International Tables for Crystallography (2013). Vol. D, Section 1.6.3, pp. 155–157.

Thus if a nonlinear crystal is pumped by two counter-propagating beams of frequency $\omega_1 = \omega_2 = \omega$, and another beam $\omega_4 = \omega$ is input at some angle, a fourth beam $\omega_3 = \omega$ results whose complex amplitude will be the complex conjugate of the ω_4 beam. Thus four-wave mixing is an important arrangement for producing *phase conjugation*.

1.6.2.10. *Faraday rotation* $\varepsilon_o \chi_{ijk} E_j^{\omega_1} B_k^{\omega_2}$

Application of a static magnetic field to certain crystals through which light of frequency ω passes causes a change in polarization state *via*

$$P_i^{\omega} = \varepsilon_o \chi_{ijk} E_j^{\omega} B_k^0.$$

The effect is to rotate the plane of polarization of the incident light, the size of the effect depending not only on the length of the medium traversed, but also on the size of the applied magnetic field. An interesting difference from ordinary optical rotation is that on reflecting the light beam back through the medium, the plane of polarization is *further* rotated rather than cancelled: this property has been used in making optical isolators.

1.6.2.11. *Quadratic magneto-optic effect* $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} B_k^{\omega_2} B_\ell^{\omega_3}$

By analogy with the quadratic electro-optic effect, application of a strong static magnetic field can modulate the polarization state of the incident light *via*

$$P_i^{\omega} = \varepsilon_o \chi_{ijk\ell} E_j^{\omega} B_k^0 B_\ell^0.$$

This effect is also known as the *Cotton–Mouton effect*.

1.6.2.12. *Linear photoelastic effect* $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} T_{k\ell}^{\omega_2}$

Also known as the *piezo-optic* effect (or *elasto-optic* effect), this is usually observed through $\chi_{ijk\ell}(\omega; \omega, 0)$, *i.e.* the applied stress is static. Thus the application of a force to an elasto-optic material results in a change in birefringence. This effect can be seen not only in crystals, but also in isotropic materials such as glass or transparent plastics. By observation of a stressed material between crossed polars, the resulting strains can be seen as coloured fringes, a useful way of examining engineering structures.

1.6.2.13. *Linear acousto-optic effect* $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} T_{k\ell}^{\omega_2}$

In the acousto-optic effect, the applied stress is at an acoustic frequency ω_2, *i.e.* the relevant susceptibility is $\chi_{ijk\ell}(\omega_1 \pm \omega_2; \omega_1, \omega_2)$. Thus a sound wave passing through an acousto-optic crystal modulates the refractive index *via*

$$P_i^{\omega_1 \pm \omega_2} = \varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} T_{k\ell}^{\omega_2}.$$

A beam of light of frequency ω_1 passing through the crystal can then be diffracted by the refractive index modulation, and so such a crystal is a useful device for converting sound waves into an optical signal for long-distance transmission along optical fibres. As $\omega_1 \gg \omega_2$, the frequency of the input light is only very slightly altered by the sound wave, and for most purposes can be neglected.

1.6.3. Linear optics

1.6.3.1. *The fundamental equation of crystal optics*

It is necessary, in order to understand fully the propagation of light through a general anisotropic crystal, to address the question of the way in which an electromagnetic wave is affected by its passage through a regular array of atoms or molecules. A full analysis of this problem at a microscopical level is complicated and was treated, for example, by Ewald (1916), who showed through consideration of a 'half-crystal' how to link the electromagnetic field outside the crystal to that inside (a good description of Ewald's work on this can be read in the book *P. P. Ewald and his Dynamical Theory of X-ray Diffraction*, published by the International Union of Crystallography, Oxford Science Publications, 1992). For the purposes needed here, it is sufficient to apply Maxwell's equations to a bulk anisotropic continuum crystal, thus taking a macroscopic approach. The treatment here follows that given by Nussbaum & Phillips (1976).

