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Phase Matching in Harmonic Generation Employing Optical Rotatory Dispersion*

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It is shown that phase matching in harmonic generation may, in principle, be achieved in a nonlinear medium which has appropriate optical rotatory dispersion. The treatment follows the analysis of Franken and Ward whereby the resultant radiative output of a dipolar array generated by a laser beam is obtained. For specific cases without double refraction, the relative intensities of second- and third-harmonic radiation are calculated, new phase-matching conditions are derived, and the nature of harmonic radiation in the presence of optical rotation is examined.

INTRODUCTION

THEORETICAL investigations have shown the crucial role of dispersion in the generation of optical harmonic radiation by a laser beam.[1-3] In the limit for which the incoming fundamental wave is not depleted in traversing a distance l in the medium, the resultant intensity of second-harmonic generation (SHG) shows an oscillatory behavior which is dependent on the dispersion of the medium,

$$I_{\text{SHG}} \propto \frac{\sin^2 \frac{1}{2} l (\Delta k)_{\text{SHG}}}{(\Delta k)_{\text{SHG}}^2}. \tag{1}$$

The magnitudes of the wave vector at the fundamental frequency and the second harmonic are given by k_1 and k_2, respectively, and

$$(\Delta k)_{\text{SHG}} = k_2 - 2k_1. \tag{2}$$

The condition for the initiation of growth of harmonic radiation is apparent from Eq. (1). I_{SHG} increases with l^2 when

$$(\Delta k)_{\text{SHG}} = 0, \tag{3}$$

the so-called phase-matching condition.

The intensity of third-harmonic generation (THG) follows a similar form when the fundamental wave is not depleted,[1,4]

$$I_{\text{THG}} \propto \frac{\sin^2 \frac{1}{2} l (\Delta k)_{\text{THG}}}{(\Delta k)_{\text{THG}}^2}, \tag{4}$$

where

$$(\Delta k)_{\text{THG}} = k_3 - 3k_1, \tag{5}$$

k_3 referring to the wave vector at the third harmonic. Phase matching similarly occurs for

$$(\Delta k)_{\text{THG}} = 0. \tag{6}$$

The above solution for THG also requires that the quadratic Kerr effect can be ignored.[1] This assumption will be continued throughout the present discussion.

The general oscillatory variation predicted by Eq. (1) has been experimentally observed,[5] and the use of birefringence properties of anisotropic crystals has led to phase matching and enhanced harmonic production.[5,6] Other schemes for the achievement of phase matching have been discussed, including the stacking of specially cut crystal plates,[1,3] the use of internal reflections in a crystal,[1] and waveguide-type crystal resonators.[7]

The purpose of the present paper is to explore the conditions under which optical rotatory dispersion may lead to phase matching in harmonic generation, and the possibilities for achieving such conditions in available materials. In addition, several characteristic features of optical rotatory dispersion in a nonlinear medium are discussed, and these are amenable to experimental confirmation. In principle, the optical rotation may arise from either natural optical activity of the medium, or from magneto-optic rotation as in the Faraday effect. An interesting discussion of frequency mixing in optically active liquids has already appeared in the literature.[8]

The physical basis for anticipating that optical rotatory dispersion may be employed in phase matching in both SHG and THG is as follows. It is well known that Eqs. (1) and (4) have associated with them a critical length called the coherence length l_{coh} which is equal to $\pi/\Delta k$. In this distance, the harmonic light wave shifts in phase by an amount π with respect to the nonlinear polarization wave. This phase mismatch leads to the zeros of Eqs. (1) and (4), and physically is correlated with the harmonic radiation flowing back into the fundamental wave. It would appear that optical rotation offers the possibility of compensating for the abovementioned phase mismatch since rotation of the plane of polarization of the harmonic light wave by an amount π is equivalent to a phase shift of π. Thus in the pres-

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[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[2] D. A. Kleinman, Phys. Rev. **128**, 1761 (1962).

[3] P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).

[4] P. D. Maker, R. W. Terhune, and C. M. Savage, in *Quantum Electronics III*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 1559.

[5] P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Letters **8**, 21 (1962).

[6] J. A. Giordmaine, Phys. Rev. Letters **7**, 19 (1962).

[7] A. Ashkin, G. D. Boyd, and D. A. Kleinman, Appl. Phys. Letters **6**, 179 (1965).

[8] J. A. Giordmaine, Phys. Rev. **137**, A1599 (1965).

