# A THEORETICAL INVESTIGATION OF BIREFRINGENCES IN CUBIC AND UNIAXIAL MAGNETIC CRYSTALS

*by*

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# ABSTRACT

In this thesis a consistent multipole theory is used to describe light propagation in non-absorbing magnetic cubic and uniaxial crystals to the order of electric octopoles and magnetic quadrupoles.

The first chapter extends Maxwell's equations for a vacuum to their macroscopic form in matter by including bound-source contributions as multipole expansions. From these the corresponding forms for ***D*** and ***H*** are obtained, which ensure origin-independence of Maxwell's equations. A multipole eigenvalue equation describing light propagation in a source-free homogeneous medium is then derived, which is the basic equation applied in this thesis.

In the second chapter it is shown how, from the multipolar form of the propagation equation for transverse waves, expressions can be derived for the various birefringences that may be exhibited in macroscopic platelets of the medium, as introduced by Jones in the formulation of his M-matrix.

The following chapter presents the derivation, by means of first-order perturbation theory, of the quantum mechanical expressions for the polarizability tensors which enter the eigenvalue wave equation. The origin independence of the expressions for the various observable quantities is then established.

In the fourth chapter the independent components of the polarizability tensors are calculated for two selected crystal point groups, namely $6\underline{2}\underline{2}$ and $\underline{4}3\underline{2}$, by way of illustration.

In chapter five the components calculated in the manner illustrated in the previous chapter are presented in tabular form. The Jones method outlined in chapter two is then applied to the crystal point group $\underline{\bar{6}m}2$, again as an illustration of the method used to determine the optical effects displayed by this point group. Chapter five concludes with a table containing a listing of the predicted optical effects calculated in this way for all of the magnetic uniaxial and cubic point groups.

The thesis concludes with chapter six, in which a summary of the results of the work undertaken is given, together with a discussion of factors influencing measurements of the predicted optical effects.

# DECLARATION

I declare that this work is a result of my own research, except where specifically indicated to the contrary, and has not been submitted for any other degree or examination to any other university.

Signed: ____________________ Date: 30/03/98

# ACKNOWLEDGEMENTS

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# CHAPTER 1

## 1.1 MAXWELL'S EQUATIONS

Gauss' law in vacuum relates, at an instant of time, the outward flux of an arbitrary time-dependent electric field $\boldsymbol{E}$ through a closed surface to the total charge Q within the surface. Thus

$$\int_S \boldsymbol{E} \cdot d\boldsymbol{a} = \frac{1}{\epsilon_o} Q \ , \tag{1.1}$$

where $d\boldsymbol{a}$ is an element of area of the closed surface $S$. For a continuous distribution of charge in vacuum the law takes the form

$$\int_S \boldsymbol{E} \cdot d\boldsymbol{a} = \frac{1}{\epsilon_o} \int_V \rho \, dV \ , \tag{1.2}$$

where $\rho$ is the charge density at the volume element $dV$ of the volume $V$ enclosed by $S$. By means of the divergence theorem

$$\int_S \boldsymbol{A} \cdot d\boldsymbol{a} = \int_V \nabla \cdot \boldsymbol{A} \, dV \ , \tag{1.3}$$

where $\boldsymbol{A}$ is some vector, the differential form of Gauss' law in a vacuum may be immediately obtained from equation (1.2), namely

$$\nabla \cdot \boldsymbol{E} = \frac{1}{\epsilon_o} \rho \ . \tag{1.4}$$

In the presence of matter a similar form may be derived in which $\boldsymbol{E}$ is the macroscopic or volume-average electric field at a macroscopic point and $\rho$ is the total charge density at that point, namely

$$\rho = \rho_c + \rho_b \quad , \tag{1.5}$$

where $\rho_c$ and $\rho_b$ are the macroscopic free and bound charge densities respectively. The following equation is thus obtained:

$$\nabla \cdot \boldsymbol{E} = \frac{\rho_c + \rho_b}{\epsilon_o} \quad . \tag{1.6}$$

This may be regarded as an alternative form to one of Maxwell's four equations of electrodynamics.

In a number of texts (e.g. Lorrain and Corson 1990) it is shown that

$$\rho_b = -\nabla \cdot \boldsymbol{P} \quad , \tag{1.7}$$

where $\boldsymbol{P}$ is the polarization density or, more descriptively, the electric dipole moment per unit macroscopic volume. By combining equations (1.6) and (1.7) one obtains

$$\nabla \cdot (\epsilon_o \boldsymbol{E} + \boldsymbol{P}) = \rho_c \quad . \tag{1.8}$$

The divergence of the vector $(\epsilon_o \boldsymbol{E} + \boldsymbol{P})$ depends only on the free charge density $\rho_c$. This vector is called the electric displacement, designated $\boldsymbol{D}$, so that

$$\nabla \cdot \boldsymbol{D} = \rho_c \quad , \tag{1.9}$$

where

$$\boldsymbol{D} = \epsilon_o \boldsymbol{E} + \boldsymbol{P} \quad . \tag{1.10}$$

Equation (1.9) is the traditional form of the Maxwell equation (1.6).

The experimental fact that free magnetic charge has not been discovered in vacuum is expressed by the analogous form of Gauss' law

$$\int_S \boldsymbol{B} \cdot d\boldsymbol{a} = 0 \quad , \tag{1.11}$$

where $\boldsymbol{B}$ is an arbitrary time-dependent magnetic field at a point in vacuum. Application of equation (1.3) yields the vacuum equation

$$\nabla \cdot \boldsymbol{B} = 0 \quad . \tag{1.12}$$

As neither free nor bound magnetic charge has been found to exist in matter on the macroscopic scale, the same form as that in equation (1.12) can be shown to apply to matter, except that now $\boldsymbol{B}$ is the macroscopic magnetic field. This is another of Maxwell's equations.

Faraday's law of electromagnetic induction in vacuum reads

$$\oint_C \boldsymbol{E} \cdot d\boldsymbol{l} = -\frac{d}{dt} \int_S \boldsymbol{B} \cdot d\boldsymbol{a} \quad , \tag{1.13}$$

where $S$ is any surface spanning the closed path $C$, of which $d\boldsymbol{l}$ is an element. By means of Stokes's theorem

$$\oint_C \boldsymbol{A} \cdot d\boldsymbol{l} = \int_S (\nabla \times \boldsymbol{A}) \cdot d\boldsymbol{a} \quad , \tag{1.14}$$

one obtains from equation (1.13)

$$\oint_C \boldsymbol{E}\cdot d\boldsymbol{l} = \int_S (\nabla \times \boldsymbol{E})\cdot d\boldsymbol{a} = -\frac{d}{dt}\int_S \boldsymbol{B}\cdot d\boldsymbol{a} = -\int_S \frac{\partial \boldsymbol{B}}{\partial t}\cdot d\boldsymbol{a} \ , \tag{1.15}$$

in which, to ensure that the closed path and its bounding surface are constant in the same reference frame, only a time variation of $\boldsymbol{B}$ at a given point is possible, as expressed by the partial derivative. Since this equation is valid for an arbitrary surface, the integrands of the surface integrals are equal at every point, and we obtain

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \ . \tag{1.16}$$

Since no free sources enter this vacuum equation, its form in matter is identical, except that now the fields are macroscopic. This is the third of Maxwell's equations, and it applies to stationary media.

For a distribution of steady current in vacuum Ampere's circuital law applies

$$\oint_C \boldsymbol{B}\cdot d\boldsymbol{l} = \mu_o \int_S \boldsymbol{J}\cdot d\boldsymbol{a} \ , \tag{1.17}$$

where $\boldsymbol{J}$ is the surface current density at the element d$\boldsymbol{a}$ of any surface $S$ bounded by the closed path $C$. By means of Stokes's theorem equation (1.17) can be transformed to yield the differential form

$$\nabla \times \boldsymbol{B} = \mu_o \boldsymbol{J} \ . \tag{1.18}$$

For time-dependent fields in vacuum this can be shown to become

$$\nabla \times \boldsymbol{B} = \mu_o(\epsilon_o \frac{\partial \boldsymbol{E}}{\partial t} + \boldsymbol{J}) \ . \tag{1.19}$$

The corresponding equation in the presence of matter has the form of equation (1.18) where $\boldsymbol{B}$ and $\boldsymbol{J}$ are macroscopic quantities with

$$\boldsymbol{J} = \boldsymbol{J}_d + \boldsymbol{J}_c + \boldsymbol{J}_b \quad . \qquad \textbf{(1.20)}$$

Here $\boldsymbol{J}_d = \epsilon_o(\partial \boldsymbol{E}/\partial t)$ is the displacement current density involving the macroscopic electric field, $\boldsymbol{J}_c$ the free current density, and $\boldsymbol{J}_b$ the density of bound currents that may arise in matter.

A number of authors (e.g. Hornreich and Shtrikman 1968, Lorrain and Corson 1990) show that

$$\boldsymbol{J}_b = \nabla \times \boldsymbol{M} + \frac{\partial \boldsymbol{P}}{\partial t} \quad , \qquad \textbf{(1.21)}$$

where $\boldsymbol{M}$ is termed the magnetization, defined to be the magnetic dipole moment per unit macroscopic volume.

From equations (1.10), (1.20), and (1.21) it follows that equation (1.18) may be written in the more traditional form for the last of Maxwell's equations, namely

$$\nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t} + \boldsymbol{J}_c \quad . \qquad \textbf{(1.22)}$$

In this

$$\boldsymbol{H} = \mu_0^{-1}\boldsymbol{B} - \boldsymbol{M} \quad . \qquad \textbf{(1.23)}$$

Although these forms for the field vectors $\boldsymbol{D}$ in equation (1.10) and $\boldsymbol{H}$ in equation (1.23) are acceptable for static uniform fields, they cannot be applied to non-uniform static or electromagnetic fields. This is a consequence of the omission in the expressions for the bound source densities in equations (1.7) and (1.21) of terms involving higher multipole moments, beginning with the electric quadrupole moment density $Q_{\alpha\beta}$, which, as will be evident in the next section, contributes to the same order of magnitude as $\boldsymbol{M}$. Furthermore, the omission of the electric quadrupole term in equations (1.7) and (1.21) leads to forms for $\boldsymbol{D}$ and $\boldsymbol{H}$ which, when used in Maxwell's equations, yield expressions for certain observables that depend on origin. This will be illustrated in Chapter 3. A successful description of optical transmission phenomena in terms of Maxwell's equations requires the use of correct multipolar forms for these field vectors.

## 1.2 MULTIPOLAR EXPRESSIONS FOR *D* AND *H*

The interaction of matter with electromagnetic radiation, whose wavelength is much greater than the linear dimensions of a macroscopic volume element, has been successfully described in terms of the multipole moments induced in a volume element by the radiation. (Buckingham 1967, Graham and Raab 1990). In order to describe such an electromagnetic effect in matter using Maxwell's equations it is necessary to include multipole contributions of comparable magnitude in the expressions for $\boldsymbol{D}$ and $\boldsymbol{H}$. The relative magnitudes of these contributions to an optical effect are ordered as follows (de Figueiredo and Raab 1981):

$$\begin{matrix}\textit{electric} \\ \textit{dipole}\end{matrix} \gg \begin{cases}\textit{electric quadrupole} \\ \textit{magnetic dipole}\end{cases} \gg \begin{cases}\textit{electric octopole} \\ \textit{magnetic quadrupole}\end{cases} \tag{1.24}$$

In this research allowance has been made for consistent inclusion of all contributions to the order of electric octopoles and magnetic quadrupoles.

A finite distribution of time-varying currents in a volume $V$ in vacuum gives rise to the retarded scalar potential $\phi(\mathfrak{R},t)$ at a point with coordinate $\mathfrak{R}$ relative to an arbitrary origin O in the distribution. In the Lorentz gauge

$$\phi(\mathfrak{R},t) = \frac{1}{4\pi\epsilon_o}\int_V \frac{\rho(\boldsymbol{r},t-|\mathfrak{R}-\boldsymbol{r}|/c)}{|\mathfrak{R}-\boldsymbol{r}|}\,dV \ . \tag{1.25}$$

In a similar way the retarded vector potential $\boldsymbol{A}(\mathfrak{R},t)$ is expressed as

$$\boldsymbol{A}(\mathfrak{R},t) = \frac{\mu_o}{4\pi}\int_V \frac{J(\boldsymbol{r},t-|\mathfrak{R}-\boldsymbol{r}|/c)}{|\mathfrak{R}-\boldsymbol{r}|}\,dV \ , \tag{1.26}$$

In equations (1.25) and (1.26) $\rho$ is the charge density and $J$ the current density at the retarded time $t-|\mathfrak{R}-\boldsymbol{r}|/c$ at a microscopic volume element $dV$ which has coordinate $\boldsymbol{r}$ relative to O.

In their derivation of a multipolar expression for the total bound current density at a macroscopic volume element Graham et al. (1992) began by performing a binomial expansion of $|\mathfrak{R}-\boldsymbol{r}|^{-1}$ in equation (1.26) and a Taylor expansion of $t-|\mathfrak{R}-\boldsymbol{r}|/c$ about $t-\mathfrak{R}/c$, in order to relate the vector potential at a distant field point ($\mathfrak{R}>>r$) to a series of multipole moments at O. In the limit $\lambda>>\mathfrak{R}$, where $\lambda$ is the wavelength of the light wave, and with a suitable averaging procedure to extend the derivation to bulk matter, the following expression for the macroscopic vector potential **A** was obtained:

$$A_\alpha(\boldsymbol{R},t) = \frac{\mu_o}{4\pi}\left(\int_V \dot{P}_\alpha(R^{-1})dV + \int_V(\tfrac{1}{2}\dot{Q}_{\alpha\beta} - \epsilon_{\alpha\beta\gamma}M_\gamma)\nabla_\beta(R^{-1})dV + \int_V(\tfrac{1}{6}\dot{Q}_{\alpha\beta\gamma} - \tfrac{1}{2}\epsilon_{\alpha\beta\delta}M_{\delta\gamma})\nabla_\gamma\nabla_\beta(R^{-1})dV + \ldots\right) , \quad \textbf{(1.27)}$$

in which the multipole moment densities are those at the coordinate $\boldsymbol{R}$=-$\mathfrak{R}$ at time $t'=t-R/c$.

Equation (1.27) is written in cartesian tensor notation, in which Greek subscripts denote cartesian components. $\epsilon_{\alpha\beta\gamma}$ is the alternating tensor and has the following properties:

When α,β, and γ are in cyclic order of x, y, and z, $\epsilon_{\alpha\beta\gamma}=1$.

When α,β, and γ are in anti-cyclic order, $\epsilon_{\alpha\beta\gamma}=-1$.

When one of α,β, or γ is a repeat of either of the two remaining subscripts, $\epsilon_{\alpha\beta\gamma}=0$.

Equations (1.26) and (1.27) can be shown to lead to the following expression for the total bound current density at a macroscopic volume element:

$$J_{b_\alpha} = \dot{P}_\alpha - \tfrac{1}{2}\nabla_\beta\dot{Q}_{\alpha\beta} + \epsilon_{\alpha\beta\gamma}\nabla_\beta M_\gamma + \tfrac{1}{6}\nabla_\gamma\nabla_\beta\dot{Q}_{\alpha\beta\gamma} - \tfrac{1}{2}\epsilon_{\alpha\beta\delta}\nabla_\gamma\nabla_\beta M_{\delta\gamma} - \cdots . \quad \textbf{(1.28)}$$

Substituting this into equation (1.20) which is then used in equation (1.18) yields

$$\epsilon_{\alpha\beta\gamma}\nabla_\beta \mu_o^{-1} B_\gamma = \frac{\partial}{\partial t}\left(\epsilon_o E_\alpha + P_\alpha - \tfrac{1}{2}\nabla_\beta Q_{\alpha\beta} + \tfrac{1}{6}\nabla_\gamma\nabla_\beta Q_{\alpha\beta\gamma} + \dots\right)$$
$$+ \epsilon_{\alpha\beta\gamma}\nabla_\beta\left(M_\gamma - \tfrac{1}{2}\nabla_\delta M_{\gamma\delta}\right) + \dots \quad + J_{c_\alpha} . \qquad \textbf{(1.29)}$$

This equation has the form

$$\epsilon_{\alpha\beta\gamma}\nabla_\beta H_\gamma = \frac{\partial D_\alpha}{\partial t} + J_{c_\alpha} , \qquad \textbf{(1.30)}$$

where

$$D_\alpha = \epsilon_o E_\alpha + P_\alpha - \tfrac{1}{2}\nabla_\beta Q_{\alpha\beta} + \tfrac{1}{6}\nabla_\gamma\nabla_\beta Q_{\alpha\beta\gamma} - \dots \qquad \textbf{(1.31)}$$

and

$$H_\gamma = \mu_0^{-1} B_\gamma - M_\gamma + \tfrac{1}{2}\nabla_\delta M_{\gamma\delta} - \dots . \qquad \textbf{(1.32)}$$

When the scalar potential $\phi$ in equation (1.25) is expanded in the same way as $\boldsymbol{A}$ in equation (1.26), a multipole expansion of the macroscopic bound charge density $\rho_b$ is obtained which, when substituted into equation (1.6), yields the Maxwell equation (1.9) with $\boldsymbol{D}$ having the identical multipole form as in equation (1.31).

## 1.3 MACROSCOPIC MULTIPOLE MOMENT DENSITIES

Due to its finite wavelength, the field of an electromagnetic wave is not constant over the linear dimension d of a molecule or a crystal unit cell. If $\lambda \gg d$ the wave may be described by its fields $\boldsymbol{E}$ and $\boldsymbol{B}$ and also by their various space derivatives

$$\nabla_\beta E_\alpha\ ,\ \nabla_\gamma \nabla_\beta E_\alpha\ ,\ \dots\ ;\quad \nabla_\beta B_\alpha\ ,\ \nabla_\gamma \nabla_\beta B_\alpha\ ,\ \dots \tag{1.33}$$

at a point in a molecule or unit cell.

An electromagnetic wave also consists of time-derivative fields, such as

$$\boldsymbol{E},\ \dot{\boldsymbol{E}},\ \ddot{\boldsymbol{E}},\ \dddot{\boldsymbol{E}},\ \dots\ . \tag{1.34}$$

However, due to the harmonic condition applying to a plane monochromatic wave

$$\ddot{\boldsymbol{E}} = -\omega^2 \boldsymbol{E} \quad , \quad \dddot{\boldsymbol{E}} = -\omega^2 \dot{\boldsymbol{E}} \quad etc. \tag{1.35}$$

where $\omega$ is the angular frequency of the light wave, there are only two independent time derivatives of each field in equation (1.33), which we take to be the field and its first time derivative.

When a plane monochromatic wave propagates in a medium, multipole moments are induced in the medium by the light wave fields and their space and time derivatives. The expressions for the induced moment densities, to the order of electric octopole and magnetic quadrupole, are (Graham and Raab 1991):

$$P_\alpha = \alpha_{\alpha\beta}E_\beta + \frac{1}{\omega}\alpha'_{\alpha\beta}\dot{E}_\beta + \frac{1}{2}a_{\alpha\beta\gamma}\nabla_\gamma E_\beta + \frac{1}{2\omega}a'_{\alpha\beta\gamma}\nabla_\gamma \dot{E}_\beta$$
$$+ \frac{1}{6}b_{\alpha\beta\gamma\delta}\nabla_\delta\nabla_\gamma E_\beta + \frac{1}{6\omega}b'_{\alpha\beta\gamma\delta}\nabla_\delta\nabla_\gamma \dot{E}_\beta + \ldots$$
$$+ G_{\alpha\beta}B_\beta + \frac{1}{\omega}G'_{\alpha\beta}\dot{B}_\beta + \frac{1}{2}H_{\alpha\beta\gamma}\nabla_\gamma B_\beta + \frac{1}{2\omega}H'_{\alpha\beta\gamma}\nabla_\gamma \dot{B}_\beta + \ldots, \quad \textbf{(1.36)}$$

$$Q_{\alpha\beta} = \rho_{\alpha\beta\gamma}E_\gamma + \frac{1}{\omega}\rho'_{\alpha\beta\gamma}\dot{E}_\gamma + \frac{1}{2}d_{\alpha\beta\gamma\delta}\nabla_\delta E_\gamma + \frac{1}{2\omega}d'_{\alpha\beta\gamma\delta}\nabla_\delta \dot{E}_\gamma + \ldots$$
$$+ L_{\alpha\beta\gamma}B_\gamma + \frac{1}{\omega}L'_{\alpha\beta\gamma}\dot{B}_\gamma + \ldots, \quad \textbf{(1.37)}$$

$$Q_{\alpha\beta\gamma} = \zeta_{\alpha\beta\gamma\delta}E_\delta + \frac{1}{\omega}\zeta'_{\alpha\beta\gamma\delta}\dot{E}_\delta + \ldots, \quad \textbf{(1.38)}$$

$$M_\alpha = \chi_{\alpha\beta}B_\beta + \frac{1}{\omega}\chi'_{\alpha\beta}\dot{B}_\beta + \ldots$$
$$+ \xi_{\alpha\beta}E_\beta + \frac{1}{\omega}\xi'_{\alpha\beta}\dot{E}_\beta + \frac{1}{2}\mathcal{L}_{\alpha\beta\gamma}\nabla_\gamma E_\beta + \frac{1}{2\omega}\mathcal{L}'_{\alpha\beta\gamma}\nabla_\gamma \dot{E}_\beta + \ldots, \quad \textbf{(1.39)}$$

$$M_{\alpha\beta} = \mathcal{H}_{\alpha\beta\gamma}E_\gamma + \frac{1}{\omega}\mathcal{H}'_{\alpha\beta\gamma}\dot{E}_\gamma + \ldots . \quad \textbf{(1.40)}$$

In these equations $P_\alpha$, $Q_{\alpha\beta}$, $Q_{\alpha\beta\gamma}$, $M_\alpha$ and $M_{\alpha\beta}$ are, respectively, the electric dipole, electric quadrupole, electric octopole, magnetic dipole, and magnetic quadrupole moments per unit macroscopic volume. Quantum mechanical expressions for the polarizability tensors which appear in the right-hand-sides of the above equations are derived in Chapter 3 of this dissertation.

These expressions indicate that all contributions to the required multipole order have been included in equations (1.36) to (1.40). The polarizability tensors are in general complex to allow for absorption. According to the definition of a property tensor given in Birss (1964), these polarizability tensors may be termed property tensors since they form a relationship between two particular measurable tensor quantities associated with the crystal.

