data were obtained in this study both for pure MBBA and in the mixture of smectic liquid crystals.

Comparison of theory with experiment showed substantial disagreement: while agreement with the corrected variants of the Maier-Saupe theory was obtained for S_2 , the experimental value of S_4 differed significantly from theory. Possible explanations of this disagreement can be offered within the framework of the remarks made above; allowance for local-field anisotropy is probably most important.²¹

A monotonic decrease of the degree of orientational order is observed in various LC with the approach to the PT point (Fig. 9).²⁰⁻²² The values of S_2 and S_4 increase when the anisotropy of the local field is taken into account; the relative changes are particularly large for S_4 and reach 100-150% near the PT. If the local-field anisotropy near T_K were not taken into account, the parameter S_4 could have been negative²⁰; this is eliminated when anisotropy is taken into account. Since the S_4/S_2 ratios are not small, allowance for

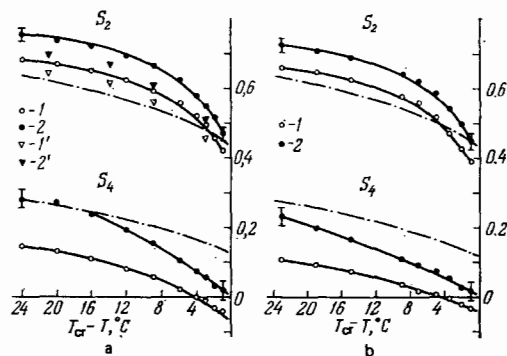


FIG. 9. Temperature variation of order parameters S_2 and S_4 in NLC E06T (a) and E08T (b) as obtained by various methods. 1, 2) Raman scattering; 1', 2') optical probing. Calculation made in the isotropic local field approximation (1, 1') and with allowance for local-field anisotropy (2, 2'). The dot-dash lines correspond to a calculation based on the Maier-Saupe theory.

higher-order moments is necessary in experimental determination of the distribution function.

2) Measurement of third-order nonlinear susceptibilities. Amplitude ARS was used in Ref. 22 to measure the dispersion curves of the third-order nonlinear susceptibility of the MBBA NLC. The measurements, which were made in both the nematic and the isotropic phases, made it possible to determine both the magnitudes and signs of the electron (nonresonant) and Raman (resonant) susceptibilities $\hat{\chi}^{nr}$ and $\hat{\chi}^r$ in the neighborhood of the strong spontaneous RS line of MBBA at $\nu = 1164$ cm⁻¹. The individual components of these tensors were measured in Ref. 23 (Table VI) in an oriented MBBA specimen. Figure 10 shows experimental curves of the dispersion of $|\chi^{(3)}|$. It was also found²² that the ratio $\hat{\chi}^r/\hat{\chi}^{nr} > 0$ and that its sign does not change at PT; the nonresonant part of the component χ_{1111}^{nr} did not change (within the limits of experimental error) at the PT, while the resonant part χ_{1111}^r was 1.5 times larger in the nematic than in the isotropic phase.

It should be noted that the possibility of SHG in the oriented NLC cells was not taken into consideration in interpreting the third-order nonlinear-susceptibility measurements in Refs. 22-23, i. e., the possibly substantial contribution of cascade processes was not taken into account; in addition, it is necessary to take into

TABLE VI. Third-order nonlinear susceptibilities in isotropic and nematic phases.^{22,23}

	$\hat{\chi}_{MBBA}^{(3)R} / \hat{\chi}_{MBBA}^{(3)NR}$	$\hat{\chi}_{MBBA}^{(3)R} / \hat{\chi}_{glass}^{(3)NR}$	$\hat{\chi}_{MBBA}^{(3)NR} / \hat{\chi}_{glass}^{(3)NR}$	$\hat{\chi}_{MBBA}^{(3)R} \cdot 10^{-14} \text{ cm}^3/\text{erg}$	$\hat{\chi}_{MBBA}^{(3)NR} \cdot 10^{-14} \text{ cm}^3/\text{erg}$
Isotropic phase $ \chi $	4 ± 0.5	21 ± 2	5.4 ± 0.5	19 ± 5	5 ± 1
Nematic phase $ \chi $	6.5 ± 1	31 ± 3	5 ± 1	29 ± 8	5 ± 2
χ_{1111}	5.4 ± 0.5	30.1 ± 2	5.9 ± 1	—	—
χ_{3333}	10.8 ± 2	24.1 ± 3	2.3 ± 2	—	—
χ_{3113}	6.20 ± 0.5	28.9 ± 1	4.65 ± 1	—	—
χ_{1311}	37.5 ± 5	112.8 ± 1	4.7 ± 1	—	—

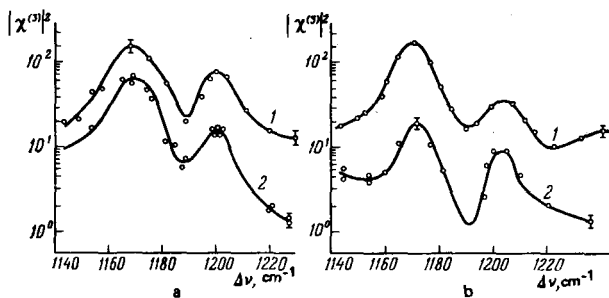


FIG. 10. Dispersion of cubic susceptibility of MBBA.²² a) isotropic phase, cell length 2 cm; $T - T_K = 0.2^\circ\text{C}$ (1), 28°C (2); b) nematic phase, NLC layer thickness $70\ \mu\text{m}$, $T_K - T = 14.4^\circ\text{C}$; thickness of glass base $l_1 = 320\ \mu\text{m}$ (1); $480\ \mu\text{m}$ (2).

account their influence on the structure of the LC in strong laser fields.

c) Induced scattering

No systematic studies of induced scattering (IS) in LC have been made. Among the results obtained thus far, we might note characteristic dependences of the IS thresholds on temperature in the PT range.⁹² The IRS threshold decreases as T approaches T_K from above (it is possible that it rises again in the immediate vicinity of T_K); the IMBS threshold, on the contrary, increases (Fig. 11a). Observation of the transverse structure of the beam passing through the LC indicated that self-focusing of the laser radiation influences the IS threshold.

The nonstationary characteristics of IS are also related to self-focusing; this is illustrated by Fig. 11b, which shows the IMBS output power as a function of the ratio of the pump power P to the critical self-focusing power P_{cr} for various ratios of the pump-pulse duration τ_p to the relaxation time τ of the EBBA (*p*-ethoxybenzylidene-*p*-butylaniline) NLC.⁸

IRS spectra in the isotropic phase of MBBA activated with dyes were investigated in Ref. 93.

The possibilities of IRS in studies of the influence of molecular structure on $\tilde{\chi}^{(3)}$ must be stressed: we may expect a significant lowering of the IRS threshold as the length of the conjugate-bond system in the LC molecule increases.

Induced Rayleigh scattering (IRIS) was studied in Ref.

94, where it was possible for the first time to measure the hydrodynamic relaxation rate of inhomogeneities in oriented water-lipid smectics.

It is interesting to discuss the spectrum of light scattering in LC.^{14,95-97} It is known that a Rayleigh-line wing due to light scattering by orientation fluctuations of individual molecules is observed in all liquids that consist of anisotropic molecules. In LC, this is caused by order-parameter fluctuations. In addition to a relatively weak but broad line centered on the laser frequency, the light-scattering spectrum of an LC contains a strong narrow line with a half-width of ~ 100 MHz.⁹⁸ This might be explained by taking into account corrections for the temporal and spatial inhomogeneity of the local field. The average-field approximation describes the orientation fluctuations in a smoothed local field and predicts a Lorentz line counter with critical linewidth behavior for the scattered radiation. In a more exact description, the problem of the reradiation by N interacting molecules reduces to a problem with N coupled oscillators (which describe the orientational motion). In the strong-damping limit, a system of N coupled oscillators has a large number of resonance lines, whose frequencies are negligibly small compared to their widths. Thus, a number of Lorentz lines with various widths, centered on the zero frequency, form in the scattering spectrum. The width of the narrowest of these lines depends critically on temperature via the smoothed local field. The other lines are much broader; they vary weakly with temperature and characterize basically the orientational fluctuations of single molecules.⁹⁸

The high accuracy and directness of nonlinear optical methods for study of pretransition effects in LC have already been demonstrated. In addition to broadening the range of LC compounds, they now offer progress in analysis of transitions between various mesophases and in analysis of heterostructures, using highly developed statistical methods to reduce the results.

