International Tables for Crystallography (2013). Vol. D, Section 1.7.3.1, pp. 186–190.

lographical frame by the standard conventions given in Chapter 1.6.

1.7.3. Propagation phenomena

1.7.3.1. *Crystalline linear optical properties*

We summarize here the main linear optical properties that govern the nonlinear propagation phenomena. The reader may refer to Chapter 1.6 for the basic equations.

1.7.3.1.1. *Index surface and electric field vectors*

The relations between the different field vectors relative to a propagating electromagnetic wave are obtained from the constitutive relations of the medium and from Maxwell equations.

In the case of a non-magnetic and non-conducting medium, Maxwell equations lead to the following wave propagation equation for the Fourier component at the circular frequency ω defined by (1.7.2.15) and (1.7.2.16) (Butcher & Cotter, 1990):

$$\nabla \mathbf{x} \nabla \mathbf{x} \mathbf{E}(\omega) = (\omega^2/c^2)\mathbf{E}(\omega) + \omega^2 \mu_0 \mathbf{P}(\omega), \qquad (1.7.3.1)$$

where $\omega = 2\pi c/\lambda$, λ is the wavelength and c is the velocity of light in a vacuum; μ_0 is the free-space permeability, $\mathbf{E}(\omega)$ is the electric field vector and $\mathbf{P}(\omega)$ is the polarization vector.

Table 1.7.2.3. *Nonzero $\chi^{(2)}$ coefficients and equalities between them under the Kleinman symmetry assumption*

Symmetry class	Independent nonzero $\chi^{(2)}$ elements under Kleinman symmetry
Triclinic	
C_1 (1)	xxx, $xyy = yxy = yyx$, $xzz = zxz = zzx$, $xyz = xzy = yxz = yzx = zxy = zyx$, $xxz = xzx = zxx$, $xxy = xyx = yxx$, yyy, $yzz = zyz = zzy$, $yyz = yzy = zyy$, zzz
Monoclinic	
C_2 (2) (twofold axis parallel to z)	$xyz = xzy = yxz = yzx = zxy = zyx$, $xxz = xzx = zxx$, $yyz = yzy = zyy$, zzz
C_s (m) (mirror perpendicular to z)	xxx, $xyy = yxy = yyx$, $xzz = zxz = zzx$, $xxy = xyx = yxx$, yyy, $yzz = zyz = zzy$
Orthorhombic	
C_{2v} ($mm2$) (twofold axis parallel to z)	$xzx = xxz = zxx$, $yyz = yzy = zyy$, zzz
D_2 (222)	$xyz = xzy = yzx = yxz = zxy = zyx$
Tetragonal	
C_4 (4)	$xzx = xxz = zxx = yzy = yyz = zyy$, zzz
S_4 ($\bar{4}$)	$xyz = xzy = yzx = yxz = zxy = zyx$, $xzx = xxz = zxx = -yzy = -yyz = -zyy$
D_4 (422)	All elements are nil
C_{4v} ($4mm$)	$xzx = xxz = zxx = yyz = yzy = zyy$, zzz
D_{2d} ($\bar{4}2m$)	$xyz = xzy = yzx = yxz = zxy = zyx$
Hexagonal	
C_6 (6)	$xzx = xxz = zxx = yyz = yzy = zyy$, zzz
C_{3h} ($\bar{6}$)	$xxx = -xyy = -yxy = -yyx$, $yyy = -yxx = -xyx = -xxy$
D_6 (622)	All elements are nil
C_{6v} ($6mm$)	$xzx = xxz = zxx = yyz = yzy = zyy$, zzz
D_{3h} ($\bar{6}2m$) (mirror perpendicular to x)	$yyy = -yxx = -xxy = -xyx$
Trigonal	
C_3 (3)	$xxx = -xyy = -yyx = -yxy$, $xzx = xxz = zxx = yyz = yzy = zyy$, $yyy = -yxx = -xxy = -xyx$, zzz
D_3 (32)	$xxx = -xyy = -yyx = -yxy$
C_{3v} ($3m$) (mirror perpendicular to x)	$yyy = -yxx = -xxy = -xyx$, $xzx = xxz = zxx = yyz = yzy = zyy$, zzz
Cubic	
T (23), T_d ($\bar{4}3m$)	$xyz = xzy = yzx = yxz = zxy = zyx$
O (432)	All elements are nil

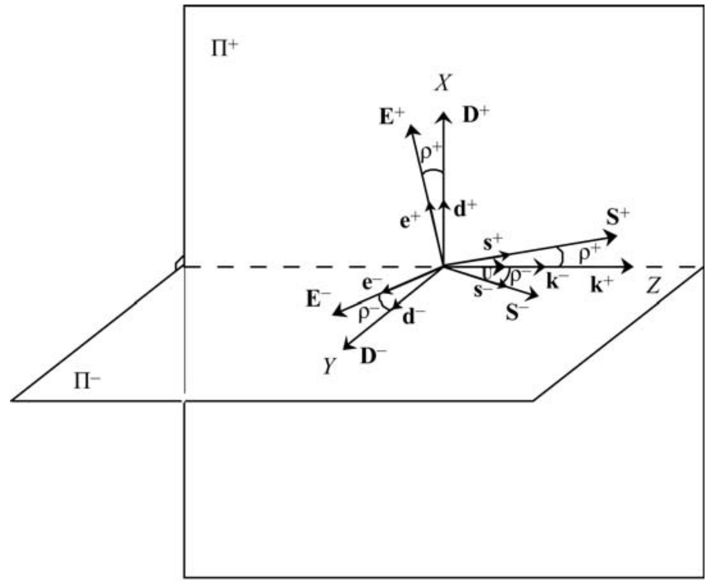

Fig. 1.7.3.1. Field vectors of a plane wave propagating in an anisotropic medium. (X, Y, Z) is the wave frame. Z is along the direction of propagation, X and Y are contained in Π^+ and Π^- respectively, by an arbitrary convention.

