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General theory of Maker fringes in crystals of low symmetry

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Abstract. A set of general equations for Maker fringes, applicable to all crystal structures and orientations, has been derived. Alternative forms of the equations are given, suitable for numerical work or for analytical reduction in cases where symmetry or other factors reduce their complexity. Formulae for special cases have been obtained from the general equations and the results compared with previously published work. The case of monoclinic symmetry has been discussed in more detail and a numerical example of the application of the formulae to the study of the *d*-coefficients is presented.

1. Introduction

Second-harmonic generation in systems with interfaces that are flat to within a coherence length inevitably leads to the production of Maker fringes [1] except in those particular orientations where phase matching occurs. The determination of the detailed structure of the $\chi^{(2)}$ tensor therefore usually involves a study of these fringes at some stage. The intensity of the second harmonic is determined by the values of the elements of $\chi^{(2)}$ and is related to the amplitude of the fringes, which follows an envelope function as the angle is varied. The spacing of the fringes is related to differences between combinations of refractive indices at the fundamental frequency (ω) and the doubled frequency (2ω). Valuable information about linear and non-linear optical properties can therefore be extracted from a careful study of the Maker fringes.

The most complete treatments of the theory of Maker fringes are to be found in the work of Kurtz and Jerphagnon [2] and Kurtz [3, 4], but the analysis is restricted to relatively high-symmetry uniaxial crystals, or in other cases to certain special orientations.

Organic materials, with very large non-linear susceptibilities, are currently of interest in optoelectronics [5], and these materials usually crystallize in the orthorhombic, monoclinic or triclinic systems, the most common form, at least among those crystals at present under investigation, being monoclinic.

In monoclinic crystals only one crystal axis necessarily coincides with a dielectric axis and the other two dielectric axes may rotate about the fixed axis as the frequency changes. In triclinic crystals there is no necessary relationship, dictated by symmetry, between the crystal and dielectric axes. In the course of investigations on monoclinic organic crystals the need for a more general treatment of the fringes has therefore arisen. It is

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also the case that, even for high-symmetry crystals, more information would be obtained if fringes generated at a variety of unsymmetrical orientations could be interpreted. Consequently, it seems pertinent to attempt to provide a generalized scheme of calculation for the Maker fringes.

In the present paper a general procedure for the analysis of Maker fringes in crystals with parallel entry and exit faces is derived, and the formulae are then specialized to give explicit equations for commonly occurring orientations, particularly in monoclinic systems. An example of the application of the equations to derive information about the relative values of d-coefficients in an unsymmetrical monoclinic case is given.

In subsequent papers the theory will be applied to the analysis of experimental data obtained for a number of monoclinic non-linear organic materials.

2. The non-linear wave equation

In a material with negligible magnetic susceptibility, the electric and magnetic radiation fields satisfy the equations

$$\nabla \times \nabla \times \boldsymbol{E} = -\mu_0 \, \partial^2 \boldsymbol{D}/\partial t^2 \tag{1a}$$

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} \tag{1b}$$

$$\partial \boldsymbol{H}/\partial t = -(1/\mu_0)\nabla \times \boldsymbol{E} \tag{1c}$$

where $\boldsymbol{P}$ is the polarization. In the parametric approximation (see for example [6]), the non-linear source term at 2ω is derived only from the primary field of frequency ω, so that the equations for the ω and 2ω Fourier components of the field can be separated. The two frequency components of the field and polarization are written

$$\boldsymbol{E}(\boldsymbol{r}, t) = \mathrm{Re}[\boldsymbol{E}(\omega)\,\mathrm{e}^{-\mathrm{i}\omega t} + \boldsymbol{E}(2\omega)\,\mathrm{e}^{-2\mathrm{i}\omega t}] \tag{2a}$$

$$\boldsymbol{P}(\boldsymbol{r}, t) = \mathrm{Re}[\boldsymbol{P}(\omega)\,\mathrm{e}^{-\mathrm{i}\omega t} + \boldsymbol{P}(2\omega)\,\mathrm{e}^{-2\mathrm{i}\omega t}] \tag{2b}$$

where

$$\boldsymbol{P}(-\Omega)^* = \boldsymbol{P}(\Omega) \tag{2c}$$

and Ω denotes either ω or 2ω.

The constitutive relations, including the second-order effect, are

$$\boldsymbol{P}^{(1)}(\Omega) = \varepsilon_0 \boldsymbol{\chi}^{(1)}(-\Omega; \Omega):\boldsymbol{E}(\Omega) \tag{3a}$$

$$\boldsymbol{P}^{(2)}(2\omega) = \varepsilon_0 \boldsymbol{\chi}^{(2)}(-2\omega; \omega, \omega):\boldsymbol{E}(\omega)\boldsymbol{E}(\omega) \tag{3b}$$

$$\boldsymbol{\varepsilon}(\Omega) = 1 + \boldsymbol{\chi}^{(1)}(-\Omega:\Omega). \tag{3c}$$

Substitution into equations (1b) and (1a) then leads to the wave equations for $\boldsymbol{E}(\omega)$ and $\boldsymbol{E}(2\omega)$, i.e.

$$\nabla \times \nabla \times \boldsymbol{E}(\omega) - (\omega/c)^2 \boldsymbol{\varepsilon}(\omega):\boldsymbol{E}(\omega) = 0 \tag{4}$$

for the fundamental and

$$\nabla \times \nabla \times \boldsymbol{E}(2\omega) - (2\omega/c)^2 \boldsymbol{\varepsilon}(2\omega):\boldsymbol{E}(2\omega) = \mathcal{P}(2\omega) \tag{5}$$

for the second harmonic, where

$$\mathcal{P}(2\omega) = (2\omega/c)^2 \boldsymbol{\chi}(-2\omega; \omega, \omega):\boldsymbol{E}(\omega)\boldsymbol{E}(\omega). \tag{6}$$

Here and in the rest of this paper the non-linear susceptibility for frequency doubling is denoted simply by χ or χ_{ijk}.

3. Laboratory set-up, coordinate system and notation

The type of experiment that is to be analysed is shown schematically in figure 1. The diagram represents a plan view of the experiment as seen from above the optical bench. The crystals are usually available in the form of thin, cleaved slices of thickness ~1 mm or of rather thicker polished slabs (~4 mm). In either case there is a pair of opposite parallel faces through which the light enters and leaves the crystal. In figure 1 these parallel faces are in the planes $z = 0$ and $z = L$. The z axis is therefore the normal to the face of the slabs; the x axis lies in the entry face of the slab and also in the plane of incidence. The y axis is normal to the plane of incidence and, with the senses of x and z as shown in the figure, points in to the plane of the paper to make xyz a right-handed set. The coordinate system xyz is a laboratory system and has no necessary relation to the internal crystal symmetry or the principal dielectric axes.

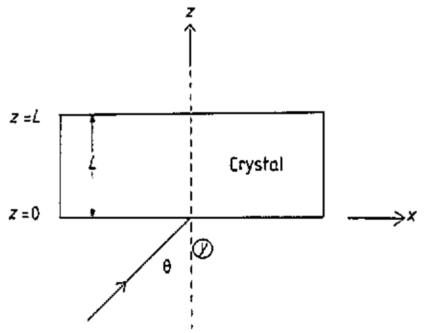

Figure 1. Coordinate system. The diagram shows a plan view, from above the optical bench, of the type of experiment envisaged. The opposite parallel faces of the crystal slab are in the $z = 0$ (entry face) and $z = L$ (exit face) planes. The xz plane is the plane of incidence; all wavevectors lie in this plane. The y axis is normal to the plane of incidence and points into the plane of the paper; the z axis is the direction of normal incidence. The angle of incidence is denoted by θ. This coordinate system is referred to as the laboratory system.

All the calculations in this paper are referred to the laboratory system of axes. The disadvantage of this procedure is that the dielectric tensors at ω and 2ω are no longer diagonal and the elements of χ are not directly referred to the conventional piezoelectric system. The disadvantages are outweighed by the necessity of working in one coordinate system that is simply related to the boundary conditions. The transformation of ε and χ from the principal axis and piezoelectric systems can be effected by standard tensor methods. The d-coefficient notation is reserved for quantities referred to the standard piezoelectric system; in the laboratory system the elements of the second-order susceptibility are always denoted by χ_{ijk}.

For an anisotropic crystal, a plane wave of frequency ω incident at an angle θ will, in general, give rise to two plane waves of the same frequency in the crystal. These will

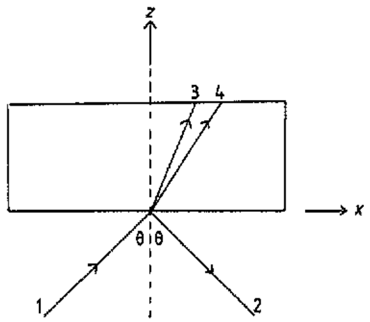

Figure 2. ω waves. Schematic representation of the waves present at the fundamental frequency ω: $I = 1$, incident wave; $I = 2$, reflected wave; $I = 3, 4$, refracted waves.

generate three polarization waves at 2ω with associated bound electromagnetic fields and there will also be two independent free-wave solutions at 2ω. In addition there are reflected, internally reflected and transmitted waves. It is convenient to label each wave with a single index, denoted in the following by I or J. The system of numbering is shown in figure 2 for ω waves and in figure 3 for 2ω waves.

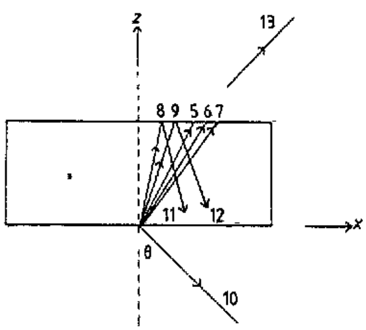

Figure 3. 2ω waves. Schematic diagram of the waves present at the double frequency 2ω: $I = 10$, reflected wave; $I = 5, 6, 7$, polarization (bound) waves; $I = 8, 9$, free waves; $I = 11, 12$, internally reflected waves; $I = 13$, transmitted wave.

