Application of the high-accuracy universal polarimeter to magnetic and absorbing crystals

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Abstract. In this paper we show that the high-accuracy universal polarimeter can be used to investigate the optical properties of (almost) any crystal through which light can be transmitted. The only extra condition is that the reciprocal linear birefringence (or the reciprocal linear dichroism) of the sample is large with respect to the other optical effects that are present. The sample is allowed to exhibit reciprocal linear birefringence and reciprocal circular birefringence. This is the situation for which the high-accuracy universal polarimeter was originally intended. We show, however, that reciprocal linear dichroism and reciprocal circular dichroism may also be present. The method can, therefore, be applied to (weakly) absorbing crystals. Furthermore, optical effects are taken into account that are related to the breaking of time-reversal symmetry. These are the non-reciprocal circular birefringence, non-reciprocal circular dichroism, non-reciprocal linear birefringence and non-reciprocal linear dichroism. This means that, under some conditions, each (weakly) absorbing, magnetic crystal can be investigated with the high-accuracy universal polarimeter. We derive a unified formula for the intensity change of the light that propagates through the polarimeter. This expression can be used to determine the (complex) eigenpolarizations of an arbitrary sample. Moreover, it is shown how this unified formula can be translated to a formula in terms of the different birefringent and dichroic optical effects. The relevant formula for a specific case can, therefore, be given directly. The method is demonstrated by means of measurements on samples of NiSO₄·6H₂O. This material shows reciprocal linear birefringence, reciprocal linear dichroism, reciprocal circular birefringence and reciprocal circular dichroism, simultaneously.

1. Introduction

The study of optical properties of single crystals has a long tradition. Nowadays, it is still very important. The main reason for this lies in the fact that optical effects in crystals are symmetry-dependent, tensorial properties. Whenever new crystalline phases are discovered that have interesting physical properties, optical studies are likely to be performed in order to study the symmetry. In addition, the occurrence of a phase transition into such a phase can be detected by means of optical measurements, because optical properties depend on the order parameter. Also fluctuations of the order parameter may be detected (Ferré and Gehring 1984). Furthermore, optical properties can be related to the band structure of a material, especially in the case of absorbing crystals.

The (new) crystalline phases that are currently of interest often have complicated structures. The symmetry of these phases is not always clear in advance. Consider, for example, the high-$T_c$ superconductors that are the subject of many investigations. It has been proposed that so-called anyons, these being excitations that obey fractional statistics, exist in these materials (Kalmeyer and Laughlin 1987, Laughlin 1988a, 1998b). The anyons are supposed to break both the spatial inversion and the time-reversal symmetry (Wen and Zee 1989, Halperin et al 1989, Kitazawa 1990, Dzyaloshinskii 1991). Many optical experiments have been performed, see Fabre and Boccara (1992) and references therein, with the aim of detecting this symmetry-breaking. The relevant optical effects that were (supposedly) observed were very small. Therefore, a serious dispute remained and, to our knowledge, the situation has not yet been clarified.

A second example of crystals with an involved structure is given by the magneto-electric crystals. In these crystals an electric polarization can be induced by an applied magnetic field and a magnetization can result from the action of an applied electric field (O’Dell et al 1963). It has been predicted that a new optical effect can exist in these magneto-electric crystals, even when no external field is applied.
It is a result of the coupling between the electric and magnetic field of the light itself. The effect is called gyrotropic, non-reciprocal or Jones birefringence (Hornreich and Shtrikman 1968, Graham and Raab 1992). Throughout this paper we use the name non-reciprocal linear birefringence. It can give rise to a shift of the principal axes of linear birefringence and a change in the propagation velocity of plane electromagnetic waves. Hornreich and Shtrikman (1968) have estimated that the shift of the principal axes is of the order of $10^{-6}$ rad, which is extremely small. As far as we know, the only experimental indication for the existence of non-reciprocal linear birefringence has been reported by Pisarev et al (1991).

As a last example, we want to discuss the case of incommensurately modulated crystals (de Wolff 1974, Janner and Janssen 1977, de Wolff et al 1981, Janner et al 1983). In these crystals an extra periodicity, the modulation, is present, which is incommensurate with the basic three-dimensional translation lattice. Therefore, the corresponding three-dimensional lattice translational symmetry is broken. It has been suggested that, for example, spatial inversion symmetry can be broken due to the presence of the modulation (Uesu and Kobayashi 1985, Kobayashi et al 1986, Meekes and Janner 1988). This has been tested by measuring the optical activity (that is, the reciprocal circular birefringence) of these crystals (see, for the most recent results, Kobayashi et al (1994) and references therein). Optical activity cannot exist in a centrosymmetric medium. In a number of cases, it has been claimed that a very small but non-zero optical activity was measured in these incommensurately modulated crystals that are, on the average, centrosymmetric. However, also these measurements remain disputed (Ortega et al 1994, Kremers and Meekes 1995, Kremers et al 1994).

There are clear resemblances between the just-described examples. In all cases, one searches for very subtle optical effects. Their measurement is usually complicated by the presence of other, much larger optical effects. The crystals are mostly optically anisotropic and in many cases also absorbing. Therefore, the subtle effects have to be separated from birefringent as well as dichroic properties in an appropriate way. Unfortunately, many experiments are still performed in which the contribution of these optical effects is conveniently neglected or wrongly taken into account. In this paper, we investigate how the high-accuracy universal polarimeter can be put to use for the correct measurement of subtle optical effects in crystals that are both birefringent and dichroic.

The high-accuracy universal polarimeter (HAUP) was introduced by Kobayashi and Uesu (1983) for the measurement of a small reciprocal circular birefringence in the presence of a considerably larger reciprocal linear birefringence. One of the important principles of this polarimetric method is that the optical system is kept very simple. In fact, it only consists of a polarizer, the sample and a second polarizer, called the analyser. In this way, the number of systematic errors that have to be taken into account is kept minimal. Furthermore, the rotation angles of both polarizers are restricted to a small range. This allows for the derivation of the so-called HAUP intensity formula, which expresses the intensity of the light, propagated through the optical system, as a function of the rotation angles of the polarizers, the properties of the sample and the intrinsic systematic errors. By fitting the intensities, measured at different combinations of polarizer angles, to the HAUP intensity formula one is able to detect values of reciprocal circular birefringence that are smaller than the magnitude of the systematic errors. Simultaneously, the reciprocal linear birefringence is found. Moreover, the rotation of the principal axes of this birefringence can also be obtained. It has been shown by Moxon and Renshaw (1990) that the HAUP method can also be applied to detect a small reciprocal linear and reciprocal circular dichroism in the presence of a considerably larger reciprocal linear birefringence (see also Moxon et al (1991)).

