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Squeezing in second-harmonic generation

Structure of the nonlinear medium, phase-matching conditions and polarization dependences†

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Abstract. The production of squeezed states in second-harmonic generation is discussed theoretically from the viewpoint of the structure of the nonlinear medium, phase-matching conditions, and the polarization state of the fields. The nonlinear coupling constants are derived in explicit form for all 102 magnetic symmetry groups for crystalline as well as electrically polarized isotropic media. The phase-matching conditions are discussed in detail. Phase mismatch is shown to accumulate along the optical path, and is calculated in full detail for various media and geometries. We refer to this as the mismatch accumulation effect. General formulae for normally ordered variances of the second-harmonic and fundamental fields are derived by perturbative procedure, and are specified for some special cases of practical interest.

1. Introduction

In recent years the problem of production of squeezed states of light has become a challenge to both theorists and experimenters working in the field of quantum optics [1]. Such states are characterized by reduced quantum fluctuations in one quadrature component of the field at the expense of increased fluctuations in the other non-commuting component. As expected, this new quantum effect should manifest itself in optical processes in which the nonlinear response of the system to the optical signal plays an important role. Theoretical predictions have shown that squeezing of quantum fluctuations can occur in a variety of nonlinear optical phenomena, in particular four-wave mixing [2–4], parametric amplification [5, 6], harmonics generation [7–12], multiphoton absorption [13, 14] and nonlinear propagation of light [11, 15]. These theoretical predictions have stimulated intensive experimental studies aimed at observations of squeezed states in a hitherto restricted number of nonlinear processes [16–20]. As experimental research is under way and many technical problems have already been overcome, there is a need for the explicit form and numerical values of the coupling constants occurring in the effective Hamiltonians [21, 22]. A more detailed description of the nonlinear medium used for generation of squeezed states and of the conditions (phase-matching, polarization of the exciting field, etc.) is also needed.

In this paper we discuss in detail the problem of squeezing in second-harmonic generation in crystals as well as in isotropic media subjected to a d.c. electric field. Second-harmonic generation is allowed in the electric-dipole approximation only in

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a medium without a centre of inversion. For isotropic media with a centre of symmetry, second-harmonic generation is forbidden in the electric-dipole approximation and becomes allowed in the electric-quadrupole and magnetic-dipole approximation [23].

The intensity of the second harmonic generated via multipolar mechanisms, however, is much smaller than that generated via the electric-dipole mechanism. In order to increase the intensity of the second harmonic the centrosymmetric medium has to be placed in a d.c. electric field [24] which lowers its symmetry (removes the centre of inversion). If the medium (a gas or liquid) consists of individual polar molecules the d.c. electric field, depending on its strength, aligns the polar molecules partially [25] or completely (electric saturation) [26]. Such molecular reorientation can be described within the framework of Boltzmann statistics enabling us to express the nonlinear coupling constants in terms of the molecular rotational invariants. The latter will be tabulated in the present work for all magnetic point groups of molecular symmetry. The effective Hamiltonian contains, in general, six different terms describing couplings between the various polarization components of the fundamental and second-harmonic beams. Each term has, moreover, its own phase-mismatch function, and the resulting mismatch functions that appear in our squeezing formulae are different from those known for the intensity of the generated beam. We shall give here general formulae for squeezing in both the fundamental and generated beams that are valid for crystals as well as for molecular systems in a d.c. electric field. Our formulae allow also for the appropriate choice of particular configurations of the polarization states of the two beams.

2. Effective Hamiltonian and equations of motion

Second-harmonic generation is a well known nonlinear optical phenomenon, its semi-classical description is a standard subject of textbooks on nonlinear optics [27–30]. A strong electric field of optical frequency ω induces, in the nonlinear medium, a polarization of frequency 2ω which in turn is the source of a field of frequency 2ω (second harmonic). The second-harmonic beam is coupled back to the fundamental beam, so that energy is transferred from the fundamental beam to the second-harmonic beam and back, depending on the phase relations between the two fields. The nonlinear polarization at frequency 2ω can be written as follows [27–30]:

$$P_i(2\omega)=\sum_{jk}\chi_{ijk}(-2\omega,\omega,\omega)E_j^{(+)}(\omega)E_k^{(+)}(\omega), \tag{1}$$

and the polarization at frequency ω induced by the field of frequency 2ω as

$$P_i(\omega)=\sum_{jk}\chi_{ijk}(-\omega,2\omega,-\omega)E_j^{(+)}(2\omega)E_k^{(-)}(\omega), \tag{2}$$

where $\chi_{ijk}(-2\omega,\omega,\omega)$ is the tensor of the second-order nonlinear susceptibility of the medium in the electric-dipole approximation, the explicit quantum-mechanical form of which is well known in the literature [27–30]. For non-dissipative media the following relation holds [30]:

$$\chi_{ijk}(-\omega,2\omega,-\omega)=2\chi_{jik}(-2\omega,\omega,\omega), \tag{3}$$

where the two susceptibility tensors are real. The electromagnetic field is assumed to be the sum of plane waves

$$\mathbf{E}^{(+)}(\mathbf{r},t)=\sum_j \mathbf{E}^{(+)}(\mathbf{k}_j,\omega_j)\exp\left[-\mathrm{i}(\omega_j t-\mathbf{k}_j\cdot\mathbf{r})\right], \tag{4}$$

and the intensity of the beam of frequency ω is given by

$$I(\omega)=\frac{cn(\omega)}{2\pi}|\mathbf{E}^{(+)}(\omega)|^2, \tag{5}$$

with $n(\omega)$ the refractive index of the medium for the frequency ω.

Using the slowly varying amplitude approximation, one obtains from the Maxwell equations the following equations for the amplitudes of the second-harmonic and fundamental fields [30]:

$$\left.\begin{aligned}\frac{\mathrm{d}E_i^{(+)}(2\omega)}{\mathrm{d}z}&=\frac{\mathrm{i}2\pi(2\omega)^2}{k^i(2\omega)c^2}\sum_{jk}\chi_{ijk}\Phi-2\omega,\omega,\omega)E_j^{(+)}(\omega)E_k^{(+)}(\omega)\\&\quad\times\exp\left(\mathrm{i}\Delta k^{ijk}z\right),\\\frac{\mathrm{d}E_i^{(+)}(\omega)}{\mathrm{d}z}&=\frac{\mathrm{i}4\pi\omega^2}{k^i(\omega)c^2}\sum_{jk}\chi_{jik}(-2\omega,\omega,\omega)E_j^{(+)}(2\omega)E_k^{(-)}(\omega)\\&\quad\times\exp\left(-\mathrm{i}\Delta k^{jik}z\right),\end{aligned}\right\} \tag{6}$$

where in deriving the second equation we have made use of the relation (3). We have assumed that both beams propagate in the z-axis direction of the laboratory reference frame and that the fields have two polarization components x and y. The propagation vectors have the values: $k^i(2\omega)=n_i(2\omega)2\omega/c$, $k^i(\omega)=n_i(\omega)\omega/c$, where $n_i(2\omega)$ and $n_i(\omega)$ are the refractive indices for the field component i of frequency 2ω and ω, respectively. We hope that the double use of i as the imaginary unit and as the Cartesian component will not lead to misunderstanding. The phase mismatch is defined by

$$\Delta k^{ijk}=\frac{\omega}{c}[-2n_i(2\omega)+n_j(\omega)+n_k(\omega)]. \tag{7}$$

Equations (6) are general classical equations describing the second-harmonic generation process. They include all possible combinations of the field components and all possible mismatch values Δk^{ijk}. The nonlinear susceptibility tensor $\chi_{ijk}(-2\omega,\omega,\omega)$ is defined in the laboratory reference frame and the fields are classical.

