NONLINEAR OPTICAL AND ELECTRO-OPTICAL PROPERTIES OF DIELECTRICS AND FERROELECTRICS†

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The article is intended as a review of significant theoretical and experimental achievements in the study of the optical and electro-optical properties of dielectrics and ferroelectrics. New experimental methods using laser technique and permitting the study of induced and natural nonlinear properties of dielectrics are described. Stress is laid on measurements of laser beam induced optical birefringence and nonlinear light scattering processes, optical rectification, second and third harmonic generation of laser beams, mixing of light wave frequencies, and d.c. harmonic field induced second generation. Tables listing the available data on nonlinear optical polarizabilities of atoms and molecules and nonlinear optical susceptibilities of ferroelectric crystals are included. Particular attention is given to facts providing new insight into the statistical-molecular structure of dielectrics, the electron, ionic and domain structure of ferroelectrics, and phase transitions. Various uses of ferroelectric crystals in nonlinear optical systems, modulators of coherent light, multipliers and frequency mixers, parametric optical generators and many other opto-electronic appliances are discussed.

1. INTRODUCTION

Since the times of the classical work of Mosotti,[1] Clausius,[2] Lorentz[3] and Debye,[4] the physics of dielectrics has grown to a vast, independent discipline, now represented by a considerable number of monographs on the electric properties of dielectrics[5–11] and their optical and electro-optical properties.[12–18] In the isotropic class, not only gaseous and liquid atomic and molecular dielectrics but also macromolecular ones[19] have been studied intensely. Nor has there been a lack of studies devoted to dielectric crystals,[20–26] in particular piezoelectric[27,28] and ferroelectric crystals.[29–31]

The 1960's witnessed the coming of cw and pulsed lasers, sources of collimated monochromatic light beams, coherent in time and space, conveying energy fluxes of enormous density.[32] These extraordinary properties of laser light have since permitted the experimental detection of numerous nonlinear optical processes in dielectrics, especially in ferroelectric crystals. Thus, out of the foundations of classical (linear) optics,[33] there

has very rapidly grown a new subject of nonlinear optics[34–37] providing novel methods for the investigation of optical and electro-optical nonlinear properties of dielectrics and ferroelectrics.

The study of liquid dielectrics in strong electric fields (e.g. the Kerr effect and dielectric saturation) yields information regarding not only the nonlinear electric properties of the constitutive atoms and molecules[38] but moreover regarding weak and strong molecular correlations.[39] The nonlinear optical properties of atoms and molecules are at present determined from measurements of optical Kerr effect[40] and second-harmonic scattering[41,42] as well as from optical harmonics generation.[43–46] In these studies, an important rôle belongs to the relation between the macroscopic symmetry of the electrically or optically polarized (but naturally isotropic) body, and the point group symmetry of its individual molecules.[47,48] By resorting to second and third harmonic generation of laser light, it has been possible to determine the nonlinear susceptibilities of numerous ferro- and piezo-electric crystals as well as other materials.[46,50]

With regard to the nonlinear properties of dielectrics and ferroelectrics, great progress has been achieved on the theoretical side and even more on the experimental side owing to new, ingenious measuring methods of high accuracy and

sensitivity. This was largely due to rapid developments in quantum electronics and laser technique which, in the form of ready-made automatized opto–electronic devices, have become the standard equipment of most physical, physico-chemical and engineering laboratories. We now have the possibility of studying with relative ease the electronic, atomic, molecular and ionic properties of matter at oscillation frequencies ranging from those of ordinary supplies of a.c. currents and those used for radar and radio waves, through microwaves, the far infrared, infrared, visible, ultraviolet, and even up to X-rays.

This report is intended as a concise review of the most significant studies of the nonlinear optical and electro–optical properties of naturally isotropic and anisotropic dielectrics and in particular those performed during the last 10 years.

2. LINEAR AND NONLINEAR PROPERTIES OF DIELECTRICS

2.1. Electrical properties

A dielectric in an electric field of strength E becomes electrically polarized. The polarization vector, P, which is a well-defined function (or, more appropriately, a functional) of E:

$$P = f(E). \qquad (1)$$

The explicit form of the functional f is specific to the medium, its structure and thermodynamical state, and depends on the field strength E.

As long as E is not very large, it is a good approximation to take the electric polarization P as linear in E. For an arbitrary body, one can write the i-component of the electric polarization vector in the form:

$$P_i(E) = P_{si} + \chi_{ij}E_j + ..., \qquad (2)$$

where P_s is the polarization vector in the absence of an external field (at $E = 0$) in bodies exhibiting spontaneous polarization (ferroelectrics), and χ_{ij} is a symmetric tensor of rank 2 defining the linear electric susceptibility of an anisotropic body. Equation (2) has been written in accordance with the repeated index summation convention. The indices i, j run through the values x, y, z in the directions of the Cartesian axes of the laboratory system.

Table I contains the elements of the linear electric susceptibility tensor χ_{ij} for the various crystallographical systems. For common, isotropic dielectrics, Eq. (2) becomes:

$$P(E) = \chi E = \frac{\varepsilon - 1}{4\pi} E, \qquad (2a)$$

where χ is the scalar electric susceptibility and ε the electric permittivity.

All gases and liquids exhibit linear electron polarizability following a Clausius–Mosotti law; polar substances exhibit, in addition, orientational

TABLE I

Elements of the symmetric tensor χ_{ij} of linear susceptibility for all crystallographic systems

Optical classification	Crystallographic system	Elements of the nonlinear susceptibility tensor		
		Number of mutually independent tensor elements	Non-zero tensor elements	
Biaxial crystals	Triclinic	6	χ_{xx} χ_{xy} χ_{xz}	
			χ_{yx} χ_{yy} χ_{yz}	
			χ_{zx} χ_{zy} χ_{zz}	
	Monoclinic	4	χ_{xx} 0 χ_{xz}	
		4	0 χ_{yy} 0	
			χ_{zx} 0 χ_{zz}	
	Orthorhombic	3	χ_{xx} 0 0	
			0 χ_{yy} 0	
			0 0 χ_{zz}	
Uniaxial crystals	Tetragonal	2	χ_{xx} 0 0	
	Trigonal		0 χ_{xx} 0	
	Hexagonal		0 0 χ_{zz}	
Anaxial/optically isotropic/crystals	Cubic	1	χ_{xx} 0 0	
	Isotropic		0 χ_{xx} 0	
	Medium		0 0 χ_{xx}	

polarization of their electric dipoles following a Debye–Langevin law, as well as co-operative dipolar[51] or, more generally, multipolar[52] polarizability. The electric permittivity of nondipolar substances is small, but that of dipolar substances attains values as large as 100. In molecular liquids, the changes in electric permittivity caused by a strong electric field are insignificant and depend more or less quadratically on the field strength.[39,53] In macromolecular solutions, complete dielectric saturation is observed experimentally.[54,55]

Ferroelectrics are a special case of pyroelectrics, i.e. of spontaneously polarized crystals. Below the Curie temperature, they exhibit spontaneous polarization, and their electric permittivity becomes a maximum at the Curie point (Table II). Above the Curie point, i.e. in the para-electric state, the temperature-dependence of electric permittivity in ferroelectrics obeys the well-known Curie–Weiss law. The emergence of a ferroelectric state (often marked by differently oriented ferroelectric domains) in dielectrics below the Curie point is due simultaneously to near-range (exchange) and far-range (dipole–dipole, ... interaction) forces. Ferroelectrics are strongly nonlinear materials. In the ferroelectric phase, the nonlinearity of orientational domain polarization considerably exceeds the nonlinearity of the polarization induced by the external electric field. In the paraelectric phase, the nonlinear properties are due entirely to induced polarization. In ferroelectrics subjected to the action of an a.c. field, if the a.c. frequency is sufficiently high so that orientational polarization is unable to follow the field, nonlinearity of distortional electron polarization becomes predominant.

2.2. Optical properties

Assume an electromagnetic wave, harmonically depending on the time t and spatial coordinates r,

$$E(r, t) = E(\omega, k) \exp\{i(k \cdot r - \omega t)\}, \qquad (3)$$

with circular frequency ω and propagation vector k, as incident on a dielectric.

By analogy to (2), the electric vector (3) of a light wave of low intensity will produce in the medium the following linear polarization, analyzed at frequency ω:

$$P_i^L(\omega, k) = \chi_{ij}(-\omega, \omega; -k, k) E_j(\omega, k), \qquad (4)$$

The linear susceptibility tensor elements χ_{ij} are given in Table I for all crystallographical classes. The dependence of χ_{ij} on the frequency ω defines time-dispersion (frequency-dispersion), whereas the dependence of χ_{ij} on the wave vector k defines spatial dispersion (i.e. natural optical activity). In particular, for isotropic bodies, and crystals belonging to the cubic system, one has in the absence of spatial dispersion,

$$\chi_{ij}(-\omega, \omega) = \chi(-\omega, \omega)\delta_{ij}, \qquad (5)$$

where δ_{ij} is the symmetric Kronecker unit tensor. The scalar linear susceptibility χ at frequency ω

TABLE II

Electric and electro–optical properties of some important ferroelectric and antiferroelectric crystals at room temperature. ε_{ij}^T and r_{ijk}^T are values at constant elastic stress T. ε_{ij}^S and r_{ijk}^S are values at constant elastic strain S.

Crystal	Class symmetry	Curie temperature T_c (in °C)	Numerical values of electric permittivity tensor elements ε_{ij}	Numerical values of electro–optic tensor elements r_{ijk} (in 10^{-10} cm/V)		
$(NH_2CH_2COOH)_3H_2SO_4$	2	49	$\varepsilon_{11} = 10,\quad \varepsilon_{22} = 70,$ $\varepsilon_{33} = 8$			
$Ba_2NaNb_5O_{15}$	mm2	560	$\varepsilon_{11} = 246,\quad \varepsilon_{22} = 242,$ $\varepsilon_{33} = 51$			
$BaTiO_3$	4 mm	120	$\varepsilon_{11}^T = 5000,\ \varepsilon_{11}^S = 2000,$ $\varepsilon_{33}^T = 200,\ \varepsilon_{33}^S = 100,$	$r_{223}^T = 1640,$ $r_{223}^S = 820,$	$r_{113}^S = 8$ $r_{333}^S = 28$	
$K_3Li_2Nb_5O_{15}$	4 mm	420	$\varepsilon_{11} = 309,\quad \varepsilon_{33} = 100,$			
KH_2PO_4 (KDP)	$\bar{4}2$ m	-158	$\varepsilon_{11} = 45,\quad \varepsilon_{33} = 21,$	$r_{123}^T = 10.3,$	$r_{321}^T = 8.8,$	$r_{123}^S = 9.7$
$NH_4H_2PO_4$ (ADP)	$\bar{4}2$ m	-125	$\varepsilon_{11} = 58,\quad \varepsilon_{33} = 14$	$r_{123}^T = 8.5,$	$r_{321}^T = 23.4,$	$r_{123}^S = 5.5$
KH_2AsO_4 (KDA)	$\bar{4}2$ m	-176	$\varepsilon_{11} = 54,\quad \varepsilon_{33} = 20,$	$r_{123}^T = 10.9,$	$r_{321}^T = 12.5$	
RbH_2PO_4 (RDA)	$\bar{4}2$ m	-126	$\varepsilon_{11} = 48,\quad \varepsilon_{33} = 24$			
$LiNbO_3$	3 m	1200	$\varepsilon_{11}^T = 84,\quad \varepsilon_{11}^S = 43,$ $\varepsilon_{33}^T = 30,\quad \varepsilon_{33}^S = 28$	$r_{222}^T = 3.3-6.7, r_{113}^S = 8.6,$ $r_{223}^T = 32,\quad r_{223}^S = 28,$	$r_{222}^S = 3.4$ $r_{333}^S = 30.8$	
$LiTaO_3$	3 m	665	$\varepsilon_{11}^T = 51,\quad \varepsilon_{11}^S = 41,$ $\varepsilon_{33}^T = 45,\quad \varepsilon_{33}^S = 43$	$r_{113}^T = 7,\quad r_{333}^S = 30,$ $r_{223}^S = 20,\quad r_{222}^S = 1$		

and the light refractive index n are related in the well-known manner:

$$n^2 - 1 = 4\pi\chi(-\omega, \omega), \qquad (6)$$

with:

$$P_L(\omega, k) = \chi^\omega E(\omega, k) = \frac{n^2 - 1}{4\pi} E(\omega, k). \quad (4a)$$