With this paper, we extend the HAUP method, so that it can be applied to absorbing crystals of all (magnetic) symmetry classes. First, it is explained how the optical properties of such a crystal can be described both in terms of material tensors and in terms of parameters that were given by Jones (1948). It is shown that the latter description is more convenient. Therefore, we want to derive the HAUP intensity formula in terms of the Jones parameters. It is realized, however, that there are many cases in which either the reciprocal linear birefringence or the reciprocal linear dichroism is large with respect to the additional optical effects. The most important goal of this paper is to show that these cases can be unified in one HAUP intensity formula. This formula is expressed in terms of the eigenpolarizations of a general sample. Subsequently, specific examples are discussed. The crystal is taken to be linearly birefringent and dichroic for all examples. The principal axes of both effects are assumed to be the same. The use of HAUP is discussed for the case that, in addition, small reciprocal circular birefringence and reciprocal circular dichroism are present. This case is demonstrated by means of measurements on NiSO$_4$·6H$_2$O. Furthermore, the case is studied in which the principal axes of reciprocal linear dichroism and reciprocal linear birefringence do not coincide. Finally, it is shown that it should be possible to detect the non-reciprocal linear birefringence in magneto-electric crystals.

2. The description of linear optical properties of crystals

The study of the linear optical properties of crystals usually starts with the investigation of the so-called proper waves. These are plane waves that can propagate in the crystal without a change in their polarization. The proper waves are found by solving the Fresnel equations, namely the combination of the Maxwell equations and the constitutive equations for plane waves (see, for example, Ramachandran and Ramaseshan (1961)). The
Table 1. Descriptions of optical effects that can occur in transmission optical measurements; R=reciprocal, N=non-reciprocal. Both the description in terms of specific parts of material tensors and in terms of Jones parameters is given. Furthermore, the occurrence (+) or absence (−) of the effects is indicated for non-absorbing crystals and for non-magnetic crystals.

<table>
<thead>
<tr>
<th>Optical effect</th>
<th>Material tensor</th>
<th>Occurrence in non-absorbing crystals</th>
<th>Occurrence in non-magnetic crystals</th>
<th>Corresponding parameter in Jones calculus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 R Linear birefringence</td>
<td>$e^a$</td>
<td>+</td>
<td>+</td>
<td>$g_{0} = (\pi/\lambda)\left(n_{\perp} - n_{\parallel}\right)$</td>
</tr>
<tr>
<td>2 R Linear dichroism</td>
<td>$e^{78}$</td>
<td>−</td>
<td>+</td>
<td>$p_{0} = (\pi/\lambda)(\kappa_{\perp} - \kappa_{\parallel})$</td>
</tr>
<tr>
<td>3 N Circular birefringence</td>
<td>$e^{18}$</td>
<td>+</td>
<td>−</td>
<td>$\omega = (\pi/\lambda)(h_{\parallel} - h_{\perp})$</td>
</tr>
<tr>
<td>4 N Circular dichroism</td>
<td>$e^a$</td>
<td>−</td>
<td>+</td>
<td>$\delta = (\pi/\lambda)(\kappa_{\parallel} - \kappa_{\perp})$</td>
</tr>
<tr>
<td>5 R Circular birefringence</td>
<td>$y^{1a}$</td>
<td>+</td>
<td>−</td>
<td>$g_{20} = (\pi/\lambda)(n_{\perp} - n_{\parallel})$</td>
</tr>
<tr>
<td>6 R Circular dichroism</td>
<td>$y^{18}$</td>
<td>−</td>
<td>+</td>
<td>$p_{20} = (\pi/\lambda)(\kappa_{\perp} - \kappa_{\parallel})$</td>
</tr>
<tr>
<td>7 N Linear birefringence</td>
<td>$y^{78}$</td>
<td>+</td>
<td>−</td>
<td>$g_{24} = (\pi/\lambda)(n_{\perp} - n_{\parallel})$</td>
</tr>
<tr>
<td>8 N Linear dichroism</td>
<td>$y^{78}$</td>
<td>−</td>
<td>+</td>
<td>$p_{24} = (\pi/\lambda)(\kappa_{\perp} - \kappa_{\parallel})$</td>
</tr>
</tbody>
</table>

Linear optical properties of a crystal depend, therefore, on the material tensors in the constitutive equations. In the case that the frequency of the light is far from the natural magnetic resonance frequencies, the magnetic permeability tensor $\mu$ can be approximated very well by the unit tensor. The constitutive equations then become (in Gaussian units)

$$D_i(r) = \varepsilon_{ij} E_j(r) + \gamma_{ijk} \frac{\delta E_j(r)}{\delta r_k}$$

This is the case that we treat in this paper. The tensor $\varepsilon$ specifies the local response and the tensor $\gamma$ specifies the non-local response of the medium. The wavelength $\lambda$ of the light is long with respect to typical lattice constants $a$ of crystals. The effects originating from the non-local response, therefore, have a magnitude of the order of $a/\lambda$ with respect to the effects caused by the local response (Agranovich and Ginzburg 1984).

A classification of optical effects can be given by separating the tensors $\varepsilon$ and $\gamma$ into real, imaginary, symmetric and antisymmetric parts:

$$\varepsilon = \varepsilon^{\text{re}} + \varepsilon^{\text{im}} = \varepsilon^a + i(\varepsilon^{78} + \varepsilon^{87})$$

$$\gamma = \gamma^{\text{re}} + \gamma^{\text{im}} = \gamma^a + i(\gamma^{78} + \gamma^{87})$$

where a single prime denotes the real part and a double prime the imaginary part. The symbols $s$ and $a$ denote that the tensor is, respectively, symmetric or antisymmetric in its first two indices.

In table 1 the possible optical effects are associated with the different parts of the tensors $\varepsilon$ and $\gamma$. Each of the optical effects can be described by two proper waves that have different polarizations and that propagate with different velocities, for each direction in the crystal. The polarizations of the proper waves are orthogonal in the case that the crystal is non-absorbing. Moreover, the propagation velocities are real in that case. They become complex, however, if the crystal does absorb light, in which case the polarizations of the proper waves are no longer necessarily orthogonal.