In the linear regime, $\mathbf{P}(\omega) = \varepsilon_0 \chi^{(1)}(\omega)\mathbf{E}(\omega)$, where ε_0 is the free-space permittivity and $\chi^{(1)}(\omega)$ is the first-order electric susceptibility tensor. Then (1.7.3.1) becomes

$$\nabla \mathbf{x} \nabla \mathbf{x} \mathbf{E}(\omega) = (\omega^2/c^2)\varepsilon(\omega)\mathbf{E}(\omega). \qquad (1.7.3.2)$$

$\varepsilon(\omega) = 1 + \chi^{(1)}(\omega)$ is the dielectric tensor. In the general case, $\chi^{(1)}(\omega)$ is a complex quantity *i.e.* $\chi^{(1)} = \chi^{(1)'} + i\chi^{(1)''}$. For the following, we consider a medium for which the losses are small ($\chi^{(1)'} \gg \chi^{(1)''}$); it is one of the necessary characteristics of an efficient nonlinear medium. In this case, the dielectric tensor is real: $\varepsilon = 1 + \chi^{(1)'}$.

The plane wave is a solution of equation (1.7.3.2):

$$\mathbf{E}(\omega, X, Y, Z) = \mathbf{e}(\omega)E(\omega, X, Y, Z)\exp[\pm ik(\omega)Z]. \qquad (1.7.3.3)$$

(X, Y, Z) is the orthonormal frame linked to the wave, where Z is along the direction of propagation.

We consider a linearly polarized wave so that the unit vector $\mathbf{e}$ of the electric field is real ($\mathbf{e} = \mathbf{e}^*$), contained in the XZ or YZ planes.

$E(\omega, X, Y, Z) = A(\omega, X, Y, Z)\exp[i\Phi(\omega, Z)]$ is the scalar complex amplitude of the electric field where $\Phi(\omega, Z)$ is the phase, and $E^*(-\omega, X, Y, Z) = E(\omega, X, Y, Z)$. In the linear regime, the amplitude of the electric field varies with Z only if there is absorption.

k is the modulus of the wavevector, real in a lossless medium: $+kZ$ corresponds to forward propagation along Z, and $-kZ$ to backward propagation. We consider that the plane wave propagates in an anisotropic medium, so there are two possible wavevectors, $\mathbf{k}^+$ and $\mathbf{k}^-$, for a given direction of propagation of unit vector $\mathbf{u}$:

$$\mathbf{k}^{\pm}(\omega, \theta, \varphi) = (\omega/c)n^{\pm}(\omega, \theta, \varphi)\mathbf{u}(\theta, \varphi). \qquad (1.7.3.4)$$

(θ, φ) are the spherical coordinates of the direction of the unit wavevector $\mathbf{u}$ in the optical frame; (x, y, z) is the optical frame defined in Section 1.7.2.

The spherical coordinates are related to the Cartesian coordinates (u_x, u_y, u_z) by

$$u_x = \cos\varphi \sin\theta \quad u_y = \sin\varphi \sin\theta \quad u_z = \cos\theta. \qquad (1.7.3.5)$$

The refractive indices $n^{\pm}(\omega, \theta, \varphi) = [\varepsilon^{\pm}(\omega, \theta, \varphi)]^{1/2}$, $(n^+ > n^-)$, real in the case of a lossless medium, are the two solutions of the Fresnel equation (Yao & Fahlen, 1984):

$$\begin{aligned} n^{\pm} &= \left[\frac{2}{-B \mp (B^2 - 4C)^{1/2}}\right]^{1/2} \\ B &= -u_x^2(b+c) - u_y^2(a+c) - u_z^2(a+b) \\ C &= u_x^2 bc + u_y^2 ac + u_z^2 ab \\ a &= n_x^{-2}(\omega), \quad b = n_y^{-2}(\omega), \quad c = n_z^{-2}(\omega). \end{aligned} \tag{1.7.3.6}$$

$n_x(\omega)$, $n_y(\omega)$ and $n_z(\omega)$ are the principal refractive indices of the index ellipsoid at the circular frequency ω.

Equation (1.7.3.6) describes a double-sheeted three-dimensional surface: for a direction of propagation **u** the distances from the origin of the optical frame to the sheets (+) and (−) correspond to the roots n^+ and n^-. This surface is called the index surface or the wavevector surface. The quantity $(n^+ - n^-)$ or $(n^- - n^+)$ is the birefringency. The waves (+) and (−) have the phase velocities c/n^+ and c/n^-, respectively.

Equation (1.7.3.6) and its dispersion in frequency are often used in nonlinear optics, in particular for the calculation of the phase-matching directions which will be defined later. In the regions of transparency of the crystal, the frequency law is well described by a Sellmeier equation, which is the case for normal dispersion where the refractive indices increase with frequency (Hadni, 1967):

$$n^{\pm}(\omega_i) < n^{\pm}(\omega_j) \quad \text{for} \quad \omega_i < \omega_j. \tag{1.7.3.7}$$

If ω_i or ω_j are near an absorption peak, even weak, $n^{\pm}(\omega_i)$ can be greater than $n^{\pm}(\omega_j)$; this is called abnormal dispersion.

The dielectric displacements $\mathbf{D}^{\pm}$, the electric fields $\mathbf{E}^{\pm}$, the energy flux given by the Poynting vector $\mathbf{S}^{\pm} = \mathbf{E}^{\pm} \times \mathbf{H}^{\pm}$ and the collinear wavevectors $\mathbf{k}^{\pm}$ are coplanar and define the orthogonal vibration planes $\Pi^{\pm}$ (Shuvalov, 1981). Because of anisotropy, $\mathbf{k}^{\pm}$ and $\mathbf{S}^{\pm}$, and hence $\mathbf{D}^{\pm}$ and $\mathbf{E}^{\pm}$, are non-collinear in the general case as shown in Fig. 1.7.3.1: the walk-off angles, also termed double-refraction angles, $\rho^{\pm} = \arccos(\mathbf{d}^{\pm} \cdot \mathbf{e}^{\pm}) = \arccos(\mathbf{u} \cdot \mathbf{s}^{\pm})$ are different in the general case; $\mathbf{d}^{\pm}$, $\mathbf{e}^{\pm}$, **u** and $\mathbf{s}^{\pm}$ are the unit vectors associated with $\mathbf{D}^{\pm}$, $\mathbf{E}^{\pm}$, $\mathbf{k}^{\pm}$ and $\mathbf{S}^{\pm}$, respectively. We shall see later that the efficiency of a nonlinear interaction is strongly conditioned by **k**, **E** and ρ, which only depend on $\chi^{(1)}(\omega)$, that is to say on the linear optical properties.