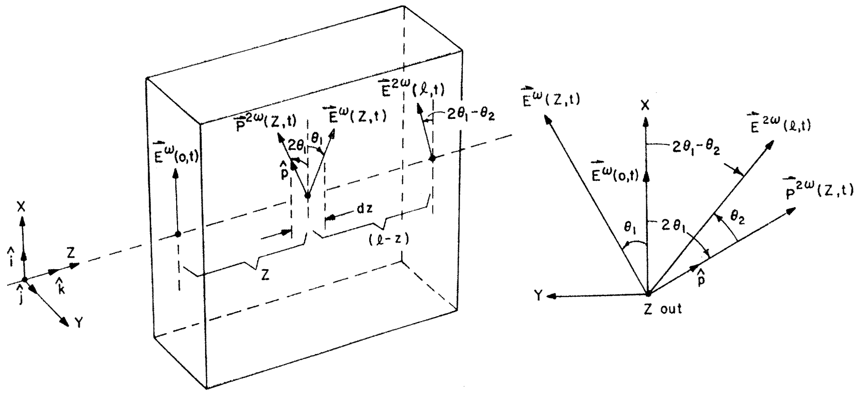

FIG. 1. Schematic representation of waves moving along the optic axis of a rotatory dispersive crystal of class 32 for SHG. The right-hand diagram is a view from the exit face of the crystal in which the propagating waves are directed out of the paper.

ence of rotatory dispersion, where the difference of rotation between the fundamental and harmonic waves is adjusted to an amount $\pm\pi$ in a length l_{coh}, the harmonic light and polarization waves should be in phase. If the comparatively smaller rotation at the lower or fundamental frequency is ignored, matching is likely to be achieved when $l_{\text{coh}} \simeq \pm\pi/\alpha$, where α is the specific rotation at the harmonic frequency. Thus a typical matching condition might likely be given by

$$\Delta k \simeq \pm\alpha \tag{7}$$

for either SHG or THG.

THEORY

The above physical considerations provide the incentive for a more detailed investigation of possible phase-matching conditions when optical rotatory dispersion is present in a dispersive nonlinear medium. The optically active, uniaxial crystals of the point group 32 have been selected for evaluation in the case where wave propagation occurs along the optic axis. Both SHG and THG are evaluated and, as will be pointed out later, the THG treatment is equally valid for the case of isotropic rotatory dispersive media. The effects of rotatory dispersion are not further complicated by double refraction because of the selected direction of propagation, and the medium is assumed to be transparent at the frequencies of interest.

Quartz,[9] which is perhaps the most studied crystal from the point of view of rotatory dispersion, falls into the crystal class 32. The specific optical rotation of quartz and other inorganic and organic crystals of class 32 are generally available in tabulated form.[10] Cinnabar (HgS) is one of them which is well known for the extraordinarily large rotation it produces. The class 32 has the property of enantiomorphism, in which both right- and left-handed crystalline forms exist. These forms are mirror images which are not superimposable upon one another in space. For purposes of this discussion it will be assumed that we are dealing with the left-handed form.

In the analysis which follows, the method of Franken and Ward[3] will be employed, whereby the resultant radiative output of an array of dipoles generated by a laser beam is obtained. The dipoles are considered to be oscillating at the harmonic frequency and the incoming fundamental wave is assumed to be unattenuated throughout the medium. Franken and Ward have applied this treatment to the case of SHG in an isotropic medium without rotatory dispersion, and obtained the result quoted above in Eq. (1). For the cases of SHG and THG to be treated here, anisotropic properties as well as the rotatory dispersion of the medium are accounted for.

A. Second-Harmonic Generation

The physical situation is depicted in Fig. 1. A plane monochromatic wave $\mathbf{E}^{\omega}(z,t)$ of frequency ω and wave vector k_1 is propagating in the z direction, and it is polarized along the x axis when incident on the front or $z=0$ plane of the crystal. The crystal axes are chosen so that the z axis corresponds to the threefold axis or optic axis of the crystal, and the x axis to a twofold axis. The crystal is considered to be of sufficient extent in the x-y plane so that edge effects are not important, and of length l along the z axis. Unit vectors $\hat{\imath}$, $\hat{\jmath}$, and $\hat{k}$ are defined in the usual way.

Upon propagating a distance z into the medium, optical rotation produces a left-handed rotation[11] of the plane of polarization of $\mathbf{E}^{\omega}$ by an amount θ_1 in the x-y plane, where

$$\theta_1 = \alpha_1 z \,, \tag{8}$$

α_1 corresponding to the specific rotation at the fundamental frequency ω. The fundamental wave at this

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[9] For a discussion of the rotatory power of quartz see, for example, R. B. Sosman, *The Properties of Silica* (The Chemical Catalog Company, Inc., New York, 1927), p. 646.

[10] *Landolt-Börnstein Zahlenwerte und Funktionen*, edited by K. H. Hellwege and A. M. Hellwege, (Springer-Verlag, Berlin, 1962), Vol. II, Part 8, pp. 434–442.