Multiple internal reflections are neglected; correction factors of the kind discussed by Kurtz and Jerphagnon [2] can be introduced into the final expressions if necessary. The first internally reflected 2ω waves, 11 and 12, must be included to obtain a consistent solution of the boundary conditions at $z = L$.

Each of the frequency components $\boldsymbol{E}(\omega)$ in equation (2) is made up of a sum over plane-wave components of the form

$$\boldsymbol{E}_I(\boldsymbol{k}_I, \boldsymbol{r}) = E_I \hat{\boldsymbol{e}}_I \, \mathrm{e}^{\mathrm{i}\boldsymbol{k}_I \cdot \boldsymbol{r}} \tag{7}$$

where each I refers to the particular frequency, ω or 2ω. The unit polarization vector $\hat{\mathbf{e}}_I$ has components e_{Ii} $(i = x, y, z)$ and the alternative notation E_{Ii} $(i = x, y, z)$ is sometimes used for the components of the field, to avoid cumbersome normalization algebra.

The wavevectors $\boldsymbol{k}_I$ remain in the plane of incidence so that $k_{Iy} = 0$ for all I. Furthermore, to satisfy the boundary conditions over the whole entry and exit faces,

$$\begin{aligned} k_{Ix} &= k_{1x} \qquad \text{when} \qquad \Omega_I = \omega \\ k_{Ix} &= 2k_{1x} \qquad \text{when} \qquad \Omega_I = 2\omega. \end{aligned} \tag{8}$$

The problem of determining the wavevectors of the free waves in the crystal therefore reduces to that of finding the k_{Iz} values. Since it is anticipated that in many cases a numerical approach to the calculation will be made, it is convenient to introduce dimensionless variables ξ_I, such that

$$\xi_I = k_{Iz}/k_{\text{vac}}(\Omega_I)$$

where

$$\begin{aligned} k_{\text{vac}}(\omega) &= \omega/c = k_1 \\ k_{\text{vac}}(2\omega) &= 2\omega/c = 2k_1. \end{aligned} \tag{9}$$

When θ and e_{1y} are fixed, the problem is completely defined in the sense that the 2ω output for any polarization can be computed as a ratio to E_1^4, provided all the material parameters $(\boldsymbol{\varepsilon}, \boldsymbol{\chi})$ are known.

Relationships between the parameters describing the waves *in vacuo* (1, 2, 10 and 13) are summarized in table 1. The quantity

$$\gamma_I = -[1/k_{\text{vac}}(\Omega_I)](\boldsymbol{k}_I \times \hat{\boldsymbol{e}}_I)_y = s e_{Iz} - \xi_I e_{Ix} \tag{10}$$

which appears in the boundary conditions for the magnetic field, is also included. In this table and throughout the paper, $s = \sin\theta$ and $c = \cos\theta$, where θ is the angle of incidence.

Table 1. External waves. The table contains relationships between the parameters characterizing the incident, reflected and transmitted waves outside the crystal. These equations, resulting from the transverse nature of the vacuum waves, have been used, implicitly, in deriving the results in the text. Here and elsewhere, $c = \cos\theta$, $s = \sin\theta$ and $\gamma_I = se_{Iz} - \xi_I e_{Ix}$.

Incident wave: $I = 1$, $\Omega_I = \omega$			
$k_{1x} = k_1 s$ $k_{1z} = k_1 c$	$\xi_1 = c$	$e_{1x} = c(1 - e_{1y}^2)^{1/2}$ $e_{1z} = -(s/c)e_{1x}$	$\gamma_1 = -e_{1x}/c$
Reflected wave[a]: $I = 2$, $\Omega_I = \omega$			
$k_{2x} = k_1 s$ $k_{2z} = -k_1 c$	$\xi_2 = -c$	$e_{2x} = c(1 - e_{2y}^2)^{1/2}$ $e_{2z} = (s/c)e_{2x}$	$\gamma_2 = e_{2x}/c$
Reflected wave[a]: $I = 10$, $\Omega_I = 2\omega$			
$k_{10x} = 2k_1 s$ $k_{10z} = -2k_1 c$	$\xi_{10} = -c$	$e_{2x} = c(1 - e_{10y}^2)^{1/2}$ $e_{2z} = (s/c)e_{10x}$	$\gamma_{10} = e_{10x}/c$
Transmitted wave: $I = 13$, $\Omega_I = 2\omega$			
$k_{13x} = 2k_1 s$ $k_{13z} = 2k_1 c$	$\xi_{13} = c$	$e_{13x} = c(1 - e_{13y}^2)^{1/2}$ $e_{13z} = -(s/c)e_{13x}$	$\gamma_{13} = -e_{13x}/c$

[a] The signs of the x components of the polarization for reflected waves are chosen arbitrarily. The sign of the amplitudes E_2 and E_{10}, determined from the boundary conditions, automatically adjusts the relative signs.

4. Solution of the wave equations

Equations (4), (5) and (6) can now be written in a more explicit form. Define the operator

$$\hat{F}(\Omega) = \{1/[k_{\text{vac}}(\Omega)]^2\} \quad [\nabla \times \nabla \times \quad -(\Omega/c)^2 \boldsymbol{\varepsilon}^{\Omega}:] \tag{11}$$

where a superscript notation has been introduced to indicate the frequency dependence of $\boldsymbol{\varepsilon}$. The action of $\hat{F}$ on fields of the form defined in equation (7) can be expressed in matrix form as

$$\hat{F}(\Omega)E_I(\Omega) = \mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{\Omega})E_I(\Omega) = \mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{\Omega})\hat{e}_I E_I \, \mathrm{e}^{\mathrm{i}k_I \cdot r} \tag{12}$$

where

$$\mathbf{F}(\xi, \boldsymbol{\varepsilon}) = \begin{pmatrix} \xi^2 - \varepsilon_{xx} & -\varepsilon_{xy} & -(s\xi + \varepsilon_{xz}) \\ -\varepsilon_{xy} & \xi^2 + s^2 - \varepsilon_{yy} & -\varepsilon_{yz} \\ -(s\xi + \varepsilon_{xz}) & -\varepsilon_{yz} & s^2 - \varepsilon_{zz} \end{pmatrix}. \tag{13}$$

The superscript notation $\boldsymbol{\varepsilon}^{\Omega_I}$, indicating that the dielectric tensor is a function of the frequency of wave I, is shortened to $\boldsymbol{\varepsilon}^I$ where this can be done without ambiguity.

The polarization vectors of the fundamental waves 3 and 4 satisfy equation (4) in the form

$$\mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{\omega})\hat{e}_I = 0 \tag{14a}$$

which only has non-trivial solutions if

$$|\mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{\omega})| = 0. \tag{14b}$$

Equation (14*b*) is Fresnel's equation of wave normals [7] expressed in the laboratory coordinate system, which leads to a quartic equation for ξ_I. In special cases the ξ_I values can be extracted analytically from this equation, which is obtained explicitly from the expansion of the determinant

$$\begin{aligned} -|\mathbf{F}(\xi, \boldsymbol{\varepsilon})| = {} & \varepsilon_{zz}\xi^4 + 2\varepsilon_{xz}s\xi^3 + [\varepsilon_{zz}(s^2 - \varepsilon_{yy}) + \varepsilon_{xx}(s^2 - \varepsilon_{zz}) + \varepsilon_{yz}^2 + \varepsilon_{xz}^2]\xi^2 \\ & + 2s[\varepsilon_{xz}(s^2 - \varepsilon_{yy}) + \varepsilon_{xy}\varepsilon_{yz}]\xi + \varepsilon_{xx}(s^2 - \varepsilon_{yy})(s^2 - \varepsilon_{zz}) + \varepsilon_{xy}^2(s^2 - \varepsilon_{zz}) \\ & + \varepsilon_{xz}^2(s^2 - \varepsilon_{yy}) - \varepsilon_{xx}\varepsilon_{yz}^2 + 2\varepsilon_{xz}\varepsilon_{xy}\varepsilon_{yz}. \end{aligned} \tag{15}$$

It follows by transformation to a principal-axis system or by direct analysis of equation (15) [7] that there are always four real roots for ξ_I of which two are positive and two negative. The two positive roots of equation (14*b*) are the values of ξ_3 and ξ_4. The vectors $\hat{e}_3$ and $\hat{e}_4$ are obtained by substituting these ξ values back into equation (14*a*).