The directions $\mathbf{S}^+$ and $\mathbf{S}^-$ are the directions normal to the sheets (+) and (−) of the index surface at the points n^+ and n^-.

For a plane wave, the time-average Poynting vector is (Yariv & Yeh, 2002)

$$\begin{aligned} \|\mathbf{S}^{\pm}(\omega)\| &= \left\|\tfrac{1}{2} Re\left[\mathbf{E}^{\pm}(\omega) \times \mathbf{H}^{\pm *}(\omega)\right]\right\| \\ &= \tfrac{1}{2} \frac{\|\mathbf{k}^{\pm}(\omega)\|}{\mu_0 \omega} \|\mathbf{E}^{\pm}(\omega)\|^2 \cos^2 \rho^{\pm}(\omega). \end{aligned} \tag{1.7.3.8}$$

$\|\mathbf{S}^{\pm}\|$ is the energy flow $I = \hbar\omega N^{\pm}$, which is a power per unit area *i.e.* the intensity, where $\hbar\omega$ is the energy of the photon and $N^{\pm}$ are the photons flows. $\rho^{\pm}(\omega)$ is the angle between $\mathbf{S}^{\pm}$ and **u**; it is detailed later on.

The unit electric field vectors $\mathbf{e}^+$ and $\mathbf{e}^-$ are calculated from the propagation equation projected on the three axes of the optical

Table 1.7.2.4. *Nonzero $\chi^{(3)}$ coefficients and equalities between them in the general case*

Symmetry class	$\chi^{(3)}$ nonzero elements
Triclinic C_1 (1), C_i ($\bar{1}$)	All 81 elements are independent and nonzero
Monoclinic C_s (*m*), C_2 (2), C_{2h} $\left(\frac{2}{m}\right)$ (twofold axis parallel to *z*)	*xxxx, xyyy, xyzz, xzyz, xzzy, xxzz, xzxz, xzzx, xxyy, xyxy, xyyx, xxxy, xxyx, xyxx, yxxx, yyyy, yyzz, yzyz, yzzy, yxzz, yzxz, yzzx, yxyy, yyxy, yyyx, yxxy, yxyx, yyxx, zzzz, zyyz, zyzy, zzyy, zxxz, zxzx, zzxx, zxyz, zxzy, zyxz, zzxy, zyzx, zzyx*
Orthorhombic C_{2v} (*mm*2), D_2 (222), D_{2h} (*mmm*) (twofold axis parallel to *z*)	*xxxx, xxzz, xzxz, xzzx, xxyy, xyxy, xyyx, yyyy, yyzz, yzyz, yzzy, yxxy, yxyx, yyxx, zzzz, zyyz, zyzy, zzyy, zxxz, zxzx, zzxx*
Tetragonal S_4 ($\bar{4}$), C_4 (4), C_{4h} $\left(\frac{4}{m}\right)$	*xxxx = yyyy, xyyy = −yxxx, xyzz = −yxzz, xzyz = −yzxz, xzzy = −yzzx, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, xxxy = −yyyx, xxyx = −yyxy, xyxx = −yxyy, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx, zxyz = −zyxz, zxzy = −zyzx, zzxy = −zzyx*
C_{4v} (4*mm*), D_{2d} ($\bar{4}$2*m*), D_4 (422), D_{4h} $\left(\frac{4}{m}mm\right)$	*xxxx = yyyy, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx*
Hexagonal C_{3h} ($\bar{6}$), C_6 (6), C_{6h} $\left(\frac{6}{m}\right)$	*xxxx = yyyy = xxyy + xyxy + xyyx, xyyy = xxxy + xxyx + xyxx = −yxxx, xyzz = −yxzz, xzyz = −yzxz, xzzy = −yzzx, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, xxxy = −yyyx, xxyx = −yyxy, xyxx = −yxyy, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx, zxyz = −zyxz, zxzy = −zyzx, zzxy = −zzyx*
C_{6v} (6*mm*), D_{3h} ($\bar{6}$2*m*), D_6 (622), D_{6h} $\left(\frac{6}{m}mm\right)$	*xxxx = yyyy = xxyy + xyxy + xyyx, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx*
Trigonal C_3 (3), C_{3i} ($\bar{3}$)	*xxxx = yyyy = xxyy + xyxy + xyyx, xyyy = xxxy + xxyx + xyxx = −yxxx, xyzz = −yxzz, xzyz = −yzxz, xzzy = −yzzx, xyyz = yxyz = yyxz = −xxxz, xyzy = yyzx = yxzy = −xxzx, xzyy = yzxy = yzyx = −xzxx, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, xxxy = −yyyx, xxyx = −yyxy, xyxx = −yxyy, xxyz = xyxz = yxxz = −yyyz, xxzy = xyzx = yxzx = −yyzy, xzxy = xzyx = yzxx = −yzyy, −zxxx = zxyy = zyxy = zyyx, −zyyy = zxxy = zxyx = zyxx, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx, zxyz = −zyxz, zxzy = −zyzx, zzxy = −zzyx*
C_{3v} (3*m*), D_3 (32), D_{3d} ($\bar{3}$*m*) (mirror perpendicular to *x*) (twofold axis parallel to *x*)	*xxxx = yyyy = xxyy + xyxy + xyyx, xxzz = yyzz, xzxz = yzyz, xzzx = yzzy, xxyy = yyxx, xyxy = yxyx, xyyx = yxxy, xxyz = xyxz = yxxz = −yyyz, xxzy = xyzx = yxzx = −yyzy, xzxy = xzyx = yzxx = −yzyy, −zyyy = zxxy = zxyx = zyxx, zzzz, zyyz = zxxz, zyzy = zxzx, zzyy = zzxx*
Cubic *T* (23), T_h (*m*3)	*xxxx = yyyy = zzzz, xxzz = yyxx = zzyy, xzxz = yxyx = zyzy, xzzx = yxxy = zyyz, xxyy = yyzz = zzxx, xyxy = yzyz = zxzx, xyyx = yzzy = zxxz*
T_d ($\bar{4}$3*m*), *O* (432), O_h (*m*3*m*)	*xxxx = yyyy = zzzz, xxzz = xxyy = yyzz = yyxx = zzyy = zzxx, xzxz = xyxy = yzyz = yxyx = zyzy = zxzx, xzzx = xyyx = yzzy = yxxy = zyyz = zxxz*