[11] The convention of left-handed rotation corresponds to counterclockwise rotation of the plane of polarization as the light wave approaches the observer. This is the situation in left-handed quartz. See e.g., J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1964), p. 261.

point has both x and y components, E_x^ω and E_y^ω, and is described by

$$\mathbf{E}^\omega(z,t)=\hat{\imath}E_0\sin(k_1z-\omega t)\cos\theta_1 +\hat{\jmath}E_0\sin(k_1z-\omega t)\sin\theta_1. \quad (9)$$

The associated second-order polarization $\mathbf{P}^{2\omega}(z,t)$ which is generated has both nonvanishing x and y components[3]:

$$P_x^{2\omega}=d_{11}[(E_x^\omega)^2-(E_y^\omega)^2]+d_{14}E_y^\omega E_z^\omega, \quad (10)$$

$$P_y^{2\omega}=-d_{14}E_x^\omega E_z^\omega-2d_{11}E_x^\omega E_y^\omega,$$

and

$$P_z^{2\omega}=0.$$

The second-order susceptibility coefficient d_{14} does not contribute in the present problem with $E_z^\omega=0$, and more generally, as a result of the Kleinman symmetry condition.[12] The coefficient d_{11} is positive for the left-handed form of crystal class 32, here under consideration. Substitution of the components of Eq. (9) into Eq. (10) gives

$$\mathbf{P}^{2\omega}(z,t)=\hat{p}d_{11}E_0^2\sin^2(k_1z-\omega t), \quad (11)$$

where the unit vector $\hat{p}$ is $\hat{\imath}\cos2\theta_1-\hat{\jmath}\sin2\theta_1$, indicating that $\mathbf{P}^{2\omega}$ is directed along $-2\theta_1$, in the x-y plane when $\mathbf{E}^\omega$ is in the direction $+\theta_1$. Thus the second-order polarization wave is right-handed or in opposite sense to the fundamental, and the magnitude of its rotation about the z axis is twice that of the fundamental.

The polarization wave described by Eq. (11) contains both a dc and second-harmonic component, i.e., $\sin^2(k_1z-\omega t)=\frac{1}{2}[1-\cos(2k_1z-2\omega t)]$, and it is the latter which is of interest here. Thus the harmonic component

$$P^{2\omega}\propto\cos(2k_1z-2\omega t), \quad (12)$$

directed along $\hat{p}$, acts as the source of SHG in the medium. Clearly the second-harmonic light wave $\mathbf{E}^{2\omega}$ is polarized along the $\hat{p}$ direction, but is rotated in the left-hand sense an amount θ_2 in traveling a distance $l-z$ to the exit face of the medium, owing to the rotatory dispersion. Thus,

$$\theta_2=\alpha_2(l-z), \quad (13)$$

where α_2 is the specific rotation at the second-harmonic frequency. The problem reduces to summing all of the $\mathbf{E}^{2\omega}$ contributions at the exit face due to the second-order polarization elements of the form of Eq. (12) distributed throughout the medium. Written in differential form, the incremental second harmonic at the exit face, $dE^{2\omega}(l,t)$, generated by the polarization within the element dz is given by

$$dE^{2\omega}(l,t)\propto dz\cos[2k_1z-2\omega(t-t')], \quad (14)$$

and for purposes of this calculation the constant of proportionality need not be evaluated. The time t is replaced by $t-t'$ in order to give the proper time phase to $\mathbf{E}^{2\omega}$ which travels a distance $l-z$ in the dispersive medium. t' is the transit time over this distance.

$$t'=(l-z)k_2/2\omega, \quad (15)$$

where k_2 is the wave vector at the harmonic frequency, 2ω.

It is now convenient to sum the various harmonic contributions at the exit face of the medium separately in the x and y directions. Thus from Eq. (14), the independent x- and y-harmonic components are

$$E_x^{2\omega}(l,t)\propto\int_0^l dz\cos[2k_1z-2\omega(t-t')]\cos(\theta_2-2\theta_1) \quad (16)$$

and

$$E_y^{2\omega}(l,t)\propto\int_0^l dz\cos[2k_1z-2\omega(t-t')]\sin(\theta_2-2\theta_1). \quad (17)$$

The necessary angular relationships are shown in the right side of Fig. 1 for the light waves approaching an observer situated along the z axis. Upon substituting expressions contained in Eqs. (2), (8), (13), and (15), and using the shorthand notation

$$(\Delta\alpha)_{\mathrm{SHG}}=\alpha_2+2\alpha_1, \quad (18)$$

it follows that

$$E_x^{2\omega}(l,t)\propto\int_0^l dz\cos[lk_2-z(\Delta k)_{\mathrm{SHG}}-2\omega t] \times\cos[\alpha_2l-(\Delta\alpha)_{\mathrm{SHG}}z] \quad (19)$$

and

$$E_y^{2\omega}(l,t)\propto\int_0^l dz\cos[lk_2-z(\Delta k)_{\mathrm{SHG}}-2\omega t] \times\sin[\alpha_2l-(\Delta\alpha)_{\mathrm{SHG}}z]. \quad (20)$$

