OPTO-ELECTRONICS 2 (1970) 125-151

Optical Harmonic Generation and Laser Light Frequency Mixing Processes in Nonlinear Media*

S. KIELICH
Institute of Physics, Nonlinear Optics Group, A. Mickiewicz University, Poznań, Grunwaldzka 6, Poland

Received 21 July 1970

The essential results achieved during the ten years since the coming of lasers, in the fields of second, third and higher harmonic generation in reflected and transmitted, continuous and pulsed laser light, frequency mixing processes in various materials, and nonlinear optical properties of liquids, gases, crystals and other materials are reported concisely from the available literature. Stress is laid on the newer and more stimulating experimental results, and on their relation with other nonlinear phenomena.

1. Introduction

In 1961, Franken and co-workers [1] performed an artfully devised experiment in which they proved that ruby laser light of wavelength 694.3 nm, focused within a quartz crystal, contained on emerging a small admixture of the second harmonic of wavelength 347.15 nm. The discovery of this phenomenon, which has its source in the nonlinear optical properties of matter, became the starting point of vast developments, further enhanced by the rapid evolution of laser techniques. This has led to the detection of a number of novel optical effects, which have since been discussed in various monographs [2-5] and review articles [6-15]. Here, we intend to give a discussion of the more important theoretical and experimental results achieved in the domains of optical harmonic generation and laser wave frequency mixing over the past ten years of nonlinear optics. The theoretical essentials of coherent nonlinear processes are to be found in the fundamental work of Armstrong *et al* [16], Bloembergen and Pershan [17], Akhmanov and Khokhlov [2], and certain other authors [18-24].

1.1. Linear and Nonlinear Optical Processes

Ordinary light propagating in a transparent body does not affect its optical properties because the electric polarisation $\mathbf{P}(\mathbf{r}, t)$ induced in it is a linear function of the strength $\mathbf{E}(\mathbf{r}, t)$ of the electric field of the light wave oscillating at frequency ω at the point of space $\mathbf{r}$ and moment of time t. A linear relationship between $\mathbf{P}(\mathbf{r}, t)$ and $\mathbf{E}(\mathbf{r}, t)$ results immediately in Lorentz's classical electron theory [25], in which an atom is dealt with as represented by an isotropic harmonic oscillator, as well as in quantum mechanics in a first approximation of perturbation calculus [26]. To a linear approximation, the solutions of Maxwell's equations satisfy the principle of superposition, which states that electromagnetic waves simultaneously traversing a linear medium propagate independently without interacting upon one another. In linear, optically transparent bodies, electromagnetic waves accordingly propagate without distortion, the refractive index depending solely on the properties and thermodynamic state of the medium but not depending on the incident light intensity.

*Invited review article given on 6 April 1970, at the IVth Polish Conference on "Radiospectroscopy and Quantum Electronics" in Poznań. This review covers only such papers as were directly accessible to the author.

All optical phenomena and laws are linear as long as the optically investigated medium is studied by means of a non-intense light probe and is not acted on by external fields or forces. An optically isotropic body, when immersed in an external electric or magnetic field, changes its refractive index and becomes optically anisotropic. The discovery of electric birefringence by Kerr took place in 1875 and of magnetic birefringence by Cotton and Mouton in 1907. The classical theories of these two effects are due to Voigt [27] and Langevin [28], and have since been developed by various authors [26, 29-31]. Still earlier, in 1846, Faraday found that polarised light traversing a medium in the direction of an applied magnetic field underwent a rotation of its plane of polarisation [26]. No counterpart to Faraday's effect is revealed by isotropic bodies subjected to the action of an electric field, but anisotropic ones exhibit the linear electro-optical phenomenon known as Pockels' effect [32]. Still other external agents, such as mechanical stress, liquid flow, acoustic fields, and so forth, cause changes in the refractive index of light [30, 33-35] and give rise to various linear optical processes. The optics of all these phenomena are sometimes referred to as parametric optics, in order to underline the role of external non-optical parameters in them.

Now, when a transparent body is traversed by light of very high intensity, its refractive index and electric permittivity become dependent on the intensity of the light beam; this has indeed been directly observed by various authors, in accordance with theoretical predictions [31, 36, 37], to be the case when using giant pulsed ruby lasers [38-40]. Lasers operating continuously or pulsed emit a parallel beam of monochromatic light, coherent in space and time, and conveying a flux of immense energy density. The very high light intensities of laser beams, never achieved with ordinary light, cause the refractive index to depend on the electric field strength $\mathbf{E}(\mathbf{r}, t)$ of the beam. An electromagnetic wave of such strength, inducing optical nonlinearity in the medium, itself undergoes distortion when propagating in the latter. By Fourier spectral analysis, the original wave of fundamental frequency ω is now additionally accompanied by harmonic components of double frequency 2ω, triple frequency 3ω, and higher harmonics [2-6].

1.2. Nonlinear Polarisations

A medium acted on by very intense electromagnetic radiation exhibits an electric polarisation $\mathbf{P}(\mathbf{r}, t)$ and a magnetic polarisation $\mathbf{M}(\mathbf{r}, t)$ which are in general nonlinear functions of both the electric and magnetic field strengths $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$. An electric, and similarly a magnetic field, harmonically varying with the time t and spatial co-ordinates $\mathbf{r}$, can be represented in the form of Fourier components:

$$\mathbf{E}(\mathbf{r}, t) = \sum_s \mathbf{E}(\omega_s, \mathbf{k}_s) \exp\{i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)\} , \tag{1}$$

where ω_s is the circular oscillation frequency and $\mathbf{k}_s$ the wave vector of the *sth* mode. Summation in (1) extends over all frequency and wave vectors, both positive and negative, with $\omega_{-s} = -\omega_s$, $\mathbf{k}_{-s} = -\mathbf{k}_s$ and, for the Fourier transform (field amplitude), $\mathbf{E}^*(\omega_s, \mathbf{k}_s) = \mathbf{E}(-\omega_s, -\mathbf{k}_s)$.

Provided the electric field strength $\mathbf{E}(\mathbf{r}, t)$ is not excessive, the electric polarisation induced in the medium can be expanded in a power series:

$$\mathbf{P}(\mathbf{r}, t) = \sum_{n=1}^{\infty} \mathbf{P}^{(n)}(\mathbf{r}, t) \tag{2}$$

with $\mathbf{P}^{(n)}(\mathbf{r}, t)$ defining electric polarisation of the *nth* order which can be represented in terms of its Fourier frequency components:

$$\mathbf{P}^{(n)}(\omega_{n+1}, \mathbf{k}_{n+1}) \exp\{i(\mathbf{k}_{n+1} \cdot \mathbf{r} - \omega_{n+1} t)\} . \tag{3}$$

Restricting ourselves, at this stage, to their dependence on the electric vector only, we obtain for the *ith* component of the dipole polarisation (3):

$$\mathbf{P}_i^{(n)}(\omega_{n+1}, \mathbf{k}_{n+1}) = \chi_{ij_1 \ldots j_n}^{\omega_{n+1}} \mathbf{E}_{j_1}(\omega_1, \mathbf{k}_1) \ldots \mathbf{E}_{j_n}(\omega_n, \mathbf{k}_n) , \tag{4}$$

where summation over recurring indices $j_1, \ldots j_n$ is implicit and

$$\chi_{ij_1 \ldots j_n}^{\omega_{n+1}} = \chi_{ij_1 \ldots j_n}(-\omega_{n+1}; \omega_1, \ldots \omega_n)$$

is a tensor of nonlinear electric susceptibility of *nth* order. The dependence of the nonlinear susceptibility tensor on the oscillation frequency is referred to as time or frequency dispersion, whereas its dependence on the wave vectors is termed spatial dispersion. When the waves interact in the medium, time and space synchronisation takes place:

$$\omega_{n+1} = \sum_{s=1}^{n} \omega_s \ , \tag{5}$$

$$\mathbf{k}_{n+1} = \sum_{s=1}^{n} \mathbf{k}_s \ . \tag{6}$$

In a quantum-mechanical interpretation, equation 5 expresses the principle of energy conservation and equation 6 that of momentum conservation for the photons. Sometimes, slight deviations $\Delta\mathbf{k}$ from the condition (6) are taken into consideration, with $|\Delta\mathbf{k}| \ll |\mathbf{k}_{n+1}|$.

Electric polarisations of higher orders (4) and, likewise, magnetic as well as cross (electromagnetic and magneto-electric) polarisations, have been discussed in both a phenomenological and quantum-mechanical approach for various isotropic and anisotropic bodies [16-24], and provide the theoretical foundations of nonlinear optics [2-15].

Equations 1 to 6 account for processes of frequency mixing of different electromagnetic waves which interact with one another in the medium; in particular, they describe the phenomena in which optical harmonics are produced. When one of the electric fields in equation 1 is very strong, or moreover if the medium is acted on by a pumping electric field

$$\mathbf{E}_p(\mathbf{r}, t) = \mathbf{E}(\omega_p, \mathbf{k}_p) \exp\{i(\mathbf{k}_p \cdot \mathbf{r} - \omega_p t)\} + c \cdot c \ , \tag{7}$$

of strength much in excess of that of the electric fields (1), and having a pumping frequency ω_p comparable to ω_s or larger, $\omega_p > \omega_s$, one has parametric interaction of electromagnetic waves. In addition to this amplification of parametrically interacting waves, one can modulate light waves in a nonlinear medium if $\omega_p \ll \omega_s$.

2. Optical Processes of the Second Order

Two electromagnetic waves, of frequencies ω_1 and ω_2 and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, induce in the medium an electric dipole polarisation of the second order:

$$\mathbf{P}_i^{(2)}(\omega_3, \mathbf{k}_3) = \chi_{ijk}^{\omega_3} \mathbf{E}_j(\omega_1, \mathbf{k}_1) \mathbf{E}_k(\omega_2, \mathbf{k}_2) \ , \tag{8}$$

where with regard to (5) and (6) the time and spatial synchronisation conditions for the co-operation of three waves are:

$$\omega_3 = \omega_1 + \omega_2 \ , \tag{5a}$$

$$\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2 + \Delta\mathbf{k} \ . \tag{6a}$$

For the third-rank tensor $\chi_{ijk}^{\omega_3} = \chi_{ijk}(-\omega_3; \omega_1, \omega_2)$ defining the nonlinear susceptibility of the second order, the following space-time permutation symmetry relations are fulfilled [8, 16]:

$$\chi_{ijk}(-\omega_3; \omega_1, \omega_2) = \chi_{jik}(\omega_1; -\omega_3, \omega_2) = \chi_{kij}(\omega_2; -\omega_3, \omega_1) \ . \tag{9}$$

These relations allow us to perform arbitrary permutations of the frequencies ω_3, ω_1, ω_2 simultaneously with the respective indices i, j, k labelling the spatial co-ordinates X, Y, Z of the laboratory reference system.

In optically inactive media without dispersion and absorption, the tensor χ_{ijk} can be regarded as totally symmetric in all indices i, j, k and as having non-zero elements in bodies without a centre of symmetry only. This symmetry conjecture of Kleinman [18] reduces the number of independent tensor elements χ_{ijk} from 27 to 10. The further reduction in number of independent elements depends on the specific crystallographical symmetry of the body and proceeds similarly as in the case of the piezoelectric tensor [41, 42]. In transparent optically active bodies, the tensor χ_{ijk} can be separated into a part $S_{ijk} = (\chi_{ijk} + \chi_{ikj})/2$ and a part $A_{ijk} = (\chi_{ijk} - \chi_{ikj})/2$, respectively symmetric and antisymmetric in the indices j and k. In naturally anisotropic bodies, the second-order effects due to the asymmetric part A_{ijk} are insignificant

as compared with those due to the symmetric part S_{ijk}. On the other hand, in isotropic bodies without a centre of symmetry, such as optically active liquids, the symmetric part vanishes, $S_{ijk} = 0$, and the sole factor causing the mixing of two waves differing as to their frequencies resides in the antisymmetric part A_{ijk}, which in this case is non-zero [23]. Akhmanov and Khokhlov [2], Butcher [4], and Giordmaine [23] have carried out a full tabulation of the non-vanishing elements of the tensor χ_{ijk} for all crystallographical classes as well as for textures and isotropic bodies.

2.1. Conditions for Second-Harmonic Generation (SHG)

When a wave of (fundamental) frequency ω propagating in the direction $\mathbf{k}$ is incident on a nonlinear medium without centre of symmetry, the polarisation induced at frequency 2ω at a point $\mathbf{r}$ in the medium is given as follows [10]:

$$\mathbf{P}_i^{(2)}(2\omega, \mathbf{r}) = \chi_{ijk}^{2\omega}\, \mathbf{E}_j(\omega, \mathbf{r})\, \mathbf{E}_k(\omega, \mathbf{r}) \tag{10}$$

the time-space synchronisation conditions now being:

$$\omega_h - 2\omega_f = 0 \ , \tag{5b}$$

$$\Delta k = k_h - 2k_f = \left(\frac{2\omega}{c}\right)(n_h - n_f) \ , \tag{6b}$$

where ω_f, $\mathbf{k}_f$, n_f are the frequency, wave vector and refractive index of the fundamental wave and ω_h, $\mathbf{k}_h$, n_h respectively those of the harmonic.

The polarisation wave (10) of doubled frequency produces along its path in the medium, at each moment of time, a second-harmonic light wave of electric field strength [10]

$$\mathbf{E}_i(2\omega, r) \approx \chi_{ijk}^{2\omega}\, \mathbf{E}_j(\omega, 0)\, \mathbf{E}_k(\omega, 0) \left\{\frac{1 - \exp i\Delta kr}{\Delta k}\right\} . \tag{11}$$

In accordance with this equation, at $\Delta k = 0$ (matching wave vectors, that is, if $n_h = n_f$), $\mathbf{E}(2\omega, r)$ grows linearly with the distance r until the fundamental wave $\mathbf{E}(\omega, \mathbf{r})$ becomes attenuated. When $\Delta k \neq 0$, the bracketed term on the right-hand side in (11) shows $\mathbf{E}(2\omega, \mathbf{r})$ to vary periodically as a function of the distance $\mathbf{r}$, the period of variation being determined by the phase coherence length [10]:

$$l_{coh} = \frac{\pi}{\Delta k} = \frac{\lambda}{4(n_h - n_f)} \ . \tag{12}$$

By (11), the intensity of the second harmonic of light at the point r is [14]:

$$I(2\omega, r) \approx (\chi^{2\omega})^2 \left\{\frac{\sin \frac{1}{2}\Delta kr}{\frac{1}{2}\Delta k}\right\}^2 I^2 \tag{13}$$

with I denoting the intensity of the incident light wave.

From equation 13, we have at our disposal at least three procedures for increasing the intensity of the second harmonic, namely:

(i) by using giant pulsed lasers providing large intensities I,

(ii) by using strongly nonlinear crystals of large susceptibility $\chi^{2\omega}$,

(iii) by resorting to the equality condition of phase velocities of the fundamental and second-harmonic waves ($\Delta k = 0$).

Giordmaine [43] and Maker *et al* [44], with the aim of increasing considerably the quantum yield of conversion of photons of the fundamental beam into photons of the second-harmonic beam, independently proposed different, well-contrived methods of index matching. Their methods follow from the synchronisation conditions (5b) and (6b) and expressions (11) to (13); the idea is, by properly orientating a sufficiently birefringent naturally anisotropic crystal, to achieve index matching between the laser beam polarised in one direction and its harmonic beam polarised in another direction.

By (12), with decreasing difference Δk, the coherence length increases and so does the length

of the path on which energy is transferred from the fundamental wave to the second harmonic. A successful way of increasing l_{coh} consists in compensating the effect of dispersion by a proper birefringence of the crystal. At $\Delta k = 0$, the conversion yield should increase monotonically with the square of distance up to 100%, converting the whole energy from fundamental to harmonic [10]. Hence, at conditions of phase matching, the conversion of light of a given frequency ω into light of double frequency 2ω is a highly effective process; in practice, conversion efficiency upward of 20% can be achieved, and when additionally resorting to cascade amplification the conversion yield of SHG can be raised to 30 to 35% [45]. Some experiments have revealed conversion saturation [46] due chiefly to a limitation of the interaction length for SHG by birefringence, causing the energy of the fundamental wave and that of the second harmonic to propagate in slightly different directions [47].