frame. We obtain, for each wave, three equations which relate the three components (e_x, e_y, e_z) to the unit wavevector components (u_x, u_y, u_z) (Shuvalov, 1981):

$$(n^{\pm})^2(e_p^{\pm} - u_p[u_x e_x^{\pm} + u_y e_y^{\pm} + u_z e_z^{\pm}]) = (n_p)^2 e_p^{\pm} \quad (p = x, y \text{ and } z) \qquad (1.7.3.9)$$

with $(e_x^{\pm})^2 + (e_y^{\pm})^2 + (e_z^{\pm})^2 = 1$.

The vibration planes $\Pi^{\pm}$ relative to the eigen polarization modes $\mathbf{e}^{\pm}$ are called the neutral vibration planes associated with $\mathbf{u}$: an incident linearly polarized wave with a vibration plane parallel to Π^+ or Π^- is refracted inside the crystal without depolarization, that is to say in a linearly polarized wave, $\mathbf{e}^+$ or $\mathbf{e}^-$, respectively. For any other incident polarization the wave is refracted in the two waves $\mathbf{e}^+$ and $\mathbf{e}^-$, which propagate with the difference of phase $(\omega/c)(n^+ - n^-)Z$.

The existence of equalities between the principal refractive indices determines the three optical classes: isotropic for the cubic system; uniaxial for the tetragonal, hexagonal and trigonal systems; and generally biaxial for the orthorhombic, monoclinic and triclinic systems [Nye (1957) and Sections 1.1.4.1 and 1.6.3.2].

1.7.3.1.2. *Isotropic class*

The isotropic class corresponds to the equality of the three principal indices: the index surface is a one-sheeted sphere, so $n^+ = n^-$, $\rho^+ = \rho^- = 0$ for all directions of propagation, and any electric field vector direction is allowed as in an amorphous material.

1.7.3.1.3. *Uniaxial class*

The uniaxial class is characterized by the equality of two principal indices, called ordinary indices $(n_x = n_y = n_o)$; the other index is called the extraordinary index $(n_z = n_e)$. Then, according to (1.7.3.6), the index surface has one umbilicus along the z axis, $n^+(\theta = 0) = n^-(\theta = 0)$, called the optic axis, which is along the fold rotation axis of greatest order of the crystal. The two other principal axes are related to the symmetry elements of the orientation class according to the standard conventions (Nye, 1957). The ordinary sheet is spherical *i.e.* $n_o(\theta, \varphi) = n_o$, so an ordinary wave has no walk-off for any direction of propagation in a uniaxial crystal; the extraordinary sheet is ellipsoidal *i.e.* $n_e(\theta, \varphi) = [(\cos^2\theta)/(n_o^2) + (\sin^2\theta)/(n_e^2)]^{-1/2}$. The sign of the uniaxial class is defined by the sign of the birefringence $n_e - n_o$. Thus, according to these definitions, (n_e, n_o) corresponds to (n^+, n^-) for the positive class $(n_e > n_o)$ and to (n^-, n^+) for the negative class $(n_e < n_o)$, as shown in Fig. 1.7.3.2.

The ordinary electric field vector is orthogonal to the optic axis $(e_z^o = 0)$, and also to the extraordinary electric field vector, leading to

$$\mathbf{e}^o(\omega_i, \theta, \varphi) \cdot \mathbf{e}^e(\omega_j, \theta, \varphi) = 0. \qquad (1.7.3.10)$$

This relation is satisfied when ω_i and ω_j are equal or different and for any direction of propagation (θ, φ).

According to these results, the coplanarity of the field vectors imposes the condition that the double-refraction angle of the extraordinary wave is in a plane containing the optic axis. Thus, the components of the ordinary and extraordinary unit electric field vectors $\mathbf{e}^o$ and $\mathbf{e}^e$ at the circular frequency ω are

$$e_x^o = -\sin\varphi \quad e_y^o = +\cos\varphi \quad e_z^o = 0 \qquad (1.7.3.11)$$

$$\begin{aligned} e_x^e &= -\cos[\theta \pm \rho^{\mp}(\theta, \omega)] \cdot \cos\varphi \\ e_y^e &= -\cos[\theta \pm \rho^{\mp}(\theta, \omega)] \cdot \sin\varphi \\ e_z^e &= \sin[\theta \pm \rho^{\mp}(\theta, \omega)] \end{aligned} \qquad (1.7.3.12)$$

Table 1.7.2.5. *Nonzero $\chi^{(3)}$ coefficients and equalities between them under the Kleinman symmetry assumption*