These integrals are easily evaluated in closed form and converted to the following harmonic functions:

$$E_x^{2\omega}(l,t)\propto[A^2+2AB\cos[(2\alpha_1-\alpha_2)l]+B^2]^{1/2} \times\sin(\delta-2\omega t) \quad (21)$$

and

$$E_y^{2\omega}(l,t)\propto[A^2-2AB\cos[(2\alpha_1-\alpha_2)l]+B^2]^{1/2} \times\sin(\delta'-2\omega t), \quad (22)$$

where

$$A=\frac{\sin\frac{1}{2}l[(\Delta k)_{\mathrm{SHG}}-(\Delta\alpha)_{\mathrm{SHG}}]}{(\Delta k)_{\mathrm{SHG}}-(\Delta\alpha)_{\mathrm{SHG}}},$$

$$B=\frac{\sin\frac{1}{2}l[(\Delta k)_{\mathrm{SHG}}+(\Delta\alpha)_{\mathrm{SHG}}]}{(\Delta k)_{\mathrm{SHG}}+(\Delta\alpha)_{\mathrm{SHG}}},$$

$$\delta=\arctan\left[\frac{-A\cos\beta_1-B\cos\beta_2}{A\sin\beta_1+B\sin\beta_2}\right],$$

$$\delta'=\arctan\left[\frac{A\sin\beta_1-B\sin\beta_2}{A\cos\beta_1-B\cos\beta_2}\right],$$

and

$$\beta_1=l\{k_2-\alpha_2-\tfrac{1}{2}[(\Delta k)_{\mathrm{SHG}}-(\Delta\alpha)_{\mathrm{SHG}}]\},$$

$$\beta_2=l\{k_2+\alpha_2-\tfrac{1}{2}[(\Delta k)_{\mathrm{SHG}}+(\Delta\alpha)_{\mathrm{SHG}}]\}.$$

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[12] D. A. Kleinman, Phys. Rev. **126**, 1977 (1962); R. C. Miller, *ibid.* **131**, 95 (1963).

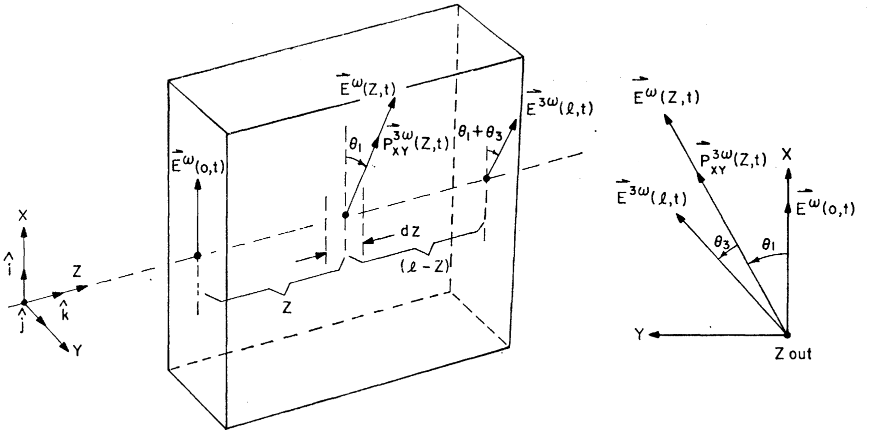

FIG. 2. Schematic representation of waves moving along the optic axis of a rotatory dispersive crystal of class 32 or a rotatory dispersive isotropic medium for THG. The right-hand diagram is a view from the exit face of the medium in which propagating waves are directed out of the paper.

The relative intensity of second-harmonic radiation at the exit face of the crystal, averaged over one period, follows directly from Eqs. (21) and (22),

$$I_{\mathrm{SHG}} \propto \frac{\sin^2\frac{1}{2}l[(\Delta k)_{\mathrm{SHG}}-(\Delta\alpha)_{\mathrm{SHG}}]}{[(\Delta k)_{\mathrm{SHG}}-(\Delta\alpha)_{\mathrm{SHG}}]^2} + \frac{\sin^2\frac{1}{2}l[(\Delta k)_{\mathrm{SHG}}+(\Delta\alpha)_{\mathrm{SHG}}]}{[(\Delta k)_{\mathrm{SHG}}+(\Delta\alpha)_{\mathrm{SHG}}]^2}. \quad (23)$$