In uniaxial crystals (symmetric around their z-axis, the optical axis of the crystal), the susceptibility tensor χ_{ij} presents two mutually independent elements: $\chi_{xx} = \chi_{yy}$, and χ_{zz}, with two refractive indices: $n_e = n_\parallel$ (extraordinary) for light oscillations parallel to the optical axis, and $n_0 = n_\perp$ (ordinary) for oscillations perpendicular thereto. We thus have, by (6), (for light propagation perpendicular to the optical z-axis),

$$n_\parallel^2 - n^2 = \frac{8\pi}{3}(\chi_{zz}^\omega - \chi_{xx}^\omega),$$

$$n_\perp^2 - n^2 = -\frac{4\pi}{3}(\chi_{zz}^\omega - \chi_{xx}^\omega), \qquad (7)$$

where $n^2 = (n_\parallel^2 + 2n_\perp^2)/3$ is the average refractive index. Uniaxial crystals are birefringent with respect to light with their natural optical birefringeence defined, in approximation, by the formula:

$$n_\parallel - n_\perp \approx \frac{2\pi}{n}(\chi_{zz}^\omega - \chi_{xx}^\omega). \qquad (7a)$$

In isotropic bodies in the absence of external forces, the refractive index n, analysed (probed) by means of a weak light beam, is a constant specific to the substance at a given wavelength. This results from the linear relation (4a)—a consequence of Lorentz's electron theory, where the atom is considered as a harmonic oscillator; the same result is obtained in the first approximation of quantum-mechanical perturbation calculus.[16] In the present linear approximation, the solution of Maxwell's equations fulfil the principle of superposition, according to which electromagnetic waves propagating simultaneously in a medium do so independently of one another, and thus undistortedly. Hence, in a linear optically transparent dielectric, the refractive index n does not vary in space and does not depend on the wave intensity as long as this intensity is insignificant and no external fields act on the body. In the above stated conditions, all optical laws and phenomena are of a linear nature and lie within the scope of linear optics.

In order that nonlinear polarization can become apparent, one must have a sufficiently large ratio of field strengths of the electric field E_ω of the light wave and of the internal field E_e acting on the optical electrons within the medium. The electric field of the nucleus acting on the electron of the hydrogen atom (the force binding the electron to the nucleus) amounts to $E_e \approx 10^9$ V/cm. In dense matter, these fields are weaker than in isolated atoms, and amount to $E_e \approx 10^8$ V/cm in crystals and to 10^7 V/cm in semiconductors. The light emitted by usual (thermal) sources and low power gas lasers conveys power in the range of $I = (1 - 10^2)$W/cm^2 whence its electric field strength can be evaluated at $E_\omega = (1 - 10^2)$ V/cm. Fields of this order of magnitude are weak in comparison with the strong internal fields E_e and suffice only for inducing linear polarization in matter. The high-power solid-state lasers now available emit light beams of intensity $I \approx (10^8 - 10^{12})$ W/cm^2, carrying electric fields of strength $E_\omega \approx (10^5 - 10^8)$ V/cm. Such fields are comparable in strength to the internal electric field E_e and thus induce significant nonlinear optical polarization. In electric fields of such strength, by the classical theory of Voigt[14], the harmonic oscillations of the electrons undergo distortion and the atoms become anisotropic oscillators, performing anharmonic (i.e. nonlinear) oscillations.

Thus, when a transparent medium is traversed by very intense light, its refractive index and electric permittivity depend on the light intensity. The effect, in conformity with theoretical predictions,[39, 57] has been observed experimentally even in liquids when applying giant pulses from ruby[58, 59] and neodymium[60] lasers. Optically induced variations in refractive index are measured in the form of the optical Kerr effect, the discovery of which is due to Mayer,[58] and in that of rotation of the polarization plane.[59] These methods permit the direct determination of the nonlinear polarizabilities of atoms and molecules.[40]

The dependence of the refractive index on light intensity moreover leads to self-focusing and self-trapping of laser light in various dielectric media. However, we shall refrain from considering these fascinating optical phenonena here, though they too provide information on the nonlinear optical polarizabilities of atoms and molecules[61] but refer the Reader to the appropriate review articles.[62-64]

An electromagnetic wave of high electric field strength, inducing optical nonlinearity in a medium, at the same time affects the process of its

own propagation. By Fourier analysis, an electromagnetic wave, distorted by the presence of optical nonlinearity in the medium, will contain, in addition to the fundamental frequency ω, a second-harmonic of double frequency 2ω, a third-harmonic of triple frequency 3ω, and so forth.[49]

Franken and his co-workers[65] observed that when red light of wavelength $\lambda_\omega = 6943$ Å from a ruby laser propagated in a quartz crystal, a harmonic radiation component arose with a wavelength twice that of the incident beam, i.e. ultraviolet light of $\lambda_{2\omega} = 3472$ Å (see Figure 1).
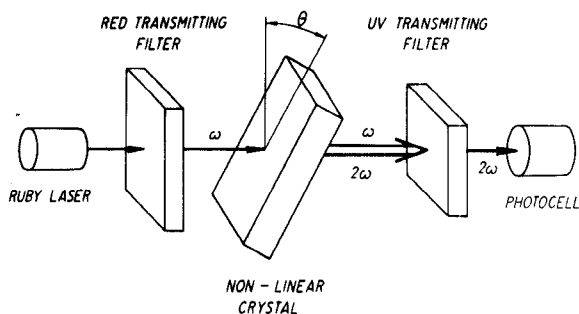

FIGURE 1 Diagram of set-up for second-harmonic generation in nonlinear crystals (e.g. quartz). The path traversed by the beam within the crystal plate is modified by varying the latter's inclination with respect to the propagation direction of the laser beam of frequency ω. The active thickness of the crystal is chosen in a manner to fulfil the conditions for proper phase matching between the fundamental wave ω and second-harmonic wave 2ω. The second-harmonic beam produced in the crystal is observed on transmission through a filter totally absorbing the fundamental (red) beam, and its intensity is recorded by means of the monochromator combined with the photomultiplier.

Quartz is a crystal without a centre of symmetry. Owing to this, the wave of frequency ω generates therein a wave of frequency 2ω which we term the second optical harmonic. The discovery of second harmonic generation of laser light has played an important rôle in the investigation of nonlinear properties of piezo- and ferro-electric crystals in the range of optical frequencies. The properties specific to ferro-electric crystals cause them to occupy a very important place among optically nonlinear materials. The numerous uses of ferro-electrics in the rapidly expanding nonlinear optics have encouraged research on the physics of ferroelectrics, especially with regard to the growing of new crystals of this type.

3. BODIES WITHOUT A CENTRE OF SYMMETRY

When matter is subjected to intense electric fields, e.g. to the light from a giant laser, the linear relation (4) is no longer sufficient and one has to resort to higher, nonlinear approximations. As long as nonlinearity is not excessive, the electric polarization can be expanded in a power series:

$$P(r, t) = P^L + P^{(2)} + P^{(3)} + \ldots, \qquad (8)$$

where $P^L = P^{(1)}$ is the first-order polarization, which depends linearly on the electric field strength in accordance with Eq. (4) and which is present in all matter.

Polarization of the second order $P^{(2)}$ depends on the square of the electric field strength (3). If in general two electromagnetic waves with the frequencies ω_1 and ω_2 and wave vectors k_1 and k_2 are incident on the medium, the induced second-order electric polarization is:

$$P_i^{(2)}(\omega_3, k_3) = \chi_{ijk}^{\omega_3, k_3} E_j(\omega_1, k_1) E_k(\omega_2, k_2), \quad (9)$$

where the third-rank tensor $\chi_{ijk}^{\omega_3, k_3} = x_{ijk}(-\omega_3, \omega_1, \omega_2; -k_3, k_1, k_2)$ defines the nonlinear susceptibility of order 2.

By Eq. (9), interaction of two waves in a quadratically nonlinear medium gives rise to a third wave, of circular frequency

$$\omega_3 = \omega_1 + \omega_2 \qquad (10)$$

and wave vector

$$k_3 = k_1 + k_2 + \Delta k. \qquad (11)$$

Equations (10) and (11) define, respectively, the conditions for space and time synchronization; in quantal interpretation, Eq. (10) is the energy conservation principle, Eq. (11) the momentum conservation principle for the photons, and Δk a slight non-conservative deviation[35].

In centrosymmetric optically inactive media (i.e. these which are characterized by a lack of spatial dispersion) all the elements of the tensor χ_{ijk} vanish. As a consequence, second-order polarization (9) occurs only in bodies without a centre of symmetry as well as in cubic and isotropic optically active bodies.[66] If $\omega_1 = \omega_2 = \omega$, the nonlinear susceptibility tensor is symmetric in the pair of indices j and k, thus $\chi_{ijk} = \chi_{ikj}$, and 18 of its 27 non-zero elements are mutually independent. In an optically transparent medium (far from electron dispersion and absorption) one has symmetry in

TABLE III

Elements of the symmetric tensor χ_{ijk} of nonlinear susceptibility

Crystallographic system	Class symmetry	Elements of the nonlinear susceptibility tensor χ_{ijk}		
		Number of non-zero elements	Number of independent elements	Elements of χ_{ijk} are denoted only by their subscripts $i, j, k = x, y, z$
Triclinic	1	27	10	$xxx, yyy, zzz, xyy = yxy = yyx, xzz = zxz = zzx,$ $xxz = xzx = zxx, xxy = xyx = yxx, yzz = zyz = zzy,$ $yyz = yzy = zyy, xyz = xzy = yxz = yzx = zxy = zyx.$
	$\bar{1}$	0	0	
Monoclinic	2	13	4	$zzz, zxx = xzx = xxz, zyy = yzy = yyz,$ $xyz = xzy = yxz = yzx = zxy = zyx.$
	m	14	6	$xxx, yyy, xyy = yxy = yyx.$ $yxx = xyx = xxy, xzz = zxz = zxx, yzz = zyz = zzy.$
	2/m	0	0	
Orthorhombic	222	6	1	$xyz = xzy = yxz = yzx = zyx = zyx.$
	mm2	7	3	$zzz, zxx = xzx = xxz, zyy = yzy = yyz.$
	mmm	0	0	
Tetragonal	4	7	2	$zzz, zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{4}$	12	2	$zxx = xzx = xxz = -zyy = -yzy = -yyz,$ $xyz = xzy = yxz = yzx = zxy = zyx.$
	4/m	0	0	
	422	0	0	
	4 mm	7	2	$zzz, zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{4}2 m$	6	1	$xyz = xzy = yxz = yzx = zxy = zyx.$
	4/mmm	0	0	
Trigonal	3	15	4	$zzz, xxx = -xyy = -yxy = -yyx,$ $yyy = -yxx = -xyx = -xxy,$ $zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{3}$	0	0	
	32	4	1	$xxx = -xyy = -yxy = -yyx.$
	3 m	11	3	$zzz, yyy = -yxx = -xyx = -xxy,$ $zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{3} m$	0	0	
Hexagonal	6	7	2	$zzz, zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{6}$	8	2	$xxx = -xyy = -yxy = -yyx,$ $yyy = -yxx = -xyx = -xxy.$
	6/m	0	0	
	622	0	0	
	6 mm	7	2	$zzz, zxx = xzx = xxz = zyy = yzy = yyz.$
	$\bar{6} m2$	4	1	$yyy = -yxx = -xyx = -xxy.$
	6/mmm	0	0	
Cubic	23	6	1	$xyz = xzy = yxz = yzx = zxy = zyx.$
	m3	0	0	
	432	0	0	
	$\bar{4}3 m$	6	1	$xyz = xzy = yxz = yzx = zxy = zyx.$
	m3m	0	0	
Axially-symmetric body		7	2	$zzz, zxx = xzx = xxz = zyy = yzy = yyz.$
Isotropic body		0	0	

all indices,[67] whence the totally symmetric tensor χ_{ijk} has 10 independent elements. A further reduction in number of non-zero elements and independent elements of the symmetric tensor χ_{ijk} depends on the crystallographical symmetry of the body (Table III).