In magnetic crystals the effects associated with $\varepsilon^a$ or with $\gamma^a$ are allowed, contrary to the case in non-magnetic crystals. These effects are non-reciprocal; the (complex) velocities of the proper wave change if the light path is reversed. However, without changing the propagation direction of the light with respect to the sample, it is still possible to separate non-reciprocal linear birefringence from reciprocal linear birefringence and non-reciprocal linear dichroism from reciprocal linear dichroism. On the other hand, the non-reciprocal circular birefringence cannot be distinguished from reciprocal birefringence and non-reciprocal circular dichroism cannot be distinguished from reciprocal circular dichroism in this way.

The tensor $\varepsilon$ has, in principle, nine different complex elements, whereas the tensor $\gamma$ can have 27 different complex elements. This means that the optical properties of a general absorbing and magnetic crystal are determined by $2 \times 36$ different numbers. It is obvious, therefore, that a description that uses the full tensors $\varepsilon$ and $\gamma$ is not convenient for the interpretation of optical experiments. In an experiment, usually one sample is present, which is traversed by the light in a specific direction. For this orientation, one wants to measure the values of each of the eight possible optical effects in table 1. A description that is very well suited for such an approach is the Jones matrix calculus (Jones 1948). It must be emphasized that this calculus was derived by Jones using a superposition method. In most cases this gives the same solutions as those that follow from solving the Fresnel equations. Sometimes, however, the Jones calculus gives different results. An example is the case of light propagating in the neighbourhood of an optic axis (the direction of zero reciprocal linear birefringence) in an optically active, biaxial crystal (Ramachandran and Ramaseshan 1961).

In this paper we use the Jones matrix calculus, but we consider only those cases for which either the reciprocal linear birefringence or the reciprocal linear dichroism is relatively large, so that the superposition method is valid (Ramachandran and Ramaseshan 1961).

The parameters that were introduced by Jones (1948) for the various optical effects have also been given in table 1. They can all be expressed in terms of a...
difference of two indices. Both the symbol $\omega$ and the symbol $\delta$ appear twice in table 1. This indicates that, in the case of the circular optical effects, it is not possible to separate reciprocal effects from non-reciprocal effects if only one direction of light propagation is used.

In the case of a general sample and light entering at normal incidence, the electric field $E(z)$ at distance $z$ from the entrance surface is determined by the Jones matrix $\mathbf{S}$ according to $E(z) = \mathbf{SE}(0)$. The Jones matrix $\mathbf{S}$ can be written in terms of the Jones parameters (Jones 1948):

$$\mathbf{S} = \exp(T_Nz) \left( \cosh(Q_Nz) + (p_0 + ig_0) \sinh(Q_Nz) / Q_N \right) \left( (p_{45} + ig_{45}) - (\omega + i\delta) \right) \sinh(Q_Nz) / Q_N^{2} \left( \cosh(Q_Nz) + (p_0 + ig_0) \sinh(Q_Nz) / Q_N \right)$$

(2)

where

$$T_N = -\frac{2\pi}{\lambda} (\vec{k} + i\vec{n})$$

$$\vec{n} = \frac{n_1 + n_2}{2}$$

$$\vec{k} = \frac{k_1 + k_2}{2}$$

$$Q_N = (p_0 + ig_0)^2 + (p_{45} + ig_{45})^2 - (\omega + i\delta)^2.$$  

The proper waves of a sample can be represented by the eigenvectors of the corresponding Jones matrix $\mathbf{S}$. If the crystal is non-absorbing $p_0$, $\delta$ and $p_{45}$ equal zero. The Jones matrix is then unitary. Consequently, the eigenvectors are orthogonal (Jones 1942). In the case that the crystal is absorbing, the eigenvectors can be non-orthogonal. At this point we want to remark that, in the use of the Jones matrix calculus, one neglects the possibility of multiple internal reflections in the sample. Moxon and Renshaw (1990) have estimated the magnitudes of the errors that can be introduced in this way.

Before using the Jones matrix of equation (2) for several specific cases, however, we construct another Jones matrix $\mathbf{S}$ in terms of the parameters that define two general eigenpolarizations (that is, proper waves), the magnitudes of the errors that can be introduced in the crystal is non-absorbing this way.

The basic HAUP set-up that is used in our laboratory has been described by Dijkstra et al (1991). Several changes were made in this set-up, which have been reported by Kremers and Meekes (1995). In the latter reference the HAUP intensity formula was re-derived for the case of small reciprocal circular birefringence in the presence of considerably larger reciprocal linear birefringence. Here, the HAUP intensity formula is derived in a similar way.

In figure 1 the basic optical system of HAUP is presented. The vectors $n_1$ and $n_2$ indicate the principal axes of the linear birefringence. If the crystal is non-absorbing, these coincide with the main axes of the (elliptic) polarizations of the proper waves. The polarizer is represented by a Jones vector $\mathbf{P}$. The polarization direction of the light emerging from the polarizer is represented by the angle $\Theta$. This angle is measured with respect to one of the directions $n_{i=1,2}$. The angle $\Lambda$ denotes, in a similar way, the polarization direction of the analyser with respect to the other direction $n_{i=2,1}$. Consequently, the polarizers are crossed when $\Theta = \Lambda$. A HAUP measurement with the origin for $\Theta$ close to $n_1$ is called the measurement of the first extinction direction. If the sample is rotated over $\frac{\pi}{2}$ rad, then $\Theta$ is measured with respect to $n_2$ as in figure 1. The second extinction direction can then be measured.

Even polarizers of very high quality do not perfectly polarize light. The polarization of the light emerging from them is still slightly elliptical. The corresponding ellipticities, denoted $p$ and $a$ respectively, have a magnitude of the order of $10^{-4}$. These are two of the systematic errors that are taken into account in the HAUP method. The Jones vectors of these non-ideal polarizers are (Dijkstra et al 1991)

$$\mathbf{P} = \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \begin{pmatrix} \cos \Theta \cos p - i \sin \Theta \sin p \\ \sin \Theta \cos p + i \cos \Theta \sin p \end{pmatrix}$$

(3)

$$\mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} -\sin \Lambda \cos a - i \cos \Lambda \sin a \\ \cos \Lambda \cos a - i \sin \Lambda \sin a \end{pmatrix}.$$  

The intensity change $\Gamma / \Gamma_0$ can be calculated if the Jones matrix $\mathbf{S}$ is specified:

$$\Gamma / \Gamma_0 = |\mathbf{A}^{\dagger} \mathbf{S} \mathbf{P}|^2.$$  

(4)

In some cases (see Dijkstra et al (1991)) it is possible to derive an explicit expression $\Gamma / \Gamma_0(\Theta, \Lambda)$ for arbitrary positions of both polarizer and analyser. Nevertheless, that expression cannot be used as such in order to extract the desired information by fitting the measured intensities.