To describe quantum effects such as squeezing we need equations for quantum fields, i.e. equations for field operators. Such equations can be obtained as Heisenberg equations from the following effective-interaction Hamiltonian

$$H_1=\hbar\sum_{ijk}[g_{ijk}(z)b_i^\dagger a_j a_k+\mathrm{h.c.}], \tag{8}$$

where the nonlinear coupling constants $g_{ijk}(z)$ are given by

$$g_{ijk}(z)=\frac{2\pi\omega}{n_i(2\omega)n_i(\omega)n_k(\omega)}\left(\frac{4\pi\hbar\omega}{V}\right)^{1/2}\chi_{ijk}(-2\omega,\omega,\omega)\exp\left(\mathrm{i}\Delta k^{ijk}z\right), \tag{9}$$

with V denoting the quantization volume, which in this case is equal to the volume of the nonlinear medium where the two beams interact. In the interaction Hamiltonian (8), the operators a_x, a_y are the annihilation operators for the two modes of the fundamental beam with polarizations along the x and y axes, and b_x, b_y are the operators for the two polarizations of the second-harmonic beam. The annihilation and creation operators satisfy the commutation rules

$$[a_i, a_j^\dagger] = [b_i, b_j^\dagger] = \delta_{ij}. \tag{10}$$

Introducing quantized fields we should replace the classical fields by

$$E_i^{(+)}(\omega) = \mathrm{i}\left(\frac{2\pi\hbar\omega}{n_i^2(\omega)V}\right)^{1/2} a_i. \tag{11}$$

There are eight terms in the interaction Hamiltonian (8). Since $a_x a_y = a_y a_x$ however, the number of different combinations of the field operators reduces to six.

Using the interaction Hamiltonian given by (8) and the commutation rules (10) one obtains the time evolution of the field operators (the Heisenberg equations of motion). On replacing the time t by $-nz/c$, where the refractive index n should be chosen appropriately with respect to the field operator (for example, $n_x(2\omega)$ for b_x, etc.), we obtain the following equations:

$$\left.\begin{aligned} \frac{\mathrm{d}b_i(z)}{\mathrm{d}z} &= \frac{\mathrm{i}n_i(2\omega)}{c}\sum_{jk} g_{ijk}(z)a_j(z)a_k(z), \\ \frac{\mathrm{d}a_i(z)}{\mathrm{d}z} &= \frac{\mathrm{i}2n_i(\omega)}{c}\sum_{jk} g_{jik}^*(z)a_k^\dagger(z)b_j(z), \end{aligned}\right\} \tag{12}$$

where again $i,j,k = x,y$. The equations for the creation operators are Hermitian conjugates of the equations (12). We thus have a system of eight coupled equations. On applying the relation (11), equations (12) go over into the equations (6) for classical fields. The equations (12), however, are operator equations that can be used to describe all quantum effects related with the non-commutability of the field operators (quantum fluctuations). Squeezing is just an effect of this kind. It will be the subject of our present considerations.

3. General solution for squeezing effect and mismatch accumulation

The system of equations (12) does not allow for a closed analytical solution. To cope with it, some approximations are needed. Equations (12) can be integrated formally, giving

$$\left.\begin{aligned} b_i(z) &= b_i(0) + \frac{\mathrm{i}n_i(2\omega)}{c}\sum_{jk}\int_0^z g_{ijk}(z')a_j(z')a_k(z')\,\mathrm{d}z', \\ a_i(z) &= a_i(0) + \frac{\mathrm{i}2n_i(\omega)}{c}\sum_{jk}\int_0^z g_{jik}^*(z')a_k^\dagger(z')b_j(z')\,\mathrm{d}z'. \end{aligned}\right\} \tag{13}$$

In the above form, equations (13) are easy to iterate, and a solution of given order in the coupling constants g_{ijk} can be obtained. This iterative procedure can be stopped short at the lowest non-vanishing term whenever the intensity of the second harmonic is much smaller than the intensity of the incoming beam. One has to keep in mind however that equations (13) are still operator equations and that the ordering

of the operators must be preserved in the iterative calculations. The observable physical quantitities are mean values of the operators over the initial state of the field. For example if the second-harmonic beam is initially (i.e. for $z=0$) in the vacuum state $|0\rangle$ such that $b_i(0)|0\rangle=0$, the intensity of the second harmonic is given by

$$\langle b_i^\dagger(z)b_i(z)\rangle=\left(\frac{n_i(2\omega)}{c}\right)^2\sum_{jklm}\langle a_j^\dagger(0)a_k^\dagger(0)a_l(0)a_m(0)\rangle \times\int_0^z g_{ijk}^*(z')\,\mathrm{d}z'\int_0^z g_{ilm}(z')\,\mathrm{d}z', \tag{14}$$

where the integrations over z' account for the phase mismatch along the path z in the nonlinear medium. Each integration can be performed explicitly, giving

$$\int_0^z g_{ijk}(z')\,\mathrm{d}z'=g_{ijk}(0)zf_1(\Delta k^{ijk}z), \tag{15}$$

where

$$f_1(x)=\frac{\exp(\mathrm{i}x)-1}{\mathrm{i}x},\quad f_1(0)=1. \tag{16}$$

If there is only one polarization component, say x, of the incoming beam and if we measure the x component of the second harmonic, then there is only one term on the right-hand side of equation (14) and we obtain the well known result for the intensity of the second harmonic with

$$|f_1(\Delta kz)|^2=\sin^2\frac{\Delta kz}{2}\Big/\left(\frac{\Delta kz}{2}\right)^2.$$

Generally, the summations in equation (14) are over the x and y components and include all contributions to the ith component of the second harmonic.

To answer the question whether squeezed states of light can be produced in the second-harmonic generation process, one has to calculate the normally ordered variances of the in-phase and/or out-of-phase quadrature components of the fields outgoing from the medium. Assuming that for $z=0$ the second-harmonic field was in the vacuum state and the incoming fundamental beam was in a coherent state, one obtains from equations (13) and the commutation relations (10) the following results:

$$\begin{aligned}\langle :[\Delta(a_i(z)+a_i^\dagger(z))]^2: \rangle &=\langle a_i^2(z)\rangle+\langle a_i^{\dagger 2}(z)\rangle+2\langle a_i^\dagger(z)a_i(z)\rangle-\langle a_i(z)\rangle^2\\ &\quad-\langle a_i^\dagger(z)\rangle^2-2\langle a_i^\dagger(z)\rangle\langle a_i(z)\rangle\\ &=-\frac{2n_i(\omega)}{c^2}\sum_{jkl}n_j(2\omega)\langle a_k(0)a_l(0)\rangle\\ &\quad\times\int_0^z g_{jil}^*(z')\int_0^z g_{jkl}(z'')\,\mathrm{d}z''\,\mathrm{d}z'+\text{c.c.},\end{aligned} \tag{17}$$

$$\langle :[\Delta(b_i(z)+b_i^{\dagger}(z))]^2: \rangle$$
$$= \frac{8n_i(2\omega)}{c^4} \sum_{jklmpqr} n_k(\omega) n_l(2\omega) \langle a_j(0) a_p(0) a_q(0) a_r(0) \rangle$$
$$\times [n_i(2\omega) \int_0^z q_{ijk}(z') \int_0^{z'} g_{lkm}^{*}(z'') \int_0^{z''} g_{lpq}(z''')\, dz'''\, dz''\, dz'$$
$$\times \int_0^z g_{imr}(z')\, dz' - n_m(\omega) \int_0^z g_{ijk}(z') \int_0^{z'} g_{lkm}^{*}(z'')$$
$$\times \int_0^{z''} g_{lpq}(z''')\, dz''' \int_0^{z''} g_{imr}(z''')\, dz'''\, dz''\, dz' \Big] + \text{c.c.} \qquad (18)$$