The free second-harmonic waves, 8, 9, 11 and 12, are obtained in the same way from

$$\mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})\hat{e}_I = 0 \tag{16a}$$

$$|\mathbf{F}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})| = 0. \tag{16b}$$

The two positive roots of the associated determinant give ξ_8 and ξ_9 and the two negative roots ξ_{11} and ξ_{12}. Only in special cases are ξ_{11} and ξ_{12} equal to $-\xi_8$ and $-\xi_9$. The amplitudes of the waves in the crystal are calculated below by solving boundary-condition equations. Suppose that this has been done for the ω waves and that E_3 and E_4 are known. If equation (5) is divided by

$$[k_{\text{vac}}(2\omega)]^2 = (2k_1)^2$$

it can be rewritten as

$$\hat{F}(2\omega)E(2\omega) = [1/(2k_1)^2]\mathcal{P}(2\omega) = P(2\omega) = \chi:(E_3 + E_4)(E_3 + E_4). \tag{17}$$

The components of P are written

$$P_i(2\omega) = \sum_{I=5}^{7} p_{Ii}\, \mathrm{e}^{2\mathrm{i}\xi_I k_1 z} E_1^2 \tag{18}$$

where

$$\xi_5 = \xi_3 \qquad \xi_6 = \xi_4 \qquad \xi_7 = \tfrac{1}{2}(\xi_3 + \xi_4). \tag{19}$$

In equation (18) the summation is over the three polarization waves, the x dependence has been omitted and

$$p_{Ii} = \chi_{ijk}\pi_{Ijk}t_I \tag{20}$$

where the summation convention over repeated coordinate indices is implied and the projection factors π_{Iij} and transmission coefficients t_I are given explicitly later in table 2. Equation (17) becomes

$$\hat{F}(2\omega)E(2\omega) = \sum_{I=5}^{7} p_I\, \mathrm{e}^{2\mathrm{i}\xi_I k_1 z} E_1^2. \tag{21}$$

The solution of equation (21) consists of a linear combination of the two free waves, 8 and 9, solutions of the homogeneous part of (21) and a particular solution of the inhomogeneous equation. The free waves 11 and 12 are not included. Their effect at the $z = 0$ boundary is assumed to be negligible, so that the amplitudes E_8 and E_9 are determined at this boundary without reference to them. The inhomogeneous field is made up from the sum of three terms, each having the same z dependence as one of the polarization components. These are obtained by solving equation (21) separately for each polarization wave:

$$\mathsf{F}(2\omega)E_I\, \mathrm{e}^{2\mathrm{i}\xi_I k_1 z} = p_I\, \mathrm{e}^{2\mathrm{i}\xi_I k_1 z} E_1^2 \qquad I = 5, 7 \tag{22}$$

or

$$\mathsf{F}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})E_I = p_I E_1^2 \tag{23}$$

$$E_I/E_1^2 = \mathsf{F}^{-1}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})p_I = |\mathsf{F}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})|^{-1}\mathsf{F}^{\mathrm{A}}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})p_I \qquad I = 5, 7 \tag{24}$$

where F^{A} is the adjoint matrix of F.

The values of ξ_I are predetermined for the polarization waves, so that $|\mathsf{F}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})|$ is not zero except in the special cases that produce phase matching. The adjoint matrix is useful when explicit formulae are to be derived in cases where symmetry somewhat simplifies the equations. The matrix $\mathsf{F}^{\mathrm{A}}(\xi, \boldsymbol{\varepsilon})$ is symmetric and its distinct components are

$$\begin{aligned}
F^{\mathrm{A}}_{xx} &= F_{\mathrm{O}}(s^2 - \varepsilon_{zz}) - \varepsilon_{yz}^2 \\
F^{\mathrm{A}}_{xy} &= \varepsilon_{xy}(s^2 - \varepsilon_{zz}) + \varepsilon_{yz}(s\xi + \varepsilon_{xz}) \\
F^{\mathrm{A}}_{xz} &= F_{\mathrm{O}}(s\xi + \varepsilon_{xz}) + \varepsilon_{xy}\varepsilon_{yz} \\
F^{\mathrm{A}}_{yy} &= F_{\mathrm{E}} - 2\varepsilon_{xz}s\xi - \varepsilon_{xz}^2 \\
F^{\mathrm{A}}_{yz} &= \varepsilon_{yz}(\xi^2 - \varepsilon_{xx}) + \varepsilon_{xy}(s\xi + \varepsilon_{xz}) \\
F^{\mathrm{A}}_{zz} &= F_{\mathrm{O}}(\xi^2 - \varepsilon_{xx}) - \varepsilon_{xy}^2
\end{aligned} \tag{25a}$$

where

$$F_O = s^2 + \xi^2 - \varepsilon_{yy} \qquad F_E = (\xi^2 - \varepsilon_{xx})(s^2 - \varepsilon_{zz}) - s^2\xi^2. \tag{25b}$$

The notation O and E relates to the factorization of the matrix into $F_O F_E$ when $\boldsymbol{\varepsilon}$ is diagonal. The values of ξ obtained from these factors refer to the ordinary and extraordinary waves, ordinary here having the meaning that the electric vector is normal to the plane of incidence.

5. The boundary conditions

At each boundary the E and H field components parallel to the boundary surface must be continuous. In the coordinate system defined, E_x, E_y, $(\nabla \times \boldsymbol{E})_x$ and $(\nabla \times \boldsymbol{E})_y$ must be continuous at $z = 0$ and $z = L$. Since k_{ly} is zero, the two curl terms can be replaced by $\xi_l e_{ly} E_l$ and $\gamma_l E_l$, respectively. At the $z = 0$ boundary the ω wave conditions are used to determine E_3 and E_4 and the 2ω wave conditions (neglecting E_{11} and E_{12}) to find E_8 and E_9. At $z = L$ the 2ω equations are solved for the transmitted wave components.

Each set of boundary conditions consists of four equations from which two of the four unknowns can always be eliminated in a symmetric and manipulatively easy manner, after which the equations will have a form such as

$$\mathbf{M}\begin{pmatrix} E'_\alpha \\ E'_\beta \end{pmatrix} = \begin{pmatrix} m_1 \\ m_2 \end{pmatrix} = \boldsymbol{m} \tag{26}$$

where $\boldsymbol{m}$ is a predetermined vector and $\mathbf{M}$ a 2×2 matrix of factors determined from the free-wave characteristics. E'_α and E'_β are the remaining unknown fields, including factors such as E_1^{-1} or E_1^{-2}. The vector on the right is sometimes the resultant of a sum over known waves:

$$\begin{pmatrix} m_1 \\ m_2 \end{pmatrix} = \sum_l \begin{pmatrix} m_{1l} \\ m_{2l} \end{pmatrix}. \tag{27}$$

The following notation is therefore introduced:

$$M = |\mathbf{M}| = \begin{vmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{vmatrix} \qquad M_1 = \begin{vmatrix} m_1 & M_{12} \\ m_2 & M_{22} \end{vmatrix} \qquad M_2 = \begin{vmatrix} M_{11} & m_1 \\ M_{21} & m_2 \end{vmatrix}$$

$$M_{1l} = \begin{vmatrix} m_{1l} & M_{12} \\ m_{2l} & M_{12} \end{vmatrix} \qquad M_{2l} = \begin{vmatrix} M_{11} & m_{1l} \\ M_{21} & m_{2l} \end{vmatrix}. \tag{28}$$

The general symbols M and m are replaced by symbols specific to each set of boundary conditions:

U, u	for ω conditions at $z = 0$
V, v	for 2ω conditions at $z = 0$
W, w	for 2ω conditions at $z = L$.

(i) Boundary conditions for ω waves at $z = 0$:

$$E_1 e_{1x} + E_2 e_{2x} = E_3 e_{3x} + E_4 e_{4x} \tag{29a}$$

$$E_1 e_{1y} + E_2 e_{2y} = E_3 e_{3y} + E_4 e_{4y} \tag{29b}$$

$$\xi_1 E_1 e_{1y} + \xi_2 E_2 e_{2y} = \xi_3 E_3 e_{3y} + \xi_4 E_4 e_{4y} \tag{29c}$$

$$\gamma_1 E_1 + \gamma_2 E_2 = \gamma_3 E_3 + \gamma_4 E_4. \tag{29d}$$

Eliminating $(E_2/E_1)e_{2x}$ and $(E_2/E_1)e_{2y}$ and using values of γ_1, γ_2, ξ_1 and ξ_2 from table 1 leads to

$$E_3/E_1 = U_1/U \qquad E_4/E_1 = U_2/U \tag{30}$$

where

$$U = \begin{vmatrix} (c+\xi_3)e_{3y} & (c+\xi_4)e_{4y} \\ e_{3x} - c\gamma_3 & e_{4x} - c\gamma_4 \end{vmatrix} \qquad \boldsymbol{u} = \begin{pmatrix} 2ce_{1y} \\ 2e_{1x} \end{pmatrix}. \tag{31}$$

The quantities t_I ($I = 5, 7$) of the preceding section are therefore given by

$$t_5 = (U_1/U)^2 \qquad t_6 = (U_2/U)^2 \qquad t_7 = U_1 U_2/U^2.$$

(ii) Boundary conditions for 2ω waves at $z = 0$:

$$E_{10} e_{10x} = E_8 e_{8x} + E_9 e_{9x} + \sum_{I=5}^{7} (E_{Ix}/E_1^2) E_1^2 \tag{32a}$$

$$E_{10} e_{10y} = E_8 e_{8y} + E_9 e_{9y} + \sum_{I=5}^{7} (E_{Iy}/E_1^2) E_1^2 \tag{32b}$$

$$\xi_{10} E_{10} e_{10y} = \xi_8 E_8 e_{8y} + \xi_9 E_9 e_{9y} + \sum_{I=5}^{7} \xi_I (E_{Iy}/E_1^2) E_1^2 \tag{32c}$$

$$\gamma_{10} E_{10} = \gamma_8 E_8 + \gamma_9 E_9 + \sum_{I=5}^{7} [s(E_{Iz}/E_1^2) - \xi_I (E_{Ix}/E_1^2)] E_1^2. \tag{32d}$$

Elimination of $E_{10}e_{10x}$ and $E_{10}e_{10y}$ leads eventually to

$$E_8/E_1^2 = \sum_{I=5}^{7} V_{1I}/V \qquad E_9/E_1^2 = \sum_{I=5}^{7} V_{2I}/V \tag{33}$$

where

$$V = \begin{vmatrix} (c+\xi_8)e_{8y} & (c+\xi_9)e_{9y} \\ e_{8x} - c\gamma_8 & e_{9x} - c\gamma_9 \end{vmatrix}$$

$$\boldsymbol{v}_I = -\begin{pmatrix} (c+\xi_I)E_{Iy}/E_1^2 \\ (1+c\xi_I)E_{Ix}/E_1^2 - csE_{Iz}/E_1^2 \end{pmatrix}. \tag{34}$$