It was realized by Kobayashi and Uesu (1983), however, that it is nowadays possible to set polarizers at positions with an accuracy of about $5 \times 10^{-6}$ rad. Therefore, the angles $\Theta$ and $\Lambda$ can be restricted to values within a range that is comparable to the magnitude...
of the systematic errors \( (\mathcal{O}(10^{-4})) \) that are present. Consequently, it is possible to expand the HAUP intensity formula \( (4) \) up to low-order terms in the angles \( \Theta \) and \( \Lambda \), in the systematic errors and in any optical parameter in the Jones matrix \( S \) that is expected to be small. The thus-obtained HAUP intensity formula can then be used to fit intensities that have been measured for a set of different polarizer angles within the above-mentioned small range.

In the next section, we first derive a HAUP intensity formula in terms of the parameters that describe two general complex eigenpolarizations. The result can be considered to be the unified HAUP intensity formula. It can be used to determine, for any sample, the complex ellipticities of the eigenpolarizations simultaneously with the (complex) birefringence. Usually, however, one is interested in measuring the values of specific optical effects as they have been given in table 1. Therefore, the HAUP intensity formula is subsequently derived by using the Jones matrix \( (2) \). It is shown that the result is analogous to the unified HAUP intensity formula. Therefore, it is possible to give expressions for the complex ellipticity angles of the eigenpolarizations in terms of the Jones parameters. The shapes of the eigenpolarizations that one finds in this way, for specific examples, agree with those that can be derived from the corresponding material tensors \( \varepsilon \) and \( \gamma \) by means of the Fresnel equations.

### 3.1. The unified HAUP intensity formula

A general polarization state of light is represented by figure 2. It is characterized by the azimuth angle \( \psi \in [0, \pi] \) and the ellipticity angle \( \chi \in [-\pi/4, \pi/4] \). The azimuth angle \( \psi \) is the angle between the major axis of the ellipse of vibration and the positive direction of the \( x \) axis of the reference coordinate system. The
ellipticity angle \( \chi \) is the arctangent of the ellipticity angle \( \varepsilon \). This ellipticity is defined as the ratio of the minor axis length and the major axis length. Its sign is positive for right-handed polarized light and negative for left-handed polarized light. The polarization state in figure 2 can be represented by a two-dimensional complex vector \( \mathbf{J} \) in the Jones matrix calculus:

\[
\mathbf{J} = \begin{pmatrix} \cos \psi \cos \chi - i \sin \psi \sin \chi \\ \sin \psi \cos \chi + i \cos \psi \sin \chi \end{pmatrix}.
\]

(5)

In principle, two independent eigenpolarizations exist for light propagating in a certain direction in a crystal, but for all cases that we consider the major axes of the two corresponding ellipses of vibration are orthogonal to each other. We do take, however, arbitrary ellipticities for both eigenpolarizations:

\[
x_1 = k_s - k_a
\]

\[
x_2 = k_s + k_a.
\]

The first eigenpolarization (\( n_1 \) in figure 1) is given azimuth angle \( \psi = 0 \). The second eigenpolarization (\( n_2 \) in figure 1) is given by the azimuth angle \( \Phi = \pi/2 \). Thus, on a Cartesian basis, the Jones vectors of the eigenpolarizations are

\[
J_1 = \begin{pmatrix} \cos(k_s - k_a) \\ i \sin(k_s - k_a) \end{pmatrix},
\]

\[
J_2 = \begin{pmatrix} i \sin(-k_s - k_a) \\ \cos(-k_s - k_a) \end{pmatrix}.
\]

(6)

From the eigenpolarizations we construct the coordinate transformation matrix \( \mathbf{R} \):

\[
\mathbf{R} = \begin{pmatrix} \cos(k_s - k_a) & i \sin(-k_s - k_a) \\ i \sin(k_s - k_a) & \cos(-k_s - k_a) \end{pmatrix}.
\]

(7)

The propagation velocities of the eigenpolarizations are taken to be \( c/n_1 \) and \( c/n_2 \), where \( n_1 \) and \( n_2 \) are the (complex) refractive indices and \( c \) is the velocity of light in a vacuum. The response of the sample on its eigenvector basis \( \{J_1, J_2\} \) is then

\[
\mathbf{W}_q = \begin{pmatrix} e^{i \Delta/2} & 0 \\ 0 & e^{-i \Delta/2} \end{pmatrix}
\]

(8)

where

\[
\Delta = \frac{2 \pi z}{\lambda} (n_1 - n_2)
\]

(9)

and \( z \) is the thickness of the sample platelet. The Jones matrix \( \mathbf{S} \) of the sample on the Cartesian basis is calculated in the following way:

\[
\mathbf{S} = \mathbf{R} \mathbf{W}_q \mathbf{R}^{-1}
\]

\[
\approx \begin{pmatrix} \cos(\Delta/2) + i \sin(\Delta/2) & -2(k_s + k_a) \sin(\Delta/2) & -2(k_s - k_a) \sin(\Delta/2) & \cos(\Delta/2) - i \sin(\Delta/2) \end{pmatrix}.
\]

(10)

In the actual calculation we have included terms up to third order in the ellipticity angles, which were assumed to be small. This assumption is valid for light propagating not too close to an optic axis. In the final result, however, only first-order terms in the ellipticity angles remained. In this paper, therefore, we have omitted quadratic or higher order terms in these angles. It is shown later that the ellipticity angles can be expressed in terms of the Jones parameters. The relevant parameters can, in turn, be related to the tensor \( \gamma \) of equation (1). The corresponding ellipticity angles are, therefore, small (\( O(\alpha/\lambda) \)) with respect to \( \Delta \), provided that \( \Delta \) is not too small.

Using the Jones matrix \( \mathbf{S} \) of equation (10) we now demonstrate how one calculates the HAUP intensity formula (4). For this, it is necessary to calculate \( \mathbf{A}^\dagger \mathbf{S} \mathbf{P} \). This has been done in the following way:

\[
\mathbf{A}^\dagger \mathbf{S} \mathbf{P} = \cos(\Delta/2)(P_1 A_1^* + P_2 A_2^*)
\]

\[
+ i \sin(\Delta/2)(P_1 A_1^* - P_2 A_2^*)
\]

\[
+ 2k_s \sin(\Delta/2)(P_1 A_1^* - P_2 A_2^*)
\]

\[
- 2k_a \sin(\Delta/2)(P_1 A_2^* + P_2 A_2^*).
\]

(11)

In appendix A the expansions for the terms \( P_1 A_1^* + P_2 A_2^* \), \( P_1 A_1^* - P_2 A_2^* \), \( P_1 A_2^* - P_2 A_2^* \), and \( P_1 A_2^* + P_2 A_2^* \) are given up to third order in \( \Theta, \Lambda, p \) and \( a \). It has been shown by Kremer and Meekes (1995) that this is sufficient for the angles \( \Lambda \) and \( \Theta \) that are used in the experiments.