The solutions (17) and (18) are general solutions obtained by retaining the first non-vanishing order terms only. Comparing (17) and (18) to (14) it is easily seen also that the phase-mismatch functions in the variances (17) and (18) are different from those in the intensity (14). Noteworthy is the phase-mismatch-accumulation effect in the variances. One could expect it to occur since the two variances are phase-dependent quantities and in this respect differ essentially from the intensity, which is phase independent. All integrations can be performed explicitly and similarly to (15). We obtain

$$\langle :[\Delta(a_i(z)+a_i^{\dagger}(z))]^2: \rangle = -\frac{z^2 n_i(\omega)}{c^2} \sum_{jkl} n_j(2\omega)$$
$$\times g_{jii}(0) q_{jkl}(0) [\alpha_k \alpha_l f_2(-\Delta k^{jii} z, \Delta k^{jkl} z) + \text{c.c.}], \qquad (19)$$

$$\langle :[\Delta(b_i(z)+b_i^{\dagger}(z))]^2: \rangle = \frac{4z^4 n_i(2\omega)}{3c^4} \sum_{jklmpqr} n_k(\omega) n_l(2\omega)$$
$$\times g_{ijk}(0) g_{lkm}(0) g_{lpq}(0) g_{imr}(0)$$
$$\times \Big\{ \alpha_j \alpha_p \alpha_q \alpha_r \Big[n_i(2\omega) f_3(\Delta k^{ijk} z, -\Delta k^{lkm} z, \Delta k^{lpq} z) f_1(\Delta k^{imr} z)$$
$$- \frac{n_m(\omega)}{2} f_4(\Delta k^{ijk} z, -\Delta k^{lkm} z, \Delta k^{lpq} z, \Delta k^{imr} z) \Big] + \text{c.c.} \Big\}, \qquad (20)$$

where the α_i $(i = x, y)$ are complex amplitudes of the incident beam obtained on taking the quantum-mechanical mean value in the coherent state of the incoming field. The mismatch functions f_2, f_3 and f_4 are

$$f_2(x_2, x_1) = -\frac{2\mathrm{i}}{x_1} [f_1(x_2 + x_1) - f_1(x_2)], \qquad (21)$$

$$f_3(x_3, x_2, x_1) = -\frac{3\mathrm{i}}{x_1} [f_2(x_3, x_2 + x_1) - f_2(x_3, x_2)] \qquad (22)$$

$$f_4(x_4, x_3, x_2, x_1) = -\frac{6\mathrm{i}}{x_1 x_2} [f_2(x_4, x_3 + x_2 + x_1)$$
$$- f_2(x_4, x_3 + x_2) - f_2(x_4, x_3 + x_1) + f_2(x_4, x_3)] \qquad (23)$$

with the $f_1(x)$ defined by equation (16). For comparison, in the intensity (14) the mismatch function has the form

$$f_1(-x_2)f_1(x_1)=\tfrac{1}{2}[f_2(-x_2,x_1)+f_2(x_1,-x_2)]. \tag{24}$$

All the functions f_1–f_4 are defined in such a way as to become unity when all their arguments tend to zero. The parameters Δk^{ijk} are defined in equation (7). So, in the general case when all Δk^{ijk} are different from zero we have a rather complicated behaviour of the variances (19) and (20) along the path z in the nonlinear medium. Nevertheless, our formulae cover all the complications that may arise in the production of squeezed states in second-harmonic generation. Whenever the variances (19) or (20) become negative we have squeezing in a particular component of the fundamental or the second-harmonic beam. Our formulae also include all possible combinations of the polarizations of the two beams. The complex amplitudes α_i can be written as $\alpha_i=|\alpha_i|\exp(i\phi_i)$ with the real amplitude $|\alpha_i|$ and phase ϕ_i. The proper choice of the initial phase of the incoming field can simplify considerably the formulae (19) and (20). For $\phi_x=\phi_y=0$ only the real parts of the mismatch functions remain and it is evident from (19) that the in-phase components of the fundamental beam are squeezed. A shift in phase by $\pi/2$ changes the in-phase components into the out-of-phase components. A shift in phase between the x and y components allows for circular polarization of the incoming beam. We should also keep in mind that the coupling constants $g_{ijk}(0)$, which are directly related to the nonlinear susceptibility tensor $\chi_{ijk}(-2\omega,\omega,\omega)$ are so far defined in the laboratory reference frame. The components of this tensor should still be expressed by the corresponding components in the crystallographical reference frame (for crystals) or by the molecular parameters (for molecular media). Some special cases will be discussed in § 4.

4. Some special cases

4.1. *Crystalline media*

The most popular nonlinear media used to generate the second harmonic are uniaxial crystals. The crystals KDP and ADP are probably the best known examples of this class. A nice feature of such crystals is the possibility of finding a direction of propagation for which one of the $\Delta k^{ijk}=0$ and phase matching conditions are met. For optically negative crystals i.e. such that $n_e(\omega)-n_0(\omega)<0$ (which is usually the case) there are two possible types of synchronism [30]: type I (oo*e*) and type II (o*ee*). Type-I synchronism means that two ordinary components of the fundamental beam produce an extraordinary component of the second harmonic. Type II means that one ordinary and one extraordinary component of the fundamental beam produce an extraordinary component of the second harmonic. If we choose our laboratory reference frame in such a way that the x component be ordinary and the y component extraordinary, Type-I phase matching means $\Delta k^{yxx}=0$ and type II means $\Delta k^{yyx}=0$. In the case of perfect phase matching one can retain in equations (19) and (20) only one term, i.e. that term for which phase matching is satisfied. This gives us for type I ($\Delta k^{yxx}=0$) the conditions

$$\langle :[\Delta(a_x(z)+a_x^\dagger z))]^2:\rangle=-\frac{2z^2n_x^2(\omega)}{c^2}g_{yxx}^2(0)|\alpha_x|^2\cos 2\phi_x, \tag{25}$$

$$\langle :[\Delta(b_y(z)+b_y^\dagger(z))]^2:\rangle=\frac{4z^4n_y^4(2\omega)}{3c^4}g_{yxx}^4(0)|\alpha_x|^4\cos 4\phi_x. \tag{26}$$

Table 1. The components $\chi_{i(jk)}(-2\omega;\omega,\omega)$ of the susceptibility tensor for all 102 magnetic classes.

Magnetic class	Components $\chi_{i(jk)}(-2\omega;\omega,\omega)$					
	$\chi_{yyy}(-2\omega;\omega,\omega)$	$\chi_{yxx}(-2\omega;\omega,\omega)$	$\chi_{xxy}(-2\omega;\omega,\omega)$	$\chi_{xxx}(-2\omega;\omega,\omega)$	$\chi_{xyy}(-2\omega;\omega,\omega)$	$\chi_{yyx}(-2\omega;\omega,\omega)$
1	a_1	$b_1+b_2+b_3$	$c_1+c_2+c_3$	$d_1+d_2+d_3$	$e_1+e_2+e_3$	$f_1+f_2+f_3$
2, *2*	0	b_1+b_2	c_1+c_2	d_1+d_2	e_1+e_2	f_1+f_2
m, *m*	a_1	b_3	c_3	d_3	e_3	f_3
222, *222*	0	b_2	c_2	d_2	e_2	f_2
mm2, *mm2*, *2mm*	0	b_1	c_1	d_1	e_1	f_1
4, *4*, 6, *6*, ∞	0	b_4	$-\frac{1}{2}b_4$	d_4	e_4	f_4
$\bar{4}$, $\bar{4}$	0	b_5+b_6	$\frac{1}{2}(b_5+b_7+b_6+b_8)$	$d_5+d_6+d_7$	e_2+e_5	f_5+f_6
422, *422*, *422*, 622, *622*, *622*	0	b_4	$-\frac{1}{2}b_4$	0	0	0
4mm, *4mm*, *4mm*, 6mm, *6mm*, *6mm*, ∞m, ∞m	0	0	0	d_4	e_4	f_4
$\bar{4}$2m, $\bar{4}2m$, $\bar{4}$m2, $\bar{4}2m$	0	b_6	$\frac{1}{2}(b_6+b_8)$	d_6+d_7	e_2	f_6
3,	a_2+a_3	$(a_2+a_3)\cos^2\theta+b_4$	$(a_2+a_3)\cos^2\theta-\frac{1}{2}b_4$	$d_4+d_8+d_9$	$e_4+e_7+e_8$	$f_4+e_7+e_8$
32, *32*	a_3	$b_4+a_3\cos^2\theta$	$-\frac{1}{2}b_4+a_3\cos^2\theta$	d_9	e_8	e_8
3m, *3m*	a_2	$a_2\cos^2\theta$	$a_2\cos^2\theta$	d_4+d_8	e_4+e_7	f_4+e_7
$\bar{6}$, $\bar{6}$,	a_2+a_3	$(a_2+a_3)\cos^2\theta$	$(a_2+a_3)\cos^2\theta$	d_8+d_9	e_7+e_8	e_7+e_8
$\bar{6}$m2, $\bar{6}2m$, $\bar{6}$m2, $\bar{6}m2$	a_2	$a_2\cos^2\theta$	$a_2\cos^2\theta$	d_8	e_7	e_7
23, $\bar{4}$3m, $\bar{4}3m$,	0	b_6	b_6	$\frac{3}{2}d_6$	f_6	f_6