3.1. Linear electro-optical effect

On putting $\omega_1 = \omega$, $k_1 = k$ and $\omega_2 = k_2 = 0$ in Eq. (9), the second-order polarization:

$$P_i^{(2)}(\omega, k) = \chi_{ijk}(-\omega, \omega, 0, k) E_j(\omega, k) E_k(0), \qquad (12)$$

defines the electro–optical process referred to as the Pockels effect:

$$\Delta\varepsilon_{ij}^{\omega}(E) = 4\pi\chi_{ijk}(-\omega, \omega, 0, k)E_k(0). \qquad (13)$$

Above

$$\Delta\varepsilon_{ij}^{\omega}(E) = \varepsilon_{ij}^{\omega}(E) - \varepsilon_{ij}^{\omega}(0). \qquad (13a)$$

defines the change in electric permittivity tensor due to a d.c. electric field, where

$$\varepsilon_{ij}^{\omega}(0) = \delta_{ij} + 4\pi\chi_{ij}(-\omega, \omega) \qquad (13b)$$

is the electric permittivity tensor in the absence of an external electric field.

It is customary to describe the change in refractive indices under the influence of a d.c. electric field as the change in reciprocal electric permittivity tensor $\Delta\varepsilon_{ij}^{-1}$ or change in polarization tensor:

$$\Delta a_{ij} = r_{ijk}E_k(0), \qquad (14)$$

with the tensor r_{ijk} of rank 3 defining the linear electro–optical effect.

The Pockels effect has a long history, dating back to the work of Kerr in 1875 and to that of Roentgen, Kundt, and Pockels.[13] The linear electro–optical effect is observed in crystals not having a centre of symmetry and hence also in ferroelectrics. When studied in the ferroelectric phase in a strong electric field, it permits the observation of hysteresis and the determination of the coercive force. In the paraelectric phase, when a centre of symmetry is present and the crystal structure is cubic, neither the Pockels effect nor birefringence are apparent. Below the Curie point, the crystal exhibits strong optical birefringence and a linear electro–optical effect.

Of late, the study of the electro–optical properties of ferroelectrics has come to be of particular importance to the production of coherent light harmonics, the modulation of laser beams, parametric processes, etc.[68, 69] Recently, Di Domenbico and Wemple[70] have developed a microscopic theory of the electro–optical properties of ferroelectrics of the oxygen octahedron type, whereas Kaminow and Johnston[71] determined the relationship existing between Raman scattering yield and the electro–optical coefficients r_{ijk}.

3.2. Optical rectification

At $\omega_1 = -\omega_2 = \omega$ and $k_1 = -k_2 = k$, polarization of the second order yields:

$$P_i^{(2)}(0) = \chi_{ijk}(0, \omega, -\omega)E_j(\omega, k)E_k^*(\omega, k). \qquad (15)$$

This is referred to as the d.c. electric field effect, which is the production of a steady polarization in a medium by the action of an intense optical electric field.[72, 73] This optical rectification is the optical frequency analogue of 'detection' by electric rectification, which is of considerable practical importance at radio frequency. For media without spatial dispersion, Eq. (15) can be written as follows:

$$P_i^{(2)}(0) = 2\chi_{ijk}(0, \omega, -\omega)I_{jk}, \qquad (15a)$$

Here, we have introduced the second-rank non-symmetric tensor of incident light intensity:

$$I_{jk} = \tfrac{1}{2}E_j(\omega)E_k^*(\omega). \qquad (15b)$$

On inspection of Eq. (15a) one sees that a light beam of high intensity I is apt to polarize electrically a body without centre of symmetry.

The d.c. nonlinear polarization of Eq. (15) is in general accompanied by generation of the second harmonic, and has been observed by Bass and his co-workers[74] in the ferroelectric crystal KDP (KH_2PO_4, potassium dihydrogen phosphate). Ward[73] made direct absolute measurements of the optical-rectification tensor elements in KDP and in the antiferroelectric ADP ($NH_4H_2PO_4$, ammonium dihydrogen phosphate). He established the following relationships between the optical rectification tensor $\chi_{ijk}(0, \omega, -\omega)$ and the linear electro–optical effect tensor $\chi_{ijk}(-\omega, \omega, 0)$:

$$\chi_{ijk}(0, \omega, -\omega) + \chi_{ikj}(0, \omega, -\omega)$$
$$= \tfrac{1}{4}\{\chi_{kji}(-\omega, \omega, 0) + \chi_{jki}(-\omega, \omega, 0)\}.$$

For KDP crystal of symmetry $\bar{4}2m$, his measurements yielded for the optical-rectification tensor elements at 27 °C and $\lambda_\omega = 6943$ Å:[73]

$$\chi_{xyz}(0, \omega, -\omega) + \chi_{xzy}(0, \omega, -\omega)$$
$$= (1.32 \pm 0.18) \times 10^{-7} \text{ e.s.u.}$$

in good agreement with electro–optical measurements.[75]

3.3 Second-harmonic generation

Consider a medium without a centre of symmetry immersed in the electric field $E(\omega, k)$ of an electromagnetic wave oscillating at frequency ω and propagating in the direction k. According to the general equation (9) with $\omega_1 = \omega_2 = \omega$ and $k_1 = k_2 = k$, the component of electric polarization of order 2 now takes the form:

$$P_i^{(2)}(2\omega, 2k) = \chi_{ijk}(-2\omega, \omega, \omega)E_j(\omega, k)E_k(\omega, k), \qquad (16)$$

The time and space synchronization conditions (10) and (11) now become:

$$\omega_h = 2\omega, \tag{10a}$$

$$\Delta k = k_{2\omega} - 2k_\omega, \tag{11a}$$

They define the conditions for generation of the second harmonic of light in a nonlinear medium (above, k_ω and $k_{2\omega}$ are respectively wave vectors of the wave oscillating at frequency ω and the second-harmonic wave oscillating at 2ω).

The intensity of the second harmonic light produced in an optically transparent medium at the point r, is given by the expression:[49]

$$I(2\omega, r) \approx (\chi^{2\omega})^2 \left\{ \frac{\sin \frac{1}{2}\Delta kr}{\frac{1}{2}\Delta k} \right\}^2 I^2, \tag{17}$$

where $I = E(\omega)E^*(\omega)/2$ is the incident intensity and, by (11a):

$$\Delta k = \left(\frac{2\omega}{c}\right)(n_{2\omega} - n_\omega), \tag{11b}$$

with n_ω and $n_{2\omega}$ denoting, respectively, the refractive index for the fundamental and second-harmonic wave.

Formula (17) suggests at least 3 ways of augmenting the intensity of the second harmonic, namely:

(i) by applying giant laser pulses of high power I and focusing them into the nonlinear material producing the second harmonic,

(ii) by using strongly nonlinear materials with large values of second-order susceptibility $\chi^{2\omega}$,

(iii) by satisfying the condition of equality between the phase velocities of the fundamental and second-harmonic waves, i.e. by fulfilling the phase matching condition or index matching condition:[76]

$$\Delta k = \left(\frac{2\omega}{c}\right)(n_{2\omega} - n_\omega) = 0. \tag{11c}$$

The smaller the difference Δk, the larger is the phase coherence length:

$$l_s = \frac{\pi}{\Delta k} = \frac{\lambda_\omega}{4(n_{2\omega} - n_\omega)}, \tag{18}$$

and hence the longer is the segment (path) on which energy is transferred from the fundamental wave to the wave oscillating at the second harmonic frequency. At $\Delta k = 0$ (the matching condition when $n_\omega = n_{2\omega}$), the intensity of the second harmonic grows approximately as the square of the thickness

of the nonlinear medium. If the matching condition is not fulfilled ($\Delta k \neq 0$), the function of Δk in Eq. (17) varies periodically with the distance causing a periodicity in r of the second-harmonic intensity. In ideal conditions, the energy of the incident wave is almost totally converted into energy of the second harmonic, i.e. the conversion yield (efficiency) can theoretically attain a value of 100%. The efficiency of conversion is affected by divergence, imperfect monochromaticity, and polarization of the laser beam as well as by the quality length and orientation of the crystal.[77] In practice, conversion efficiencies amount to about 50%[78] and, in special conditions, can be enhanced to almost 100%.[79] By resorting to KDP and ADP crystals, ultraviolet $\lambda_{2\omega} = 2573$ Å has been produced in continuous second-harmonic generation of argon ion laser light of wavelength $\lambda_\omega = 5145$ Å.[79a] Geusic et al[79b] reported that a continuous $\lambda_{2\omega} = 5320$ Å solid-state source utilizing the nonlinear material $Ba_2NaNb_5O_{15}$ inside the cavity of a $\lambda_\omega = 10,640$ Å YAlG:Nd laser has generated 1.1 W of coherent green power.

The tensor elements χ_{ijk} listed in Table III make it possible to adapt Eq. (16) to various particular cases of crystallographical symmetry. Thus, for instance, in class mm2 we obtain the following result (for brevity, we omit the dependence on wave vectors):

$$P_x^{(2)}(2\omega) = 2\chi_{xxz}(-2\omega, \omega, \omega)E_x(\omega)E_z(\omega),$$

$$P_y^{(2)}(2\omega) = 2\chi_{yyz}(-2\omega, \omega, \omega)E_y(\omega)E_z(\omega),$$

$$P_z^{(2)}(2\omega) = \chi_{zxx}(-2\omega, \omega, \omega)E_x^2(\omega)$$
$$+ \chi_{zyy}(-2\omega, \omega, \omega)E_y^2(\omega) + \chi_{zzz}(-2\omega, \omega, \omega)E_z^2(\omega) \tag{16a}$$

With regard to the Kleinman symmetry conditions,[67] these five mutually independent components reduce to three:

$$\chi_{xxz} = \chi_{zxx}, \chi_{yyz} = \chi_{zyy} \text{ and } \chi_{zzz}.$$

For the classes 4, 4mm, 6 and 6mm we have but two mutually independent components: $\chi_{xxz} = \chi_{yyz}$ and χ_{zzz}. For the class $\bar{4}2m$, second-order polarization (16) has the following components:

$$P_x^{(2)}(2\omega) = 2\chi_{xyz}(-2\omega, \omega, \omega)E_y(\omega)E_z(\omega),$$

$$P_y^{(2)}(2\omega) = 2\chi_{xyz}(-2\omega, \omega, \omega)E_z(\omega)E_x(\omega),$$

$$P_z^{(2)}(2\omega) = 2\chi_{zxy}(-2\omega, \omega, \omega)E_x(\omega)E_y(\omega), \tag{16b}$$

and the two independent components occurring here reduce to a single one if Kleinman's condition

is fulfilled. In the last case $\chi_{xyz} = \chi_{zxy}$, and Eqs (16b) extend to the classes 222, 23, $\overline{4}$3m also.

Equations (16a) and (16b) are appropriate for those classes to which the majority of uniaxial ferroelectric and antiferroelectric crystals belong.

3.4 Nonlinear optical susceptibilities of ferroelectric crystals

Since the earliest experiments of Franken,[65] the second harmonic has been observed in numerous piezo- and ferro-electric crystals as well as in other nonlinear materials when using pulsed crystal lasers and semiconductor or gas lasers.[46] The nonlinear crystal should be available in the form of a single crystal and has to exhibit considerable asymmetricity of its properties, a high refractive index and strong optical birefringence, and transparency throughout a wide spectral range. However, when the growing of single crystals is not feasible or presents difficulties, the powder method[80] can be resorted to; it is simple and convenient, and permits rapid assays of the nonlinear optical properties of new materials[50] (see Figure 2).
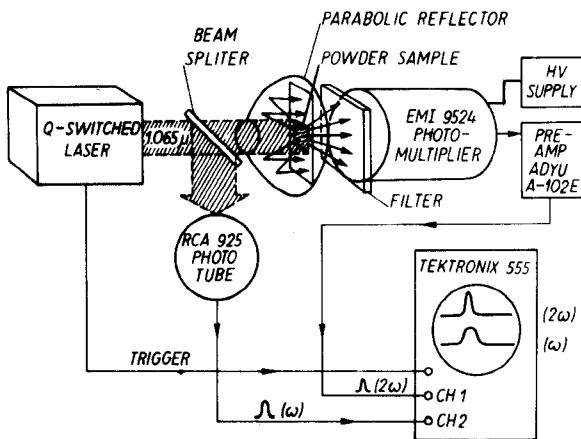

FIGURE 2 Kurtz and Perry's setup[80] for second harmonic generation in powders. The non-focused beam of an Nd:CaWO$_4$ or Nd:YAG Q-switched laser is incident on a thin (about 0.2 mm) powder layer of the crystal under investigation. The fundamental frequency beam is eliminated by a series of filters. The second harmonic is detected by a photomultiplier and made apparent on a cathode–oscilloscope screen. With the aim of enhancing second harmonic collection by the detector, a parabolic reflector with aperture transmitting the incident laser beam is placed between the laser and the sample.

