1.6. Classical linear crystal optics

By A. M. Glazer and K. G. Cox†

1.6.1. Introduction

The field of classical crystal optics is an old one, and in the last century, in particular, it was the main subject of interest in the study of crystallography. Since the advent of X-ray diffraction, however, crystal optics tended to fall out of widespread use, except perhaps in mineralogy, where it has persisted as an important technique for the classification and identification of mineral specimens. In more recent times, however, with the growth in optical communications technologies, there has been a revival of interest in the optical properties of crystals, both linear and nonlinear. There are many good books dealing with classical crystal optics, which the reader is urged to consult (Hartshorne & Stuart, 1970; Wahlstrom, 1959; Bloss, 1961). In addition, large collections of optical data on crystals exist (Groth, 1906–1919; Winchell, 1931, 1939, 1951, 1954, 1965; Kerr, 1959). In this chapter, both linear and nonlinear optical effects will be introduced briefly in a generalized way. Then the classical derivation of the refractive index surface for a crystal will be derived. This leads on to a discussion on the practical means by which conventional crystal optics can be used in the study of crystalline materials, particularly in connection with mineralogical study, although the techniques described apply equally well to other types of crystals. Finally, some detailed explanations of certain linear optical tensors will be given.

1.6.2. Generalized optical, electro-optic and magneto-optic effects

When light of a particular cyclic frequency ω is incident on a crystal of the appropriate symmetry, in general an electrical polarization **P** may be generated within the crystal. This can be expressed in terms of a power series with respect to the electric vector of the light wave (Nussbaum & Phillips, 1976; Butcher & Cotter, 1990; Kaminow, 1974):

$$P = \sum \varepsilon_o \chi^{(i)} E^i = \varepsilon_o \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right), \quad (1.6.2.1)$$

where the $\chi^{(i)}$ are susceptibilities of order i. Those working in the field of electro-optics tend to use this notation as a matter of course. The susceptibility $\chi^{(1)}$ is a linear term, whereas the higher-order susceptibilities describe nonlinear behaviour.

However, it is convenient to generalize this concept to take into account other fields (*e.g.* electrical, magnetic and stress fields) that can be imposed on the crystal, not necessarily due to the incident light. The resulting polarization can be considered to arise from many different so-called electro-optic, magneto-optic and photoelastic (elasto-optic) effects, expressed as a series expansion of P_i in terms of susceptibilities $\chi_{ijk\ell\ldots}$ and the applied fields **E**, **B** and T. This can be written in the following way:

$$P_i = P_i^0 + \varepsilon_o \chi_{ij} E_j^\omega + \varepsilon_o \chi_{ij\ell} \nabla_\ell E_j^\omega + \varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$$
$$+ \varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} E_k^{\omega_2} E_\ell^{\omega_3} + \varepsilon_o \chi_{ijk} E_j^{\omega_1} B_k^{\omega_2}$$
$$+ \varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} B_k^{\omega_2} B_\ell^{\omega_3} + \varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} T_{k\ell}^{\omega_2} + \ldots.$$
$$(1.6.2.2)$$

Here, the superscripts refer to the frequencies of the relevant field terms and the susceptibilities are expressed as tensor components. Each term in this expansion gives rise to a specific effect that may or may not be observed, depending on the crystal symmetry and the size of the susceptibility coefficients. Note a possible confusion: in the notation $\chi^{(i)}$, i is equal to one less than its rank. It is important to understand that these terms describe various properties, both linear and nonlinear. Those terms that describe the effect purely of optical frequencies propagating through the crystal give rise to *linear* and *nonlinear* optics. In the former case, the input and output frequencies are the same, whereas in the latter case, the output frequency results from sums or differences of the input frequencies. Furthermore, it is apparent that nonlinear optics depends on the intensity of the input field, and so is an effect that is induced by the strong optical field.