4. SELF-ACTION EFFECTS OF STRONG RADIATION IN LC

The use of light self-action effects in LC, especially in the PT range, where the specific properties of LC become most conspicuous, is an example of how the use of new materials can yield essentially new informa-

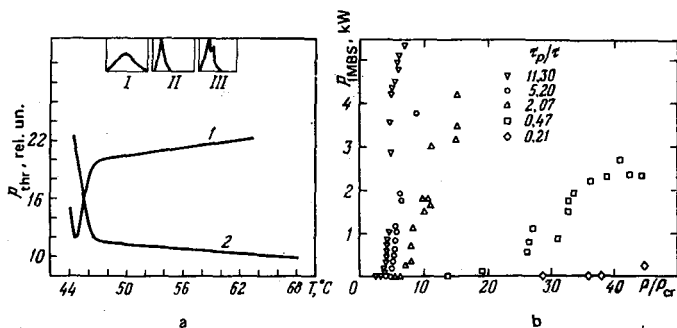


FIG. 11. a) Threshold power of IRS (1) and IMBS (2)⁹² (the laser-pump pulse (I) and the scattered-radiation pulses at $T = 44.8^\circ\text{C}$ (III) and 45.1°C (II) are shown at the top); b) backward IMBS output power vs. pump power at various values of τ_p/τ (EBBA NLC).⁸

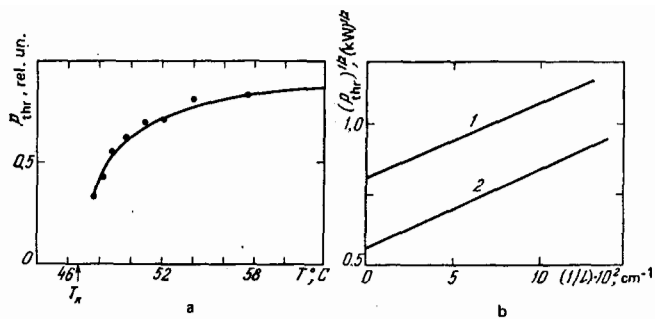


FIG. 12. Self-focusing threshold power P_{thr} vs. temperature of MBBA in isotropic phase (a) and vs. cell length (b) at $T = 53^\circ\text{C}$ (1) and 47.8°C (2).⁹⁹

tion on the course of classical nonlinear effects. First of all we are dealing here with self-focusing of light (SF), with its importance for nonlinear optics. The problem of quantitative description of SF and comparison of experiment with theory is a highly urgent one, and there are practically no reliable experimental data for nonstationary SF. This problem has been solved for LC, where the only quantitative experimental results thus far have been obtained on nonstationary SF in a liquid;¹³⁾ in addition, by varying the temperature of a single LC specimen, it is possible to investigate SF in all regimes: from stationary ($\tau_p \gg \tau$) through the intermediate range ($\tau_p \sim \tau$) to the nonstationary regime ($\tau_p < \tau$). LC may also provide the first case of a medium in which the nature of SF is strongly influenced by the SD of nonlinear response.

a) Self-focusing of light

1) Experimental observation. Stationary and nonstationary regimes. The first data on SF in LC were obtained in Ref. 92 in a study of the IRS and IMBS thresholds in the PT range. A later study⁹⁹ reported on the results of the first direct observations of SF; SF was investigated as a function of the length and temperature of a cell containing MBBA in the isotropic phase. The experimental results basically agreed with theoretical predictions¹⁰⁰: as a result of strong molecular anisotropy, comparatively weak laser fields are capable of causing appreciable ordering of the LC's isotropic phase.

The work was done with an MBBA NLS (PT temperature about 46.8°C). The threshold power of the SF beam was studied as a function of temperature in a cell of length $l = 30$ cm; P_{thr} was also measured as a function of cell length at various temperatures (Fig. 12). The plots of $\sqrt{P_{thr}}$ against $1/l$ are linear, in agreement with theory. It is significant that the threshold power of SF in MBBA is nearly two orders below the corresponding value for CS_2 .

Measurements of nonstationary SF are of the greatest interest.^{9,103} By varying the temperature of a suit-

¹³⁾ Since the values of τ lie in the picosecond range for ordinary liquids, observation of nonstationary SF would require picosecond laser pulses, techniques for generations of which are not now adequately developed.

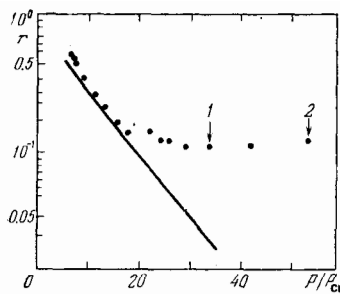


FIG. 13. Beam self-focusing radius vs. power. The arrows indicate the IMBS (1) and IRS (2) threshold powers.¹⁰

able LC compound, it is possible to vary the relaxation time τ in a range from $\tau \gg \tau_p$ to $\tau \ll \tau_p$; this means that both quasistationary and nonstationary SF can be studied with the same pulse from a Q-switched laser. The refractive-index increment δn induced by the laser field E ($n = n_0 + \delta n |E|^2$) is given by the expression¹⁰¹

$$\delta n(t) = \frac{n_2}{\tau} \int_{-\infty}^t |E(t')|^2 \times \exp\left(-\frac{t-t'}{\tau}\right) dt', \quad (17)$$

where n_2 is a parameter of the medium. If $\tau_p \gg \tau$

$$\delta n(t) = n_2 |E(t)|^2, \quad (18)$$

and if $\tau_p \ll \tau$

$$\delta n(t) = \frac{n_2}{\tau} \int_{-\infty}^t |E(t')|^2 dt'. \quad (19)$$

Theoretical analysis of SF has advanced rather far for the first case¹⁰¹; analysis of nonstationary SF is possible basically with the aid of numerical methods.¹⁰²

The results of experimental nonstationary SF studies in the isotropic phase of the MBBA NLC⁹ (a single-mode ruby laser with $\tau_p = 10$ nsec and a peak power of 50 kW was used) agree well with the corresponding calculations.¹⁰² An almost exponential decrease of the radius of a self-focusing beam with increasing power was obtained (Fig. 13); the minimum beam size was limited at $P/P_{cr} = 20$ ($P_{cr} = 0.12$ kW), an effect that the authors believed due to two-photon absorption.

Systematic and complete measurements have been made for EBBA NLC in the isotropic phase.¹⁰³ The results were used to find the T -dependence of the nonlinearity parameters:

$$\begin{aligned} n_2 &= 6.35 \cdot 10^{-9} \text{ (cgs esu} \cdot \text{K)} (T - T^*)^{-1}, \\ \tau &= e^{(2800\text{K}/T)} \cdot 7.0 \cdot 10^{-11} \text{ (nsec} \cdot \text{K)} (T - T^*)^{-1}, \end{aligned} \quad (20)$$

where $T^* = T_K - 1.0$ K, and also of the critical power P_{cr} (Table VII).

Complete quantitative comparison of theory and ex-

TABLE VII. Parameters of self-focusing in EBBA.¹⁰³

$T, ^\circ\text{C}$	τ, nsec	τ_p/τ	$n_2, 10^{-11} \text{ cgs esu}$	P_{cr}, kW
79.7	72.5	0.24	237	0.071
96.0	7.25	2.07	33.4	0.503
112.0	2.87	5.2	48.2	0.926
130.8	1.33	11.3	11.8	1.420

periment over the entire range of parameters is hampered by the lack of detailed numerical calculations. The factors that limit the diameter of the beam in SF and polarization effects, with allowance for which the nonstationarity of the process may result in sharp anisotropy of the beam, also require further investigation.¹⁰⁴

2) Self-focusing near a phase transition. Influence of SD of nonlinear susceptibility. In addition to the sharp temperature dependence of the relaxation times in the PT range, there is a characteristic increase in the relative contribution of spatial-nonlocalism effects in nonlinear establishment of orientation.¹⁰⁵ SD effects are more conspicuous in LC than in ordinary liquids; still, they remain weak, because the influence of the dispersion on SF threshold characteristics may be evident only in the immediate vicinity of the PT point, which is difficult of access in experiment. At the same time, certain qualitatively new aspects of SF are related to the SD of nonlinearity.