Symmetry class	Independent nonzero elements of $\chi^{(3)}$ under Kleinman symmetry
Triclinic C_1 (1), C_i ($\bar{1}$)	$xxxx, xyyy = yxyy = yyxy = yyyx, xzzz = zxzz = zzxz = zzzx, xyzz = xzyz = xzzy = yxzz = yzxz = yzzx = zxyz = zxzy = zyxz = zyzx = zzxy = zzyx, xyyz = xyzy = xzyy = yxyz = yxzy = yyxz = yyzx = yzxy = yzyx = zxyy = zyxy = zyyx, xxzz = xzxz = xzzx = zxxz = zxzx = zzxx, xxxz = xxzx = xzxx = zxxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, xxxy = xxyx = xyxx = yxxx, xxyz = xxzy = xyxz = xyzx = xzxy = xzyx = yxxz = yxzx = yzxx = zxxy = zxyx = zyxx, yyyy, yzzz = zyzz = zzyz = zzzy, yyzz = yzyz = yzzy = zyyz = zyzy = zzyy, yyyz = yyzy = yzyy = zyyy, zzzz$
Monoclinic C_s (m), C_2 (2), C_{2h} $\left(\frac{2}{m}\right)$ (twofold axis parallel to z)	$xxxx, xyyy = yxyy = yyxy = yyyx, xyzz = xzyz = xzzy = yxzz = yzxz = yzzx = zxyz = zxzy = zyxz = zyzx = zzxy = zzyx, xxzz = xzxz = xzzx = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, xxxy = xxyx = xyxx = yxxx, yyyy, yyzz = yzyz = yzzy = zyyz = zyzy = zzyy, zzzz$
Orthorhombic C_{2v} ($mm2$), D_2 (222), D_{2h} (mmm) (twofold axis parallel to z)	$xxxx, xxzz = xzxz = xzzx = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, yyyy, yyzz = yzyz = yzzy = zyyz = zyzy = zzyy, zzzz$
Tetragonal S_4 ($\bar{4}$), C_4 (4), C_{4h} $\left(\frac{4}{m}\right)$	$xxxx = yyyy, xyyy = yxyy = yyxy = yyyx = -xxxy = -xxyx = -xyxx = -yxxx, xxzz = xzxz = xzzx = yyzz = yzyz = yzzy = zyyz = zyzy = zzyy = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, zzzz$
C_{4v} ($4mm$), D_{2d} ($\bar{4}2m$), D_4 (422), D_{4h} $\left(\frac{4}{m}mm\right)$	$xxxx = yyyy, xxzz = xzxz = xzzx = yyzz = yzyz = yzzy = zyyz = zyzy = zzyy = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, zzzz$
Hexagonal C_{3h} ($\bar{6}$), C_6 (6), C_{6h} $\left(\frac{6}{m}\right)$, C_{6v} ($6mm$), D_{3h} ($\bar{6}2m$), D_6 (622), D_{6h} $\left(\frac{6}{m}mm\right)$	$xxxx = yyyy = xxyy + xyxy + xyyx, xxzz = xzxz = xzzx = yyzz = yzyz = yzzy = zyyz = zyzy = zzyy = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, zzzz$
Trigonal C_3 (3), C_{3i} ($\bar{3}$)	$xxxx = yyyy = xxyy + xyxy + xyyx, xyyz = xyzy = xzyy = -xxxz = -xxzx = -xzxx = yxyz = yxzy = yyxz = yyzx = yzxy = yzyx = -zxxx = zxyy = zyxy = zyyx, xxzz = xzxz = xzzx = yyzz = yzyz = yzzy = zyyz = zyzy = zzyy = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, xxyz = xxzy = xyxz = xyzx = xzxy = xzyx = -yyyz = -yyzy = -yzyy = yxxz = yxzx = yzxx = -zyyy = zxxy = zxyx = zyxx, zzzz$
C_{3v} ($3m$), D_3 (32), D_{3d} ($\bar{3}m$) (mirror perpendicular to x) (twofold axis parallel to x)	$xxxx = yyyy = xxyy + xyxy + xyyx, xxzz = xzxz = xzzx = yyzz = yzyz = yzzy = zyyz = zyzy = zzyy = zxxz = zxzx = zzxx, xxyy = xyxy = xyyx = yxxy = yxyx = yyxx, xxyz = xxzy = xyxz = xyzx = xzxy = xzyx = -yyyz = -yyzy = -yzyy = yxxz = yxzx = yzxx = -zyyy = zxxy = zxyx = zyxx, zzzz$
Cubic T (23), T_h ($m3$), T_d ($\bar{4}3m$), O (432), O_h ($m3m$)	$xxxx = yyyy = zzzz, xxzz = xzxz = xzzx = xxyy = xyxy = xyyx = yyzz = yzyz = yzzy = yyxx = yxyx = yxxy = zzyy = zyzy = zyyz = zzxx = zxzx = zxxz$

with $-\rho^{+}(\theta, \omega)$ for the positive class and $+\rho^{-}(\theta, \omega)$ for the negative class. $\rho^{\pm}(\theta, \omega)$ is given by

$$\begin{aligned}\rho^{\pm}(\theta, \omega) &= \arccos(\mathbf{d}^{\pm} \cdot \mathbf{e}^{\pm}) = \arccos(\mathbf{u}^{\pm} \cdot \mathbf{s}^{\pm}) \\ &= \arccos\left\{\left[\frac{\cos^2\theta}{n_o^2(\omega)} + \frac{\sin^2\theta}{n_e^2(\omega)}\right]\left[\frac{\cos^2\theta}{n_o^4(\omega)} + \frac{\sin^2\theta}{n_e^4(\omega)}\right]^{-1/2}\right\}.\end{aligned} \quad (1.7.3.13)$$

Note that the extraordinary walk-off angle is nil for a propagation along the optic axis ($\theta = 0$) and everywhere in the xy plane ($\theta = \pi/2$).

1.7.3.1.4. *Biaxial class*

In a biaxial crystal, the three principal refractive indices are all different. The graphical representations of the index surfaces are given in Fig. 1.7.3.3 for the positive biaxial class ($n_x < n_y < n_z$) and for the negative one ($n_x > n_y > n_z$), both with the usual conventional orientation of the optical frame. If this is not the case, the appropriate permutation of the principal refractive indices is required.