If the input electrical fields are static (the term 'static' is used here to mean zero or low frequency compared with that of light), the resulting effects are either linear or nonlinear electrical effects, in which case they are of no interest here. There is, however, an important class of effects in which both static and optical fields are involved: linear and nonlinear electro-optic effects. Here, the use of the terms linear and nonlinear is open to confusion, depending on whether it is the electrical part or the optical part to which reference is made (see for example below in the discussion of the linear electro-optic effect). Similar considerations apply to applied magnetic fields to give linear and nonlinear magneto-optic effects and to applied stresses, the *photoelastic* effects. Table 1.6.2.1 lists the most important effects according to the terms in this series. The susceptibilities are written in the form $\chi(\omega_1; \omega_2, \omega_3, \ldots)$ to indicate the frequency ω_1 of the output electric field, followed after the semicolon by the input frequencies $\omega_1, \omega_2, \ldots$.

Table 1.6.2.1. *Summary of linear and nonlinear optical properties*

Type of polarization term	Susceptibility	Effect
P_i^0	$\chi(0; 0)$	Spontaneous polarization
$\varepsilon_o \chi_{ij} E_j^\omega$	$\chi(\omega; \omega)$	Dielectric polarization, refractive index, linear birefringence
$\varepsilon_o \chi_{ij\ell} \nabla_\ell E_j^\omega$	$\chi(\omega; \omega)$	Optical rotation (gyration)
$\varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$	$\chi(0; 0, 0)$	Quadratic electric effect
	$\chi(\omega; \omega, 0)$	Linear electro-optic effect or Pockels effect
	$\chi(\omega_1 \pm \omega_2; \omega_1, \omega_2)$	Sum/difference frequency generation, two-wave mixing
	$\chi(\omega; \omega/2, \omega/2)$	Second harmonic generation (SHG)
	$\chi(0; \omega/2, \omega/2)$	Optical rectification
	$\chi(\omega_3; \omega_1, \omega_2)$	Parametric amplification
$\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} E_k^{\omega_2} E_\ell^{\omega_3}$	$\chi(\omega; 0, 0)$	Quadratic electro-optic effect or Kerr effect
	$\chi(\omega; \omega/2, \omega/2, 0)$	Electric-field induced second harmonic generation (EFISH)
	$\chi(-\omega_1; \omega_2, \omega_3, -\omega_4)$	Four-wave mixing
$\varepsilon_o \chi_{ijk} E_j^{\omega_1} B_k^{\omega_2}$	$\chi(\omega; \omega, 0)$	Faraday rotation
$\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} B_k^{\omega_2} B_\ell^{\omega_3}$	$\chi(\omega; \omega, 0, 0)$	Quadratic magneto-optic effect or Cotton–Mouton effect
$\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} T_{k\ell}^{\omega_2}$	$\chi(\omega; \omega, 0)$	Linear elasto-optic effect or photoelastic effect
	$\chi(\omega_1 \pm \omega_2; \omega_1, \omega_2)$	Linear acousto-optic effect

† The sudden death of Keith Cox is deeply regretted. He died in a sailing accident on 27 August 1998 in Scotland at the age of 65.

1.6.2.1. Spontaneous polarization P_i^0

A spontaneous polarization of a crystal can be created in some polar crystals after a strong static electric field is first applied and then removed. Subsequent application of an electric field in the opposite direction can then reverse the sense of the spontaneous polarization. By analogy with the well known similar phenomenon of ferromagnetism, such crystals are known as ferroelectrics (Jona & Shirane, 1962; Lines & Glass, 1979). This effect is therefore not an optical effect, but is included here for the sake of completeness. For a crystal to be a ferroelectric, it cannot have a centre of symmetry.