(iii) Boundary conditions for 2ω waves at $z = L$: Factors $f_I = e^{2i\xi^I k_1 L}$ now appear as a result of the phaseshifts between $z = 0$ and $z = L$. The four equations are

$$E_{13}e_{13x}f_{13} - E_{11}e_{11x}f_{11} - E_{12}e_{12x}f_{12} = \sum_{I=5}^{9} (E_{Ix}/E_1^2)f_I E_1^2 \tag{35a}$$

$$E_{13}e_{13y}f_{13} - E_{11}e_{11y}f_{11} - E_{12}e_{12y}f_{12} = \sum_{I=5}^{9} (E_{Iy}/E_1^2)f_I E_1^2 \tag{35b}$$

$$\xi_{13}E_{13}e_{13y}f_{13} - \xi_{11}E_{11}e_{11y}f_{11} - \xi_{12}E_{12}e_{12y}f_{12} = \sum_{I=5}^{9} (E_{Iy}/E_1^2)\xi_I f_I E_1^2 \tag{35c}$$

$$\gamma_{13}E_{13}f_{13} - \gamma_{11}E_{11}f_{11} - \gamma_{12}E_{12}f_{12} = \sum_{I=5}^{9} [s(E_{Iz}/E_1^2) - \xi_I(E_{Ix}/E_1^2)]f_I E_1^2. \tag{35d}$$

In this case it is easiest to eliminate the E_{13} components first and solve for E_{11} and E_{12}. The values of E_{11} and E_{12} are then substituted back into the first two equations to find the components of E_{13}. Following this procedure leads to

$$\frac{E_{11}}{E_1^2}f_{11} = \sum_{I=5}^{9} f_I \frac{W_{1I}}{W} \qquad \frac{E_{12}}{E_1^2}f_{12} = \sum_{I=5}^{9} f_I \frac{W_{2I}}{W} \tag{36}$$

where

$$W = \begin{vmatrix} (c - \xi_{11})e_{11y} & (c - \xi_{12})e_{12y} \\ e_{11x} + c\gamma_{11} & e_{12x} + c\gamma_{12} \end{vmatrix} \tag{37}$$

$$w_I = -\begin{pmatrix} (c - \xi_I)E_{Iy}/E_1^2 \\ (1 - c\xi_I)E_{Ix}/E_1^2 + csE_{Iz}/E_1^2 \end{pmatrix}.$$

Substitution into equations (35a) and (35b) then gives

$$E_{13}e_{13i}f_{13} = E_1^2 \sum_{I=5}^{9} f_I \left(\frac{W_{1I}}{W}e_{11i} + \frac{W_{2I}}{W}e_{12i} + \frac{E_{Ii}}{E_1^2}\right) \tag{38}$$

$$= E_1^2 \sum_{I=5}^{9} f_I Q_{Ii} \qquad i = x, y \tag{39}$$

where

$$Q_{Ii} = (W_{1I}/W)e_{11i} + (W_{2I}/W)e_{12i} + E_{Ii}/E_1^2 \qquad i = x, y. \tag{40}$$

The phase factor f_{13} is unimportant and can be omitted. The transmitted second-harmonic intensities of the x and y components are proportional to

$$|E_{13i}|^2 = E_1^4 \left|\sum_{I=5}^{9} f_I Q_{Ii}\right|^2 = E_1^4 \left(\sum_{I=5}^{9} Q_{Ii}^2 + \sum_{\substack{I=5 \\ I\neq J}}^{9} \sum_{J=5}^{9} e^{2ik_1(\xi_I - \xi_J)L} Q_{Ii} Q_{Ji}\right) \tag{41}$$

$$|E_{13i}|^2 = E_1^4 \left[\left(\sum_{I=5}^{9} Q_{Ii}\right)^2 - 4\sum_{I=5}^{9} \sum_{J=I+1}^{9} Q_{Ii}Q_{Ji} \sin^2[k_1(\xi_I - \xi_J)L]\right]. \tag{42}$$

For the limiting case of a very thin crystal ($L \to 0$), equation (42) predicts that the second-harmonic intensity is given by

$$\lim_{L\to 0} |E_{13i}|^2 = E_1^4 \left(\sum_{I=5}^{9} Q_{Ii}\right)^2. \tag{43}$$

If all multiple reflections were included coherently, the intensity obtained from a very thin slab should tend to zero. The magnitude of the first term on the right of equation (42) is therefore of the order of the contributions neglected in the approximation used in this model and it is omitted in the rest of the analysis. It can be shown directly in special cases that the L-independent term is small compared to the second term in equation (42). With this approximation the second-harmonic intensities reduce to

$$|E_{13i}|^2 = -4 \sum_{I=5}^{9} \sum_{J=I+1}^{9} Q_{Ii} Q_{Ji} \sin^2[k_1(\xi_I - \xi_J)L] E_1^4. \tag{44}$$

Maker fringes are produced by interference between the free and bound second-harmonic waves. The formula describes all possible types of Maker fringes and additional interference effects between one free wave and the other and among the three bound waves. The mutual interference of the two free waves is analogous to the conoscopic interference occurring in the linear optics of biaxial crystals. Since the dispersion due to birefringence and the frequency dispersion are often effects of comparable magnitude, it is to be expected that, in more complicated optical geometries that do not isolate one or other phenomenon, mixed effects may sometimes be observed.

Maximum information will be obtained if the second-harmonic intensities are measured for two cases of orthogonal polarization, most conveniently chosen to be normal and parallel to the plane of incidence. Denoting the intensities in the two cases, respectively, by $\mathscr{I}_O$ and $\mathscr{I}_E$ and relating the total parallel intensity to that of the x polarization direction by a factor $(1/c^2)$ gives

$$\mathscr{I}_O/E_1^2 = -4 \sum_{I=5}^{9} \sum_{J=I+1}^{9} Q_{Iy} Q_{Jy} \sin^2[k_1(\xi_I - \xi_J)L] \tag{45}$$

$$\mathscr{I}_E/E_1^2 = -(4/c^2) \sum_{I=5}^{9} \sum_{J=I+1}^{9} Q_{Ix} Q_{Jx} \sin^2[k_1(\xi_I - \xi_J)L]. \tag{46}$$

The equations derived to this point are sufficient to allow a numerical computation of the angular dependence of the second-harmonic intensity to be made provided that the $\boldsymbol{\varepsilon}^{\omega}$, $\boldsymbol{\varepsilon}^{2\omega}$ and $\boldsymbol{\chi}$ tensors are known. All ξ_I values can be found from equations (14*b*), (16*b*) and (19) and the corresponding $\hat{\boldsymbol{e}}_I$ vectors for the free waves from the associated linear equations, (14*a*) and (16*a*). Standard numerical methods are readily available. The quantity γ_I can be constructed from ξ_I and $\hat{\boldsymbol{e}}_I$. The ω fields, E_3 and E_4, can then be found from (30) and (31), the polarization waves from (20) and (24), the free 2ω waves from (33) and (34), and the W and Q values from (37) and (40).

The above procedure could be used with numerical optimization to refine incompletely determined $\boldsymbol{\chi}$ matrices, or to check observations made with new geometries when the elements of $\boldsymbol{\chi}$ have been determined in more symmetrical arrangements or by the phase-matching method. Very often some of the elements will have been estimated using Kleinman symmetry [6, 8] and the application of the more general equations should allow this approximation to be tested.

With new organic materials the information available will often be fragmentary and an independent determination of the tensor by the Maker fringe method will be necessary. In these circumstances it will be advantageous to arrange the formulae to isolate the contributions of individual elements of the tensor. For low-symmetry crystals this end is not completely attainable but the formulae can be rearranged in a manner that allows the contributions of individual elements and small groups of elements to be more explicitly exhibited. This rearrangement is carried out in the next section and applied, in section 7, to particular cases where there is some simplification through symmetry.

6. Derivation of a more explicit general formula

In equation (38) and subsequent equations, each phase factor appears once in each term of the summation; so that each spatial periodicity in the fringes is identified uniquely in the final formula. This is computationally convenient, but when attempting to identify the contributions of small groups of coefficients, it is better to extract them from the polarization terms and group them together. To do this the free fields must be expressed explicitly in terms of the bound fields. A further advantage that then accrues is that each phase-matching denominator, $|\mathbf{F}(\xi_I, \varepsilon^{2\omega})|(I = 5, 7)$, is separated as a factor in only one term of the sum. Small values of these denominators can often so enhance the contribution of a particular term as to make a substantial reduction in the number of d-coefficients that effectively contribute to the signal.

In the following, $\alpha = 8, 9$ is an index used to identify the free waves at 2ω. The repeated index summation convention is implied over the coordinate indices (j, k, l, m, n) but not over the indices I, α that label the different waves. Expressions for the various coefficients that are introduced during the rearrangement are collected together in table 2.