2.2. SHG in Transmitted Light

Since the original experiments of Franken *et al* [1], the second harmonic of light has been observed in various piezoelectric and ferroelectric crystals as well as in other nonlinear material, resorting to pulsed crystal lasers as well as semiconductor and gas, pulsed and continuously operating lasers. We shall now proceed to a discussion of the more important results of experiments on SHG in transmitted light.

The crystal laser operating on neodymium-activated calcium tungstate ($CaWO_4 : Nd^{3+}$) emits light of wavelength 1.0582 μm, which is well adapted to the observation of the second harmonic, which has a wavelength of 529.1 nm lying in a region where the human eye is highly sensitive. Miller [48] applied a laser of this kind for SHG in quartz, ferroelectric crystalline $BaTiO_3$, KDP, ADP, CdS [49] and strongly nonlinear $LiNbO_3$ and $LiTaO_3$ crystals [50]. Geusic *et al* [51] observed SHG at 532nm in Ba_2NaNbO_{15} and $K_6Li_4NbO_3$ using a lightly focused, continuously pumped, repetitively Q-switched Nd : YAG laser emitting light of wavelength 1.064 μm. Using ruby lasers (694.3 nm) and neodymium lasers (1.06 μm), SHG was studied in some novel, strongly nonlinear materials, namely HIO_3 [52] and $LiIO_3$ [53]. Recently, Jerphagnon [54] corrected earlier values of the nonlinear susceptibilities of $LiIO_3$ by Maker's fringe technique [44] using a Nd^{3+} : YAG laser with an acoustic Q-switching system. Also, Gurski [55] reported on simultaneous mode-locking and quasi-CW SHG in high-temperature $LiNbO_3$ or $Ba_2NaNb_5O_{15}$ with a Nd^{3+} : YAG laser achieved by electro-optic modulation of the nonlinear medium. Recently, blue light at 473.0 nm generated in KDP and HIO_3 as internal Q-switched SHG of the 946.0 nm line of a Nd^{3+} : YAG laser [56] has been observed.

Graja [57], Kurtz [58] and Rez [59] went over to SHG in crystal powders, thus by-passing the tedious procedures of single crystal preparation. The powder method is simple and convenient; it makes possible rapid assessments of the nonlinear optical properties of various new materials, particularly crystals of organic dyes, which exhibit strong nonlinearity and intense SHG [60-64].

Gas lasers (continuous and pulsed), notwithstanding their low power, yield coherence lengths in SHG which are larger by several orders than those from ruby lasers. The use of gas lasers permits the achievement of a higher degree of accuracy in SHG studies, obtaining quantitative data on the quantum yield and nonlinear susceptibilities, and a more precise measurement of the accuracy of frequency doubling as well as of the harmonic linewidth. Ashkin *et al* [65] observed continuous SHG using the infra-red transition 1.1526 μm of the He-Ne gas laser with a focused and non-focused beam, and remeasured the second-order susceptibility component d_{36} of KDP finding a value five times larger than that measured with a ruby laser [43, 44]. Patel [66], resorting to a CO_2 laser with focused fundamental continuous wave 10.5915 μm, measured SHG at 5.2958 μm in tellurium crystal, zinc blende crystals (InAs, ZnS, etc.), hexagonal crystals (CdS) and a trigonal crystal (Se). Bjorkholm and Siegman [67] used optimally focused beams from a CW He-Ne gas laser operating at 632.8 nm and performed an accurate absolute measurement of SHG in ADP crystal. An identical laser was also used for the observation of SHG in piezoelectric $BeSO_4 . 4H_2O$ crystal [68].

Rabin and Bey [69] have discussed the theory of SHG in crystals with natural optical

activity and derived new phase-matching conditions. Simon and Bloembergen [70] studied experimentally SHG in the optically active crystals $NaClO_3$ and $NaBrO_3$ of the cubic class 23 and obtained in place of equation (12) for the coherence length

$$l_{\mathrm{coh}}^{\pm} = \frac{\lambda}{4(n_{\mathrm{h}}^{\pm} - n_{\mathrm{f}}^{\mp})} \tag{14}$$

two different values corresponding to the right and left senses of circularly polarised waves.

Investigation has also dealt with various other aspects of SHG with focused and non-focused laser beams [71, 72]: simultaneous generation of two waves of double frequency [73], conical refraction in SHG in biaxial crystals [74], and the influence of temperature and domain structure on SHG in ferroelectric crystals [48, 60, 61, 75, 76]. Particularly noteworthy is the extensive paper by Kleinman *et al* [71] which contains a detailed study of many experimental and theoretical aspects of SHG by focused laser beams.

2.3. SHG in Reflected Light

In accordance with a general theory for the generation of harmonic light at the boundary of a nonlinear medium developed by Bloembergen and Pershan [17], generation of harmonic waves is not restricted to experiments in transmitted light but extends to reflected light as well. A widely readable account of the essentials of this phenomenon, and a review of the papers up to 1965, are to be found in Bloembergen's paper [77].

The incident laser beam at frequency ω induces, after refraction, a polarisation at the harmonic frequency 2ω which in the case of bodies without a centre of inversion is given by equation (10). SHG in reflection was first observed by Ducuing and Bloembergen [78], when a GaAs mirror (or a piezoelectric mirror such as Te or InSb of symmetry $\bar{4}3$ m) was submerged in a linear dispersive fluid and illuminated with a ruby laser.

The reflected second harmonic has a direction different from that of the reflected fundamental beam; the variation of its intensity (SHR) with the angle of incidence of the primary ruby or neodymium glass laser beam has been measured by Chang and Bloembergen [79]. Bloembergen and Lee [80] observed the internal reflected SHI generated at 486 nm by an incident beam totally reflected by a nonlinear medium ($NaClO_3$ or KH_2PO_4) immersed in an optically denser linear fluid (1-bromonaphthalene). The incident beam was the stimulated Stokes beam induced by a Q-switched ruby laser in H_2 gas. In accordance with theory [17, 81], this experiment shows anomalously high, reflected harmonic intensities because phase matching is important for the reflected intensity at the critical angle for total reflection. Recently, a detailed discussion of total reflection phenomena in SHG has been given by Bloembergen *et al* [82].

The general theory of nonlinear polarisation [20, 22, 24] leads to the conclusion that, in addition to the dipolar polarisation of second order in the electric dipole approximation of equation (10), yet other multipolar contributions playing a particularly important role in bodies with a centre of symmetry (where the electric dipole-dipolar term vanishes) have to be taken into account. The electric quadrupole approximation to the dipolar polarisation of the second order at frequency 2ω is given [20, 24] by:

$$P_i^{(2)}(2\omega, 2\mathbf{k}) = \kappa_{ijkl}^{2\omega} E_j(\omega, \mathbf{k}) \nabla_k E_l(\omega, \mathbf{k}) \ . \tag{15}$$

Above, $\kappa_{ijkl}^{2\omega}$ is a tensor of rank 4 defining nonlinear dipolar susceptibility in the quadrupolar approximation. Its elements are non-zero even in media which possess a centre of symmetry.

A contribution of the same order of magnitude as that of equation (15) comes from quadrupolar polarisation of the second order in the electric dipolar approximation [20, 24]:

$$Q_{ij}^{(2)}(2\omega, 2\mathbf{k}) = \kappa_{ijkl}^{2\omega} E_k(\omega, \mathbf{k}) E_l(\omega, \mathbf{k}) \ . \tag{16}$$

The SHI generated by electric quadrupolar processes in bodies with a centre of symmetry (15) and (16) is considerably weaker than that of radiation due to the electric dipole mechanism (10), which takes place in bodies without a centre of symmetry. The ratio of the quadrupolar polarisation (16) and dipolar polarisation (10) is of the order of magnitude of $ka = 2\pi\mathbf{a}/\lambda$, with $\mathbf{a}$ denoting the linear dimensions of the microsystems specifically characterising the

system (atomic or molecular size, crystal lattice constants). In the optical wave range, this ratio is of the order of 10^{-3}, in agreement with experiment [67].

For full generality, when dealing with SHG processes one has moreover to consider electric and magnetic polarisations due to the action of the magnetic field of electromagnetic waves on the medium, as well as magnetic polarisations induced by electric fields [20, 24]. In a second approximation, the electric dipolar polarisation due to the simultaneous action of an electric and magnetic field is [83, 84]:

$$P_i^{(2)}(2\omega, 2\mathbf{k}) = \eta_{ijk}^{2\omega} E_j(\omega, \mathbf{k}) H_k(\omega, \mathbf{k}) \ , \tag{17}$$

where the pseudotensor of magneto-electric susceptibility $\eta_{ijk}^{2\omega}$ has non-zero elements even in the case of isotropic bodies [84] in which the polarisation of equation (17) takes the form [83]:

$$\mathbf{P}^{(2)}(2\omega, 2\mathbf{k}) = \eta^{2\omega} \mathbf{E}(\omega, \mathbf{k}) \times \mathbf{H}(\omega, \mathbf{k}) \ . \tag{17a}$$

Jha [83], from equations (15) to (17), carried out a theoretical discussion of SHG reflected from metal surfaces. The effect was first observed by Brown *et al* [85] at reflection of a giant pulsed laser beam from the surface of a silver mirror. In later experiments, it was studied at reflection from other metals (Ag, Au, Ge, Cu, Bi [86-89]), semiconductors and alkali halides (CaF_2, NaF, KCl, NaCl [90]). SHG at reflection on metals and semiconductors is due primarily to the quadrupolar-type nonlinearity from both bound and free electrons, involving intra- and interband transitions. Recently, Wang [91] reported first SHG measurements at reflection of ruby laser light from several liquid-air interfaces (e.g. H_2O, CS_2, C_6H_6).

2.4. Light Frequency Mixing

The process of frequency mixing of the oscillations of two waves (leading to sum $\omega_1 + \omega_2$ or difference $\omega_1 - \omega_2$ frequencies) in nonlinear media is accounted for by polarisation of the second order, equation (8). Mixing of monochromatic light beams from two ruby lasers, one operating at liquid nitrogen temperature and the other at room temperature and thus yielding a difference in wavelength of about 1 nm, was first achieved by Bass *et al* [92]. The two beams were focused on the surface of a TGS crystal and the light beams emerging from it were observed with a quartz spectrograph of high resolution. On the photographic plate, three closely situated lines were obtained, the line to the right corresponding to SHG by the cooled laser and the one to the left to SHG by the laser operating at room temperature, whereas the central line revealed the sum frequency $\omega_1 + \omega_2$. These processes disappeared when the crystal was above its Curie temperature (50°C), in which region TGS is known to be centrosymmetric.

An interesting experiment is due to Miller and Savage [93]. In it, a ruby laser beam was mixed with the beam of a $CaWO_4 : Nd^{3+}$ laser (1.0582 μm) in a variety of crystals (KDP, ADP, $BaTiO_3$). In addition to the second harmonic of either beam, a beam of the sum frequency 418.9 nm was observed. When the two laser beams do not overlap in time no mixed signal is observed; when they begin to overlap, a small mixed signal appears; finally, when the two beams exactly overlap, a large mixed signal output is observed. The SHG and mixing efficiencies are considerably enhanced when velocity matching occurs. Also, six sum frequencies of the waves of an He-Ne gas laser, which contained four lines, namely 1.153 μm, 1.161 μm, 1.198 μm and 1.177 μm, were observed in $LiNbO_3$ [94].

Bradley *et al* [95] reported the observation in ADP of the sum of two tunable frequencies contained in the single pulse output of a gain switched ruby laser. This renders possible the direct simultaneous comparison of the conversion efficiencies and relative intensities of the three lines $I(2\omega_1)$, $I(2\omega_2)$ and $I(\omega_1 + \omega_2)$. It is shown that when the two fundamental frequencies ω_1 and ω_2 completely overlap in space and time, the value of the ratio $R = I(\omega_1 + \omega_2)/[I(2\omega_1)\, I(2\omega_2)]^{1/2}$ approaches 4, as expected from nonlinear optical theory.

Zernike and Berman [96] reported first observations of far-infra-red radiation generated in a mixing process in quartz crystal as the difference frequency between two near-infra-red frequencies, 1.059 μm and 1.073 μm, of neodymium glass lasers. Faust and Henry [97] observed sum and difference frequency generation when visible laser light was mixed in a GaP crystal with each of five infra-red laser frequencies lying near the lattice resonance (reststrahl).

A method of converting infra-red radiation to visible by mixing it with highly collimated ruby laser radiation in $LiNbO_3$ has been described by Midwinter [98]. Faries *et al* [99] observed tunable far-infra-red radiation from the difference frequency between two temperature-tuned ruby laser beams by mixing in $LiNbO_3$ or quartz. Also, far-infra-red generation by non-phase-matched difference-frequency mixing in bulk nonlinear media has been observed [100, 101]. Van Tran and Patel [102] have demonstrated that magnetoplasma effects in semiconductors can be used for phase-matched nonlinear interactions in the far-infra-red, specifically difference-frequency generation in the 100 μm range by mixing the 9.6 μm and 10.6 μm CO_2 laser transitions in *n*-InSb. Somewhat earlier, Chang *et al* [103] produced millimetre wave difference frequencies by mixing CO_2 gas laser lines in a GaAs-filled waveguide designed for phase-matched interactions.

Recently, Patel and Van Tran [104] reported the first observations of generation of circularly polarised far-infra-red radiation at 100 μm by phase-matched difference frequency mixing between two circularly polarised infra-red radiations at 9.6 μm and 10.6 μm. Brown [105] proposed observation of far-infra-red difference-frequency generation by reflection from the surface of metals and semiconductors. Sodha *et al* [106] considered the generation of combination frequencies of waves in a homogeneous plasma.

Giordmaine [23] drew attention to the feasibility of wave mixing in optically active liquids in which frequency doubling does not occur. Experimentally this has been performed by Rentzepis *et al* [107], who observed coherent optical sum-frequency generation in aqueous arabinose ($C_5H_{10}O_5$) solutions and other optically active liquids. In their experiment, a ruby laser beam and its second harmonic produced at 347.15 nm in KDP intersected in the liquid to generate collimated sum-frequency emission at 231.4 nm. Cohan and Hameka [108] proposed a theory of sum-frequency generation in gases and liquids for the case of resonance, and suggested an experiment in which only one of the incident beams comes from a laser source while the other is ordinary polarised monochromatic light of variable frequency. This, indeed, is a case of mixing, in a liquid, of coherent light and non-coherent light; it had already been put to effect [109] in KDP crystal by mixing the light of a ruby laser with that of a mercury lamp. Bey and Rabin [110] performed a general theoretical analysis of the co-operation of circularly polarised waves in optically active bodies.

3. Optical Processes of the Third Order

Three waves with frequencies ω_1, ω_2, ω_3 and wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ incident on a medium will give rise to polarisation of the third order which, by equation 4, is of the following form in the dipolar approximation:

$$P_i^{(3)}(\omega_4, \mathbf{k}_4) = \chi_{ijkl}^{\omega_4} E_j(\omega_1, \mathbf{k}_1) E_k(\omega_2, \mathbf{k}_2) E_l(\omega_3, \mathbf{k}_3) , \tag{18}$$

where, in accordance with the synchronisation conditions (5) and (6), we now have for the interaction of four waves [111]:

$$\omega_4 = \omega_1 + \omega_2 + \omega_3 , \tag{5c}$$

$$\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \Delta\mathbf{k} . \tag{6c}$$

For the tensor of third-order non-linear susceptibility we have the following time-space permutation symmetry relations [3, 16]:

$$\begin{aligned} \chi_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3) &= \chi_{jikl}(\omega_1; -\omega_4, \omega_2, \omega_3) \\ &= \chi_{klji}(\omega_2; -\omega_4, \omega_1, \omega_3) = \chi_{lijk}(\omega_3; -\omega_4, \omega_1, \omega_2) . \end{aligned} \tag{19}$$

The tensor χ_{ijkl} has non-zero elements even in the case of isotropic bodies possessing a centre of symmetry, i.e. also in that of gases and liquids. The non-vanishing tensor elements have been tabulated for all the crystallographical classes [4, 111]. In bodies in which optical dispersion is absent or negligibly small, the tensor χ_{ijkl} can be dealt with as totally symmetric. In isotropic bodies χ_{ijkl} has twenty-one non-zero elements only three of which are mutually independent, and we can write in the general case [112]:

$$\chi_{ijkl} = \chi_{xxyy}\,\delta_{ij}\,\delta_{kl} + \chi_{xyxy}\,\delta_{ik}\,\delta_{jl} + \chi_{yxxy}\,\delta_{il}\,\delta_{kj} \tag{20}$$

where use has been made of the relation [4]:

$$\chi_{xxxx} = \chi_{yyyy} = \chi_{zzzz} = \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy} ,$$

δ_{ij} denoting Kronecker's unit symmetric tensor.