Franken's experiment[65] on second-harmonic generation in quartz was repeated by Miller[81] in a version applying a crystal laser operating on neodymium-activated calcium tungstenate (CaWO$_4$: Nd^{+3}), which emits light at $\lambda_\omega = 10{,}582$ Å convenient for observing the second harmonic at wavelength $\lambda_{2\omega} = 5291$ Å which lies in the range of high sensitivity of the human eye. In the next stage of experiments, uniaxial ferroelectric crystals such as KDP and ADP,[82,83] BaTiO$_3$,[84] LiNbO$_3$ and LiTaO$_3$,[85] biaxial ones like TGS (triglycine sulphate, with the chemical formula (NH$_2$CH$_2$–COOH)$_3$ H$_2$SO$_4$)[86] as well as the ferroelastic-ferroelectric crystals β-Gd$_2$(MoO$_4$)$_3$ and β-Tb$_2$(MoO$_4$)$_3$[87] have been found to be highly effective in second-harmonic production. The method of second-harmonic generation has served for determining the nonlinear susceptibilities of many other ferroelectric crystals[88–94] listed in Table IV. Also, methods for the accurate determination of relative nonlinear susceptibilities[91] and of their sign[89] have been devised.

In recent years, techniques of ultra-short light pulses (of order 10^{-12} sec) have been developed and applied to second-harmonic production in KDP, ADP, LiNbO$_3$ and other crystals.[95] Moreover, the conditions for second-harmonic generation in ferroelectric crystals by concentrated beams have been studied in detail, as well as phase matching and generation yield conditions.[96] Of late, the ferroelectric crystal LiNbO$_3$ has been used for the measurement of photon correlation and resonance generation of second harmonic,[97a] and simultaneous mode-locking and quasi-CW SHG have been achieved in LiNbO$_3$ and Ba$_2$NaNb$_5$O$_{15}$ with a Nd^{3+}:YAG laser by electro–optical modulation of the nonlinear medium.[97b]

Although quantum-mechanical theories of nonlinear optical susceptibilities have long been available,[72,98] direct numerical calculations based on simple models and various approximations[99] have been carried out for but few ferroelectric crystals.[100] Calculations of nonlinear optical susceptibilities can be made in a simple way for piezo- and ferro-electric crystals by resorting to Miller's relation:[83]

$$\chi_{ijk}^{2\omega} = \chi_{ii}^{2\omega} \chi_{jj}^{\omega} \chi_{kk}^{\omega} \delta_{ijk}^{2\omega}, \qquad (19)$$

between the nonlinear susceptibility tensor elements $\chi_{ijk}^{2\omega}$ and the principal components of the linear susceptibilities $\chi_{ii}^{2\omega}$, χ_{jj}^{ω} and χ_{kk}^{ω} at second-harmonic frequency 2ω and fundamental frequency ω.

TABLE IV

Numerical values of elements of the nonlinear susceptibility tensor $\chi_{ijk}^{2\omega}$ for ferroelectric crystals, from second harmonic generation of light

Crystal	Class symmetry	T_c Curie point (in °C)	Values of light refractive indices	Laser wavelength (in Å)	Numerical values of tensor elements $\chi_{ijk}^{2\omega}$ (in 10^{-9} e.s.u.)	Reference
$Ba_2NaNb_5O_{15}$	mm2	560	$n_x = 2.71$ $n_y = 2.259$ $n_z = 2.260$	10,640	$\chi_{311}^{2\omega} = -42.0$ $\chi_{322}^{2\omega} = -49.6$ $\chi_{333}^{2\omega} = -50.5$	88, 89
$BaTiO_3$	4 mm	120	$n_0 = 2.338$ $n_e = 2.298$	10,582	$\chi_{311}^{2\omega} = -57$ $\chi_{333}^{2\omega} = -21$	83, 84, 89
$K_3Li_2Nb_5O_{15}$	4 mm	420	$n_0 = 2.208$ $n_e = 2.112$	10,640	$\chi_{311}^{2\omega} = 23.2$ $\chi_{333}^{2\omega} = 42.0$	90a
$PbTiO_3$	4 mm	492		10,640	$\chi_{311}^{2\omega} = \mp 12.8$ $\chi_{113}^{2\omega} = \mp 11.4$ $\chi_{333}^{2\omega} = \pm 2.6$	90b
KH_2PO_4/KDP/	$\bar{4}2$ m	-158	$n_0 = 1.502$ $n_e = 1.464$	10,640	$\chi_{123}^{2\omega} = 1.5$	50, 91
$NH_4H_2PO_4$/ADP/	$\bar{4}2$ m	-125	$n_0 = 1.504$ $n_0 = 1.467$	10,640 6943	$\chi_{321}^{2\omega} = 1.8$ $\chi_{321}^{2\omega} = 1.4$	50 83, 84
KH_2AsO_4/KDA/	$\bar{4}2$ m	-176	$n_0 = 1.563$ $n_e = 1.515$	10,582 6943	$\chi_{321}^{2\omega} = 1.7$ $\chi_{321}^{2\omega} = 1.5$	83, 84 92
RbH_2PO_4/RDA/	$\bar{4}2$ m	-126	$n_0 = 1.502$ $n_e = 1.474$	6943	$\chi_{321}^{2\omega} = 1.6$	93
$LiNbO_3$	3 m	1200	$n_0 = 2.241$ $n_e = 2.158$	10,582	$\chi_{222}^{2\omega} = 9.5$ $\chi_{311}^{2\omega} = 17.9$ $\chi_{333}^{2\omega} = 124.5$	85, 89
$LiTaO_3$	3 m	665	$n_0 = 2.139$ $n_e = 2.143$	10,582	$\chi_{222}^{2\omega} = 6.5$ $\chi_{311}^{2\omega} = -3.9$ $\chi_{333}^{2\omega} = -60$	85, 89
$LiIO_3$	6		$n_0 = 1.860$ $n_e = 1.719$	10,640	$\chi_{311}^{2\omega} = -17.9$ $\chi_{333}^{2\omega} = -18.6$	89, 94

Available studies show that, in ferroelectric crystals, SHG depends predominantly on the energy levels in the ultraviolet ('electronic' levels) whereas optical rectification and the linear electro-optical effect are contributed to by processes which depend simultaneously on the ultraviolet and infrared ('ionic') levels. As usual, by 'electronic' and 'ionic' we mean levels with transition wavelengths shorter or longer, respectively, than the limits of the region of optical transparency.[99] The three methods previously discussed sub (3.1–3.3) permit the determination of the percentage contributions from:[100]

(i) 'electronic–electronic' processes,
(ii) 'electronic–ionic' processes, and
(iii) (ionic–ionic' processes to the tensor of non-linear susceptibility χ_{ijk}.

Recently, Rabin[101] has proposed the application of optical second-harmonics generation to the study of defects in crystals, namely ones having a macroscopic centre of inversion in the ideal state, whereas lattice defects introduced into a crystal may alter the local point symmetry in the medium, and in fact may convert local inversion symmetry to that which corresponds to a noncentrosymmetric point group.

3.5. Mixing of light wave frequencies

Second-order polarization in the general form (9) defines the process of mixing of the frequencies of two waves in a nonlinear medium[102] leading, beside the processes of generation of the second harmonics $2\omega_1$, and $2\omega_2$, to the generation of summation frequencies $\omega_1 + \omega_2$ as well as of difference frequencies $\omega_1 - \omega_2$.

The earliest experiment consisting in the mixing, in a TGS crystal, of the frequencies of two monochromatic light beams from two distinct ruby lasers (the one operating at liquid nitrogen temperature and the other at room temperature) is

due to Bass et al.[103] The two beams were focused into a TGS crystal and the light beams emerging from it were observed with a high resolution quartz spectrograph. The photographic plate revealed three closely situated lines, the one 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 corresponded to the sum frequency $\omega_1 + \omega_2$. These processes vanished when the crystal was above its Curie temperature (50°C), in which region TGS is known to be centro-symmetric.

An interesting experiment is due to Miller and Savage[104] in which a ruby laser beam was mixed with the beam of a $CaWO_4 : Nd^{3+}$ laser in a variety of ferroelectric crystals: KDP, ADP and $BaTiO_3$. In addition to the second harmonic of either beam, a beam of the sum frequency 4189 Å was observed. Frequency mixing experiments have also been performed in $LiNbO_3$ crystal using a He–Ne gas laser,[85] as well as in KDP crystal by mixing the coherent light of a ruby laser and non-coherent light of a mercury lamp[105]. Bradley et al.[106] reported the observation in ADP of megawatt tunable second-harmonic and sum frequency generation at 2800 Å from a dye laser. Faries et al.[107] observed tunable far-infrared radiation from the difference frequency between two temperature-tuned ruby laser beams by mixing in $LiNbO_3$, whereas Yajima and Takeuchi[108] observed far-infrared difference-frequency generation by pico-second laser pulses. A method of converting infrared radiation to visible light by optical mixing in $LiNbO_3$ has also been described.[102,109]

4. BODIES HAVING A CENTRE OF SYMMETRY

In a body possessing a centre of symmetry, in the absence of natural optical or magnetic activity, second-order electric polarization $P^{(2)}$ does not appear in the dipolar approximation. For such bodies, the polarization term which next appears in the expansion (8) after the linear polarization P^L is a dipole polarization of the third order, $P^{(3)}$. If in general the medium is acted on simultaneously by three electromagnetic waves of frequencies ω_1, ω_2 and ω_3 and wave vectors k_1, k_2 and k_3, the component of third-order dipole polarization can be expressed in the form:[46,110]

$$P_i^{(3)}(\omega_4, k_4) = \chi_{ijkl}(-\omega_4, \omega_1, \omega_2, \omega_3) E_j(\omega_1, k_1)$$
$$\times E_k(\omega_2, k_2) E_l(\omega_3, k_3), \qquad (20)$$

the time and space synchronization conditions being given as follows[111]:

$$\omega_4 = \omega_1 + \omega_2 + \omega_3,$$
$$k_4 = k_1 + k_2 + k_3 + \Delta k. \qquad (21)$$

The fourth-rank tensor χ_{ijkl} describing the nonlinear susceptibility of order 3 has non-zero elements even for isotropic bodies (i.e. ones having a centre of symmetry) and, thus, for gases and usual liquids also. In the general case, the tensor χ_{ijkl} has 81 non-zero elements. As one proceeds from one crystallographical class to another, symmetry conditions cause a reduction in number of non-zero elements[36,37] (see Table V). In the case of the cubic system and isotropic bodies, the tensor χ_{ijkl} presents 21 non-vanishing elements, only 3 of which are mutually independent, namely:[112]

$$\chi_{ijkl} = \chi_{xxyy}\delta_{ij}\delta_{kl} + \chi_{xyxy}\delta_{ik}\delta_{jl} + \chi_{yxxy}\delta_{il}\delta_{kj} \qquad (22)$$

with the supplementary relation[36]

$$\chi_{xxxx} = \chi_{yyyy} = \chi_{zzzz} = \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy} \qquad (22a)$$

TABLE V

Tensor elements χ_{ijkl} of third-order susceptibility, for all crystallographic classes, on the assumption of total symmetricity in the indices i, j, k and l. The tensor elements are expressed by their subscripts only

1. Triclinic. The two classes 1 (C_1) and $\bar{1}$ (C_i) have 81 non-zero tensor elements, 15 of which are independent:

xxxx,
yyyy,
zzzz,
xxyy = xyxy = xyyx = yyxx = yxyx = yxxy,
xxzz = xzxz = xzzx = zzxx = zxzx = zxxz,
yyzz = yzyz = yzzy = zzyy = zyzy = zyyz,
xxxy = xxyx = xyxx = yxxx,
yyyx = yyxy = yxyy = xyyy,
xzzz = zxzz = zzxz = zzzx,
yzzz = zyzz = zzyz = zzzy,
xxxz = xxzx = xzxx = zxxx,
yyyz = yyzy = yzyy = zyyy,
xxyz = xyxz = xyzx = xxzy = xzxy = xzyx =
    = yxxz = yxzx = yzxx = zxxy = zxyx = zyxx,
yyxz = yxyz = yxzy = yyzx = yzyx = yzxy =
    = xyyz = xyzy = xzyy = zyyx = zyxy = zxyy,
xzzy = xzyz = xyzz = yxzz = yzxz = yzzx =
    = zxyz = zyxz = zyzx = zxzy = zzyx = zzxy.