From the expressions for the property tensors given in Chapter 3, the following relationships are evident:

$$\alpha_{\alpha\beta} = \alpha_{\beta\alpha} \quad , \quad \alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha} \quad , \tag{1.41}$$

$$\rho_{\alpha\beta\gamma} = a_{\gamma\alpha\beta} \quad , \quad \rho'_{\alpha\beta\gamma} = -a'_{\gamma\alpha\beta} \quad , \tag{1.42}$$

$$\zeta_{\alpha\beta\gamma\delta} = b_{\delta\alpha\beta\gamma} \quad , \quad \zeta'_{\alpha\beta\gamma\delta} = -b'_{\delta\alpha\beta\gamma} \quad , \tag{1.43}$$

$$\xi_{\alpha\beta} = G_{\beta\alpha} \quad , \quad \xi'_{\alpha\beta} = -G'_{\beta\alpha} \quad , \tag{1.44}$$

$$\mathcal{H}_{\alpha\beta\gamma} = H_{\gamma\alpha\beta} \quad , \quad \mathcal{H}'_{\alpha\beta\gamma} = -H'_{\gamma\alpha\beta} \quad , \tag{1.45}$$

$$\mathscr{L}_{\alpha\beta\gamma} = L_{\beta\gamma\alpha} \quad , \quad \mathscr{L}'_{\alpha\beta\gamma} = -L'_{\beta\gamma\alpha} \quad . \tag{1.46}$$

The multipole moment densities in equations (1.36) to (1.40) are the average per unit macroscopic volume of the following moments of a charge distribution (Raab 1975):

$$p_\alpha = \sum_i q_i r_{i_\alpha} \quad , \tag{1.47}$$

$$q_{\alpha\beta} = \sum_i q_i r_{i_\alpha} r_{i_\beta} \quad , \tag{1.48}$$

$$q_{\alpha\beta\gamma} = \sum_i q_i r_{i_\alpha} r_{i_\beta} r_{i_\gamma} \quad , \tag{1.49}$$

$$m_\alpha = \sum_i \frac{q_i}{2m_i} l_{i_\alpha} \quad , \tag{1.50}$$

$$m_{\alpha\beta} = \sum_i \frac{q_i}{3m_i}\left(r_{i_\beta} l_{i_\alpha} + l_{i_\alpha} r_{i_\beta}\right) \quad , \tag{1.51}$$

in which $\boldsymbol{r}_i$ is the displacement from an arbitrary origin of charge $q_i$ with mass $m_i$ and orbital angular momentum $\boldsymbol{l}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i$, where $\boldsymbol{p}_i$ is its linear momentum.

## 1.4 AN EIGENVALUE WAVE EQUATION

It is convenient to express the electric field of a plane monochromatic wave in the form:

$$\boldsymbol{E} = \boldsymbol{E}_o e^{-i\omega(t - nr\cdot\sigma/c)} \ . \tag{1.52}$$

In this equation σ is the unit vector perpendicular to the plane wave front, and n is the refractive index of the medium for light propagating in the direction σ, with a polarization state described by the amplitude $\boldsymbol{E}_o$ which may be complex.

From Maxwell's equation (1.16) and equation (1.52), expressions can be derived in terms of $\boldsymbol{E}$ for the fields and their space and time derivatives in equations (1.36) to (1.40). The multipole moment densities in these equations are then substituted into equation (1.29) to obtain the following equation:

$$\left\{ n^2\sigma_\alpha\sigma_\beta - (n^2-1)\delta_{\alpha\beta} + \frac{1}{\epsilon_o}\tilde{\alpha}_{\alpha\beta} + \frac{n}{c\epsilon_o}\tilde{U}_{\alpha\beta} + \frac{n^2}{c^2\epsilon_o}\tilde{V}_{\alpha\beta} \right\} E_{o_\beta} = 0 \ . \tag{1.53}$$

This is the basic equation to the order of electric octopole and magnetic quadrupole for describing the propagation of a plane monochromatic wave in a source-free magnetic medium. In this equation the tensors denoted by a tilde have the form

$$\tilde{T}_{\alpha\beta} = T^s{}_{\alpha\beta} - iT^a{}_{\alpha\beta} \ . \tag{1.54}$$

The explicit expressions for the these different tensors are given below.

$$\alpha^{s}_{\alpha\beta} = \alpha_{\alpha\beta} = \alpha_{\beta\alpha} \ , \tag{1.55}$$

$$\alpha^{a}_{\alpha\beta} = \alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha} \ , \tag{1.56}$$

$$U^{s}_{\alpha\beta} = \sigma_{\gamma}\left\{-\epsilon_{\beta\gamma\delta}G_{\alpha\delta} - \epsilon_{\alpha\gamma\delta}G_{\beta\delta} + \frac{1}{2}\omega(a'_{\alpha\beta\gamma} + a'_{\beta\alpha\gamma})\right\} = U^{s}_{\beta\alpha} \ , \tag{1.57}$$

$$U^{a}_{\alpha\beta} = \sigma_{\gamma}\left\{-\epsilon_{\beta\gamma\delta}G'_{\alpha\delta} + \epsilon_{\alpha\gamma\delta}G'_{\beta\delta} - \frac{1}{2}\omega(a_{\alpha\beta\gamma} - a_{\beta\alpha\gamma})\right\} = -U^{a}_{\beta\alpha} \ , \tag{1.58}$$

$$V^{s}_{\alpha\beta} = \sigma_{\gamma}\sigma_{\delta}\left\{-\frac{1}{6}\omega^{2}(b_{\alpha\beta\gamma\delta} + b_{\beta\alpha\gamma\delta}) + \frac{1}{4}\omega^{2}d_{\alpha\gamma\beta\delta} - \frac{1}{2}\omega(\epsilon_{\alpha\gamma\epsilon}H'_{\beta\epsilon\delta} + \epsilon_{\beta\gamma\epsilon}H'_{\alpha\epsilon\delta}) \right.$$
$$\left. + \frac{1}{2}\omega(\epsilon_{\alpha\gamma\epsilon}L'_{\beta\delta\epsilon} + \epsilon_{\beta\gamma\epsilon}L'_{\alpha\delta\epsilon}) + \epsilon_{\alpha\gamma\epsilon}\epsilon_{\beta\delta\phi}X_{\epsilon\phi}\right\} = V^{s}_{\beta\alpha} \ , \tag{1.59}$$

$$V^{a}_{\alpha\beta} = \sigma_{\gamma}\sigma_{\delta}\left\{-\frac{1}{6}\omega^{2}(b'_{\alpha\beta\gamma\delta} - b'_{\beta\alpha\gamma\delta}) + \frac{1}{4}\omega^{2}d'_{\alpha\gamma\beta\delta} - \frac{1}{2}\omega(\epsilon_{\alpha\gamma\epsilon}H_{\beta\epsilon\delta} - \epsilon_{\beta\gamma\epsilon}H_{\alpha\epsilon\delta}) \right.$$
$$\left. + \frac{1}{2}\omega(\epsilon_{\alpha\gamma\epsilon}L_{\beta\delta\epsilon} - \epsilon_{\beta\gamma\epsilon}L_{\alpha\delta\epsilon}) + \epsilon_{\alpha\gamma\epsilon}\epsilon_{\beta\delta\phi}X'_{\epsilon\phi}\right\} = -V^{a}_{\beta\alpha} \ . \tag{1.60}$$

The respective symmetry and antisymmetry of the tensors indicated with superscripts *s* and *a* can be deduced from the tensor expressions derived in Chapter 3. By setting $\alpha$ in equation (1.53) equal to x, y, and z in turn, and summing over repeated subscripts, we obtain three linear homogeneous equations in the components of $\boldsymbol{E}_o$. These can be cast in the form of the following matrix eigenvalue equation:

$$\begin{bmatrix} n^2(1-\sigma_x^2)-\tilde{S}_{xx} & -n^2\sigma_x\sigma_y-\tilde{S}_{xy} & -n^2\sigma_x\sigma_z-\tilde{S}_{xz} \\ -n^2\sigma_x\sigma_y-\tilde{S}_{yx} & n^2(1-\sigma_y^2)-\tilde{S}_{yy} & -n^2\sigma_y\sigma_z-\tilde{S}_{yz} \\ -n^2\sigma_x\sigma_z-\tilde{S}_{zx} & -n^2\sigma_y\sigma_z-\tilde{S}_{zy} & n^2(1-\sigma_z^2)-\tilde{S}_{zz} \end{bmatrix} \begin{bmatrix} E_{o_x} \\ E_{o_y} \\ E_{o_z} \end{bmatrix} = \begin{bmatrix} E_{o_x} \\ E_{o_y} \\ E_{o_z} \end{bmatrix}, \qquad \textbf{(1.61)}$$

in which the eigenvalues are constrained to be unity, and where

$$\tilde{S}_{\alpha\beta} = \frac{1}{\epsilon_o}\tilde{\alpha}_{\alpha\beta} + \frac{n}{c\epsilon_o}\tilde{U}_{\alpha\beta} + \frac{n^2}{c^2\epsilon_o}\tilde{V}_{\alpha\beta} . \qquad \textbf{(1.62)}$$

For any given propagation direction $\sigma$ the medium supports only those polarization forms whose amplitudes are the eigenvectors of equation (1.61). Their associated refractive indices can be found from the condition that the eigenvalues are unity. Alternatively, the condition that not all of the components of $\boldsymbol{E}_o$ vanish is that the determinant of their coefficients should be zero, that is

$$\begin{vmatrix} n^2(\sigma_x^2-1)+1+\tilde{S}_{xx} & n^2\sigma_x\sigma_y+\tilde{S}_{xy} & n^2\sigma_x\sigma_z+\tilde{S}_{xz} \\ n^2\sigma_x\sigma_y+\tilde{S}_{yx} & n^2(\sigma_y^2-1)+1+\tilde{S}_{yy} & n^2\sigma_y\sigma_z+\tilde{S}_{yz} \\ n^2\sigma_x\sigma_z+\tilde{S}_{zx} & n^2\sigma_y\sigma_z+\tilde{S}_{zy} & n^2(\sigma_z^2-1)+1+\tilde{S}_{zz} \end{vmatrix} = 0 . \qquad \textbf{(1.63)}$$

This determinantal equation is used in Chapter 2 to obtain general expressions for the various optical effects that arise due to light propagation in magnetic crystals.

# CHAPTER 2

## 2.1 THE JONES CALCULUS

The state of polarization of a plane electromagnetic wave with its electric field transverse to the direction of propagation is fully described by its two orthogonal field components, say $E_x$ and $E_y$ for a wave propagating along the positive z axis. In the formulation of the calculus which bears his name Jones used a complex form of the field of such a wave and represented it by a 2x1 column vector

$$\boldsymbol{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} \quad . \tag{2.1}$$

Its elements are thus complex in general and through their real and imaginary parts **E** contains four pieces of information concerning the light beam. These are the amplitudes and phases of the two components which, as is known for a Lissajou figure, constitute one way of specifying an ellipse as the most general form of polarization.

Consider such a wave incident on a medium, which may change the polarization of the beam without depolarizing it. Let the incident beam in a given direction be described by the vector **E** and the emergent beam, assumed to be in the same direction, by the vector **E'**. Then for a linear response of the medium to the field of the incident light wave

$$E' = \mathrm{M}\, E\,, \tag{2.2}$$

where M represents the effect of the medium in transforming ***E*** into ***E'***. As ***E*** and ***E'*** are 2x1 column vectors, M must be a 2x2 matrix with four elements which are complex in general. Their real and imaginary parts thus represent in general eight distinct optical properties of the medium.

In 1941 Jones initially introduced the matrix representation of a medium to describe the effects on a polarized plane monochromatic light wave of a non-depolarizing crystal which could be birefringent, optically active, and absorbing. Only later (1948) did he extend his theory to a general dielectric medium in which all eight properties may be present together. The basis of Jones' approach was to assign each of the eight optical effects to a separate macroscopically very thin plate of medium, and then to integrate to produce the total effect. For the light wave propagating through a medium of length z with a field given by equation (1.52) Jones showed that the matrix M is given by

$$\mathrm{M} = exp(Tz)\begin{bmatrix} cosh(Qz)+\frac{1}{2}(\mathrm{N}_1-\mathrm{N}_2)Q^{-1}sinh(Qz) & \mathrm{N}_4Q^{-1}sinh(Qz) \\ \mathrm{N}_3Q^{-1}sinh(Qz) & cosh(Qz)-\frac{1}{2}(\mathrm{N}_1-\mathrm{N}_2)Q^{-1}sinh(Qz) \end{bmatrix}. \tag{2.3}$$

In this

$$T = i\tilde{\eta}\ , \quad Q^2 = -(\tilde{\omega}^2+\tilde{g}_o^{\,2}+\tilde{g}_{45}^{\,2})\ , \tag{2.4}$$

and $N_1$, $N_2$, $N_3$ and $N_4$ are the elements of a matrix N, which is determinate at each point along the path of the light beam in the medium. For a homogeneous dielectric

$$N = \begin{bmatrix} N_1 & N_4 \\ N_3 & N_2 \end{bmatrix} = \begin{bmatrix} i(\tilde{\eta}-\tilde{g}_o) & -\tilde{\omega}-i\tilde{g}_{45} \\ \tilde{\omega}-i\tilde{g}_{45} & i(\tilde{\eta}+\tilde{g}_o) \end{bmatrix} . \tag{2.5}$$

The quantities denoted with a tilde in equation (2.5) are complex and are given by:

$$\begin{aligned} \tilde{\eta} &= \eta + i\kappa \ , \\ \tilde{\omega} &= \omega + i\delta \ , \\ \tilde{g}_o &= g_o + ip_o \ , \\ \tilde{g}_{45} &= g_{45} + ip_{45} \ . \end{aligned} \tag{2.6}$$

The right-hand-sides of these equations consist of eight independent differential parameters. These parameters are related to the following optical properties of a medium:

refraction, which relates to the parameter denoted by $\eta$, and absorption, which is associated with $\kappa$; circular birefringence, associated with the parameter indicated by $\omega$, and circular dichroism, related to $\delta$; linear birefringence, which is related to $g_o$, and is relative to a pair of orthogonal axes, and the associated dichroism, which relates to the parameter $p_o$; and finally a linear birefringence, associated with the term $g_{45}$, with respect to the bisectors of the axes mentioned above, and the associated dichroism, related to the parameter $p_{45}$. In non-absorbing media these eight parameters reduce to four, namely: $\eta$, $\omega$, $g_o$, and $g_{45}$.

Jones defined the differential parameters given in equation (2.6) in terms of the relevant refractive indices and extinction coefficients for different polarization states of a light beam in the following way:

$$\tilde{\eta} = \frac{2\pi}{\lambda}(n + ik) = \frac{2\pi}{\lambda}\tilde{n} \quad , \tag{2.7}$$

$$\tilde{\omega} = \frac{\pi}{\lambda}[n_r - n_l + i(k_r - k_l)] = \frac{\pi}{\lambda}(\tilde{n}_r - \tilde{n}_l) \quad , \tag{2.8}$$

$$\tilde{g}_0 = \frac{\pi}{\lambda}[n_y - n_x + i(k_y - k_x)] = \frac{\pi}{\lambda}(\tilde{n}_y - \tilde{n}_x) \quad , \tag{2.9}$$

$$\tilde{g}_{45} = \frac{\pi}{\lambda}[n_- - n_+ + i(k_- - k_+)] = \frac{\pi}{\lambda}(\tilde{n}_- - \tilde{n}_+) \quad . \tag{2.10}$$

Here $\tilde{n}$ is the complex refractive index for randomly polarized light. It consists of the refractive index n and extinction coefficient k, where, for the choice of sign of the exponent in equation (1.52),

$$\tilde{n} = n + ik \quad . \tag{2.11}$$

The corresponding quantities for the polarization states are denoted by the following subscripts:

r and l for right- and left-circularly polarized light,

x and y for light linearly polarized along the x and y axes,

and + and - for light linearly polarized along the bisectors of the x and y axes and of the x and -y axes.

The Jones M-matrix in equation (2.3) has been used to suggest experiments by which the various optical properties in equations (2.7) to (2.10) may be measured, particularly when several coexist (Raab 1982, Graham and Raab 1994).

A light wave whose electric field is perpendicular to its propagation direction σ is termed an N-ray (Graham and Raab 1990). A wave which has an electric field component along its propagation path is called an S-ray (ibid.), and will not be considered in this research as the Jones calculus is not applicable to such rays.

If the light path is taken to be along a crystallographic axis, then the form of the determinant in equation (1.63) allows immediate identification of whether an N-ray exists. For example light propagating along the z-axis has σ=(0,0,1). An N-ray occurs when in equation (1.63)

$$\tilde{S}_{zx} = \tilde{S}_{zy} = 0 \quad , \tag{2.12}$$

from which, using equations (1.62) and (1.54) to (1.60), it follows that

$$\tilde{S}_{xz} = \tilde{S}_{yz} = 0 \quad . \tag{2.13}$$

Equation (1.63) thus reduces to the following general form:

$$\begin{vmatrix} -n^2+1+\tilde{S}_{xx} & \tilde{S}_{xy} \\ \tilde{S}_{yx} & -n^2+1+\tilde{S}_{yy} \end{vmatrix} = 0 \quad . \tag{2.14}$$

It can be seen from equations (1.55) to (1.60) that, for non-absorbing media, the tensor **S** has the Hermitian property:

$$\tilde{S}_{ij} = \tilde{S}^{*}_{ji} \quad . \tag{2.15}$$

This leads to the following general form, within the electric octopole-magnetic quadrupole approximation, for equation (2.14):

$$\begin{vmatrix} -n^2+1+\mathrm{a}+\mathrm{b}n+\mathrm{c}n^2 & \mathrm{d}+\mathrm{e}n+\mathrm{f}n^2+i(\mathrm{g}+\mathrm{h}n+\mathrm{j}n^2) \\ \mathrm{d}+\mathrm{e}n+\mathrm{f}n^2-i(\mathrm{g}+\mathrm{h}n+\mathrm{j}n^2) & -n^2+1+\mathrm{k}+\mathrm{l}n+\mathrm{m}n^2 \end{vmatrix} = 0 \quad . \tag{2.16}$$

It is evident from this and (1.53) to (1.60) that the terms indicated with small letters in this have the following multipole orders:

| | | |
|---|---|---|
| a, d, g, k | : | electric dipole |
| b, e, h, l | : | electric quadrupole-magnetic dipole |
| c, f, j, m | : | electric octopole-magnetic quadrupole |

In order to apply Jones' approach to determine the various optical effects experienced by the wave propagating through the crystal, we rewrite equation (2.16) as:

$$\begin{vmatrix} -n^2+1+A+B & C+iD \\ C-iD & -n^2+1+A-B \end{vmatrix} = 0 \ , \tag{2.17}$$

where

$$A = \tfrac{1}{2}(a+k) + \tfrac{1}{2}n(b+l) + \tfrac{1}{2}n^2(c+m) \ , \tag{2.18}$$

$$B = \tfrac{1}{2}(a-k) + \tfrac{1}{2}n(b-l) + \tfrac{1}{2}n^2(c-m) \ , \tag{2.19}$$

$$C = d + en + fn^2 \ , \tag{2.20}$$

$$D = g + hn + jn^2 \ . \tag{2.21}$$

To obtain the four distinct optical effects identified by Jones in non-absorbing media, we proceed by considering four optical plates independently. In the absence of absorption $A$, $B$, $C$, and $D$ are real quantities.

Plate 1: $A \neq 0$, $B = C = D = 0$.

Equation (2.17) then becomes:

$$\begin{vmatrix} -n^2+1+A & 0 \\ 0 & -n^2+1+A \end{vmatrix} = 0 \ . \tag{2.22}$$

This equation has two equal roots, given by

$$\begin{aligned} n^2 &= 1 + A \\ &= 1 + \tfrac{1}{2}(a+k) + \tfrac{1}{2}n(b+l) + \tfrac{1}{2}n^2(c+m) \ , \end{aligned} \tag{2.23}$$

which reduce to the correct vacuum limit of $n=1$ when $A=0$.

Hence

$$n = \tfrac{1}{2}\left[\, Y + \left(Y^2+4(1-Z)(1+X)\right)^{\frac{1}{2}} \,\right]\left[\, 1-Z \,\right]^{-1} \ , \tag{2.24}$$

where

$$X = \tfrac{1}{2}(a+k) \ , \tag{2.25}$$

$$Y = \tfrac{1}{2}(b+l) \ , \tag{2.26}$$

$$Z = \tfrac{1}{2}(c+m) \ . \tag{2.27}$$

Since $Z$ contains terms to the order of electric octopole and magnetic quadrupole, it is clear that

$$Z \ll 1 \ . \tag{2.28}$$

We therefore use the binomial expansion

$$(1+x)^{\alpha} = 1 + \frac{\alpha}{1!}x + \frac{\alpha(\alpha-1)}{2!}x^2 + \ldots + \frac{\alpha(\alpha-1)\ldots(\alpha-n+1)}{n!}x^n + \ldots \quad \mathit{for}\ -1<x<1 \ , \tag{2.29}$$

which leads to

$$(1-Z)^{-1} = 1 + Z - \frac{Z^2}{2} + \dots$$
$$\approx 1 + Z \ , \tag{2.30}$$

since the higher order terms are negligibly small. Equation (2.24) then becomes

$$n = \tfrac{1}{2}\left[\, Y + \left(Y^2 + 4(1-Z)(1+X)\right)^{\frac{1}{2}} \right] \left[1 + Z\right] . \tag{2.31}$$

To first order in the multipole terms *X, Y,* and *Z,* this reduces to

$$n = \tfrac{1}{2} Y + (1+X)^{\frac{1}{2}} + \tfrac{1}{2} Z (1+X)^{\frac{1}{2}} \ . \tag{2.32}$$

The two polarization eigenvectors corresponding to the two equal roots in equation (2.23) are orthogonal linear polarizations along the crystallographic x- and y-axes. Thus all polarization forms experience the same refraction along the chosen light path. This is the first optical effect described by Jones.

<u>Plate 2</u>: $B \neq 0$ , $A = C = D = 0.$

Equation (2.17) becomes:

$$\begin{vmatrix} -n^2 + 1 + B & 0 \\ 0 & -n^2 + 1 - B \end{vmatrix} = 0 \ . \tag{2.33}$$

The solutions of this are given by

$$n_x^2 = 1 + B$$
$$= 1 + \tfrac{1}{2}(a-k) + \tfrac{1}{2}n_x(b-l) + \tfrac{1}{2}n_x^2(c-m) \quad , \tag{2.34}$$

and

$$n_y^2 = 1 - B$$
$$= 1 - \tfrac{1}{2}(a-k) - \tfrac{1}{2}n_y(b-l) - \tfrac{1}{2}n_y^2(c-m) \quad . \tag{2.35}$$

The two eigenvectors are again orthogonal linear polarizations along the x and y crystallographic axes, but now with different refractive indices, so that a linear birefringence is evident. To first order in the multipole terms this is calculated to be:

$$n_x - n_y = (1+X)^{\frac{1}{2}} - (1-X)^{\frac{1}{2}} + Y + \tfrac{1}{2}Z\left[(1+X)^{\frac{1}{2}} + (1-X)^{\frac{1}{2}}\right] \quad , \tag{2.36}$$

where

$$X = \tfrac{1}{2}(a-k) \quad , \tag{2.37}$$

$$Y = \tfrac{1}{2}(b-l) \quad , \tag{2.38}$$

$$Z = \tfrac{1}{2}(c-m) \quad . \tag{2.39}$$

When a≠k, for instance for propagation perpendicular to an optic axis in a uniaxial crystal, then (a-k) is the leading multipole contribution and the higher order terms may be neglected. This is the second of Jones' optical effects.

Plate 3: $C \neq 0$ , $A = B = D = 0$.

Equation (2.17) reduces to:

$$\begin{vmatrix} -n^2+1 & C \\ C & -n^2+1 \end{vmatrix} = 0 \quad . \qquad \textbf{(2.40)}$$

The two solutions of this equation are:

$$n^2 = 1 \pm C \quad . \qquad \textbf{(2.41)}$$

From this we obtain the following two values for the refractive indices:

$$n_+ = (1+d)^{\frac{1}{2}} + \frac{1}{2}e + \frac{1}{2}f(1+d)^{\frac{1}{2}} \quad , \qquad \textbf{(2.42)}$$

and

$$n_- = (1-d)^{\frac{1}{2}} - \frac{1}{2}e - \frac{1}{2}f(1-d)^{\frac{1}{2}} \quad . \qquad \textbf{(2.43)}$$

Substituting these roots into the two equations on which the two rows of equation (2.40) are based yields

$$\frac{E_{0_y}}{E_{0_x}} = \pm 1 \quad . \tag{2.44}$$

The two eigenvectors thus represent linear vibrations along the bisectors of the two crystallographic axes that are perpendicular to the direction of propagation. To first order in the multipole terms equations (2.42) and (2.43) lead to the following birefringence

$$n_- - n_+ = (1-d)^{\frac{1}{2}} - (1+d)^{\frac{1}{2}} - e - \tfrac{1}{2}f\left[(1+d)^{\frac{1}{2}} + (1-d)^{\frac{1}{2}}\right] \quad . \tag{2.45}$$

This linear birefringence was first identified by Jones, and has been named after him (Graham and Raab 1983).