3.1. Third-Harmonic Generation (THG)

In isotropic optically inactive bodies, in the absence of frequency and spatial dispersion and of magnetic optical activity, third-order polarisation at 3ω is given, with regard to (19) and (20), by [39]:

$$P_i^{(3)}(3\omega, \mathbf{r}) = 3\chi_{xxyy}(-3\omega; \omega, \omega, \omega)\, E_j(\omega, \mathbf{k})\, E_j(\omega, \mathbf{k})\, E_i(\omega, \mathbf{k}) \tag{21}$$

(we now have $\chi_{xxyy} = \chi_{xyxy} = \chi_{yxxy}$).

The THG of intensity

$$I(3\omega, \mathbf{r}) \approx (\chi^{3\omega})^2 \left\{\frac{\sin \frac{1}{2} \Delta k r}{\frac{1}{2} \Delta k}\right\}^2 I^3 \tag{22}$$

(when the medium is perfectly transmitting) caused by this polarisation is obviously the most highly effective when the matching condition:

$$\Delta k = \left(\frac{3\omega}{c}\right)(n_{3\omega} - n_{\omega}) = 0$$

is fulfilled.

The first attempts at obtaining an ultraviolet third harmonic at 231.4 nm using a ruby laser are due to Terhune *et al* in calcite [113] and subsequently in cubic crystals (LiF, KCl, CaF, etc.) and liquids [39, 114]. Bey *et al* [115] provided the earliest experimental evidence that phase matching can be achieved in harmonic processes by the introduction of anomalous dispersion into a normally unmatched medium. They obtained phase-matched THG at 353.0 nm of the neodymium laser line by introducing dye molecules into a liquid medium (thus, fuchsin red dye dissolved in hexafluoroacetone sesquihydrate). These experiments were extended by Chang and Galbraith [116] to other solvents of different index mismatch and to another dye, methylene blue. Bey *et al* [117] reported highly interesting THG studies, which prove that a linearly polarised laser beam generates a third-harmonic signal, while a circularly polarised beam does not, in accordance with theory. This experiment can lead to a variety of applications when determining the state of polarisation of laser light, when modulating it, and when measuring ultrashort light pulses such as those produced by mode-locked lasers.

Ward and New [118] observed THG at 231.4 nm in gases (He, Ne, Ar, etc.) using a focused ruby laser beam.

Goldberg and Schnur [119] investigated harmonic generation in liquid crystals with the aim of checking earlier SHG studies in these bodies [120], in particular cholesteryl nonanoate (CN) as well as other cholesteric and nematic liquid crystals. The solid phase of CN revealed a high SH intensity (of the same order as in quartz crystal powder) which, on heating, decreased steeply by four orders of magnitude in the vicinity of 79°C on transition from solid to cholesteric phase. In the inverse process of slow cooling from the isotropic liquid phase through the cholesteric and smectic mesophases, a clear SH signal was observed only at the point of recrystallisation to the solid. THG was apparent in all phases, both at heating and cooling, its intensity in the solid phase being 100 times stronger than in the liquid phase. Similar results have been obtained in other liquid crystals [121]; in no case did they exhibit SHG when in mesomorphic phases, which have to be regarded as centro-symmetric. The above-cited studies have made apparent some role, in the process of harmonic generation, of the molecular correlations which play an important part in multi-harmonic light scattering and optical birefringence in isotropic media [122].

Recently, Bey *et al* [123] extended earlier work by Bloembergen and Lee [80] to THG in light reflected from liquids. Here, a Q-switched pulse from a neodymium laser was internally reflected from a liquid the refractive index of which was tuned by the anomalous dispersion

of a dye additive. An increase of more than two orders of magnitude in the intensity of reflected THG was observed near the critical angle for total internal reflection when the dye was adjusted for phase matching. Also, Wang and Baardsen [124] recently reported studies of THG reflected from the boundary of solids including metals, semiconductors, alkali halides and glass.

3.2. DC Field-Induced Optical Harmonics

When equation 18 is rewritten with $\omega_3 = \mathbf{k}_3 = 0$, $\omega_1 = \omega_2 = \omega$ and $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$, the third-order polarisation

$$P_i^{(3)}(2\omega, \mathbf{r}) = \chi_{ijkl}(-2\omega, \omega, \omega, 0)\, E_j(\omega, \mathbf{k})\, E_k(\omega, \mathbf{k})\, E_l(0) \tag{23}$$

describes SHG in a body subjected to the action of a DC electric field $\mathbf{E}(0)$.

Terhune, Maker, and Savage [113] studied the optical harmonics of ruby laser light in calcite, which has a centre of symmetry; they found a weak SH due to quadrupolar polarisation, equation 16, and on applying a DC electric field observed a considerable increase in SHG us a quadratic function of the field strength. The experiment was repeated by Bjorkholm and Siegman [67] with accurate CW (He-Ne laser) measurements of the electric quadrupole-type SHG and electric field-induced SHG in calcite relative to the SHG obtained in ADP crystals, finding a displacement of the parabolic curve of SH power as a function of the applied field $\mathbf{E}(0)$.

McFee [125] observed SHG at 530 nm when a DC electric field and CO_2 laser beams are applied simultaneously to narrow band-gap semiconductors (InAs, InSb). Lee *et al* [126] showed the SH intensity produced in reflection by a ruby laser beam incident on silver or silicon surfaces to vary significantly when a DC electric field is applied normal to the surface. Suvorov and Sonin [127] investigated SHG in TGS crystal acted on by an electric field at various synchronisations in the temperature range 20 to 90° C.

Recently, Mayer [128] studied SHG in non-dense molecular substances immersed in a DC electric field. In non-dipolar gases SHG is caused by nonlinear polarisation of the electron shell whereas, when some degree of condensation is exceeded, reorientation of induced dipoles intervenes also [84]. In dipolar gases, DC electric field-induced SHG is due chiefly to reorientation of the permanent molecular dipoles [112]. In strongly dipolar substances (C_2H_5I, C_2H_5Br, CH_3I) Mayer [128] observed an anomalous increase in SHG at DC field strengths close to breakdown, presumably arising by electric saturation of reorientation of the molecular dipoles [129]. Sodha and Kaw [130] showed that SHG is possible in a plasma in a DC electric field.

Van Tran *et al* [131] observed an enhancement of THG in InSb due to interband transitions and resonance in the presence of a magnetic field, as predicted theoretically by Lax *et al* [132] and Kołodziejczak [133]. Sodha and Kaw [134] proposed a theory of THG in magnetoplasma.

3.3. Four-Wave Mixing Processes

Equation 18 describes the mixing of three waves in a medium which gives rise to a fourth wave of sum frequency (5c) or other, difference frequencies. Midwinter and Warner [111] extended the theory of the phase matching technique of Giordmaine [43] and Maker *et al* [44] to the case of interaction between four waves. They suggested three different experimental situations involving (i) three waves (the lower frequencies) polarised orthogonally to the fourth, (ii) two orthogonal to the fourth, (iii) one orthogonal to the fourth.

Maker and Terhune [39] discussed resonant and non-resonant mixing of waves at three different frequencies and carried out measurements of parametric generation of Raman light in suitably transparent material (liquids, other isotropic bodies, and cubic crystals). The situation has moreover been studied when the beats between the laser and the Stokes frequency and the SH frequency are involved [11, 135]. Rado [136] was the first to perform four-wave mixing experiments in several gases (He, N_2, O_2, CO, CO_2, etc.), which permitted the determination of values of third-order nonlinear susceptibility coefficients.

Wynne [137] investigated third-order difference mixing of CO_2 laser waves in semicon-

ductors (GaAs, Ge, Si, InAs) and discussed contributions from the bound, valence and conduction electrons to the nonlinear susceptibility tensor

$$\chi_{ijkl}(-\omega_3; \omega_1, \omega_2, -\omega_2) ,$$

where the frequencies ω_1 and ω_2 are emitted by the laser and $\omega_3 = 2\omega_1 - \omega_2$ is the radiation due to mixing. Also, mixing processes of four circularly polarised waves in optically active bodies have been studied [70, 110].

4. Harmonics Generated by Picosecond Laser Pulses

Ruby or neodymium lasers produce giant light pulses of a power not less than 1 MW and duration shorter than 10^{-6} sec. The peak power of the oscillations of the light pulse can be enhanced by raising the energy of the pulse or reducing its duration. The four years preceding the writing of this article have witnessed a rapid development of the quantum electronics technique of ultrashort pulses from Nd : YAG lasers with a duration of 10^{-11} to 10^{-12} sec [138, 139], which can be shortened to 10^{-13} to 10^{-14} sec by resorting to the optical Kerr effect [140]. Information on light pulses of so short a duration (or rather on the intensity autocorrelation function) can be obtained by the method of harmonic production [141] (i.e. by mixing the pulses with delayed replicas of themselves in a harmonic-generator crystal) or by a simpler technique using two- or three-photon fluorescence [142, 143]. Basov *et al* [144] showed that amplification of picosecond neodymium laser light pulses results in a peak the power of which exceeds 10^{12} W.

From a theoretical analysis [145, 146] of SHG by ultrashort pulses, Shapiro [147] proceeded to an investigation of the duration of the second harmonic of short Nd-glass laser pulses as a function of the length of a $LiNbO_3$ crystal. Orlov *et al* [148] studied extensively the spectral and angular distributions of SHG in KDP and $LiNbO_3$ by picosecond Nd-glass laser pulses.

Eckardt and Lee [149] worked out a new technique for the measurement of picosecond light pulses applying the suggestions of Bey *et al* [117] concerning the unique polarisation properties of optical THG in phase-matchable dye solutions. It is generally known that, in materials strongly absorbing the fundamental frequency, the observation of THG is rendered difficult because the required high fundamental intensity I often gives rise to significant damage due to energy deposition. The requirement of high I and a tolerable rate of energy deposition was met by the use of a picosecond pulse train from a mode-locked Nd^{3+} glass laser. In this way, Bloembergen *et al* [150] were able to observe THG by picosecond laser pulses in reflection from semiconductors and metals and to study its dependence on the angle of incidence, light polarisation, and crystallographic orientation. Recently Wang and Baardsen [151] reported measurements of optical THG in ADP crystals both in reflection and along the phase-matched directions using mode-locked and nonmode-locked Nd-doped glass lasers.

In relation with the evolution of the technique of ultrashort laser pulse generation, much attention is given to the study of optical transient phenomena. Various nonlinear phenomena, when studied in the electric field of a picosecond laser pulse, proceed according to a shape which is entirely different from that of the same process in the field of a micro- or nanosecond pulse. The time of duration of ultrashort pulses (10^{-11} to 10^{-13} sec) is comparable to the relaxation time of molecules, the time required for nonlinearities to become steady [152], and the times of group-wise delay of light waves co-operating in a medium. This group delay time, which defines the wave unstationarities, is in principle essential to the processes of harmonic generation and parametric processes caused by ultrashort pulses [145, 148, 153].

5. Higher Harmonic Optical Processes

By equation 4, which defines polarisation of the *nth* order, one can in general produce higher harmonics than the third, thus the fourth, fifth harmonic, and so forth. Akhmanov, Khokhlov and their co-workers succeeded in performing experiments in which they first observed the fourth [45, 154] and, quite recently, the fifth harmonic of laser light [155]. They used a giant neodymium laser to excite a frequency conversion cascade system consisting of three KDP crystals in series. The first, at room temperature, generated the SH of wavelength

$\lambda_2 = 530.0$ nm, while the second produced the third harmonic at $\lambda_3 = 353.3$ nm or the fourth harmonic at $\lambda_4 = 265.0$ nm [45]. The aim of the third KDP crystal was to mix the harmonics produced by the first two in order to produce the sum frequencies $\omega_5 = \omega_2 + \omega_3$ or $\omega_5 = \omega_1 + \omega_4$, thus yielding the fifth harmonic 5ω. Since in KDP and ADP the synchronisation conditions for summation of the fundamental frequency ω_1 and fourth harmonic ω_4 are not fulfilled at room temperature, the third crystal was cooled to $-70°C$ in these experiments. At transition through the synchronisation temperature, a steep 10^3 to 10^4-fold increase in fifth harmonic power attaining 1 kW in the non-focused beam was observed. The fifth harmonic of light produced at $\lambda_5 = 212.0$ nm by the above method is the shortest ultraviolet electromagnetic wave to have been obtained hitherto by the method of cascade light harmonic generation in nonlinear crystals.

On replacing the third crystal in Khokhlov's experiment by a cell containing a solution of organic scintillators, the ultraviolet frequency can be retuned throughout the 400-200 nm range [154]. Previously, ultraviolet radiation at 257.3 nm had been produced in KDP and ADP crystals in continuous SHG with the light of an argon ion laser of wavelength 514.5 nm [156]. More recently, various authors [157] have observed tunable laser emission in the range from 385 to 600 nm using the 337.1 nm N_2 laser line as the pumping source and a number of dyes and scintillators in several solvents. Also, laser higher-harmonic frequency mixing experiments have been successfully performed at far infra-red frequencies [158] and infra-red frequencies (in the 9 μm region [159]).

We refrain from a discussion of the optical parametric oscillators, which permit coherent light to be obtained in a wide range of frequencies as well as its continuous frequency modulation, because the subject is dealt with exhaustively in the review articles by Akhmanov and Khokhlov, and Giordmaine [160], as well as more recently in reviews by Boyd and Kleinman, and Harris [161].

6. Harmonic Light Scattering

Beside elastic scattering at the fundamental frequency ω, laser light of sufficiently high intensity I causes scattering processes of higher orders at double frequency 2ω, triple frequency 3ω, and so forth, so that the total scattered intensity can be expressed by the series [162]:

$$I_S = S^{\omega} I + S^{2\omega} I^2 + S^{3\omega} I^3 + \ldots , \tag{24}$$

where the constant S^{ω} accounts for the linear scattering studied unremittingly since the days of Lord Rayleigh and Smoluchowski [26, 30, 35].

The constant S_2^{ω} defines nonlinear scattering of light at doubled frequency, as observed by Terhune, Maker, and Savage [163], who used the beam of a giant ruby laser collimated in a liquid whose molecules possessed no centre of symmetry (H_2O, CCl_4, CH_3CN). Moreover, SH scattering has been observed in methane under a pressure of 100 atm. [164]. In gaseous media, SH scattering is very sensitive to the molecular symmetry, and occurs only if molecules not presenting a centre of symmetry in the ground state undergo a nonlinear polarisation of the second order at the frequency 2ω [162-166]. Liquids, on the other hand, reveal the role of molecular correlations of the radial and angular kinds [122, 162, 167-169] owing to which, for example, some small amount of SH scattering can appear in the case of centrosymmetric molecules possessing a permanent electric quadrupole [122]. In the course of this year, Maker published an extensive paper [170] containing a discussion of the spectral linewidths of SH scattering in a variety of liquids. High intensities of nonlinearly scattered light are to be expected from solutions of macromolecules [171] and colloid particles [172].

Freund [173] observed SH scattering due to angular fluctuations in NH_4Cl close to the critical point. The phenomenon provides information concerning phase transitions in solids (e.g. the order-disorder transition) [174]. Measurements of SH scattering in NH_4Cl as a function of the temperature and scattering angle have yielded a measure of the ordering correlation length of NH_4^+ ions, and have moreover made apparent the existence of domains with variously oriented ions [173, 174].