2. Monoclinic. All three classes 2 (C_2), m (C_3) and 2/m (C_{2h}) have 41 non-zero tensor elements, 9 of which are independent:

xxxx; yyyy; zzzz;
xxyy = xyxy = xyyx = yyxx = yxyx = yxxy;
xxzz = xzxz = xzzx = zzxx = zxzx = zxxz;
yyzz = yzyz = yzzy = zzyy = zyzy = zyyz;
xxxy = xxyx = xyxx = yxxx;
yyyx = yyxy = yxyy = xyyy;
xzzy = xzyz = xyzz = yxzz = yzxz = yzzx =
    = zxyz = zyxz = zyzx = zxzy = zzyx = zzxy;

3. Orthorhombic. The classes 222 (D_2), mm2 (C_{2v}) and mmm (D_{2h}) have 21 non-zero tensor elements, 6 of which are independent.

$xxxx$; $yyyy$; $zzzz$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$;

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz$;

$yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$;

4. Tetragonal. The classes 4 (C_4), $\bar{4}$ (S_4) and 4/m (C_{4h}) have 29 non-zero tensor elements, 5 of which are independent:

$zzzz$; $xxxx = yyyy$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$;

$xxxy = xxyx = xyxx = yxxx = -yyyx = -yyxy =$

$= -yxyy = -xyyy$

The classes 422 (D_4), 4 mm (C_{4v}), 4 mm (D_{4h}) and $\bar{4}2$ m (D_{2d}) have 21 non-zero tensor elements, 4 of which are independent:

$zzzz$; $xxxx = yyyy$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$,

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$,

5. Trigonal. The classes 3 (C_3) and $\bar{3}$ (C_{3i}) have 53 non-zero tensor elements, 5 of which are independent:

$zzzz$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$;

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$;

$xxxz = xxzx = xzxx = zxxx = -yxyz = -yyzx =$

$= -yzyx = -yyxz = -yxzy = -yzxy = -xyyz =$

$= -xyzy = -xzyy = -zxyy = -zyxy = -zyyx$;

$yyyz = yyzy = yzyy = zyyy = -xyxz = -xxzy =$

$= -xzxy = -xxyz = -xyzx = -xzyx = -yxxz =$

$= -yxzx = -yzxx = -zyxx = -zxyx = -zxxy$;

$(xxxx = yyyy = xxyy + xyxy = xyyx)$

The classes 3m (C_{3v}), $\bar{3}$m (D_{3d}) and 32 (D_3) have 37 non-zero tensor elements, 4 of which are independent:

$zzzz$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$,

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$,

$yyyz = yyzy = yzyy = zyyy = -xyxz = -xxzy =$

$= -xzxy = -xxyz = -xyzx = -xzyx = -yxxz =$

$= -yxzx = -yzxx = -zyxx = -zxyx = -zxxy$

$(xxxx = yyyy = xxyy + xyxy + xyyx)$

6. Hexagonal. The classes 6 (C_6), $\bar{6}$ (C_{3h}) and 6/m (C_{6h}), 622 (D_6), 6 mm (C_{6v}); $\bar{6}$ m2 (D_{3h}) 6/mmm (D_{6h}) have 19 non-zero tensor elements, only 3 of which are independent:

$zzzz$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$,

$xxzz = xzxz = xzzx = zzxx = zxzx = zxxz =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$;

$(xxxx = yyyy = xxyy + xyxy + xyyx)$

7. Cubic. All classes of this system 23 (T), m3 (T_h), 432 (O), $\bar{4}3$ m (T_d) and m3m (O_h) have 21 non-zero tensor elements, only 2 of which are independent:

$xxxx = yyyy = zzzz$;

$xxyy = xyxy = xyyx = yyxx = yxyx = yxxy =$

$= zzxx = zxzx = zxxz = xxzz = xzxz = xzzx =$

$= yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$;

8. Isotropic medium. Non-zero elements as in the cubic system, but only 1 independent element owing to the relation:

$xxxx = xxyy + xyxy + xyyx$.

9. Axially-symmetric medium.
Groups C_∞, $C_{\infty v}$, $C_{\infty h}$ and $D_{\infty h}$.
Non-zero and independent tensor elements as in the classes of the hexagonal system.

If the centro-symmetrical medium exhibits spatial dispersion, the following second-order polarization[46] appears in the electric quadrupolar approximation:

$$P_i^{(2)}(\omega_3, \mathbf{k}_3) = \chi_{ijkl}(-\omega_3, \omega_1, \omega_2, k) E_j(\omega_1, \mathbf{k}_1)$$
$$\times \nabla_l E_k(\omega_2, \mathbf{k}_2) \qquad (23)$$

with the fourth-rank tensor χ_{ijkl} describing the nonlinear susceptibility in dipole–quadrupole approximation, where ∇ is the spatial derivation operator. Equation (23) shows that this nonlinearity is induced by the gradient of the electric field, i.e. its variation from one point of space to another.

4.1. Tripling of oscillation frequency

If a single, intense wave frequency $\omega = \omega_1 = \omega_2 = \omega_3$ and wave vector $\mathbf{k} = \mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}_3$ is incident on a centro-symmetrical medium, the tensor χ_{ijkl} (in the absence of electron dispersion) is totally symmetric, and with regard to the relation (22) the third-order polarization (20) takes the form:

$$P_i^{(3)}(3\omega, 3\mathbf{k}) = 3\chi_{xxyy}(-3\omega, \omega, \omega, \omega) E_i(\omega, \mathbf{k})$$
$$\times E_i(\omega, \mathbf{k}) E_j(\omega, \mathbf{k}). \qquad (24)$$

The preceding polarization describes the tripling of oscillation frequency in a centro-symmetrical medium. The highest efficiency of third-harmonic generation is achieved when the phase matching condition:

$$\Delta k = \left(\frac{3\omega}{c}\right)(n_{3\omega} - n_\omega) = 0, \qquad (21a)$$

is fulfilled. Here, n_ω and $n_{3\omega}$ are the refractive indices for the fundamental frequency ω and tripled frequency (third-harmonic frequency) 3ω, respectively.

Terhune and his co-workers were the first to attempt the production of a ultra-violet third harmonic of ruby at $\lambda_{3\omega} = 2313$ Å in calcite[113], the cubic ionic crystals LiF, KCl, NaCl and others,

as well as in dielectric liquids.[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 third-harmonic generation at 3530 Å of the neodymium laser line at 10,600 Å by the addition of dye molecules to a liquid medium (fuchsin red dye in solution 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, proving that a linearly polarized laser beam generates a third-harmonic signal whereas a circularly polarized beam does not, in accordance with theory. This experiment offers a variety of applications when determining the state of polarization of laser light, when modulating it, and when measuring ultra-short light pulses such as those produced by mode-locked lasers. Ward and New[118] observed THG at 2314 Å in gases (He, Ne, Ar, etc.) using a focused ruby laser beam.

Goldberg and Schnur[119] investigated harmonics generation in liquid crystals, in particular cholesteryl nonanoate (CN) as well as other cholesteric and nematic liquid crystals. The solid phase of CN exhibited a high SH intensity (of the same order as in quartz crystal powder) which, on heating, fell steeply by 4 orders of magnitude in the neighbourhood 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 recrystallization to the solid. THG was apparent from all three 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;[120] in no case did they exhibit SHG when in mesomorphic phases, which have to be regarded as centro-symmetric. Recently, Rentzepis et al.[121] reported that the efficiency for third-harmonic conversion in pure organic liquids is found to be by a factor of 100 larger than for fused silica. The above-cited studies prove that some rôle in the process of harmonics generation is played by the molecular correlations so highly relevant to multiharmonic light scattering and optical birefringence in isotropic media.[122]

Also, the conditions for frequency tripling in infrared by anharmonic molecular vibrations have been analyzed[123a] and a technique for the efficient production of ultraviolet radiation by THG in phase-matched metal vapours proposed.[123b]

Ferroelectric crystals have been applied to the production of the second and third and, simultaneously, fourth and even fifth harmonics of light.[124]

4.2. D.c. field-induced second optical harmonic

When Eq. (20) is re-written with $\omega_3 = k_3 = 0$ and $\omega_1 = \omega_2 = \omega$, $k_1 = k_2 = k$, the third-order polarization

$$P_i^{(3)}(2\omega, k) =$$

$$\chi_{ijkl}(-2\omega, \omega, \omega, 0)\, E_j(\omega, k)\cdot E_k(\omega, k)\, E_l(0) \qquad (25)$$

describes SHG in a body subjected to the action of a d.c. electric field $E(0)$.

Terhune, Make and Savage[113] studied the optical harmonics of ruby laser light in calcite, which has a centre of symmetry. They found a weak second harmonic due to quadrupolar polarization, Eq. (23), and on applying a d.c. electric field observed a considerable rise in SHG quadratic in the field strength. Their experiment was repeated by Bjorkholm and Siegman[125] 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. The study revealed a displacement of the parabolic curve of SH power with growing applied field strength $E(0)$.

McFee[126] observed SHG at 5300 Å when a d.c. electric field and CO_2 laser beam are applied simultaneously to narrow band-gap semiconductors (InAs, InSb). Suvorov et al.[127] investigated SHG in TGS crystal acted on by a d.c. electric field at various synchronizations in the temperature range from 20 to 90°C finding a large increase of SHG in the field direction.

Recently, Mayer et al.[43] studied SHG in molecular gases immersed in a d.c. electric field. In non-dipolar rarefied gases, SHG is caused solely by nonlinear polarization of the electron shell, whereas upward of some degree of condensation, reorientation of induced dipoles also contributes to SHG.[44] In dipolar gases, d.c. electric field-induced SHG is due chiefly to reorientation of the permanent electric dipoles. In strongly dipolar substances (C_2H_5I, C_2H_5Br, CH_3I) Mayer[43] observed an anomalous increase in SHG at d.c.

field strengths close to breakdown, presumably arising from electric saturation of reorientation of the molecular dipoles.[44]

Of late, Finn and Ward[45] measured d.c. field-induced SHG by a focussed ruby laser beam in the inert gases.