Plate 4: $D \neq 0$ , $A = B = C = 0$.

The general equation (2.17) becomes:

$$\begin{vmatrix} -n^2+1 & iD \\ -iD & -n^2+1 \end{vmatrix} = 0 \quad . \tag{2.46}$$

This has two possible solutions:

$$n^2 = 1 \pm D \quad . \tag{2.47}$$

Substitution of these roots into the two equations represented by the determinant in equation (2.46) yields

$$\frac{E_{0_y}}{E_{0_x}} = \mp i \ . \qquad \textbf{(2.48)}$$

These describe right- and left-circularly polarized light, corresponding to the upper and lower signs respectively. Solving equation (2.47) to first order in the multipole terms then leads to the circular birefringence

$$n_r - n_l = (1+\mathrm{g})^{\frac{1}{2}} - (1-\mathrm{g})^{\frac{1}{2}} + \mathrm{h} + \frac{1}{2}\mathrm{j}\left[(1+\mathrm{g})^{\frac{1}{2}} + (1-\mathrm{g})^{\frac{1}{2}}\right] \ . \qquad \textbf{(2.49)}$$

In this $n_r$ and $n_l$ are the refractive indices for right and left circularly polarized light respectively. It is evident from (2.49) that circular birefringence may arise from the electric dipole term g which is a term in $\alpha'$, as (1.53) to (1.56) show. This contribution occurs in ferromagnetic crystals (Graham and Raab 1991). The next higher multipole term is that in h, which is of electric quadrupole-magnetic dipole order, followed by that in j.

In this dissertation the above approach will be used to identify the different optical properties of each of the uniaxial and cubic magnetic point groups. Examples of the application of this method will be illustrated in Chapter 5.

# CHAPTER 3

## 3.1 QUANTUM MECHANICAL EXPRESSIONS FOR POLARIZABILITY TENSORS

Quantitative expressions for polarizability tensors allow one to deduce the intrinsic symmetry of their tensor subscripts, as well as any relationships that may exist between various of the tensors. In addition, one can deduce from such an expression the order of magnitude of a tensor.

These quantitative expressions for the tensors used in this thesis are derived from quantum mechanics by means of first-order perturbation theory, in which the electromagnetic perturbation Hamiltonian is expressed in the Barron-Gray gauge (Barron and Gray 1973, Raab 1975).

The forms of the multipole moment densities induced in a magnetic medium by a plane monochromatic wave were obtained phenomenologically in Chapter 1, for instance that for the electric dipole moment density:

$$\begin{aligned} P_\alpha = {} & P_\alpha^{(0)} + \alpha_{\alpha\beta}E_\beta + \frac{1}{\omega}\alpha'_{\alpha\beta}\dot{E}_\beta + \frac{1}{2}a_{\alpha\beta\gamma}\nabla_\gamma E_\beta + \frac{1}{2\omega}a'_{\alpha\beta\gamma}\nabla_\gamma \dot{E}_\beta \\ & + \frac{1}{6}b_{\alpha\beta\gamma\delta}\nabla_\delta\nabla_\gamma E_\beta + \frac{1}{6\omega}b'_{\alpha\beta\gamma\delta}\nabla_\delta\nabla_\gamma \dot{E}_\beta + \ldots \\ & + G_{\alpha\beta}B_\beta + \frac{1}{\omega}G'_{\alpha\beta}\dot{B}_\beta + \frac{1}{2}H_{\alpha\beta\gamma}\nabla_\gamma B_\beta + \frac{1}{2\omega}H'_{\alpha\beta\gamma}\nabla_\gamma \dot{B}_\beta + \ldots \quad . \end{aligned} \qquad (3.1)$$

We now show how such expressions can be formally derived by means of quantum mechanics.

The quantum mechanical expectation value of the induced electric dipole moment density, represented by the operator

$$\boldsymbol{P} = \frac{\sum q\,r}{\Delta V} \ , \qquad \textbf{(3.2)}$$

in a time-dependent state $|n(t)\rangle$ is, to first order in the perturbation due to the electromagnetic wave,

$$\begin{aligned} \langle n(t)|P_\alpha|n(t)\rangle &= \langle n^{(0)}(t) + n^{(1)}(t) + \ldots|P_\alpha|n^{(0)}(t) + n^{(1)}(t) + \ldots\rangle \\ &= \langle P_\alpha^{(0)}\rangle + \langle n^{(0)}(t)|P_\alpha|n^{(1)}(t)\rangle + \langle n^{(1)}(t)|P_\alpha|n^{(0)}(t)\rangle + \ldots \\ &= \langle P_\alpha^{(0)}\rangle + 2\Re e\langle n^{(0)}(t)|P_\alpha|n^{(1)}(t)\rangle + \ldots \ , \end{aligned} \qquad \textbf{(3.3)}$$

since $\boldsymbol{P}$ is Hermitian.

In equation (3.3) the ket $|n^{(0)}(t)\rangle$ is the solution of Schrödinger's time-dependent equation for the *n*th state of the unperturbed system described by the Hamiltonian $H^{(0)}$, namely

$$H^{(0)}|n^{(0)}(t)\rangle = i\hbar\frac{\partial}{\partial t}|n^{(0)}(t)\rangle \ . \qquad \textbf{(3.4)}$$

Because the unperturbed system is time-independent, Schrödinger's energy eigenvalue equation also applies. Thus

$$H^{(0)}|n^{(0)}(t)\rangle = E_n^{(0)}|n^{(0)}(t)\rangle \ , \qquad \textbf{(3.5)}$$

where $E_n^{(0)}$ is the energy eigenvalue of the *n*th unperturbed state of the system.

It follows from equations (3.4) and (3.5) that

$$|n^{(0)}(t)\rangle = e^{-iE_n^{(0)}t/\hbar}\,|n^{(0)}(0)\rangle \quad . \tag{3.6}$$

The ket $|n^{(1)}(t)\rangle$ in equation (3.3) is the first-order perturbation ket for the nth state. Any state of a system may be expressed as a linear combination of the eigenstates of a Hermitian operator on the vector space representing that system. Thus using the unperturbed kets of $H^{(0)}$ in equation (3.6), we may write

$$|n^{(1)}(t)\rangle = \sum_j a_j(t)\,|j^{(0)}(t)\rangle \quad . \tag{3.7}$$

It can be shown from time-dependent perturbation theory that

$$a_j(t) = -\frac{i}{\hbar}\int_0^t e^{-i\omega_{nj}t}\,H_{jn}^{(1)}\,dt \quad , j \neq n \quad , \tag{3.8}$$

where

$$H_{jn}^{(1)} = \langle j^{(0)}(0)|H^{(1)}|n^{(0)}(0)\rangle \tag{3.9}$$

and

$$\omega_{nj} = (E_n^{(0)} - E_j^{(0)})/\hbar \quad . \tag{3.10}$$

Equation (3.3) then becomes:

$$\langle n(t)|P_\alpha|n(t)\rangle = \langle P_\alpha^{(0)}\rangle + 2\Re e\sum_{j\neq n} a_j(t)e^{i\omega_{nj}t}\langle n^{(0)}(0)|P_\alpha|j^{(0)}(0)\rangle + \ldots \quad . \tag{3.11}$$

The semi-classical Hamiltonian for describing a system of particles in a macroscopic volume element ΔV in an electromagnetic field is

$$H = \sum \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + V + \sum q\phi \quad , \tag{3.12}$$

where V is the unperturbed potential energy operator and q the charge of a particle in ΔV with mass m and momentum operator **p**.

Barron and Gray (1973) showed that the following potentials **A** and $\phi$ at a point $\boldsymbol{r}$ at time t in a source-free region of space

$$A_\alpha(\boldsymbol{r},t) = \epsilon_{\alpha\beta\gamma}\left\{\tfrac{1}{2}[B_\beta(\boldsymbol{r},t)]_o r_\gamma + \tfrac{1}{3}[\nabla_\delta B_\beta(\boldsymbol{r},t)]_o r_\gamma r_\delta + \tfrac{1}{8}[\nabla_\epsilon \nabla_\delta B_\beta(\boldsymbol{r},t)]_o r_\gamma r_\delta r_\epsilon + \ldots\right\} , \tag{3.13}$$

and

$$\phi(\boldsymbol{r},t) = [\phi(\boldsymbol{r},t)]_o - [E_\alpha(\boldsymbol{r},t)]_o r_\alpha - \tfrac{1}{2}[\nabla_\beta E_\alpha(\boldsymbol{r},t)]_o r_\alpha r_\beta - \ldots \quad , \tag{3.14}$$

field the correct Taylor expansions of the electric and magnetic fields, as given by

$$\boldsymbol{E} = -\nabla\phi - \frac{\partial \boldsymbol{A}}{\partial t} \quad , \tag{3.15}$$

and

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} \quad , \tag{3.16}$$

where ***E*** and ***B*** are arbitrary time-dependent fields.

In equations (3.13) and (3.14) $[\,]_o$ signifies that the expression must be evaluated at the origin. The Hamiltonian in equation (3.12) can then be shown to have the form:

$$H = \sum \frac{1}{2m}p^2 + V + q[\Phi]_o - p_\alpha[E_\alpha]_o - \tfrac{1}{2}q_{\alpha\beta}[\nabla_\beta E_\alpha]_o - \tfrac{1}{6}q_{\alpha\beta\gamma}[\nabla_\gamma\nabla_\beta E_\alpha]_o - \dots$$
$$- m_\alpha[B_\alpha]_o - \tfrac{1}{2}m_{\alpha\beta}[\nabla_\beta B_\alpha]_o - \dots \, , \qquad \textbf{(3.17)}$$

where $p_\alpha$ , $q_{\alpha\beta}$ , $q_{\alpha\beta\gamma}$ ,$m_\alpha$ , and $m_{\alpha\beta}$ are the quantum mechanical multipole moment operators for the macroscopic volume element. These correspond to the classical multipole moments defined in equations (1.47) to (1.51).

Thus it follows from equation (3.17) that in the electric octopole - magnetic quadrupole approximation the first-order perturbation Hamiltonian is given by the expression (Raab 1975):

$$H^{(1)} = q[\Phi]_o - p_\alpha[E_\alpha]_o - \tfrac{1}{2}q_{\alpha\beta}[\nabla_\beta E_\alpha]_o - \tfrac{1}{6}q_{\alpha\beta\gamma}[\nabla_\gamma\nabla_\beta E_\alpha]_o$$
$$- m_\alpha[B_\alpha]_o - \tfrac{1}{2}m_{\alpha\beta}[\nabla_\beta B_\alpha]_o - \dots \, . \qquad \textbf{(3.18)}$$

It is the unique advantage of the Barron-Gray gauge that the first-order perturbation Hamiltonian appears in an explicit multipole form.

From equations (1.16) and (1.52) it is possible to express $\boldsymbol{B}$ in terms of $\boldsymbol{E}$ for a plane monochromatic wave. Thus in tensor form

$$B_\alpha = \frac{n}{c}\,\epsilon_{\alpha\beta\gamma}\sigma_\beta E_\gamma \; . \qquad \textbf{(3.19)}$$

It can be shown that

$$\int_0^t e^{-i\omega_{nj}t}[E_\alpha(\boldsymbol{r},t)]_o dt = E_\alpha^{(0)}\int_0^t e^{-i\omega_{nj}t}e^{-i\omega t}dt$$

$$= \frac{1}{i}\frac{e^{-i\omega_{nj}t}}{\omega^2-\omega_{nj}^2}\left\{\omega_{nj}e^{-i\omega t} - \omega e^{-i\omega t}\right\}E_\alpha^{(0)}$$

$$= \frac{1}{i}\frac{e^{-i\omega_{nj}t}}{\omega^2-\omega_{nj}^2}\left\{\omega_{nj}[E_\alpha(\boldsymbol{r},t)]_o - i[\dot{E}_\alpha(\boldsymbol{r},t)]_o\right\} . \tag{3.20}$$

This result together with equations (3.18) and (3.19) and the explicit form for $\boldsymbol{E}$ given in equation (1.52), when substituted into equation (3.8), yields:

$$a_j(t) = -\frac{i}{\hbar}\int_0^t e^{-i\omega_{nj}t}\Big[q_{jn}[\phi]_o - p_{\alpha_{jn}}[E_\alpha]_o - \tfrac{1}{2}q_{\alpha\beta_{jn}}[\nabla_\beta E_\alpha]_o - \tfrac{1}{6}q_{\alpha\beta\gamma_{jn}}[\nabla_\gamma\nabla_\beta E_\alpha]_o$$
$$- m_{\alpha_{jn}}[B_\alpha]_o - \tfrac{1}{2}m_{\alpha\beta_{jn}}[\nabla_\beta B_\alpha]_o - \ldots\Big]dt$$
$$= \frac{1}{\hbar}\frac{e^{-i\omega_{nj}t}}{\omega^2-\omega_{nj}^2}\Big[p_{\alpha_{jn}}(\omega_{nj}[E_\alpha]_o - i[\dot{E}_\alpha]_o) + \tfrac{1}{2}q_{\alpha\beta_{jn}}(\omega_{nj}[\nabla_\beta E_\alpha]_o - i[\nabla_\beta \dot{E}_\alpha]_o)$$
$$+ \tfrac{1}{6}q_{\alpha\beta\gamma_{jn}}(\omega_{nj}[\nabla_\gamma\nabla_\beta E_\alpha]_o - i[\nabla_\gamma\nabla_\beta \dot{E}_\alpha]_o) + m_{\alpha_{jn}}(\omega_{nj}[B_\alpha]_o - i[\dot{B}_\alpha]_o)$$
$$+ \tfrac{1}{2}m_{\alpha\beta_{jn}}(\omega_{nj}[\nabla_\beta B_\alpha]_o - i[\nabla_\beta \dot{B}_\alpha]_o) + \ldots\Big] . \tag{3.21}$$

In this $q_{jn}=0$ because $q$ is a constant and the distinct states $|j\rangle$ and $|n\rangle$ are orthogonal. From this equation and equation (3.11), and from the hermiticity of the multipole moment operators, it follows that

$$\langle n(t)|P_\alpha|n(t)\rangle = \langle P_\alpha^{(0)}\rangle + \sum_{j\neq n}\frac{2}{\hbar}\frac{1}{\omega^2-\omega_{nj}^2}\,\Re e\Big\{P_{\alpha_{nj}}\Big[p_{\beta_{jn}}(\omega_{nj}[E_\beta]_o - i[\dot{E}_\beta]_o)$$

$$+ \frac{1}{2}q_{\beta\gamma_{jn}}(\omega_{nj}[\nabla_\gamma E_\beta]_o - i[\nabla_\gamma \dot{E}_\beta]_o) + \frac{1}{6}q_{\beta\gamma\delta_{jn}}(\omega_{nj}[\nabla_\delta\nabla_\gamma E_\beta]_o - i[\nabla_\delta\nabla_\gamma \dot{E}_\beta]_o)$$

$$+ m_{\beta_{jn}}(\omega_{nj}[B_\beta]_o - i[\dot{B}_\beta]_o) + \frac{1}{2}m_{\beta\gamma_{jn}}(\omega_{nj}[\nabla_\gamma B_\beta]_o - i[\nabla_\gamma \dot{B}_\beta]_o) + \ldots\Big]\Big\}\,. \qquad \textbf{(3.22)}$$

Comparison of this quantum mechanical expansion with the classical expression given in equation (3.1) yields a quantum mechanical expression for each of the polarizability tensors for the macroscopic volume element ΔV. For instance, the polarizability $\alpha_{\alpha\beta}$ is given by:

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n} Z_{jn}\omega_{jn}\Re e\,\langle n|P_\alpha|j\rangle\langle j|p_\beta|n\rangle\ . \qquad \textbf{(3.23)}$$

Here $\omega_{jn}=-\omega_{nj}$ was used, together with

$$Z_{jn} = (\omega_{jn}^2 - \omega^2)^{-1}\ , \qquad \textbf{(3.24)}$$

which is a dispersion line shape function. Absorption has been neglected in this work in order to determine which birefringences would be manifest for different propagation directions as a consequence of the symmetry of non-absorbing crystals.

Since

$$\boldsymbol{P} = \frac{\boldsymbol{p}}{\Delta V}\ , \qquad \textbf{(3.25)}$$

equation (3.23) may be written as

$$\alpha_{\alpha\beta} = \frac{2}{\hbar} \Delta V \sum_{j \neq n} Z_{jn} \omega_{jn} \Re e \langle n | P_\alpha | j \rangle \langle j | P_\beta | n \rangle = \alpha_{\beta\alpha} \quad , \tag{3.26}$$

in which the hermiticity of **P** was used. Similarly, from the hermitian property of other multipole moment operators,

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega \Im m \langle n | P_\alpha | j \rangle \langle j | P_\beta | n \rangle = -\alpha'_{\beta\alpha} \quad , \tag{3.27}$$

$$a_{\alpha\beta\gamma} = \frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega_{jn} \Re e \langle n | P_\alpha | j \rangle \langle j | Q_{\beta\gamma} | n \rangle \quad , \tag{3.28}$$

$$a'_{\alpha\beta\gamma} = -\frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega \Im m \langle n | P_\alpha | j \rangle \langle j | Q_{\beta\gamma} | n \rangle \quad , \tag{3.29}$$

$$b_{\alpha\beta\gamma\delta} = \frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega_{jn} \Re e \langle n | P_\alpha | j \rangle \langle j | Q_{\beta\gamma\delta} | n \rangle \quad , \tag{3.30}$$

$$b'_{\alpha\beta\gamma\delta} = -\frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega \Im m \langle n | P_\alpha | j \rangle \langle j | Q_{\beta\gamma\delta} | n \rangle \quad , \tag{3.31}$$

$$G_{\alpha\beta} = \frac{2}{\hbar} \Delta V \sum_{j} Z_{jn} \omega_{jn} \Re e \langle n | P_\alpha | j \rangle \langle j | M_\beta | n \rangle \quad , \tag{3.32}$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\, \Im m\langle n|P_\alpha|j\rangle\langle j|M_\beta|n\rangle \quad , \tag{3.33}$$

$$H_{\alpha\beta\gamma} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|P_\alpha|j\rangle\langle j|M_{\beta\gamma}|n\rangle \quad , \tag{3.34}$$

$$H'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\, \Im m\langle n|P_\alpha|j\rangle\langle j|M_{\beta\gamma}|n\rangle \quad . \tag{3.35}$$

In a similar way the quantum mechanical expressions can be obtained for the polarizability tensors in the definitions of $Q_{\alpha\beta}$, $Q_{\alpha\beta\gamma}$, $M_\alpha$, and $M_{\alpha\beta}$ in equations (1.37) to (1.40). They can be shown to have the following forms:

$$\rho_{\alpha\beta\gamma} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|Q_{\alpha\beta}|j\rangle\langle j|P_\gamma|n\rangle = a_{\gamma\alpha\beta} \quad , \tag{3.36}$$

$$\rho'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\, \Im m\langle n|Q_{\alpha\beta}|j\rangle\langle j|P_\gamma|n\rangle = -a'_{\gamma\alpha\beta} \quad , \tag{3.37}$$

$$\zeta_{\alpha\beta\gamma\delta} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|Q_{\alpha\beta\gamma}|j\rangle\langle j|P_\delta|n\rangle = b_{\delta\alpha\beta\gamma} \quad , \tag{3.38}$$

$$\zeta'_{\alpha\beta\gamma\delta} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\, \Im m\langle n|Q_{\alpha\beta\gamma}|j\rangle\langle j|P_\delta|n\rangle = -b'_{\delta\alpha\beta\gamma} \quad , \tag{3.39}$$

$$d_{\alpha\beta\gamma\delta} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|Q_{\alpha\beta}|j\rangle\langle j|Q_{\gamma\delta}|n\rangle = d_{\gamma\delta\alpha\beta} \quad , \tag{3.40}$$

$$d'_{\alpha\beta\gamma\delta} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega \Im m\langle n|Q_{\alpha\beta}|j\rangle\langle j|Q_{\gamma\delta}|n\rangle = -d'_{\gamma\delta\alpha\beta} \quad , \tag{3.41}$$

$$\xi_{\alpha\beta} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|M_{\alpha}|j\rangle\langle j|P_{\beta}|n\rangle = G_{\beta\alpha} \quad , \tag{3.42}$$

$$\xi'_{\alpha\beta} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega \Im m\langle n|M_{\alpha}|j\rangle\langle j|P_{\beta}|n\rangle = -G'_{\beta\alpha} \quad , \tag{3.43}$$

$$\begin{aligned} \chi_{\alpha\beta} = {} & \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|M_{\alpha}|j\rangle\langle j|M_{\beta}|n\rangle \\ & + \sum \left(\frac{q^2}{4m}\right)\langle n|r_{\alpha}r_{\beta} - r^2\delta_{\alpha\beta}|n\rangle \quad = \chi_{\beta\alpha} \quad , \end{aligned} \tag{3.44}$$

$$\chi'_{\alpha\beta} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega \Im m\langle n|M_{\alpha}|j\rangle\langle j|M_{\beta}|n\rangle = -\chi'_{\beta\alpha} \quad , \tag{3.45}$$

$$\mathcal{H}_{\alpha\beta\gamma} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn} \Re e\langle n|M_{\alpha\beta}|j\rangle\langle j|P_{\gamma}|n\rangle = H_{\gamma\alpha\beta} \quad , \tag{3.46}$$

$$\mathcal{H}'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\,\Im m\langle n|M_{\alpha\beta}|j\rangle\langle j|P_\gamma|n\rangle = -H'_{\gamma\alpha\beta} \quad , \tag{3.47}$$

$$L_{\alpha\beta\gamma} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn}\Re e\langle n|Q_{\alpha\beta}|j\rangle\langle j|M_\gamma|n\rangle \quad , \tag{3.48}$$

$$L'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\,\Im m\langle n|Q_{\alpha\beta}|j\rangle\langle j|M_\gamma|n\rangle \quad , \tag{3.49}$$

$$\mathcal{L}_{\alpha\beta\gamma} = \frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega_{jn}\Re e\langle n|M_\alpha|j\rangle\langle j|Q_{\beta\gamma}|n\rangle = L_{\beta\gamma\alpha} \quad , \tag{3.50}$$

$$\mathcal{L}'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\Delta V \sum_j Z_{jn}\omega\,\Im m\langle n|M_\alpha|j\rangle\langle j|Q_{\beta\gamma}|n\rangle = -L'_{\beta\gamma\alpha} \quad . \tag{3.51}$$

The full permutation symmetry which exists in the subscripts of the electric quadrupole and octopole moment operators can be used to show the intrinsic symmetry of the polarizability tensors containing matrix elements of these two moments. The expressions given above also allow one to deduce any relationships which may exist between tensors, and where relevant these are included in the expressions.