Inspection of this expression shows that phase matching is achieved when either $(\Delta k)_{\mathrm{SHG}}=(\Delta\alpha)_{\mathrm{SHG}}$ or $(\Delta k)_{\mathrm{SHG}}=-(\Delta\alpha)_{\mathrm{SHG}}$; substituting from Eq. (18), the phase-matching conditions are

$$(\Delta k)_{\mathrm{SHG}}=\pm(\alpha_2+2\alpha_1). \quad (24)$$

B. Third-Harmonic Generation

The intensity of THG is next calculated for propagation along the optic or z axis of a crystal of class 32, and the physical situation is depicted in Fig. 2. The basic assumptions of Subsec. A above still obtain, whereby the plane of polarization of the fundamental wave described by Eqs. (8) and (9) is rotated through an angle θ_1 in traveling a distance z into the crystal. The principal modification from the earlier-treated SHG case results from the form of the third-order polarization and its relative direction with respect to $\mathbf{E}^{\omega}$. Maker and Terhune[13] have given the third-order polarization for point symmetry 32, and with $E_z^{\omega}=0$ required in the present situation, the x and y components of these polarizations take the form

$$P_x^{3\omega}=3C_{1122}E_x^{\omega}[(E_x^{\omega})^2+(E_y^{\omega})^2]$$

and

$$P_y^{3\omega}=3C_{1122}E_y^{\omega}[(E_x^{\omega})^2+(E_y^{\omega})^2], \quad (25)$$

where the constant c_{1122} is a nonvanishing component of the fourth-rank electric susceptibility tensor. The z component of third-order polarization $P_z^{3\omega}$ is nonzero, but it is of no interest for present purposes for harmonic waves propagating in the z direction. The third-harmonic light wave $\mathbf{E}^{3\omega}(z,t)$ propagating in the z direction is generated by the third-order polarization in the x-y plane,

$$\mathbf{P}_{xy}^{3\omega}(z,t)=\hat{\imath}P_x^{3\omega}+\hat{\jmath}P_y^{3\omega}. \quad (26)$$

It is clear upon substituting E_x^{ω} and E_y^{ω} from Eq. (9) into Eq. (25), and this result into Eq. (26), that the magnitude of third-order polarization in the x-y plane is given by

$$P_{xy}^{3\omega} \propto \sin^3(k_1z-\omega t), \quad (27)$$

and it is directed along the fundamental electric vector which generated it, as shown in Fig. 2. This situation is distinctly different from that of SHG where the nonlinear polarization lagged the fundamental electric field by an amount $3\theta_1$, and rotated in opposite sense. Here the third-order polarization in the x-y plane follows the fundamental electric field and rotates with it.

It was pointed out earlier that the treatment of THG along the optic axis of a rotatory dispersive crystal of point symmetry 32 is also applicable to THG in other nonlinear media with rotatory dispersion. In particular this is the situation for an isotropic medium, such as an optically active liquid, or for an isotropic medium with magneto-optic rotation. The form of the third-order polarization in an isotropic medium,[13]

$$P_i^{3\omega}=3C_{1122}E_i^{\omega}(\mathbf{E}^{\omega}\cdot\mathbf{E}^{\omega}), \quad (28)$$

where i refers to the x, y, and z components, gives the same representation as that given in Eq. (27) for the magnitude of the third-order polarization, and it also points in the same direction as the fundamental wave, $\mathbf{E}^{\omega}$.

The polarization described by Eq. (27) contains both the fundamental and the third harmonic, i.e.,

$$\sin^3(k_1z-\omega t)=\tfrac{1}{4}[3\sin(k_1z-\omega t)-\sin(3k_1z-3\omega t)],$$

and it is the component leading to THG in the z

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[13] P. D. Maker and R. W. Terhune, Phys. Rev. **137**, A801 (1965).

direction which is of interest, namely,

$$P_{xy}^{3\omega}\propto \sin(3k_1z-3\omega t)\,. \tag{29}$$

The third-harmonic light wave is initially polarized along the axis of $P_{xy}^{3\omega}$ which points along $\mathbf{E}^{\omega}$, but thereafter as a free-running wave in the rotatory dispersive medium it is rotated in the left-hand sense θ_3 in traveling a distance $l-z$ to the exit face at $z=l$. Thus

$$\theta_3=\alpha_3(l-z)\,, \tag{30}$$

where α_3 is the specific rotation at the third-harmonic frequency.