Consider the relationship between the dielectric displacement **D** and an electric field **E** which in tensor terms is given by

$$D_i = \varepsilon_o \varepsilon_{ij} E_j, \qquad (1.6.3.1)$$

where ε_o is the vacuum dielectric permittivity and ε_{ij} is a second-rank tensor, the relative dielectric tensor. Correspondingly, there is an induced polarization **P** related to **E** *via*

$$P_k = \varepsilon_o \chi_{k\ell} E_\ell, \qquad (1.6.3.2)$$

where $\chi_{k\ell}$ is another second-rank tensor, called the dielectric susceptibility tensor. Note that the restriction to a linear relationship between **D** and **E** (or **P** and **E**) confines the theory to the region of *linear optics*. Addition of higher-order terms (see above) gives *nonlinear optics*. (Nonlinear optics is discussed in Chapter 1.7.)

$$\operatorname{curl} \mathbf{H} = \partial \mathbf{D}/\partial t \qquad (1.6.3.3)$$

$$\operatorname{curl} \mathbf{E} = -\partial \mathbf{B}/\partial t, \qquad (1.6.3.4)$$

where **B** and **H** are the magnetic induction and magnetic field intensity, respectively. It is customary at this point to assume that the crystal is non-magnetic, so that $\mathbf{B} = \mu_o \mathbf{H}$, where μ_o is the vacuum magnetic permeability. If plane-wave solutions of the form

$$\mathbf{E} = \mathbf{E}_o \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \qquad (1.6.3.5)$$

$$\mathbf{H} = \mathbf{H}_o \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \qquad (1.6.3.6)$$

$$\mathbf{D} = \mathbf{D}_o \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \qquad (1.6.3.7)$$

are substituted into equations (1.6.3.3) and (1.6.3.4), the following results are obtained:

$$\mathbf{k} \times \mathbf{H} = \omega \mathbf{D} \qquad (1.6.3.8)$$

$$\mathbf{k} \times \mathbf{E} = -\omega \mathbf{B}. \qquad (1.6.3.9)$$

These equations taken together imply that **D**, **H** and **k** are vectors that are mutually orthogonal to one another: note that in general **E** and **D** need not be parallel. Similarly **B** (and hence **H**), **E** and **k** are mutually orthogonal. Now, on substituting (1.6.3.9) into (1.6.3.8),

$$\frac{1}{\mu_o \omega^2} \mathbf{k} \times (\mathbf{k} \times \mathbf{E}) = -\mathbf{D}. \qquad (1.6.3.10)$$

Defining the propagation vector (or wave normal) **s** by

$$\mathbf{s} = \frac{c}{\omega} \mathbf{k} = n\hat{\mathbf{s}}, \qquad (1.6.3.11)$$

where $\hat{\mathbf{s}}$ is the unit vector in the direction of **s** and n is the *refractive index* for light propagating in this direction, equation (1.6.3.10) then becomes

$$\frac{1}{\mu_o c^2} \mathbf{s} \times (\mathbf{s} \times \mathbf{E}) = -\mathbf{D}. \qquad (1.6.3.12)$$

Via the vector identity $\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = (\mathbf{A} \cdot \mathbf{C})\mathbf{B} - (\mathbf{A} \cdot \mathbf{B})\mathbf{C}$, this result can be transformed to

$$-(\mathbf{s} \cdot \mathbf{s})\mathbf{E} + (\mathbf{s} \cdot \mathbf{E})\mathbf{s} = -\mu_o c^2 \mathbf{D}. \qquad (1.6.3.13)$$

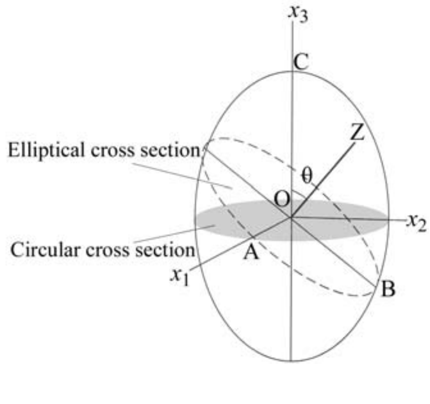

Fig. 1.6.3.1. The optical indicatrix.

$\mathbf{s} \cdot \mathbf{s}$ is equal to n^2 and $\mathbf{s} \cdot \mathbf{E}$ can be expressed simply in tensor form as $\sum_j s_j E_j$. Now, with equation (1.6.3.1), the fundamental equation of linear crystal optics is found:

$$\sum_j (\varepsilon_{ihj} + s_i s_j) E_j = n^2 I E_i, \qquad (1.6.3.14)$$

where I is the unit matrix.