In the remaining classes $\bar{1}$, $\bar{1}$, 2/m, *2*/m, 2/*m*, *2*/*m*, mmm, *mm*m, *mmm*, mm*m*, 4/m, *4*/m, 4/*m*, *4*/*m*, 4/mmm, *4*/mm*m*, 4/m*mm*, 4/*mm*m, 4/*mmm*, $\bar{3}$, *$\bar{3}$*, $\bar{3}$m, $\bar{3}m$, *$\bar{3}$m*, 6/m, *6*/m, 6/*m*, *6*/*m*, 6/mmm, *6*/mm*m*, 6/m*mm*, 6/*mmm*, 6/*m*mm, *6*/m*mm*, m3, *m*3, 432, *432*, m3m, *m*3m, m3*m*, *m*3*m*, ∞/m, ∞/m, ∞/mm, ∞/mm, ∞/m*m*, Y, K, Y_h, K_h all the components vanish.

with

$b_4=\sin 2\theta\,\chi_{XYZ}$,

$d_4=-\sin^3\theta\,\chi_{ZZZ}-\cos^2\theta\sin\theta\,(2\chi_{XXZ}+\chi_{ZXX})$,

$e_4=-\sin\theta\,\chi_{ZXX}$,

$f_4=-\sin\theta\,\chi_{XXZ}$,

$b_5=\sin 2\theta\sin 2\phi\,\chi_{XXZ}$, $b_6=-\sin 2\theta\cos 2\phi\,\chi_{XYZ}$, $b_7=\sin 2\theta\sin 2\phi\,\chi_{ZXX}$,

$b_8=-\sin 2\theta\cos 2\phi\,\chi_{ZXY}$,

$d_5=-\cos^2\theta\sin\theta(2\chi_{XXZ}+\chi_{ZXX})$, $d_6=-2\cos^2\theta\sin\theta\sin 2\phi\,\chi_{XYZ}$, $d_7=-\cos^2\theta\sin\theta\sin 2\phi\,\chi_{ZXY}$,

$e_5=\sin\theta\cos 2\phi\,\chi_{ZXX}$,

$f_5=\sin\theta\cos 2\phi\,\chi_{XXZ}$, $f_6=\sin\theta\sin 2\phi\,\chi_{XYZ}$,

$a_2=-\sin\phi\,(4\cos^2\phi-1)\,\chi_{XXX}$, $a_3=-\cos\phi\,(4\cos^2\phi-3)\,\chi_{YYY}$,

$d_8=\cos^3\theta\cos\phi\,(4\cos^2\phi-3)\,\chi_{XXX}$, $d_9=-\cos^3\theta\sin\phi\,(4\cos^2\phi-1)\,\chi_{YYY}$,

$e_7=-\cos\theta\cos\phi\,(4\cos^2\phi-3)\,\chi_{XXX}$, $e_8=-\cos\theta\sin\phi\,(4\cos^2\phi-1)\,\chi_{YYY}$.

Equations (25) and (26) reproduce the results already known in the literature [7–11]. It is seen from equation (19) that type-II synchronism ($\Delta k^{yyx} = \Delta k^{yxy} = 0$) cannot be used to produce squeezed states in the fundamental beam. For the harmonic beam we have

$$\langle : [(b_y(z) + b_y^\dagger(z))]^2 : \rangle = \frac{8z^4 n_y^2(2\omega)[n_x^2(\omega) + n_y^2(\omega)]}{3c^4} g_{yyx}^4(0)|\alpha_x|^2|\alpha_y|^2 \cos 2(\phi_x + \phi_y), \quad (27)$$

and squeezing can be obtained with the proper choice of ϕ_x and ϕ_y. It is also seen from (25)–(27) that for circular polarization of the incoming beam and for type-I phase matching one half of the incoming intensity will not be effective while for type-II synchronism the total intensity will be effective in producing squeezed states. The coupling constants $g_{yxx}(0)$ and $g_{yyx}(0)$ are defined in the laboratory reference frame, and to make the above formulae applicable to crystals of various symmetry classes the susceptibility tensors defining the coupling constants have to be transformed into the crystallographical coordinate system (see the Appendix). If the phase matching conditions are not satisfied there is no single dominant term contributing to the variances. In this case it is still possible to obtain squeezing, but all contributions must be added according to equations (19) and (20). Some simplifications can be achieved owing to the symmetry of the crystal, as is seen from table 1.

4.2. *Weakly oriented molecular media*

It has been shown some time ago that molecular media placed in a d.c. electric field can be sources of second-harmonic generation [26, 29]. In the classical statistical-molecular approach the macroscopic tensor of nonlinear susceptibility can be written as [26]

$$\chi_{ijk}(-2\omega, \omega, \omega; \mathbf{E}^0) = \rho \int (\beta_{ijk}^{2\omega} + \gamma_{ijkl}^{2\omega} \mathbf{E}_l^0 + \ldots) f(\Omega, \mathbf{E}^0)\, \mathrm{d}\Omega, \quad (28)$$

where $\rho = N/V$ denote the number density of molecules whose orientation Ω with respect to the d.c. field vector $\mathbf{E}^0$ is given by the classical distribution function $f(\Omega, \mathbf{E}^0)$.

In the expansion (28) the tensor $\beta_{ijk}^{2\omega}$ describes the second-order nonlinear polarizability of the molecules. The variation of this tensor owing to the d.c. field is described by the tensor $\gamma_{ijkl}^{2\omega}$. The frequency dependence of the two hyperpolarizability tensors can be derived from the classical Lorentz–Voigt theory or quantum-mechanically using the Kramers–Heisenberg formulae [27–31].

If the molecules are polar and have a permanent electric-dipole moment $\boldsymbol{\mu}$, then in a linear approximation with respect to the static field $\mathbf{E}^0$ the Boltzmann distribution function takes the form [26]

$$f(\Omega, \mathbf{E}^0) = f(\Omega)\left(1 + \frac{\boldsymbol{\mu} \cdot \mathbf{E}^0}{kT}\right), \quad (29)$$

where $f(\Omega)$ is the distribution function in the absence of an external field, corresponding to entirely random orientation of the molecules.

According to (28) and (29) we have in the linear approximation

$$\chi_{ijk}^{2\omega}(\mathbf{E}^0) = \rho\left[\langle \gamma_{ijkl}^{2\omega} \rangle_\Omega + \frac{1}{kT} \langle \beta_{ijk}^{2\omega} \mu_l \rangle_\Omega\right] E_l^0. \quad (30)$$

The rotational averaging in (30) can be performed explicitly [29], and assuming that the d.c. field is directed along the y axis we obtain for the macroscopic tensor $\chi^{2\omega}_{ijk}(\mathbf{E}^0)$ (we use here a shortened notation) the following non-zero components:

$$\left.\begin{aligned}
\chi^{2\omega}_{xxy}(E^0_y)&=\chi^{2\omega}_{xyx}(E^0_y)=\frac{\rho}{30}\left[3\gamma^{2\omega}_{\alpha\alpha\beta\beta}-\gamma^{2\omega}_{\alpha\beta\beta\alpha}+\frac{1}{kT}(3\beta^{2\omega}_{\alpha\alpha\beta}\mu_\beta-\beta^{2\omega}_{\alpha\beta\beta}\mu_\alpha)\right]E^0_y,\\
\chi^{2\omega}_{yxx}(E^0_y)&=\frac{\rho}{15}\left[2\gamma^{2\omega}_{\alpha\beta\beta\alpha}-\gamma^{2\omega}_{\alpha\alpha\beta\beta}+\frac{1}{kT}(2\beta^{2\omega}_{\alpha\beta\beta}\mu_\alpha-\beta^{2\omega}_{\alpha\alpha\beta}\mu_\beta)\right]E^0_y,\\
\chi^{2\omega}_{yyy}(E^0_y)&=2\chi^{2\omega}_{xxy}(E^0_y)+\chi^{2\omega}_{yxx}(E^0_y),
\end{aligned}\right\}\tag{31}$$

where summation is to be performed over repeated Greek indices. On performing this summation and using the available tables [32] defining the relations between the non-zero components of the nonlinear polarizability tensors $\beta^{2\omega}_{\alpha\beta\gamma}$ and $\gamma^{2\omega}_{\alpha\beta\gamma\delta}$, we have found the explicit form of the susceptibility tensors (31) for all 102 magnetic point groups of molecular symmetry. The results are given in table 2. For isotropic media there are only four non-zero components of the nonlinear susceptibility tensor and only three of them are different. The two molecular mechanisms contributing to the second-harmonic generation process are clearly visible in equations (31). The one, described by the tensor $\gamma^{2\omega}_{\alpha\beta\gamma\delta}$ is related to distortion of the electronic structure in the d.c. electric field, whereas the other is related to the alignment of the permanent molecular dipoles along the d.c. field direction [29, 33].