As in the case for SHG, the problem reduces to accounting for all of the $\mathbf{E}^{3\omega}$ contribution at the exit face due to the third-order polarization given in Eq. (29) with an appropriately retarded time. The differential element is given by

$$dE^{3\omega}(l,t)\propto dz\,\sin[3k_1z-3\omega(t-t')]\,, \tag{31}$$

where

$$t'=(l-z)k_3/3\omega\,, \tag{32}$$

and k_3 is the wave vector at the third-harmonic frequency. Taking account of the separate x and y components,

$$E_x^{3\omega}(l,t)\propto \int_0^l dz\,\sin[3k_1z-3\omega(t-t')]\,\cos(\theta_1+\theta_3) \tag{33}$$

and

$$E_y^{3\omega}(l,t)\propto \int_0^l dz\,\sin[3k_1z-3\omega(t-t')]\,\sin(\theta_1+\theta_3)\,. \tag{34}$$

Substituting from Eqs. (5), (8), (30), and (32), and using

$$(\Delta\alpha)_{\mathrm{THG}}=\alpha_3-\alpha_1\,, \tag{35}$$

it follows that

$$E_x^{3\omega}(l,t)\propto \int_0^l dz\,\sin[lk_3-z(\Delta k)_{\mathrm{THG}}-3\omega t]\times\cos[\alpha_3l-(\Delta\alpha)_{\mathrm{THG}}z]\,, \tag{36}$$

$$E_y^{3\omega}(l,t)\propto \int_0^l dz\,\sin[lk_3-z(\Delta k)_{\mathrm{THG}}-3\omega t]\times\sin[\alpha_3l-(\Delta\alpha)_{\mathrm{THG}}z]\,. \tag{37}$$

Upon integration, the following harmonic functions are obtained:

$$E_x^{3\omega}(l,t)\propto [C^2+2CD\cos[(\alpha_1+\alpha_3)l]+D^2]^{1/2}\times\sin(\epsilon-3\omega t)\,, \tag{38}$$

$$E_y^{3\omega}(l,t)\propto [C^2-2CD\cos[(\alpha_1+\alpha_3)l]+D^2]^{1/2}\times\sin(\epsilon'-3\omega t)\,, \tag{39}$$

where

$$C=\frac{\sin\frac{1}{2}l[(\Delta k)_{\mathrm{THG}}-(\Delta\alpha)_{\mathrm{THG}}]}{(\Delta k)_{\mathrm{THG}}-(\Delta\alpha)_{\mathrm{THG}}}\,,$$

$$D=\frac{\sin\frac{1}{2}l[(\Delta k)_{\mathrm{THG}}+(\Delta\alpha)_{\mathrm{THG}}]}{(\Delta k)_{\mathrm{THG}}+(\Delta\alpha)_{\mathrm{THG}}}\,,$$

$$\epsilon=\arctan\left[\frac{C\sin\gamma_1+D\sin\gamma_2}{C\cos\gamma_1+D\cos\gamma_2}\right],$$

$$\epsilon'=\arctan\left[\frac{C\cos\gamma_1-D\cos\gamma_2}{-C\sin\gamma_1+D\sin\gamma_2}\right],$$

and

$$\gamma_1=l\{k_3-\alpha_3-\tfrac{1}{2}[(\Delta k)_{\mathrm{THG}}-(\Delta\alpha)_{\mathrm{THG}}]\}\,,$$

$$\gamma_2=l\{k_3+\alpha_3-\tfrac{1}{2}[(\Delta k)_{\mathrm{THG}}+(\Delta\alpha)_{\mathrm{THG}}]\}\,.$$

The relative intensity of THG at the exit face of the crystal, averaged over one period, follows from Eqs. (38) and (39),

$$I_{\mathrm{THG}}\propto\frac{\sin^2\frac{1}{2}l[(\Delta k)_{\mathrm{THG}}-(\Delta\alpha)_{\mathrm{THG}}]}{[(\Delta k)_{\mathrm{THG}}-(\Delta\alpha)_{\mathrm{THG}}]^2}+\frac{\sin^2\frac{1}{2}l[(\Delta k)_{\mathrm{THG}}+(\Delta\alpha)_{\mathrm{THG}}]}{[(\Delta k)_{\mathrm{THG}}+(\Delta k)_{\mathrm{THG}}]^2}\,. \tag{40}$$

Phase matching is achieved with $(\Delta k)_{\mathrm{THG}}=\pm(\Delta\alpha)_{\mathrm{THG}}$ and from Eq. (35) the matching conditions are

$$(\Delta k)_{\mathrm{THG}}=\pm(\alpha_3-\alpha_1)\,. \tag{41}$$

DISCUSSION

The intensity of SHG and THG for the cases of rotatory dispersion, Eqs. (23) and (40), show parallel analytical form,

$$I\propto\frac{\sin^2\frac{1}{2}l(\Delta k-\Delta\alpha)}{(\Delta k-\Delta\alpha)^2}+\frac{\sin^2\frac{1}{2}l(\Delta k+\Delta\alpha)}{(\Delta k+\Delta\alpha)^2}\,, \tag{42}$$

analogous to the parallel form of Eqs. (1) and (4) for SHG and THG without optical rotation,

$$I\propto\sin^2\tfrac{1}{2}l\Delta k/(\Delta k)^2\,. \tag{43}$$

It is clear that in the limit of vanishing rotatory dispersion the above expressions become identical.