In summary, the following expressions indicate the symmetry which exists in the tensor subscripts:

$$\alpha_{\alpha\beta} = \alpha_{\beta\alpha}, \quad \alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}, \quad a_{\alpha\beta\gamma} = a_{\alpha\gamma\beta}, \quad a'_{\alpha\beta\gamma} = a'_{\alpha\gamma\beta},$$
$$b_{\alpha\beta\gamma\delta} = b_{\alpha\beta\delta\gamma} = b_{\alpha\delta\beta\gamma} = b_{\alpha\gamma\beta\delta}, \quad b'_{\alpha\beta\gamma\delta} = b'_{\alpha\beta\delta\gamma} = b'_{\alpha\delta\beta\gamma} = b'_{\alpha\gamma\beta\delta},$$
$$d_{\alpha\beta\gamma\delta} = d_{\gamma\delta\alpha\beta} = d_{\delta\gamma\alpha\beta} = d_{\gamma\delta\beta\alpha}, \quad d'_{\alpha\beta\gamma\delta} = -d'_{\gamma\delta\alpha\beta} = -d'_{\delta\gamma\alpha\beta} = -d'_{\gamma\delta\beta\alpha},$$
$$\chi_{\alpha\beta} = \chi_{\beta\alpha}, \quad \chi'_{\alpha\beta} = -\chi'_{\beta\alpha}, \quad L_{\alpha\beta\gamma} = L_{\beta\alpha\gamma}, \quad L'_{\alpha\beta\gamma} = -L'_{\beta\alpha\gamma}. \tag{3.52}$$

## 3.2 ORIGIN INDEPENDENCE OF MULTIPOLE MOMENT OPERATORS

Van Vleck (1932) derived a quantum mechanical expression for the static magnetic susceptibility of a molecule, which, in addition to matrix elements of the magnetic dipole moment operator, contained matrix elements involving the displacement **r** of a charge from an arbitrary origin in the molecule. He showed this expression to be independent of the choice of origin. This origin independence is an essential property of an expression for a physical observable which is itself independent of origin.

The change in each multipole moment operator can be calculated for a displacement **R** of the origin to which these multipole moments are referred. These changes are readily obtained from the operator versions of the classical multipole moments in (1.47) to (1.51).

For instance, if ***P'*** is the electric dipole moment density referred to origin O', displaced by ***R*** from origin O to which ***P*** is referred, then the origin shift in ***P*** is

$$\Delta P_\alpha = P'_\alpha - P_\alpha = \left( \sum q r'_\alpha - \sum q r_\alpha \right)(\Delta v)^{-1}$$

$$= \left[ \sum q(r_\alpha - R_\alpha) - \sum q r_\alpha \right] (\Delta v)^{-1}$$

$$= -R_\alpha (\Delta v)^{-1} \sum q \quad . \qquad \textbf{(3.53)}$$

Similarly

$$\Delta Q_{\alpha\beta} = -R_\alpha P_\beta - R_\beta P_\alpha + R_\alpha R_\beta (\Delta v)^{-1} \sum q \quad , \qquad \textbf{(3.54)}$$

$$\Delta Q_{\alpha\beta\gamma} = -R_\alpha Q_{\beta\gamma} - R_\beta Q_{\alpha\gamma} - R_\gamma Q_{\alpha\beta} + R_\alpha R_\beta P_\gamma + R_\alpha R_\gamma P_\beta + R_\beta R_\gamma P_\alpha - R_\alpha R_\beta R_\gamma (\Delta v)^{-1} \sum q \quad , \qquad \textbf{(3.55)}$$

$$\Delta M_\alpha = -\epsilon_{\alpha\beta\gamma} R_\beta (\Delta v)^{-1} \sum (q/2m) p_\gamma \quad , \qquad \textbf{(3.56)}$$

$$\Delta M_{\alpha\beta} = -2R_\beta M_\alpha + \tfrac{2}{3}\delta_{\alpha\beta} R_\gamma M_\gamma - \epsilon_{\alpha\gamma\delta} R_\gamma (\Delta v)^{-1} \sum (q/3m)(r_\beta p_\delta + r_\delta p_\beta)$$
$$+ \epsilon_{\alpha\gamma\delta} R_\beta R_\gamma (\Delta v)^{-1} \sum (2q/3m) p_\delta - i\hbar \epsilon_{\alpha\beta\gamma} R_\gamma (\Delta v)^{-1} \sum (q/3m) \quad . \qquad \textbf{(3.57)}$$

From these origin shifts, together with the expressions given in equations (3.26) to (3.51), the change in each polarizability tensor can be calculated for the displacement ***R*** of origin. From the expression in equation (3.26) the origin shift in $\alpha_{\alpha\beta}$ is calculated as follows:

$$\Delta\alpha_{\alpha\beta} = \frac{2}{\hbar}\Delta V \sum_{j\neq n} Z_{jn}\omega_{jn}\Re e\left\{<n|P_\alpha+\Delta P_\alpha|j><j|P_\beta+\Delta P_\beta|n> - <n|P_\alpha|j><j|P_\beta|n>\right\}$$

$$= \frac{2}{\hbar}\Delta V \sum_{j\neq n} Z_{jn}\omega_{jn}\Re e\left\{<n|P_\alpha|j><j|P_\beta|n> + <n|\Delta P_\alpha|j><j|P_\beta|n> + <n|P_\alpha|j><j|\Delta P_\beta|n> - <n|P_\alpha|j><j|P_\beta|n>\right\}$$

$$= 0 \quad , \qquad \textbf{(3.58)}$$

since from equation (3.53) the term

$$<n|\Delta P_\alpha|j><j|\Delta P_\beta|n> \qquad \textbf{(3.59)}$$

is of second order in **R** and can thus be neglected, while

$$<n|j> = <j|n> = 0 \qquad \textbf{(3.60)}$$

due to orthogonality.

In a similar way the origin shifts of the remaining tensors can be calculated. These are:

$$\Delta\alpha'_{\alpha\beta} = 0 \quad , \qquad \textbf{(3.61)}$$

$$\Delta a_{\alpha\beta\gamma} = -R_\gamma\alpha_{\alpha\beta} - R_\beta\alpha_{\alpha\gamma} \quad , \qquad \textbf{(3.62)}$$

$$\Delta a'_{\alpha\beta\gamma} = -R_\gamma \alpha'_{\alpha\beta} - R_\beta \alpha'_{\alpha\gamma} \quad , \tag{3.63}$$

$$\Delta G_{\alpha\beta} = -\frac{1}{2}\omega\, \epsilon_{\beta\gamma\delta} R_\gamma \alpha'_{\alpha\delta} \quad , \tag{3.64}$$

$$\Delta G'_{\alpha\beta} = \frac{1}{2}\omega\, \epsilon_{\beta\gamma\delta} R_\gamma \alpha_{\alpha\delta} \quad , \tag{3.65}$$

$$\Delta b_{\alpha\beta\gamma\delta} = -R_\delta a_{\alpha\beta\gamma} - R_\gamma a_{\alpha\beta\delta} - R_\beta a_{\alpha\gamma\delta} + R_\gamma R_\delta \alpha_{\alpha\beta} + R_\beta R_\gamma \alpha_{\alpha\delta} + R_\beta R_\delta \alpha_{\alpha\gamma} \, , \tag{3.66}$$

$$\Delta b'_{\alpha\beta\gamma\delta} = -R_\delta a'_{\alpha\beta\gamma} - R_\gamma a'_{\alpha\beta\delta} - R_\beta a'_{\alpha\gamma\delta} + R_\gamma R_\delta \alpha'_{\alpha\beta} + R_\beta R_\gamma \alpha'_{\alpha\delta} + R_\beta R_\delta \alpha'_{\alpha\gamma} \, , \tag{3.67}$$

$$\begin{aligned} \Delta d_{\alpha\beta\gamma\delta} = {} & -R_\alpha a_{\beta\gamma\delta} - R_\beta a_{\alpha\gamma\delta} - R_\gamma a_{\delta\alpha\beta} - R_\delta a_{\gamma\alpha\beta} \\ & + R_\alpha R_\gamma \alpha_{\beta\delta} + R_\alpha R_\delta \alpha_{\beta\gamma} + R_\beta R_\gamma \alpha_{\alpha\delta} + R_\beta R_\delta \alpha_{\alpha\gamma} \quad , \end{aligned} \tag{3.68}$$

$$\begin{aligned} \Delta d'_{\alpha\beta\gamma\delta} = {} & -R_\alpha a'_{\beta\gamma\delta} - R_\beta a'_{\alpha\gamma\delta} + R_\gamma a'_{\delta\alpha\beta} + R_\delta a'_{\gamma\alpha\beta} \\ & + R_\alpha R_\gamma \alpha'_{\beta\delta} + R_\alpha R_\delta \alpha'_{\beta\gamma} + R_\beta R_\gamma \alpha'_{\alpha\delta} + R_\beta R_\delta \alpha'_{\alpha\gamma} \quad , \end{aligned} \tag{3.69}$$

$$\Delta\chi_{\alpha\beta} = \frac{1}{2}\omega(\epsilon_{\alpha\gamma\delta}R_\gamma G'_{\delta\beta} + \epsilon_{\beta\gamma\delta}R_\gamma G'_{\delta\alpha}) + \frac{1}{4}\omega^2\epsilon_{\alpha\gamma\delta}\epsilon_{\beta\epsilon\phi}R_\gamma R_\epsilon \alpha_{\delta\phi} \quad , \tag{3.70}$$

$$\Delta\chi'_{\alpha\beta} = -\frac{1}{2}\omega(\epsilon_{\alpha\gamma\delta}R_\gamma G_{\delta\beta} - \epsilon_{\beta\gamma\delta}R_\gamma G_{\delta\alpha}) + \frac{1}{4}\omega^2\epsilon_{\alpha\gamma\delta}\epsilon_{\beta\epsilon\phi}R_\gamma R_\epsilon \alpha'_{\delta\phi} \quad , \tag{3.71}$$

$$\Delta H_{\alpha\beta\gamma} = -2R_\gamma G_{\alpha\beta} + \frac{2}{3}\delta_{\beta\gamma}R_\delta G_{\alpha\delta} - \frac{1}{3}\omega\epsilon_{\beta\delta\epsilon}R_\delta a'_{\alpha\gamma\epsilon} + \frac{2}{3}\omega\epsilon_{\beta\delta\epsilon}R_\gamma R_\delta \alpha'_{\alpha\epsilon} \quad , \tag{3.72}$$

$$\Delta H'_{\alpha\beta\gamma} = -2R_\gamma G'_{\alpha\beta} + \frac{2}{3}\delta_{\beta\gamma}R_\delta G'_{\alpha\delta} + \frac{1}{3}\omega\epsilon_{\beta\delta\epsilon}R_\delta a_{\alpha\gamma\epsilon} - \frac{2}{3}\omega\epsilon_{\beta\delta\epsilon}R_\gamma R_\delta \alpha_{\alpha\epsilon} \quad , \tag{3.73}$$

$$\Delta L_{\alpha\beta\gamma} = -R_\alpha G_{\beta\gamma} - R_\beta G_{\alpha\gamma} + \frac{1}{2}\omega\epsilon_{\gamma\delta\epsilon}R_\delta(R_\alpha \alpha'_{\beta\epsilon} + R_\beta \alpha'_{\alpha\epsilon} + a'_{\epsilon\alpha\beta}) \quad , \tag{3.74}$$

$$\Delta L'_{\alpha\beta\gamma} = -R_\alpha G'_{\beta\gamma} - R_\beta G'_{\alpha\gamma} - \frac{1}{2}\omega\epsilon_{\gamma\delta\epsilon}R_\delta(R_\alpha \alpha_{\beta\epsilon} + R_\beta \alpha_{\alpha\epsilon} - a_{\epsilon\alpha\beta}) \quad . \tag{3.75}$$

By means of the relationships

$$\epsilon_{\alpha\beta\gamma}\epsilon_{\gamma\delta\epsilon} = \delta_{\alpha\delta}\delta_{\beta\epsilon} - \delta_{\alpha\epsilon}\delta_{\beta\delta} \tag{3.76}$$

and

$$\delta_{\alpha\beta}A_{\beta\gamma\delta...} = A_{\alpha\gamma\delta...} \quad , \qquad \textbf{(3.77)}$$

where $A_{\alpha\gamma\delta...}$ represents any tensor, it can be shown from the above origin shifts that the expressions for the terms of different multipole order in the propagation equation, namely equations (1.55) to (1.60), are independent of origin. Origin independence, as a form of translational invariance, is a necessary requirement for a physical observable. Thus the expressions for the refractive indices and birefringences derived from the wave equation satisfy this requirement.

# CHAPTER 4

## 4.1 SYMMETRY CLASSIFICATION OF THE POLARIZABILITY TENSORS

Neumann's principle states that every physical property of a system must possess at least the full symmetry of the system, but may possess higher symmetry (Birss 1964). In this chapter we illustrate how Birss' tables of tensor components for all crystal point group symmetries can be used to determine which crystal symmetries may exhibit the various birefringences which were identified in Chapter 2.

Under space inversion polar vectors undergo a change of sign. Axial vectors, however, remain invariant under this operation. These are specific instances of the general transformation rules for polar and axial tensors by which these tensors are defined. Thus a polar tensor $T_{\alpha\beta\gamma...}$ transforms under both proper and improper rotation of axes according to

$$T_{\alpha\beta\gamma...} = T_{ijk...}\ a_i^{\alpha}\ a_j^{\beta}\ a_k^{\gamma}\ ...\ , \tag{4.1}$$

where $a_i^{\alpha}$ is the direction cosine of the angle between the i-axis of one set of cartesian axes and the $\alpha$-axis of another, both of these sets of axes possessing a common origin. A space transformation which changes right-handed coordinate axes into left-handed axes, and vice versa, is an improper transformation. A proper transformation leaves the handedness of a set of axes unchanged. For an axial tensor:

$$T_{\alpha\beta\gamma\ldots} = \pm T_{ijk\ldots}\ a_i^{\alpha}\ a_j^{\beta}\ a_k^{\gamma}\ \ldots \quad . \qquad \textbf{(4.2)}$$

Here the positive and negative signs apply to proper and improper transformations respectively.

Jackson (1975) compiled a table in which were listed various polar and axial mechanical and electromagnetic quantities. In this table the electric field vector ***E*** is shown to be polar, and the magnetic field vector ***B*** axial.

The effect of time-reversal allows property tensors to be divided into two types: tensors whose components remain ***i***nvariant under time-reversal are called ***i***-tensors, and those whose components **c**hange sign are called ***c***-tensors (Birss 1964).

By inspection of equations (1.36) to (1.40), the various property tensors may be classified as follows:

**TABLE 4.1**: Classification of the polarizability tensors

| Relative multipole order | *i*-tensors | | *c*-tensors | |
|---|---|---|---|---|
| | polar | axial | polar | axial |
| electric dipole | $\alpha_{\alpha\beta}$ | | $\alpha'_{\alpha\beta}$ | |
| electric quadrupole<br>magnetic dipole | $a_{\alpha\beta\gamma}$ | $G'_{\alpha\beta}$ | $a'_{\alpha\beta\gamma}$ | $G_{\alpha\beta}$ |
| electric octopole<br>magnetic quadrupole | $b_{\alpha\beta\gamma\delta}$,<br>$d_{\alpha\beta\gamma\delta}$,$X_{\alpha\beta}$ | $H'_{\alpha\beta\gamma}$,$L'_{\alpha\beta\gamma}$ | $b'_{\alpha\beta\gamma\delta}$,<br>$d'_{\alpha\beta\gamma\delta}$,$X'_{\alpha\beta}$ | $H_{\alpha\beta\gamma}$,$L_{\alpha\beta\gamma}$ |

The polarizability tensors contributing to each of the quantities a, b, c, ... in equation (2.16) can be identified with reference to equations (1.62) and (1.63). The various contributions to these quantities are indicated in the table below:

**TABLE 4.2**: Quantities in equation (2.16) and their associated property tensors

| Quantity | Associated Property Tensors |
|---|---|
| a, k, d | $\alpha_{\alpha\beta}$ |
| g | $\alpha'_{\alpha\beta}$ |
| b, e, l | $a'_{\alpha\beta\gamma}$, $G_{\alpha\beta}$ |
| h | $a_{\alpha\beta\gamma}$, $G'_{\alpha\beta}$ |
| c, f, m | $b_{\alpha\beta\gamma\delta}$, $d_{\alpha\beta\gamma\delta}$, $\chi_{\alpha\beta}$, $H'_{\alpha\beta\gamma}$, $L'_{\alpha\beta\gamma}$ |
| j | $b'_{\alpha\beta\gamma\delta}$, $d'_{\alpha\beta\gamma\delta}$, $\chi'_{\alpha\beta}$, $H_{\alpha\beta\gamma}$, $L_{\alpha\beta\gamma}$ |

## 4.2 CALCULATION OF TENSOR COMPONENTS FOR SELECTED POINT GROUPS

The quantum mechanical expressions for the polarizability tensors given in Chapter 3 allow one to deduce any intrinsic symmetry of each of these tensors. This intrinsic symmetry can be used together with the tensor symmetry properties for the specific point group under consideration, which are given in the tables of Birss (1963), to derive the non-vanishing independent components of each tensor within this point group. Examples of this procedure are detailed below for certain members of the hexagonal and cubic classes.

### 4.2.1 Hexagonal Point Group - 6<u>22</u>

The non-vanishing tensor components for this point group are shown below, together with any relationships between them due to their point group symmetry, as determined from Birss' tables, and/or any intrinsic symmetry, as derived in Chapter 3.

$$\alpha_{xx} = \alpha_{yy} \quad , \alpha_{zz} \quad ; \tag{4.3}$$

$$\alpha'_{xy} = -\alpha'_{yx} \quad ; \tag{4.4}$$

$$a_{xyz} = -a_{yxz} = a_{xzy} = -a_{yzx} \quad ; \tag{4.5}$$

$$a'_{zzz} \quad , a'_{xxz} = a'_{yyz} = a'_{xzx} = a'_{yzy} \; , a'_{zxx} = a'_{zyy} \quad ; \tag{4.6}$$

$$G'_{xx} = G'_{yy} \quad , G'_{zz} \quad ; \tag{4.7}$$

$$G_{xy} = -G_{yx} \quad ; \tag{4.8}$$

$$L'_{xzy} = -L'_{yzx} = L'_{zxy} = -L'_{zyx} \quad ; \tag{4.9}$$

$$L_{zzz} \quad , \; L_{xxz} = L_{yyz} \; , \; L_{xzx} = L_{yzy} = L_{zxx} = L_{zyy} \quad ; \tag{4.10}$$

$$H'_{xyz} = -H'_{yxz} \quad , \; H'_{xzy} = -H'_{yzx} \quad , \; H'_{zxy} = -H'_{zyx} \quad ; \tag{4.11}$$

$$H_{zzz} \quad , \; H_{xxz} = H_{yyz} \quad , \; H_{xzx} = H_{yzy} = H_{zxx} = H_{zyy} \quad ; \tag{4.12}$$

$$\begin{gathered} b_{xxxx} = b_{yyyy} = 3\,b_{xxyy} \quad , \; b_{zzzz} \quad , \\ b_{xxyy} = b_{yyxx} = b_{xyyx} = b_{yxxy} = b_{xyxy} = b_{yxyx} \quad , \\ b_{xxzz} = b_{yyzz} = b_{xzzx} = b_{yzzy} = b_{xzxz} = b_{yzyz} \quad , \\ b_{zzxx} = b_{zzyy} = b_{zxxz} = b_{zyyz} = b_{zxzx} = b_{zyzy} \quad ; \end{gathered} \tag{4.13}$$

$$\begin{gathered} b'_{xzyz} = -b'_{yzxz} = b'_{xyzz} = -b'_{yxzz} = b'_{xzzy} = -b'_{yzzx} \quad , \\ b'_{yxxx} = -3b'_{xyxx} = -3b'_{xxyx} = -3b'_{xxxy} = \\ = -b'_{xyyy} = 3b'_{yxyy} = 3b'_{yyxy} = 3b'_{yyyx} \quad ; \end{gathered} \tag{4.14}$$

$$d_{xxxx} = d_{yyyy} = d_{xxyy} + 2d_{xyxy} \quad , \; d_{zzzz} \quad ,$$
$$d_{xxyy} = d_{yyxx} \quad , \; d_{xyyx} = d_{yxxy} = d_{xyxy} = d_{yxyx} \quad , \tag{4.15}$$
$$d_{xxzz} = d_{yyzz} = d_{zzxx} = d_{zzyy} \quad ,$$
$$d_{xzzx} = d_{yzzy} = d_{xzxz} = d_{yzyz} = d_{zxxz} = d_{zyyz} = d_{zxzx} = d_{zyzy} \quad ;$$

$$d'_{zxzy} = -d'_{zyzx} = d'_{zxyz} = -d'_{zyxz} = d'_{xzyz} = -d'_{yzxz} = d'_{xzzy} = -d'_{yzzx} \quad ,$$
$$d'_{xxxy} = d'_{xxyx} = -d'_{xyxx} = -d'_{yxxx} = \tag{4.16}$$
$$= d'_{xyyy} = d'_{yxyy} = -d'_{yyxy} = -d'_{yyyx} \quad ;$$

$$\mathrm{X}_{xx} = \mathrm{X}_{yy} \quad , \; \mathrm{X}_{zz} \quad ; \tag{4.17}$$

$$\mathrm{X}'_{xy} = -\mathrm{X}'_{yx} \quad . \tag{4.18}$$

By means of the above results it is possible to calculate the components of the tensors that appear in equation (1.62). Using equation (1.57) and the symmetry relationships given in equations (4.6) and (4.8) above we find that

$$U^{s}_{xx} = \sigma_z \left\{ 2G_{xy} + \omega a'_{xxz} \right\} \quad , \tag{4.19}$$

$$U^{s}_{xy} = 0 = U^{s}_{yx} \quad , \tag{4.20}$$

$$U^{s}_{xz} = \sigma_x \left\{ -G_{xy} + \frac{1}{2}\omega(a^{'}_{xxz} + a^{'}_{zxx}) \right\} = U^{s}_{zx} \quad , \tag{4.21}$$

$$U^{s}_{yy} = \sigma_z \left\{ 2G_{xy} + \omega a^{'}_{xxz} \right\} \quad , \tag{4.22}$$

$$U^{s}_{yz} = \sigma_y \left\{ -G_{xy} + \frac{1}{2}\omega(a^{'}_{xxz} + a^{'}_{zxx}) \right\} = U^{s}_{zy} \quad , \tag{4.23}$$

$$U^{s}_{zz} = \sigma_z \left\{ \omega a^{'}_{zzz} \right\} \quad . \tag{4.24}$$

From equation (1.58) and the relationships in equations (4.5) and (4.7) we obtain:

$$U^{a}_{xx} = 0 \quad , \tag{4.25}$$

$$U^{a}_{xy} = \sigma_z \left\{ -2G^{'}_{xx} - \omega a_{xyz} \right\} = -U^{a}_{yx} \quad , \tag{4.26}$$

$$U^{a}_{xz} = \sigma_y \left\{ G'_{xx} + G'_{zz} - \frac{1}{2}\omega a_{xyz} \right\} = -U^{a}_{zx} \quad , \tag{4.27}$$

$$U^{a}_{yy} = 0 \quad , \tag{4.28}$$

$$U^{a}_{yz} = \sigma_x \left\{ -G'_{xx} - G'_{zz} + \frac{1}{2}\omega a_{xyz} \right\} = -U^{a}_{zy} \quad , \tag{4.29}$$

$$U^{a}_{zz} = 0 \quad . \tag{4.30}$$

The symmetry relationships given in equations (4.9), (4.11), (4.13), (4.15), and (4.17) together with equation (1.59) yield the following:

$$\begin{aligned} V^{s}_{xx} = {} & \sigma_x^{2}\left\{ -\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 (d_{xxyy} + 2d_{xyxy}) \right\} + \\ & \sigma_y^{2}\left\{ -\frac{1}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 d_{xxyy} - \omega H'_{xzy} + X_{zz} \right\} + \\ & \sigma_z^{2}\left\{ -\frac{1}{3}\omega^2 b_{xxzz} + \frac{1}{4}\omega^2 d_{xzxz} + \omega (H'_{xyz} - L'_{xzy}) + X_{xx} \right\} \quad , \end{aligned} \tag{4.31}$$

$$V^{s}_{xy} = \sigma_x \sigma_y \left\{ -\frac{2}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 (d_{xxyy} + d_{xyxy}) + \omega H'_{xzy} - X_{zz} \right\} = V^{s}_{yx} \quad , \tag{4.32}$$

$$V^s_{xz} = \sigma_x\sigma_z\left\{ -\frac{1}{3}\omega^2(b_{xxzz}+b_{zzxx}) + \frac{1}{4}\omega^2(d_{xxzz}+d_{xzxz}) - \frac{1}{2}\omega(H'_{xyz}+H'_{zxy}) - \chi_{xx}\right\} = V^s_{zx} \quad \textbf{(4.33)}$$

$$\begin{aligned} V^s_{yy} = {} & \sigma_x^2\left\{ -\frac{1}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 d_{xxyy} - \omega H'_{xzy} + \chi_{zz}\right\} + \\ & \sigma_y^2\left\{ -\omega^2 b_{xxyy} + \frac{1}{4}\omega^2(d_{xxyy}+2d_{xyxy})\right\} + \\ & \sigma_z^2\left\{ -\frac{1}{3}\omega^2 b_{xxzz} + \frac{1}{4}\omega^2 d_{xzxz} + \omega(H'_{xyz} - L'_{xzy}) + \chi_{xx}\right\} \ , \end{aligned} \quad \textbf{(4.34)}$$

$$V^s_{yz} = \sigma_y\sigma_z\left\{ -\frac{1}{3}\omega^2(b_{xxzz}+b_{zzxx}) + \frac{1}{4}\omega^2(d_{xxzz}+d_{xzxz}) - \frac{1}{2}\omega(H'_{xyz}+H'_{zxy}) - \chi_{xx}\right\} = V^s_{zy} \quad \textbf{(4.35)}$$

$$\begin{aligned} V^s_{zz} = {} & (\sigma_x^2+\sigma_y^2)\left\{ -\frac{1}{3}\omega^2 b_{zzxx} + \frac{1}{4}\omega^2 d_{xzxz} + \omega(H'_{zxy} + L'_{zxy}) + \chi_{xx}\right\} + \\ & \sigma_z^2\left\{ -\frac{1}{3}\omega^2 b_{zzzz} + \frac{1}{4}\omega^2 d_{zzzz}\right\} \ . \end{aligned} \quad \textbf{(4.36)}$$