Expanding the right-hand side of equation (33) gives the free-wave amplitudes E_8 and E_9 in terms of the bound-wave components

$$E_\alpha = \sum_{I=5}^{7} A_{\alpha Ij} E_{Ij} \tag{47}$$

and, using equations (37) and (40), each Q_{Ii} can be written in terms of the corresponding electric field

$$Q_{Ii} = B_{Iij} E_{Ij}. \tag{48}$$

From equation (39) the transmitted field vector is

$$E_{13i} = \sum_{I=5}^{9} f_I B_{Iij} E_{Ij}. \tag{49}$$

The free fields, $I = 8, 9$, in equation (49) must be separated and expanded in terms of the bound fields:

$$E_{13i} = \sum_{I=5}^{7} f_I B_{Iij} E_{Ij} + \sum_{\alpha=8}^{9} f_\alpha B_{\alpha ij} E_{\alpha j}. \tag{50}$$

Table 2. Formulae for the evaluation of coefficients. The formulae in this table provide, in conjunction with equations (25), (55), (56), (59) and (60), the basis for an algorithm for the evaluation of the right-hand side of equation (57). The wave parameters, ξ_I and $\hat{e}_I$ must be known (see section 4) and the $\chi^{(2)}$ tensor is implicit in the X_{Ik}.

$$U = (c+\xi_3)e_{3y}(e_{4x} - c\gamma_4) - (c+\xi_4)e_{4y}(e_{3x} - c\gamma_3)$$

$$U_1 = 2[ce_{1y}(e_{4x} - c\gamma_4) - e_{1x}(c+\xi_4)e_{4y}]$$

$$U_2 = 2[e_{1x}(c+\xi_3)e_{3y} - ce_{1y}(e_{3x} - c\gamma_3)]$$

$$t_5 = (U_1/U)^2 \qquad t_6 = (U_2/U)^2 \qquad t_7 = U_1U_2/U^2$$
$$\pi_{5jk} = e_{3j}e_{3k} \qquad \pi_{6jk} = e_{4j}e_{4k} \qquad \pi_{7jk} = e_{3j}e_{4k} + e_{4j}e_{3k}$$

$$V = (c+\xi_8)e_{8y}(e_{9x} - c\gamma_9) - (c+\xi_9)e_{9y}(e_{8x} - c\gamma_8)$$

$$A_{8Ix} = (1/V)(c+\xi_9)e_{9y}(1+c\xi_I) \qquad A_{9Ix} = -(1/V)(c+\xi_8)e_{8y}(1+c\xi_I)$$
$$A_{8Iy} = -(1/V)(c+\xi_I)(e_{9x} - c\gamma_9) \qquad A_{9Iy} = (1/V)(c+\xi_I)(e_{8x} - c\gamma_8)$$
$$A_{8Iz} = -(1/V)(c+\xi_9)e_{9y}sc \qquad A_{9Iz} = (1/V)(c+\xi_8)e_{8y}sc$$

$$W = e_{11y}(c-\xi_{11})(e_{12x} + c\gamma_{12}) - (c-\xi_{12})e_{12y}(e_{11x} + c\gamma_{11})$$

Let

$$g_{1i} = e_{11i}(c-\xi_{12})e_{12y} - e_{12i}(c-\xi_{11})e_{11y}$$
$$g_{2i} = e_{11i}(e_{12x} + c\gamma_{12}) - e_{12i}(e_{11x} + c\gamma_{11})$$

then

$$B_{Iix} = \delta_{ix} + (1/W)g_{1i}(1-c\xi_I) \qquad B_{Iiy} = \delta_{iy} - (1/W)g_{2i}(c-\xi_I) \qquad B_{Iiz} = (sc/W)g_{1i}$$

$$C_{\alpha i} = e_{\alpha x}\delta_{ix} + e_{\alpha y}\delta_{iy} + (1/W)[g_{1i}(1-c\xi_\alpha)e_{\alpha x} - g_{2i}(c-\xi_\alpha)e_{\alpha y} + g_{1i}sce_{\alpha z}]$$

Substituting from equation (47) for the free-wave fields, the second sum on the right of equation (50) becomes

$$\sum_{\alpha=8}^{9} f_\alpha B_{\alpha ij}E_{\alpha j} = \sum_{\alpha=8}^{9} f_\alpha B_{\alpha ij}\sum_{I=5}^{7} A_{\alpha Ik}E_{Ik}e_{\alpha j} = \sum_{I=5}^{7}\sum_{\alpha=8}^{9} f_\alpha B_{\alpha Ik}e_{\alpha k}A_{\alpha Ij}E_{Ij} \tag{51}$$

and inserting this expression into equation (50) gives

$$E_{13i} = \sum_{I=5}^{7}(f_IB_{Iij} + f_8B_{8ik}e_{8k}A_{8Ij} + f_9B_{9Ik}e_{9k}A_{9Ij})E_{Ij}. \tag{52}$$

The summations over k can be carried out first and are written as

$$C_{\alpha i} = B_{\alpha ik}e_{\alpha k}. \tag{53}$$

Explicit expressions for the bound fields are introduced from equations (20) to (24), leading to

$$E_{13i} = E_1^2\sum_{I=5}^{7}(f_IB_{Iij} + f_8C_{8i}A_{8Ij} + f_9C_{9i}A_{9Ij})F_I^{-1}F_{Ijk}^{\mathrm{A}}\chi_{klm}\pi_{Ilm}t_I \tag{54}$$

where

$$F_I = |\mathsf{F}(\xi_I, \varepsilon^{2\omega}) \qquad F_{Ijk}^{\mathrm{A}} = F_{jk}^{\mathrm{A}}(\xi_I, \varepsilon^{2\omega}). \tag{55}$$

The summation over the j coordinate index is carried out and an effective second-order susceptibility X_{Ik}, connecting fields in the I polarization state to 2ω polarization in the k coordinate direction, is introduced:

$$X_{Ik} = \pi_{Ilm}\chi_{klm}. \tag{56}$$

The final equation is

$$E_{13i} = E_1^2 \sum_{I=5}^{7} (S_{iIk} f_I + C_{8i} T_{8Ik} f_8 + C_{9i} T_{9Ik} f_9) F_I^{-1} X_{Ik} t_I \tag{57}$$

where

$$S_{iIk} = B_{Iij} F_{Ijk}^{\wedge} \tag{58}$$

$$T_{\alpha Ik} = A_{\alpha Ij} F_{Ijk}^{\wedge} \tag{59}$$

$$C_{\alpha i} = B_{\alpha ik} e_{\alpha k}. \tag{60}$$

Equation (57) can be interpreted physically. Starting from the right, t_I are the transmission factors from the incident wave to the products of the ω waves in the crystal. The X_{Ik} are the non-linear coefficients producing second-harmonic polarization of the material from the products of the fundamental waves. From this second-order polarization, bound electric fields are generated by the factors $S_{iIk} F_I^{-1}$ and free electric fields by $C_{\alpha i} T_{\alpha Ik} F_I^{-1}$. Transmission factors at the second surface are included in S and T. In this rearranged form the formula contracts in a very straightforward way to various special cases. Some of these are discussed in the next section.

7. Special cases

7.1. No angular dispersion of the dielectric axes: dielectric and laboratory axes aligned

It is often the case, even in monoclinic crystals, that the directions of the dielectric axes are fixed by molecular symmetry, at least to a sufficiently good approximation to ensure that there is effectively no angular dispersion over the frequency range of a particular doubling experiment. If it is then possible to cut crystals so that the laboratory and dielectric axes coincide at one of the frequencies, they will remain aligned at the other. This is the case to be treated in the present section. The three principal values at each frequency will still, in general, be distinct. The conditions for the particular specialization of the general theory defined above are almost always satisfied in work on orthorhombic crystals [9], where the directions of the dielectric axes are fixed by crystal symmetry, and the natural cleavage and growth directions will be related to the same axes.

Most of the formulae given below have appeared in the literature and one reason for including them is to show that the general equations derived in the previous section do, in fact, reduce correctly to more familiar special cases.

The essential simplification arises from the reduction of the dielectric tensors to diagonal form:

$$\varepsilon_{ij}^{\Omega} = \varepsilon_i^{\Omega} \delta_{ij}. \tag{61}$$

All internal waves can then be classified as ordinary (O, electric vector normal to plane of incidence) or extraordinary (E, electric vector in plane of incidence), and the solutions for the free waves can be chosen as follows:

$I = 3, 8, 11$ ordinary

$I = 4, 9, 12$ extraordinary.

The polarization waves $I = 5$ and $I = 6$ are then respectively O and E.

Table 3. Wave parameters for the case of section 7.1. (no angular dispersion; laboratory and dielectric axes aligned).

O waves: $I = 3, 5, 8, 11$

$e_{Ix} = e_{Iz} = 0 \qquad e_{Iy} = 1 \qquad \gamma_I = 0$

$\xi_3 = (\varepsilon_y^{\omega} - s^2)^{1/2} \qquad \xi_8 = (\varepsilon_y^{2\omega} - s^2)^{1/2} \qquad \xi_{11} = -\xi_8 \qquad \xi_5 = \xi_3$

E waves: $I = 4, 6, 9, 12$

$e_{Iy} = 0$

$\xi_4 = [(\varepsilon_x^{\omega}/\varepsilon_z^{\omega})(\varepsilon_z^{\omega} - s^2)]^{1/2} \qquad \xi_9 = [(\varepsilon_x^{2\omega}/\varepsilon_z^{2\omega})(\varepsilon_z^{2\omega} - s^2)]^{1/2} \qquad \xi_{12} = -\xi_9 \qquad \xi_6 = \xi_4$

$e_{Ix} = (\varepsilon_z^{I}/\varepsilon_x^{I})\xi_I^2/\delta_I \qquad e_{Iz} = -s\xi_I/\delta_I \qquad \gamma_I = -\xi_I\varepsilon_z^{I}/\delta_I$

where

$\delta_I = [(\varepsilon_z^{I} - s^2)^2 + s^2\xi_I^2]^{1/2}$

$F_I = F_{\mathrm{O}}(\xi_I, \boldsymbol{\varepsilon}^{2\omega})F_{\mathrm{E}}(\xi_I, \boldsymbol{\varepsilon}^{2\omega}) = -\varepsilon_z^{2\omega}(\xi_I^2 - \xi_8^2)(\xi_I^2 - \xi_9^2)$

$t_5 = \left(\dfrac{2ce_{1y}}{c + \xi_3}\right)^2 \qquad t_6 = \left(\dfrac{2e_{1x}(\varepsilon_x^{\omega}/\varepsilon_z^{\omega})\delta_4}{\xi_4(\xi_4 + c\varepsilon_x^{\omega})}\right)^2$

Explicit formulae for ξ_I and $\hat{e}_I$ can now be obtained from the equations of section 4 and these are collected in table 3. The coefficients calculated by substitution from table 3 into table 2 are listed in table 4. The number of non-zero S, T and C coefficients is reduced by half compared to the general case. Equation (57) then yields reduced expressions for the x and y components of the transmitted 2ω field:

$$E_{13x} = E_1^2 \sum_{I=5}^{7} [(S_{xIx}X_{Ix} + S_{xIz}X_{Iz})f_I + C_{9x}(T_{9Ix}X_{Ix} + T_{9Iz}X_{Iz})f_9]F_I^{-1}t_I \tag{62}$$

$$E_{13y} = E_1^2 \sum_{I=5}^{7} (S_{yIy}f_I + C_{8y}T_{8Iy}f_8)F_I^{-1}x_{Iy}t_I. \tag{63}$$

Separate formulae will be derived for the four combinations of input and output polarization.