Spatial nonlocalism of nonlinear susceptibility due to laser heating and the intrinsic SD of the order parameter may result in the appearance of quasiwaveguide SF regimes; the SD of nonlinearity also explains the saturation of minimum beam radius that is observed in experiments at high powers and the stability against layering of the beam into individual filaments, even at appreciable excesses over threshold, which is uncommon for ordinary liquids.

The variation of the slow complex amplitude A of the linearly polarized wave is described by the equation¹⁰¹

$$\left(\frac{\partial}{\partial z} + \frac{i}{2k} \Delta_{\perp} + \frac{1}{v_{gr}} \frac{\partial}{\partial t} + \delta\right) A = \frac{4\pi\omega i \epsilon_a S A}{3nc}; \quad (21)$$

here z is the propagation coordinate, k is the wave number, $\Delta_{\perp} = \partial^2/\partial x^2 + \partial^2/\partial y^2$ and v_{gr} is the group velocity. The establishment of the order parameter is described by

$$\eta \frac{\partial S}{\partial t} + a(T - T^*) S = L \Delta_{\perp} S + \frac{2\epsilon_a |A|^2}{9}, \quad (22)$$

where $L = a(T - T^*)L_{or}/4$, L_{or} is the molecular correlation radius, δ is the absorption coefficient, and η is the viscosity. Near the PT, the relaxation time $\tau \sim \eta/\alpha(T - T^*)$ varies sharply with temperature, so that the influence of laser heating may be decisive, especially in a quasistationary regime. The variation of the medium's temperature is described by the heat conduction equation¹⁰⁵

$$C\rho \frac{\partial T}{\partial t} = \kappa \Delta_{\perp} T + \frac{\delta c n |A|^2}{8\pi}; \quad (23)$$

where κ is the thermal conductivity, C is the heat capacity, and ρ is the density.

System (21)–(23) was analyzed in the paraxial approximation; it has also been subject to detailed numerical analysis.¹⁰⁵ The "repulsive forces" governed by the SD of the order parameter and by heating of the medium prevent SF and come to dominate at small spatial scales: the diameter of the beam oscillates and its largest cross section is equal to its entrance cross section. With increasing power and weakening of the order-parameter SD, the depth of the beam-width beats

decreases sharply just above threshold. The weak heating of the medium at small excesses over threshold does not affect the stabilization of the minimum cross section, but the nonlocalism of the heating asserts itself strongly at high powers, preventing collapse of the beam—the depth of the beats increases. Mutual compensation of these effects results in the stabilization of minimum laser-beam cross section that was recorded in Ref. 103.

b) Defocusing of light. The thermal-lens effect

The thermal-lens effect (TLE) was first observed experimentally in Ref. 106; it has since been the object of many theoretical investigations (see Ref. 101). The TLE results from the change in the refractive index on laser heating of the medium; SF is observed in materials with $dn/dT > 0$ and defocusing at $dn/dT < 0$. The far-field pattern shows interference with a characteristic ring structure.¹⁰⁷

The TLE in a thin layer of MBBA NCL was investigated in Ref. 108; as a result of the LC's birefringence, both SF and defocusing were observed, depending on the polarization of the laser beam. The experiment was performed with a 30- μm MBBA cell at temperatures from 10 to 43°C. The laser radiation (argon laser with outputs up to 180 mW in a beam 100 μm in diameter) was incident perpendicular to the plane of the cell and could be polarized either parallel (E_{\parallel}) or perpendicular (E_{\perp}) to the director. The authors observed the appearance of a ring structure, with the polarization E_{\perp} corresponding to a spot of smaller diameter than E_{\parallel} at a given laser power. In Ref. 109, the TLE was used to measure the heat capacity C_p and thermal conductivity Λ of the isotropic MBBA phase near $T = T_K$. A microcomputer was used in the experiment so that the fluctuations of the measured parameters could be monitored and the experiment could be repeated several times in the same temperature range. The optical length of the cell with the MBBA LC was 1 cm; the temperature was stable to within $\pm 0.01^\circ\text{C}$. Easily observed thermal lenses were formed at a power of 50 mW.

A modified Jamin interferometer was used to record the refractive-index change Δn as a function of temperature (Fig. 14). Appropriate reduction of the results yielded C_p , Λ , and the diffusion coefficient as functions of temperature (see also Ref. 125).

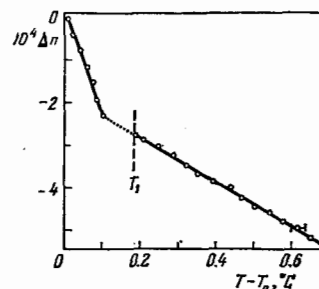


FIG. 14. Variation of Δn with temperature in TLE.¹⁰⁹ T_1 is the induced-transparency temperature of the specimen. T_0 is the temperature at which the ring structure is blurred by the turbidity of the medium.

c) Light-induced change in LC structure

The changes in the structure of LC under the action of magnetic and electric fields, static and low-frequency, have been studied in detail both theoretically and experimentally.^{2,4} The current broadening of research on nonlinear optical effects makes analysis of LC deformation by high-intensity electromagnetic fields a priority problem. An example of these deformations is the increase in the pitch of the cholesteric structure in the field of a traveling wave¹¹⁰ with a frequency outside of the circular-dichroism band.⁶⁶ Such a structure can be induced in the liquid by a spiral standing wave.¹¹¹ Here the index of dichroism is proportional to the intensity and the rotatory power is a square-law function, with estimates indicating that its magnitude is comparable to the rotatory power for optically active crystals.¹¹²

Recently, there has been substantial interest in the study of the characteristics of various physical systems by measuring the decay time of periodic gratings induced in such media with the aid of laser fields. Gratings of this kind are investigated in holographic and laser systems (DFB lasers^{76,74}) and resonant media.^{113,114} LC, whose high sensitivity to external fields makes it easy to create such periodic structures, are promising from this standpoint.^{5,94,115} Structures induced within laser resonators are especially valuable here.^{116,117}

1) Induction of line gratings in LC. Observations of reorientations of LC in a laser field were reported in Ref. 5. Regions with an unstable orientation different from the original planar orientation form in the LC layer; the reorientation is stable at energy densities $\geq 0.1 \text{ J/cm}^2$. A reversible record with high spatial resolution could be obtained from the irradiated LC layer.

Active Rayleigh-scattering spectroscopy was used in a study of LC gratings in Ref. 94 to determine the relaxation rates of local water-concentration fluctuations in oriented water-lipid smectics (WLS). (WLS are good models for biological membranes.) The grating in Ref. 94 was created by superposing argon-laser beams ($\lambda = 5145 \text{ \AA}$) in the specimen, where the intensity distribution took the form

$$I = F(x, y, z) [1 + \cos(q_0 x + \psi)], \quad (24)$$

where $q_0 = 4\pi/\lambda \cdot \sin(\theta/2)$, θ is the angle between beams, the function $F(x, y, z)$ describes the profiles of the beams, and ψ is the phase shift between them. Formation of the diffraction grating causes local heating at the interference maxima, and this changes the refractive index. Disappearance of the Bragg diffraction maxima on the induced grating is observed with a probing HeNe laser when one of the argon-laser beams is switched off, so that the relaxation time can be determined. The main source of error is the presence, in addition to Bragg diffraction on the periodic part of (24), of diffraction on inhomogeneities of the weakly variable function $F(x, y, z)$. This effect can be eliminated by heterodyning; the Bragg signal then has typical efficiency of the order of 10^{-3} . The experiment made is possible to observe both relaxation of water-concentration fluctuations in a WLS with a time constant $\tau_w^{-1}(q_0) = Dq_0^2$ and