1.6.3.2. *The optical indicatrix*

Equation (1.6.3.14) is the relevant starting point for the derivation of the way in which light propagates in an anisotropic medium. To solve it in a particular case, treat it as an eigenvector–eigenvalue problem: the E_i are the eigenvectors and n^2 the eigenvalues. For example, take the case of a uniaxial crystal. The dielectric tensor is then given by

$$\begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}. \qquad (1.6.3.15)$$

Assume that light propagates along a direction in the x_2x_3 plane, at an angle θ to the x_3 axis. Then, using (1.6.3.11), it is seen that

$$\begin{aligned} s_1 &= 0 \\ s_2 &= n \sin\theta \\ s_3 &= n\cos\theta \end{aligned} \qquad (1.6.3.16)$$

and

$$s_i s_j = \begin{pmatrix} 0 & 0 & 0 \\ 0 & n^2 \sin^2\theta & n^2 \sin\theta\cos\theta \\ 0 & n^2\sin\theta\cos\theta & n^2\cos\theta \end{pmatrix}. \qquad (1.6.3.17)$$

Substituting into equation (1.6.3.14) yields

$$\begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} + n^2\sin^2\theta & n^2\sin\theta\cos\theta \\ 0 & n^2\sin\theta\cos\theta & \varepsilon_{33} + n^2\cos\theta \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} = \begin{pmatrix} n^2 & 0 & 0 \\ 0 & n^2 & 0 \\ 0 & 0 & n^2 \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}. \qquad (1.6.3.18)$$

Solving this for the eigenvalues n gives

$$n_1^2 = \varepsilon_{11} \qquad (1.6.3.19)$$

as one solution and

$$\frac{1}{n_2^2} = \frac{\cos^2\theta}{\varepsilon_{11}} + \frac{\sin^2\theta}{\varepsilon_{33}} \qquad (1.6.3.20)$$

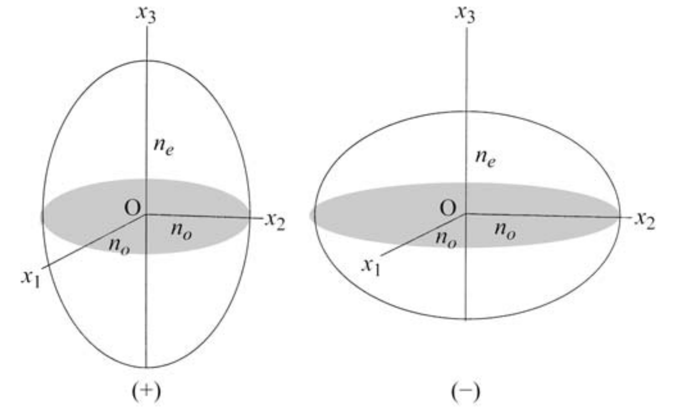

Fig. 1.6.3.2. Positive and negative uniaxial indicatrix.

as the other. This latter solution can be rewritten as

$$\frac{1}{n_2^2} = \frac{\cos^2\theta}{n_o^2} + \frac{\sin^2\theta}{n_e^2}, \qquad (1.6.3.21)$$

showing how the observed refractive index n_2 varies between the limits set by n_o and n_e, called the *ordinary* and *extraordinary* refractive index, respectively (sometimes these are denoted by ω and ε, respectively). Equation (1.6.3.21) can be thought of as the equation of a uniaxial ellipsoid (circular cross section) with the lengths of the semi-axes given by n_o and n_e. This is illustrated in Fig. 1.6.3.1, where **OZ** is the direction of propagation of the light ray at an angle θ to x_3. Perpendicular to **OZ**, an elliptical cross section is cut from the uniaxial ellipsoid with semi-axes *OA* equal to n_o and *OB* given by (1.6.3.21): the directions **OA** and **OB** also correspond to the eigenvectors of equation (1.6.3.4).