7.1.1. Ordinary incidenct wave. The only polarization wave generated is the ordinary wave $I = 5$, and equations (62) and (63) are further reduced to

$$E_{13x} = E_1^2[(S_{x5x}\chi_{xyy} + S_{x5z}\chi_{zyy})f_5 + C_{9x}(T_{95x}\chi_{xyy} + T_{95z}\chi_{zyy})f_9]F_5^{-1}t_5 \tag{64}$$

$$E_{13y} = E_1^2(S_{y5y}f_5 + C_{8y}T_{85y}f_8)F_5^{-1}t_5\chi_{yyy} \tag{65}$$

Table 4. Non-Zero coefficients for the case of section 7.1 (no angular dispersion; laboratory and dielectric axes aligned).

$T_{9Ix} = \dfrac{\delta_9(\xi_I^2 - \xi_8^2)(\xi_9^2 + c\varepsilon_x^{2\omega}\xi_I)}{\xi_9(\xi_9 + c\varepsilon_x^{2\omega})}$	$S_{xIx} = -\dfrac{c(\xi_I^2 - \xi_8^2)\xi_9(\xi_I + \xi_9)\varepsilon_z^{2\omega}}{(\xi_9 + c\varepsilon_x^{2\omega})}$
$T_{8Iy} = \dfrac{(c + \xi_I)\varepsilon_z^{2\omega}(\xi_I^2 - \xi_9^2)}{(c + \xi_8)}$	$S_{yIy} = -\varepsilon_z^{2\omega}(\xi_I^2 - \xi_9^2)\left(\dfrac{\xi_I + \xi_8}{c + \xi_8}\right)$
$T_{9Iz} = -\dfrac{\delta_9(\xi_I^2 - \xi_8^2)\varepsilon_x^{2\omega}s(\xi_I + c\varepsilon_x^{2\omega})}{\xi_9(\xi_9 + c\varepsilon_x^{2\omega})\varepsilon_z^{2\omega}}$	$S_{xIz} = \dfrac{c(\xi_I^2 - \xi_8^2)(\xi_9 + \xi_I)s\varepsilon_x^{2\omega}}{(\xi_9 + c\varepsilon_x^{2\omega})}$
$C_{8y} = 2\xi_8/(c + \xi_8)$	$C_{9x} = \dfrac{2\varepsilon_z^{2\omega}c\xi_9^2}{\delta_9(\xi_9 + c\varepsilon_x^{2\omega})}$

where

$$X_{5i} = \pi_{5lm}\chi_{ilm} = e_{3l}e_{3m}\chi_{ilm} = \delta_{ly}\delta_{my}\chi_{ilm} = \chi_{iyy} \tag{46}$$

has been used. Extracting the Maker fringe intensities as in equations (42) to (46) gives, in an obvious notation,

$$\mathcal{I}_{\mathrm{O}\to\mathrm{E}} = -(4E_1^4/c^2)F_5^{-2}t_5^2C_{9x}(S_{x5x}\chi_{xyy} + S_{x5z}\chi_{zyy}) \times (T_{95x}\chi_{xyy} + T_{95z}\chi_{zyy})\sin^2[k_1(\xi_5 - \xi_9)L] \tag{66}$$

$$\mathcal{I}_{\mathrm{O}\to\mathrm{O}} = -4E_1^4F_5^{-2}t_5^2C_{8y}S_{y5y}T_{85y}\chi_{yyy}^2\sin^2[k_1(\xi_5 - \xi_8)L]. \tag{67}$$

Substitution of values from table 4 produces the final expressions:

$$\mathcal{I}_{\mathrm{O}\to\mathrm{E}} = 8E_1^4\frac{\varepsilon_x^{2\omega}}{(\varepsilon_z^{2\omega})^2}\left(\frac{2c}{c+\xi_3}\right)^4\frac{\xi_9(\xi_5+\xi_9)}{(\xi_9 + c\varepsilon_x^{2\omega})^3} \times [(\varepsilon_z^{2\omega})/\varepsilon_x^{2\omega})(\xi_9^2 + c\varepsilon_x^{2\omega}\xi_5)\chi_{xyy} - s(\xi_5 + c\varepsilon_x^{2\omega})\chi_{zyy}] \times (\varepsilon_z^{2\omega}\xi_9\chi_{xyy} - s\varepsilon_x^{2\omega}\chi_{zyy})\sin^2[k_1(\xi_5-\xi_9)L]/(\xi_5^2 - \xi_9^2)^2 \tag{68}$$

$$\mathcal{I}_{\mathrm{O}\to\mathrm{O}} = 8E_1^4\left(\frac{2c}{c+\xi_3}\right)^4\frac{\xi_8(\xi_5+\xi_8)(c+\xi_5)}{(c+\xi_8)^3}\frac{\sin^2[k_1(\xi_5-\xi_8)L]}{(\xi_5^2-\xi_8^2)^2}\chi_{yyy}^2. \tag{69}$$

7.1.2. Extraordinary incident wave. The only polarization wave is $I = 6$, so that (62) and (63) become

$$E_{13x} = E_1^2[(S_{x6x}X_{6x} + S_{x6z}X_{6z})f_6 + C_{9x}(T_{96x}x_{6x} + T_{96z}X_{6z})f_9]F_6^{-1}t_6 \tag{70}$$

and

$$E_{13y} = E_1^2(S_{y6y}f_6 + C_{8y}T_{86y}f_8)F_6^{-1}X_{6y}t_6. \tag{71}$$

In this case the final reduction involves a further adjustment of the quantities X_{6i} since the projection factors are no longer trivial:

$$X_{6i} = \pi_{ilm}\chi_{ilm} = e_{4l}e_{4m}\chi_{ilm} = e_{4x}^2\chi_{ixx} + 2e_{4x}e_{4z}\chi_{ixz} + e_{4z}^2\chi_{izz} = (1/\delta_4^2)\{[(\varepsilon_z^{\omega})^2/\varepsilon_x^{\omega}]\xi_4^4\chi_{ixx} - 2(\varepsilon_z^{\omega}/\varepsilon_x^{\omega})s\xi_4^3\chi_{ixz} + s^2\xi_4^2\chi_{izz}\} = (\varepsilon_z^{\omega}\xi_4/\varepsilon_x^{\omega}\delta_4)^2X'_{6i} \tag{72}$$

where

$$X'_{6i} = \xi_4^2\chi_{ixx} - 2(\varepsilon_x^{\omega}/\varepsilon_z^{\omega})s\xi_4\chi_{ixy} + (\varepsilon_x^{\omega}/\varepsilon_z^{\omega})^2s^2\chi_{izz}. \tag{73}$$

Then

$$\mathcal{I}_{\mathrm{E}\to\mathrm{E}} = 8E_1^4\frac{\varepsilon_x^{2\omega}}{(\varepsilon_z^{2\omega})^2}\left(\frac{2c}{\xi_4 + c\varepsilon_x^{\omega}}\right)^4\frac{\xi_9(\xi_6+\xi_9)}{(\xi_9 + c\varepsilon_x^{2\omega})^3}(\xi_9\varepsilon_z^{2\omega}X'_{6x} - s\varepsilon_x^{2\omega}X'_{6z}) \times [(\varepsilon_z^{2\omega}/\varepsilon_x^{2\omega})(\xi_9^2 + c\varepsilon_x^{2\omega}\xi_6)X'_{6x} - s(\xi_6 + c\varepsilon_x^{2\omega})X'_{6z}] \times \sin^2[k_1(\xi_6-\xi_9)L]/(\xi_6^2-\xi_9^2)^2 \tag{74}$$

and

$$\mathscr{P}_{\mathrm{E}\to\mathrm{O}} = 8E_1^4 \left(\frac{2c}{\xi_4 + c\varepsilon_x^{\omega}}\right)^4 \frac{\xi_8(c+\xi_6)(\xi_6+\xi_8)}{(c+\xi_8)^3} \frac{\sin^2[k_1(\xi_6-\xi_8)L]}{(\xi_6^2-\xi_8^2)^2} (X'_{6y})^2. \tag{75}$$

Equations (68), (69), (74) and (75) include as special cases almost all the formulae that have been published in the literature [2, 3, 4, 9], since the experiments described have, in the large majority of cases, involved conditions where there is no angular dispersion and where laboratory and dielectric axes are aligned. The additional restrictions usually found in published formulae arise from the symmetry of the $\boldsymbol{\chi}$ tensor for particular crystallographic groups. These particular forms can easily be introduced into the above equations.

The notation used in previous work, which is usually based on the work of Jerphagnon and Kurtz [2], differs from that in the present paper. The conversion between the two can be effected through the equation

$$\xi_I = n_I \cos\theta'_I \tag{76}$$

where n_I is the refractive index for the wave I and θ'_I is the angle of refraction. When the plane of incidence is a principal dielectric plane, n_I can be calculated from

$$1/n_I^2 = (\cos^2\theta'_I)/n_x^2 + (\sin^2\theta'_I)/n_z^2 \qquad n_x = \varepsilon_x^{1/2} \qquad n_z = \varepsilon_z^{1/2} \tag{77}$$

Table 5. Case of section 7.2: formulae for variables in equations (80) (plane of incidence is a principal dielectric plane; in monoclinic crystals the monoclinic axis is normal to the plane of incidence).