Now let us assume that the laser beam propagates along the laboratory z-axis, perpendicularly to the d.c. electric field $E(0)$ applied along the y-axis. Equations (23) and (25) in this case yield, for an isotropic body, the following two mutually perpendicular polarization components:

$$P_x^{(3)}(2\omega) = \chi_1^{2\omega} E_x(\omega) E_y(\omega) E_y(0),$$

$$P_y^{(3)}(2\omega) = \{\chi_2^{2\omega} E_x^2(\omega) + \chi_3^{2\omega} E_y^2(\omega)\} E_y(0),$$ (25a)

where we have introduced the constants:

$$\chi_1^{2\omega} = \chi_{xxyy}(-2\omega, \omega, \omega, 0) + \chi_{xyxy}(-2\omega, \omega, \omega, 0),$$

$$\chi_2^{2\omega} = \chi_{xyyx}(-2\omega, \omega, \omega, 0),$$

$$\chi_3^{2\omega} = \chi_{xxyy}(-2\omega, \omega, \omega, 0) + \chi_{xyxy}(-2\omega, \omega, \omega, 0)$$

$$+ \chi_{xyyx}(-2\omega, \omega, \omega, 0) = \chi_{yyyy}(-2\omega, \omega, \omega, 0).$$ (25b)

Equation (25a) permits the determination of the nonlinear susceptibility constants (25b). Namely, using linearly polarized light, we are able to determine $\chi_3^{2\omega}$ with light oscillations parallel to the d.c. field direction, and $\chi_2^{2\omega}$ with light oscillations perpendicular to $E_y(0)$. By using circularly polarized light, we can determine $\chi_1^{2\omega}$ by measuring the component $P_x^{(2)}(2\omega)$, whereas the measurement of $P_y^{(2)}(2\omega)$ will yield the value of $\chi_2^{2\omega} + \chi_3^{2\omega}$. Along these lines a method for the experimental determination of the tensor elements $\chi_{ijkl}(-2\omega, \omega, \omega, 0)$ of isotropic bodies from SHG studies in the presence of a d.c. electric field has been proposed recently by Mayer.[43]

In the absence of dispersion and absorption, we have:[99]

$$\chi_{xxyy} = \chi_{xyxy} = \chi_{xyyx} = \tfrac{1}{3}\chi_{yyyy},$$

whence we derive the following symmetry relations:[44]

$$\chi_1^{2\omega} + \chi_2^{2\omega} = \chi_3^{2\omega},$$

$$\chi_1^{2\omega} : \chi_2^{2\omega} : \chi_3^{2\omega} = 2 : 1 : 3.$$ (26)

For molecular dipolar substances of density ρ, in the absence of molecular interaction, the macroscopic constant of nonlinear susceptibility takes the form:[44]

$$\chi_3^{2\omega} = \frac{\rho}{20}\left(c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT} b_{\alpha\alpha\beta}^{2\omega} p_\beta\right),$$ (26a)

where p_β is the dipole moment component of the molecule and the tensors $b_{\alpha\beta\gamma}^{2\omega} = b_{\alpha\beta\gamma}(-2\omega, \omega, \omega)$ and $c_{\alpha\beta\gamma\delta}^{2\omega} = c_{\alpha\beta\gamma\delta}(-2\omega, \omega, \omega, 0)$ describe, respectively, its nonlinear polarizabilities of orders 2 and 3 at frequency 2ω.

In the microscopic approach, by (26a), the nonlinear susceptibility consists of two parts. One part does not depend directly on temperature. It is due to the purely distortional process, residing in nonlinear polarization of the electron shell (Voigt effect). The tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$, which describes it, has non-zero elements even for atoms in the ground state. The other part is directly dependent on temperature. It is related with the statistical Langevin process[128] of reorientation of the dipoles p_β by the electric field, and with the second-order nonlinear polarization $b_{\alpha\alpha\beta}^{2\omega}$.

4.3. Optically induced birefringence

Let us now put $\omega_A = \omega_1 \neq \omega_I = \omega_2 = -\omega_3$ and $k_4 = 0$ in Eq. (20). This results in the following nonlinear polarization, induced in an isotropic medium by an intense wave of frequency ω_I but analyzed (measured) by using a weak wave of frequency ω_A:

$$P_i^{(3)}(\omega_A) =$$

$$\chi_{xxyy}(-\omega_A, \omega_A, \omega_I, -\omega_I) E_i(\omega_A) E_j(\omega_I) E_j^*(\omega_I) +$$
$$\chi_{xyxy}(-\omega_A, \omega_A, \omega_I, -\omega_I) E_j(\omega_A) E_i(\omega_I) E_j^*(\omega_I) +$$
$$\chi_{xyyx}(-\omega_A, \omega_A, \omega_I, -\omega_I) E_j(\omega_A) E_j(\omega_I) E_i^*(\omega_I).$$ (27)

The existence of this nonlinear polarization causes the variations in electric permittivity of the isotropic medium to become anisotropic in accordance with the general formula:

$$\Delta\varepsilon_{ij}(\omega_A) =$$
$$4\pi\{\chi_{xxyy}(-\omega_A, \omega_A, \omega_I, -\omega_I)\delta_{ij} E_k(\omega_I) E_k^*(\omega_I) +$$
$$\chi_{xuxy}(-\omega_A, \omega_A, \omega_I, -\omega_I) E_i(\omega_I) E_j^*(\omega_I) +$$
$$\chi_{xyyx}(-\omega_A, \omega_A, \omega_I, -\omega_I) E_j(\omega_I) E_i^*(\omega_I)\},$$ (28)

Assuming the analyzing (measuring) light beam to propagate along the z-axis, the difference in

diagonal permittivity tensor elements is, by (28),

$$\Delta\varepsilon_{xx}(\omega_A) - \Delta\varepsilon_{yy}(\omega_A) = 4\pi\{\chi_{xyxy}(-\omega_A, \omega_A, \omega_I, -\omega_I)$$

$$+ \quad \chi_{xyyx}(-\omega_A, \omega_A, \omega_I, -\omega_I)\}$$

$$\times \{E_x(\omega_I) E_x^*(\omega_I) - E_y(\omega_I) E_y^*(\omega_I)\}. \quad (29)$$

The preceding formula gives the optical bire-fringence (analysed by means of linearly polarized light of frequency ω_A) which is induced in isotropic media by intense light of frequency ω_I. We have here the optical Kerr effect, discovered by Mayer[58] and studied since by various methods.[60, 129, 130] Figure 3 shows the method used by Martin and Lalanne.[60, 129]
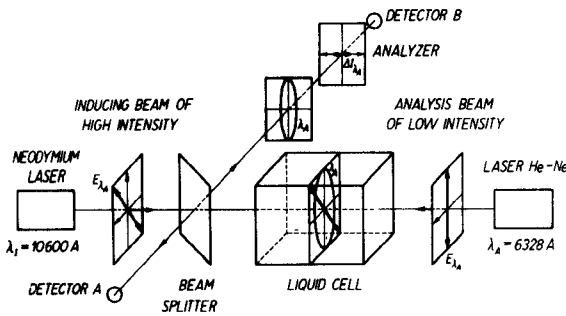

FIGURE 3   Principle of optically induced birefringence experiment.[129] The liquid irradiated with the intense plane-polarized wave λ_I behaves like a uniaxial crystal with optical axis parallel to the electric vector $E(\lambda_I)$. The analysing wave λ_A of low intensity, plane-polarized (e.g. vertically), becomes elliptical (the two laser beams, i.e. the one inducing the non-linearity and the analysing one are polarized at 45° to one another and propagate in opposite directions). An analyser whose plane of polarization is perpendicular to that of the initial polarized (that is to say, horizontally), permits the measurement of this ellipticity. In the absence of an intense wave, no signal appears on the detector B because the analyser and polarizer are crossed (are at right angles). During propagation of the intense wave, the component $\Delta I(\lambda_A)$ of the analysed, wave is detected at B. The intensity of the strong inducing beam is measured by means of the detector A.

For molecular substances, in the absence of dispersion and absorption, the nonlinear sus-ceptibilities for optical birefringence can be ex-pressed as follows:[39, 57]

$$\chi_{xyxy}(-\omega_A, \omega_A, \omega_I, -\omega_I)$$

$$= \chi_{xyyx}(-\omega_A, \omega_A, \omega_I, -\omega_I)$$

$$= \frac{\rho}{90}\left\{3c_{\alpha\beta\alpha\beta}^{\omega_A, \omega_I} - c_{\alpha\alpha\beta\beta}^{\omega_A, \omega_I}\right.$$

$$\left. + \frac{1}{kT}(3a_{\alpha\beta}^{\omega_A} a_{\alpha\beta}^{\omega_I} - a_{\alpha\alpha}^{\omega_A} a_{\beta\beta}^{\omega_I})\right\}, \quad (29a)$$

where $a_{\alpha\beta}^{\omega_A}$ and $a_{\alpha\beta}^{\omega_I}$ are tensors of rank 2 describing the linear molecular polarizabilities measured at frequencies ω_A and ω_I respectively. The tensor $c_{\alpha\beta\gamma\delta}^{\omega_A, \omega_I} = c_{\alpha\beta\gamma\delta}(-\omega_A, \omega_A, \omega_I, -\omega_I)$ of rank 4 des-cribes the nonlinear polarizability of order 3 at frequencies ω_A and ω_I.

It is obvious from Equations (29) and (29a) that the measurement of optical Kerr effect permits the direct numerical determination of the anisotropy of linear polarizabilities as well as of the mean value of nonlinear polarizabilities of atoms and molecules.[40, 129]

The general formula (28) leads to the following difference between non-diagoital tensor elements of electric permittivity:

$$\Delta\varepsilon_{xy}(\omega_A) - \Delta\varepsilon_{yx}(\omega_A)$$

$$= 4\pi\{\chi_{xyxy}(-\omega_A, \omega_A, \omega_I, -\omega_I)$$

$$- \chi_{xyyx}(-\omega_A, \omega_A, \omega_I, -\omega_I)\}$$

$$\times \{E_x(\omega_I) E_y^*(\omega_I) - E_y(\omega_I) E_x^*(\omega_I)\}. \quad (30)$$

We have here a quantity measurable by using circularly or elliptically polarized light.[59, 110] Equation (30) permits only the determination of variations in nonlinear electron polarizability of molecules.[59, 61]

4.4. Self-induced optical birefringence

When but a single, intense light beam of frequency acts on an isotropic medium, by insertion of $\omega = \omega_A = \omega_I$ into Eq. (27) and by taking into account Eq. (22a) one obtains the following mutually perpendicular polarization components (perpendicular to the direction of propagation of the beam):

$$P_x^{(3)}(\omega) = \chi_{xxxx}(-\omega, \omega, \omega, -\omega) E_x(\omega)$$

$$\times \{E_x(\omega) E_x^*(\omega) + E_y(\omega) E_y^*(\omega)\}$$

$$+ \chi_{xyyx}(\omega, -\omega, \omega, -\omega) E_y(\omega)$$

$$\times \{E_y(\omega) E_x^*(\omega) - E_x(\omega) E_y^*(\omega)\},$$

$$P_y^{(3)}(\omega) = \chi_{yyyy}(-\omega, \omega, \omega, -\omega) E_y(\omega)$$

$$\times \{E_x(\omega) E_x^*(\omega) + E_y(\omega) E_y^*(\omega)\}$$

$$+ \chi_{xyyx}(-\omega, \omega, \omega, -\omega) E_x(\omega)$$

$$\times \{E_x(\omega) E_y^*(\omega) - E_y(\omega) E_x^*(\omega)\}. \quad (31)$$

Hence, the difference in diagonal electric permit-tivity tensor elements amounts to:

$$\Delta\varepsilon_{xx}(\omega) - \Delta\varepsilon_{yy}(\omega) = 4\pi\chi_{xyyx}(-\omega, \omega, \omega, -\omega)$$

$$\times \{E_x(\omega) E_x^*(\omega) - E_y(\omega) E_y^*(\omega)\}, \quad (31a)$$

defining an effect of optical birefringence self-induced by linearly polarized light.[57,58]

Likewise, we derive from Eq. (31) the following difference between non-diagonal elements of the electric permittivity tensor:

$$\Delta\varepsilon_{xy}(\omega) - \Delta\varepsilon_{yx}(\omega) = 8\pi\chi_{xyyx}(-\omega, \omega, \omega, -\omega)$$

$$\times \{E_y(\omega) E_x^*(\omega) - E_x(\omega) E_y^*(\omega)\} \qquad (31b)$$

which describes the effect of self-induced rotation of the polarization ellipse detected by Maker et al.[59] when using intense elliptically polarized laser light.

4.5. Kerr effect

Insert now $\omega_A = \omega$ and $\omega_I = 0$ in Eq. (29). This leads to the expression:

$$\Delta\varepsilon_{xx}(\omega) - \Delta\varepsilon_{yy}(\omega) =$$

$$8\pi\chi_{xyyx}(-\omega, \omega, 0, 0) \{E_x^2(0) - E_y^2(0)\}, \qquad (32)$$

describing the optical birefringence induced in an isotropic medium by a strong d.c. electric field, i.e. the well-known Kerr effect.