In the quantum mechanical approach, scattering at double frequency is a three-photon

process in which the molecule absorbs two photons of light incident at frequency ω and emits a photon at frequency 2ω. One has also to consider (beside this elastic SH scattering) processes of nonlinear Raman scattering of the second order [165] in which two photons at frequencies ω_1 and ω_2 are incident on a molecule, which then scatters inelastically a third photon at frequency $\omega_1 + \omega_2 + \omega_{kl}$, the frequency ω_{kl} being that of transition by the molecule from the quantum state k to l. In general one has to envisage nonlinear Raman scattering processes of higher orders, at frequencies $\omega_1 + 2\omega_2 \pm \omega_{kl}$, $\omega_1 + \omega_2 + \omega_3 \pm \omega_{kl}$, and others [24, 165], providing valuable information on the nonlinear optical properties of atoms and molecules [175].

A very recent paper by Strizhevsky and Obukhovsky [176] proposes a microscopic theory of nonlinear light scattering in crystals of the type of GaP, ZnSe and ZnO. The authors show that in the general case of dipole active transverse vibrations the nonlinearly scattered intensity is determined (i) by the nature of the mechanical phonon, (ii) by the interaction between the phonons and transverse electromagnetic field as a result of which the phonons change into polaritons, (iii) by non-resonance processes of crystal polarisation by the exciting field.

7. Nonlinear Optical Susceptibilities of Media

Obviously, the processes in which optical harmonics of laser light are produced in a medium (a crystal, liquid, or gas etc.) depend strongly on the symmetry and structure proper to it. The study of these new nonlinear phenomena has been an incentive to search for and to obtain various new materials exhibiting the properties required for strong harmonic generation. The nonlinear properties of a substance can be established experimentally by testing it in harmonic processes, or can be predicted theoretically by calculation. Crystals, in order to be useful in nonlinear optics, have to exhibit considerable asymmetry of their properties, a high refractive index, high optical birefringence, transparency in a wide spectral range, and the advantage of being available as single crystals. However, if there are difficulties in the way of growing single crystals, one can proceed by the powder method [57-59], which has permitted the study of a number of new nonlinear substances [58, 62]. There exist Tables assembling the nonlinear data of over 100 organic and inorganic, natural and synthetic crystals [177].

The investigation of optical harmonics in transmitted light provides information regarding the microscopic structure of the medium as a whole as well as its phase transitions, whereas studies in reflected light provide optical data on the surface properties of the medium, on double electric layers, and on surface phenomena at the boundary of two media (thus, gas-solid, liquid-solid, gas-liquid, electrolyte-semiconductor boundaries).

7.1. Atoms and Molecules

The investigation of harmonic and other nonlinear processes (static [178, 179] and optical [36, 37, 180, 181] Kerr effect, nonlinear optical activity [182, 183]) in gases and liquids enables us to gain direct information on the nonlinear optical properties of the individual atoms and molecules [122, 176, 181]. The nonlinear optical properties of molecules are described by the tensor of second-order polarisability b_{ijk} and that of third-order polarisability $-c_{ijkl}$, the components of which can be determined by experiment or by direct calculation.

The dipole moment of second order induced in a molecule at frequency $\omega_3 = \omega_1 + \omega_2$ is:

$$m_i^{(2)}(\omega_3) = \beta b_{ijk}(-\omega_3 ; \omega_1, \omega_2)\, E_j(\omega_1)\, E_k(\omega_2) , \tag{25}$$

where the ordering factor β is equal to 1/4 for $\omega_1 = \omega_2$ and to 1/2 if the two frequencies are different. In the static case ($\omega_1 = \omega_2 = 0$), β amounts to 1/2 for the case of a single field and to 1 for that of two different fields. Beyond dispersion and absorption, we have the following relations between the tensors defining nonlinear second-order processes:

$$\begin{aligned} 2b_{ijk}(-\omega_3; \omega_1, \omega_2) &= b_{ijk}(-2\omega; \omega, \omega) \\ &= 4b_{ijk}(-\omega; \omega, 0) = 2b_{ijk}(0; 0, 0) . \end{aligned}$$

Static values b_{ijk} (0; 0, 0) have been calculated theoretically for various dipolar linear molecules [181, 184-186]; values of b_{ijk} $(-\omega; \omega, 0)$ can be determined from Kerr effect [181] or

Rayleigh light scattering [37, 179] measurements. Components of the tensor $b_{ijk}(-2\omega; \omega, \omega)$ can be determined from measurements of nonlinear light scattering at double frequency [163, 164, 176] defined by the constant $S^{2\omega}$ in the expansion (24) or of SHG in a DC electric field [84, 128, 129].

To a third approximation, the dipole moment induced at frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ in a molecule is:

$$m_i^{(4)}(\omega_4) = \gamma c_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) \ . \tag{26}$$

Here, the ordering factor γ is 1/4 if all the frequencies are different, 1/8 if two differ, 1/24 for $\omega_1 = \omega_2 = \omega_3$ and 1/6 in the single-field static case. Neglecting dispersion and absorption, we have the relations:

$$\begin{aligned} 6c_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3) &= 6c_{ijkl}(-\omega_1; \omega_1, \omega_2, -\omega_2) \\ &= 3c_{ijkl}(\omega_1 - 2\omega_2; -\omega_1, \omega_2, \omega_2) = c_{ijkl}(-3\omega; \omega, \omega, \omega) \\ &= 6c_{ijkl}(-2\omega; \omega, \omega, 0) = 3c_{ijkl}(-\omega; \omega, \omega, -\omega) \\ &= 12c_{ijkl}(-\omega; \omega, 0, 0) = 4c_{ijkl}(0; 0, 0, 0) \ . \end{aligned}$$

Direct calculations of third-order polarisabilities have been carried out for inert gases in the static [181, 187] and optical [189-192] cases. Static values c_{ijkl} have also been calculated for linear molecules [181, 185, 192] as well as planar molecules [193]. Values $c_{ijkl}(-\omega; \omega, 0, 0)$ have been determined for numerous molecules from the static Kerr [179, 181, 187, 194, 195] and optical [40, 180, 196] Kerr effects. Values of $c_{ijkl}(-3\omega; \omega, \omega, \omega)$ are determined from THG studies in gases and liquids [39, 113, 118] or from depolarisation of third-harmonic scattered light [176, 197] as defined by the constant $S^{3\omega}$ in the expansion (24), $c_{ijkl}(-2\omega, \omega, \omega, 0)$ from SHG in a DC electric field [84, 128, 129], and $c_{ijkl}(\omega_1 - 2\omega_2; -\omega_1, \omega_2, \omega_2)$ from difference frequency generation [136].

7.2 Solids

Nonlinear optical susceptibilities of solids have been determined by optical harmonic investigation and have been calculated both classically and quantum mechanically. A useful and important relationship between the second-order nonlinear susceptibility tensor $\chi_{ijk}^{2\omega}$ and the linear optical susceptibility tensor χ_{ij}^{ω} has been given by Miller [198] in the form:

$$\chi_{ijk}^{2\omega} = \chi_{ii}^{2\omega} \chi_{jj}^{\omega} \chi_{kk}^{\omega} \delta_{ijk}^{2\omega} \tag{27}$$

which holds, e.g. for nonlinear piezoelectric crystals. With unrestricted generality, we have the following relation:

$$\chi_{ijk}^{\omega_3} = \chi_{il}^{\omega_3} \chi_{jm}^{\omega_1} \chi_{kn}^{\omega_2} \delta_{lmn}^{\omega_3} \ . \tag{27a}$$

Although quantum-mechanical theories of nonlinear optical susceptibilities of the second, third [16, 19, 199-203] and higher orders [21, 24, 203-205] have been available for a number of years, it was only two years ago that numerical computations of non-zero tensor elements began, and that only for certain cases, thus for semiconductors of the groups III-V [206-209] the group IV [207], and for covalent crystals [210, 211]. Semiconductor compounds of groups III-V provide the first example of successful, *ab initio* theoretical calculations of a nonlinear susceptibility in condensed matter for relatively simple structures. In these calculations, the authors applied various models and approximations, which enabled them to derive numerical susceptibility values and to confront these values with the values resulting by Miller's rule (27) and by experiment.

Jha and Bloembergen [207], when investigating the nonlinear susceptibilities of semiconductors, calculated separately the bound or valence electron contribution and the conduction-electron contribution from simple tetrahedral bonding orbitals. For numerical evaluations, they used hydrogenic-type wave functions and on neglecting overlap obtained, in contradiction to experiment, a negative sign of the susceptibility. Flytzanis and Ducuing [206] obtained better agreement using Slater-type wave functions and a variational perturbation procedure to determine the effective charge of the bond and taking into account semi-

TABLE I Numerical values of linear and nonlinear polarisabilities of atoms and molecules calculated theoretically or determined from experimental data. Only mean values $a = a_{ii}/3$, $b = b_{iii}/3 = b_{333}$ (for the axial symmetry), $b = b_{123}$ (for the tetrahedral symmetry) and $c = c_{iijj}/5 = c_{3333}$ are given.*

Units	10^{-24} cm^3	10^{-30} cm^5/e.s.u.			10^{-36} cm^7/e.s.u.^{2}				
Gas or liquid	a^{ω}	b^0	b^{ω}	$b^{2\omega}$	c^0	c^{ω}	$c^{2\omega}$	$c^{3\omega}$	$c^{2\omega-\omega'}$
He	0.205				0.021 [190]	0.027 [194]	0.023 [190]	0.024 [190]	0.068 [136]
					0.021 [188]	0.022 [190]		0.021 [189]	
Ne	0.394					0.051 [187]		0.041 [189]	
						0.055 [181]		0.214 [118]	
Ar	1.66					0.59 [187]		3.024 [118]	1.39 [136]
						0.73 [181]		0.672 [189]	
Kr	2.52					1.4 [187]		9.264 [118]	
						1.6 [181]		1.704 [189]	
Xe	4.11					3.9 [187]		23.496 [118]	
						4.0 [181]		5.328 [189]	
H_2	0.79				0.2 [185]		0.36 [128]	1.920 [118]	
N_2	1.76							2.568 [118]	1.21 [136]
O_2	1.60						0.64 [128]		1.17 [136]
HF	2.46	−0.16 [184]							
CO	1.95	±0.43 [184]			1.0 [185]		1.81 [128]		1.62 [136]
		0.19 [185]							
		0.18 [192]							
NO	1.72								3.78 [136]
LiH	3.35	−3.44 [184]							
BF	3.13	0.98 [184]							
CO_2	2.65							2.744 [118]	1.80 [136]
NH_3	2.26	−0.045 [186]	−3.9 [181]						
CH_4	2.6	0.04 [186]		0.01 [164]		2.6 [181]	1.48 [128]		2.65 [136]
		−0.21 [181]							
CCl_4	10.5			0.03 [164]		12.0 [181]	3.6 [128]		
						7.2 [195]			
						6.51 [179]			
						2.15 [180]			
CH_3F	3.55	−0.089 [186]	−1.11 [186]						
$CHCl_3$	8.23		14.4 [181]			4.8 [180]	4.4 [128]		
H_2O	1.46	+0.11 [186]							
CS_2	8.74					56.5 [179]			
						50.1 [180]			
						54.4 [181]			
						63.9 [195]			
C_2H_6	4.47						4.8 [128]		5.58 [136]
C_6H_6	10.32					−3 ±6 [195]			
C_6H_{12}	10.87					1.2 [180]			
$C_6H_5CH_3$	12.29					27.2 [180]			
$C_6H_5NO_2$	12.17					85.0 [180]			
CH_3I	7.28						8.0 [128]		
SF_6	4.47				1.2 [194]				2.25 [136]

*The author thanks Professor G. Mayer for a preprint (G. Hauchecorne, F. Kerhervé, and G. Mayer, *J. Phys. Paris*, (1970, in press) with detailed and systematical results on the nonlinear polarisabilities of orders 2 and 3 for a large number of molecular substances in the gaseous and condensed states. Also, Dr M. A. Duguay was kind enough to communicate his results concerning the hyper-polarisability of fused silica (M. A. Duguay and J. W. Hansen, Amer. Opt. Soc. Meeting in Philadelphia, April, 1970). The data of the above papers are not included in Table I.

(32 (1971) 47-62),

empirically corrections for the local field. Philips and Van Vechten [210] applied the dielectric theory of electronegativity differences to calculate the nonlinear susceptibilities of covalent crystals. Levine [211], by resorting to a simple model relating the anharmonic motion of the bond charge to the third and fourth order susceptibilities, achieved satisfactory agreement with experiment (see Tables IV and V).

Patel *et al* [212] first used a Q-switched CO_2 laser beam for studying the nonlinear susceptibility of semiconductors (which are not transparent in the visible) by measuring the difference frequencies $2\omega_1 - \omega_2$ at 11.8 μm and $2\omega_2 - \omega_1$ at 8.7 μm, with near phase-matched mixing in significantly long crystals. They observed a new type of nonlinearity, which arises from the non-parabolicity of the conduction-band electrons in semiconductors (InAs, GaAs, etc.). The problem was studied in detail, calculating contributions to the nonlinear susceptibility from this non-parabolicity [137, 213], and assuming non-spherical and non-parabolic energy bands and the existence of a momentum relaxation time [214, 215]. Earlier, Chang, Ducuing, and Bloembergen [216] proposed a method for measuring dispersion of the

TABLE II Relative values of nonlinear susceptibility tensor elements $\chi^{2\omega}{}_{ijk}$ determined from SHG measurements (the d_{36}-value in KDP crystal is taken as unity).

Crystal	Symmetry	λ (μm)	Relative values $d_{ij}{}^{2\omega}$	l_{coh}	Reference
KH_2PO_4 (KDP)	$\bar{4}2$ m	0.6943	$d_{36} = 1.00$	18.5	[49]
			$d_{14} = 0.95 \pm 0.06$	7.3	
		1.0582	$d_{36} = 1.00$	22.0	
			$d_{14} = 1.01 \pm 0.05$	14.6	
		1.064	$d_{36} = 1.00$	22.86	[221]
KD_2PO_4 (DKDP)	$\bar{4}2$ m	0.6943	$d_{36} = 0.75 \pm 0.02$	20.6	[49]
			$d_{14} = 0.76 \pm 0.04$	7.7	
		1.0582	$d_{36} = 0.92 \pm 0.04$	21.2	
			$d_{14} = 0.91 \pm 0.03$	15.8	
$NH_4H_2PO_4$ (ADP)	$\bar{4}2$ m	0.6943	$d_{36} = 0.93 \pm 0.06$*	17.7	[49]
			$d_{14} = 0.89 \pm 0.04$	6.7	
		1.0582	$d_{36} = 0.99 \pm 0.06$*	21.0	
			$d_{14} = 0.98 \pm 0.05$	13.2	
		1.064	$d_{36} = 1.21 \pm 0.05$	21.18	[221]
$BaTiO_3$	4 mm	1.0582	$d_{15} = 35 \pm 3$	3.1	[48]
			$d_{31} = 37 \pm 3$	5.8	[49]
			$d_{33} = 14 \pm 1$	4.1	
Quartz (SiO_2)	32	1.0582	$d_{11} = 0.82 \pm 0.04$	20	[48]
			$d_{14} = 0.00 \pm 0.05$		
		1.064	$d_{11} = 0.77 \pm 0.04$	20.65	[221]
$AlPO_4$	32	1.06	$d_{11} = 0.84 \pm 0.07$		[3]
CdS	6 mm	1.0582	$d_{15} = 35 \pm 2$	1.8	[48]
			$d_{31} = 32 \pm 2$	1.7	[49]
			$d_{33} = 63 \pm 4$	1.8	
ZnO	6 mm	1.06	$d_{15} = 4.7 \pm 0.4$		[3]
			$d_{31} = 4.3 \pm 0.4$		
			$d_{33} = 13.4 \pm 0.4$		

*Recently, Miller obtained corrected values: $d_{36}{}^{ADP} = (1.03 \pm 0.06)\, d_{36}{}^{KDP}$ for 0.6943 μm and $d_{36}{}^{ADP} = (1.18 \pm 0.06)\, d_{36}{}^{KDP}$ for 1.0582 μm which are in agreement with the latest accurate measurements of Jerphagnon and Kurtz [221].

complex nonlinear susceptibility tensor χ_{ijk} of semiconductors (it is real only if the medium is transparent for the fundamental and harmonic frequency but is complex if the medium absorbs either). More recent work deals with nonlinear susceptibility dispersion of other materials [217] and accurate measurements of its sign and relative values [218-227]. Di Domenico and Wemple [220] developed a microscopic theory of the electro-optical and nonlinear optical properties of oxygen-octahedra ferroelectrics in the energy-bond approach.

