International Tables for Crystallography (2013). Vol. D, Section 1.7.3.1.3, pp. 188–189.

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

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

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:

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

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:

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

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:

$$e_x^e = 0 \quad e_y^e = 0 \quad e_z^e = 1. \tag{1.7.3.16}$$

(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:

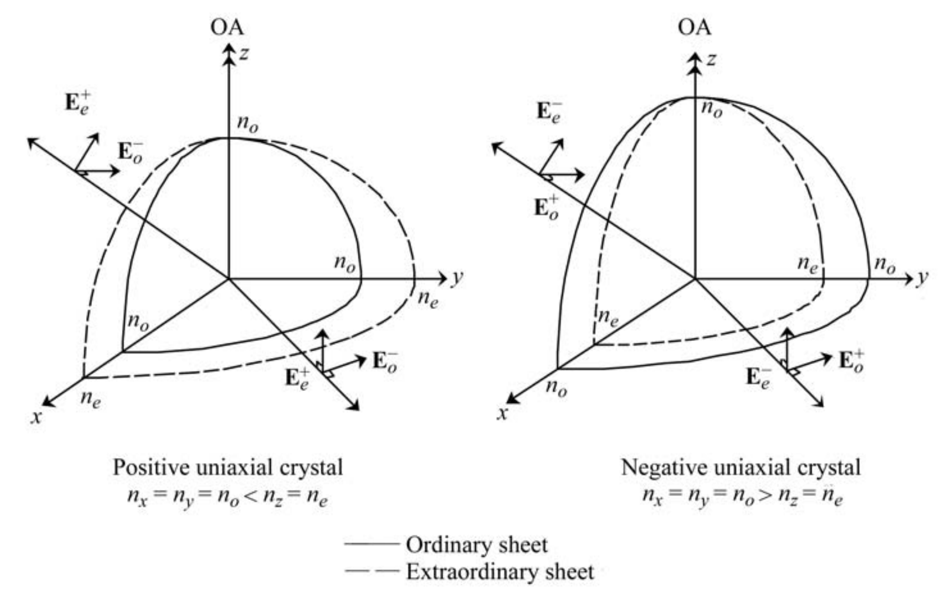

Fig. 1.7.3.2. Index surfaces of the negative and positive uniaxial classes. $\mathbf{E}_{o,e}^\pm$ are the ordinary (o) and extraordinary (e) electric field vectors relative to the external (+) or internal (−) sheets. OA is the optic axis.

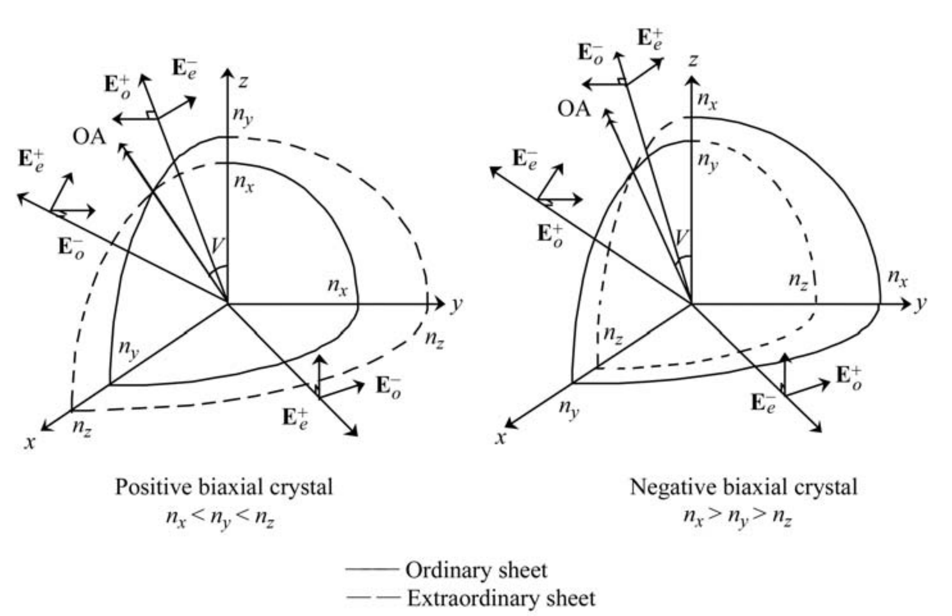

Fig. 1.7.3.3. Index surfaces of the negative and positive biaxial classes. $\mathbf{E}_{o,e}^\pm$ are the ordinary (o) and extraordinary (e) electric field vectors relative to the external (+) or internal (−) sheets for a propagation in the principal planes. OA is the optic axis.

references