1.6.2.2. Dielectric polarization $\varepsilon_o \chi_{ij} E_j^\omega$

Application of an electric field **E** of frequency ω to a crystal results in a polarization response whose size depends on the dielectric susceptibility $\chi^{(1)}$. This is a second-rank tensor that is applicable to *all* materials, and is often quoted in terms of the dielectric constant $\varepsilon = \varepsilon_o(1 + \chi)$. For electric fields at optical frequencies, the dielectric constant is equal to the square of the refractive index for light propagating in a certain direction and in a particular polarization state. This effect can only be termed optical if the frequency of the electric field lies at optical frequencies. There is no difference between input and output frequencies, and so the susceptibility is written in the form $\chi_{ij}(\omega; \omega)$. Because there is no change in frequency, this is a linear optical effect.

1.6.2.3. Optical rotation (gyration) $\varepsilon_o \chi_{ij\ell} \nabla_\ell E_j^\omega$

This is the phenomenon often known as *optical activity* (Born & Wolf, 1993; Agranovich & Ginzburg, 1984) in which plane-polarized light of frequency ω passing through a medium has its polarization rotated through an angle depending on the path length through the medium. It is seen most easily along uniaxial directions in crystals with the appropriate symmetry. Centrosymmetric crystals cannot show optical rotation. Because no change in frequency occurs, it can be considered to be a linear optical effect.

1.6.2.4. Quadratic electric effect $\varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$

If $\omega_1 = \omega_2 = 0$, *i.e.* the susceptibility is $\chi_{ijk}(0; 0, 0)$, the resulting polarization is given by

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

This is therefore a polarization induced in the crystal by a strong static electric field. It is a nonlinear electrical effect, and so it is not an optical property.

1.6.2.5. Linear electro-optic effect $\varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$

If $\omega_1 = \omega$ and $\omega_2 = 0$, *i.e.* $\chi_{ijk}(\omega; \omega, 0)$, this contribution becomes

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

and corresponds to the situation where light of frequency ω passes into the crystal at the same time as a static electric field is applied. The effect, sometimes known as the *Pockels effect*, is to change the polarization state of the incident light, effectively by altering the refractive indices of the crystal. This physical property is governed by the third-rank electro-optic susceptibility $\chi^{(2)}$, components χ_{ijk}, which follow the same symmetry constraints as the piezoelectric tensor. Crystals therefore must lack a centre of symmetry for this effect to be observable. Although this can be classified as a nonlinear effect, because more than one incident field is involved, it is customary to call it a linear electro-optic effect, as only a single electrical field is used, and moreover there is no change in the frequency of the incident light.

1.6.2.6. Sum/difference frequency generation (two-wave mixing) $\varepsilon_o \chi_{ijk} E_j^{\omega_1} E_k^{\omega_2}$

It can happen that when two different light fields of frequencies ω_1 and ω_1, such as can be obtained from two lasers, propagate through a crystal, the resulting output frequency can be the sum or difference of the two incident frequencies, through the susceptibility $\chi_{ijk}(\omega_1 \pm \omega_2; \omega_1, \omega_2)$. A particular case is of interest: suppose $\omega_1 = \omega_2 = \omega/2$ *i.e.* $\chi_{ijk}(\omega; \omega/2, \omega/2)$, to get

$$P_i^\omega = \varepsilon_o \chi_{ijk} E_j^{\omega/2} E_k^{\omega/2}.$$

Here, the light, on passing through the crystal, interacts with itself to produce a doubling of the frequency. This important effect is known as *second harmonic generation* or SHG and is used for generating different laser frequencies starting from a fundamental frequency. The observation of SHG is also often a good indicator of the lack of a centre of inversion in a crystal. As two optical fields are involved, the incident field inducing the second one, this is a true nonlinear optical effect.

Another effect can be envisaged in which the susceptibility is $\chi_{ijk}(0; \omega/2, -\omega/2)$, *i.e.* there is a cancellation of the two incident frequencies to produce a polarization in the crystal. This is called *optical rectification*.

Parametric amplification is an effect caused when an incident beam at frequency ω_1 is incident on a nonlinear optical crystal at the same time as an intense pump beam frequency ω_2, where $\omega_2 > \omega_1$. The ω_1 wave is then amplified accompanied by an 'idler' wave of frequency $\omega_3 = \omega_2 - \omega_1$.