In the orthorhombic system, the three principal axes are fixed by the symmetry; one is fixed in the monoclinic system; and none are fixed in the triclinic system. The index surface of the biaxial class has two umbilici contained in the xz plane, making an angle V with the z axis:

$$\sin^2 V(\omega) = \frac{n_y^{-2}(\omega) - n_x^{-2}(\omega)}{n_z^{-2}(\omega) - n_x^{-2}(\omega)}. \quad (1.7.3.14)$$

The propagation along the optic axes leads to the internal conical refraction effect (Schell & Bloembergen, 1978; Fève *et al.*, 1994).

1.7.3.1.4.1. *Propagation in the principal planes*

It is possible to define ordinary and extraordinary waves, but only in the principal planes of the biaxial crystal: the ordinary electric field vector is perpendicular to the z axis and to the extraordinary one. The walk-off properties of the waves are not the same in the xy plane as in the xz and yz planes.

(1) In the xy plane, the extraordinary wave has no walk-off, in contrast to the ordinary wave. The components of the electric field vectors can be established easily with the same considerations as for the uniaxial class:

$$\begin{aligned} e_x^o &= -\sin[\varphi \pm \rho^{\mp}(\varphi, \omega)] \\ e_y^o &= \cos[\varphi \pm \rho^{\mp}(\varphi, \omega)] \\ e_z^o &= 0, \end{aligned} \quad (1.7.3.15)$$

with $+\rho^{-}(\varphi, \omega)$ for the positive class and $-\rho^{+}(\varphi, \omega)$ for the negative class. $\rho^{\pm}(\varphi, \omega)$ is the walk-off angle given by (1.7.3.13), where θ is replaced by φ, n_o by n_y and n_e by n_x:

$$e_x^e = 0 \quad e_y^e = 0 \quad e_z^e = 1. \quad (1.7.3.16)$$

(2) The yz plane of a biaxial crystal has exactly the same characteristics as any plane containing the optic axis of a uniaxial crystal. The electric field vector components are given by (1.7.3.11) and (1.7.3.12) with $\varphi = \pi/2$. The ordinary walk-off is nil and the extraordinary one is given by (1.7.3.13) with $n_o = n_y$ and $n_e = n_z$.

(3) In the xz plane, the optic axes create a discontinuity of the shape of the internal and external sheets of the index surface leading to a discontinuity of the optic sign and of the electric field vector. The birefringence, $n_e - n_o$, is nil along the optic axis, and its sign changes on either side. Then the yz plane, xy plane and xz plane from the x axis to the optic axis have the same optic sign, the opposite of the optic sign from the optic axis to the z axis. Thus a positive biaxial crystal is negative from the optic axis to the z axis. The situation is inverted for a negative biaxial crystal. It implies the following configuration of polarization:

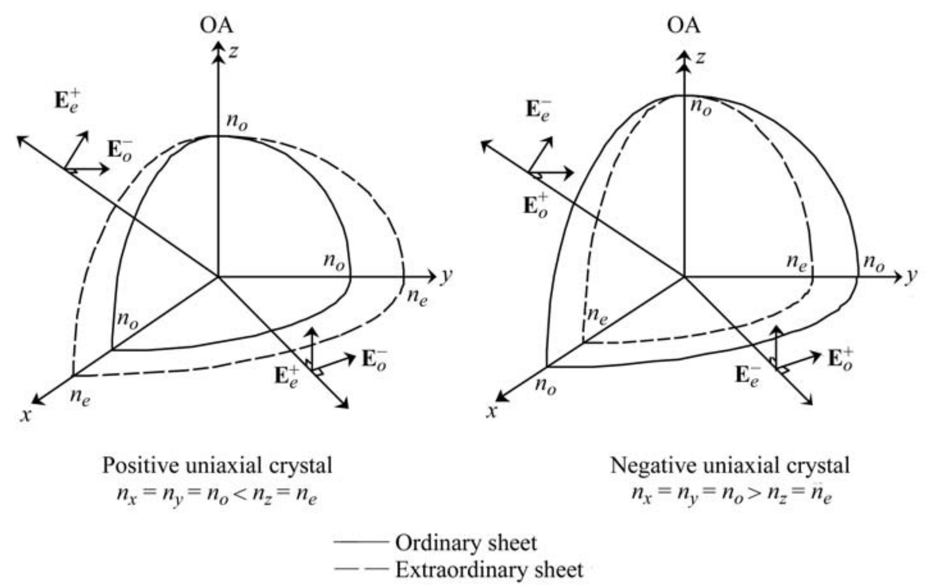

Fig. 1.7.3.2. Index surfaces of the negative and positive uniaxial classes. $\mathbf{E}_{o,e}^{\pm}$ are the ordinary (o) and extraordinary (e) electric field vectors relative to the external (+) or internal (−) sheets. OA is the optic axis.

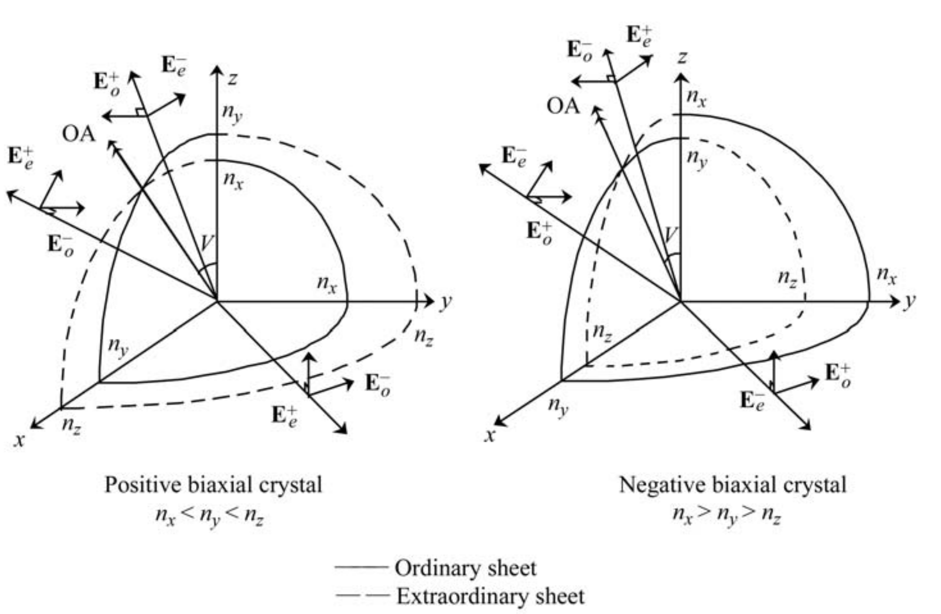

Fig. 1.7.3.3. Index surfaces of the negative and positive biaxial classes. $\mathbf{E}_{o,e}^{\pm}$ are the ordinary (o) and extraordinary (e) electric field vectors relative to the external (+) or internal (−) sheets for a propagation in the principal planes. OA is the optic axis.