O waves: $I = 3, 5, 7, 8$

ξ_I and $\hat{e}_I$ as in table 3

E waves: $I = 4, 6, 9, 12$

$$e_{Iy} = 0$$

$$\xi_4 = \xi_{\mathrm{D}}^{\omega}\left(1 - \frac{(\varepsilon_{xz}^{\omega})^2}{\varepsilon_{xx}^{\omega}\varepsilon_{zz}^{\omega}}\right)^{1/2} - s\frac{\varepsilon_{xz}^{\omega}}{\varepsilon_{zz}^{\omega}} \qquad \xi_6 = \xi_4$$

$$\xi_9 = \xi_{\mathrm{D}}^{2\omega}\left(1 - \frac{(\varepsilon_{xz}^{2\omega})^2}{\varepsilon_{xx}^{2\omega}\varepsilon_{zz}^{2\omega}}\right)^{1/2} - s\frac{\varepsilon_{xz}^{2\omega}}{\varepsilon_{zz}^{2\omega}}$$

$$\xi_{12} = -\xi_{\mathrm{D}}^{2\omega}\left(1 - \frac{(\varepsilon_{xz}^{2\omega})^2}{\varepsilon_{xx}^{2\omega}\varepsilon_{zz}^{2\omega}}\right)^{1/2} - s\frac{\varepsilon_{xz}^{2\omega}}{\varepsilon_{zz}^{2\omega}}$$

where

$$\xi_{\mathrm{D}}^{\Omega_I} = \left(\frac{\varepsilon_{xx}^{\Omega_I}}{\varepsilon_{zz}^{\Omega_I}}(\varepsilon_{zz}^{\Omega_I} - s^2)\right)^{1/2}$$

$$e_{Ix} = (\varepsilon_{zz}^{\Omega_I} - s^2)/\delta_I \qquad e_{Iz} = -(s\xi_I + \varepsilon_{xz}^{\Omega_I})/\delta_I$$

$$\delta_I = [(\varepsilon_{zz}^{\Omega_I} - s^2)^2 + (s\xi_I + \varepsilon_{xz}^{\Omega_I})^2]^{1/2}$$

$$\sigma_{Ix} = \varepsilon_{zz}^{\omega}(1 + c\xi_I) - s(s - c\varepsilon_{xz}^{2\omega})$$

$$\sigma_{Iz} = -s(\xi_I + c\varepsilon_{xx}^{2\omega}) - \varepsilon_{xz}^{2\omega}(1 + c\xi_I)$$

$$\tau_{Ix} = \gamma_{12}(s^2 - \varepsilon_{zz}^{2\omega}) - e_{12x}(\xi_I\varepsilon_{zz}^{2\omega} + s\varepsilon_{xz}^{2\omega})$$

$$\tau_{Iz} = \gamma_{12}(s\xi_I + \varepsilon_{xz}^{2\omega}) + e_{12x}(\xi_I\varepsilon_{xz}^{2\omega} + s\varepsilon_{xx}^{2\omega})$$

$$v_9 = (se_{12z} - \xi_{12}e_{12x} + \xi_9 e_{12x})e_{9x} - se_{12x}e_{9z}$$

for extraordinary waves, and for ordinary waves

$$n_l = n_y = \varepsilon_y^{1/2}. \tag{78}$$

In more general cases there is no simple expression for n_l. Denominators of the form $\xi_l^2 - \xi_j^2$ become

$$\xi_l^2 - \xi_j^2 = n_l^2 \cos^2\theta_l' - n_j^2 \cos^2\theta_j' = n_l^2 - n_j^2 \tag{79}$$

where Snell's law has been used to remove $\sin^2\theta'$ terms.

As an example, the reduction of equation (75) to an equation used in [9], in a study of orthorhombic crystals, is described in the appendix.

7.2. *Plane of incidence is a principal dielectric plane for frequencies ω and 2ω*

This is a more general case than the one described in the previous section. The laboratory axes in the plane of incidence are not necessarily dielectric axes and the dielectric axes in this plane may change direction as the frequency varies. Such conditions are found in monoclinic crystals when the unique monoclinic axis, which is a dielectric axis at all frequencies by symmetry, is normal to the plane of incidence. The other axis in the face of the crystal will usually be a crystal axis, not coinciding with a dielectric axis. Dispersion of the axes, if it is present, will, in terms of the coordinate system of this paper, be confined to a rotation about the y axis.

As in the previous example, all waves can be classified as O or E and explicit solutions for the ξ_l and $\hat{e}_l$ can be obtained. These are given in table 5. The values of the intermediate quantities of table 2 are not shown in this case, but table 5 also contains definitions of some combinations of variables appearing in the final equations for the intensity, which are given below:

$$\mathcal{I}_{\mathrm{E}\to\mathrm{O}} = 4E_1^4 \left(\frac{2c}{e_{4x} - c\gamma_4}\right)^4 \frac{(\xi_8 - \xi_{11})(\xi_6 - \xi_{11})(c + \xi_6)}{(c + \xi_8)^2(c - \xi_{11})} \frac{\sin^2[k_1(\xi_6 - \xi_8)L]}{(\xi_6^2 - \xi_8^2)^2} X_{6y}^2 \tag{80a}$$

$$\mathcal{I}_{\mathrm{E}\to\mathrm{E}} = -4E_1^4 \left(\frac{2c}{e_{4x} - c\gamma_4}\right)^4 \frac{v_9(\tau_{6x}X_{6x} + \tau_{6z}X_{6z})(\sigma_{6x}X_{6x} + \sigma_{6z}X_{6z})}{(e_{12x} + c\gamma_{12})^2(e_{9x} - c\gamma_9)[\varepsilon_{zz}^{2\omega}(\xi_6 + \xi_9) + 2s\varepsilon_{xz}^{2\omega}]^2} \times \frac{\sin^2[k_1(\xi_6 - \xi_9)L]}{(\xi_6 - \xi_9)^2} \tag{80b}$$

$$\mathcal{I}_{\mathrm{O}\to\mathrm{E}} = -4E_1^4 \left(\frac{2c}{c + \xi_3}\right)^4 \frac{v_9(\tau_{5x}X_{5x} + \tau_{5z}X_{5z})(\sigma_{5x}X_{5x} + \sigma_{5z}X_{5z})}{(e_{12x} + c\gamma_{12})^2(e_{9x} - c\gamma_9)[\varepsilon_{zz}^{2\omega}(\xi_5 + \xi_9) + 2s\varepsilon_{xz}^{2\omega}]^2} \times \frac{\sin^2[k_1(\xi_5 - \xi_9)L]}{(\xi_5 - \xi_9)^2} \tag{80c}$$

$$\mathcal{I}_{\mathrm{O}\to\mathrm{O}} = 4E_1^4 \left(\frac{2c}{c + \xi_3}\right)^4 \frac{(\xi_8 - \xi_{11})(\xi_5 - \xi_{11})(c + \xi_5)}{(c - \xi_{11})(c + \xi_8)^2} \frac{\sin^2[k_1(\varepsilon_5 - \xi_8)L]}{(\xi_5^2 - \xi_8^2)^2}. \tag{80d}$$

In section 8 some numerical results computed with equation (80*a*) are described.

8. An example of the application of the formulae

To give an indication of the way in which the rather complex formulae of the preceding sections can be applied to extract information about the *d*-coefficients, a preliminary example of the new kinds of fringe system that arise in monoclinic crystals is described. Here, only computed results are presented, but fringes of the type described have been observed and will be reported in detail in a later paper.

The organic material 2(α)-methylbenzylamino-5-nitropyridine (MBANP) [10–12] crystallizes in the monoclinic non-centrosymmetric space group $P2_1$, for which the form of the *d*-tensor is given in [8]. The linear optical properties of the crystal have been reported [11, 12] and the d_{22} coefficient, corresponding to *b*-axis polarization of the fundamental and second-harmonic waves, has been measured [11, 12]. The dielectric axes rotate by about 26° between the two frequencies (equivalent to 1.064 μm and 532 nm) in a standard YAG doubling experiment. Slabs of crystal with parallel faces aligned with the (1 0 0), (0 1 0) and (0 0 1) crystallographic planes can be obtained. The (1 0 0) crystal can be aligned so that the correspondence between crystal and laboratory axes is

$$x \rightarrow c \qquad y \rightarrow b \qquad z \rightarrow a^*$$

where a^* is the piezoelectric axis normal to *b* and *c*. The laboratory system now coincides with the piezoelectric system provided that the conventional labelling of the piezoelectric a^* and *c* axes as *x* and *z* is interchanged. The corresponding interchanges in the standard *d*-matrix labelling are easily made. The Maker fringes should conform to the analysis of section 7.2. Taking the case where the ω wave is E and the orthogonal second-harmonic output O is detected, equation (80*a*) is applicable. The non-linear susceptibilities are contained in the quantity X_{6y}, which reduces for the appropriate *d*-matrix to

$$X_{6y} = e_{4x}^2 d_{23} + 2e_{4x}e_{4z}d_{25} + e_{4z}^2 d_{21}.$$

At normal incidence e_{4z} is zero and the amplitude of the Maker fringe envelope is then determined completely by d_{23}. An examination of the angular variation of the polarization vectors shows that, for angles of incidence less than about 30°, the e_{4z} term is very much smaller than the others, so that the fringe pattern is essentially determined by the values of the two coefficients, d_{23} and d_{25}. The details of the shape of the pattern are also very dependent on the other factors occurring in equation (80*a*), all of which can be calculated provided the linear optical properties are known. Figures 4 and 5 show the results of such a calculation for MBANP. The d_{23} and d_{25} values used to compute the fringes have initially been taken from theoretical work in which the molecular hyperpolarizability tensor is first calculated by a semi-empirical quantum-mechanical method [13] and the crystal χ tensor estimated using oriented gas model internal field factors, based on the measured refractive indices. Such an approach is only expected to be reliable in a semiquantitative sense. The results of the calculation in this case indicate that d_{23} and d_{25} are of roughly comparable magnitude but have opposite signs. These values of d_{23} and d_{25}, used in equation (80*a*), produce the fringes of figure 4. The relative signs of the two components were then arbitrarily reversed; the new computed fringes were then as shown in figure 5. It is apparent that the shape of the asymmetric fringe pattern depends very sensitively on the relative values of the contributing *d*-values. The lack of symmetry about the normal to the crystal face occurs because the dielectric axis in the plane of incidence are inclined to the face. The position of the centre of the fringe pattern—where the fringe spacing is greatest—corresponds to a minimum in the