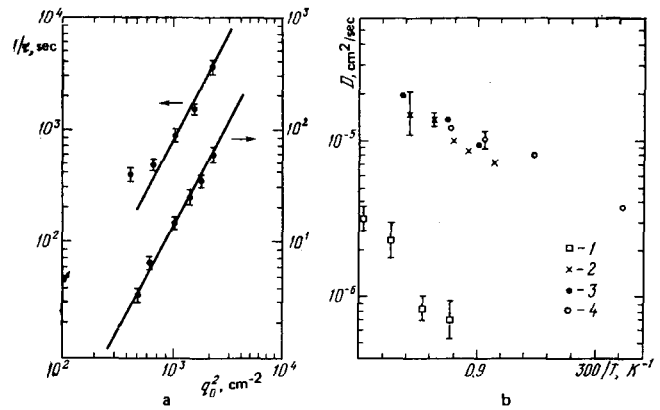


FIG. 15. a) Fluctuation relaxation rate in IRIS as a function of grating period $2\pi/q_0$ (the upper row of circles represent thermal diffusion, the lower row water-concentration fluctuations; the solid lines represent theory);⁹⁴ b) temperature dependence of D for WLS specimens containing various amounts of water⁹⁴ (1) 10%; 2) 17%; 3) 21%; 4) 24%].

thermal decay with $\tau_T^{-1}(q_0) = \chi q_0^2$ (D and χ are coefficients of proportionality).

The results obtained in Ref. 94 (Fig. 15) provided the first experimental proof of the importance of concentration relaxation, thereby confirming the validity of the hydrodynamic WLS model.

2) Change in pitch of cholesteric structure in traveling-wave field. When a strong circularly polarized wave propagates along the axis of a CLC, its period should increase,¹¹⁰ and the wavelength range in which Bragg reflection occurs should therefore be shifted. For small anisotropies $|\varepsilon_a/\varepsilon_o| \ll 1$, the variation of the reciprocal period is described by

$$K_{22}(q - q_0) = -\frac{\varepsilon_a^2 E_0^2}{32} \frac{\omega^2}{c^2} \left(\frac{\omega}{c} \sqrt{\varepsilon} + 2q_0 \right) \left[\varepsilon q_0^2 \left(\frac{\omega}{c} \sqrt{\varepsilon} + q_0 \right)^2 \right]^{-1}, \quad (25)$$

where E_0 is the amplitude of the light wave and K_{22} is the constant of elasticity. The range of validity of this result is limited to the rather high fields at which the $\varepsilon(E)$ dependence can assert itself. Absorption (and the associated laser heating of the medium) and, in thin specimens, the boundary effect, may make observation of the effect difficult.

3) Induction of cholesteric structure in NLC by the field of a spiral standing wave (SSW). We present the basic results from calculation of a new effect—the light-induced transition from the nematic to the cholesteric phase of an LC in the field of a laser SSW.¹¹⁸

The variation of the slow amplitudes of the circularly polarized field components in the LC is described by the equations⁶⁸

$$\left(\frac{d^2}{dz^2} + \frac{\omega^2 \varepsilon_0}{c^2} \right) A_{\pm} + \frac{\omega^2 \varepsilon_a}{2c^2} A_{\mp} e^{\pm 2i\theta} = 0. \quad (26)$$

The light wave is assumed plane and θ is the angular variable that determines the director components. The influence of the light field on θ is taken into account with Euler-Lagrange equation

$$\frac{d^2 \theta}{dz^2} = \varepsilon_a [\text{Re}(A_+ A_-^*) \sin 2\theta + i \text{Im}(A_+ A_-^*) \cos 2\theta] \frac{1}{4K_{22}}. \quad (27)$$

It follows from (27) that a cholesteric structure is established in the medium if the field is a superposition of two colliding circularly polarized waves:

$$\theta = kz, \quad A_{\pm} = 2E_0 e^{\pm i k z}, \quad k = \frac{\omega}{c} \sqrt{\epsilon_0 + \frac{\epsilon_a}{2}}. \quad (28)$$

The solution (28) is valid for an unbounded medium; as in the case of the Fredericks transition,^{2,4} inclusion of boundary conditions results in the appearance of a threshold-type dependence of the field on specimen thickness.

The induced structure is distorted near the boundaries of an LC of finite thickness with arbitrary boundary conditions. The inhomogeneity-region dimension L_1 can be found on the assumption that the SSW distortions are small. Considering the least favorable boundary condition $\theta(0) = \pi/2$, $\theta(z > l/2) \approx kz$ (l is the thickness), we obtain

$$\theta = kz + \arcsin\left(\operatorname{sch} \frac{z}{\bar{z}}\right), \quad (29)$$

where $\bar{z}^2 = K_{22}/2\epsilon_a E_0^2$. Thus, the inhomogeneity region becomes smaller as the intensity increases, and the threshold intensity required to satisfy the inequality $L_1 < l/2$ is

$$I_{\text{thr}} = \frac{81cK_{22}\sqrt{\epsilon_0}}{4\pi\epsilon_a l^3}. \quad (30)$$

When short laser pulses are considered, Eq. (27) must be supplemented with a term for viscosity:

$$\eta \frac{\partial \theta}{\partial t} = K_{22} \frac{\partial^2 \theta}{\partial z^2} - \epsilon_a E^2(t) \sin[2(\theta - kz)]. \quad (31)$$

This equation is valid if the pulse duration $\tau_p > l/c$; $l > L_1$. An approximate solution that gives good accuracy for all z in the case of short, powerful pulses and correctly describes the establishment of the steady state is

$$\theta = kz - \arctg e^{-W/W_1} \operatorname{tg} kz, \quad (32)$$

here

$$W(t) = \frac{c\sqrt{\epsilon_0}}{4\pi} \int E^2(t) dt, \quad W_1 = \frac{\eta I_{\text{thr}}}{k^3 K_{22}}.$$

When a pulsed laser source is used, the most important characteristic requiring estimation is the time to establish a structure, which is determined from (32): $\tau_y = \eta c \sqrt{\epsilon_0} / 8\pi \epsilon_a I$. Structure is established after a time of the order of τ_p if

$$W \gg \frac{\eta c \sqrt{\epsilon_0}}{8\pi \epsilon_a}. \quad (33)$$

Numerical estimates made by formulas (30) and (33) for MBBA give a threshold power $P_{\text{thr}} \approx 5$ mW and an energy $W_{\text{thr}} \approx 30$ J/cm² ($l = 100$ μ m, beam radius 30 μ m). The effect should therefore be observable not only in the fields of powerful pulsed lasers (nonstationary regime), but also in gas-laser fields (stationary regime).

The basic experimental difficulty is evidently that of producing SSW in LC (compare with Ref. 124). It is also necessary to consider other possible effects (thermal, for example) of exposure of the LC to the laser wave, effects that might reorient the LC. Major difficulties also arise in observation of the induced structure. They are considerable even for induced line gratings²⁴; the best way to detect cholesteric structure

is to observe the reflected wave with wave vector \mathbf{k}' that satisfies the resonance Bragg condition $\mathbf{k}' = \mathbf{k}_0 + \mathbf{k}_r$, where \mathbf{k}_0 is the wave vector of the weak probing wave and $\mathbf{k}_r \equiv \mathbf{q}$. Here the angular width of resonance is determined by the formula $\Delta\varphi = 1/kl_0$, where l_0 is the extinction length, $l_0 = 4 \sin \alpha \epsilon_0 \lambda / (1 + \cos \alpha) \cdot 2\pi \epsilon_a$. It amounts to several degrees, and it is necessary that $l \gg l_0$ to register the reflected wave.

(d) LC interresonator nonlinear elements

The operation of a new optical device—the bistable Fabry-Perot resonator (FPR) was recently proposed and demonstrated; it shows sharply nonlinear properties (for example, possesses hysteresis) and can function as an optical shutter, discriminator, front shaper, or optical memory element.¹¹⁷ Devices of this type contain an electrooptical phase modulator with feedback or a medium with a refractive-index nonlinearity inside an FPR in which a saturating absorber is placed. NLC are especially interesting in the latter case.