Equation (1.60) and the relationships in equations (4.10), (4.12),(4.14), (4.16), and (4.18) give rise to the following tensor components:

$$V^a_{xx} = V^a_{yy} = V^a_{zz} = 0 \ , \quad \textbf{(4.37)}$$

$$V^a_{xy} = (\sigma_x^2+\sigma_y^2)\left\{-\frac{2}{3}\omega^2 b'_{xxxy}+\frac{1}{4}\omega^2 d'_{xxxy}-\frac{1}{2}\omega\,(H_{xzx}-L_{xxz})\right\} +$$
$$\sigma_z^2\left\{-\frac{1}{3}\omega^2 b'_{xyzz}+\frac{1}{4}\omega^2 d'_{xzyz}+\omega\,(H_{xxz}-L_{xzx})+\chi'_{xy}\right\} = -V^a_{yx} \quad , \qquad \textbf{(4.38)}$$

$$V^a_{xz} = \sigma_y\sigma_z\left\{-\frac{1}{3}\omega^2 b'_{xyzz}+\frac{1}{4}\omega^2 d'_{xzyz}-\frac{1}{2}\omega\,(H_{zzz}+H_{xxz}-H_{zxx}-L_{zzz})-\chi'_{xy}\right\} = -V^a_{zx} \ , \qquad \textbf{(4.39)}$$

$$V^a_{yz} = -\sigma_x\sigma_z\left\{-\frac{1}{3}\omega^2 b'_{xyzz}+\frac{1}{4}\omega^2 d'_{xzyz}-\frac{1}{2}\omega\,(H_{zzz}+H_{xxz}-H_{zxx}-L_{zzz})-\chi'_{xy}\right\} = -V^a_{zy} \ . \qquad \textbf{(4.40)}$$

### 4.2.2 Cubic Point Group - 432

The following non-vanishing components exist for the different property tensor components for this point group, with any relationships between them also shown:

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz} \quad ; \qquad \textbf{(4.41)}$$

$$a'_{xyz} = a'_{xzy} = a'_{zxy} = a'_{yxz} = a'_{yzx} = a'_{zyx} \quad ; \qquad \textbf{(4.42)}$$

$$G'_{xx} = G'_{yy} = G'_{zz} \quad ; \tag{4.43}$$

$$L_{xyz} = L_{xzy} = L_{zxy} = L_{yxz} = L_{yzx} = L_{zyx} \quad ; \tag{4.44}$$

$$H'_{xyz} = H'_{zxy} = H'_{yzx} = -H'_{xzy} = -H'_{yxz} = -H'_{zyx} \quad ; \tag{4.45}$$

$$H_{xyz} = H_{xzy} = H_{zxy} = H_{yxz} = H_{yzx} = H_{zyx} \quad ; \tag{4.46}$$

$$\begin{aligned} & b_{xxxx} = b_{yyyy} = b_{zzzz} \quad , \\ & b_{xxyy} = b_{yyxx} = b_{xyyx} = b_{yxxy} = b_{xyxy} = b_{yxyx} = \\ & = b_{xxzz} = b_{yyzz} = b_{xzzx} = b_{yzzy} = b_{xzxz} = b_{yzyz} = \\ & = b_{zzxx} = b_{zzyy} = b_{zxxz} = b_{zyyz} = b_{zxzx} = b_{zyzy} \quad ; \end{aligned} \tag{4.47}$$

$$\begin{aligned} & b'_{xxyy} = -b'_{yyxx} = b'_{xyyx} = -b'_{yxxy} = b'_{xyxy} = -b'_{yxyx} = \\ & = -b'_{xxzz} = b'_{yyzz} = -b'_{xzzx} = b'_{yzzy} = -b'_{xzxz} = b'_{yzyz} = \\ & = b'_{zzxx} = -b'_{zzyy} = b'_{zxxz} = -b'_{zyyz} = b'_{zxzx} = -b'_{zyzy} \quad ; \end{aligned} \tag{4.48}$$

$$d_{xxxx} = d_{yyyy} = d_{zzzz} \quad ,$$
$$d_{xxyy} = d_{yyxx} = d_{xxzz} = d_{yyzz} = d_{zzxx} = d_{zzyy} \quad ,$$
$$d_{xyyx} = d_{yxxy} = d_{xyxy} = d_{yxyx} = d_{xzzx} = d_{yzzy} =$$
$$= d_{xzxz} = d_{yzyz} = d_{zxxz} = d_{zyyz} = d_{zxzx} = d_{zyzy} \quad ; \qquad \textbf{(4.49)}$$

$$d'_{xxyy} = -d'_{yyxx} = -d'_{xxzz} = d'_{zzxx} = d'_{yyzz} = -d'_{zzyy} \quad ; \qquad \textbf{(4.50)}$$

$$X_{xx} = X_{yy} = X_{zz} \quad . \qquad \textbf{(4.51)}$$

In a similar way to that used for the hexagonal point group 6<u>22</u> the components of the tensors that appear in equation (1.62) can be calculated for this cubic point group. These are:

$$U^{s}_{xx} = 0 \quad , \qquad \textbf{(4.52)}$$

$$U^{s}_{xy} = \sigma_z\left\{\omega a'_{xyz}\right\} = U^{s}_{yx} \quad , \qquad \textbf{(4.53)}$$

$$U^{s}_{xz} = \sigma_y \left\{ \omega a'_{xyz} \right\} = U^{s}_{zx} \quad , \tag{4.54}$$

$$U^{s}_{yy} = 0 \quad , \tag{4.55}$$

$$U^{s}_{yz} = \sigma_x \left\{ \omega a'_{xyz} \right\} = U^{s}_{zy} \quad , \tag{4.56}$$

$$U^{s}_{zz} = 0 \quad , \tag{4.57}$$

$$U^{a}_{xx} = 0 \quad , \tag{4.58}$$

$$U^{a}_{xy} = \sigma_z \left\{ -2G'_{xx} \right\} = -U^{a}_{yx} \quad , \tag{4.59}$$

$$U^{a}_{xz} = -\sigma_y \left\{ -2G'_{xx} \right\} = -U^{a}_{zx} \quad , \tag{4.60}$$

$$U^{a}_{yy} = 0 \quad , \tag{4.61}$$

$$U^{a}_{yz} = \sigma_x \left\{ -2G'_{xx} \right\} = -U^{a}_{zy} \quad , \tag{4.62}$$

$$U^{a}_{zz} = 0 \quad , \tag{4.63}$$

$$\begin{aligned} V^{s}_{xx} = {} & \sigma_x^{\,2} \left\{ -\frac{1}{3}\omega^2 b_{xxxx} + \frac{1}{4}\omega^2 d_{xxxx} \right\} + \\ & (\sigma_y^{\,2} + \sigma_z^{\,2}) \left\{ -\frac{1}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 d_{xyxy} + \omega H'_{xyz} + \chi_{xx} \right\} \quad , \end{aligned} \tag{4.64}$$

$$V^{s}_{xy} = \sigma_x \sigma_y \left\{ -\frac{2}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 (d_{xxyy} + d_{xyxy}) - \omega H'_{xyz} - \chi_{xx} \right\} = V^{s}_{yx} \quad , \tag{4.65}$$

$$V^{s}_{xz} = \sigma_x \sigma_z \left\{ -\frac{2}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 (d_{xxyy} + d_{xyxy}) - \omega H'_{xyz} - \chi_{xx} \right\} = V^{s}_{zx} \quad , \tag{4.66}$$

$$\begin{aligned} V^{s}_{yy} = {} & \sigma_y^{\,2} \left\{ -\frac{1}{3}\omega^2 b_{xxxx} + \frac{1}{4}\omega^2 d_{xxxx} \right\} + \\ & (\sigma_x^{\,2} + \sigma_z^{\,2}) \left\{ -\frac{1}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 d_{xyxy} + \omega H'_{xyz} + \chi_{xx} \right\} \quad , \end{aligned} \tag{4.67}$$

$$V^{s}_{yz} = \sigma_y\sigma_z\left\{ -\frac{2}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 (d_{xxyy} + d_{xyxy}) - \omega H'_{xyz} - \chi_{xx} \right\} = V^{s}_{zy} \quad , \tag{4.68}$$

$$\begin{aligned} V^{s}_{zz} = {} & \sigma_z^{\,2}\left\{ -\frac{1}{3}\omega^2 b_{xxxx} + \frac{1}{4}\omega^2 d_{xxxx} \right\} + \\ & (\sigma_x^{\,2} + \sigma_y^{\,2})\left\{ -\frac{1}{3}\omega^2 b_{xxyy} + \frac{1}{4}\omega^2 d_{xyxy} + \omega H'_{xyz} + \chi_{xx} \right\} \quad , \end{aligned} \tag{4.69}$$

$$V^{a}_{xx} = 0 \quad , \tag{4.70}$$

$$V^{a}_{xy} = \sigma_x\sigma_y\left\{ -\frac{2}{3}\omega^2 b'_{xxyy} + \frac{1}{4}\omega^2 d'_{xxyy} - \omega(H_{xyz} - L_{xyz}) \right\} = -V^{a}_{yx} \quad , \tag{4.71}$$

$$V^{a}_{xz} = -\sigma_x\sigma_z\left\{ -\frac{2}{3}\omega^2 b'_{xxyy} + \frac{1}{4}\omega^2 d'_{xxyy} - \omega(H_{xyz} - L_{xyz}) \right\} = -V^{a}_{zx} \quad , \tag{4.72}$$

$$V^{a}_{yy} = 0 \quad , \tag{4.73}$$

$$V^{a}_{yz} = \sigma_y\sigma_z\left\{ -\frac{2}{3}\omega^2 b'_{xxyy} + \frac{1}{4}\omega^2 d'_{xxyy} - \omega(H_{xyz} - L_{xyz}) \right\} = -V^{a}_{zy} \quad , \tag{4.74}$$

$$V^{a}_{zz} = 0 \quad . \tag{4.75}$$

Once it has been ascertained in each of these point groups whether N-rays exist, which is the case if equations (2.12) and (2.13) are satisfied, then the above expressions for the tensor components can be used to calculate the quantities in equation (2.16) and hence the relevant birefringences that, in principle, should be observable in each magnetic crystal point group of the cubic and uniaxial classes.

# CHAPTER 5

## 5.1 RESULTS

The procedure outlined in Chapter 4 has been followed for each of the magnetic point groups of the cubic and uniaxial classes. The non-vanishing components of the tensors in equations (1.57) to (1.60) so obtained are listed in Tables 5.1 to 5.4. These components are found from those appearing in Birss' tables for all non-magnetic and magnetic crystal point groups, relative to crystallographic axes with origin at the centre of symmetry. These axes serve as principal axes for the polarizability tensor $\alpha_{\alpha\beta}$ for all cubic and uniaxial crystals, for which for the cubic symmetries $\alpha_{xx}=\alpha_{yy}=\alpha_{zz}$ whereas for the uniaxials $\alpha_{xx}=\alpha_{yy}\neq\alpha_{zz}$.

### 5.1.1 The Cubic Point Groups

All components of the magnetic tensors $\alpha'_{\alpha\beta}$ and $U^{s}_{ii}$ vanish for the cubic point groups. The components of the remaining tensors are listed in Table 5.1 on the following pages.

**TABLE 5.1**: The components of $U_{\alpha\beta}$ and $V_{\alpha\beta}$ relative to crystallographic axes for cubic point groups.

| Cubic Class | $U^s_{xy}$ | $U^s_{yz}$ | $U^s_{zx}$ |
|---|---|---|---|
| $23, \underline{m}3, \underline{4}3\underline{2}, \bar{4}3m, \underline{m}3m$ | $\sigma_z C_4$ | $\sigma_x C_4$ | $\sigma_y C_4$ |
| $m3, 432, \underline{\bar{4}}3\underline{m}, m3m, m3\underline{m}, \underline{m}3\underline{m}$ | 0 | 0 | 0 |

| Cubic Class | $U^a_{xy}$ | $U^a_{yz}$ | $U^a_{zx}$ |
|---|---|---|---|
| $23, 432, \underline{4}3\underline{2}$ | $-\sigma_z K_1$ | $-\sigma_x K_1$ | $-\sigma_y K_1$ |
| $m3, \underline{m}3, \bar{4}3m, \underline{\bar{4}}3\underline{m}, m3m,$ $m3\underline{m}, \underline{m}3\underline{m}, \underline{m}3m$ | 0 | 0 | 0 |

| Cubic Class | $V^a_{xy}$ | $V^a_{yz}$ | $V^a_{zx}$ |
|---|---|---|---|
| 23,m3 | $\sigma_x\sigma_y K_2$ | $\sigma_y\sigma_z K_2$ | $\sigma_x\sigma_z K_2$ |
| $\underline{4}3\underline{2},\underline{\bar{4}}3\underline{m},m3\underline{m}$ | $\sigma_x\sigma_y K_3$ | $\sigma_y\sigma_z K_3$ | $\sigma_x\sigma_z K_3$ |
| $\underline{m}3,432,\bar{4}3m,m3m,\underline{m}3\underline{m},\underline{m}3m$ | 0 | 0 | 0 |

| Cubic Class | $V^s_{xx}$ | $V^s_{yy}$ | $V^s_{zz}$ |
|---|---|---|---|
| $23,m3,\underline{m}3$ | $\sigma_x^2C_1+\sigma_y^2C_2+\sigma_z^2C_3$ | $\sigma_x^2C_3+\sigma_y^2C_1+\sigma_z^2C_2$ | $\sigma_x^2C_2+\sigma_y^2C_3+\sigma_z^2C_1$ |
| $432,\underline{4}3\underline{2},\bar{4}3m,$ $\underline{\bar{4}}3\underline{m},m3m,m3\underline{m},$ $\underline{m}3\underline{m},\underline{m}3m$ | $\sigma_x^2C_1+(\sigma_y^2+\sigma_z^2)C_6$ | $(\sigma_x^2+\sigma_z^2)C_6+\sigma_y^2C_1$ | $(\sigma_x^2+\sigma_y^2)C_6+\sigma_z^2C_1$ |

| Cubic Class | $V^s_{xy}$ | $V^s_{yz}$ | $V^s_{zx}$ |
|---|---|---|---|
| $23, m3, \underline{m}3$ | $\sigma_x\sigma_y C_5$ | $\sigma_y\sigma_z C_5$ | $\sigma_x\sigma_z C_5$ |
| $432, \underline{4}3\underline{2}, \bar{4}3m, \underline{\bar{4}}3\underline{m}, m3m,$ $m3\underline{m}, \underline{m}3\underline{m}, \underline{m}3m$ | $\sigma_x\sigma_y C_7$ | $\sigma_y\sigma_z C_7$ | $\sigma_x\sigma_z C_7$ |

$C_1=-\tfrac{1}{3}\omega^2 b_{xxxx}+\tfrac{1}{4}\omega^2 d_{xxxx}$ $\quad$ $C_2=-\tfrac{1}{3}\omega^2 b_{xxyy}+\tfrac{1}{4}\omega^2 d_{xyxy}-\omega(H'_{xzy}-L'_{xyz})+\chi_{xx}$

$C_3=-\tfrac{1}{3}\omega^2 b_{yyxx}+\tfrac{1}{4}\omega^2 d_{xyxy}+\omega(H'_{xyz}-L'_{xyz})+\chi_{xx}$ $\quad$ $C_4=\omega a'_{xyz}$

$C_5=-\tfrac{1}{3}\omega^2(b_{xxyy}+b_{yyxx})+\tfrac{1}{4}\omega^2(d_{xxyy}+d_{xyxy})-\tfrac{1}{2}\omega(H'_{xyz}-H'_{xzy})-\chi_{xx}$

$C_6=-\tfrac{1}{3}\omega^2 b_{xxyy}+\tfrac{1}{4}\omega^2 d_{xyxy}+\omega H'_{xyz}+\chi_{xx}$ $\quad$ $C_7=-\tfrac{2}{3}\omega^2 b_{xxyy}+\tfrac{1}{4}\omega^2(d_{xxyy}+d_{xyxy})-\omega H'_{xyz}-\chi_{xx}$

$K_1=2G'_{xx}$ $\quad$ $K_2=-\tfrac{1}{3}\omega^2(b'_{xxyy}-b'_{yyxx})+\tfrac{1}{4}\omega^2 d'_{xxyy}-\tfrac{1}{2}\omega(H_{xzy}+H_{xyz}-2L_{xyz})$

$K_3=-\tfrac{2}{3}\omega^2 b'_{xxyy}+\tfrac{1}{4}\omega^2 d'_{xxyy}-\omega(H_{xyz}-L_{xyz})$

### 5.1.2 The Hexagonal Point Groups

Only for certain classes of the hexagonal system does the time-odd tensor $\alpha'_{\alpha\beta}=-\alpha'_{\beta\alpha}$ exist, namely $6$, $\bar{6}$, $6/m$, $6\underline{22}$, $6\underline{mm}$, $\bar{6}\underline{m2}$, and $6/m\underline{mm}$, and then only the components $\alpha'_{xy}=-\alpha'_{yx}$.

**TABLE 5.2**: The components of $U_{\alpha\beta}$ and $V_{\alpha\beta}$ relative to crystallographic axes for hexagonal point groups.

| Hexagonal Class | $U^s_{xx}$ | $U^s_{yy}$ | $U^s_{zz}$ |
|---|---|---|---|
| $6,\underline{\bar{6}},6/\underline{m}$ | $\sigma_z C_1$ | $\sigma_z C_1$ | $\sigma_z C_{12}$ |
| $\underline{6},\bar{6},\underline{6}/m$ | $\sigma_x C_{15}+\sigma_y C_{14}$ | $-\sigma_x C_{15}-\sigma_y C_{14}$ | 0 |
| $6/m,\underline{6}/\underline{m},6/mmm,\underline{6}/\underline{m}m\underline{m},$ $6/m\underline{mm},622,6\underline{mm},\underline{\bar{6}m}2,$ $6/\underline{mmm}$ | 0 | 0 | 0 |
| $\underline{6}2\underline{2},\underline{6}m\underline{m},\bar{6}m2,\bar{6}\underline{m2},\underline{6}/mm\underline{m}$ | $\sigma_x C_{15}$ | $-\sigma_x C_{15}$ | 0 |
| $6\underline{22},6mm,\underline{\bar{6}}m\underline{2},6/\underline{m}mm$ | $\sigma_z C_1$ | $\sigma_z C_1$ | $\sigma_z C_{12}$ |

| Hexagonal Class | $U^s_{xy}$ | $U^s_{yz}$ | $U^s_{zx}$ |
|---|---|---|---|
| $6,\underline{\bar{6}},6/\underline{m}$ | 0 | $-\sigma_x C_8+\sigma_y C_7$ | $\sigma_x C_7+\sigma_y C_8$ |
| $\underline{6},\bar{6},\underline{6}/m$ | $\sigma_x C_{14}-\sigma_y C_{15}$ | 0 | 0 |
| $6/m,\underline{6}/\underline{m},6/mmm,\underline{6}/\underline{m}m\underline{m},6/m\underline{mm}$ | 0 | 0 | 0 |
| $622,6\underline{mm},\underline{\bar{6}m}2,6/\underline{mmm}$ | 0 | $-\sigma_x C_8$ | $\sigma_y C_8$ |
| $\underline{6}2\underline{2},\underline{6}m\underline{m},\bar{6}m2,\bar{6}\underline{m2},\underline{6}/mm\underline{m}$ | $-\sigma_y C_{15}$ | 0 | 0 |
| $6\underline{22},6mm,\underline{\bar{6}}m\underline{2},6/\underline{m}mm$ | 0 | $\sigma_y C_7$ | $\sigma_x C_7$ |

| Hexagonal Class | $U^a_{xy}$ | $U^a_{yz}$ | $U^a_{zx}$ |
|---|---|---|---|
| $6,\underline{6}$ | $\sigma_z K_1$ | $-\sigma_x K_5+\sigma_y K_4$ | $-\sigma_x K_4-\sigma_y K_5$ |
| $622,\underline{6}2\underline{2},6\underline{22}$ | $\sigma_z K_1$ | $-\sigma_x K_5$ | $-\sigma_y K_5$ |
| $6mm,\underline{6}m\underline{m},6\underline{mm}$ | 0 | $\sigma_y K_4$ | $-\sigma_x K_4$ |
| $\bar{6},\underline{\bar{6}},6/m,\underline{6}/\underline{m},6/\underline{m},\underline{6}/m,\bar{6}m2,\underline{\bar{6}m}2,\underline{\bar{6}}m\underline{2},$ $\bar{6}\underline{m2},6/mmm,\underline{6}/\underline{m}m\underline{m},$ $6/m\underline{mm},6/\underline{mmm},6/\underline{m}mm,\underline{6}/mm\underline{m}$ | 0 | 0 | 0 |