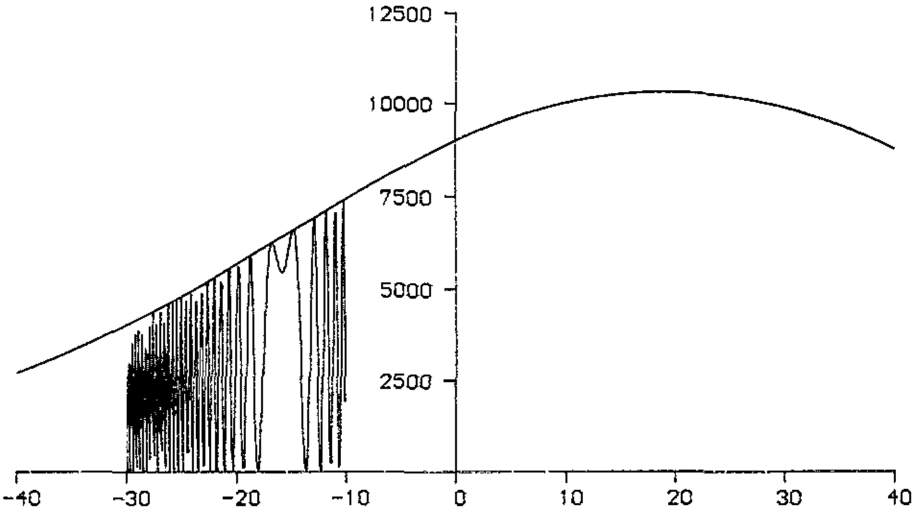

Figure 4. Computed fringes for the case of section 8. The elements d_{23} and d_{25} are as obtained from theory. The fringes are shown only where they can be easily resolved on the scale of the diagram, near the centre of the system. The envelope function is shown over the whole range. The intensity scale is arbitrary.

argument of the $\sin^2$ term in equation (80*a*) and this again is a sensitive function of the angular variation of the combination of refractive index principal values (refered to different principal axes) on which it depends. Further confirmatory evidence for the values of the linear optical parameters can therefore also be obtained from an analysis of the asymmetry of the fringes. Kurtz [3] has discussed the effect of the relative sign of different, simultaneously contributing, *d*-coefficients on the fringes in uniaxial crystals. The effect treated here includes, as an additional complication, the rotation of the

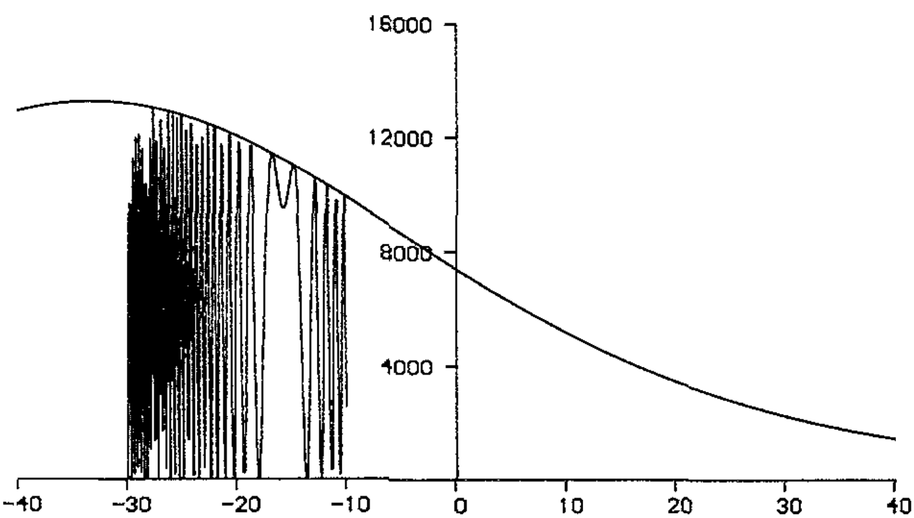

Figure 5. Computed fringes for the case of section 8. As for figure 4, but with the sign of d_{25} reversed.

principal axes between the two frequencies. Numerical work, in which approximate treatments were attempted and parameters arbitrarily varied, has indicated that it is essential to include the effect of the rotation of the axes systematically if a reliable interpretation of the fringes is to be obtained.

Fringes, showing features such as those described above, have been observed in MBANP, and an analysis of the data will be presented in a later publication.

The example relates to a comparatively simple case but even here it has proved necessary to base the analysis on a treatment that takes account of the low symmetry of the crystal. In attempting a full determination of a d-matrix for such a crystal it will evidently be desirable to extract as much information as possible from orientations where one or two d-coefficients can be isolated. The values so obtained will reduce the number of unknown parameters left in the equations that must be applied in the less tractable situations.

9. Conclusions

A set of general equations for Maker fringes, applicable to all crystal structures and orientations, has been derived. Alternative forms of the equations have been presented in sections 5 and 6. The former, having a simpler but more implicit structure, is suited to numerical work, the latter to analytical manipulation leading to the identification of the major contributions to the intensity that often emerge as a consequence of crystal symmetry or because of the predominance of terms associated with a particular phase-matching denominator.

It has been shown (section 7) that, when dielectric axes are fixed in direction and aligned with laboratory axes, the general equations reduce to forms that have previously appeared in the literature for special cases. New formulae for special cases that occur in monoclinic crystals are given.

In section 8 an example is described in which it is shown that the new equations can usefully be employed to extract information about the relative signs and magnitudes of d-coefficients.

The system of equations developed in this paper is currently being used, in conjunction with experimental studies of Maker fringes, to attempt to make complete determinations of the d-matrices of several organic crystals.

Acknowledgments

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Appendix. Example of relationship to literature notation

The orthorhombic point group, $mm2$, has a d-matrix of the form

$$\boldsymbol{d} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}. \tag{A1}$$

With an alignment of the laboratory (xyz) and piezoelectric ($x_0y_0z_0$) axes such that $x_0 \rightarrow x, y_0 \rightarrow z$ and $z_0 \rightarrow y$, the effective second-order susceptibility, from equation (73), for generating E → O type Maker fringes (equation 75) becomes

$$X'_{6y} = \xi_4^2 d_{31} + (\varepsilon_x^\omega/\varepsilon_z^\omega)^2 s^2 d_{32}. \tag{A2}$$

Using table 3, and equations (76), (77), (78) and (79), equation (75) gives

$$\mathscr{I}_{\mathrm{E}\rightarrow\mathrm{O}}(\theta) =$$

$$128E_1^4 \frac{(\cos\theta + n^\omega\cos\theta'_\omega)(n^\omega\cos\theta'_\omega + n_y^{2\omega}\cos\theta'_{2\omega})(n^\omega\cos\theta)^4 n_y^{2\omega}\cos\theta'_{2\omega}}{[n^\omega\cos\theta'_\omega + (n_x^\omega)^2\cos\theta]^4(\cos\theta + n_y^{2\omega}\cos\theta'_{2\omega})^3(n^\omega + n_y^{2\omega})^2(n^\omega - n_y^{2\omega})}$$
$$\times\, d_{31}^2[\cos^2\theta'_\omega - (n_x^\omega/n_z^\omega)^4\sin^2\theta'_\omega(d_{32}/d_{31})]^2$$
$$\times\, \sin^2[k_1(n^\omega\cos\theta'_\omega - n_y^{2\omega}\cos\theta'_{2\omega})] \tag{A3}$$

where $n^\omega \equiv n_4$ is given by equation (77). The 'normalized enveloped function' is often used; it is obtained by taking the ratio of the coefficient of the $\sin^2$ term at θ to its value at $\theta = 0$. Recalling that, at $\theta = 0$, $n^\omega = n_x^\omega$, substitution in equation (A3) gives

$$\mathscr{I}_{\mathrm{E}\rightarrow\mathrm{O}}(0) = 128E_1^4 \frac{n_y^{2\omega}}{(1+n_x^\omega)^3(n_x^\omega + n_y^{2\omega})(1+n_y^{2\omega})^3(n_x^\omega - n_y^{2\omega})^2}$$
$$\times\, \sin^2[k_1(n_x^\omega - n_y^{2\omega})L] \tag{A4}$$

and the normalized ratio is

$$\frac{(n_x^\omega + n_y^{2\omega})(n_x^\omega - n_y^{2\omega})(1+n_y^{2\omega})^3(1+n_x^\omega)^3(\cos\theta + n^\omega\cos\theta'_\omega)(n^\omega\cos\theta'_\omega + n_y^{2\omega}\cos\theta'_{2\omega})}{(n^\omega + n_y^{2\omega})^2(n^\omega - n_y^{2\omega})^2(n_y^{2\omega}\cos\theta'_{2\omega} + \cos\theta)^3[(n_x^\omega)^2\cos\theta + n^\omega\cos\theta'_\omega]^4}$$
$$\times\, d_{31}^2[\cos^2\theta'_\omega - (n_x^\omega/n_z^\omega)^4\sin^2\theta'_{2\omega}(d_{32}/d_{31})]^2. \tag{A5}$$

If the interchange $y \rightarrow z$ is made to allow for the different labelling of the laboratory system in [9], then equation (A5) is identical with equation (6) of that reference.

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