Note that all parameters \( \Delta, k_s \), and \( k_a \) are complex numbers in absorbing crystals. Therefore, we substitute

\[
\Delta - i E \text{ for } \Delta, \quad k_s' + i k_a'' \text{ for } k_s \text{ and } k_a' + i k_a'' \text{ for } k_a.
\]

(12)

Before calculating \( \mathbf{A}^\dagger \mathbf{S} \mathbf{P} \) it must be noted that the angle \( \Lambda \) is usually not used in HAUP experiments. Instead, the position of the analyser is read with respect to the situation in which both polarizers are crossed (Kobayashi and Uesu 1983). In this alternative reading system, the position of the analyser is indicated by the angle \( Y \), in such a way that, for \( Y = 0 \), the polarizers are crossed. Furthermore, it is necessary to discuss another systematic error, \( \delta Y \), that is encountered in HAUP measurements. This systematic error describes a small deviation of the actual analyser position from its supposed position. The origin of this error can, in large part, be found in mechanical inaccuracies in the system that is used to rotate the polarizers (see Kremer and Meekes (1995) and references therein). One can change to the new reading system for the analyser by substituting \( \Theta + Y + \delta Y \) for \( \Lambda \) in all terms in appendix A. Indeed, in this way one has that \( \Lambda - \Theta = Y + \delta Y \). The systematic error \( \delta Y \) is small (\( O(10^{-3}) \)) and is therefore treated in the same way as the other small parameters.

The HAUP intensity formula, derived up to third-order terms in \( \delta Y, Y, \Theta, p \) and \( a \), can then be written in the following form (Moxon and Renshaw 1990):

\[
\Gamma / \Gamma_0 = \left(1 + Y Y^2 C_{(3x3)}^{ep}(\Theta, \Theta^2) \right).
\]

(13)

The matrix elements of \( C_{(3x3)}^{ep} \) are given in appendix B. The superscript \( ep \) denotes eigenpolarization, referring
to the fact that the angles $\Theta$ in this expression are supposed to be read with respect to a major axis of an eigenpolarization.

Experimentally, the exact position of such an eigenpolarization is difficult to find. Therefore, it is better to use a reference for the angle $\Theta$ that can be found more accurately. An extinction direction is chosen for this reference. It corresponds to that orientation of the sample between crossed polarizers for which the transmitted intensity is minimal. In our set-up the extinction direction is found by rotating both polarizers simultaneously, while keeping them crossed, until the intensity is minimal. The position of the polarizer at an extinction direction is denoted $\Theta_0$. This position can be calculated from equation (13). It is the value of $\Theta$ for which

$$\frac{\delta I}{\delta \Theta} |_{Y=0} = 0.$$  \hspace{1cm} (14)

This gives the following expression for $\Theta_0$:

$$\Theta_0 = -\frac{1}{2} \delta Y \left( \frac{(p + a) \sin \Delta - \delta Y \sinh E}{2 \cosh E - 2 \cos \Delta} + k'_a - k'_b \right).$$ \hspace{1cm} (15)

Note that $\Theta_0$ differs from the position of the eigenpolarization ($\Theta = 0$). This difference is not only caused by the optical properties of the sample, but also, in large part, by the systematic errors, $p$, $a$ and $\delta Y$. This shows the importance of taking these systematic errors into account appropriately. The value of $\Theta_0$ is measured with respect to an arbitrary origin in a HAUP experiment. Nevertheless, if the behaviour of $\Theta_0$ can be recorded as a function of $\Delta$ or $E$ it is still possible to use $\Theta_0$ for the determination of changes in $k'_a - k'_b$.

It will be clear that the position $\Theta_0$ can be found very accurately. Therefore, it is used as origin for the reading of polarizer angles. The corresponding HAUP intensity formula for this reading system is obtained by substituting $\Theta + \Theta_0$ for $\Theta$ and expression (15) for $\Theta_0$ in equation (13).

Finally, the unified HAUP intensity formula is obtained:

$$\frac{\Gamma}{\Gamma_0} = (1 + Y^2) C^{(3,3)}_{(3,3)} \begin{pmatrix} 1 \\ \Theta \\ \Theta^2 \end{pmatrix}. \hspace{1cm} (16)$$

where

$$C^{(3,3)}_{(3,3)} = \begin{bmatrix} 2(k'_a - k'_b) - (p - a) \sin \Delta \\ (p + a) \sinh E + \delta Y \sin \Delta \\ \cosh E - \cos \Delta \end{bmatrix} \begin{bmatrix} 1 \\ \Theta \\ \Theta^2 \end{bmatrix}.$$ \hspace{1cm} (17)

All other elements of $C^{(3,3)}_{(3,3)}$ are zero, except for $C^{(3,3)}_{11}$. This term has not explicitly been worked out, because it is not used to extract optical parameters from a measurement. The superscript $\Theta_0$ indicates that, for this HAUP intensity formula, an extinction direction has to be used as origin for the reading of the angles $\Theta$. Note that we have found a different sign for $E$ in the expression for $C^{(3,3)}_{22}$ to that found by Dijkstra et al. (1991). More important, though, is the fact that we have not used the assumption that $E$ is small with respect to $\Delta$, as opposed to Moxon and Renshaw (1990) and Dijkstra et al. (1991).

The unified formula (16) corresponds to the measurement of the first extinction direction. The polarization of the light emerging from the polarizer has a direction close to $n_1$. The same formula can, nevertheless, be used when the second extinction direction is measured. The polarization direction of the polarizer is then close to $n_2$. In the derivation of the HAUP intensity formula one only has to interchange the ellipticity angles $x_1$ and $x_2$. This comes down to changing the signs of $k'_a$ and $k'_b$. The same formula (16) can, therefore, be used for the second extinction direction if the signs of $k'_a$, $k'_b$, $\Delta$ and $E$ are reversed.

It is important, however, to determine the values of the systematic errors for each extinction direction separately (see Kremers and Meekes (1995)), because they can behave in an unpredictable way.