Direction **OA** is therefore the direction of the electric polarization transverse to the propagation direction, so that the refractive index measured for light polarized along **OA** is given by the value n_o. For light polarized along **OB**, the refractive index would be given by equation (1.6.3.7). When **OZ** is aligned along x_3, a circular cross section of radius n_o is obtained, indicating that for light travelling along **OZ** and with any polarization the crystal would appear to be optically isotropic. The ellipsoid described here is commonly known as the *optical indicatrix*, in this case a *uniaxial indicatrix*.

Two cases are recognized (Fig. 1.6.3.2). When $n_o < n_e$, the indicatrix is a prolate ellipsoid and is defined to be positive; when $n_o > n_e$, it is oblate and defined to be negative. Note that when $n_o = n_e$ the indicatrix is a sphere, indicating that the refractive index is the same for light travelling in any direction, *i.e.* the crystal is optically isotropic. The quantity $\Delta n = n_e - n_o$ is called the *linear birefringence* (often simply called *birefringence*). In general, then, for light travelling in any direction through a uniaxial crystal, there will be two rays, the ordinary and the extraordinary, polarized perpendicular to each other and travelling with different velocities. This splitting of a ray of light into two rays in the crystal is also known as *double refraction*.

The origin of the birefringence in terms of the underlying crystal structure has been the subject of many investigations. It is obvious that birefringence is a form of optical anisotropy (the indicatrix is not spherical) and so it must be linked to anisotropy in the crystal structure. Perhaps the most famous early study of this link, which is still worth reading, is that of Bragg (1924), who showed that it was possible to calculate rough values for the refractive indices, and hence birefringence, of calcite and aragonite. His theory relied upon the summation of polarizability contributions from the Ca^{2+} and O^{2-} ions.

Returning now to the theory of the indicatrix, more general solution of the fundamental equation (1.6.3.14) leads to a triaxial

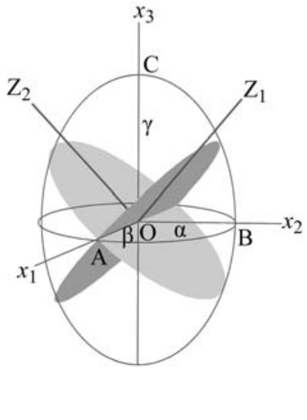

Fig. 1.6.3.3. Biaxial indicatrix, showing the two optic axes and corresponding circular cross sections.

ellipsoid, *i.e.* one in which all three semi-axes are different from one another (Fig. 1.6.3.3).

It is conventional to label the three axes according to the size of the refractive index by $n_\gamma > n_\beta > n_\alpha$ (or simply $\gamma > \beta > \alpha$). In such an ellipsoid, there are always two special directions lying in the γ–α plane, known as the *optic axial plane*, and perpendicular to which there are circular cross sections (shown shaded) of radius β. Thus these two directions are optic axes down which the crystal appears to be optically isotropic, with a measured refractive index β for light of any polarization. For this reason, crystals with this type of indicatrix are known as *biaxial*. When the angle between the optic axes, denoted conventionally as $2V$, is acute about the γ axis, the crystal is *positive biaxial*, and when it is acute about α the crystal is *negative biaxial*. Note that as $2V$ becomes smaller, the biaxial indicatrix becomes closer to a uniaxial indicatrix (positive or negative). In all general directions the crystal is optically anisotropic. Thus, for light along x_3, the measured refractive indices will be α and β for light polarized along x_1 and x_2, respectively; for light along x_2, α and γ are measured for light polarized along x_1 and x_3, respectively; and along x_1, β and γ are measured for light polarized along x_2 and x_3, respectively. There are therefore three different linear birefringences to measure: γ–β, β–α and γ–α.

The different indicatrices are oriented in the crystal according to symmetry considerations (Table 1.6.3.1), and so their observation can form valuable and reliable indicators of the crystal system.