(i) From the x axis to the optic axis, $\mathbf{e}^o$ and $\mathbf{e}^e$ are given by (1.7.3.11) and (1.7.3.12) with $\varphi = 0$. The walk-off is relative to the extraordinary wave and is calculated from (1.7.3.13) with $n_o = n_x$ and $n_e = n_z$.

(ii) From the optic axis to the z axis, the vibration plane of the ordinary and extraordinary waves corresponds respectively to a rotation of $\pi/2$ of the vibration plane of the extraordinary and ordinary waves for a propagation in the areas of the principal planes of opposite sign; the extraordinary electric field vector is given by (1.7.3.12) with $\varphi = 0$, $-\rho^-(\varphi, \omega)$ for the positive class and $+\rho^+(\varphi, \omega)$ for the negative class, and the ordinary electric field vector is out of phase by π in relation to (1.7.3.11), that is

$$e_x^o = 0 \quad e_y^o = -1 \quad e_z^o = 0. \qquad (1.7.3.17)$$

The extraordinary walk-off angle is given by (1.7.3.13) with $n_o = n_x$ and $n_e = n_z$.

The $\pi/2$ rotation on either side of the optic axes is well observed during internal conical refraction (Fève *et al.*, 1994).

Note that for a biaxial crystal, the walk-off angles are all nil only for a propagation along the principal axes.

1.7.3.1.4.2. *Propagation out of the principal planes*

It is impossible to define ordinary and extraordinary waves out of the principal planes of a biaxial crystal: according to (1.7.3.6) and (1.7.3.9), $\mathbf{e}^+$ and $\mathbf{e}^-$ have a nonzero projection on the z axis. According to these relations, it appears that $\mathbf{e}^+$ and $\mathbf{e}^-$ are not perpendicular, so relation (1.7.3.10) is never verified. The walk-off angles ρ^+ and ρ^- are nonzero, different, and can be calculated from the electric field vectors:

$$\rho^{\pm}(\theta, \varphi, \omega) = \varepsilon \arccos[\mathbf{e}^{\pm}(\theta, \varphi, \omega) \cdot \mathbf{u}(\theta, \varphi, \omega)] - \varepsilon\pi/2. \qquad (1.7.3.18)$$

$\varepsilon = +1$ or -1 for a positive or a negative optic sign, respectively.

1.7.3.2. *Equations of propagation of three-wave and four-wave interactions*

1.7.3.2.1. *Coupled electric fields amplitudes equations*

The nonlinear crystals considered here are homogeneous, lossless, non-conducting, without optical activity, non-magnetic and are optically anisotropic. The nonlinear regime allows interactions between γ waves with different circular frequencies $\omega_i, i = 1, \ldots, \gamma$. The Fourier component of the polarization vector at ω_i is $\mathbf{P}(\omega_i) = \varepsilon_0 \chi^{(1)}(\omega_i)\mathbf{E}(\omega_i) + \mathbf{P}^{NL}(\omega_i)$, where $\mathbf{P}^{NL}(\omega_i)$ is the nonlinear polarization corresponding to the orders of the power series greater than 1 defined in Section 1.7.2.

Thus the propagation equation of each interacting wave ω_i is (Bloembergen, 1965)

$$\nabla x \nabla x \mathbf{E}(\omega_i) = (\omega_i^2/c^2)\varepsilon(\omega_i)\mathbf{E}(\omega_i) + \omega_i^2 \mu_0 \mathbf{P}^{NL}(\omega_i). \qquad (1.7.3.19)$$

The γ propagation equations are coupled by $\mathbf{P}^{NL}(\omega_i)$:

(1) for a three-wave interaction, $\gamma = 3$,

$$\mathbf{P}^{NL}(\omega_1) = \mathbf{P}^{(2)}(\omega_1) = \varepsilon_0 \chi^{(2)}(\omega_1 = \omega_3 - \omega_2) \cdot \mathbf{E}(\omega_3) \otimes \mathbf{E}^*(\omega_2),$$
$$\mathbf{P}^{NL}(\omega_2) = \mathbf{P}^{(2)}(\omega_2) = \varepsilon_0 \chi^{(2)}(\omega_2 = \omega_3 - \omega_1) \cdot \mathbf{E}(\omega_3) \otimes \mathbf{E}^*(\omega_1),$$
$$\mathbf{P}^{NL}(\omega_3) = \mathbf{P}^{(2)}(\omega_3) = \varepsilon_0 \chi^{(2)}(\omega_3 = \omega_1 + \omega_2) \cdot \mathbf{E}(\omega_1) \otimes \mathbf{E}^*(\omega_2);$$