| Hexagonal Class | $V^s_{xx}$ | $V^s_{yy}$ | $V^s_{zz}$ |
|---|---|---|---|
| $6,\underline{6},\bar{6},\underline{\bar{6}},6/m,\underline{6}/\underline{m},6/\underline{m},\underline{6}/m$ | $\sigma_x^2C_2+\sigma_x\sigma_yC_3+\sigma_y^2C_4+\sigma_z^2C_5$ | $\sigma_x^2C_4-\sigma_x\sigma_yC_3+\sigma_y^2C_2+\sigma_z^2C_5$ | $(\sigma_x^2+\sigma_y^2)C_{13}+\sigma_z^2C_{11}$ |
| $622,\underline{6}2\underline{2},6\underline{2}\underline{2},6mm,\underline{6}m\underline{m},6\underline{m}\underline{m},\bar{6}m2,\underline{\bar{6}}\underline{m}2,\underline{\bar{6}}m\underline{2},\bar{6}\underline{m}\underline{2},6/mmm,\underline{6}/\underline{m}m\underline{m},6/m\underline{m}\underline{m},6/\underline{m}\underline{m}\underline{m},6/\underline{m}mm,\underline{6}/mm\underline{m}$ | $\sigma_x^2C_2+\sigma_y^2C_4+\sigma_z^2C_5$ | $\sigma_x^2C_4+\sigma_y^2C_2+\sigma_z^2C_5$ | $(\sigma_x^2+\sigma_y^2)C_{13}+\sigma_z^2C_{11}$ |

| Hexagonal Class | $V^s_{xy}$ | $V^s_{yz}$ | $V^s_{zx}$ |
|---|---|---|---|
| $6,\underline{6},\bar{6},\underline{\bar{6}},6/m,\underline{6}/\underline{m},6/\underline{m},\underline{6}/m$ | $\frac{1}{2}(\sigma_y^2-\sigma_x^2)C_2+\sigma_x\sigma_yC_6$ | $-\sigma_x\sigma_zC_{10}+\sigma_y\sigma_zC_9$ | $\sigma_x\sigma_zC_9+\sigma_y\sigma_zC_{10}$ |
| $622,\underline{6}2\underline{2},6\underline{2}\underline{2},6mm,\underline{6}m\underline{m},6\underline{m}\underline{m},\bar{6}m2,\underline{\bar{6}}\underline{m}2,\underline{\bar{6}}m\underline{2},\bar{6}\underline{m}\underline{2},6/mmm,\underline{6}/\underline{m}m\underline{m},6/m\underline{m}\underline{m},6/\underline{m}\underline{m}\underline{m},6/\underline{m}mm,\underline{6}/mm\underline{m}$ | $\sigma_x\sigma_yC_6$ | $\sigma_y\sigma_zC_9$ | $\sigma_x\sigma_zC_9$ |

| Hexagonal Class | $V^a_{xy}$ | $V^a_{yz}$ | $V^a_{zx}$ |
|---|---|---|---|
| $6,\bar{6},6/m$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_3$ | $-\sigma_x\sigma_zK_7+\sigma_y\sigma_zK_6$ | $-\sigma_x\sigma_zK_6-\sigma_y\sigma_zK_7$ |
| $\underline{6},\underline{\bar{6}},\underline{6}/\underline{m}$ | 0 | $(\sigma_x^2-\sigma_y^2)K_9-2\sigma_x\sigma_yK_8$ | $(\sigma_y^2-\sigma_x^2)K_8-2\sigma_x\sigma_yK_9$ |
| $\underline{6}/m,6/\underline{m},6/\underline{mmm},6/\underline{m}mm,\underline{6}/mm\underline{m}$ | 0 | 0 | 0 |
| $622,6mm,\bar{6}m2,6/mmm$ | 0 | $\sigma_y\sigma_zK_6$ | $-\sigma_x\sigma_zK_6$ |
| $\underline{6}2\underline{2},\underline{6}m\underline{m},\underline{\bar{6}}\underline{m}2,\underline{\bar{6}}m\underline{2},\underline{6}/\underline{m}m\underline{m}$ | 0 | $(\sigma_x^2-\sigma_y^2)K_9$ | $-2\sigma_x\sigma_yK_9$ |
| $6\underline{22},6\underline{mm},\bar{6}\underline{m2},6/m\underline{mm}$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_3$ | $-\sigma_x\sigma_zK_7$ | $-\sigma_y\sigma_zK_7$ |

$C_1=2G_{xy}+\omega a'_{xxz}$

$C_2=-\frac{1}{3}\omega^2b_{xxxx}+\frac{1}{4}\omega^2d_{xxxx}$

$C_3=-\frac{2}{3}\omega^2b_{xxxy}-\omega(H'_{xzx}-L'_{xxz})$

$C_4=-\frac{1}{3}\omega^2b_{xxyy}+\frac{1}{4}\omega^2d_{xyxy}-\omega H'_{xzy}+\chi_{zz}$

$C_5=-\frac{1}{3}\omega^2b_{xxzz}+\frac{1}{4}\omega^2d_{xzxz}+\omega(H'_{xyz}-L'_{zxy})+\chi_{xx}$

$C_6=-\frac{2}{3}\omega^2b_{xxyy}+\frac{1}{4}\omega^2(d_{xxyy}+d_{xyxy})+\omega H'_{xzy}-\chi_{zz}$

$C_7=-G_{xy}+\frac{1}{2}\omega(a'_{xxz}+a'_{zxx})$

$C_8=G_{xx}-G_{zz}+\frac{1}{2}\omega a'_{xyz}$

$C_9=-\frac{1}{3}\omega^2(b_{xxzz}+b_{zzxx})+\frac{1}{4}\omega^2(d_{xxzz}+d_{xzxz})-\frac{1}{2}\omega(H'_{xyz}+H'_{zxy})-\chi_{xx}$

$C_{10}=-\frac{1}{3}\omega^2b_{xyzz}-\frac{1}{2}\omega(H'_{zzz}-H'_{xxz}-H'_{zxx}+2L'_{zxx}-L'_{zzz})$

$C_{11}=-\frac{1}{3}\omega^2b_{zzzz}+\frac{1}{4}\omega^2d_{zzzz}$

$C_{12}=\omega a'_{zzz}$

$C_{13}=-\frac{1}{3}\omega^2b_{zzxx}+\frac{1}{4}\omega^2d_{xzxz}+\omega(H'_{zxy}+L'_{zxy})+\chi_{xx}$

$C_{14}=-\omega a'_{yyy}$

$C_{15}=\omega a'_{xxx}$

$K_1=-2G'_{xx}-\omega a_{xyz}$

$K_2=-\frac{2}{3}\omega^2b'_{xxxy}+\frac{1}{4}\omega^2d'_{xxxy}-\frac{1}{2}\omega(H_{xzx}-L_{xxz})$

$K_3=-\frac{1}{3}\omega^2b'_{xyzz}+\frac{1}{4}\omega^2d'_{xzyz}+\omega(H_{xxz}-L_{zxx})+\chi'_{xy}$

$K_4=-G'_{xy}-\frac{1}{2}\omega(a_{xxz}-a_{zxx})$

$K_5=G'_{xx}+G'_{zz}-\frac{1}{2}\omega a_{xyz}$ $\qquad$ $K_6=-\frac{1}{3}\omega^2(b'_{xxzz}-b'_{zzxx})+\frac{1}{4}\omega^2 d'_{xxzz}+\frac{1}{2}\omega(H_{xyz}-H_{zxy}-2L_{zxy})$

$K_7=-\frac{1}{3}\omega^2 b'_{xyzz}+\frac{1}{4}\omega^2 d'_{xzyz}-\frac{1}{2}\omega(H_{zzz}+H_{xxz}-H_{zxx}-L_{zzz})-\chi'_{xy}$

$K_8=-1/6\,\omega^2(b'_{xxxz}-b'_{zxxx})+\frac{1}{4}\omega^2 d'_{xxxz}-\frac{1}{2}\omega(H_{yyy}-L_{yyy})$

$K_9=1/6\,\omega^2(b'_{yyyz}-b'_{zyyy})-\frac{1}{4}\omega^2 d'_{yyyz}-\frac{1}{2}\omega(H_{xxx}-L_{xxx})$

### 5.1.3 The Trigonal Point Groups

For the trigonal point groups 3, $\bar{3}$, $3\underline{2}$, $\bar{3}\underline{m}$, and $3\underline{m}$, the only components of $\alpha'_{\alpha\beta}$ that exist are $\alpha'_{xy}=-\alpha'_{yx}$. For the remaining groups all components of $\alpha'_{\alpha\beta}$ are zero.

**TABLE 5.3**: The components of $U_{\alpha\beta}$ and $V_{\alpha\beta}$ relative to crystallographic axes for the trigonal point groups.

| Trigonal Class | $U^s_{xx}$ | $U^s_{yy}$ | $U^s_{zz}$ |
|---|---|---|---|
| $3,\underline{\bar{3}}$ | $\sigma_x C_1+\sigma_y C_2+\sigma_z C_3$ | $-\sigma_x C_1-\sigma_y C_2+\sigma_z C_3$ | $\sigma_z C_{18}$ |
| $\bar{3},\bar{3}m,\bar{3}\underline{m}$ | 0 | 0 | 0 |
| $32,3\underline{m},\underline{\bar{3}m}$ | $\sigma_x C_1$ | $-\sigma_x C_1$ | 0 |
| $3\underline{2},3m,\underline{\bar{3}}m$ | $\sigma_y C_2+\sigma_z C_3$ | $-\sigma_y C_2+\sigma_z C_3$ | $\sigma_z C_{18}$ |

| Trigonal Class | $U^s_{xy}$ | $U^s_{yz}$ | $U^s_{zx}$ |
|---|---|---|---|
| $3,\underline{3}$ | $\sigma_x C_2 - \sigma_y C_1$ | $-\sigma_x C_{13} + \sigma_y C_{12}$ | $\sigma_x C_{12} + \sigma_y C_{13}$ |
| $\bar{3},\bar{3}m,\bar{3}\underline{m}$ | 0 | 0 | 0 |
| $32,3\underline{m},\underline{\bar{3}m}$ | $-\sigma_y C_1$ | $-\sigma_x C_{13}$ | $\sigma_y C_{13}$ |
| $3\underline{2},3m,\underline{\bar{3}}m$ | $\sigma_x C_2$ | $\sigma_y C_{12}$ | $\sigma_x C_{12}$ |

| Trigonal Class | $U^a_{xy}$ | $U^a_{yz}$ | $U^a_{zx}$ |
|---|---|---|---|
| 3 | $\sigma_z K_1$ | $-\sigma_x K_8 + \sigma_y K_9$ | $-\sigma_x K_9 - \sigma_y K_8$ |
| $\bar{3},\underline{\bar{3}},\bar{3}m,\bar{3}\underline{m},\underline{\bar{3}m},\underline{\bar{3}}m$ | 0 | 0 | 0 |
| $32,3\underline{2}$ | $\sigma_z K_1$ | $-\sigma_x K_8$ | $-\sigma_y K_8$ |
| $3m,3\underline{m}$ | 0 | $\sigma_y K_9$ | $-\sigma_x K_9$ |

| Trigonal Class | $V^s_{xx}$ | $V^s_{yy}$ | $V^s_{zz}$ |
|---|---|---|---|
| $3,\bar{3},\underline{\bar{3}}$ | $\sigma_x^2C_4+\sigma_x\sigma_yC_5+\sigma_x\sigma_zC_6+\sigma_y^2C_7+\sigma_y\sigma_zC_8+\sigma_z^2C_9$ | $\sigma_x^2C_7-\sigma_x\sigma_yC_5-\sigma_x\sigma_zC_6+\sigma_y^2C_4-\sigma_y\sigma_zC_8+\sigma_z^2C_9$ | $(\sigma_x^2+\sigma_y^2)C_{19}+\sigma_z^2C_{20}$ |
| $32,3\underline{2},3m,3\underline{m},\bar{3}m,\bar{3}\underline{m},\underline{\bar{3}m},\underline{\bar{3}}m$ | $\sigma_x^2C_4+\sigma_y^2C_7+\sigma_y\sigma_zC_8+\sigma_z^2C_9$ | $\sigma_x^2C_7+\sigma_y^2C_4-\sigma_y\sigma_zC_8+\sigma_z^2C_9$ | $(\sigma_x^2+\sigma_y^2)C_{19}+\sigma_z^2C_{20}$ |

| Trigonal Class | $V^s_{xy}$ | $V^s_{yz}$ | $V^s_{zx}$ |
|---|---|---|---|
| $3,\bar{3},\underline{\bar{3}}$ | $(\sigma_x^2-\sigma_y^2)C_{10}+\sigma_x\sigma_yC_{11}+\sigma_x\sigma_zC_8-\sigma_y\sigma_zC_6$ | $\frac{1}{2}(\sigma_x^2-\sigma_y^2)C_{15}-2\sigma_x\sigma_yC_{14}-\sigma_x\sigma_zC_{17}+\sigma_y\sigma_zC_{16}$ | $(\sigma_x^2-\sigma_y^2)C_{14}+\sigma_x\sigma_yC_{15}+\sigma_x\sigma_zC_{16}+\sigma_y\sigma_zC_{17}$ |
| $32,3\underline{2},3m,3\underline{m},\bar{3}m,\bar{3}\underline{m},\underline{\bar{3}m},\underline{\bar{3}}m$ | $\sigma_x\sigma_yC_{11}+\sigma_x\sigma_zC_8$ | $\frac{1}{2}(\sigma_x^2-\sigma_y^2)C_{15}+\sigma_y\sigma_zC_{16}$ | $\sigma_x\sigma_yC_{15}+\sigma_x\sigma_zC_{16}$ |

| Trigonal Class | $V^{a}_{xy}$ | $V^{a}_{yz}$ | $V^{a}_{zx}$ |
|---|---|---|---|
| $3,\bar{3}$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_3$ | $\frac{1}{2}(\sigma_x^2-\sigma_y^2)K_5-2\sigma_x\sigma_yK_4-\sigma_x\sigma_zK_7+\sigma_y\sigma_zK_6$ | $(\sigma_y^2-\sigma_x^2)K_4-\sigma_x\sigma_yK_5-\sigma_x\sigma_zK_6-\sigma_y\sigma_zK_7$ |
| $\underline{\bar{3}},\underline{\bar{3}m},\underline{\bar{3}}m$ | 0 | 0 | 0 |
| $32,3m,\bar{3}m$ | 0 | $\frac{1}{2}(\sigma_x^2-\sigma_y^2)K_5+\sigma_y\sigma_zK_6$ | $-\sigma_x\sigma_yK_5-\sigma_x\sigma_zK_6$ |
| $3\underline{2},3\underline{m},\bar{3}\underline{m}$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_3$ | $-2\sigma_x\sigma_yK_4-\sigma_x\sigma_zK_7$ | $(\sigma_y^2-\sigma_x^2)K_4-\sigma_y\sigma_zK_7$ |

$C_1=\omega a'_{xxx}$ $\quad C_2=-\omega a'_{yyy}$ $\quad C_3=2G_{xy}+\omega a'_{xxz}$

$C_4=-\frac{1}{3}\omega^2b_{xxxx}+\frac{1}{4}\omega^2d_{xxxx}$ $\quad C_5=-\frac{2}{3}\omega^2b_{xxxy}-\omega(H'_{xzx}-L'_{xxz})$

$C_6=-\frac{2}{3}\omega^2b_{xxxz}+\frac{1}{2}\omega^2d_{xxxz}-\omega(H'_{yyy}-L'_{yyy})$ $\quad C_7=-\frac{1}{3}\omega^2b_{xxyy}+\frac{1}{4}\omega^2d_{xyxy}-\omega H'_{xzy}+\chi_{zz}$

$C_8=\frac{2}{3}\omega^2b_{yyyz}-\frac{1}{2}\omega^2d_{yyyz}-\omega(H'_{xxx}-L'_{xxx})$ $\quad C_9=-\frac{1}{3}\omega^2b_{xxzz}+\frac{1}{4}\omega^2d_{xzxz}+\omega(H'_{xyz}-L'_{zxy})+\chi_{xx}$

$C_{10}=\frac{1}{3}\omega^2b_{xxxy}+\frac{1}{2}\omega(H'_{xzx}-L'_{xxz})$ $\quad C_{11}=-\frac{2}{3}\omega^2b_{xxyy}+\frac{1}{4}\omega^2(d_{xxyy}+d_{xyxy})+\omega H'_{xzy}-\chi_{zz}$

$C_{12}=-G_{xy}+\frac{1}{2}\omega(a'_{xxz}+a'_{zxx})$ $\quad C_{13}=G_{xx}-G_{zz}+\frac{1}{2}\omega a'_{xyz}$

$C_{14}=-1/6\,\omega^2(b_{xxxz}+b_{zxxx})+\frac{1}{4}\omega^2d_{xxxz}+\frac{1}{2}\omega(H'_{yyy}-L'_{yyy})$ $\quad C_{15}=\frac{1}{3}\omega^2(b_{yyyz}+b_{zyyy})-\frac{1}{2}\omega^2d_{yyyz}+\omega(H'_{xxx}-L'_{xxx})$

$C_{16}=-\frac{1}{3}\omega^2(b_{xxzz}+b_{zzxx})+\frac{1}{4}\omega^2(d_{xxzz}+d_{xzxz})-\frac{1}{2}\omega(H'_{xyz}+H'_{zxy})-\chi_{xx}$

$C_{17}=-\frac{1}{3}\omega^2b_{xyzz}-\frac{1}{2}\omega(H'_{zzz}-H'_{xxz}-H'_{zxx}+2L'_{zxx}-L'_{zzz})$ $\quad C_{18}=\omega a'_{zzz}$

$C_{19}=-\frac{1}{3}\omega^2b_{zzxx}+\frac{1}{4}\omega^2d_{xzxz}+\omega(H'_{zxy}+L'_{zxy})+\chi_{xx}$ $\quad C_{20}=-\frac{1}{3}\omega^2b_{zzzz}+\frac{1}{4}\omega^2d_{zzzz}$

$K_1=-2G'_{xx}-\omega a_{xyz}$ $\quad K_2=-\frac{2}{3}\omega^2b'_{xxxy}+\frac{1}{4}\omega^2d'_{xxxy}-\frac{1}{2}\omega(H_{xzx}-L_{xxz})$

$K_3=-\frac{1}{3}\omega^2b'_{xyzz}+\frac{1}{4}\omega^2d'_{xzyz}+\omega(H_{xxz}-L_{zxx})+\chi'_{xy}$ $\quad K_4=-1/6\,\omega^2(b'_{xxxz}-b'_{zxxx})+\frac{1}{4}\omega^2d'_{xxxz}-\frac{1}{2}\omega(H_{yyy}-L_{yyy})$

$K_5=\frac{1}{3}\omega^2(b'_{yyyz}-b'_{zyyy})-\frac{1}{2}\omega^2d'_{yyyz}-\omega(H_{xxx}-L_{xxx})$

$K_6=-\frac{1}{3}\omega^2(b'_{xxzz}-b'_{zzxx})+\frac{1}{4}\omega^2d'_{xxzz}+\frac{1}{2}\omega(H_{xyz}-H_{zxy}-2L_{zxy})$

$K_7=-\frac{1}{3}\omega^2 b'_{xyzz}+\frac{1}{4}\omega^2 d'_{xzyz}-\frac{1}{2}\omega(H_{zzz}+H_{xxz}-H_{zxx}-L_{zzz})-\chi'_{xy}$ $\quad K_8=G'_{xx}+G'_{zz}-\frac{1}{2}\omega a_{xyz}$

$K_9=-G'_{xy}-\frac{1}{2}\omega(a_{xxz}-a_{zxx})$

### 5.1.4 The Tetragonal Point Groups

Only the components $\alpha'_{xy}=-\alpha'_{yx}$ of $\alpha'_{\alpha\beta}$ do not vanish for the following tetragonal point groups: 4, $\bar{4}$, 4/m, 4$\underline{22}$, 4$\underline{mm}$, $\bar{4}\underline{2m}$, and 4/m$\underline{mm}$. For the other tetragonal classes all components of $\alpha'_{\alpha\beta}$ are zero.

**TABLE 5.4**: The components of $U_{\alpha\beta}$ and $V_{\alpha\beta}$ relative to crystallographic axes for the tetragonal point groups.