1.6.3.3. *The dielectric impermeability tensor*

It has been seen how the refractive indices can be described in a crystal in terms of an ellipsoid, known as the indicatrix. Thus for orthogonal axes chosen to coincide with the ellipsoid axes, one can write

$$\frac{x_1^2}{n_1^2} + \frac{x_2^2}{n_2^2} + \frac{x_3^2}{n_3^2} = 1, \qquad (1.6.3.22)$$

where $n_1 = (\varepsilon_{11})^{1/2}$, $n_2 = (\varepsilon_{22})^{1/2}$ and $n_3 = (\varepsilon_{33})^{1/2}$. One can write this equation alternatively as

$$\eta_{11}x_1^2 + \eta_{22}x_2^2 + \eta_{33}x_3^2 = 1, \qquad (1.6.3.23)$$

where the $\eta_{ii} = 1/\varepsilon_{ii}$ are the *relative dielectric impermeabilities*. For the indicatrix in any general orientation with respect to the coordinate axes

$$\eta_{11}x_1^2 + \eta_{22}x_2^2 + \eta_{33}x_3^2 + 2\eta_{12}x_1x_2 + 2\eta_{23}x_2x_3 + 2\eta_{31}x_3x_1 = 1. \qquad (1.6.3.24)$$

Thus the dielectric impermeability tensor is described by a second-rank tensor, related inversely to the dielectric tensor.

1.6.4. Practical observation of crystals

1.6.4.1. *The polarizing microscope*

There are countless applications of polarizing microscopy. One of the largest fields of use is in mineralogy and petrology, where the requirement is to identify naturally occurring minerals, the optical properties of which have already been determined elsewhere. Medical applications of a similar sort exist, for instance in the identification of the minerals present in bladder or kidney stones. The chemist or materials scientist who has synthesised a crystalline material may also wish to identify it from known properties, or it may be a new substance that needs to be described. For other purposes it might, for example, be necessary to determine the orientation (relative to crystallographic axes) of mineral specimens, *e.g.* in the cutting of synthetic corundum for the manufacture of watch jewels. This section explains the point of view of an observer who wishes to record and measure optical properties, for whatever reason. Although much of what follows is discussed in terms of mineral crystals, it is equally valid for crystals in general, whether organic or inorganic.

The polarizing microscope incorporates five major features not found in ordinary microscopes. These are:

(i) A *polarizer*, normally a sheet of Polaroid, which is part of the microscope substage assembly. This produces plane-polarized light before the light reaches the specimen. In some microscopes, the polarizer can be rotated, though applications of this technique are rare. In the commonly used petrological microscope, the vibration direction of the polarizer is set in what is called the E–W direction, that is, as the user of the microscope sees the field of view, the vibration direction is from side to side.

(ii) An extra, high-power *condenser* situated in the substage immediately below the specimen. The condenser is switched in and out of the optical path as required.

(iii) A *rotating stage*, circular in plan and graduated in degrees. For a number of purposes, specimens can be rotated through known angles.

(iv) An *analyser*, a second polarizing device, situated in the microscope tube above the specimen. Its vibration direction is set at right angles to that of the polarizer, *i.e.* usually N–S. Like the condenser, this can be inserted into the optical path as needed.

(v) A *Bertrand lens*, also in the microscope tube and insertable as required, which has the function of transferring images from the back (upper) focal plane of the objective to the front (lower) focal plane of the eyepiece. The Bertrand lens and the extra substage condenser are used together to convert the microscope from the *orthoscopic* to the *conoscopic* configuration (see later).

In addition, polarizing microscopes have slotted tubes that allow the insertion of a variety of extra devices generally known as accessory plates. Most common amongst these are the sensitive-tint plate (or 1λ plate) and the quartz wedge.

Objective lenses of various magnifying powers are mounted in a rotating turret. Apart from magnification (typically *ca* ×5 for low power, and ×40 or more for high power), the *numerical aperture* (n.a.) of a lens is an important feature. This is defined as the diameter divided by the focal length. This is a measure of the angle of the cone of light that can enter the objective. In the

Table 1.6.3.1. *Symmetry constraints on the optical indicatrix*

Crystal system	Indicatrix	Orientation constraints
Cubic	Isotropic (sphere)	None
Tetragonal Trigonal Hexagonal	Uniaxial	Circular cross section perpendicular to **c**
Orthorhombic	Biaxial	All indicatrix axes aligned along **a**, **b** and **c**
Monoclinic	Biaxial	One indicatrix axis aligned along **b** (second setting)
Triclinic	Biaxial	None

references