When phase matching is achieved in the presence of rotatory dispersion, Eq. (24) for SHG and Eq. (41) for THG, we have

$$\Delta k=\pm\Delta\alpha\,,$$

and the initial growth of harmonic radiation depends on l, according to

$$I\propto l^2+\sin^2l\Delta\alpha/(\Delta\alpha)^2\,.$$

The phase-matching conditions calculated with optical rotation are in essential agreement with Eq. (7), developed on the basis of physical considerations. It is clear that the detailed form of $\Delta\alpha$ depends critically on the relation of the nonlinear polarization to the fundamental light wave. In the case treated for THG, $(\Delta\alpha)_{\mathrm{THG}}$ is simply given by the difference in specific rotations $\alpha_3-\alpha_1$; however, when a more complicated spatial relationship between the fundamental wave and the nonlinear polarization exists, as in the case of SHG, $(\Delta\alpha)_{\mathrm{SHG}}$ is appropriately modified as in Eq. (18). The results indicate that Eq. (7) can be considered to be a reasonable working relationship for a rotatory dispersive medium.

The basic difference between the second-harmonic and third-harmonic light waves produced along the optic axis of crystals of class 32 arises from nonlinear polarizations rotating in opposite sense with respect to the fundamental wave. Figures 1 and 2 show left-handed optical rotation of $\mathbf{E}^{\omega}$ results in doubly rapid right-handed rotation of $\mathbf{P}_{xy}{}^{2\omega}$ for SHG, and equal left-handed rotation of $\mathbf{P}^{3\omega}$ for THG. Assuming normal rotatory dispersion in this treatment, the free-running harmonic waves $\mathbf{E}^{2\omega}$ and $\mathbf{E}^{3\omega}$, once generated in the medium, both rotate in the left-handed sense. Upon meeting the exit face of the crystal, the rotatory dispersion ceases, and the plane of polarization of the various contributing harmonic waves is thereafter frozen. The solutions obtained for the intensity of SHG and for THG clearly indicate that for a plane-polarized fundamental incoming wave, the resultant harmonic light leaving the crystal is in general elliptically polarized. Depending on the magnitudes of the dispersion and optical rotatory power of the medium, the elliptical radiation may degenerate into circular or plane-polarized harmonic radiation. The ellipticity of the harmonic radiation can be anticipated from the phases (δ and δ') and amplitudes in Eqs. (21) and (22) for SHG, and the corresponding phases (ϵ and ϵ') and amplitudes in Eqs. (38) and (39) for THG.

Equations (42) and (43) indicate characteristic differences in the harmonic light intensities due to the presence or absence of rotatory dispersion. Both solutions are oscillatory as a function of optical path length l in the medium; however, their finer details are decidedly different. These distinguishing features are shown in Fig. 3, plotted for the specific case where $\Delta k=10^3\ \mathrm{cm}^{-1}$ and $\Delta\alpha=10^2\ \mathrm{cm}^{-1}$. In the upper portion of the figure, Eq. (42) is plotted over one period, and in the lower portion, each of the terms in (42) is individually shown. The latter are of the same analytical form as Eq. (43), corresponding to the case without rotatory dispersion. It is clear that while the intensity function without rotatory dispersion has distinct zeros between each oscillation, this is not the case for rotatory dispersion. It can, in general, be shown that where the ratio $\Delta k/\Delta\alpha$ is an irrational number, there are no exact zeros other than the one occurring at the front face, $l=0$. (For the example given in Fig. 3 the ratio is 10; here zeros repeat after every 9 of the longer or 11 of the shorter cycles of the lower curves.)

Beside the removal of zeros in intensity with every oscillation, it should be noted that rotatory dispersion produces characteristic minima which are roughly half the intensity of neighboring maxima. Furthermore, there is distortion of the intensity curve caused by the rotatory dispersion which is not present in the symmetrical curves without rotation.