| Tetragonal Class | $U^s_{xx}$ | $U^s_{yy}$ | $U^s_{zz}$ |
|---|---|---|---|
| 4,$\underline{\bar{4}}$,4/$\underline{m}$ | $\sigma_z C_1$ | $\sigma_z C_1$ | $\sigma_z C_6$ |
| $\underline{4}$,$\bar{4}$,$\underline{4}$/$\underline{m}$ | $\sigma_z C_1$ | $-\sigma_z C_1$ | 0 |
| 4/m,$\underline{4}$/m,4/mmm,$\underline{4}$/mm$\underline{m}$,4/m$\underline{mm}$ | 0 | 0 | 0 |
| 422,4$\underline{mm}$,$\underline{\bar{4}}$2$\underline{m}$,4/$\underline{mmm}$ | 0 | 0 | 0 |
| $\underline{4}$22,$\underline{4}$m$\underline{m}$,$\bar{4}$2m,$\bar{4}\underline{2m}$,$\underline{4}$/$\underline{m}$m$\underline{m}$ | 0 | 0 | 0 |
| 4$\underline{22}$,4mm,$\underline{\bar{4}2}$m,4/$\underline{m}$mm | $\sigma_z C_1$ | $\sigma_z C_1$ | $\sigma_z C_6$ |

| Tetragonal Class | $U^s_{xy}$ | $U^s_{yz}$ | $U^s_{zx}$ |
|---|---|---|---|
| $4,\underline{\bar{4}},4/\underline{m}$ | 0 | $-\sigma_x C_{10}+\sigma_y C_9$ | $\sigma_x C_9+\sigma_y C_{10}$ |
| $\underline{4},\bar{4},\underline{4}/\underline{m}$ | $\sigma_z C_{15}$ | $\sigma_x C_{16}-\sigma_y C_9$ | $\sigma_x C_9+\sigma_y C_{16}$ |
| $4/m,\underline{4}/m,4/mmm,\underline{4}/mm\underline{m},4/m\underline{mm}$ | 0 | 0 | 0 |
| $422,4\underline{mm},\underline{\bar{4}}2\underline{m},4/\underline{mmm}$ | 0 | $-\sigma_x C_{10}$ | $\sigma_y C_{10}$ |
| $\underline{4}22,\underline{4}m\underline{m},\bar{4}2m,\bar{4}\underline{2m},\underline{4}/\underline{m}m\underline{m}$ | $\sigma_z C_{15}$ | $\sigma_x C_{16}$ | $\sigma_y C_{16}$ |
| $4\underline{22},4mm,\underline{\bar{4}2}m,4/\underline{m}mm$ | 0 | $\sigma_y C_9$ | $\sigma_x C_9$ |

| Tetragonal Class | $U^a_{xy}$ | $U^a_{yz}$ | $U^a_{zx}$ |
|---|---|---|---|
| 4,$\underline{4}$ | $\sigma_z K_1$ | $-\sigma_x K_4+\sigma_y K_3$ | $-\sigma_x K_3-\sigma_y K_4$ |
| $\bar{4}$,$\underline{\bar{4}}$ | 0 | $\sigma_x K_{10}-\sigma_y K_3$ | $-\sigma_x K_3-\sigma_y K_{10}$ |
| 4/m,$\underline{4}$/m,4/$\underline{m}$,$\underline{4}$/$\underline{m}$,4/mmm,$\underline{4}$/mm$\underline{m}$, 4/m$\underline{mm}$,4/$\underline{mmm}$,4/$\underline{m}$mm,$\underline{4}$/$\underline{m}$m$\underline{m}$ | 0 | 0 | 0 |
| 422,$\underline{4}$22,4$\underline{22}$ | $\sigma_z K_1$ | $-\sigma_x K_4$ | $-\sigma_y K_4$ |
| 4mm,$\underline{4}$m$\underline{m}$,4$\underline{mm}$ | 0 | $\sigma_y K_3$ | $-\sigma_x K_3$ |
| $\bar{4}$2m,$\underline{\bar{4}}$2$\underline{m}$,$\underline{\bar{4}2}$m,$\bar{4}\underline{2m}$ | 0 | $\sigma_x K_{10}$ | $-\sigma_y K_{10}$ |

| Tetragonal Class | $V^s_{xx}$ | $V^s_{yy}$ | $V^s_{zz}$ |
|---|---|---|---|
| 4,$\underline{4}$,$\bar{4}$,$\underline{\bar{4}}$,4/m,$\underline{4}$/m,4/$\underline{m}$,$\underline{4}$/$\underline{m}$ | $\sigma_x^2C_2+\sigma_x\sigma_yC_3+\sigma_y^2C_4+\sigma_z^2C_5$ | $\sigma_x^2C_4-\sigma_x\sigma_yC_3+\sigma_y^2C_2+\sigma_z^2C_5$ | $(\sigma_x^2+\sigma_y^2)C_{13}+\sigma_z^2C_{14}$ |
| 422,$\underline{4}$22,4$\underline{22}$,4mm,$\underline{4}$m$\underline{m}$,4$\underline{mm}$, $\bar{4}$2m,$\underline{\bar{4}}$2$\underline{m}$,$\underline{\bar{4}2}$m,$\bar{4}\underline{2m}$,4/mmm, $\underline{4}$/mm$\underline{m}$,4/m$\underline{mm}$,4/$\underline{mmm}$, 4/$\underline{m}$mm,$\underline{4}$/$\underline{m}$m$\underline{m}$ | $\sigma_x^2C_2+\sigma_y^2C_4+\sigma_z^2C_5$ | $\sigma_x^2C_4+\sigma_y^2C_2+\sigma_z^2C_5$ | $(\sigma_x^2+\sigma_y^2)C_{13}+\sigma_z^2C_{14}$ |

| Tetragonal Class | $V^s_{xy}$ | $V^s_{yz}$ | $V^s_{zx}$ |
|---|---|---|---|
| $4,\underline{4},\bar{4},\underline{\bar{4}},4/m,\underline{4}/m,4/\underline{m},\underline{4}/\underline{m}$ | $(\sigma_x^2-\sigma_y^2)C_7+\sigma_x\sigma_yC_8$ | $-\sigma_x\sigma_zC_{12}+\sigma_y\sigma_zC_{11}$ | $\sigma_x\sigma_zC_{11}+\sigma_y\sigma_zC_{12}$ |
| $422,\underline{4}22,4\underline{22},4mm,\underline{4}m\underline{m},4\underline{mm},\bar{4}2m,\underline{\bar{4}}2\underline{m},\underline{\bar{4}2}m,\bar{4}\underline{2m},4/mmm,\underline{4}/mm\underline{m},4/m\underline{mm},4/\underline{mmm},4/\underline{m}mm,\underline{4}/\underline{m}m\underline{m}$ | $\sigma_x\sigma_yC_8$ | $\sigma_y\sigma_zC_{11}$ | $\sigma_x\sigma_zC_{11}$ |

| Tetragonal Class | $V^a_{xy}$ | $V^a_{yz}$ | $V^a_{zx}$ |
|---|---|---|---|
| $4,\bar{4},4/m$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_7$ | $-\sigma_x\sigma_zK_6+\sigma_y\sigma_zK_5$ | $-\sigma_x\sigma_zK_5-\sigma_y\sigma_zK_6$ |
| $\underline{4},\underline{\bar{4}},\underline{4}/m$ | $(\sigma_x^2-\sigma_y^2)K_2+\sigma_x\sigma_yK_9$ | $\sigma_x\sigma_zK_{11}-\sigma_y\sigma_zK_8$ | $-\sigma_x\sigma_zK_8-\sigma_y\sigma_zK_{11}$ |
| $4/\underline{m},\underline{4}/\underline{m},4/\underline{mmm},4/\underline{m}mm,\underline{4}/\underline{m}m\underline{m}$ | 0 | 0 | 0 |
| $\underline{4}22,\underline{4}m\underline{m},\underline{\bar{4}}2\underline{m},\underline{\bar{4}2}m,\underline{4}/mm\underline{m}$ | $\sigma_x\sigma_yK_9$ | $-\sigma_y\sigma_zK_8$ | $-\sigma_x\sigma_zK_8$ |
| $4\underline{22},4\underline{mm},\bar{4}\underline{2m},4/m\underline{mm}$ | $(\sigma_x^2+\sigma_y^2)K_2+\sigma_z^2K_7$ | $-\sigma_x\sigma_zK_6$ | $-\sigma_y\sigma_zK_6$ |
| $422,4mm,\bar{4}2m,4/mmm$ | 0 | $\sigma_y\sigma_zK_5$ | $-\sigma_x\sigma_zK_5$ |

$$C_1=2G_{xy}+\omega a'_{xxz}$$

$$C_2=-\tfrac{1}{3}\omega^2 b_{xxxx}+\tfrac{1}{4}\omega^2 d_{xxxx}$$

$$C_3=-\tfrac{2}{3}\omega^2 b_{xxxy}+\tfrac{1}{2}\omega^2 d_{xxxy}-\omega(H'_{xzx}-L'_{xxz})$$

$$C_4=-\tfrac{1}{3}\omega^2 b_{xxyy}+\tfrac{1}{4}\omega^2 d_{xyxy}-\omega H'_{xzy}+\chi_{zz}$$

$$C_5=-\tfrac{1}{3}\omega^2 b_{xxzz}+\tfrac{1}{4}\omega^2 d_{xzxz}+\omega(H'_{xyz}-L'_{zxy})+\chi_{xx}$$

$$C_6=wa'_{zzz}$$

$$C_7=-1/6\,\omega^2\,(b_{xxxy}+b_{yxxx})+\tfrac{1}{4}\omega^2 d_{xxxy}+\tfrac{1}{2}\omega(H'_{xzx}-L'_{xxz})$$

$$C_8=-\tfrac{2}{3}\omega^2 b_{xxyy}+\tfrac{1}{4}\omega^2(d_{xxyy}+d_{xyxy})+\omega H'_{xzy}-\chi_{zz}$$

$$C_9=-G_{xy}+\tfrac{1}{2}\omega(a'_{xxz}+a'_{zxx})$$

$$C_{10}=G_{xx}-G_{zz}+\tfrac{1}{2}\omega a'_{xyz}$$

$$C_{11}=-\tfrac{1}{3}\omega^2(b_{xxzz}+b_{zzxx})+\tfrac{1}{4}\omega^2(d_{xxzz}+d_{xzxz})-\tfrac{1}{2}\omega(H'_{xyz}+H'_{zxy})-\chi_{xx}$$

$$C_{12}=-\tfrac{1}{3}\omega^2 b_{xyzz}-\tfrac{1}{2}\omega(H'_{zzz}-H'_{xxz}-H'_{zxx}+2L'_{zxx}-L'_{zzz})$$

$$C_{13}=-\tfrac{1}{3}\omega^2 b_{zzxx}+\tfrac{1}{4}\omega^2 d_{xzxz}+\omega(H'_{zxy}+L'_{zxy})+\chi_{xx} \quad C_{14}=-\tfrac{1}{3}\omega^2 b_{zzzz}+\tfrac{1}{4}\omega^2 d_{zzzz}$$

$$C_{15}=-2G_{xx}+\omega a'_{xyz}$$

$$C_{16}=G_{xx}+\tfrac{1}{2}\omega(a'_{xyz}+a'_{zxy})$$

$$K_1=-2G'_{xx}-\omega a_{xyz}$$

$$K_2=-1/6\,\omega^2(b'_{xxxy}-b'_{yxxx})+\tfrac{1}{4}\omega^2 d'_{xxxy}-\tfrac{1}{2}\omega(H_{xzx}-L_{xxz})$$

$$K_3=-G'_{xy}-\tfrac{1}{2}\omega(a_{xxz}-a_{zxx})$$

$$K_4=G'_{xx}+G'_{zz}-\tfrac{1}{2}\omega a_{xyz}$$

$$K_5=-\tfrac{1}{3}\omega^2(b'_{xxzz}-b'_{zzxx})+\tfrac{1}{4}\omega^2 d'_{xxzz}+\tfrac{1}{2}\omega(H_{xyz}-H_{zxy}-2L_{zxy})$$

$$K_6=-\tfrac{1}{3}\omega^2 b'_{xyzz}+\tfrac{1}{4}\omega^2 d'_{xzyz}-\tfrac{1}{2}\omega(H_{zzz}+H_{xxz}-H_{zxx}-L_{zzz})-\chi'_{xy}$$

$$K_7=-\tfrac{1}{3}\omega^2 b'_{xyzz}+\tfrac{1}{4}\omega^2 d'_{xzyz}+\omega(H_{xxz}-L_{zxx})+\chi'_{xy}$$

$$K_8=-\tfrac{1}{3}\omega^2(b'_{xxzz}-b'_{zzxx})+\tfrac{1}{4}\omega^2 d'_{xxzz}+\tfrac{1}{2}\omega(H_{xyz}+H_{zxy}-2L_{zxy})$$

$$K_9=-\tfrac{2}{3}\omega^2 b'_{xxyy}+\tfrac{1}{4}\omega^2 d'_{xxyy}-\omega(H_{xzy}-L_{xyz})$$

$$K_{10}=G'_{xx}-\tfrac{1}{2}\omega(a_{xyz}-a_{zxy})$$

$$K_{11}=-\tfrac{1}{3}\omega^2(b'_{xyzz}-b'_{zzxy})+\tfrac{1}{4}\omega^2 d'_{xyzz}-\tfrac{1}{2}\omega(H_{xxz}+H_{zxx}-2L_{zxx})$$

## 5.2 DETERMINATION OF OPTICAL EFFECTS IN $\bar{6}m2$

The different optical effects apparent in crystals belonging to the $\bar{6}m2$ point group will be determined as an example of the application of the method outlined in Chapter 2.

### 5.2.1 Propagation along the z-axis.

With $\sigma=(0,0,1)$ equation (1.63) together with the tensor components given in Table 5.2 leads to the following determinantal equation:

$$\begin{vmatrix} -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_5 & 0 & 0 \\ 0 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_5 & 0 \\ 0 & 0 & 1+\frac{1}{\epsilon_o}\alpha_{zz}+\frac{n^2}{c^2\epsilon_o}C_{13} \end{vmatrix} = 0\ . \qquad \textbf{(5.1)}$$

The first two equations from which this determinant is obtained indicate the propagation of N-rays, since equations (2.12) and (2.13) are satisfied. The third equation, however, shows that there is a wave which has an electric field in the direction of propagation. This is termed an additional ray. This type of wave will not be considered further in this dissertation.

The determinant in equation (5.1) reduces to the following 2x2 determinant:

$$\begin{vmatrix} -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_5 & 0 \\ 0 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_5 \end{vmatrix} = 0 \ . \qquad \textbf{(5.2)}$$

In order to obtain this equation in the form of (2.17), equations (2.18) to (2.21) are used to derive the following expressions for the relevant coefficients:

$$A = \frac{1}{\epsilon_o}\alpha_{xx} + \frac{n^2}{c^2\epsilon_o}C_5 \ , \qquad \textbf{(5.3)}$$

$$B = 0 \ , \qquad \textbf{(5.4)}$$

$$C = 0 \ , \qquad \textbf{(5.5)}$$

$$D = 0 \ . \qquad \textbf{(5.6)}$$

Equation (5.2) then becomes

$$\begin{vmatrix} -n^2+1+A & 0 \\ 0 & -n^2+1+A \end{vmatrix} = 0 \ . \qquad \textbf{(5.7)}$$

This is identical in form to equation (2.22). It can hence be concluded that for propagation down the optic axis no birefringence will be exhibited by a crystal that belongs to this point group.

### 5.2.2 Propagation along the y-axis.

When light is propagated along $\sigma=(0,1,0)$, equation (1.63) becomes:

$$\begin{vmatrix} -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_4 & 0 & \frac{n}{c\epsilon_o}C_{10} \\ 0 & 1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_2 & \frac{in^2}{c^2\epsilon_o}K_9 \\ \frac{n}{c\epsilon_o}C_{10} & -\frac{in^2}{c^2\epsilon_o}K_9 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{zz}+\frac{n^2}{c^2\epsilon_o}C_{15} \end{vmatrix} = 0 \ . \quad \textbf{(5.8)}$$

These are clearly not N-rays, since the equations equivalent to equations (2.12) and (2.13) for y-propagation are not satisfied. The Jones method for the determination of optical effects can therefore not be applied for this propagation direction.

### 5.2.3 Propagation along the x-axis.

For $\sigma$=(1,0,0) equation (1.63) becomes:

$$\begin{vmatrix} 1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_2 & 0 & 0 \\ 0 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_4 & -\frac{n}{c\epsilon_o}C_{10}-\frac{in}{c^2\epsilon_o}K_9 \\ 0 & -\frac{n}{c\epsilon_o}C_{10}+\frac{in^2}{c^2\epsilon_o}K_9 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{zz}+\frac{n^2}{c^2\epsilon_o}C_{15} \end{vmatrix} = 0 \ . \tag{5.9}$$

Apart from an additional wave, there are two other rays which propagate along the +x axis, both N-rays as inspection of the determinant shows. For them equation (5.9) reduces to

$$\begin{vmatrix} -n^2+1+\frac{1}{\epsilon_o}\alpha_{xx}+\frac{n^2}{c^2\epsilon_o}C_4 & -\frac{n}{c\epsilon_o}C_{10}-\frac{in}{c^2\epsilon_o}K_9 \\ -\frac{n}{c\epsilon_o}C_{10}+\frac{in^2}{c^2\epsilon_o}K_9 & -n^2+1+\frac{1}{\epsilon_o}\alpha_{zz}+\frac{n^2}{c^2\epsilon_o}C_{15} \end{vmatrix} = 0 \ . \tag{5.10}$$

The coefficients in equation (2.17) become

$$A = \frac{1}{2\epsilon_o}(\alpha_{xx}+\alpha_{zz}) + \frac{n^2}{2c^2\epsilon_o}(C_4+C_{15}) \ , \tag{5.11}$$

$$B = \frac{1}{2\epsilon_o}(\alpha_{xx}-\alpha_{zz}) + \frac{n^2}{2c^2\epsilon_o}(C_4-C_{15}) \quad , \tag{5.12}$$

$$C = -\frac{n}{c\epsilon_o}C_{10} \quad , \tag{5.13}$$

$$D = -\frac{n^2}{c^2\epsilon_o}K_9 \quad . \tag{5.14}$$

Since none of these coefficients vanish, the analysis in Chapter 2 indicates that this crystal will display all three types of birefringence. The first of these is a linear birefringence relative to the y and z crystallographic axes of the crystal, namely

$$n_y - n_z = (1+X)^{\frac{1}{2}} - (1-X)^{\frac{1}{2}} + Y + \tfrac{1}{2}Z\left[(1+X)^{\frac{1}{2}} + (1-X)^{\frac{1}{2}}\right] \quad , \tag{5.15}$$

where

$$X = \frac{1}{2\epsilon_o}(\alpha_{xx}-\alpha_{zz}) \quad , \tag{5.16}$$

$$Y = 0 \quad , \tag{5.17}$$

and

$$Z = \frac{1}{2c^2\epsilon_o}(C_4 - C_{15})$$

$$= \frac{1}{2c^2\epsilon_o}\Big[-\tfrac{1}{3}\omega^2 b_{xxyy} + \tfrac{1}{4}\omega^2 d_{xyxy} - \omega H'_{xzy} + X_{zz}$$

$$+ \tfrac{1}{3}\omega^2 b_{zzxx} - \tfrac{1}{4}\omega^2 d_{xzxz} - \omega(H'_{zxy} + L'_{zxy}) + X_{xx}\Big] \quad . \tag{5.18}$$

Although the term $(C_4\text{-}C_{15})$ is much smaller than the $(\alpha_{xx}\text{-}\alpha_{xx})$ term, since the former is of electric octopole-magnetic quadrupole order, it is included at this stage for completeness.

The second is a linear birefringence relative to the bisectors of these axes, namely that named after Jones (Graham and Raab 1983):

$$n_- - n_+ = \frac{1}{c\epsilon_o}C_{10}$$

$$= \frac{1}{c\epsilon_o}(G_{xx} - G_{zz} + \tfrac{1}{2}\omega a'_{xyz}) \quad . \tag{5.19}$$

The third is a circular birefringence, given by

$$n_r - n_l = -\frac{1}{c^2\epsilon_o}K_9$$

$$= -\frac{1}{c^2\epsilon_o}\Big[\tfrac{1}{6}\omega^2(b'_{yyyz} - b'_{zyyy}) - \tfrac{1}{4}\omega^2 d'_{yyyz} - \tfrac{1}{2}\omega(H_{xxx} - L_{xxx})\Big] \quad . \tag{5.20}$$

The above procedure was followed for all the cubic and uniaxial point groups, leading to predictions of the optical effects that result from contributions by the polarizability tensors of different multipole order. These predictions are displayed in Table 5.5.

## 5.3 SUMMARY

In this chapter, with the theory taken to the order of electric octopole and magnetic quadrupole, the multipole contributions to the wave equation were determined for all magnetic crystals of the cubic and uniaxial systems. The details of the relevant expressions in terms of multipole polarizability tensors are presented in Section 5.1. With the wave equation cast in determinantal form, inspection of its elements allows immediate identification to be made, as described in Chapter 2, of whether N-rays may propagate for the chosen light path, since the Jones calculus applies only to such rays, and also of whether any of the three platelet birefringences that enter Jones' M-matrix may occur. The simplest propagation directions to treat in this way are those along the three orthogonal crystallographic axes. An illustration of the procedure is given in Section 5.2, where the symmetry class $\underline{\bar{6}\mathrm{m}}2$ was analysed. Indications of the existence of these three birefringences in the cubic and uniaxial point groups are presented in Table 5.5. The symbols in an entry in the table, such as $\alpha L'H'bd\chi$, are those for the polarizability tensors that contribute to the birefringence.

All tensor contributions to the order of electric octopole and magnetic quadrupole are included in the results in this dissertation for the sake of completeness. However, not all of these contributions will be detectable experimentally, as the effects of tensors related to higher order multipoles will in some cases be masked by the much larger relative effects of lower order multipole contibutions. An instance of this is where the effect of the $V^{s}_{\alpha\beta}$ tensor in linear birefringence in uniaxial crystals is masked due to the presence of the $\alpha^{s}_{\alpha\beta}$ tensor, which produces a much greater contribution to this effect.

Where in Table 5.5 an entry in the linear birefringence column is indicated in parentheses, this means that the linear birefringence which has been calculated to be along the bisectors of the crystallographic axes which lie perpendicular to the propagation direction is not accompanied by a normal linear birefringence, and hence is not considered a Jones birefringence. This birefringence is measurable as a normal linear birefringence with the crystallographic axes rotated through an angle of 45°.

**Table 5.5 Symmetry Indications for the Existence of Birefringences for *N* Rays in the Magnetic Crystal Groups within the Electric-Octopole Magnetic-Quadrupole Approximation**

| ystem | Group | *z*-Propagation *N*-Rays? | $(n_y - n_x)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *y*-Propagation *N*-Rays? | $(n_x - n_z)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *x*-Propagation *N*-Rays? | $(n_z - n_y)$ | $(n_- - n_+)$ | $(n_r - n_l)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| :tragonal | $4$ | Yes | 0 | 0 | *α'G'ab'd'LHχ'* | No | - | - | - | No | - | - | - |
| | $\underline{4}$ | Yes | *Ga'* | *Ga'* | *G'a* | No | - | - | - | No | - | - | - |
| | $\bar{4}$ | Yes | *Ga'* | *Ga'* | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\underline{\bar{4}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $4/m$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\underline{4}/m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $4/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{4}/\underline{m}$ | Yes | *Ga'* | *Ga'* | 0 | No | - | - | - | No | - | - | - |
| | $422$ | Yes | 0 | 0 | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* |
| | $\underline{4}22$ | Yes | *(Ga')* | 0 | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* |
| | $4\underline{22}$ | Yes | 0 | 0 | *α'G'aLHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $4mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{4}m\underline{m}$ | Yes | *(Ga')* | 0 | 0 | No | - | - | - | No | - | - | - |
| | $4\underline{mm}$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\bar{4}2m$ | Yes | *(Ga')* | 0 | 0 | Yes | *αL'H'bdχ* | *Ga'* | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* |
| | $\underline{\bar{4}}2\underline{m}$ | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | *Ga'* | *G'a* | Yes | *αL'H'bdχ* | *Ga'* | *G'a* |
| | $\underline{\bar{4}2}m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\bar{4}\underline{2m}$ | Yes | *(Ga')* | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $4/mmm$ | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 |
| | $\underline{4}/mm\underline{m}$ | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 |
| | $4/m\underline{mm}$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $4/\underline{mmm}$ | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | *Ga'* | 0 | Yes | *αL'H'bdχ* | *Ga'* | *0* |
| | $4/\underline{m}mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{4}/\underline{m}m\underline{m}$ | Yes | *(Ga')* | 0 | 0 | Yes | *αL'H'bdχ* | *Ga'* | 0 | Yes | *αL'H'bdχ* | *Ga'* | *0* |
| rigonal | $3$ | Yes | 0 | 0 | *α'G'aLHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\bar{3}$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\underline{\bar{3}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $32$ | Yes | 0 | 0 | *G'a* | No | - | - | - | Yes | *αa'L'H'bdχ* | *Ga'L'H'bd* | *G'aLHb'd'* |
| | $3\underline{2}$ | Yes | 0 | 0 | *α'G'aLHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $3m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $3\underline{m}$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\bar{3}m$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | *αL'H'bdχ* | *L'H'bd* | *LHb'd'* |
| | $\bar{3}\underline{m}$ | Yes | 0 | 0 | *α'LHb'd'χ'* | No | - | - | - | No | - | - | - |
| | $\underline{\bar{3}m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | *αa'L'H'bdχ* | *Ga'L'H'bd* | 0 |
| | $\underline{\bar{3}}m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |

| System | Group | *N*-Rays? | *z*-Propagation $(n_y-n_x)$ | $(n_- - n_+)$ | $(n_r-n_l)$ | *N*-Rays? | *y*-Propagation $(n_x-n_z)$ | $(n_- - n_+)$ | $(n_r-n_l)$ | *N*-Rays? | *x*-Propagation $(n_z-n_y)$ | $(n_- - n_+)$ | $(n_r-n_l)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hexagonal | $6$ | Yes | 0 | 0 | $\alpha'G'aLHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\underline{6}$ | Yes | 0 | 0 | $G'a$ | No | - | - | - | No | - | - | - |
| | $\bar{6}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\underline{\bar{6}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $6/m$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\underline{6}/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $6/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}/m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $622$ | Yes | 0 | 0 | $G'a$ | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $G'a$ | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $G'a$ |
| | $\underline{6}2\underline{2}$ | Yes | 0 | 0 | $G'a$ | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | $G'aLHb'd'$ |
| | $6\underline{22}$ | Yes | 0 | 0 | $\alpha'G'aLHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}m\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $6\underline{mm}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\bar{6}m2$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | 0 |
| | $\underline{\bar{6}m}2$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $LHb'd'$ |
| | $\underline{\bar{6}}m\underline{2}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\bar{6}\underline{m2}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6/mmm$ | Yes | 0 | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | 0 | 0 |
| | $\underline{6}/\underline{m}m\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha L'H'bd\chi$ | 0 | $LHb'd'$ |
| | $6/m\underline{mm}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6/\underline{mmm}$ | Yes | 0 | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | 0 | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | 0 |
| | $6/\underline{m}mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}/mm\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | 0 |
| Cubic | $23$ | Yes | $L'H'b$ | $a'$ | $G'$ | Yes | $L'H'b$ | $a'$ | $G'$ | Yes | $L'H'b$ | $a'$ | $G'$ |
| | $m3$ | Yes | $L'H'b$ | 0 | 0 | Yes | $L'H'b$ | 0 | 0 | Yes | $L'H'b$ | 0 | 0 |
| | $\underline{m}3$ | Yes | $L'H'b$ | $a'$ | 0 | Yes | $L'H'b$ | $a'$ | 0 | Yes | $L'H'b$ | $a'$ | 0 |
| | $432$ | Yes | 0 | 0 | $G'$ | Yes | 0 | 0 | $G'$ | Yes | 0 | 0 | $G'$ |
| | $\underline{4}3\underline{2}$ | Yes | $(a')$ | 0 | $G'$ | Yes | $(a')$ | 0 | $G'$ | Yes | $(a')$ | 0 | $G'$ |
| | $\bar{4}3m$ | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 |
| | $\underline{\bar{4}}3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $m3m$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $m3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $\underline{m}3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $\underline{m}3m$ | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 |

# CHAPTER 6

## 6.1 DISCUSSION OF RESULTS

Table 5.5, in conjunction with Tables 5.1 to 5.4 and equations (2.36), (2.45), and (2.49), allows the actual expressions to be written down, in terms of multipole polarizability tensors, for the birefringences that will exist for N-rays propagating along a given crystallographic axis in any cubic or uniaxial magnetic crystal. Such a quantitative expression indicates which macroscopic tensor component, or components, are responsible for a particular birefringence, and enables one to assess the magnitude of the effect, and hence the prospect of measuring it.