Such a medium has no linear anisotropy and

$$n_x(\omega)=n_y(\omega)=n(\omega),\ n_x(2\omega)=n_y(2\omega)=n(2\omega).$$

Thus, the refractive indices are distinguished only by their frequency dependences due to dispersion. This means that all Δk^{ijk} defined by equation (7) are the same and do not depend on ijk. This fact simplifies considerably the general formulae (19) and (20) for squeezing in such a system. We have in this case

$$\langle :[\Delta(a_y(z)+a_y^\dagger(z))]^2:\rangle=-\frac{z^2n(\omega)n(2\omega)}{c^2}g_{yxx}(0)[g_{yxx}(0)\alpha_x^2+g_{yyy}(0)\alpha_y^2]\times f_2(-\Delta kz,\Delta kz)+\text{c.c.}\tag{32}$$

where we have taken into account (31). It should be noted here that only the y component of the fundamental beam can be squeezed. This is due to our choice of the direction of the d.c. field. The detailed molecular form of the coupling constants $g_{ijk}(0)$ for various symmetry groups can be found using table 2. If the phases ϕ_x and ϕ_y of the incoming beam are zero, we have a still simpler expression

$$\langle :[\Delta(a_y(z)+a_y^\dagger(z))]^2:\rangle=-\frac{z^2n(\omega)n(2\omega)}{c^2}g_{yxx}(0)[g_{yxx}(0)|\alpha_x|^2+g_{yyy}(0)|\alpha_y|^2]2\,\mathrm{Re}f_2(-\Delta kz,\Delta kz),\tag{33}$$

where

$$\mathrm{Re}f_2(-\Delta kz,\Delta kz)=\mathrm{sinc}^2\frac{\Delta kz}{2},\tag{34}$$

with $\mathrm{sinc}\,x=\sin x/x$. In this case we obtain the standard mismatch function known from the intensity formula.

Table 2. The components $\chi_{xxy}(-2\omega;\omega,\omega;E_y^0)$ and $\chi_{yxx}(-2\omega;\omega,\omega,E_y^0)$ of the susceptibility tensors for all 102 magnetic point groups, in the case of weak reorientation.

Magnetic point groups	$\chi_{xxy}(-2\omega;\omega,\omega;E_y^0)$		$\chi_{yxx}(-2\omega;\omega,\omega;E_y^0)$	
	$g_1+\frac{3}{2}g_2-\frac{1}{2}g_3$	$u_1+u_2+u_3$	$g_1-g_2+2g_3$	$w_1+w_2+w_3$
1,	$g_1+\frac{3}{2}g_2-\frac{1}{2}g_3$	$u_1+u_2+u_3$	$g_1-g_2+2g_3$	$w_1+w_2+w_3$
$\bar{1}$, $\bar{I}$, 2/m, *2*/m, 2/*m*, *2*/*m*, 222, *222*, mmm, *mmm*, *mmm*, mm*m*,	$g_1+\frac{3}{2}g_2-\frac{1}{2}g_3$	0	$g_1-g_2+2g_3$	0
m, *m*	$g_1+\frac{3}{2}g_2-\frac{1}{2}g_3$	u_1+u_2	$g_1-g_2+2g_3$	w_1+w_2
2, *2*, mm2, *mm*2, *2m*m,	$g_1+\frac{3}{2}g_2-\frac{1}{2}g_3$	u_3	$g_1-g_2+2g_3$	w_3
4, *4*, 4mm, *4mm*, *4mm*,	$g_4+\frac{3}{2}g_5-\frac{1}{2}g_6$	u_4	$g_4-g_5+2g_6$	w_4
$\bar{4}$, *$\bar{4}$*, 4/m, *4*/m, 4/*m*, *4*/*m*, 422, *422*, *422*, $\bar{4}$2m, *$\bar{4}$2m*, *$\bar{4}$m2*, *$\bar{4}$2m*, 4/mmm, *4*/mm*m*, 4/m*mm*, *4*/*mmm*, 4/*m*mm, *4*/*mm*m,	$g_4+\frac{3}{2}g_5-\frac{1}{2}g_6$	0	$g_4-g_5+2g_6$	0
3, 3m, 3*m*, 6, *6*, 6mm, *6m*m, *6mm*, ∞, ∞m, ∞*m*,	g_7	u_4	g_{11}	w_4
$\bar{3}$, *$\bar{3}$*, 32, *32*, $\bar{3}$m, *$\bar{3}$m*, *$\bar{3}$m*, $\bar{6}$, *$\bar{6}$*, 6/m, *6*/m, 6/*m*, *6*/*m*, 622, *622*, *622*, $\bar{6}$m2, *$\bar{6}$*2*m*, *$\bar{6}$m2*, *6*/mmm, *6*/*mmm*, 6/m*mm*, 6/ *mmm*, 6/*m*mm, *6*/m*mm*, ∞/m, ∞/*m*, ∞/mm, ∞/*m*m, ∞/m*m*	g_7	0	g_{11}	0
23, m3, *m*3	g_8	0	g_{12}	0
432, *432*, $\bar{4}$3m, *$\bar{4}$3m*, m3m, *m*3m, m3*m*, *m*3*m*	g_9	0	g_{13}	0
Y, Y_h, K, K_h	g_{10}	0	g_{14}	0

$$g_4=\frac{\rho}{15}(2\gamma_{1111}+\gamma_{3333})E_y^0,$$

$$g_5=\frac{2\rho}{15}(\gamma_{1122}+\gamma_{1133}+\gamma_{3311})E_y^0,$$

$$g_6=\frac{2\rho}{15}(\gamma_{1221}+\gamma_{1331}+\gamma_{3113})E_y^0,$$

$$g_7=\frac{\rho}{15}[\gamma_{3333}+7\gamma_{1122}+3(\gamma_{1133}+\gamma_{3311})+\gamma_{1221}-\gamma_{1331}-\gamma_{3113}]E_y^0,$$

$$g_8=\frac{\rho}{10}[2\gamma_{3333}+3(\gamma_{1122}+\gamma_{2211})-\gamma_{1221}-\gamma_{2112}]E_y^0,$$

$$g_9=\frac{\rho}{5}(\gamma_{3333}+3\gamma_{1122}-\gamma_{1221})E_y^0,$$

$$g_{10}=\rho\gamma_{1122}E_y^0,$$

$$g_{11}=\frac{\rho}{15}[\gamma_{3333}+2\gamma_{1122}+6\gamma_{1221}-2(\gamma_{1133}+\gamma_{3311})+4(\gamma_{1331}+\gamma_{3113})]E_y^0,$$

$$g_{12}=\frac{\rho}{5}[\gamma_{3333}-\gamma_{1122}-\gamma_{2211}+2(\gamma_{1221}+\gamma_{2112})]E_y^0,$$

$$g_{13}=\frac{\rho}{5}(\gamma_{3333}-2\gamma_{1122}+4\gamma_{1221})E_y^0,$$

$$g_{14}=\rho\gamma_{1221}E_y^0,$$

$$u_4=\frac{\rho\mu_3E_y^0}{15kT}(\beta_{333}+3\beta_{113}-\beta_{311}),$$

$$w_4=\frac{\rho\mu_3E_y^0}{15kT}(\beta_{333}-2\beta_{113}+4\beta_{311}).$$

The corresponding formulae for the second-harmonic field are

$$\langle :[\Delta(b_x(z)+b_x^\dagger(z))]^2 : \rangle = \frac{4z^4 n^2(2\omega)n(\omega)}{3c^4} \times {}^6 6g_{xxy}^2(0)[66g_{yyy}(0)66g_{yxx}(0)(\alpha_x^2+\alpha_y^4)+(66g_{yyy}^2(0) + g_{yxx}^2(0)+4g_{xxy}^2(0))\alpha_x^2\alpha_y^2]F(\Delta kz)+\text{c.c.}, \quad (35)$$