Systems of this kind with “artificially” created nonlinearity have a number of advantages: they can function at low optical levels, are free of limitations on power or on operating time, and work over a broad range of wavelengths, which is limited only by reflection at the mirrors and by absorption; in addition, switching between the stable operating points can be accomplished either electrically or optically.

The first studies of a nonlinear FPR using the Kerr effect in the MBBA isotropic phase were carried out in Ref. 116. Good agreement between theory and experiment was obtained on the assumption that the refractive-index changes induced by the field influence only the phase shift $\Delta\Phi$.

If a plane wave $E_{\text{in}}(t) = \mathcal{E}_i(t) e^{-i\omega t}$ strikes the FPR, the field at its output has the form

$$E_{\text{out}}(t) = T \exp\left[i\omega\left(\frac{n_0 d}{c} - t\right)\right] \int_{-\infty}^t \left(\frac{d\mathcal{E}_i(t')}{dt'}\right) \frac{1 - R_\alpha \exp[i\Phi(t') - (t-t')/\tau_c]}{1 - R_\alpha \exp[i\Phi(t')}} dt', \quad (34)$$

where $\tau_c = t_R / |1 - R_\alpha \exp(i\Phi)|$ is the buildup time of the field in the resonator, T and R are the transmission and reflection coefficients of the FPR mirrors, d is the length of the resonator, $R_\alpha = R \exp(-\alpha d)$, α is the damping coefficient, which includes all losses, and $t_R = 2dn_0/c$. The phase shift $\Delta\Phi$ induced by the optical field satisfies the Debye relaxation equation

$$\tau_D \frac{\partial \Delta\Phi}{\partial t} + \Delta\Phi = \frac{3d\omega}{c} n_2 (|E_{\text{fwd}}|^2 + |E_{\text{bwd}}|^2) \quad (35)$$

(here τ_D is the Debye relaxation time, E_{fwd} and E_{bwd} are the forward and backward waves inside the FPR, and $|E_{\text{out}}|^2 = n_0 T |E_{\text{fwd}}|^2$). Equations (34) and (35) fully describe the dynamic properties of the FPR and can be solved numerically.

For MBBA at $T = 45^\circ\text{C}$ we have $n_2 = 1.5 \cdot 10^{-9}$ cgs esu, $\tau_0 = 174$ nsec, and $\alpha = 0.22$ cm⁻¹; experimentally, $\tau_c = 0.55$ nsec ($d = 1$ cm, $R = 0.98$). A Q-switched ruby laser was used to induce $\delta n(\tau_p \sim 12$ nsec, $I = 10$ MW/cm², $r_0 = 0.13$ cm); the phase shift was measured with an He-Ne laser. The measurements were made at detun-

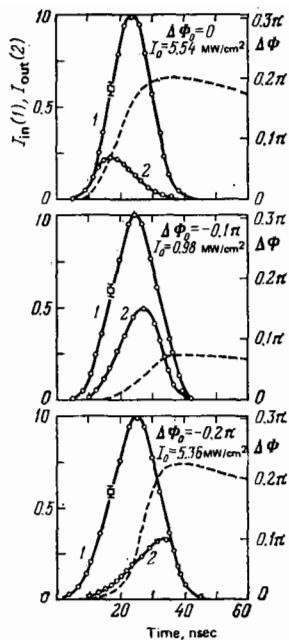


FIG. 16. Input $I_{in}(t)$ (1) and output $I_{out}(t)$ (2) intensities of nonlinear FPR as functions of time at three values of the delay $\Delta\Phi_0$.¹¹⁶ The solid curves were calculated from Eqs. (34)–(35), the dashed curves represent the field-induced phase lag $\Delta\Phi(t)$; I_0 is the peak input-signal intensity.

ings $\Delta\Phi_0 = 0, -0.1\pi$, and -0.2π , each of which corresponded to a certain mode of the nonlinear FPR in the steady state (Fig. 16).

When $\tau_c \ll \tau_p \ll \tau_D$, the plot of $|E_{out}(t_{max})|^2$ against $|E_{in}(t_{max})|^2$, where the time $t = t_{max}$ corresponds to the maximum of $\Delta\Phi$, settles onto the characteristic curve for the steady state of a nonlinear FPR (Fig. 17). Three different operating modes are possible here: power limiting (a), differential amplification (b), and a bistable mode (c). The shape of the curve changes as

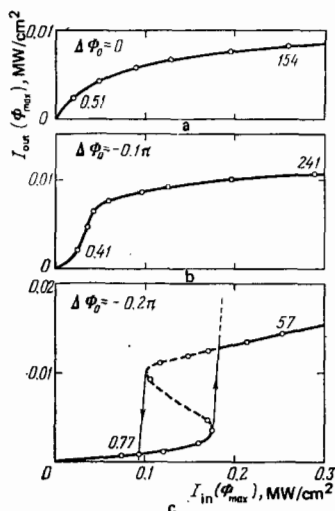


FIG. 17. I_{out} as a function of I_{in} at maximum phase lag $\Delta\Phi_{max}$ for three values of $\Delta\Phi_0$.¹¹⁶ The dashed lines are the steady-state characteristics of the nonlinear FPR. The solid curves were computer-generated for a quasistationary regime ($\tau = 2$ nsec, peak intensity 0.3 MW/cm²).

τ_D decreases. In case (c), this change is manifested chiefly in the range with negative curvature. Shapes similar to the characteristic switching curve are obtained in the limit of very small τ_0 .

CONCLUSION

The results cited in the present review demonstrate the promise of nonlinear optical conversions in LC both from the standpoint of LC physics and from the standpoint of nonlinear optics itself.¹⁴⁾ Practical applications are also expected here: the use of LC as a base for miniature, low-power laser elements and systems. The possibility of investigating critical phenomena by methods of nonlinear optics opens up a new approach to study of PT, and here we may expect to acquire important physical information. Special note should be taken of the ARS method, which enables us to make local measurements of nucleation in the new phase and to observe frequency-addition effects (harmonic generation, parametric processes), which determine the higher moments of the LC's distribution functions, as well as to investigate relaxation times in periodic structures induced by the laser field in the LC. There is also great interest in the possibilities of intraresonator modulation of LC parameters.

Although the nonlinear conversions obtained thus far in LC have not been very efficient (except for light self-focusing), this is due less to the general properties of LC than to the fact that "random" LC have been investigated up to the present time and no deliberate search for the most efficient LC has been made. Considering the already delineated methods of synthesizing liquid-crystal materials with high nonlinearity, we may expect broad practical use of LC elements in nonlinear optical systems (nonlinear mirrors, shutters, etc., including also elements controlled by laser radiation). A natural extension of these approaches is investigation of the generation characteristics of dye lasers in LC matrices. The lowering of the generation threshold of such lasers in the PT range and the broadband tunability that have already been observed experimentally will no doubt be of both practical and purely scientific interest.

Among the nonlinear effects still awaiting investigation in LC, we should note nonlinear OA and other electro- and magneto-optical effects; the usually strong SD of the nonlinear susceptibilities of LC indicates that these effects are very prominent. We note also the promise of effects of wavefront inversion¹²⁶ in LC on the basis of four-photon interaction.^{127 15)}

The authors are grateful to S. A. Akhmanov for supporting the preparation of the present paper and for helpful discussions.

¹⁴⁾This is confirmed by the results of the recent All-Union Scientific and Technical Conference on "Interaction of Laser Radiation with Liquid Crystals" (Dilizhan, 23–27 October 1978).

¹⁵⁾This was drawn to our attention by Ya. B. Zel'dovich.