In considering the orders of magnitude of the various multipole tensors, we note from equations (3.26) and (3.27) that both $\alpha_{\alpha\beta}$ and $\alpha'_{\alpha\beta}$ contain the matrix elements only of the electric dipole moment density $\boldsymbol{P}$, which is the leading term in the multipole expansion of $\boldsymbol{D}$ in equation (1.31). Other such expansions of electrodynamic quantities, for instance the vector potential or the current density (Graham, Pierrus and Raab 1992), show that the electric dipole contribution stands alone as the leading term in the expansion, followed in the next term by both the electric quadrupole and magnetic dipole contributions, and then by those of the electric octopole and magnetic quadrupole. These different multipole orders have been shown theoretically to explain the various birefringences observed in non-magnetic and some magnetic crystals, in particular those listed in Table 5.5.

The well-known linear birefringence in uniaxial crystals like quartz and calcite, which occurs when propagation is perpendicular to the optic axis, and also that in biaxials, such as mica, has long been explained in terms of the difference between principal components of the electric polarizability tensor $\alpha_{\alpha\beta}$. Some values of $n_o$-$n_e$ for different crystals at room temperature and sodium yellow light are (Jenkins and White 1950)

Quartz : -0.00911

Calcite : 0.17195

For a wavelength of 632.8nm (Landolt and Bornstein 1979)

KDP : 0.0398

Because all birefringences, whatever their cause, measure the difference between two refractive indices for orthogonal polarization states, a direct comparison of observed orders of magnitude can be made for different types of birefringence. While the above linear birefringences fall typically in the approximate range $10^{-2}$ to $10^{-1}$, circular birefringence, as a traditional manifestation of optical activity, has values for $n_r$-$n_l$ exemplified as follows (American Institute of Physics Handbook):

Quartz : $7 \times 10^{-5}$ for a wavelength of 589.3nm

This is seen to be roughly two orders of magnitude smaller than the familiar linear birefringences in uniaxial and biaxial crystals. Theory shows that the tensors responsible for circular birefringence in non-magnetic uniaxial and biaxial crystals are $a_{\alpha\beta\gamma}$ and $G'_{\alpha\beta}$, with both entering the tensor expression for $n_r$-$n_l$ (For cubic crystals and isotropic fluids there is no contribution from $a_{\alpha\beta\gamma}$). Equations (3.28) and (3.33) show that $a_{\alpha\beta\gamma}$ contains matrix elements of $P_\alpha$ and the electric quadrupole moment density $Q_{\alpha\beta}$, while $G'_{\alpha\beta}$ involves both $P_\alpha$ and $M_\alpha$, the magnetic dipole moment density. Thus relative to $\alpha_{\alpha\beta}$ the tensors $a_{\alpha\beta\gamma}$ and $G'_{\alpha\beta}$ are of order electric quadrupole and magnetic dipole. Their contribution to circular birefringence is typically two orders of magnitude smaller than that of the electric dipole tensor $\alpha_{\alpha\beta}$ to linear birefringence. Despite the much smaller magnitude of $n_r$-$n_l$, it is readily measured in practice. To show this we note that the rotation of the plane of linearly polarized light through an angle $\phi$ is related to $n_r$-$n_l$ by

$$\phi = \frac{2\pi\ell}{\lambda}(n_r - n_l) \quad , \qquad \textbf{(6.1)}$$

(Jenkins and White 1950) where $\ell$ is the path length in the medium and $\lambda$ the wavelength of the light. For $\ell$=0.5cm, $\lambda$=500nm, and $n_r$-$n_l$=$10^{-4}$, one obtains

$$\phi = 2\pi\, rad = 360° \quad . \qquad \textbf{(6.2)}$$

Thus although circular birefringence in non-magnetic crystals is due to the electric quadrupole and magnetic dipole tensors $a_{\alpha\beta\gamma}$ and $G'_{\alpha\beta}$, respectively, and is typically two orders of magnitude smaller than the normal linear birefringence that characterises uniaxial and biaxial crystals, nevertheless it can be readily and accurately measured. Indeed, for many substances the rotation $\phi$ exceeds 360° for the path lengths used, and for its actual value to be certain, $\phi$ should be measured for a number of samples of different thickness.

When the theory is taken to the next multipole order, namely electric octopole-magnetic quadrupole, one is led to ask whether the birefringence, due to tensors of this order, as indicated in Table 5.5, are too small to be measurable. The experimental record shows that Lorentz measured a linear birefringence of about $10^{-6}$ in a crystal of rock salt (1922), following his prediction of this effect in certain cubic crystals (1878). Subsequent measurements by others (Pastrnak and Vedam 1971, Pastrnak and Cross 1971) of a linear birefringence in a variety of non-magnetic cubic crystals yielded a similar order of magnitude. A theoretical explanation of this birefringence in terms of electric octopole and magnetic quadrupole contributions was published in 1990 (Graham and Raab), and this is confirmed for certain magnetic cubic crystals in the present work, as Table 5.5 shows.

The conclusion from the last paragraphs is that, where a birefringence is shown by theory to be due to non-magnetic polarizability tensors of multipole orders up to and including electric octopole-magnetic quadrupole, its accurate measurement is experimentally possible, at least where it is the only birefringence occurring for a given light path. Where two birefringences of different multipole origin occur simultaneously, as for propagation perpendicular to the optic axis in quartz, for example, where both linear and circular birefringences exist, special techniques may be used, for instance the method of intensity differentials (Raab 1975), high-precision polarimetry (Kobayashi and Uesu 1983, Kobayashi et al 1983), and the tilter method (Kaminsky and Glazer 1996).

In order for the various optical properties of a crystal to be identifiable from Table 5.5, we need to know which of the property tensors are associated with each optical effect. The tensor $\alpha_{\alpha\beta}$ is the polarizability tensor which accounts for first-order refraction effects in matter.

$G'_{\alpha\beta}$ and $a_{\alpha\beta\gamma}$ describe optical activity, which has been described previously in this chapter. Hobden's method (1968, 1969) experimentally confirmed optical activity in the non-magnetic tetragonal classes $\bar{4}2m$ and $\bar{4}$. In this method, Hobden exploited the intersection of the dispersion curves of the refractive indices of the ordinary and extraordinary rays to enable him to measure optical activity without the presence of the much larger effect of a linear birefringence.

The tensors $b_{\alpha\beta\gamma\delta}$, $d_{\alpha\beta\gamma\delta}$, $H'_{\alpha\beta\gamma}$, $L'_{\alpha\beta\gamma}$, and $\chi_{\alpha\beta}$ are related to second order refraction phenomena, for instance linear birefringence in cubic crystals, which was first predicted on grounds of symmetry by Lorentz in rock salt and then in m3 crystals by Condon and Seitz (1932) and later explained by Graham and Raab (1990), and the Jones birefringence in certain non-magnetic crystals (Jones 1948, Graham and Raab 1983, Graham and Raab 1994). A linear birefringence in cubic crystals has been observed (Lorentz 1922, Pastrnak and Vedam 1971, Pastrnak and Cross 1971). Table 5.5 confirms this higher-order linear birefringence in the cubic classes 23, m3, and $\underline{m}3$. The Jones birefringence has been predicted for the non-magnetic classes 32 and $\bar{3}m$ (Graham and Raab 1994), and in Table 5.5 is also predicted for the magnetic class $\underline{\bar{3}m}$.

Pastrnak and Vedam (1971) measured the magnitude of electric octopole-magnetic quadrupole effects to be $\Delta n \approx 5 \times 10^{-6}$. Because many magnetic crystals are strongly coloured it may prove difficult to work in the region of an absorption band, but where this is possible the magnitude of such a higher-order effect would be greatly enhanced.

Of the time-odd tensors, $\alpha'_{\alpha\beta}$ exists only for crystals which possess a spontaneous magnetic moment, and it describes the intrinsic Faraday effect in ferromagnetic materials (Suits, Argyle and Freiser 1966, Graham and Raab 1991a). Crystals for which the $\alpha'_{\alpha\beta}$ tensor vanishes identically are antiferromagnetic.

The second-rank axial *c*-tensor $G_{\alpha\beta}$ and the third-rank polar *c*-tensor $a'_{\alpha\beta\gamma}$ give rise to non-reciprocal linear birefringence in magnetic crystals, either a linear birefringence relative to the crystallographic axes, or a Jones birefringence relative to the bisectors of these axes. Being non-reciprocal, these birefringences change sign when the light path is reversed. This property should enable them to be seperated experimentally from reciprocal effects due to *i*-tensors.

For N-rays the tensors $b'_{\alpha\beta\gamma\delta}$, $d'_{\alpha\beta\gamma\delta}$, $H_{\alpha\beta\gamma}$, $L_{\alpha\beta\gamma}$, and $\chi'_{\alpha\beta}$ of electric octopole-magnetic quadrupole are responsible for a Faraday-type rotation. For z-propagation this is always accompanied by the much larger contribution due to the electric dipole *c*-tensor $\alpha'_{\alpha\beta}$, so that the higher-order effect would be impossible to detect. However, for propagation along the x-axis in certain trigonal and hexagonal crystals, these tensors contribute independently of the $\alpha'_{\alpha\beta}$ tensor, and should thus, in principle, be measurable. Table 5.5 indicates that all the crystals for which this effect has been predicted are antiferromagnetic. This is surprising, as these crystals possess no net magnetic dipole moment which would be associated with an internal magnetic field producing the Faraday-type rotation. A similar effect has been predicted for propagation along the body-diagonal in cubic antiferromagnets. (Graham and Raab 1991)

Some of the optical effects predicted in Table 5.5 merit particular discussion. In 1963 Brown, Shtrikman and Treves reported their theoretical study of the optical properties of magnetic materials using symmetry considerations and found that in addition to the expected effects of linear birefringence and optical activity, both of which are reciprocal, and a non-reciprocal (Faraday-type) rotation, certain magnetic crystals should exhibit a new spontaneous optical effect, namely a non-reciprocal gyrotropic birefringence. Subsequently Hornreich and Shtrikman (1968) found this birefringence to manifest itself as a rotation of the principal optical axes together with a change in the velocity of propagation of the wave in the medium. Whereas ferromagnetic crystals with their net magnetic dipole moment may exhibit a non-reciprocal rotation, gyrotropic birefringence may exist in the absence of such a moment. In addition, these authors recognised that this effect is due not only to the magnetoelectric tensor, as Birss and Shrubsall (1967) had predicted, but that it depends also on electric quadrupole contributions. Graham and Raab (1994) showed that the gyrotropic birefringence predicted in $Cr_2O_3$ by Hornreich and Shtrikman (1968) can be decomposed into three linear birefringences: the usual reciprocal property relative to crystallographic axes, a non-reciprocal birefringence relative to these same axes, and a non-reciprocal Jones birefringence relative to the bisectors of these axes.

From Table 5.5 it is clear that there is a number of crystal classes in which the non-reciprocal Jones birefringence and a normal linear birefringence occur simultaneously for propagation perpendicular to the optic axis. The crystals belonging to these classes are thus considered to be gyrotropic. Most of these crystals are magnetoelectric, having a non-zero ***G*** tensor which contributes to the Jones birefringence. The relevant point groups are 422, $\underline{4}22$, $\bar{4}2m$, $\underline{\bar{4}}2\underline{m}$, $4/\underline{mmm}$, $\underline{4}/\underline{m}m\underline{m}$, 32, $\bar{3}\underline{m}$, 622, $\bar{6}\underline{m}2$, and $6/\underline{mmm}$.

It is of interest to note that there is one point group in which a reciprocal Jones birefringence occurs simultaneously with a linear birefringence for propagation perpendicular to the optic axis, namely the point group $\bar{3}m$. In this case the Jones birefringence would be difficult to detect, as it arises from the electric octopole-magnetic quadrupole tensors ***L'***, ***H'***, ***b***, and ***d***. This is an instance in which the Jones birefringence may exist in a medium which does not exhibit gyrotropic birefringence, if this term is understood in its original sense of being non-reciprocal.

There are a few point groups where, for propagation along the optic axis, the non-reciprocal Jones birefringence coexists with a non-reciprocal linear birefringence, both due to the *c*-tensors ***G*** and ***a'***. These groups are $\underline{4}$, $\bar{4}$, and $\underline{4}/\underline{m}$. This result is consistent with earlier predictions that gyrotropic birefringence linear in ***G*** should occur for z-propagation in tetragonal crystals when $G_{xx}=-G_{yy}$ (Bonfim and Gehring 1980), and when

$G_{xy}$=-$G_{yx}$ (Ferré and Gehring 1984).

The Jones birefringence was predicted for the above 15 uniaxial magnetic point groups by Graham and Raab (1983).

Contrary to the findings of Birss and Shrubsall (1967), there are some gyrotropic crystals in which the magnetoelectric tensor vanishes. These are the cubic point groups 23 and $\underline{m}3$, which exhibit a non-reciprocal Jones birefringence linear in ***a'***. The latter effect was predicted by Graham and Raab (1992).

Where in Table 5.5 a birefringence relative to the bisectors of the crystallographic axes occurs in the absence of normal linear birefringence, as in the point groups $\underline{4}22$, $\underline{4}m\underline{m}$, $\bar{4}2m$, $\bar{4}\underline{2}\underline{m}$, and $\underline{4}/\underline{m}m\underline{m}$ for z-propagation, and $\underline{4}3\underline{2}$, $\bar{4}3m$, and $\underline{m}3m$ for x-, y-, or z-propagation, the former is not considered a true Jones birefringence, as it may be expressed as the normal effect with its fast and slow axes rotated through an angle of 45°.

## 6.2 IDENTIFICATION OF CRYSTALS

Table 6.1 contains a listing of the magnetic uniaxial and cubic point groups which can be uniquely distinguished from the other magnetic symmetry classes through birefringence measurements. Since the different non-magnetic point groups to which the various magnetic crystals belong can be distinguished from one another through X-ray diffraction techniques, it suffices that magnetic crystals need only be uniquely identifiable within each non-magnetic point group. This table indicates that 58 of the 70 uniaxial and cubic crystals can be uniquely identified in this way. The 12 crystal classes which are not able to be uniquely identified are listed in Table 6.2.

The distinguishing birefringences of the point groups listed in Table 6.1 provide in principle an alternative approach to neutron diffraction for the determination of the magnetic point groups of the relevant crystals.

## Table 6.1 List of Uniquely Identifiable Crystal Groups

| | | z-Propagation | | | | y-Propagation | | | | x-Propagation | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| stem | Group | N-Rays? | $(n_y-n_x)$ | $(n_- - n_+)$ | $(n_r-n_l)$ | N-Rays? | $(n_x-n_z)$ | $(n_- - n_+)$ | $(n_r-n_l)$ | N-Rays? | $(n_z-n_y)$ | $(n_- - n_+)$ | $(n_r-n_l)$ |
| ragonal | 4 | Yes | 0 | 0 | α'G'ab'd'LHχ' | No | - | - | - | No | - | - | - |
| | $\underline{4}$ | Yes | Ga' | Ga' | G'a | No | - | - | - | No | - | - | - |
| | $\bar{4}$ | Yes | Ga' | Ga' | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\underline{\bar{4}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | 4/m | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\underline{4}/\underline{m}$ | Yes | Ga' | Ga' | 0 | No | - | - | - | No | - | - | - |
| | 422 | Yes | 0 | 0 | G'a | Yes | αL'H'bdχ | Ga' | G'a | Yes | αL'H'bdχ | Ga' | G'a |
| | $\underline{4}22$ | Yes | (Ga') | 0 | G'a | Yes | αL'H'bdχ | Ga' | G'a | Yes | αL'H'bdχ | Ga' | G'a |
| | $4\underline{22}$ | Yes | 0 | 0 | α'G'aLHb'd'χ' | No | - | - | - | No | - | - | - |
| | 4mm | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{4}m\underline{m}$ | Yes | (Ga') | 0 | 0 | No | - | - | - | No | - | - | - |
| | $4\underline{mm}$ | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\bar{4}2m$ | Yes | (Ga') | 0 | 0 | Yes | αL'H'bdχ | Ga' | G'a | Yes | αL'H'bdχ | Ga' | G'a |
| | $\underline{\bar{4}}2\underline{m}$ | Yes | 0 | 0 | 0 | Yes | αL'H'bdχ | Ga' | G'a | Yes | αL'H'bdχ | Ga' | G'a |
| | $\underline{\bar{4}2}m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\bar{4}\underline{2m}$ | Yes | (Ga') | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $4/m\underline{mm}$ | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $4/\underline{mmm}$ | Yes | 0 | 0 | 0 | Yes | αL'H'bdχ | Ga' | 0 | Yes | αL'H'bdχ | Ga' | 0 |
| | $4/\underline{m}mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{4}/\underline{m}m\underline{m}$ | Yes | (Ga') | 0 | 0 | Yes | αL'H'bdχ | Ga' | 0 | Yes | αL'H'bdχ | Ga' | 0 |
| gonal | 3 | Yes | 0 | 0 | α'G'aLHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\bar{3}$ | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\underline{\bar{3}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | 32 | Yes | 0 | 0 | G'a | No | - | - | - | Yes | αa'L'H'bdχ | Ga'L'H'bd | G'aLHb'd' |
| | $3\underline{2}$ | Yes | 0 | 0 | α'G'aLHb'd'χ' | No | - | - | - | No | - | - | - |
| | 3m | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $3\underline{m}$ | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\bar{3}m$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | αL'H'bdχ | L'H'bd | LHb'd' |
| | $\bar{3}\underline{m}$ | Yes | 0 | 0 | α'LHb'd'χ' | No | - | - | - | No | - | - | - |
| | $\underline{\bar{3}m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | αa'L'H'bdχ | Ga'L'H'bd | 0 |
| | $\underline{\bar{3}}m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |

| | | *z*-Propagation | | | | *y*-Propagation | | | | *x*-Propagation | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| System | Group | *N*-Rays? | $(n_y - n_x)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *N*-Rays? | $(n_x - n_z)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *N*-Rays? | $(n_z - n_y)$ | $(n_- - n_+)$ | $(n_r - n_l)$ |
| Hexagonal | $6$ | Yes | 0 | 0 | $\alpha'G'aLHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\underline{6}$ | Yes | 0 | 0 | $G'a$ | No | - | - | - | No | - | - | - |
| | $\bar{6}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\underline{\bar{6}}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $6/m$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $622$ | Yes | 0 | 0 | $G'a$ | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $G'a$ | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $G'a$ |
| | $\underline{6}2\underline{2}$ | Yes | 0 | 0 | $G'a$ | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | $G'aLHb'd'$ |
| | $6\underline{22}$ | Yes | 0 | 0 | $\alpha'G'aLHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6\underline{mm}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $\bar{6}m2$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | 0 |
| | $\underline{\bar{6}}\underline{m}2$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | $LHb'd'$ |
| | $\underline{\bar{6}}m\underline{2}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\bar{6}\underline{m2}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6/mmm$ | Yes | 0 | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | 0 | 0 |
| | $\underline{6}/\underline{m}m\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha L'H'bd\chi$ | 0 | $LHb'd'$ |
| | $6/m\underline{mm}$ | Yes | 0 | 0 | $\alpha'LHb'd'\chi'$ | No | - | - | - | No | - | - | - |
| | $6/\underline{mmm}$ | Yes | 0 | 0 | 0 | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | 0 | Yes | $\alpha L'H'bd\chi$ | $Ga'$ | 0 |
| | $6/\underline{m}mm$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}/mm\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | Yes | $\alpha a'L'H'bd\chi$ | 0 | 0 |
| Cubic | $23$ | Yes | $L'H'b$ | $a'$ | $G'$ | Yes | $L'H'b$ | $a'$ | $G'$ | Yes | $L'H'b$ | $a'$ | $G'$ |
| | $m3$ | Yes | $L'H'b$ | 0 | 0 | Yes | $L'H'b$ | 0 | 0 | Yes | $L'H'b$ | 0 | 0 |
| | $\underline{m}3$ | Yes | $L'H'b$ | $a'$ | 0 | Yes | $L'H'b$ | $a'$ | 0 | Yes | $L'H'b$ | $a'$ | 0 |
| | $432$ | Yes | 0 | 0 | $G'$ | Yes | 0 | 0 | $G'$ | Yes | 0 | 0 | $G'$ |
| | $\underline{4}3\underline{2}$ | Yes | $(a')$ | 0 | $G'$ | Yes | $(a')$ | 0 | $G'$ | Yes | $(a')$ | 0 | $G'$ |
| | $\bar{4}3m$ | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 |
| | $\underline{\bar{4}}3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $\underline{m}3m$ | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 | Yes | $(a')$ | 0 | 0 |

## Table 6.2 List of Indistinguishable Crystal Groups

| | | | *z*-Propagation | | | | *y*-Propagation | | | | *x*-Propagation | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| System | Group | *N*-Rays? | $(n_y - n_x)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *N*-Rays? | $(n_x - n_z)$ | $(n_- - n_+)$ | $(n_r - n_l)$ | *N*-Rays? | $(n_z - n_y)$ | $(n_- - n_+)$ | $(n_r - n_l)$ |
| Tetragonal | $\underline{4}/m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $4/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | 4/mmm | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 |
| | $\underline{4}/mm\underline{m}$ | Yes | 0 | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 | Yes | *αL'H'bdχ* | 0 | 0 |
| Hexagonal | $\underline{6}/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $6/\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}/m$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | 6mm | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| | $\underline{6}m\underline{m}$ | Yes | 0 | 0 | 0 | No | - | - | - | No | - | - | - |
| Cubics | m3m | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $m3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |
| | $\underline{m}3\underline{m}$ | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 | Yes | 0 | 0 | 0 |

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