The latest results [222] show that Ag_3SbS_3 (pyrargyrite, which can be grown in large single crystals similarly to Ag_3AsS_3 (proustite) [223]) is a suitable low absorption material for use as a standard in the accurate determination of nonlinear optical susceptibilities at 10.6 μm. Similarly to the hitherto used standard materials such as quartz, KDP and ADP, which have recently been studied exhaustively [221], crystalline Ag_3SbS_3 is suitable for pulsed parametric oscillation in the infra-red, and up-conversion. Its large birefringence and lack of temperature dependence indicate that phase-matching normal to the optical axis will not be achievable. Previously, the sole materials known to permit phase-matched SHG at 10.6 μm were tellurium and selenium [66], whose inadequate optical quality, large double refraction and optical activity made reproducible measurements difficult.

Data regarding the tensor of second-order susceptibility can also be gained from the well-known linear electro-optical effect defined by the polarisation:

$$P_i^{(2)}(\omega, \mathbf{k}) = \chi_{ijk}(-\omega; \omega, 0)\, E_j(\omega, \mathbf{k})\, E_k(0) \tag{28}$$

TABLE III Optical susceptibilities of some new nonlinear materials determined by SHG investigation.*

Material	Symmetry	λ (μm)	$d_{ij}(-2\omega, \omega, \omega)$	Reference
$LiNbO_3$	3 m	1.06	$d_{22} = (6.3 \pm 0.6)\, d_{36}^{KDP}$ $d_{31} = (11.9 \pm 1.7)\, d_{36}^{KDP}$ $d_{33} = (83 \pm 21)\, d_{36}^{KDP}$	[50]
$LiTaO_3$	3 m	1.06	$d_{22} = (4.3 \pm 0.5)\, d_{36}^{KDP}$ $d_{31} = (2.6 \pm 0.5)\, d_{36}^{KDP}$ $d_{33} = (40 \pm 5)\, d_{36}^{KDP}$	[50]
$AgAsS_3$	3 m	1.152	$d_{22} = 50\, d_{36}^{KDP}$ $d_{31} = 30\, d_{36}^{KDP}$	[64]
Ag_3SbS_3	3 m	10.6	$d_{22} = (32 \pm 10) \times 10^{-9}$ cm/volt $d_{31} = (30 \pm 10) \times 10^{-9}$ cm/volt	[222]
$K_6Li_4NbO_3$	4 mm	1.064	$d_{31} = (19.3 \pm 4)\, d_{11}^{Q}$ $d_{33} = (35 \pm 5)\, d_{11}^{Q}$	[51]
$K_3Li_2Nb_5O_{15}$	4 mm	1.06	$d_{31} = (19 \pm 4)\, d_{11}^{Q}$	[63]
Ba_2NaNbO_{15}	2 mm	1.064	$d_{31} = (35 \pm 7)\, d_{11}^{Q}$ $d_{32} = (41.3 \pm 4)\, d_{11}^{Q}$ $d_{33} = (42 \pm 3)\, d_{11}^{Q}$	[51]
HIO_3	222	1.06	$d_{14} = (21 \pm 4)\, d_{11}^{Q}$	[52]
$LiIO_3$	6	1.06	$d_{31} = (31 \pm 3)\, d_{36}^{KDP}$ $d_{31} = (38 \pm 6)\, d_{31}^{Q}$	[53]
		1.064	$d_{31} = (11.9 \pm 1.0)\, d_{36}^{KDP}$ $d_{33} = (12.4 \pm 1.0)\, d_{36}^{KDP}$	[54]
$NaClO_3$	23	0.6943	$d_{14} = 3.3 \times 10^{-9}$ e.s.u.	[70]
$NaBrO_3$	23	0.6943	$d_{14} = 1.35 \times 10^{-9}$ e.s.u.	[70]

*d_{36}^{KDP}: susceptibility of KDP crystal, d_{11}^{Q}: susceptibility of quartz.

TABLE IV Nonlinear optical properties of semiconductors of the III, IV and V groups (symmetry $\bar{4}3m$).

Material	$n(\omega)$	$n(2\omega)$	l_{coh} (measured) (μm)		$d_{14}^{2\omega}$ in units of 10^{-6} e.s.u. experimental*		theoretical	
InAs	3.49	3.54	53 ± 2	[219]	1.0 ± 0.3	[66]	1.0†	
			60 ± 10	[66]	1.2 ± 0.3	[86]	0.96	[211]
					1.0	[219]	2.05	[206]
GaAs	3.27	3.30	104 ± 7	[219]	0.88 ± 0.3	[66]	0.64†	
			111 ± 10	[66]	0.9 ± 0.2	[86]	0.57	[211]
					0.45	[219]	0.95	[206]
GaP	3.05	3.11	46 ± 3	[219]	0.26	[219]	0.41†	
					0.105	[97]	0.34	[211]
							0.70	[206]
GaSb	3.80	3.82	134 ± 7	[219]	1.51	[219]	1.70†	
							1.2	[211]
							0.80	[206]

*Experimental values of $d_{14}^{2\omega}$ from SHG measurements with a CO_2 gas laser yielding light of wavelength 10.6 μm.
†Values calculated from Miller's empirical rule [198, 219].

resulting from equation 8, and from the optical-rectification effect [6]:

$$P_i^{(2)}(0) = \chi_{ijk}(0; \omega, -\omega)\, E_j(\omega, \mathbf{k})\, E_k^*(\omega, \mathbf{k}) \tag{29}$$

which consists in the production of a steady polarisation in a medium subjected to an optical laser field of intensity $E_j\, E_k^*$.

Measurements of the susceptibilities appearing in equations 28 and 29 have been carried out for KDP and ADP [228] crystals as well as for ferroelectric crystals [220, 224, 225, 227, 229, 230].

TABLE V Experimental and theoretical values of nonlinear optical susceptibilities for semiconductor crystals.

Crystal	Symmetry	$d_{ij}^{2\omega}$ in units of 10^{-7} e.s.u.	
		experimental [66, 86, 211, 224]	calculated [211]
InSb	$\bar{4}3$ m	$d_{14} = 16.5 \pm 3.5$	$d_{14} = 19.0$
CdTe		4.0 ± 1.5	3.5
ZnTe		3.1 ± 0.7	3.0
ZnSe		1.4 ± 0.4	1.4
ZnS		0.7 ± 0.2	0.85
CuCl		0.2 ± 0.1	0.32
CdSe	6 mm	$d_{15} = 1.15 \pm 0.35$	$d_{15} = d_{31} = 1.3$
		$d_{31} = 1.05 \pm 0.35$	
		$d_{33} = 2.00 \pm 0.7$	$d_{33} = 2.6$
CdS		$d_{15} = 0.60 \pm 0.09$	$d_{15} = d_{31} = 0.6$
		$d_{31} = 0.55 \pm 0.09$	
		$d_{33} = 1.00 \pm 0.15$	$d_{33} = 1.25$
ZnS		$d_{15} = 0.50 \pm 0.15$	$d_{15} = d_{31} = 0.48$
		$d_{31} = 0.45 \pm 0.15$	
		$d_{33} = 0.89 \pm 0.3$	$d_{33} = 0.95$
ZnO		$d_{15} = -0.07 \pm 0.03$	$d_{15} = d_{31} = -0.12$
		$d_{31} = -0.07 \pm 0.03$	
		$d_{33} = -0.22 \pm 0.05$	$d_{33} = -0.28$
AlN			$d_{33} = -0.41$
SiC			$d_{33} = -1.98$
BeO		$d_{33} = -0.0075$	$d_{33} = -0.013$
SiO_2		$d_{33} = 0.012$	$d_{33} = 0.012$

Likewise, the third-order susceptibility can be determined from light intensity birefringence, which results from the polarisation measured at frequency ω_1 induced by intense light of frequency ω_2:

$$P_i^{(3)}(\omega_1) = \chi_{ijkl}(-\omega_1; \omega_1, \omega_2, -\omega_2)\, E_j(\omega_1)\, E_k(\omega_2)\, E_l^*(\omega_2) \ . \tag{30}$$

The nonlinear susceptibility occurring in equation 30 has been measured mostly in isotropic bodies [38-40, 231, 232]. At $\omega_2 = 0$, equation 30 describes the static Kerr effect discussed for alkali metal vapours [233] and studied recently by the new laser technique in liquids consisting of tetrahedral and anisotropic molecules [234].

As shown theoretically and experimentally by Freund [235], second-order susceptibilities are accessible to investigation by nonlinear diffraction of optical harmonic radiations at angles of incidence for which Bragg's law is satisfied. This novel nonlinear effect arises owing to a periodic spatial modulation of the nonlinear susceptibility, and is absent in dielectrics with a spatially uniform linear susceptibility.

8. Final Remarks

In the search for new materials for the production of optical harmonics, account should be taken not only of their high nonlinearity but also of the existence of matching directions in them, which permit an increase in harmonic intensities by several orders of magnitude. This raises the equally important point of finding new methods of phase velocity synchronisation not only in anisotropic bodies but, in the first place, in isotropic ones. In naturally anisotropic bodies, optical dispersion can be compensated owing to the presence of natural linear optical birefringence [43, 44], whereas in isotropic ones matching can be achieved by resorting to the dispersion of circular birefringence occurring in optically active substances [69, 115]. Boyd *et al* [236] have just reported observations of acoustically induced phase-matched optical harmonic generation in GaAs. It is to be hoped that yet other, ingenious methods of matching, resorting to other effects and factors (electric fields, magnetic fields, flow, mechanical stress, etc.) may be found.

Nonlinear optical properties of matter are also apparent in a variety of processes and

phenomena unmentioned in this paper. Here belong, in the first place, parametric processes [160, 161, 237-241], emission and parametric scattering [242-246], various stimulated scattering effects [11, 15, 135, 247], multi-photon processes [9, 12, 248, 249], self-focusing and self-trapping [13, 40, 250-253], optical saturation [254, 255], optical Kerr effect [36, 37, 180, 256, 257], nonlinear optical activity and dichroism [182, 183, 258]. These effects, when the medium is a solid, are essentially determined by electronic and ionic processes; in isotropic bodies, they depend, often decisively (beside electronic processes), on processes of optical molecular reorientation [36, 37] and molecular spatial redistribution [37, 122, 250].

In dealing with the above-discussed nonlinear effects, much importance is attached to the analysis of radiation field coherence [259] and of the fluctuational-statistical processes accompanying the generation of optical harmonics [260-262]. Papers are moreover available on harmonic generation by bounded laser beams [263], the role of resonators [264, 265] and of different degrees of mode-locking [266] and matching [267-269], as well as other aspects of harmonic generation [270-274] and nonlinear optical mixing [275-277] including such media as a plasma [278] and an electron gas [279]. Also, general perturbation theories of nonlinear interaction between intense electromagnetic waves and matter have been developed in a classical [280], semi-classical [205, 281] and quantum-electrodynamical approach [257, 282], to within arbitrarily high orders of the perturbations and electric and magnetic multipoles [24, 248].

Successful studies of the optical properties of highly nonlinear materials and the understanding of the mechanism by which intense electromagnetic waves interact in matter have rendered possible, in the course of the past ten years, the achievement of rapid progress in the production of light harmonics in continuous, pulsed and ultrashort generation. In some cases, it has proved feasible to raise the second harmonic conversion yield to almost 100% [156, 274], permitting the use of optical second harmonics as a source of intense coherent green and ultraviolet radiation. The production of sum and difference frequencies provides a tunable source of far infra-red and millimetre wavelength radiation. Optical harmonics and their polarisation properties have found application in methods for the measurement of picosecond light pulses.

Coherent light in the visible and near infra-red can be obtained with parametric optical oscillators [238], which permit continuous tuning (i) by mechanical rotation of the crystal in the resonator [160, 161], (ii) by temperature-variation of matching angles, and (iii) by the linear electro-optical effect, a method of low inertia of order 10^{-12} sec [239, 283]. An alternative is to hand in the organic lasers [157, 284], which tune the frequency in a rather wide range. However, parametric oscillators have the advantage [238] over dye lasers in that they permit operation in the far infra-red range, a broader tuning frequency interval, CW operation, and applications for selective excitation in molecular nonlinear spectroscopy as well as in chemical studies [12, 285].

The analysis of nonlinear processes consisting in the generation of optical harmonics and the mixing of laser light frequencies provides an important new method for studying the properties of crystals and other materials, i.e. their optical dispersion, the positions and intensities of absorption bands, macroscopic and microscopic structural symmetry, and for determining numerical values of nonlinear optical susceptibilities. Harmonic investigations in transmitted and reflected light have allowed experimental verification of the laws of reflection and refraction which, in general, are nonlinear [17]. In order to understand and predict the behaviour and proper functioning of various new opto-electronic devices operating in conditions of very intense laser radiation, it is important to know how long the usual laws of optics remain valid and when nonlinear laws of light reflection and refraction begin to intervene. Although the harmonic intensities in reflected light are considerably weaker than in transmitted light (particularly under phase-matched conditions), they nevertheless permit the investigation of nonlinearity in absorbing materials. Thus not only their internal structure but also their surface properties, especially at contact with other substances, are accessible for study. We obtain knowledge of the electronic, atomic and molecular properties of matter at frequencies ranging from the ultraviolet through the visible, infra-red, and far infra-red

into the millimetre band. The new optical effects are by no means an image of the (natural and induced) nonlinear optical properties of matter in the electric dipole approximation only; in bodies with a centre of symmetry, the essence of certain of these effects resides in higher, multipolar electric and magnetic polarisations [20, 24, 248]. Multi-harmonic light scattering [122, 170], nonlinear diffraction [235] and nonlinear refractive index studies [250, 253] provide invaluable information concerning multi-molecular correlation functions and permit the quantitative checking of the superposition principles of the distribution functions dealt with in statistical mechanics [286-290].

The uncanny properties and enormous intensity of laser light have induced material media to respond fascinatingly and unexpectedly with an array of optical effects of extreme beauty in the course of the ten years which have elapsed since the coming of lasers.

Acknowledgements

I wish to thank very sincerely all Authors who had the kindness to make available to me their preprints and reprints, thus helping me to write this review. Thanks are also due to K. Flatau, M.Sci., for his part in the English translation and for his stimulating discussions.