- ¹L. G. Koreneva, V. F. Zolin, and B. L. Davydov, *Molekul'yarnye kristally v nelineinoy optike (Molecular Crystals in Nonlinear Optics)*, Nauka, Moscow, 1975.
- ²P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford, 1974. (Russ. Transl., Mir, M., 1977.)
- ³R. L. Stratonovich, *Zh. Eksp. Teor. Fiz.* 70, 1290 (1976); 73, 1061 (1977) [*Sov. Phys. JETP* 43, 672 (1976); 46, 562 (1977)].
- ⁴L. M. Blinov, *Usp. Fiz. Nauk* 114, 67 (1974) [*Sov. Phys. Usp.* 17, 658 (1975)]; *Elektrooptika i magnitooptika zhidkikh kristallov (Electrooptics and Magneto-optics of Liquid Crystals)*, Nauka, Moscow, 1978.
- ⁵V. A. Pilipovich, A. A. Kovalev, G. L. Nekrasov, Yu. V. Razvin, and S. V. Serak, *DAN BSSR* 22, 36, 234 (1978).
- ⁶F. S. Felber and J. H. Marburger, *Appl. Phys. Lett.* 28, 731 (1976).
- ⁷G. K. L. Wong and Y. R. Shen, *Phys. Rev. Lett.* 30, 895 (1976); *Physica*, 59, 2068 (1973); *Phys. Rev. Ser. A* 10, 1277 (1974).
- ⁸E. G. Hanson, Y. R. Shen, and G. K. L. Wong, *ibid.* 14, 1281 (1976); *J. Appl. Phys.* 48, 65 (1977).
- ⁹G. K. L. Wong and Y. R. Shen, *Phys. Rev. Lett.* 32, 527 (1974).
- ¹⁰E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.* 36, 193 (1976).
- ¹¹W. H. De Jeu, in: *Solid State Physics*/Ed. H. Erenreich, F. Seitz, D. Turnbull, N. Y.: Academic Press, 34 (1978).
- ¹²J. R. Lalanne, B. Martin, B. Poulguy, and Kelich, *Mol. Cryst. Liq. Cryst.* 42, 351 (1977).
- ¹³J. A. Janik *et al.*, *Physica Ser. BC*, B92 (1977).
- ¹⁴Y. R. Shen, in: *Proc. of the Intern. School of Physics Enrico Fermi. Course LXIV: Nonlinear Spectroscopy*/Ed. N. Bloembergen. Bologna, Italy: Societa Italiana di Fisica, 1977, p. 210; [Russ. Transl. *Nelineinaya spektroskopiya (translation editor S. A. Akhmanov)*, Mir, Moscow, 1979, p. 259.]
- ¹⁵S. M. Arakelyan, G. L. Grigoryan, S. Ts. Nersisyan, M. A. Nshanyan, and Yu. S. Chilingaryan, *Pis'ma Zh. Eksp. Teor. Fiz.* 28, 202 (1978); [*JETP Lett.* 28, 186 (1978)]; in: *Tezisy dokladov Vsesoyuznogo nauchno-tekhnicheskogo soveshchaniya "Vzaimodeistvie lazernogo izlucheniya s zhidkimi kristallami" (Abstracts of Papers at All-Union Scientific-Technical Conference on "Interaction of Laser Radiation with Liquid Crystals")*, Erevan, 1978, p. 7.
- ¹⁶Y. W. Shelton and Y. R. Shen, *Phys. Rev. Lett.* 25, 23 (1970); 26, 538 (1971); *Phys. Rev. Ser. A* 5, 1867 (1972).
- ¹⁷S. A. Akhmanov, G. A. Lyakhov and N. V. Suyazov, *Kvantovaya Elektron. (Moscow)* 4, 556 (1977) [*Sov. J. Quantum Electron.* 7, 308 (1977)].
- ¹⁸S. A. Akhmanov and R. V. Khokheov, *Problemy nelineinoy optiki (Problems of Nonlinear Optics)*, VINITI, Moscow, 1964.
- ¹⁹V. D. Shigorin, *Tr. FIAN SSSR* 98, 78 (1977).
- ²⁰Shen Jen, N. A. Clark, P. S. Pershan, and E. B. Priestley, *Phys. Rev. Lett.* 34, 1552 (1973); *J. Chem. Phys.* 66, 4635 (1977); *Mol. Cryst. Liq. Cryst.* 23, 369.
- ²¹E. M. Aver'yanov and V. F. Shabanov, *Kristallografiya* 23, 320 (1978) [*Sov. Phys. Crystallogr.* 23, 177 (1978)]; *Opt. Spektrosk.* 44, 703 (1978) [*Opt. Spectrosc. (USSR)* 44, 410 (1978)]; V. F. Shabanov, E. M. Aver'yanov, P. Adomenas, and V. P. Spiridonov, *Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR*, Preprint No. IFSO-79F, Krasnoyarsk, 1978.
- ²²A. F. Bunkin, S. G. Ivanov, N. I. Koroteev, A. V. Rezov, and M. L. Sybeva, *Vestn. Mosk. un-ta. Ser. Fizika, Astronomiya* 18, 35 (1977).
- ²³V. M. Avetisyan, N. N. Badalyan, and M. A. Khurshudyan, in: *Tezisy dokladov na IX Vsesoyuzn. konfer. po kogherentnoi i nelineinoy optike (Abstracts of Papers at Ninth All-Union Conference on Coherent and Nonlinear Optics)*, Moscow, 1978, Part I, p. 156.
- ²⁴M. A. Anisimov, *Usp. Fiz. Nauk* 114, 249 (1974) [*Sov. Phys. Usp.* 17, 722 (1975)].
- ²⁵I. P. Il'chishin, E. L. Tikhonov, M. T. Shpak, and A. A. Doroshkin, *Pis'ma Zh. Eksp. Teor. Fiz.* 24, 336 (1976) [*JETP Lett.* 24, 303 (1976)].
- ²⁶S. Kuroda and K. Kubota, *Appl. Phys. Lett.* 29, 737 (1976).
- ²⁷R. S. Akopyan, G. A. Lyakhov, Yu. P. Svirko, and Yu. S. Chilingaryan, *Collection cited in Ref. 15*, p. 30.
- ²⁸I. G. Chistyakov, *Usp. Fiz. Nauk* 89, 563 (1976) [*Sov. Phys. Usp.* 9, 551 (1967)]; *Zhidkie kristally (Liquid Crystals)*, Nauka, Moscow, 1966.
- ²⁹A. P. Kapustin, *Elektroopticheskie i akusticheskie svoystva zhidkikh kristallov (Electrooptical and Acoustic Properties of Liquid Crystals)*, Nauka, Moscow, 1973; *Éksperimental'nye issledovaniya zhidkikh kristallov (Experimental Studies of Liquid Crystals)*, Nauka, Moscow, 1978.
- ³⁰M. Stephen and J. P. Straley, *Rev. Mod. Phys.* 46, 617 (1974).
- ³¹Y. Chandrasekhar, *Rept. Progr. Phys.* 39, 613, 1976.
- ³²R. Williams, *Phys. Rev. Lett.* 21, 342 (1968); *J. Chem. Phys.* 50, 1324 (1969).
- ³³H. J. Kimura, *J. Phys. Soc. Japan* 30, 1273, 1971.
- ³⁴R. Alben, J. R. McColl, and S. Shin, *Sol. State Comm.* 11, 1081 (1972).
- ³⁵G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Serge, *Mol. Phys.* 30, 1345 (1975). P. J. Flory and J. Leonard, *J. Am. Chem. Soc.* 87, 2102 (1965). A. Wulf and A. G. DeRocco, *J. Chem. Phys.* 55, 12 (1971).
- ³⁶P. I. Bos, I. Pirs, P. Uklya, I. W. Doani, and M. E. Neubert, *Mol. Cryst. Liq. Cryst.* 40, 773 (1977).
- ³⁷A. G. Khachaturyan, *Phys. Lett. Ser. A* 51, 103 (1975); *J. Phys. and Chem. Solids* 36, 1055 (1975).
- ³⁸Ya. B. Zel'dovich, *Zh. Eksp. Teor. Fiz.* 67, 2357 (1974) [*Sov. Phys. JETP* 40, 1170 (1975)].
- ³⁹S. M. Arakelyan, L. E. Arushanyan, M. A. Nshanyan, and Yu. S. Chilingaryan, *Fiz. Tverd. Tela (Leningrad)* 20, 3131 (1978) [*Sov. Phys. Solid State* 20, 1806 (1978)].
- ⁴⁰I. G. Chistyakov and L. G. Vistin', *Kristallografiya* 19, 195 (1974) [*Sov. Phys. Crystallogr.* 19, 119 (1975)].
- ⁴¹V. M. Agranovich and V. L. Ginzburg, *Kristallooptika s uchedom prostranstvennoy dispersii i teoriya ékstonov (Crystal Optics in Light of Spatial Dispersion and Exciton Theory)*, Nauka, Moscow, 1975.
- ⁴²L. N. Ovander, *Usp. Fiz. Nauk* 86, 1 (1965) [*Sov. Phys. Usp.* 8, 337 (1965)].
- ⁴³V. M. Fain, *Kvantovaya radiofizika. T. 1: Fotony i nelineinyye sredy (Quantum Radiophysics. Volume 1: Photons and nonlinear Media)*, Nauka, Moscow, 1972.
- ⁴⁴S. A. Pikin and V. L. Indenbom, *Usp. Fiz. Nauk* 125, 251 (1978) [*Sov. Phys. Usp.* 21, 487 (1978)].
- ⁴⁵J. A. Giordmaine, *Phys. Rev.* 138, A1599 (1965).
- ⁴⁶S. P. Straley, *ibid.* Ser. A 10, 1881 (1974).
- ⁴⁷L. D. Landau and E. M. Lifshits, *Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media)*, Gostekhizdat, Moscow, 1957.
- ⁴⁸L. D. Barron, *Nature* 238, 17 (1972).
- ⁴⁹R. B. Meyer, *Mol. Cryst. Liq. Cryst.* 40, 33 (1977).
- ⁵⁰D. Meyerhofer, A. Sussman, and R. J. Williams, *Appl. Phys.* 43, 3685 (1972).
- ⁵¹B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov, and N. I. Chernova, *Pis'ma Zh. Eksp. Teor. Fiz.* 25, 80 (1977) [*JETP Lett.* 25, 70 (1977)].
- ⁵²J. Freund and P. M. Rentzepis, *Phys. Rev. Lett.* 18, 393 (1967).
- ⁵³G. Durand and C. H. Lee, *C. R. Acad. Sci.* 264, 1397 (1967); *Mol. Cryst. Liq. Cryst.* 5, 171 (1968).
- ⁵⁴R. Blintz and B. Jaeksch, *Ferroelectrics and Antiferroelectrics. Lattice Dynamics*, [Russ. Transl., Mir, M., 1975.]
- ⁵⁵S. A. Akhmanov and A. S. Chirkin, *Statisticheskie yavleniya v nelineinoy optike (Statistical Phenomena in Nonlinear Optics)*, Izd-vo Mosk. un-ta, Moscow, 1971.