The molecular-statistical theory of Kerr effect in gases leads to the following expression for the nonlinear susceptibility of Eq. (32):[15,16,39]

$$\chi_{xyyx}(-\omega, \omega, 0, 0) = \frac{\rho}{90}\left\{3c^{\omega}_{\alpha\beta\alpha\beta} - c^{\omega}_{\alpha\alpha\beta\beta}\right.$$

$$+ \frac{1}{kT}(3a^{\omega}_{\alpha\beta} a^0_{\alpha\beta} - a^{\omega}_{\alpha\alpha} a^0_{\beta\beta})$$

$$+ \frac{2}{kT}(3b^{\omega}_{\alpha\beta\alpha}P_\beta - b^{\omega}_{\alpha\alpha\beta}P_\beta)$$

$$\left. + \frac{1}{k^2T^2}(3a^{\omega}_{\alpha\beta}P_\alpha P_\beta - a^{\omega}_{\alpha\alpha}P_\beta P_\beta)\right\}. \qquad (32a)$$

Above, the first right-hand term, not dependent directly on temperature, corresponds to a Voigt effect[14] consisting in nonlinear distortion of the atom or molecule by the square of the d.c. electric field strength. The second term is directly temperature-dependent and defines a Langevin effect[128] of reorientation of anisotropic molecules by the d.c. field. The remaining two terms have been calculated by Born[15] and others[16,131,132] and play the decisive rôle in dipolar substances.

4.6. Nonlinear optical polarizabilities of atoms and molecules

The linear optical properties of atoms and molecules are accounted for by the second-rank polarizability tensor $a_{ij}(\omega)$ occurring in the formula for the induced dipole moment of the first order:

$$m_i^{(1)}(\omega) = a_{ij}(-\omega, \omega) E_j(\omega). \qquad (33)$$

The linear polarizability tensor elements a_{ij} are

TABLE VI
Number of non-zero elements (N) and of mutually independent elements (I) of the symmetric polarizability tensors a_{ij}, b_{ijk} and c_{ijkl} for all point groups

| Point Group | Polarizability tensor elements | | | | | |
| | a_{ij} | | b_{ijk} | | c_{ijkl} | |
	I	N	I	N	I	N
C_1	6	9	10	27	15	81
C_i	6	9	0	0	15	81
C_s	4	5	6	14	9	41
C_2	4	5	4	13	9	41
C_{2h}	4	5	0	0	9	41
C_{2v}	3	3	3	7	6	21
D_2	3	3	1	6	6	21
D_{2h}	3	3	0	0	6	21
C_4	2	3	2	7	5	29
S_4	2	3	2	12	5	29
C_{4h}	2	3	0	0	5	29
C_{4v}	2	3	2	7	4	21
D_{2d}	2	3	1	6	4	21
D_4	2	3	0	0	4	21
D_{4h}	2	3	0	0	4	21
C_3	2	3	4	15	5	53
S_6	2	3	0	0	5	53
C_{3v}	2	3	3	11	4	37
D_3	2	3	1	4	4	37
D_{3d}	2	3	0	0	4	37
C_{3h}	2	3	2	8	3	21
C_6	2	3	2	7	3	21
C_{6h}	2	3	0	0	3	21
D_{3h}	2	3	1	4	3	21
C_{6v}	2	3	2	7	3	21
D_6	2	3	0	0	3	21
D_{6h}	2	3	0	0	3	21
T	1	3	1	6	2	21
T_h	1	3	0	0	2	21
T_d	1	3	1	6	2	21
O	1	3	0	0	2	21
O_h	1	3	0	0	2	21
$C_{\infty v}$	2	3	2	7	3	21
$D_{\infty h}$	2	3	0	0	3	21
K_h	1	3	0	0	1	21
K	1	3	0	0	1	21
D_{4d}	2	3	0	0	3	21
D_{5h}	2	3	0	0	3	21
D_{5d}	2	3	0	0	3	21
D_{6d}	2	3	0	0	3	21

determined from molecular refraction, scattered light depolarization, Kerr effect[17,133] and optical birefringence[40] studies and are accessible to direct calculation by the methods of quantum mechanics.

The nonlinear optical properties of molecules are accounted for by induced dipole moments of orders 2 and 3:

$$m_i^{(2)}(\omega_3) = b_{ijk}(-\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2), \quad (34)$$

$$m_i^{(3)}(\omega_4) = c_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$$
$$\times E_j(\omega_1) E_k(\omega_2) E_l(\omega_3). \quad (35)$$

Table VI gives the number of non-zero elements and independent elements of the linear polariz-

TABLE VII

Numerical values of linear and nonlinear polarizabilities of atoms and molecules calculated theoretically and determined from experimental data. Only mean values are given: $a = a_{ii}/3, b = b_{ii3}/3 = b_{333}$ (for the axial symmetry), $b = b_{123}$ (for tetrahedral symmetry), and $c = c_{iijj}/5 = c_{3333}$

Units:	10^{-24} cm³	10^{-30} cm⁵/e.s.u.			10^{-36} cm⁷/e.s.u.²			
atom, molecule	a^∞	b^0	b^ω	$b^{2\omega}$	c^0	c^ω	$c^{2\omega}$	$c^{3\omega}$
He	0.205				0.021[141] 0.021[142]	0.027[146] 0.022[141]	0.023[141]	0.024[141] 0.021[143]
Ne	0.394				0.051[146] 0.055[38]		0.24[45]	0.041[143] 0.214[118]
Ar	1.66				0.59[146] 0.73[38]		2.74[45] 2.74[45]	3.024[118] 0.672[143]
Kr	2.52				1.4[146] 1.6[38]		6.69[45]	9.264[118] 1.704[143]
Xe	4.11				3.9[146] 4.0[38]		18.52[45]	23.496[118] 5.328[143]
H₂	0.79				0.20[135]	0.28[144]	0.36[43]	1.920[118]
N₂	1.76					0.7[144]		2.568[118]
O₂	1.60						0.64[43]	
HF	2.46	−0.16[134]						
CO	1.95	±0.43[134] 0.19[135] 0.18[136]			1.0[135]		1.81[43]	
NO	1.72							
LiH	3.35	−3.44[137]						
BF	3.13	0.98[134]						
CO₂	2.65					4.5[143]		2.744[118]
NH₃	2.26	−0.045[137]	−3.9[38]			2.6[38]	1.48[43]	
CH₄	2.6	0.21[38] 0.19[138]		0.01[41]			0.39	
CCl₄	10.5			0.03[41]		3.1[40] 7.2[151] 6.51[147]	3.6[43] 0.21	
CH₃F	3.55	−0.089[137]	−1.11[38]			1.28[149]		
CHF₃	2.81			−0.06[43]		0.92[149]	−0.27[43]	
CHCl₃	8.23		14.4[38]	0.33[43]		4.8[40]	4.4[43]	
H₂O	1.46	+0.11[138]						
CS₂	8.74					56.5[147] 50.1[40] 54.4[38] 63.9[151] 57.4[148]		
C₂H₆	4.47					1.9[148]	4.8[43]	
C₆H₆	10.32					6.46[148]		
C₆H₁₂	10.87					1.2[40]		
C₆H₅CH₃	12.29					27.2[40]		
C₆H₅NO₂	12.17					85.0[40]		
CH₃I	7.28			0.84[43]			9.0[43]	
SF₆	4.47					1.2[146]	0.26[43]	
C₂H₅I				1.1[43]			13.6[43]	

ability tensor a_{ij} and nonlinear polarizability tensors b_{ijk} and c_{ijkl} for all point groups. In the case of total symmetricity of the tensor b_{ijk}, its elements for the various point groups are the same as those of the tensor χ_{ijk} in Table III; likewise, those of c_{ijkl} become identical to the elements of the susceptibility tensor χ_{ijkl} in Table V.

Static values of the nonlinear polarizability $b_{ijk}^0 = b_{ijk}(0; 0, 0)$ have been calculated theoretically for some dipolar molecules.[134–138] The tensor elements $b_{ijk}^\omega = b_{ijk}(-\omega; \omega, 0)$ can be determined from Kerr effect measurements[38] or molecular light scattering in liquids.[132] Values of $b_{ijk}^{2\omega} = b_{ijk}(-2\omega; \omega, \omega)$ can be derived from the study of nonlinear light scattering at doubled frequency[41, 139] or second-harmonic generation by a gas in the presence of a d.c. electric field.[43–44]

Direct theoretical calculations of the third-order nonlinear polarizability c_{ijkl} have been performed for atoms of the inert gases and for simple molecules.[140–143] Values of the tensor elements $c_{ijkl}^\omega = c_{ijkl}(-\omega; \omega, 0, 0)$ have been determined for numerous molecules from static Kerr effect studies,[144–150] and those of $c_{ijkl}^\omega = c_{ijkl}(-\omega; \omega, \omega, -\omega)$ from optical Kerr effect measurements.[40, 151] Second-harmonic light generation when measured in gases in the presence of a d.c. electric field[43–45] permits the determination of the elements of $c_{ijkl}^{2\omega} = c_{ijkl}(-2\omega; \omega, \omega, 0)$; these tensor elements can also be obtained from second-harmonic scattering by centro-symmetric liquids.[42] Finally, the elements of the tensor $c_{ijkl}^{3\omega} = c_{ijkl}(-3\omega; \omega, \omega, \omega)$ are obtained by investigation of third-harmonic generation in gases and liquids.[114, 118]

Numerical values of nonlinear polarizability tensor elements b_{ijk} and c_{ijkl}, determined by the above mentioned methods and calculated theoretically, are listed in Table VII.

5. GASEOUS AND LIQUID DIELECTRICS

The investigation of nonlinear optical phenomena in isotropic dielectrics is a method of very high cognitive value, as it provides insight into the induced anisotropic optical properties of these media as well as the electro-optical properties induced in them by strong d.c., a.c. electric and optical fields. The induced macroscopic non-linearities, measured by various modern experimental methods and treated mathematically by statistical and quantum mechanics, provide knowledge of the nonlinear properties of the micro-

systems, i.e. of the atoms, molecules or macromolecules, as the case may be. Particularly important is the study of matter in the gas state and in very dilute solutions. This leads directly to data bearing on the individual microsystems, since any perturbations from interatomic or intermolecular correlations can be excluded from our considerations. For instance, the third-order nonlinear polarizability c_{ijkl} of atoms is determined directly from the measurement of optical birefringence,[40, 57] third-harmonic scattering,[139] and third-harmonic generation.[118, 123] The electro–optical nonlinear polarizability of atoms is directly measurable by Kerr effect[38, 140] and by the method of second-harmonic generation by a gas placed in a d.c. electric field.[43, 44] The same methods yield the nonlinear polarizabilities of centro-symmetric molecules. With regard to molecules without a centre of symmetry, the most important part belongs to the second-order nonlinear polarizability b_{ijk} which, in the optical case, can immediately be determined only from second-harmonic scattering,[41, 139, 152] but is directly available in the electro–optical case from Kerr's effect[38, 149] and second-harmonic generation by electrically polarized dipolar gases.[43, 44]

The theoretical calculations for isolated quantum systems interacting with an electromagnetic field, though differing widely as to the approximations on which they are based, lead to numerical values for the nonlinear polarizabilities of atoms and molecules of the same order of magnitude as those resulting from experiment (Table VII). Quantum-mechanical calculations are necessarily rather complicated and, at least for the time being, are restricted to atoms and the simpler molecules, but one should take into consideration that this approach has developed but of late and that these are no more than the first steps. Theoretical as well as experimental studies in this direction require an extension to the entire range of frequencies, including both nonlinear electron dispersion[98, 139, 153] and dielectric dispersion.[11, 154] The technique of ultra-short light pulses, of a duration of the order of 10^{-8} to 10^{-12} sec and thus comparable to the relaxation times of molecules,[155] permits the separation from one another of different nonlinear processes, which require different times to reach the steady state. In this way it is feasible, in certain conditions, to separate the processes of nonlinear electron polarizability from those of molecular reorientation, as the latter are unable to cause a macroscopic nonlinearity in so short a time. The

question as to whether these two effects are numerically of the same order of magnitude or whether one of them (and which) is predominant, unavoidably depends on the internal structure and size of the molecules, that is to say on whether a given molecule or macromolecule is more highly susceptible to nonlinear distortion in the optical field or to reorientation by it. Obviously, the problem can also be solved traditionally by studies of the nonlinear effects in function of temperature.