Considering the form of the HAUP intensity formula (17), we fit the intensities that are measured in a HAUP experiment against a polynomial equation of the form

$$\Gamma = (1 + Y^2) C^{(3,3)}_{(3,3)} \begin{pmatrix} 1 \\ \Theta \\ \Theta^2 \end{pmatrix}. \hspace{1cm} (18)$$

Note, that $\Gamma_0$ is included in the fitting parameters $C_{ij}$.

The fitting procedure that we use is a linear least squares method (Deming and Morgan 1979). Not all elements of $C^{(3,3)}_{(3,3)}$, which are the actual fitting parameters, need to be free in the fit. We only allow for $C_{11}$, $C_{21}$, $C_{12}$, $C_{22}$, $C_{31}$ and $C_{13}$ to be non-zero. $C_{12}$ is allowed to be non-zero, because this fitting parameter indicates how well the position of the extinction direction has been determined. It can even be used to improve the results by means of the so-called $\Delta \Theta$ correction (see for a detailed analysis Kremers and Meekes (1995)). The thus-obtained fitting parameters $C_{ij}$ give the values of the expressions for the corresponding matrix elements $C^{(3,3)}_{ij}$ of equation (17). It is clear that both $E$ and $\cos \Delta$ can simply be calculated from $C_{22}$ and $C_{31}$.

At this point one is left with the problem of finding the values of $k'_a$, $k'_b$, $k''_a$ and $k''_b$. These have to be extracted from the fitting parameter $C_{21}$ and the measured value for the extinction direction $\Theta_0$. The measurement of a single extinction direction is not sufficient to do this. Two extinction directions have to be measured to separate $k_a$ from $k_b$. The procedure of extracting these ellipticity angles is treated explicitly for the case of measurements on NiSO$_4$·6H$_2$O in section 4. Here, we proceed with the derivation of the HAUP intensity formula, using the Jones matrix of equation (2). In fact, the same equations (17) are found and $k'_a$, $k'_b$, $k''_a$ and $k''_b$ can be expressed in terms of Jones parameters.
Table 2. The relation between the description of the HAUP method in terms of eigenpolarizations and in terms of Jones parameters.

<table>
<thead>
<tr>
<th>HAUP parameters</th>
<th>( \Delta )</th>
<th>( E )</th>
<th>( k_j )</th>
<th>( k'_j )</th>
<th>( k''_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jones parameters</td>
<td>2g_0z</td>
<td>2p_0z</td>
<td>( \frac{1}{2} \frac{g_0\omega - p_0\delta}{p_0^2 + g_0^2} )</td>
<td>( \frac{1}{2} \frac{g_0p_45 - p_0g_45}{p_0^2 + g_0^2} )</td>
<td>( \frac{1}{2} \frac{g_0\delta + p_0\omega}{p_0^2 + g_0^2} )</td>
</tr>
</tbody>
</table>

3.2. The HAUP intensity formulae in terms of optical effects

With this paper we want to show that HAUP can have a much wider application in crystal optics than the simultaneous measurement of small reciprocal circular birefringence and large reciprocal linear birefringence. We consider those cases in which the Jones parameters \( g_{45}, p_{45}, \omega \) and \( \delta \) can be considered small with respect to \( g_0 \) and \( p_0 \).

We expand the matrix elements of (2) up to first order in the small parameters \( g_{45}, p_{45}, \omega \) and \( \delta \). The small optical effects only appear up to first order in the final expressions, even if one derives the HAUP intensity formula up to third order in all small parameters. This has been checked explicitly for all cases. Therefore, the following expansions can be used:

\[
\begin{align*}
\cosh(QNZ) &= \cosh((p_0 + ig_0)z) + O(2) \\
&= \cosh(g_0 - ip_0)z + O(2) \\
\sinh(QNZ) &= \sinh((p_0 + ig_0)z) + O(2) \\
&= \frac{g_0 + ip_0}{p_0^2 + g_0^2} \sin((g_0 - ip_0)z) + O(2),
\end{align*}
\]

where \( O(2) \) denotes terms to second order. With these expansions the Jones matrix (2) becomes

\[
\Sigma \approx \exp[-(\kappa + i\gamma)2\pi z/\lambda] \left( \begin{array}{c}
\cos((g_0 - ip_0)z) + i \sin((g_0 - ip_0)z) \\
\left( (g_0p_{45} - p_0g_{45} - g_0\omega - p_0\delta) \\
+i(g_0p_{45} + p_0g_{45} + g_0\delta + p_0\omega) \right) \sin((g_0 - ip_0)z) \\
\left( (g_0p_{45} - p_0g_{45} - g_0\omega + p_0\delta) \\
+i(g_0p_{45} + p_0g_{45} - g_0\delta - p_0\omega) \right) \sin((g_0 - ip_0)z) \\
\cos((g_0 - ip_0)z) - i \sin((g_0 - ip_0)z)
\end{array} \right)
\]

The only Jones parameters that do not change their sign upon a change in the extinction direction are \( \delta \) and \( \omega \). Therefore, it follows that, given the substitutions of equation (12), the matrix (20) has the same form as the matrix (10) except for the factor \( \exp[-(\kappa + i\gamma)2\pi z/\lambda] \). The relation between the parameters is given in table 2. The HAUP intensity formula for this case is, consequently, given by

\[
\Gamma/\Gamma_0 = \exp \left( -2\kappa \frac{2\pi z}{\lambda} \right) (1 + Y^2) \Omega_{HAUP}^{\Theta_0} \left( \begin{array}{c}
1 \\
\Theta^2
\end{array} \right)
\]

where the matrix elements \( C_{ij}^{\Theta_0} \) are obtained by substitutions in equation (17) according to the scheme given in table 2. Moreover, the expression for \( \Theta_0 \) is found from the same substitutions in equation (15). In most experiments not all optical effects of table 1 have to be taken into account. Several specific cases will now be addressed that can be expected to be of interest.

3.2.1. Uni-axial or orthorhombic bi-axial crystals that are absorbing and non-magnetic. First, we study the case in which non-reciprocal linear birefringence and non-reciprocal linear dichroism are absent: \( g_{45} = p_{45} = 0 \). Furthermore, we suppose that the crystal is uni-axial or orthorhombic bi-axial, so that the reciprocal linear birefringence and reciprocal linear dichroism have mutual principal axes. This is accounted for by means of the parameters \( g_0 \) and \( p_0 \). There are many non-magnetic, coloured crystals that belong to this case.