- ⁵⁶N. B. Baranova, Yu. V. Bogdanov, and Ya. B. Zel'dovich, *Usp. Fiz. Nauk* **123**, 349 (1977) [*Sov. Phys. Usp.* **20**, 870 (1977)].
- ⁵⁷B. F. Levine and C. G. Bethe, *Appl. Phys. Lett.* **24**, 445 (1974), G. Hauchecorne, and G. Kerherve Mayer, *J. de Phys.* **32**, 47 (1971).
- ⁵⁸J. Ducuing, cited in Ref. 14, p. 276.
- ⁵⁹R. C. Miller, *Appl. Phys. Lett.* **5**, 17 (1964).
- ⁶⁰J. P. Hermann, D. Ricard, and J. Ducuing, *ibid.* **23**, 178 (1973).
- ⁶¹A. V. Bortkevich and Ya. S. Bobovich, *Opt. Spektrosk.* **29**, 895 (1970) [*Opt. Spectrosc. (USSR)* **29**, 475 (1970)].
- ⁶²A. I. Kitaigorodskii, *Molekulyarnye kristally (Molecular Crystals)*, Nauka, Moscow, 1971.
- ⁶³L. G. Gurevich and Yu. G. Khronopulo, *Zh. Eksp. Teor. Fiz.* **51**, 1499 (1966) [*Sov. Phys. JETP* **24**, 1012 (1967)].
- ⁶⁴V. A. Belyakov and V. E. Dmitrienko, *Fiz. Tverd. Tela (Leningrad)* **15**, 2724, 3540 (1973); **17**, 491 (1975); [*Sov. Phys. Solid State* **15**, 1811, 2365 (1974); **17**, 307 (1975)].
- ⁶⁵V. L. Pokrovskii and E. I. Kats, *Zh. Eksp. Teor. Fiz.* **73**, 774 (1977) [*Sov. Phys. JETP* **46**, 405 (1977)].
- ⁶⁶W. Maier and A. Saupe, *Zs. Naturforsch.* **13**, 564 (1958); **14**, 882 (1959); **15**, 287 (1960).
- ⁶⁷H. N. DeVries, *Acta Cryst.* **4**, 219 (1951).
- ⁶⁸E. I. Kats, *Zh. Eksp. Teor. Fiz.* **59**, 1854 (1970) [*Sov. Phys. JETP* **32**, 1004 (1971)].
- ⁶⁹R. Drenner, G. Meier, and A. Saupe, *Mol. Cryst. Liq. Cryst.* **33**, 17 (1971). K. A. Suresh, *ibid.* **35**, 267 (1973).
- ⁷⁰V. E. Dmitrienko and V. A. Belyakov, *Zh. Eksp. Teor. Fiz.* **73**, 681 (1977) [*Sov. Phys. JETP* **46**, 356 (1977)].
- ⁷¹O. S. Eritsyanyan, *Izv. AN Arm. SSR. Ser. Fizika* **12**, 118 (1977).
- ⁷²L. S. Goldberg and J. H. Shnur, *Appl. Phys. Lett.* **14**, 306 (1969); *Radio Electr. Eng.* **39**, 279 (1970).
- ⁷³S. A. Akopyan, S. M. Arakelyan, R. V. Kochikyan, S. Ts. Nersisyan, and Yu. S. Chilingaryan, *Kvantovaya Elektron. (Moscow)* **4**, 1441 (1977) [*Sov. J. Quantum Electron.* **7**, 814 (1977)]; cited in Ref. 15, p. 63.
- ⁷⁴S. A. Akhmanov and G. A. Lyakhov, *Zh. Eksp. Teor. Fiz.* **66**, 96 (1974) [*Sov. Phys. JETP* **39**, 43 (1974)].
- ⁷⁵R. W. Terhune, P. D. Maker, and S. M. Savage, *Phys. Rev. Lett.* **8**, 404 (1962).
- ⁷⁶H. Kogelnik and C. V. Shank, *Appl. Phys.* **43**, 2327 (1972). S. Harris, *Appl. Phys. Lett.* **9**, 114 (1966).
- ⁷⁷K. I. Volyak and A. S. Gorshkov, *Izv. vuzov. Ser. Radiofizika* **16**, 635 (1973).
- ⁷⁸A. S. Gorshkov and V. F. Marchenko, *ibid.* **10**, 825 (1967).
- ⁷⁹L. N. Deryugin, A. T. Reutov, and P. P. Tarashchenko, *Mikroelektronika* **3**, 317 (1974).
- ⁸⁰S. Ya. Vyshkind and M. I. Rabinovich, *Izv. Vuzov. Ser. Radiofizika* **15**, 1502 (1972).
- ⁸¹T. Bischofberger and E. Courtens, *Phys. Rev. Lett.* **32**, 163 (1974).
- ⁸²A. J. Martin, G. Meier, and A. Saupe, *Symp. Far. Soc.* **5**, 115 (1971). M. J. Schadt, *Chem. Phys.* **56**, 1494 (1972).
- ⁸³J. O. Kesler, in: *Liquid Crystals and Ordered Fluids: Proc. of American Chemical Society Symposium on Ordered Fluids and Liquid Crystals - 1969/Ed. J. F. Jonson and R. S. Porter, M. Morita, S. Imanura, and R. Yatabe*, *J. Phys. Soc. Japan*, **37**, 1710 (1974).
- ⁸⁴V. N. Tsvetkov and E. I. Ryumtsev, *Kristallografia* **13**, 290 (1968) [*Sov. Phys. Crystallogr.* **13**, 225 (1968)]; H. J. Coler and B. R. Jennings, *Mol. Cryst. Liq. Cryst.* **31**, 571 (1976).
- ⁸⁵J. C. Filippini, C. R. Ac. Sci. Ser. B **275**, 349 (1972); *J. de Phys.* **36**, C1-137 (1975). A. R. Tohnslon, *J. Appl. Phys.*, **44**, 2971 (1973). M. Schadt and W. Helfrich, *Mol. Cryst. Liq. Cryst.* **17**, 355 (1972).
- ⁸⁶V. L. Pokrovskii, *Zh. Eksp. Teor. Fiz.* **71**, 1880 (1976) [*Sov. Phys. JETP* **44**, 987 (1976)]. P. Prost and B. Lalanne, *Phys. Rev.* **8**, 2090 (1973).
- ⁸⁷T. Bischofberger and Y. R. Shen, *Prepr. Univ. Calif.* LBL-6096, 1977.
- ⁸⁸S. A. Akhmanov and N. I. Koroteev, *Usp. Fiz. Nauk* **123**, 405 (1977) [*Sov. Phys. Usp.* **20**, 899 (1977)].
- ⁸⁹E. B. Priestley and P. S. Pershan, *Mol. Cryst. Liq. Cryst.* **23**, 369 (1973). J. P. Heger, *J. de Phys. Lett.* **36**, PL-209 (1975). K. Miyano, *Phys. Lett. Ser. A* **63**, 37 (1977).
- ⁹⁰M. P. Fontana and S. Bini, *Phys. Rev. Ser. A* **14**, 1555 (1976); D. Dvorjetski, V. Volterra, and E. Wiener-Avneer, *Phys. Rev. Ser. A* **12**, 681 (1975); A. Sakamoto, K. Yoshino, U. Kubo and Y. Inuishi, *Japan J. Appl. Phys.* **13**, 1691 (1974).
- ⁹¹P. P. Crooker, *Mol. Cryst. Liq. Cryst.* **42**, 283 (1977).
- ⁹²D. V. G. L. Narasimha Rao and D. K. Agrawal, *Phys. Lett. Ser. A* **37**, 383 (1971).
- ⁹³I. P. Il'chishin, E. A. Tikhonov, and M. T. Shpak, *Ukr. fiz. zh.* **22**, 1915 (1977).
- ⁹⁴Winston Chan and P. S. Pershan, *Phys. Rev. Lett.* **39**, 1368 (1977).
- ⁹⁵K. Miyano and Y. R. Shen, *Phys. Rev. Ser. A* **15**, 2471 (1977).
- ⁹⁶N. M. Amer, Y. S. Lin, and Y. R. Shen, *Sol. State Comm.* **16**, 115 (1975).
- ⁹⁷T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.* **25**, 503 (1970).
- ⁹⁸C. Flytzanis and Y. R. Shen, *ibid.* **33**, 14 (1974).
- ⁹⁹D. V. G. L. Narasimha Rao and S. Yayaraman, *Appl. Phys. Lett.* **23**, 539 (1973).
- ¹⁰⁰P. G. De Gennes, *Phys. Lett. Ser. A* **30**, 454 (1969).
- ¹⁰¹S. A. Akhmanov, A. P. Sukhorukov, and R. V. Khokhlov, *Usp. Fiz. Nauk* **93**, 19 (1967) [*Sov. Phys. Usp.* **10**, 609 (1968)].
- ¹⁰²Y. A. Flec and R. L. Carman, *Appl. Lett.* **21**, 267 (1968); F. Shimizu, *IBM J. Res. Dev.* **17**, 286 (1973).
- ¹⁰³E. G. Hanson, Y. R. Shen, and G. K. L. Wong, *Appl. Phys.* **14**, 65 (1977).
- ¹⁰⁴S. A. Akopyan *et al.*, Paper at Eighth All-Union Conference on Coherent and Nonlinear Optics, Tbilisi, 1976.
- ¹⁰⁵G. A. Lyakhov and V. A. Makarov, *Vestn. Mosk. Un-ta. Ser. Fizika, astronomiya* **20**, 3 (1979); S. M. Arakelyan *et al.*, *Izv. vuzov. Ser. Radiofizika* **22**, 55 (1979).
- ¹⁰⁶Y. P. Gordon *et al.*, *J. Appl. Phys.* **36**, 3 (1965).
- ¹⁰⁷F. W. Dalby *et al.*, *Appl. Phys. Lett.* **16**, 362 (1970).
- ¹⁰⁸V. Volterra and E. Wiener-Avneer, *Opt. Comm.* **12**, 194 (1974).
- ¹⁰⁹G. Koren, *Phys. Rev. Ser. A* **13**, 1177 (1976).
- ¹¹⁰S. G. Dmitriev, *Zh. Eksp. Teor. Fiz.* **65**, 2466 (1973) [*Sov. Phys. JETP* **38**, 1231 (1974)].
- ¹¹¹A. Kastler, *C. R. Acad. Sci. Ser. B* **271**, 999 (1970).
- ¹¹²G. A. Lyakhov, *Zh. Eksp. Teor. Fiz.* **64**, 768 (1973) [*Sov. Phys. JETP* **37**, 390 (1973)].
- ¹¹³D. Heiman, R. W. Helwarth, M. D. Levenson, and G. Martin, *Phys. Lett.* **36**, 189 (1976).
- ¹¹⁴V. M. Arutyunyan and A. Zh. Muradyan, cited in Ref. 23, Part 2, p. 41.
- ¹¹⁵R. M. Herman, R. J. Serinko, and T. A. Wiggins, *Post-Dead. Session of XX Intern. Quantum Electronics Conference, Atlanta, USA*, 1978.
- ¹¹⁶T. Bischofberger and Y. R. Shen, *Appl. Phys. Lett.* **32**, 156 (1978).
- ¹¹⁷P. W. Smith and E. H. Turner, *ibid.* **30**, 280 (1977); T. N. C. Venkatesan and S. L. McCall, *Appl. Phys. Lett.* **30**, 282 (1977). V. N. Lugovoy, *Opt. Acta* **24**, 243 (1977).
- ¹¹⁸G. A. Lyakhov and V. A. Makarov, *Vestn. Mosk. un-ta. Ser. Fizika, astronomiya* **18**, 106 (1977).
- ¹¹⁹V. I. Emel'yanov and Yu. L. Klimontovich, *Pis'ma Zh. Tekh. Fiz.* **4**, 180 (1978) [*Sov. Tech. Phys. Lett.* **4**, 74 (1978)]; cited in Ref. 15, p. 5.
- ¹²⁰V. F. Shabanov, V. P. Ermakov, E. M. Aver'yanov, and B. I. Ostrovskii, *ibid.* p. 59.
- ¹²¹F. Poldy, W. Dvolaitzky, and C. Tawpin, *J. de Phys.* **37**, Colloq. C3, C3-77 (1976).
- ¹²²V. A. Belyakov, V. E. Dmitrienko and V. P. Orlov, *Usp.*