References

1. P. A. FRANKEN, A. E. HILL, C. W. PETERS, and G. WEINREICH, *Phys. Rev. Lett.* **7** (1961) 118-119
2. S. A. AKHMANOV and R. V. KHOKHLOV, "Problemy Nyelineynoy Optiki" (Akad. Nauk SSSR, Moscow, 1964).
3. N. BLOEMBERGEN, "Nonlinear Optics" (W. A. Benjamin, New York, 1965).
4. P. N. BUTCHER, "Nonlinear Optical Phenomena" (Ohio State University, 1965).
5. G. BIRNBAUM, "Optical Masers" (Academic Press, New York, 1964); V. M. FAYN and J. I. KHANIN, "Kvantovaya Radiofizika" (Moscow, Soviet Radio, 1965).
6. P. A. FRANKEN and J. F. WARD, *Rev. Mod. Phys.* **35** (1963) 23-39.
7. J. C. CANIT, *J. Physique* **26** (1965) 433-440.
8. P. S. PERSHAN, "Nonlinear Optics" in Progress in Optics, vol. 5 (1966) 85-144 (New York: Interscience, Amsterdam: North-Holland).
9. A. M. BONCH-BRUYEVICH and W. A. KHODOVOY, *Usp. Fiz. Nauk* **85** (1965) 3-64.
10. R. W. MINCK, R. W. TERHUNE, and C. C. WANG, *Appl. Opt.* **5** (1966) 1595-1612.
11. N. BLOEMBERGEN, *Amer. J. Phys.* **35** (1967) 989-1023; D. H. RANK, *J. Opt. Soc. Amer.* **60** (1970) 443-447.
12. W. L. PETICOLAS, *Ann. Rev. Phys. Chem.* **18** (1967) 233-260.
13. S. A. AKHMANOV, A. P. SUKHORUKOV, and R. V. KHOKHLOV, *Usp. Fiz. Nauk* **93** (1967) 19-70; S. A. AKHMANOV and R. V. KHOKHLOV, *ibid* **95** (1968) 231-247.
14. R. W. TERHUNE and P. D. MAKER, "Nonlinear Optics in Lasers", vol. 2, edited by A. K. Levine (Marcel Dekker, Inc. New York) (1968) 295.
15. V. S. STARUNOV and I. L. FABIELINSKIY, *Usp. Fiz. Nauk* **98** (1969) 441-491.
16. J. A. ARMSTRONG, N. BLOEMBERGEN, J. DUCUING, and P. S. PERSHAN, *Phys. Rev.* **127** (1962) 1918-1939.
17. N. BLOEMBERGEN and P. S. PERSHAN, *ibid* **128** (1962) 606-622.
18. D. A. KLEINMAN, *ibid* **126** (1962) 1977-1979; *ibid* **128** (1962) 1761-1775.
19. R. LOUDON, *Proc. Phys. Soc.* **80** (1962) 952-961.
20. P. S. PERSHAN, *Phys. Rev.* **130** (1963) 919-928.
21. P. N. BUTCHER and T. P. MCLEAN, *Proc. Phys. Soc.* **81** (1963) 219-232; *ibid* **83** (1964) 579-589.
22. E. ADLER, *Phys. Rev.* **134** (1964) A 728-733.
23. J. A. GIORDMAINE, *ibid* **138** (1965) A 1599-1606.
24. S. KIELICH, *Proc. Phys. Soc.* **86** (1965) 709-725; *Acta Physica Polon.* **29** (1966) 875-898.
25. H. A. LORENTZ, "The Theory of Electrons" (B. G. Teubner, Leipzig, 1909); L. ROSENFELD, "Theory of Electrons" (North-Holland Publishing Company, Amsterdam, 1951).
26. M. BORN, "Optik" (J. Springer, Berlin, 1933).
27. W. VOIGT, *Ann. Physik* **4** (1901) 197-208.
28. P. LANGEVIN, *Le Radium* **7** (1910) 249.
29. J. H. VAN VLECK, "The Theory of Electric and Magnetic Susceptibilities" (University Press, Oxford, 1932); D. W. DAVIES, "The Theory of the Electric and Magnetic Properties of Molecules" (Wiley, London, 1967).
30. M. V. VOLKENSHTEYN, "Molekularnaya Optika" (Moscow, Gostekhizdat, 1951).

31. S. KIELICH, *Acta Phys. Polon.* **17** (1958) 239-255; S. KIELICH and A. PIEKARA, *ibid* **18** (1959) 439-472.
32. F. POCKELS, "Lehrbuch der Kristallooptik" (Leipzig, 1906).
33. J. FRENKEL, "Kinetic Theory of Liquids" (Oxford University Press, London, 1946).
34. L. D. LANDAU and E. M. LIFSHITZ, "Electrodynamics of Continuous Media" (Pergamon Press, Inc. New York, 1960).
35. I. L. FABIÉLINSKIY, "Molekularnoye Rassieyaniye Svyeta" (Moscow, GRFML, 1965).
36. A. D. BUCKINGHAM, *Proc. Phys. Soc.* B **69** (1956) 344-349.
37. S. KIELICH, *Acta Phys. Polon.* **19** (1960) 573-597; **30** (1966) 683-707; **31** (1967) 689-713.
38. G. MAYER and F. GIRES, *C.R. Acad. Sc., Paris* **258** (1964) 2039-2042; G. HAUCHECORNE and G. MAYER, *ibid* B **261** (1965) 4014-4017; M. PAILLETTE, *ibid* B **262** (1966) 264-267; *ibid* **266** (1968) 920-922; *ibid* **267** (1968) 882-885; F. GIRES, *Annales Radioélectricité* **23** (1968) 281-305.
39. P. D. MAKER and R. W. TERHUNE, *Phys. Rev.* **137** (1965) A 801-818.
40. C. C. WANG, *ibid* **152** (1966) 149-156; F. SHIMIZU, *J. Phys. Soc. Japan* **22** (1967) 1070-1077.
41. J. E. MIDWINTER and J. WARNER, *Brit. J. Appl. Phys.* **16** (1965) 1135-1142; J. WARNER, *Opto-Electronics* **1** (1969) 25-28.
42. J. F. NYE, "Physical Properties of Crystals" (Clarendon Press, Oxford, 1957).
43. J. A. GIORDMAINE, *Phys. Rev. Letts.* **8** (1962) 19-20.
44. P. D. MAKER, R. W. TERHUNE, M. NISENOFF, and C. M. SAVAGE, *ibid* **8** (1962) 21-22.
45. S. A. AKHMANOV, A. I. KOVRIGIN, A. S. PISKARSKAS, and R. V. KHOKHLOV, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **2** (1965) 233-235.
46. C. C. WANG and G. W. RACETTE, *J. Appl. Phys.* **36** (1965) 3281-3284.
47. G. D. BOYD, A. ASHKIN, J. M. DZIEDZIC, and D. A. KLEINMAN, *Phys. Rev.* **137** (1965) A 1305-1320.
48. R. C. MILLER, *ibid* **131** (1963) 95-97; *ibid* **134** (1964) A 1313-1319.
49. R. C. MILLER, D. A. KLEINMAN, and A. SAVAGE, *Phys. Rev. Lett.* **11** (1963) 146-149.
50. G. D. BOYD, R. C. MILLER, K. NASSAU, W. L. BOND, and A. SAVAGE, *Appl. Phys. Lett.* **5** (1964) 234-236; R. C. MILLER and A. SAVAGE, *ibid* **9** (1966) 169-171; W. F. HAGEN and P. C. MAGNATE, *J. Appl. Phys.* **40** (1969) 219-224; P. M. BRIDENBAUGH, J. R. CARRUTHERS, J. M. DZIEDZIC, and F. R. NASH, *Appl. Phys. Lett.* **17** (1970) 104-106; C. R. JEGGO and G. D. BOYD, *J. Appl. Phys.* **41**, (1970) 2742-2743.
51. L. G. VAN UITERT, S. SINGH, H. J. LEVINSTEIN, J. E. GEUSIC, and W. A. BONNER, *Appl. Phys. Lett.* **11** (1967) 161-165; *ibid* **12** (1968) 224; R. L. BYERS, S. E. HARRIS, D. J. KHIZANGA, and J. F. YOUNG, *J. Appl. Phys.* **40** (1969) 444-445; J. E. GEUSIC, H. J. LEVINSTEIN, J. J. RUBIN, S. SINGH, and L. G. VAN UITERT, *Appl. Phys. Letts.* **11** (1967) 269-271; *ibid* E **12** (1968) 224.
52. S. K. KURTZ, T. T. PERRY, and J. G. BERGMAN JR., *Appl. Phys. Lett.* **12** (1968) 186-188.
53. G. NATH and S. HAUSSUHL, *ibid* **14** (1969) 154-156; *Phys. Lett.* **29A** (1969) 91-92.
54. J. JERPHAGNON, *Appl. Phys. Lett.* **16** (1970) 298-299; F. R. NASH, J. G. BERGMAN, G. D. BOYD, and E. H. TURNER, *J. Appl. Phys.* **40** (1969) 5201-5206.
55. T. R. GURSKI, *Appl. Phys. Lett.* **15** (1969) 5-6.
56. R. W. WALLACE and S. E. HARRIS, *ibid* **15** (1969) 111-112.
57. A. GRAJA, *Phys. Status Solidi* **27K** (1968) 93-97; *Acta Physica Polonica* **36** (1969) 283-285; A **37** (1970) 539-558.
58. S. K. KURTZ and T. T. PERRY, *J. Appl. Phys.* **39** (1968) 3798-3813.
59. A. A. FILIMONOV, V. S. SUVOROV, and I. S. REZ, *Zh. Eksperim i Teor. Fiz.* **56** (1969) 1519-1523.
60. H. FAY, W. J. ALFORD, and H. M. DESS, *Appl. Phys. Lett.* **12** (1968) 89-92.
61. J. G. BERGMAN, A. ASHKIN, A. A. BALLMAN, J. M. DZIEDZIC, H. J. LEVINSTEIN, and R. G. SMITH, *ibid* **12** (1968) 92-94.
62. S. K. KURTZ, *IEEE J. Quantum Electr.* **QE-4** (1968) 578-584.
63. L. G. VAN UITERT, J. J. RUBIN, and W. A. BONNER, *ibid* **QE-4** (1968) 622-627; R. R. RICE, H. FAY, H. M. DESS, and W. J. ALFORD, *J. Electrochem. Soc.* **116** (1969) 839-843.
64. M. BASS, D. BUA, R. MOZZI, and R. R. MONCHAMP, *Appl. Phys. Letts.* **15** (1969) 393-396; L. D. DERKACHOVA, A. I. KRIMOVA, and I. P. SONINA, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **11** (1970) 469-472.
65. A. ASHKIN, G. D. BOYD, and J. M. DZIEDZIC, *Phys. Rev. Lett.* **11** (1963) 14-17.
66. C. K. N. PATEL, *ibid* **15** (1965) 1027-1030; *ibid* **16** (1966) 613-616.
67. J. E. BJORKHOLM and A. E. SIEGMAN, *Phys. Rev.* **154** (1967) 851-860.
68. G. F. DOBRZAŃSKI, M. P. GOLOVIEY, and G. I. KOSOUROV, *Zh. Eksperim i Teor. Fiz. Pisma v Redaktsiyu,* **10** (1969) 263-265.
69. H. RABIN and P. P. BEY, *Phys. Rev.* **156** (1967) 1010-1016.
70. H. J. SIMON and N. BLOEMBERGEN, *ibid* **171** (1968) 1104-1114.

71. J. E. BJORKHOLM, *ibid* **142** (1966) 126-136; D. A. KLEINMANN, A. ASHKIN, and G. D. BOYD, *ibid* **145** (1966) 338-379.
72. S. A. AKHMANOV, A. P. SUKHORUKOV, and R. V. KHOKHLOV, *Zh. Eksperim. Teor. Fiz.* **50** (1966) 474-486.
73. M. P. GOLOVIEY and G. J. KOSOUROV, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **9** (1969) 225-226; A. P. SUKHORUKOV and I. V. TOMOV, *Izv. Vysshikh Uchebnykh Zavedeniy* **13** (1970) 266-270.
74. H. SHIH and N. BLOEMBERGEN, *Phys. Rev.* **184** (1969) 895-904.
75. A. S. SONIN and V. S. SUVOROV, *Fiz. Tviordogo Tiela* **10** (1968) 1031-1035.
76. H. VOGT, H. HAPP, and H. G. HÄFELE, *Phys. Stat. Solidi* (a) **1** (1970) 439-450.
77. N. BLOEMBERGEN, *Optica Acta* **13** (1966) 311-322.
78. J. DUCUING and N. BLOEMBERGEN, *Phys. Lett.* **10** (1963) 474-476.
79. R. K. CHANG and N. BLOEMBERGEN, *Phys. Rev.* **144** (1966) 775-780.
80. N. BLOEMBERGEN and C. H. LEE, *Phys. Rev. Lett.* **19** (1967) 835-837.
81. R. FISCHER, *Phys. Status Solidi* **19** (1967) 757-765.
82. N. BLOEMBERGEN, H. J. SIMON, and C. H. LEE, *Phys. Rev.* **181** (1969) 1261-1271.
83. S. S. JHA, *ibid* **140** (1965) A 2020-2030; *ibid* **145** (1966) 500-506.
84. S. KIELICH, *Acta Physica Polonica* A **37** (1970) 205-219.
85. F. BROWN, R. E. PARKS, and A. M. SLEEPER, *Phys. Rev. Lett.* **14** (1965) 1029-1031.
86. N. BLOEMBERGEN, R. K. CHANG, and C. H. LEE, *ibid* **16** (1966) 986-989.
87. F. BROWN and M. MATSUOKA, *Phys. Rev.* **185** (1969) 985-987.
88. N. BLOEMBERGEN, R. K. CHANG, C. H. LEE, and S. S. JHA, *ibid* **174** (1968) 813-822; *ibid* **178** (1969) E 1528.
89. G. I. LEVIYEV and E. G. YASHCHIN, *Zh. Eksperim. i Teor. Fiz. Pisma v Redakt.* **10** (1969) 257-260; G. V. KRIVOSHCHIOKOV and G. V. STROGANOV, *Fiz. Tviordogo Tiela* **11** (1969) 2663-2665.
90. C. C. WANG and A. N. DUMIŃSKI, *Phys. Rev. Lett.* **20** (1968) 668-671; *ibid* **21** (1968) E 266.
91. C. C. WANG, *Phys. Rev.* **178** (1969) 1457-1461.
92. M. BASS, P. A. FRANKEN, A. E. HILL, C. W. PETERS, and G. WEINREICH, *Phys. Rev. Lett.* **8** (1962) 18-20.
93. R. C. MILLER and A. SAVAGE, *Phys. Rev.* **128** (1962) 2175-2179.
94. R. C. MILLER, G. D. BOYD, and A. SAVAGE, *Appl. Phys. Lett.* **6** (1965) 77-79.
95. D. J. BRADLEY, G. MAGYAR, and M. C. RICHARDSON, *ibid* **11** (1967) 51-53; D. J. BRADLEY, *Optical Acta* **15** (1968) 431-450.
96. F. ZERNIKE JR. and P. R. BERMAN, *Phys. Rev. Lett.* **15** (1965) 999-1001.
97. W. L. FAUST and C. H. HENRY, *ibid* **17** (1966) 1265-1268.
98. J. E. MIDWINTER, *Appl. Phys. Lett.* **12** (1968) 68-69.
99. D. W. FARIES, K. A. GEHRING, P. L. RICHARD, and Y. R. SHEN, *Phys. Rev.* **180** (1969) 363-365.
100. T. YAJIMA and K. INOUE, *Phys. Lett.* **26A** (1968) 281; *IEEE J. Quantum Electr.* **QE-5** (1969) 140-146.
101. F. ZERNIKE, *Phys. Rev. Lett.* **22** (1969) 931.
102. N. VAN TRAN and C. K. N. PATEL, *ibid* **22** (1969) 463-466.
103. T. Y. CHANG, N. VAN TRAN, and C. K. N. PATEL, *Appl. Phys. Lett.* **13** (1968) 357-359; V. J. CORCORAN, R. E. CUPP, J. J. GALLAGHER, and W. T. SMITH, *ibid* **16** (1970) 316-318.
104. C. K. N. PATEL and N. VAN TRAN, *ibid* **15** (1969) 189-191.
105. F. BROWN, *IEEE J. Quantum Electr.* **QE-5** (1969) 586-589.
106. M. S. SODHA, B. K. SAWHNEY, and R. L. SAWHNEY, *J. Phys. D.* **3** (1969) 377-387; M. S. SODHA and P. K. KAW, *Proc. Phys. Soc.* **88** (1966) 373-386; L. STENLO, *Phys. Rev.* **B1** (1970) 2821-2823
107. P. M. RENTZEPIS, J. A. GIORDMAINE, and K. W. WECHT, *Phys. Rev. Lett.* **16** (1966) 792-794; J. A. GIORDMAINE and P. M. RENTZEPIS, *J. Chim. Physique* **1** (1967) 215-221.
108. N. V. COHAN and H. F. HAMEKA, *J. Chem. Phys.* **45** (1966) 3825-3826.
109. A. W. SMITH and N. BRASLAU, *J. Appl. Phys.* **34** (1963) 2105-2106.
110. P. P. BEY and H. RABIN, *Phys. Rev.* **162** (1967) 794-800.
111. J. E. MIDWINTER and J. WARNER, *Brit. J. Appl. Phys.* **16** (1965) 1667-1674.
112. S. KIELICH, *Acta Physica Polonica* **36** (1969) 621-631.
113. R. W. TERHUNE, P. D. MAKER, and C. M. SAVAGE, *Phys. Rev. Lett.* **8** (1962) 404-406.
114. P. D. MAKER, R. W. TERHUNE, and C. M. SAVAGE, Third Conference on Quantum Electronics, Paris, 1963 (Columbia University Press, New York, 1964) 1559-1579.
115. P. P. BEY, J. F. GIULIANI, and H. RABIN, *Phys. Rev. Lett.* **19** (1967) 819-821; *IEEE J. Quantum Electr.* **QE-4** (1968) 932-939.
116. R. K. CHANG and L. K. GALBRAITH, *Phys. Rev.* **171** (1968) 993-996.
117. P. P. BEY, J. F. GIULIANI, and H. RABIN, *Phys. Lett.* **26A** (1968) 128-129.