The optical effects of such a sample can be found by fitting the measured intensities against the HAUP experiment to the polynomial equation (18). The obtained fitting parameters \( C_{ij} \) give the values of the corresponding elements \( C_{ij}^{\Theta_0} \). It is seen that the determination of both the reciprocal linear dichroism, \( \Delta \kappa = [\lambda/(2\pi)]E \), and the value of \( \cos \Delta \) are independent of the presence of small reciprocal circular birefringence or small reciprocal circular dichroism. From \( \cos \Delta \) the value of \( \Delta \) can usually be constructed if the reciprocal linear birefringence is known for a certain temperature and wavelength \( \lambda \) (Kremers and Meekes 1995). Sometimes one is certain that, for a part of the measurements, \( k'_j \) is zero. The value of \( p - a \) can then be determined from the values of the fitting parameter \( C_{21} \) by means of a linear least squares fit for this part, because \( \Delta \) and \( E \) are known. Subsequently, \( k'_j \) can be calculated from \( C_{21} \) for the other part.

Suppose that one has been able, in this or another way, to extract the value of \( 2k''_j \) from the fitting parameter \( C_{21} \) and the value of \( 2k''_j \) from the measured \( \Theta_0 \). The circular birefringence and the circular dichroism can then be calculated using

\[
\Delta - n_1 = (Ek'_j + \Delta k'_j) \frac{\lambda}{\pi z} \quad (22)
\]

\[
\kappa - k_1 = (\Delta k''_j + Ek''_j) \frac{\lambda}{\pi z} \quad (23)
\]

In many practical cases the reciprocal linear dichroism is also small. Then, one has

\[
n_1 - n_1 = (\Delta k''_j) \frac{\lambda}{\pi z} \quad (24)
\]
\[ \kappa - \kappa_1 = (\Delta k_2)^\lambda \frac{\lambda}{\pi \xi}. \quad (25) \]

if second-order terms in the small parameters can be neglected.

### 3.2.2. Linear birefringence and linear dichroism with differential principal axes, bi-axial crystals, no circular effects

The principal axes for reciprocal linear birefringence and reciprocal linear dichroism were taken to have the same directions in the previous subsection. Here, we want to demonstrate that these effects can also be measured simultaneously in non-orthorhombic bi-axial crystals. Their principal axes do not necessarily coincide then. For the time being, we do not consider any circular optical effects: \( \delta = 0 \) and \( \omega = 0 \).

We assume that the principal axes of the reciprocal linear dichroism make a small angle, \( \alpha_{pg} \), with the principal axes of the reciprocal linear birefringence. The latter are taken to be the coordinate axes. The reciprocal linear birefringence is, therefore, described by the parameter \( g_0 \). To account for the fact that the reciprocal linear dichroism has different principal axes one must include both \( p_0 \) and \( p_{45} \). The parameter \( p_{45} \) is small with respect to \( p_0 \) and \( g_0 \) because we have assumed that the angle \( \alpha_{pg} \) is small. This angle can be calculated from \( p_0 \) and \( p_{45} \) (Jones, 1948):

\[ \tan(2\alpha_{pg}) = p_{45}/p_0. \quad (26) \]

From table 2 it can be seen that, in this case, the (small) angle \( \tan(2\alpha_{pg}) \) gives rise to eigenpolarizations that have equal ellipticity. This means that they have the same handedness. Therefore, the eigenpolarizations are non-orthogonal, contrary to the case presented in section 3.2.1. By measuring two successive extinction directions in a HAUP experiment it is, therefore, possible to discriminate between that case and the present one.

In the case that circular birefringence and circular dichroism are also present, it is still possible to extract all optical effects from the HAUP measurement. Again, this is done by measuring two extinction directions. From the polynomial fits of both measurements one calculates the symmetric and antisymmetric parts \( k_2 \) and \( k_0 \). After that, all optical parameters can be obtained by comparison with the expressions in table 2. Of course, it is necessary to know the value of \( p - a \). This value is usually determined by measurements in circumstances in which \( k_2 \) and \( k_0 \) are known to be zero.

The HAUP method can also be used in cases in which the angle \( \alpha_{pg} \) is large. For this, however, it is necessary that \( p_0 \) is also small with respect to \( g_0 \). For many coloured bi-axial crystals that is still a valid approximation. The angle \( \alpha_{pg} \) can take any value if \( p_0 \) and \( p_{45} \) have the same order of magnitude. Moreover, because \( p_0 \) is small, the equations (17) can be expanded correspondingly.

### Figure 3. The linear birefringence \( \Delta n = n_1 - n_2 \) of NiSO4 \( \cdot \) 6H2O for light propagating at two different angles \( \phi \) with respect to the optic axis; (○) lower curve \( \phi = 15^\circ \) and (□) upper curve \( \phi = 90^\circ \).

### 3.2.3. The measurement of non-reciprocal effects: non-reciprocal linear birefringence and non-reciprocal linear dichroism

In this section we demonstrate the way in which HAUP can be used to measure the non-reciprocal linear birefringence or the non-reciprocal linear dichroism. Again, a crystal is considered that is both linearly birefringent and linearly dichroic. In addition, we include non-reciprocal linear birefringence by means of the Jones parameter \( g_{45} \) and we take \( p_{45} \) equal to zero. Later, we discuss the case in which non-reciprocal linear dichroism is present. The rotation \( \alpha_{45} \) of the principal axes of the linear birefringence is given by (Jones 1948)

\[ \tan(2\alpha_{45}) = g_{45}/g_0. \quad (27) \]

As explained before, it is expected that the non-reciprocal linear birefringence is very small \( (O(10^{-6} \text{ rad}) \), see Hornreich and Shtrikman (1968).

The HAUP intensity formula that is obtained in this way is highly analogous to the one found in section 3.2.2 for dichroic, bi-axial crystals. It will not be surprising that the latter also represents the case of non-reciprocal linear dichroism. Suppose that, in a crystal, the principal axes of reciprocal linear dichroism and reciprocal linear birefringence would be symmetry restricted to the same directions if the magnetic ordering were neglected. It is possible that the actual symmetry of the magnetically ordered crystal allows for non-reciprocal linear dichroism. This, in turn, causes the existence of a (small) angle between the principal axes of linear dichroism and linear birefringence, which is exactly the situation treated in section 3.2.2. The difference between the two situations is, however, that, in the case of non-reciprocal linear dichroism, the Jones matrix would change if the direction of light propagation through the crystal were reversed. In non-magnetic crystals, on the other hand, the Jones matrix is always invariant under reversal of the light path.