$$\langle :[\Delta(b_y(z)+b_y^\dagger(z))]^2 : \rangle = \frac{4z^4 n^2(2\omega)n(\omega)}{3c^4} \times [g_{yxx}^4(0)\alpha_x^4+g_{yyy}^4(0)\alpha_y^4+(g_{yyy}^3(0)g_{yxx}(0) + g_{yyy}(0)g_{yxx}^3(0)+4g_{yyy}(0)g_{yxx}(0)g_{xxy}^2(0))\alpha_x^2\alpha_y^2]F(\Delta kz), +\text{c.c.}, \quad (36)$$

where we have used the notation

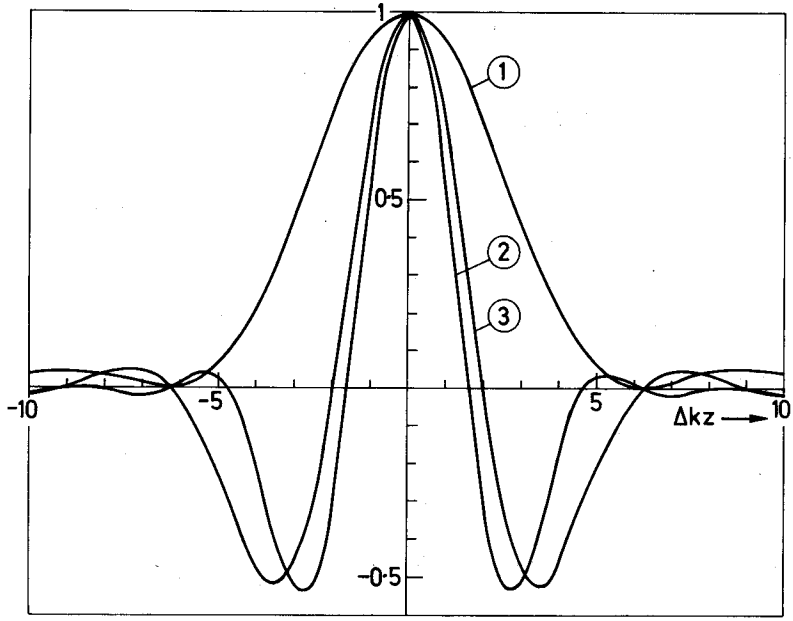
$$\begin{aligned} F(\Delta kz) &= n(2\omega)F_1(\Delta kz) - \frac{n(\omega)}{2}F_2(\Delta kz) \\ &= n(2\omega)f_3(\Delta kz, -\Delta kz, \Delta kz)f_1(\Delta kz) \\ &\quad -\frac{n(\omega)}{2}f_4(\Delta kz, -\Delta kz, \Delta kz, \Delta kz). \end{aligned} \quad (37)$$

It is worth noting that the expressions (35) and (36) become negative if we take $\phi_x=\phi_y=\pi/4$. This now corresponds to a change of the in-phase component $b_i+b_i^\dagger$ into the out-of-phase component $i(b_i-b_i^\dagger)$ of the second-harmonic field. With this choice of the initial phases, the mismatch is described by the real part of $F(\Delta kz)$ only. We then have

$$\left.\begin{aligned} \operatorname{Re} F_1(\Delta kz) &= \frac{12}{(\Delta kz)^2}\left[2\operatorname{sinc}^2\Delta kz - \operatorname{sinc}^2\frac{\Delta kz}{2} - \operatorname{sinc} 2\Delta kz\right], \\ \operatorname{Re} F_2(\Delta kz) &= \frac{12}{(\Delta kz)^2}\left[2\operatorname{sinc}\Delta kz - \operatorname{sinc}^2\Delta kz - \operatorname{sinc}^2\frac{\Delta kz}{2}\right]. \end{aligned}\right\} \quad (38)$$

Equations (38) show that even in this simple case the mismatch function is rather complicated, although it involves typical sinc x functions. The mismatch functions (34) and (38) are illustrated graphically in the figure. It is seen that the functions (38) have peaks much narrower than the peak of the function (34). They moreover change their signs when the mismatch becomes sufficiently great, and squeezing in the second-harmonic beam is lost. This means that the second-harmonic beam is much more sensitive to the phase mismatch than the fundamental beam.

A further simplification of the formulae (35) and (36) is obtained if there is only one polarization state (x or y) of the incoming beam. This reduces the number of terms to one. Even in this case however the mismatch function remains unchanged. To write the formulae for a circularly polarized incoming beam it suffices to put $\phi_y=\phi_x\pm\pi/2$. This of course, again does not affect the mismatch function. The formulae (35) and (36) are valid for an arbitrary choice of the initial phases of the incoming beam. In general, also $\operatorname{Im} F(\Delta kz)$ contributes to the variances.



Plot of the mismatch functions: the functions: (1) $\mathrm{Re}\, f_2(-\Delta kz, \Delta kz)$; (2) $\mathrm{Re}\, F_1(\Delta kz)$; and (3) $\mathrm{Re}\, F_2(\Delta kz)$.

4.3. *Strongly oriented molecular media*

If the d.c. electric field is strong, the linear approximation used in §4.2. is not justified. In this case the averaging in (28) has to be performed with the distribution function [26]

$$f(\Omega, \mathbf{E}^0) = \frac{\exp(p\cos\theta)}{\int \exp(p\cos\theta)\,\mathrm{d}\Omega}, \tag{39}$$

which is valid for axially symmetric dipolar molecules with the angle θ between the dipole moment $\boldsymbol{\mu}$ and the electric field $\mathbf{E}^0$. The parameter $p = \boldsymbol{\mu}\mathbf{E}^0/kT$. Since in the strong field the molecular reorientation mechanism is predominant we neglect $\gamma^{2\omega}_{\alpha\beta\gamma\delta}$ in our further considerations. The nonlinear susceptibility tensor $\chi^{2\omega}_{ijk}(E^0_y)$ can now be written in the form [26]

$$\left.\begin{aligned}
\chi^{2\omega}_{xxy}(E^0_y) &= \chi^{2\omega}_{xyx}(E^0_y) = \frac{\rho}{2}[(\beta^{2\omega}_{333} - \beta^{2\omega}_{311})L_1(p) \\
&\quad + (2\beta^{2\omega}_{113} + \beta^{2\omega}_{311} - \beta^{2\omega}_{333})L_3(p)], \\
\chi^{2\omega}_{yxx}(E^0_y) &= \frac{\rho}{2}[(\beta^{2\omega}_{333} - 2\beta^{2\omega}_{113} + \beta^{2\omega}_{311})L_1(p) \\
&\quad + (2\beta^{2\omega}_{113} + \beta^{2\omega}_{311} - \beta^{2\omega}_{333})L_3(p)], \\
\chi^{2\omega}_{yyy}(E^0_y) &= \rho[(2\beta^{2\omega}_{113} + \beta^{2\omega}_{311})L_1(p) \\
&\quad + (\beta^{2\omega}_{333} - 2\beta^{2\omega}_{113} - \beta^{2\omega}_{311})L_3(p)],
\end{aligned}\right\} \tag{40}$$

where $L_1(p)$ and $L_3(p)$ are generalized Langevin functions that are defined analytically and illustrated graphically in [26, 29]. Similarly to the weak reorientation case there are four non-zero components of the susceptibility tensor. The difference resides in their molecular contents. If the field is so strong that all the molecular dipoles are aligned along the d.c. field direction, the Langevin functions tend to unity (for $p \to \bar{\infty}$), and the susceptibility tensor components (40) are expressed directly by the components of the molecular hyperpolarizability tensor $\beta^{2\omega}_{\alpha\beta\gamma}$. So in the case of electric saturation the susceptibility tensor is of an exceptionally simple form. It has non-zero components for the following molecular symmetry groups only: 3, 4, *4*, 6, *6*, ∞, 3m, *3m*, 4mm, *4mm*, *4mm*, 6mm, *6mm*, *6mm*, ∞m and ∞m. For the remaining symmetry groups the tensor vanishes.

The formulae for squeezing have exactly the same form as in the case of weak reorientation, except for the values of the susceptibility tensor components.