Turning our attention now to real materials, and the achievement of phase matching, the possibilities appear to be limited. Coherence lengths typically of the order of 10^{-3} cm require specific rotations of roughly 10^3 rad/cm in order to meet the matching requirements of Eqs. (24) and (41). Of the crystal class 32, both

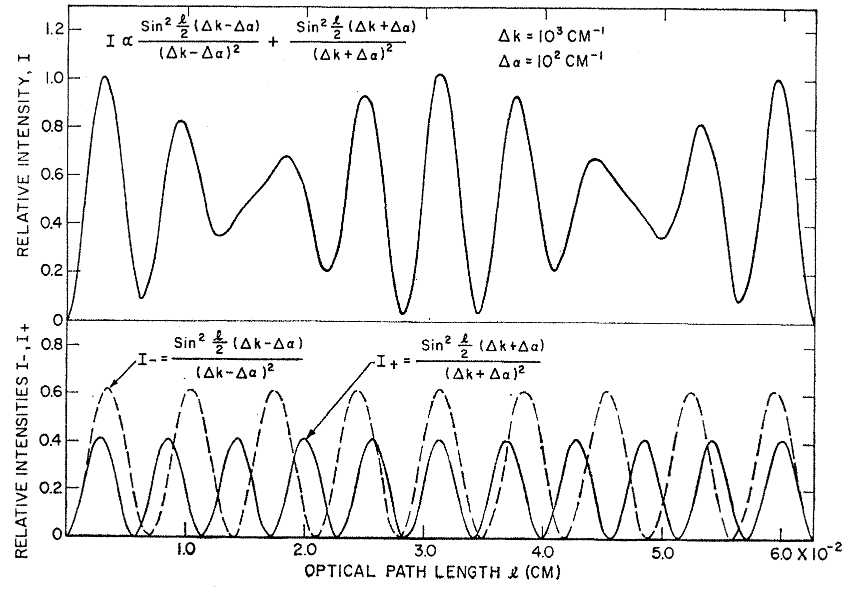

FIG. 3. General plot of the profile of the intensity of SHG and THG in a rotatory dispersive medium over one period, according to Eq. (42) (upper curve). The two component terms of Eq. (42) are plotted individually (lower curves), and correspond to typical intensity profiles in media without rotatory dispersion.

quartz and cinnabar are known to produce large natural rotations in the visible and ultraviolet, roughly in the range of 10 to 10^2 rad/cm, but these values fall short of the magnitude required. The situation is not improved by moving to longer wavelength; although coherence lengths are greater, the magnitude of natural optical rotation is in general at least correspondingly diminished. Likewise, the rotations obtained by the application of a magnetic field appear to be smaller than natural rotations for even the largest of currently available fields.

The few materials which are capable of producing the necessarily sizable specific rotations are materials which are generally prepared in thin films or very thin platelets. The so-called liquid crystals, for example cholesteryl benzoate, have natural rotations exceeding 10^3 rad/cm,[10,14] and certain magnetic materials such as the chromium trihalides[15] have built-in magneto-optic rotations which are correspondingly large. These materials generally show transmission limitations which place a further restriction on their use; nevertheless in the absence of other alternatives they might provide interesting possibilities for examining phase matching in appropriate SHG and THG experiments. Clearly, there would be a premium in the discovery of new highly rotatory media or methods for producing the same which were free of the above-mentioned limitations of size and optical quality.

CONCLUSIONS

The discussion has shown that rotatory dispersion may, in principle, be employed in producing phase matching in the harmonic generation process. This possibility anticipated on the basis of simple physical arguments is supported by more detailed analytical considerations. The analytical treatment follows that of Franken and Ward with appropriate modification to include rotatory dispersion for SHG and THG along the optic axis of crystals of point symmetry 32. The treatment for THG is equally applicable to isotropic media. The analysis can be extended to other rotatory dispersive crystals where new matching conditions may exist. Because the Franken-Ward–type treatment is carried out in the limit of no depletion of the incoming fundamental wave, it would be of interest to carry out an analogous treatment for rotatory dispersion leading to the coupled fundamental- and harmonic-wave solutions.[1] Our preliminary results along this line have supported the findings reported in this paper for the limiting case. It is intended that the coupled-wave treatment will be discussed in a subsequent communication.

The phase-matching conditions derived for the case of crystal class 32 are not achievable in either quartz or cinnabar, two crystals of this class with appreciable rotatory powers. Likewise, Verdet constants are not large enough to result in the matched conditions with the largest of magnetic fields available, and the natural rotation of liquids appear also to fall short of that required.

It would appear that only in the instance of enormously large rotatory powers, corresponding to those observed for certain liquid and magnetic crystals, could a matching condition of the form of Eq. (7) be approached. The exact form of the matching condition would of course be dependent on the particular crystal symmetry. Although there are restrictions relating to size and optical characteristics, these special materials offer interesting possibilities for studies of harmonic generation. Other experimental work in which excessive rotatory powers are not required is offered by the predictions in the text relating to ellipticity and intensity profile of harmonic radiation. Such experiments could be carried out in a variety of rotatory dispersive media which have more suitable optical properties.

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