118. J. F. WARD and G. H. C. NEW, *Phys. Rev.* **185** (1969) 57-72.
119. L. S. GOLDBERG and J. M. SCHNUR, *Appl. Phys. Lett.* **14** (1969) 306-308; *Radio and Electronic Engineer* **39** (1970) 279-285.
120. I. FREUND and P. M. RENTZEPIS, *Appl. Phys. Lett.* **18** (1967) 393-394; G. DURAND and C. H. LEE, *Comptes Rendus* **264B** (1967) 1397-1399; *Mol. Crys.* **5** (1968) 171-183.
121. J. W. SHELTON and Y. R. SHEN, *Phys. Rev. Lett.* **25** (1970) 23-26.
122. S. KIELICH, *Acta Physica Polonica* **33** (1968) 89-104; *ibid* 141-143; *IEEE J. Quantum Electr.* **QE-4** (1968) 744-752.
123. P. P. BEY, J. F. GIULIANI, and H. RABIN, *Phys. Rev.* **184** (1969) 849-858.
124. C. C. WANG and E. L. BAARDSEN, *ibid* **185** (1969) 1079-1082; *ibid* B **1** (1970) 2827.
125. J. H. MCFEE, *Appl. Phys. Lett.* **11** (1967) 228-230.
126. C. H. LEE, R. K. CHANG, and N. BLOEMBERGEN, *Phys. Rev. Lett.* **18** (1967) 167-170.
127. V. S. SUVOROV and A. S. SONIN, *Zh. Eksperim. i Teor. Fiz.* **54** (1968) 1044-1050.
128. G. MAYER, *C.R. Acad. Sci.* **267B** (1968) 54-57.
129. S. KIELICH, *IEEE J. Quantum Electr.* **QE-5** (1969) 562-568; *Optics Communications* **1** (1969) 86-88; *Opto-electronics* **2** (1970) 5-20.
130. M. S. SODHA and P. K. KAW, *J. Phys. Soc. Japan* **21** (1966) 2684-2694; G. P. GUPTA, *Proc. Phys. Soc.* **92** (1967) 1122-1133.
131. N. VAN TRAN, J. H. MCFEE, and C. K. N. PATEL, *Phys. Rev. Lett.* **21** (1968) 735-738.
132. B. LAX, W. ZAWADZKI, and M. H. WEILER, *ibid*, **18** (1967) 462.
133. J. KOŁODZIEJCZAK, *Phys. Stat. Solidi* **24** (1967) 323-329; *ibid* **29** (1968) 645-652.
134. M. S. SODHA and P. K. KAW, *Progress Theoretical Physics* **34** (1965) 557-573.
135. J. A. GIORDMAINE and W. KAISER, *Phys. Rev.* **144** (1966) 676-688.
136. W. G. RADO, *Appl. Phys. Lett.* **11** (1967) 123-125.
137. J. J. WYNNE, *Phys. Rev.* **178** (1969) 1295-1303.
138. J. A. GIORDMAINE, M. A. DUGAY, and J. W. HANSEN, *IEEE J. Quantum Electr.* **QE-4** (1968) 252-255.
139. J. P. LAUSADE and A. YARIV, *Appl. Phys. Lett.* **13** (1968) 65-66.
140. R. A. FISCHER, P. L. KELLEY, and T. K. GUSTAFSON, *ibid* **14** (1969) 140-143.
141. J. A. ARMSTRONG, *ibid* **10** (1967) 16-18; W. H. GLENN and M. J. BRIENZA, *ibid* **10** (1967) 221-224; J. R. KLAUDER, M. A. DUGUAY, J. A. GIORDMAINE, and S. L. SHAPIRO, *ibid* **13** (1968) 174-176; M. A. DUGUAY and J. W. HANSEN, *ibid* **13** (1968) 178-180; J. R. KLAUDER, *ibid* **14** (1969) 147-148.
142. J. A. GIORDMAINE, P. M. RENTZEPIS, S. L. SHAPIRO, and K. W. WECHT, *ibid* **11** (1967) 216-218; S. L. SHAPIRO and M. A. DUGUAY, *Phys. Lett.* **28A** (1969) 698-699; J. K. KARASIUK, P. P. PASHININ, and A. M. PROKHOROV, *Zh. Eksperim. i Teor. Fiz. Pišma v Redaktsiyu* **7** (1968) 117-119; P. M. RENTZEPIS, C. J. MITSCHELE, and A. C. SAXMAN, *Appl. Phys. Lett.* **17** (1970) 122-125.
143. D. J. BRADLEY, G. H. C. NEW, B. SUTHERLAND, and S. J. CAUGHEY, *Phys. Lett.* **28A** (1969) 532-533; H. E. ROVE and T. LI, *IEEE J. Quantum Electr.* **QE-6** (1970) 49-67.
144. N. G. BASOV, P. G. KRIUKOV, V. S. LETOKHOV, and YA. V. SENATSKII, *IEEE J. Quantum Electr.* **QE-4** (1968) 606-609; N. G. BASOV, P. G. KRIUKOV, YU. V. SENATSKII, and S. V. CHEKALIN, *Zh. Eksperim. i Teor. Fiz.* **57** (1969) 1175-1183.
145. J. COMLY and E. GARMIRE, *Appl. Phys. Lett.* **12** (1968) 7-9.
146. R. C. MILLER, *Phys. Lett.* **26A** (1968) 177-178; S. A. AKHMANOV, A. P. SUKHORUKOV, and A. S. CHIRKIN, *Zh. Eksperim. i Teor. Fiz.* **55** (1968) 1430-1448.
147. S. L. SHAPIRO, *Appl. Phys. Lett.* **13** (1968) 19-21.
148. R. YU. ORLOV, T. USMANOV, and A. S. CHIRKIN, *Zh. Eksperim. i Teor. Fiz.* **57** (1969) 1069-1080.
149. R. C. ECKART and C. H. LEE, *Appl. Phys. Lett.* **15** (1969) 425-427.
150. N. BLOEMBERGEN, W. K. BURNS, and M. MATSHUOKA, *Optics Communications* **1** (1969) 195-198.
151. C. C. WANG and E. L. BAARDSEN, *Appl. Phys. Lett.* **15** (1969) 396-398.
152. R. G. BREWER and C. H. LEE, *Phys. Rev. Lett.* **21** (1968) 267-270.
153. S. A. AKHMANOV, A. S. CHIRKIN, K. N. DRABOVICH, A. I. KOVRIGIN, R. V. KHOKHLOV, and A. P. SUKHORUKOV, *IEEE J. Quantum Electr.* **QE-4** (1968) 598-605.
154. G. A. ABAKUMOV, A. P. SIMONOV, V. V. FADEEV, L. A. KHARITONOV, R. V. KHOKHLOV, *Zh. Eksperim. i Teor. Fiz. Pišma v Redaktsiyu* **9** (1969) 15-18; A. G. ABAKUMOV, A. P. SIMONOV, V. V. FADEEV, M. A. KASYMDGANOV, L. A. KHARITONOV, and R. V. KHOKHLOV, *Opto-electronics* **1** (1969) 205-208.
155. A. G. AKHMANOV, S. A. AKHMANOV, B. V. ZHDANOV, A. I. KOVRIGIN, N. K. PODSOMSKAYA, and R. V. KHOKHLOV, *Zh. Eksperim. i Teor. Fiz. Pišma v Redaktsiyu* **10** (1969) 244-248.
156. M. W. DOWLEY and E. B. HODGES, *IEEE J. Quantum Electr.* **QE-4** (1968) 552-558; M. W. DOWLEY, *Appl. Phys. Lett.* **13** (1968) 395-397.
157. H. P. BROIDA and S. C. HAYDON, *Appl. Phys. Lett.* **16** (1970) 142-144; J. A. MYER, C. L. JOHNSON,

E. KIERSTEAD, E. D. SHARMA, and J. ITZKAN, *ibid* **16** (1970) 3-5; C. V. SHANK, A. DIENES, A. M. TROZZOLO, and J. A. MYER, *ibid* **16** (1970) 405-407.

158. L. O. HOCKER and A. JAVAN, *Phys. Lett.* **26A** (1968) 255-256; L. O. HOCKER, J. G. SMALL, and A. JAVAN, *ibid* **29A** (1969) 321-322.
159. V. DANEU, D. SOKOLOF, A. SANCHEZ, and A. JAVAN, *Appl. Phys. Lett.* **15** (1969) 398-401.
160. S. A. AKHMANOV and R. V. KHOKHLOV, *Usp. Fiz. Nauk.* **88** (1966) 439-460; J. A. GIORDMAINE, Italian Physical Society Proc. International School Phys. "Enrico Fermi", Course 42, 1967. Edited by R. J. Glauber (Academic Press, New York, 1968).
161. G. D. BOYD and D. A. KLEINMAN, *J. Appl. Phys.* **39** (1968) 3597-3639; S. E. HARRIS, *Proc. IEEE,* [illegible] 57 (1969) 2096 - 2113.
162. S. KIELICH, *Bull. Soc. Amis. Sci. Lett. Poznań* **13** B. **17** (1962-1963) 43-58; *Acta Phys. Polonica* **25** (1964) 85-99.
163. R. W. TERHUNE, P. D. MAKER, and C. M. SAVAGE, *Phys. Rev. Lett.* **14** (1965) 681-684.
164. P. D. MAKER, in "Physics of Quantum Electronics", p. 60 (McGraw-Hill, New York, 1966).
165. S. KIELICH, *Acta Physica Polonica* **26** (1964) 135-154.
166. S. J. CYVIN, J. E. RAUCH, and J. C. DECIUS, *J. Chem. Phys.* **43** (1965) 4083-4095; S. A. AKHMANOV and D. N. KLYSHKO, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **2** (1965) 171-175.
167. R. BERSOHN, Y. H. PAO, and H. L. FRISCH, *J. Chem. Phys.* **45** (1966) 3184-3198; *Intern. J. Quantum Chem.* **1** S (1967) 829-837.
168. D. L. WEINBERG, *J. Chem. Phys.* **47** (1967) 1307-1313.
169. V. L. STRIZHEVSKY and V. M. KLIMENKO, *Zh. Eksperim. i Teor. Fiz.* **53** (1967) 244-253.
170. P. D. MAKER, *Phys. Rev.* A **1** (1970) 923-951.
171. R. BERSOHN, *J. Am. Chem. Soc.* **86** (1964) 3505-3507; B. FANCONI and W. L. PETICOLAS, *J. Chem. Phys.* **50** (1969) 2244-2246.
172. S. KIELICH, *J. Colloid Interface Sci.* **27** (1968) 432-441; *Appl. Phys. Lett.* **13** (1968) 371-373; *Acta Phys. Polonica* **37A** (1970) 719-731.
173. I. FREUND, *Phys. Rev. Lett.* **19** (1967) 1288-1291; *Chem. Phys. Lett.* **1** (1968) 551-554.
174. M. LUBAN, N. WISER, and A. J. GREENFIELD, *J. Phys. Chem. Solid St. Phys.* **3** (1970) 1-7; I. FREUND and L. KOPF, *Phys. Rev. Lett.* **24** (1970) 1017-1021.
175. S. KIELICH, *J. Physique* **28** (1967) 519-534.
176. V. L. STRIZHEVSKY and V. V. OBUKHOVSKY, *Zh. Eksperim. i Teor. Fiz.* **58** (1970) 929-936.
177. R. BECHMAN and S. K. KURTZ, "Second harmonic generation of light in crystalline solids" in Landolt-Börnstein, Group III, vol. 2, 167-209. (Springer-Verlag, Berlin, 1969).
178. A. D. BUCKINGHAM and J. A. POPLE, *Proc. Phys. Soc. London* A **68** (1955) 905-909.
179. S. KIELICH, *Acta Physica Polonica* **22** (1962) 299-327; *Molecular Physics* **6** (1963) 49-59.
180. S. KIELICH, *Proc. Phys. Soc. London* **90** (1967) 847-858.
181. A. D. BUCKINGHAM and B. J. ORR, *Quart. Rev.* **21** (1967) 195-212.
182. S. KIELICH, *Opto-electronics* **1** (1969) 75-87; *Optics Communications* **1** (1969) 129-131.
183. P. W. ATKINS and R. G. WOLLEY, *J. Chem. Soc.* (1969) 515-519.
184. J. M. O'HARE and R. P. HURST, *J. Chem. Phys.* **46** (1967) 2356-2366.
185. A. D. MCLEAN and M. YOSHIMINE, *ibid* **46** (1967) 3682-3683.
186. G. P. ARRIGHINI, M. MAESTRO, and R. MOCCIA, *Sympos. Faraday Soc.* **2** (1968) 48-53.
187. L. L. BOYLE, A. D. BUCKINGHAM, R. L. DISCH, and D. A. DUNMUR, *J. Chem. Phys.* **45** (1966) 1318-1323; L. BOYLE, *Int. J. Quantum Chem.* **1** (1967) 595-604; *ibid* **3** (1969) 231-243; R. LOCQUENEUX and P. SMET, *C.R. Acad. Sc. Paris,* B **267** (1968) 433-436.
188. M. N. GRASSO, K. T. CHUNG, and R. P. HURST, *Phys. Rev.* **167** (1968) 1-6.
189. E. L. DAVES, *ibid* **169** (1968) 47-48.
190. P. SITZ and R. YARIS, *J. Chem. Phys.* **49** (1968) 3546-3557.
191. R. R. ALFANO and S. L. SHAPIRO, *Phys. Rev. Lett.* **24** (1970) 1217-1220.
192. R. G. BREWER and A. D. MCLEAN, *ibid* **21** (1968) 271-274.
193. A. SZWEIG, *Chem. Phys. Lett.* **1** (1967) 195-199; A. V. LUZANOV, YU. B. MALYKHANOV, and M. M. MESTECHKIN, *Optika i Spektroskopia* **28** (1970) 836-838.
194. A. D. BUCKINGHAM and D. A. DUNMUR, *Trans. Faraday Soc.* **64** (1968) 1776-1783.
195. G. H. MEETEN, *ibid* **64** (1968) 2267-2272.
196. L. D. YEVLEVA and M. A. KOVNER, *Optika i Spektroskopia* **36** (1969) 601-606.
197. S. KIELICH and M. KOZIEROWSKI, *Acta Physica Polonica* A **38** (1970) 271-273.
198. R. C. MILLER, *Appl. Phys. Lett.* **5** (1964) 17-19.
199. P. L. KELLEY, *J. Phys. Chem. Solids* **24** (1963) 607-616.
200. V. M. FAIN and E. G. YASHCHIN, *Zh. Eksperim. i Teor. Fiz.* **46** (1964) 695-709; *ibid* **49** (1965) 1118-1125.