1.6.2.7. Quadratic electro-optic effect $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} E_k^{\omega_2} E_\ell^{\omega_3}$

This effect, known also as the *Kerr effect*, results from setting $\omega_1 = \omega$, $\omega_2 = \omega_3 = 0$, *i.e.* the susceptibility is $\chi_{ijk\ell}(\omega; \omega, 0, 0)$, thus:

$$P_i^\omega = \varepsilon_o \chi_{ijk\ell} E_j^\omega E_k^0 E_\ell^0.$$

Like the linear electro-optic effect described above, a static electric field applied to the medium causes a change in the refractive indices, which then affects the polarization of the transmitted light. The difference here is that the Kerr effect is displayed by all transparent media, including liquids. In an otherwise optically isotropic system, application of a strong static field makes the system optically anisotropic: this change from isotropic to anisotropic can be used to produce a fast optical shutter. Because the light frequency is unchanged, this can be termed a linear optical effect, but on the other hand, because it depends on the square of the static electric field, it is a nonlinear electrical effect.

1.6.2.8. Electric-field induced second harmonic generation $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} E_k^{\omega_2} E_\ell^{\omega_3}$

If $\omega_1 = \omega_2 = \omega/2$ and $\omega_3 = 0$, *i.e.* the susceptibility is $\chi_{ijk\ell}(\omega; \omega/2, \omega/2, 0)$, the resulting polarization is

$$P_i^\omega = \varepsilon_o \chi_{ijk\ell} E_j^{\omega/2} E_k^{\omega/2} E_\ell^0.$$

A second-harmonic response is obtained, but this time induced by a static electric field. This is called *electric-field-induced SHG* or EFISH. It is a nonlinear optical effect that is created by a linear electric effect.

1.6.2.9. Four-wave mixing $\varepsilon_o \chi_{ijk\ell} E_j^{\omega_1} E_k^{\omega_2} E_\ell^{\omega_3}$

One use of a third-order nonlinear optical susceptibility is in the important area of four-wave mixing. In this case, the complex amplitude of the induced polarization at the frequency $\omega_1 = \omega_2 + \omega_3 - \omega_4$ is given by

$$P_i^{\omega_1} = \varepsilon_o \chi_{ijk\ell}(-\omega_1; \omega_2, \omega_3, -\omega_4) E_j^{\omega_2} E_k^{\omega_3} E_\ell^{*\omega_4}.$$

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 electro-

magnetic 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 $\mathbf{D}$ and an electric field $\mathbf{E}$ which in tensor terms is given by

$$D_i = \varepsilon_o \varepsilon_{ij} E_j, \tag{1.6.3.1}$$

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 $\mathbf{P}$ related to $\mathbf{E}$ *via*

$$P_k = \varepsilon_o \chi_{k\ell} E_\ell, \tag{1.6.3.2}$$

where $\chi_{k\ell}$ is another second-rank tensor, called the dielectric susceptibility tensor. Note that the restriction to a linear relationship between $\mathbf{D}$ and $\mathbf{E}$ (or $\mathbf{P}$ and $\mathbf{E}$) 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.)

$$\operatorname{curl} \mathbf{H} = \partial \mathbf{D} / \partial t \tag{1.6.3.3}$$

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

where $\mathbf{B}$ and $\mathbf{H}$ 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

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

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

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

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

$$\mathbf{k} \times \mathbf{H} = \omega \mathbf{D} \tag{1.6.3.8}$$

$$\mathbf{k} \times \mathbf{E} = -\omega \mathbf{B}. \tag{1.6.3.9}$$

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

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

Defining the propagation vector (or wave normal) $\mathbf{s}$ by

$$\mathbf{s} = \frac{c}{\omega} \mathbf{k} = n\hat{\mathbf{s}}, \tag{1.6.3.11}$$

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

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

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

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

references