In dense media, beside radial and angular molecular correlations,[39,132] a particularly important part is played by the fluctuational electric molecular fields F, the existence of which causes the atoms and molecules immersed in such a medium to exhibit certain effective polarizabilities.[156] Very essential is the case when the fields of electric molecular multipoles give rise to nonlinear polarizations of the second and third order as a result of which the tensor of effective polarizability of the molecule appears in the form:[132,156]

$$a_{ij}(F) = a_{ij} + b_{ijk}F_k + \tfrac{1}{2}c_{ijkl}F_kF_l + \dots \quad (36)$$

Owing to this circumstance, the nonlinear polarizability tensors b_{ijk} and c_{ijkl} become accessible to numerical determinations by the study of molecular light scattering in dense substances also.

Similarly to the expansion (36), one obtains the following tensor of effective second-order nonlinear polarizability of a molecule immersed in the medium:

$$b_{ijk}(F) = b_{ijk} + c_{ijkl}F_l + \dots, \quad (37)$$

showing that in substances consisting of centro-symmetric molecules (for which the molecular tensor b_{ijk} is zero in the ground state) nonlinear optical processes such as second-harmonic scattering can indeed take place. This is so because the molecular field F fluctuating in time and space[122] lowers the symmetry of the molecule (by destroying its centre of symmetry) and simultaneously induces a local anisotropy in the region of short-range neighbourhood. This leads to the co-operative second-harmonic scattering observed by Lalanne, Martin and this author in liquids with naturally centro-symmetric molecules, such as carbon disulphide, benzene, cyclohexane, etc.[42] We are thus able to determine the nonlinear polarizabilities of molecules not only in situations when they are induced by a strong, externally applied electric field but moreover in ones when their

induction is due to the molecular electric fields present in dense media.

We hope to have shown convincingly that there are now at our disposal a vast variety of new methods for the study of nonlinear properties of atoms and molecules. These comprise methods of nonlinear molecular spectroscopy[157] and the nonlinear spectroscopy of picosecond pulses.[158] It may be worth stressing that nonlinear processes in isotropic bodies are highly sensitive with respect to statistical inhomogeneities in regions on the fluctuational scale and thus provide valuable information concerning the microstructure of the bodies under investigation[122] as well as regarding interactions between the statistical structure of matter and the electromagnetic field.[159]

Although solutions of macromolecules and colloids are highly susceptible to both the d.c. electric[19,54,55] and optical field[160] with regard to the producing of strong nonlinearities, the nonlinear properties of macromolecules as such have hitherto not been subjected to investigation, and notwithstanding some appeals for a systematic study of nonlinear optical effects in polymers and colloids (we have in mind particularly electric anisotropy and optical birefringence induced by laser light[160] as well as nonlinear Rayleigh and Raman scattering[161]), no communications announcing experimental results are as yet available.

6. SOLID DIELECTRICS

We shall restrict the discussion of solid dielectrics chiefly to ferroelectric crystals. Their physical properties have of late been reviewed by Nettleton[162] as well as at the VII-th Soviet Union Conference on Ferroelectrics in 1970[163] and in various papers on electron and ionic motion and order–disorder in ferroelectrics,[164] nonlinear coloration effects and optical gap of $BaTiO_3$,[165] as well as electro–optical and photo-elastic behaviour[166] and laser-irradiation-induced damage in $LiNbO_3$ and KDP.[167,168] Ferroelectrics are noteworthy among solid dielectrics for their high electric permittivity, strong piezo-effect, dielectric hysteresis loop, interesting electro–optical properties and truly astounding nonlinear optical effects. In fact, it is due to the discovery of lasers and the subsequent growth of quantum electronics that we now are in an excellent position to proceed to the most varied studies of the nonlinear optical

properties of ferroelectric crystals, which have already found application in nonlinear optical systems, modulators of coherent light, multipliers and frequency mixers, parametric optical generators, and a number of modern opto-electronic devices.[169,170] These many-sided uses of ferroelectrics have, at the same time, stimulated the development of the physics of ferroelectrics in recent years. The optical structure of previously known ferroelectrics has been investigated in greater detail, and numerous new classes of these compounds have been discovered revealing a wide range of crystallographical structure (e.g. that of potassium-tungstene bronze) and chemical composition. Nonlinear theories have been worked out in a phenomenological–thermodynamical and (at least basic) microscopic approach. In particular, attempts have been made to deal with optical nonlinearities as a result of changes in the band structure of the crystal under the influence of electromagnetic fields. In many a case it is useful to resort to the model of an anharmonic oscillator, where the potential energy U of the vibrating ion of the crystal is given by the expression:

$$U = A_2 r^2 + A_4 r^4 + A_6 r^6 + \ldots \qquad (38)$$

with r denoting the displacement of the ion with respect to the centre of the elementary cell, A_2 the coefficient of harmonic elastic vibrations, and A_4 and A_6 the anharmonicity factors.

The electro–optical properties of a dielectric are quite generally rendered by the following polarization tensor:

$$\Delta a_{ij} = r_{ijk} E_k + R_{ijkl} E_k E_l + \ldots \qquad (39)$$

the first term describing the previously discussed linear electro–optical effect (14), whose presence is restricted to crystals without a centre of symmetry, and the second term with the fourth-rank tensor R_{ijkl} describing the quadratic electro–optical effect, which can occur in any dielectric (including liquids, where one has Kerr's effect). The two effects have been studied theoretically and experimentally, leading to the conclusion that BO_6 octahedra play the major rôle in $LiNbO_3$ and $LiTaO_3$ as well as in the structurally related tungstene bronze and perovskite oxygen-octahedra ferroelectrics.[70,166] The BO_6 octahedra are moreover essential to second-harmonic generation in oxygen-octahedra ferroelectrics (of the ABO_3 type) i.e. to nonlinear optical susceptibility of order 2.[100]

Investigation of the temperature-dependence of the linear as well as of the nonlinear optical properties of ferroelectrics provide new information

on the solid-state phase transitions. In crystals apt to undergo a phase transition of the first kind (thus, $BaTiO_3$[84]), a steep fall to zero of the nonlinear optical susceptibility tensor elements is observed in the Curie point. The temperature-dependence of this tensor can be written in the form of the following expansion:[84]

$$\chi_{ijk}^{2\omega}(T) = \chi_{ijk}^{2\omega}(0) + \chi_{ijkl}^{2\omega} P_{sl}(T) + \ldots, \qquad (40)$$

where $\chi_{ijk}^{2\omega}(0)$ defines the nonlinear optical susceptibility — a temperature-independent characteristic of the paraelectric phase. The change in nonlinear susceptibility in going through the phase transition is described by the second term in (40), $P_s(T)$ being the temperature-dependent spontaneous electric polarization.

Thus, in view of what has been said, the phenomenon of optical harmonics production, and in particular that of SHG, is intimately related with the structure of the ferroelectric crystal. The effect itself has come to be a very useful tool for the study of the nonlinear optical properties of solid dielectrics and of their phase transitions. However, we gain information on the nonlinear properties of ferroelectrics (see the list in Table IV) not only from SHG studies but in particular from parametric scattering of intense light[171] as well as d.c. electric field-induced SHG[93] and acoustically induced SHG in elastic anisotropic dielectrics.[172]

When the intensity of laser light incident on an essentially nonabsorbing material is too high, the interaction between the light wave and the material can cause either surface damage or damage within the volume (internal damage). Also, e.g. when an $LiNbO_3$ or $LiTaO_3$ crystal is irradiated with a high-intensity laser beam, the latter is distorted on transmission owing to optically induced refractive index inhomogeneities. This effect, known as 'optical damage', occurs in other materials too. Although methods are available for the limiting of the degree of index inhomogeneity, we as yet but imperfectly understand the mechanism underlying it and the processes leading to its limitation.[167,168] It is currently believed that the damage results from the migration of charged carriers from the illuminated region and their subsequent trapping beyond. It would appear that the conductivity of the trapping sites of the crystal are modified by the presence of hydrogen in such a way that the resulting inhomogeneity is minimized. There can, however, be no doubt but that laser-induced damage depends both on the nature of the pulse beam and that of the ferroelectric crystal itself.

Parameters necessary for characterizing a pulse of laser light are:[167] the wave length and spectral width, energy and pulse duration, transverse mode pattern and longitudinal mode content, transverse dimension at the surface, position of focal point (if any) or beam waist, polarization state, and pulse repetition rate. Parameters characterizing the crystal are: species, technology of growth (including purity considerations), presence of twinning, ferroelectric domain structure, surface (cleaved or polished), surface quality (smoothness, flatness, cleanliness), mutual orientation of crystallographical axes and light beam vectors k and E, temperature, and ambient atmosphere.

To be suitable for nonlinear optics, a crystal has to be highly homogeneous and should be of good optical quality. Since the break-up into domains renders ferro- and anti-ferroelectric crystals unfit for optical use below the Curie point, one generally resorts to crystals in the paraelectric phase (thus, KDP and ADP). Certain ferroelectrics ($LiNbO_3$) can be obtained in the ferroelectric phase in the form of single-domain crystals and can be used successfully below the Curie point also. Crystals of high optical quality are: ferroelectric KDP, Ba_2-$NaNb_5O_{15}$, $LiNbO_3$, etc. They have to be free of optical and electric domains as well as of cracks, low strain, physical surface damage or bulk index inhomogeneity, and have to possess chemical stability over a reasonably wide temperature range and atmospheric conditions, as well as mechanical hardness and ease of polish. Considering that the crystals, already answering the above-stated exceptionally strong optical demands, have to be available in the form of large single crystals, we get an idea of the costs of their production. In this situation the powder method of studying the nonlinear optical properties of ferroelectrics[80] gains in importance. It is cheap and, at the same time, simple.

Our knowledge of the structure and anisotropic properties of ferroelectrics[162,163,173] has recently gained much by nonlinear susceptibility studies in the optical[99,100,174] and microwave[175] ranges. New methods of measuring the nonlinear susceptibilities of ferroelectrics as functions of temperature,[176] relative methods of measuring nonlinearities,[177] and methods for the determination of the sign and absolute values of nonlinear susceptibilities have been proposed.[89,91] The rôle of hydrogen in polarization reversal of ferroelectrics[178] and the dependence of second-harmonic generation of $LiNbO_3$ on melt composition have

been studied.[179] Procedures for the nondestructive testing of the elastic properties of ferroelectric thin films by harmonic generation of dispersive Rayleigh waves[180] have been worked out. Also, investigations have been made of phase transitions in ferroelectrics as a result of interactions between the soft optic mode and acoustic phonons.[181] These studies have contributed largely to recent theories of phase transitions in ferroelectrics,[182,183] the theory of piezoelectricity,[184] and that of Raman scattering in dielectric crystals.[185]

A significant problem of nonlinear ferroelectrics optics is the validity of Kleinman's symmetry conjecture[67] that the susceptibility tensor χ_{ijk} relating the nonlinear dielectric polarization of very transparent crystals and the electric field of the laser beam are symmetric with respect to any rearrangement of the indices i, j, k. These Kleinman relations reduce for a given material and appropriate conditions the number of independent elements of the tensor χ_{ijk}. In the general case when nonlinear dispersion is present, Kleinman's relations are not fulfilled, and one can observe second harmonic generation where it is normally forbidden.[186] Recently, too, the theoretical and experimental conditions for second harmonic generation have been discussed in more detail.[187] Infrared difference-frequency generation has also been produced in $LiNbO_3$ using a tunable dye laser,[188] as well as far-infrared generation by picosecond light pulses.[189] UV light emission by the second harmonic of a dye laser has been observed.[190] Nonlinear susceptibilities, parametric gain, and oscillation conditions for three- and four-wave interactions have been studied.[191] Since research of this kind calls for new nonlinear materials,[192,193] the class of known ferroelectrics and piezoelectrics has undergone a rapid enlargement.

All in all, the processes of generation of optical harmonics, laser wave frequency mixing, multiharmonic scattering, optical rectification and optically induced birefringence provide novel, highly promising methods for the investigation of isotropic as well as anisotropic dielectrics, namely their nonlinear optical dispersion and nonlinear susceptibilities, and for determining their microscopic and macroscopic symmetries and the relations between them. Although hardly 10 years have elapsed since the discovery of these methods, they have already contributed to the establishing of new branches of physics: nonlinear molecular optics,[37,194] nonlinear crystallo-optics and nonlinear optical spectroscopy of fluids[158] and solids.[195]

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