201. H. CHANG and P. B. MILLER, *Phys. Rev.* **134A** (1964) 683-687.
202. W. J. CASPERS, *ibid* **133A** (1964) 1249-1251.
203. J. F. WARD, *Rev. Mod. Phys.* **37** (1965) 1-18.
204. Y. R. SHEN, *Phys. Rev.* **167** (1968) 818-821.
205. R. L. PATERSON, *Rev. Mod. Phys.* **39** (1967) 69-77; T. KAWASAKI, *Prog. Theor. Phys. Japan* **39** (1968) 331-348.
206. C. FLYTZANIS and J. DUCUING, *Phys. Lett.* **26A** (1968) 315-316; *Phys. Rev.* **178** (1968) 1218-1228.
207. S. S. JHA and N. BLOEMBERGEN, *Phys. Rev.* **171** (1968) 891-898; *IEEE J. Quantum Electr.* **QE-4** (1968) 670-673.
208. M. WEILER, W. ZAWADZKI, and B. LAX, *Phys. Rev.* **163** (1967) 733-742; M. SUFCZYŃSKI, *Phys. Lett.* **26A** (1968) 325; K. S. RUSTAGI, *ibid* **29A** (1969) 185-186.
209. J. A. VAN VECHTEN and D. E. ASPNES, *ibid* **30A** (1969) 346-347.
210. J. C. PHILIPS and J. A. VAN VECHTEN, *Phys. Rev.* **183** (1969) 709-711.
211. B. F. LEVINE, *Phys. Rev. Lett.* **22** (1969) 787-790; *ibid* **25** (1970) 440-442.
212. C. K. N. PATEL, R. E. SLUSHER, and P. A. FLEURY, *Phys. Rev. Lett.* **17** (1966) 1011-1014.
213. P. A. WOLFF and G. A. PEARSON, *ibid* **17** (1966) 1015-0000.
214. J. KOŁODZIEJCZAK, *Acta Physica Polonica* **33** (1968) 183-192.
215. C. C. WANG and N. W. RESSLER, *Phys. Rev.* **188** (1969) 1291-1293; K. C. RUSTAGI and S. S. JHA, *Phys. Lett.* **30A** (1969) 518-519; M. S. SODHA, P. K. DUBEY, S. K. SHARMA, and P. K. KAW, *Phys. Rev.* **1B** (1970) 3426-3430.
216. R. K. CHANG, J. DUCUING, and N. BLOEMBERGEN, *Phys. Rev. Lett.* **15** (1965) 6-8; *ibid* 415-418.
217. W. L. FAUST, C. H. HENRY, and R. H. EICK, *Phys. Rev.* **173** (1968) 781-786.
218. J. E. BJORKHOLM, *Appl. Phys. Lett.* **13** (1968) 36-37; *IEEE J. Quantum Electr.* **QE-4** (1968) 970-972.
219. J. J. WYNNE and N. BLOEMBERGEN, *Phys. Rev.* **188** (1969) 1211-1220.
220. M. DIDOMENICO, JR. and S. H. WEMPLE, *J. Appl. Phys.* **40** (1969) 720-752.
221. J. JERPHAGNON and S. K. KURTZ, *Phys. Rev.* **1** *B* (1970) 1739-1744; *ibid* (1970) 1667-1681.
222. J. H. MCFEE, G. D. BOYD, A. ASHKIN, and S. K. KURTZ, *J. Appl. Phys.* **40** (1969) 2860-2863; W. B. GANDRUD G. D. BOYD, J. H. MCFEE, and F. H. WEHMEIER, *Appl. Phys. Lett.* **16** (1970) 59-61.
223. B. TREVELYAN, *Opto-electronics* **1** (1969) 9-12; W. BARDSLEY, P. H. DAVIES, M. V. HOBDEN, K. F. HULME, O. JONES, W. POMEROY, and J. WARNER, *ibid* **1** (1969) 29-31.
224. R. C. MILLER and W. A. NORDLAND, *Appl. Phys. Lett.* **16** (1970) 174-176.
225. I. S. REZ, *Usp. Fiz. Nauk* **93** (1967) 633-674.
226. D. A. MCARTHUR and R. A. MCFARLANE, *Appl. Phys. Lett.* **16** (1970) 452-454.
227. G. BURNS and A. W. SMITH, *IEEE J. Quantum Electr.* **QE-4** (1968) 584-587.
228. J. F. WARD and P. A. FRANKEN, *Phys. Rev.* **133** (1964) A 183-190; J. F. WARD, *Phys. Rev.* **143** (1966) 569-574.
229. C. G. B. GARRETT, *IEEE J. Quantum Electr.* **QE-4** (1968) 70-84; H. FAY, *J. Opt. Soc. Amer.* **59** (1969) 1399-1404; W. D. JOHNSTON, *Phys. Rev.* **1**, (1970) 3494-3503.
230. W. D. JOHNSTON JR. and I. P. KAMINOV, *Phys. Rev.* **188** (1969) 1209-1211.
231. A. P. VEDUTA and B. P. KIRSANOV, *Zh. Eksperim. i Teor. Fiz.* **54** (1968) 1374-1379.
232. R. W. HELLWARTH and N. GEORGE, *Opto-electronics* **1** (1969) 213-217.
233. L. L. BOYLE and C. A. COULSON, *Molec. Phys.* **11** (1966) 165-174.
234. N. GEORGE, R. W. HELLWARTH, and C. R. COOKE, *Electron Technology, Warsaw* **2** (1969) 229-236; M. A. DUGUAY and J. W. HANSEN, *Appl. Phys. Lett.* **15** (1969) 192-194; M. PAILLETTE, *Ann. Phys. Paris*, [illegible] 4 (1969) 671 - 712.
235. I. FREUND, *Phys. Rev. Lett.* **21** (1968) 1404-1406.
236. G. D. BOYD, F. R. NASH, and D. F. NELSON, *ibid* **24** (1970) 1298-1301.
237. J. A. GIORDMAINE and R. C. MILLER, *ibid* **14** (1965) 973-976; P. L. GORDON, S. E. SCHWARZ, C. V. SHANK, and O. R. WOOD, *Appl. Phys. Lett.* **14** (1969) 235-237.
238. A. G. AKHMANOV, S. A. AKHMANOV, R. V. KHOKHLOV, A. J. KOVRIGIN, A. S. PISKARSKOS, and A. P. SUKHORUKOV, *IEEE J. Quantum Electr.* **QE-4** (1968) 828-831.
239. G. D. BOYD and A. ASHKIN, *Phys. Rev.* **146** (1966) 187-198; J. E. MIDWINTER, *IEEEJ. Quantum Electr.* **QE-4** (1968) 716-720; M. K. OSHMAN and S. E. HARRIS, *ibid* (1968) 491-502; E. O. AMMANN, M. K. OSHMAN, J. D. FOSTER, and J. M. YARBOROUGH, *Appl. Phys. Lett.* **15** (1969) 131-133; E. O. AMMANN, J. M. YARBOROUGH, M. K. OSHMAN, and P. C. MONTGOMERY, *ibid* **16** (1970) 309-312.
240. P. N. BUTCHER, E. LOUDON, and T. P. MCLEAN, *Proc. Phys. Soc.* **85** (1965) 565-581.
241. C. H. HENRY and C. G. B. GARRETT, *Phys. Rev.* **171** (1968) 1058-1064; C. Y. SHE, *Phys. Rev.* **176** (1968) 461-467.

242. T. G. GIALLORENZI and C. L. TANG, *Phys. Rev.* **166** (1968) 225-233; *ibid* **184** (1969) 353-355; C. L. TANG, *ibid* **182** (1969) 367-374.
243. D. MAGDE and H. MAHR, *ibid* **171** (1968) 393-398; D. A. KLEINMAN, *ibid* **174** (1968) 1027-1041.
244. H. CLAUSEN, *Acta Phys. Austriaca* **22** (1966) 311-324; J. H. EBERLY and W. M. FRANK, *Nuovo Cimento* **41** (1966) 113-122.
245. R. L. CARMAN, R. Y. CHIAO, and P. L. KELLEY, *Phys. Rev. Lett.* **17** (1966) 1281-1283; A. A. GRINBERG, S. M. RYBKIN, J. M. FISHMAN, and J. D. JAROSHETSKIY, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **6** (1967) 490-493; *ibid* **7** (1968) 324-327; D. L. WEINBERG, *Appl. Phys. Lett.* **14** (1969) 32-34; J. G. MEADORS, W. T. KAVAGE, and E. K. DAMON, *ibid* **14** (1969) 360-361; YU. M. KIRYN, S. G. RAYTYAN, A. E. SEMENOV, and B. M. CHERNOBOROD, *Zh. Eksperim. i Teor. Fiz. Pisma v Redaktsiyu* **11** (1970) 340-342.
246. D. N. KLYSHKO and N. T. NAZAROVA, *Zh. Eksperim. i Teor. Fiz.* **58** (1970) 878-886.
247. N. BLOEMBERGEN and Y. R. SHEN, *Phys. Rev.* **133** (1964) A37-49.
248. S. KIELICH, *Acta Physica Polonica* **30** (1966) 393-414.
249. S. CARUSOTTO, G. FORNACA, and E. POLACCO, *Phys. Rev.* **165** (1968) 1391-1398.
250. R. W. HELLWARTH, *Phys. Rev.* **152** (1966) 156-165; *ibid* **163** (1967) 205.
251. Y. R. SHEN and Y. J. SHAHAM, *Phys. Rev.* **163** (1967) 224-232.
252. M. TAKATSUJI, *ibid* **165** (1968) 171-177; J. HANUS, *ibid* **178** (1969) 420-428.
253. S. KIELICH, *J. Physique* **29** (1968) 619-630; *Chem. Phys. Lett.* **2** (1968) 112-116.
254. R. G. BREWER, J. R. LIFSITZ, E. GARMIRE, R. Y. CHIAO, and C. H. TOWNES, *Phys. Rev.* **166** (1968) 326-331.
255. S. KIELICH, *Acta Phys. Polonica* **34** (1968) 1093-1104; *J. Colloid Interface Sci.* **33** (1970) 142-149.
256. R. W. HELLWARTH, International School of Physics "E. Fermi" Course 42, 1967. Edited by R. J. Glauber (Academic Press, New York, 1968) 563-573; *J. Chem. Phys.* **52** (1970) 2128-2138.
257. M. TAKATSUJI, *Phys. Rev.* **155** (1967) 980-986; P. W. ATKINS and L. D. BARRON, *Proc. Roy. Soc.* A **304** (1968) 303-317; *ibid* A **306** (1968) 119-134; R. PECORA, *J. Chem. Phys.* **50** (1969) 2650-2566.
258. S. A. AKHMANOV and V. I. ZHARIKOV, *Zh. Eksperim. i Teor. Fiz.* **6** (1967) 644-648; A. M. MAKSUSHENKO and O. V. STOLBOVA, *Optika i Spektroskopia* **28** (1970) 600-601.
259. L. MANDEL and E. WOLF, *Rev. Mod. Phys.* **37** (1965) 231-287.
260. J. DUCUING and N. BLOEMBERGEN, *Phys. Rev.* **133** (1964) A 1493-1502.
261. S. A. AKHMANOV, A. I. KOVRIGIN, A. S. CHIRKIN, and O. N. CHUNAYEV, *Zh. Eksperim. i Teor. Fiz.* **50** (1966) 829-843; S. A. AKHMANOV, A. S. CHIRKIN, and V. G. TUNKIN, *Opto-electronics* **1** (1969) 196-204; F. DAVISON, J. KLEBBA, C. LAURENCE, and F. TITTEL, *Appl. Phys. Lett.* **17** (1970) 117-120.
262. P. N. BUTCHER and N. R. OGG, *Proc. Phys. Soc.* **86** (1965) 699-708.
263. S. A. AKHMANOV and A. S. CHIRKIN, *Radiotekhnika i Elektronika* **11** (1966) 1915-1926; S. A. AKHMANOV, A. P. SUKHORUKOV, and R. V. KHOKHLOV, *Zh. Eksperim. i Teor. Fiz.* **50** (1966) 474-486.
264. S. A. AKHMANOV, V. G. DMITRIYEV, and V. P. MODENOV, *Radiotekhnika i Elektronika* **4** (1965) 649-657.
265. R. ASBY, *Phys. Rev.* **187** (1969) 1062-1076; *Opto-electronics* **1** (1969) 165-171.
266. A. A. GRÜTTER, H. P. WEBER, and R. DÄNDLIKER, *Phys. Rev.* **185** (1969) 629-643.
267. R. FISCHER, *Ann. Physik* **21** (1968) 144-166.
268. B. G. HUTH and Y. C. KIANG, *J. Appl. Phys.* **40** (1969) 4976-4977; M. W. MCGEOCH and R. C. SMITH, *IEEE J. Quantum Electr.* **QE-6** (1970) 203-205; R. G. SMITH, *ibid* (1970) 215-223.
269. P. CHMELA, *Optik*, **28**, (1968) 346-359; *ibid* **29** (1969) 561-569.
270. E. MATHIEU, *Z. angew. Math. und Phys.* **20** (1969) 433-439.
271. G. S. AGARWAL, *Optics Communications* **1** (1969) 132-134; F. LEBON, *Phys. Stat. Sol.* **41** (1970) 297-307.
272. R. GOYAL and H. PRAKASH, *Nuovo Cimento* B **63** (1969) 185-191; Y. UEDA and K. SHIMODA, *J. Phys. Soc. Japan* **28** (1970) 196-204.
273. W. H. GLENN, *IEEE J. Quantum Electr.* **5** (1969) 284-290; J. E. MURRAY and S. E. HARRIS, *J. Appl. Phys.* **41** (1970) 609-000.
274. J. E. GEUSIC, H. J. LEVINSTEIN, S. SINGH, R. G. SMITH, and L. G. VAN UITERT, *Appl. Phys. Lett.* **12** (1968) 306-310; O. D. VOLOSOV and M. J. RASHCHEKTAEVA, *Optika i Spektroskopia* **28** (1970) 105-111.
275. M. TAKATSUJI, *Japanese J. Appl. Phys.* **5** (1966) 389-400; D. A. KLEINMAN and G. D. BOYD, *J. Appl. Phys.* **40** (1969) 546-566.
276. F. DE MARTINI, *Phys. Lett.* A **30** (1969) 319-320; J. P. COFFINET and F. DE MARTINI, *Phys. Rev. Lett.* **22** (1969) 60-62.
277. Y. KLINGER and F. ARAMS, *Proc. IEEE* **57** (1969) 1797-1798.
278. N. BLOEMBERGEN and Y. R. SHEN, *Phys. Rev.* **141** (1966) 298-305.

279. S. S. JHA, *Phys. Rev.* **150** (1966) 413-418.
280. J. B. KELLER and M. H. MILLMAN, *Phys. Rev.* **181** (1969) 1730-1747; O. G. BOKOV, L. SH. SHEKHTER, and M. V. YUDOVICH, *Optika i Spektroskopia* **28** (1970) 228-231.
281. H. R. REISS, *Phys. Rev.* A **1** (1970) 803-818.
282. R. L. FULTON, *J. Chem. Phys.* **50** (1969) 3355-3377.
283. G. V. KRIVOSHCHEKOV, S. V. KRUGLOV, S. T. MARENNIKOV, and V. N. POLIVANOV, *Zh. Eksperim. i Teor. Fiz. Pišma v Redaktsiyu* **7** (1968) 84-87.
284. D. J. BRADLEY, A. J. F. DURRANT, G. M. GALE, M. MOORE, and P. D. SMITH, *IEEE J. Quantum Electr.* **QE-4** (1968) 707-711; J. KATZENSTEIN, G. MAGYAR and A. C. SELDEN, *Opto-electronics* **1** (1969) 13-19; A. M. BONCH-BRUEVICH, N. N. ZATSEPINA, T. K. RAZUMOVA, G. M. RUBANOVA, I. F. TUPITSYN, and V. N. SHUVALOVA, *Optika i Spektroskopia* **28** (1970) 100-104.
285. H. W. SCHRÖTTER, *Naturwissenschaften* **54** (1967) 607-612; A. F. HAUGHT, *Ann. Rev. Phys. Chem.* **19** (1968) 343-370; W. J. JONES, *Quarterly Reviews* **23** (1969) 73-97; D. J. BRADLEY, *Phys. Bull.* **21** (1970) 116-122.
286. S. KIELICH, *J. Chem. Phys.* **46** (1967) 4090-4099; *Acta Phys. Polonica* **33** (1968) 65-79.
287. H. B. LEVINE and G. BIRNBAUM, *Phys. Rev. Lett.* **20** (1968) 439-441; J. P. MCTAGUE and G. BIRNBAUM, *Phys. Rev. Lett.* **21** (1968) 661-664.
288. M. THIBEAU, B. OKSENGORN, and B. VODAR, *J. Phys. Paris* **29** (1968) 287-296.
289. J. R. LALANNE, *J. Physique Paris* **30** (1969) 643-653.
290. J. P. MCTAGUE, P. A. FLEURY, and D. B. DU PRÉ, *Phys. Rev.* **188** (1969) 303-308.