We have assumed here that the molecules are mutually independent, i.e. that there is no interaction between them. In dense fluids, however, the many-body mutual interactions of the molecules [34] (the short-range and long-range forces), the Lorentz or Onsager local fields [35, 36], and fluctuations of the molecular fields [29, 34] play an essential role and should be taken into account.

5. Conclusions

We have derived general results for normally ordered variances of the second-harmonic and fundamental fields when the two beams have traversed a distance z in the nonlinear medium. Our results are then specified for crystals as well as for electrically oriented isotropic media. The structure of the nonlinear medium which is crucial for the second-harmonic generation process is considered in detail. The non-zero components of the nonlinear susceptibility tensor responsible for second-harmonic generation are calculated explicitly for all symmetry groups of crystals and molecules. Our results include moreover all possible mismatch functions. We have shown that in squeezing the mismatch functions are different from those that hold for intensity. Mismatch is found to accumulate along the optical path. We refer to this novel result as the 'mismatch accumulation effect'. Squeezing as a phase-dependent effect is in this respect different from intensity. The phase matching conditions for crystals are also discussed in detail. In particular, when the phase-matching conditions are satisfied our results reproduce the results known in the literature. Our formulae include two possible polarizations of the harmonic and fundamental beams and can be easily applied for circular polarization of the incoming beam. We have shown that o*ee* synchronism cannot be used for producing squeezed states in the fundamental beam. For isotropic media, the formula for squeezing in the fundamental beam has a quite simple form with the same mismatch function as for the intensity. For the harmonic beam the formulae for squeezing are more complicated but still accessible to interpretation. Our results showing the possibility of squeezing in second-harmonic generation give at the same time an account of some possible complications that can appear in real experiments.

Appendix

The coupling constants occurring in formula (9) are defined in the laboratory frame of reference, chosen with its z axis in the propagation direction of the two

beams. To gain information regarding the influence of crystal symmetry on the generation of second harmonics and/or squeezed states we have to express the susceptibility tensor components $\chi_{ijk}(-2\omega;\omega,\omega)$ of formula (9) by way of susceptibility tensor components $\chi_{\alpha\beta\gamma}(-2\omega;\omega,\omega)$ in the crystallographical system of reference X, Y, Z.

The laboratory system of coordinates x, y, z goes over into the crystallographical system of coordinates X, Y, Z on two successive rotations: the first about the z axis by an angle ϕ, and the second about the new $y' = Y$ axis by an angle θ. In this way, the following well known transformation relation is fulfilled between the susceptibility tensor components in the two systems of reference:

$$\chi_{i(jk)}(-2\omega;\omega,\omega)=C_{i\alpha}C_{j\beta}C_{k\gamma}\chi_{\alpha(\beta\gamma)}(-2\omega;\omega,\omega), \tag{A 1}$$

where the $C_{i\alpha}$ are elements of the transformation matrix

$$C=\begin{bmatrix}\cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta\\ -\sin\phi & \cos\phi & 0\\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta\end{bmatrix}, \tag{A 2}$$

with the indices i, j, k referring to the laboratory coordinates and taking the values x, y, z, and α, β, γ referring to the crystallographical coordinates and taking the values X, Y, Z.

On carrying out the transformation, we obtain

$$\chi_{yyy}(-2\omega;\omega,\omega)=a_1, \tag{A 3}$$

$$\chi_{yxx}(-2\omega;\omega,\omega)=b_1+b_2+b_3, \tag{A 4}$$

$$\chi_{xxy}(-2\omega;\omega,\omega)=c_1+c_2+c_3, \tag{A 5}$$

$$\chi_{xxx}(-2\omega;\omega,\omega)=d_1+d_2+d_3, \tag{A 6}$$

$$\chi_{xyy}(-2\omega;\omega,\omega)=e_1+e_2+e_3, \tag{A 7}$$

$$\chi_{yyx}(-2\omega;\omega,\omega)=f_1+f_2+f_3, \tag{A 8}$$

where

$$\begin{aligned}a_1 = &-\sin\phi[\sin^2\phi\,\chi_{XXX}+\cos^2\phi(2\chi_{YYX}+\chi_{XYY})]\\ &+\cos\phi[\cos^2\phi\,\chi_{YYY}+\sin^2\phi(2\chi_{XXY}+\chi_{YXX})],\end{aligned} \tag{A 9}$$

$$b_1=\tfrac{1}{2}\sin 2\theta\sin 2\phi(\chi_{XXZ}-\chi_{YYZ}), \tag{A 10}$$

$$b_2=\sin 2\theta(\sin^2\phi\chi_{XYZ}-\cos^2\phi\,\chi_{YXZ}), \tag{A 11}$$

$$\begin{aligned}b_3=&\cos^2\theta\{\sin\phi[\cos^2\phi(-\chi_{XXX}+2\chi_{YYX})-\sin^2\phi\,\chi_{XYY}]\\ &+\cos\phi[\sin^2\phi(\chi_{YYY}-2\chi_{XXY})+\cos^2\phi\,\chi_{YXX}]\}\\ &\sin^2\theta(-\sin\phi\,\chi_{XZZ}+\cos\phi\,\chi_{YZZ}),\end{aligned} \tag{A 12}$$

$$c_1=\tfrac{1}{4}\sin 2\theta\sin 2\phi(\chi_{XXZ}-\chi_{YYZ}+\chi_{ZXX}-\chi_{ZYY}), \tag{A 13}$$

$$c_2=\tfrac{1}{2}\sin 2\theta(-\cos 2\phi\,\chi_{ZXY}-\cos^2\phi\,\chi_{XYZ}+\sin^2\phi\,\chi_{YXZ}), \tag{A 14}$$

$$c_3=\cos^2\theta\{\sin\phi[\cos^2\phi(-\chi_{XXX}+\chi_{XYY})+\cos 2\phi\,\chi_{YYX}]$$
$$+\cos\phi[\sin^2\phi(\chi_{YYY}-\chi_{YXX})+\cos 2\phi\,\chi_{XXY}]\}$$
$$+\sin^2\theta(-\sin\phi\,\chi_{ZZX}+\cos\phi\,\chi_{ZZY}), \tag{A 15}$$

$$d_1=-\sin^3\theta\,\chi_{ZZZ}-\cos^2\theta\sin\theta[\cos^2\phi(2\chi_{XXZ}+\chi_{ZXX})$$
$$+\sin^2\phi(2\chi_{YYZ}+\chi_{ZYY})], \tag{A 16}$$

$$d_2=-\cos^2\theta\sin\theta\sin 2\phi(\chi_{XYZ}+\chi_{YXZ}+\chi_{ZXY}), \tag{A 17}$$

$$d_3=\cos^3\theta\{\cos\phi[\cos^2\phi\,\chi_{XXX}+\sin^2\phi(2\chi_{YYX}+\chi_{XYY})]$$
$$+\sin\phi[\sin^2\phi\,\chi_{YYY}+\cos^2\phi(2\chi_{XXY}+\chi_{YXX})]\}$$
$$+\cos\theta\sin^2\theta[\cos\phi(2\chi_{ZZX}+\chi_{XZZ})+\sin\phi(2\chi_{ZZY}+\chi_{YZZ})], \tag{A 18}$$

$$e_1=-\sin\theta(\sin^2\phi\,\chi_{ZXX}+\cos^2\phi\,\chi_{ZYY}), \tag{A 19}$$

$$e_2=\sin\theta\sin 2\phi\,\chi_{ZXY}, \tag{A 20}$$

$$e_3=\cos\theta\{\cos\phi[\sin^2\phi(\chi_{XXX}-2\chi_{YYX})+\cos^2\phi\,\chi_{XYY}]$$
$$+\sin\phi[\cos^2\phi(\chi_{YYY}-2\chi_{XXY})+\sin^2\phi\,\chi_{YXX}]\}, \tag{A 21}$$

$$f_1=-\sin\theta(\sin^2\phi\,\chi_{XXZ}+\cos^2\phi\,\chi_{YYZ}), \tag{A 22}$$

$$f_2=\tfrac{1}{2}\sin\theta\sin 2\phi(\chi_{XYZ}+\chi_{YXZ}), \tag{A 23}$$

$$f_3=\cos\theta\{\cos\phi[\sin^2\phi(\chi_{XXX}-\chi_{XYY})+\cos 2\phi\,\chi_{YYX}]$$
$$+\sin\phi[\cos^2\phi(\chi_{YYY}-\chi_{YXX})-\cos 2\phi\,\chi_{XXY}]\}. \tag{A 24}$$

Making use of the tables in [32], which give the dependence between the non-zero components of the tensor $\chi_{\alpha(\beta\gamma)}(-2\omega;\omega,\omega)$, we have obtained the components $\chi_{i(jk)}(-2\omega;\omega,\omega)$ of the susceptibility for all the 102 magnetic classes. For the results, see table 1.