(2) for a four-wave interaction

$$\mathbf{P}^{NL}(\omega_1) = \mathbf{P}^{(3)}(\omega_1) = \varepsilon_0 \chi^{(3)}(\omega_1 = \omega_4 - \omega_2 - \omega_3) \cdot \mathbf{E}(\omega_4) \otimes \mathbf{E}^*(\omega_2) \otimes \mathbf{E}^*(\omega_3),$$
$$\mathbf{P}^{NL}(\omega_2) = \mathbf{P}^{(3)}(\omega_2) = \varepsilon_0 \chi^{(3)}(\omega_2 = \omega_4 - \omega_1 - \omega_3) \cdot \mathbf{E}(\omega_4) \otimes \mathbf{E}^*(\omega_1) \otimes \mathbf{E}^*(\omega_3),$$
$$\mathbf{P}^{NL}(\omega_3) = \mathbf{P}^{(3)}(\omega_3) = \varepsilon_0 \chi^{(3)}(\omega_3 = \omega_4 - \omega_1 - \omega_2) \cdot \mathbf{E}(\omega_4) \otimes \mathbf{E}^*(\omega_1) \otimes \mathbf{E}^*(\omega_2)$$
$$\mathbf{P}^{NL}(\omega_4) = \mathbf{P}^{(3)}(\omega_4) = \varepsilon_0 \chi^{(3)}(\omega_4 = \omega_1 + \omega_2 + \omega_3) \cdot \mathbf{E}(\omega_1) \otimes \mathbf{E}(\omega_2) \otimes \mathbf{E}(\omega_3).$$

The complex conjugates $\mathbf{E}^*(\omega_1)$ come from the relation $\mathbf{E}^*(\omega_i) = \mathbf{E}(-\omega_i)$.

We consider the plane wave, (1.7.3.3), as a solution of (1.7.3.19), and we assume that all the interacting waves propagate in the same direction Z. Each linearly polarized plane wave corresponds to an eigen mode $\mathbf{E}^+$ or $\mathbf{E}^-$ defined above. For the usual case of beams with a finite transversal profile and when Z is along a direction where the double-refraction angles can be nonzero, *i.e.* out of the principal axes of the index surface, it is necessary to specify a frame for each interacting wave in order to calculate the corresponding powers as a function of Z: the coordinates linked to the wave at ω_i are written (X_i, Y_i, Z), which can be relative to the mode (+) or (−). The systems are then linked by the double-refraction angles ρ: according to Fig. 1.7.3.1, we have $X_j^+ = X_i^+ + Z\tan[\rho^+(\omega_j) - \rho^+(\omega_i)]$, $Y_j^+ = Y_i^+$ for two waves (+) with $\rho^+(\omega_j) > \rho^+(\omega_i)$, and $X_j^- = X_i^-$, $Y_j^- = Y_i^- + Z\tan[\rho^-(\omega_j) - \rho^-(\omega_i)]$ for two waves (−) with $\rho^-(\omega_j) > \rho^-(\omega_i)$.

The presence of $\mathbf{P}^{NL}(\omega_i)$ in equations (1.7.3.19) leads to a variation of the γ amplitudes $E(\omega_i)$ with Z. In order to establish the equations of evolution of the wave amplitudes, we assume that their variations are small over one wavelength λ_i, which is usually true. Thus we can state

$$\frac{1}{k(\omega_i)}\left|\frac{\partial E(\omega_i, X_i, Y_i, Z)}{\partial Z}\right| \ll \left|E(\omega_i, X_i, Y_i, Z)\right| \text{ or } \left|\frac{\partial^2 E(\omega_i, X_i, Y_i, Z)}{\partial Z^2}\right| \ll k(\omega_i)\left|\frac{\partial E(\omega_i, X_i, Y_i, Z)}{\partial Z}\right|. \qquad (1.7.3.20)$$

This is called the slowly varying envelope approximation.

Stating (1.7.3.20), the wave equation (1.7.3.19) for a forward propagation of a plane wave leads to

$$\frac{\partial E(\omega_i, X_i, Y_i, Z)}{\partial Z} = j\mu_0 \frac{\omega_i^2}{2k(\omega_i)\cos^2\rho(\omega_i)} \mathbf{e}(\omega_i) \cdot \mathbf{P}^{NL}(\omega_i, X_i, Y_i, Z) \times \exp[-jk(\omega_i)Z]. \qquad (1.7.3.21)$$

We choose the optical frame (x, y, z) for the calculation of all the scalar products $\mathbf{e}(\omega_i) \cdot \mathbf{P}^{NL}(\omega_i)$, the electric susceptibility tensors being known in this frame.

For a three-wave interaction, (1.7.3.21) leads to

$$\frac{\partial E_1(X_1, Y_1, Z)}{\partial Z} = j\kappa_1\left[\mathbf{e}_1 \cdot \varepsilon_0 \chi^{(2)}(\omega_1 = \omega_3 - \omega_2) \cdot \mathbf{e}_3 \otimes \mathbf{e}_2\right] \times E_3(X_3, Y_3, Z)E_2^*(X_2, Y_2, Z)\exp(j\Delta k Z)$$
$$\frac{\partial E_2(X_2, Y_2, Z)}{\partial Z} = j\kappa_2\left[\mathbf{e}_2 \cdot \varepsilon_0 \chi^{(2)}(\omega_2 = \omega_3 - \omega_1) \cdot \mathbf{e}_3 \otimes \mathbf{e}_1\right] \times E_3(X_3, Y_3, Z)E_1^*(X_1, Y_1, Z)\exp(j\Delta k Z)$$
$$\frac{\partial E_3(X_3, Y_3, Z)}{\partial Z} = j\kappa_3\left[\mathbf{e}_3 \cdot \varepsilon_0 \chi^{(2)}(\omega_3 = \omega_1 + \omega_2) \cdot \mathbf{e}_1 \otimes \mathbf{e}_2\right] \times E_1(X_1, Y_1, Z)E_2(X_2, Y_2, Z)\exp(-j\Delta k Z), \qquad (1.7.3.22)$$

with $\mathbf{e}_i = \mathbf{e}(\omega_i)$, $E_i(X_i, Y_i, Z_i) = E(\omega_i, X_i, Y_i, Z)$, $\kappa_i = (\mu_o \omega_i^2)/[2k(\omega_i)\cos^2\rho(\omega_i)]$ and $\Delta k = k(\omega_3) - [k(\omega_1) + k(\omega_2)]$, called the phase mismatch. We take by convention $\omega_1 < \omega_2$ $(< \omega_3)$.

references