- Fiz. Nauk 127, 221 (1979) [Sov. Phys. Usp. 22, 63 (1979)].
- ¹²³J. A. Janik *et al.*, Pramana Suppl. No. 1, 253 (1975).
- ¹²⁴V. Evtuhov and A. E. Siegman, Appl. Optics 4, 142 (1965).
- ¹²⁵S. Kuroda, M. Kimura, and K. Kubota, Mol. Cryst. Liq. Cryst. 33, 235 (1976).
- ¹²⁶Ya. B. Zel'dovich, V. I. Popovichev, V. V. Ragul'skii, and F. S. Faizullov, Pis'ma Zh. Eksp. Teor. Fiz. 15, 160 (1972) [JETP Lett. 15, 109 (1972)].
- ¹²⁷R. W. Hellwarth, JOSA 67 (1), 1 (1977).
- ¹²⁸M. V. Loseva *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. 25, 80 (1977); 28, 404 (1978) [JETP Lett. 25, 70 (1977); 28, 374 (1978)].
- ¹²⁹L. A. Beresnev, L. M. Blinov, and Z. M. Élashvili, *ibid.* 28, 390 (1978) [28, 360 (1978)].
- ¹³⁰S. M. Arakelyan, O. S. Eritsyán, A. S. Karayan, and Yu. S. Chilingaryan, Paper at Third Conference on Cholesteric Liquid Crystals, Kiev-Borzel', 1979.

Translated by R. W. Bowers