On summation over recurring Greek indices in formulae (31) we obtain:

$$\chi_{xxy}(-2\omega;\omega,\omega;E_y^0)=g_1+\tfrac{3}{2}g_2-\tfrac{1}{2}g_3+u_1+u_2+u_3, \tag{A 25}$$

$$\chi_{yxx}(-2\omega;\omega,\omega;E_y^0)=g_1-g_2+2g_3+w_1+w_2+w_3, \tag{A 26}$$

with

$$g_1=\frac{\rho}{15}(\gamma_{1111}+\gamma_{2222}+\gamma_{3333})E_y^0, \tag{A 27}$$

$$g_2=\frac{\rho}{15}(\gamma_{1122}+\gamma_{1133}+\gamma_{2211}+\gamma_{2233}+\gamma_{3311}+\gamma_{3322})E_y^0, \tag{A 28}$$

$$g_3=\frac{\rho}{15}(\gamma_{1221}+\gamma_{1331}+\gamma_{2112}+\gamma_{2332}+\gamma_{3113}+\gamma_{3223})E_y^0, \tag{A 29}$$

$$u_1=\frac{\rho\mu_1E_y^0}{30kT}[2\beta_{111}+3(\beta_{221}+\beta_{331})-\beta_{122}-\beta_{133}], \tag{A 30}$$

$$u_2=\frac{\rho\mu_2E_y^0}{30kT}[2\beta_{222}+3(\beta_{112}+\beta_{332})-\beta_{211}-\beta_{233}], \tag{A 31}$$

$$u_3=\frac{\rho\mu_3 E_y^0}{30kT}[2\beta_{333}+3(\beta_{113}+\beta_{223})-\beta_{311}-\beta_{322}], \tag{A 32}$$

$$w_1=\frac{\rho\mu_1 E_y^0}{15kT}[\beta_{111}-\beta_{221}-\beta_{331}+2(\beta_{122}+\beta_{133})], \tag{A 33}$$

$$w_2=\frac{\rho\mu_2 E_y^0}{15kT}[\beta_{222}-\beta_{112}-\beta_{332}+2(\beta_{211}+\beta_{233})]$$

$$w_3=\frac{\rho\mu_3 E_y^0}{15kT}[\beta_{333}-\beta_{113}-\beta_{223}+2(\beta_{311}+\beta_{322})]. \tag{A 35}$$

On making use of the tables [32] giving in explicit form the nonlinear polarizability tensor $\gamma_{\alpha(\beta\gamma)\delta}^{(-2\omega;\omega,\omega)}$ and $\beta_{\alpha(\beta\gamma)}^{(-2\omega;\omega,\omega)}$ we obtained the components $\chi_{xxy}^{(-2\omega;\omega,\omega;E_y^0)}$ and $\chi_{yxx}^{(-2\omega;\omega,\omega;E_y^0)}$ of the susceptibility tensors for all 102 magnetic point groups. The results are assembled in table 2.

References

[1] WALLS, D. F., 1983, *Nature, Lond.*, **306,** 141, and references therein.
[2] YUEN, H. P., and SHAPIRO, J. H., 1979, *Optics Lett.*, **4,** 334.
[3] REID, M. D., and WALLS, D. F., 1985, *Phys. Rev.* A, **31,** 1622.
[4] PEŘINA, J., PEŘINOVA, V., SIBILIA, C., and BERTOLOTTI, M., 1984, *Optics Commun.*, **49,** 285.
[5] MILBURN, G. J., and WALLS, D. F., 1983, *Phys. Rev. A*, **27,** 392.
[6] CAVES, C. M., and SHUMAKER, B. L., 1985, *Phys. Rev. A*, **31,** 3068.
[7] MANDEL, L., 1982, *Optics Commun.*, **42,** 437.
[8] KOZIEROWSKI, M., and KIELICH, S., 1983, *Phys. Lett.* A, **94,** 213.
[9] LUGIATO, L. A., STRINI, G., and DE MARTINI, F., 1983, *Optics Lett.*, **8,** 256.
[10] PEŘINA, J., PEŘINOVA, V., and KODOUSEK, J., 1984, *Optics Commun.*, **49,** 210.
[11] KIELICH, S., KOZIEROWSKI, M., and TANAŚ, R., 1985, *Optica Acta*, **32,** 1023, and references therein.
[12] COLLETT, M. J., and WALLS, D. F., 1985, *Phys. Rev.* A, **32,** 2887.
[13] ZUBAIRY, M. S., RAZMI, M. S. K., IQBAL, S., and IDRESS, M., 1983, *Phys. Lett.* A, **98,** 168.
[14] LOUDON, R., 1984, *Optics Commun.*, **49,** 67.
[15] TANAŚ, R., and KIELICH, S., 1984, *Optica Acta*, **31,** 81.
[16] LEVENSON, M. D., SHELBY, R. M., ASPECT, A., REID, M. D., and WALLS, D. F., 1985, *Phys. Rev.* A, **32,** 1550.
[17] MAEDA, M. W., KUMAR, P., and SHAPIRO, J. H., 1985, *Phys. Rev.* A, **32,** 3803.
[18] SLUSHER, R. E., HOLLBERG, L. W., YURKE, B., MERTZ, J. C., and VALLEY, J. F., 1985, *Phys. Rev. Lett.*, **55,** 2409.
[19] LEVENSON, M. D., SHELBY, R. M., DEVOE, R. G., and PERLMUTTER, S. H., 1986, *XIV International Conference on Quantum Electronics, Digest of Technical Papers* (Washington, D.C.: Optical Society of America), p. 56.
[20] KIMBLE, H. J., and HALL, J. L., 1986, *XIV International Conference on Quantum Electronics, Digest of Technical Papers* (Washington, D.C.: Optical Society of America), p. 86.
[21] KIELICH, S., 1965, *Acta Phys. Polon.*, **28,** 459.
[22] SHEN, Y. R., 1967, *Phys. Rev.*, **155,** 921.
[23] PERSHAN, P. S., 1963, *Phys. Rev.*, **130,** 919.
[24] TERHUNE, R. W., MAKER, P. D., and SAVAGE, C. M., 1962, *Phys. Rev. Lett.*, **1,** 404.
[25] MAYER, G., 1968, *C. r. hebd. Séanc. Acad. Sci., Paris*, **267,** 54.
[26] KIELICH, S., 1969, *IEEE Jl quant. Electron.*, **5,** 562.
[27] BLOEMBERGEN, N., 1965, *Nonlinear Optics* (New York: Benjamin).

[28] BUTCHER, P. N., 1965, *Nonlinear Optical Phenomena* (Ohio State University).
[29] KIELICH, S., 1981, *Nonlinear Molecular Optics* (Moscow: Nauka) in Russian.
[30] SHEN, Y. R., 1985, *The Principles of Nonlinear Optics* (New York: Wiley).
[31] KIELICH, S., 1965, *Proc. phys. Soc.*, **86,** 709.
[32] BIRSS, R. R., 1964, *Symmetry and Magnetism* (Amsterdam: North-Holland).
[33] HAUCHECORNE, G., KERHERVÉ, K., and MAYER, G., 1971, *J. Phys., Paris*, **32,** 47.
[34] KIELICH, S., 1979, *Nonlinear Behaviour of Molecules, Atoms and Ions in Electric*, Magnetic or Electromagnetic Fields edited by L. Néel (Amsterdam: Elsevier), p. 111.
[35] BEDEAUX, D., and BLOEMBERGEN, N., 1973, *Physica*, **69,** 57.
[36] KASPROWICZ-KIELICH, B., and KIELICH, S., 1975, *Adv. Molec. Relaxation Processes*, **7,** 275.