The experiment that we suggest for the measurement of non-reciprocal linear birefringence or non-reciprocal
linear dichroism is, therefore, a temperature-dependent HAUP measurement of a uni-axial or bi-axial orthorhombic crystal that undergoes at some temperature a phase transition into a magnetically ordered state. The symmetry of this state must, of course, allow for non-reciprocal linear birefringence or non-reciprocal linear dichroism. Unfortunately, both spatial inversion symmetry and time-reversal symmetry must then be broken (Brown et al. 1963). This implies that the crystal can also be circularly birefringent and circularly dichroic. Therefore, one has to take these effects into account, but they can be separated if two extinction directions are measured. Another way to detect non-reciprocal effects is to perform an additional HAUP measurement in which the orientation of the sample with respect to the direction of light propagation is reversed.

4. Experimental results

4.1. The example of NiSO₄·6H₂O

In order to demonstrate how one can separate the parameters that represent small optical effects from a HAUP intensity formula, we have chosen the example of the greenish-coloured NiSO₄·6H₂O. This crystal is interesting for several reasons. It is a uni-axial crystal, of space group P4₁2₁2 that exhibits reciprocal linear birefringence (Stadnicka et al. 1987), reciprocal linear dichroism (Moxon et al. 1991), reciprocal circular birefringence (Underwood et al. 1938) and reciprocal circular dichroism (Grinter et al. 1970). All of these optical effects, except the linear birefringence, show a clear variation with wavelength. In the case of the cited references, the circular birefringence and the circular dichroism were determined by means of measurements along the optic axis. Both the linear birefringence and the linear dichroism are then zero. The advantage of HAUP is that circular birefringence and circular dichroism can also be measured in directions along which linear birefringence and linear dichroism are non-zero.

Previous HAUP experiments by Moxon et al. (1991) have shown that, for NiSO₄·6H₂O, it is possible to measure linear and circular dichroism, under the assumption that the linear dichroism is small. They were unable, however, to detect the circular birefringence. Moreover, the behaviour of the circular dichroism as a function of wavelength was shown, but only in arbitrary units. Unfortunately, they did not specify the orientation of the sample that was used in their experiment.

Here, we present the results of HAUP measurements on NiSO₄·6H₂O for two different sample orientations. In the first sample, of thickness \( z = 0.70 \) mm, the light propagates in a direction that makes an angle of 15°·40' with the optic axis. In the second sample, of thickness \( z = 0.10 \) mm, the light propagates in a direction perpendicular to the optic axis. For both samples we have determined the values of linear birefringence, linear dichroism, circular birefringence and circular dichroism as a function of wavelength. In each case, two extinction directions were measured.

4.2. The HAUP intensity formula for NiSO₄·6H₂O

In the case of NiSO₄·6H₂O it is safe to assume, for visible light, that linear dichroism is small with respect to the linear birefringence (Moxon et al. 1991). Therefore, we conveniently expand the expressions for \( C_{ij}^{\Theta_0} \) and \( \Theta_0 \) for small linear dichroism. The other expressions are used in their original form. Thus, we get the following HAUP intensity formula:

\[
\Gamma/\Gamma_0 = \exp\left(-2\kappa \frac{2\pi z}{\lambda}(1 Y Y^2)C_{ij}^{\Theta_0}\left(\begin{array}{c} 1 \\ \Theta \\ \Theta^2 \end{array}\right)\right) \tag{28}
\]

where the matrix elements \( C_{ij}^{\Theta_0} \) are given by equation (17) if we substitute

\[
k_i \approx \frac{\pi z}{\lambda} \left( n_r - n_1 \right) \Delta.
\]

The expanded expression for \( \Theta_0 \) is

\[
\Theta_0 \approx -\frac{1}{2}\delta Y + \frac{1}{2}(p + a)\cot((\Delta/2) - \frac{\pi z}{\lambda} \frac{k_r - k_1}{\Delta}). \tag{29}
\]

4.3. Determination of the optical properties of NiSO₄·6H₂O

The intensities measured in the HAUP experiments were fitted to the polynomial equation (18). During this fitting procedure the so-called \( \Delta \Theta \) correction (Kremers and Meekes 1995) was performed. From the fitting parameters \( C_{ij} \) one has to determine the optical properties.

First the factor \( \Gamma_0 \exp[-2\kappa (2\pi z/\lambda)] \) is determined:

\[
\Gamma_0 \exp\left(-2\kappa \frac{2\pi z}{\lambda}\right) = [C_{31}(C_{13} - (C_{22} - C_{33}))]^{1/2} \tag{30}
\]

and all fitting parameters are divided by this factor. Then, the linear birefringence \( \Delta n = [\lambda/(2\pi z)]\Delta \) is constructed from \( \cos^2(\Delta/2) \):

\[
\cos^2(\Delta/2) = \frac{1}{2}(1 + C_{31}) - \frac{1}{4}C_{22}. \tag{31}
\]

At \( \lambda = 500 \) nm the linear birefringence is \( n_o - n_e = 1.517 - 1.493 = 0.024 \) (Stadnicka et al. 1987). Using this information, the linear birefringence as a function of wavelength can be derived from the \( \cos^2(\Delta/2) \) values. In figure 3 the result is shown for both samples.

The linear dichroism \( \Delta \kappa = [\lambda/(2\pi z)]E \) is calculated from

\[
E = \ln(C_{31}). \tag{32}
\]

The results have been plotted in figure 4. They show that the linear dichroism can, indeed, be taken to be small with respect to the linear birefringence. Therefore, we can use the expansion made above (section 4.2). The linear dichroism shows a peak at \( \lambda = 400 \) nm. The
onset of another peak is observed at $\lambda = 625$ nm. This agrees with the results of Moxon et al. (1991).

The obtained fitting parameters $C_{21}$, as a function of the wavelength of the light, are given in figure 5. There is a much larger variation in the maxima (and minima) for the measurement with $\phi = 90^\circ$. This indicates that the wavelength variation of $k'_1$ is largest for that sample.

Consider, now, the expression for this fitting parameters $C_{21}$. The value of $28Y$ can be found if there is a wavelength at which $\sin \Delta = 0$ and $E \approx 0$. Thus, we find $28Y (\lambda = 611 \text{ nm}) = -1.1 \times 10^{-5}$ and $28Y (\lambda = 530 \text{ nm}) = -2.2 \times 10^{-4}$ from figure 5. The value of $p + a$ is obtained by plotting the measured values of $\Theta_0$ against $\cot(\Delta/2)$ in a region in which the circular dichroism can be neglected. In this case, this is the same region as that in which the linear dichroism is small (Moxon et al 1991). Thus, we have found $p + a = -2.3 \times 10^{-4}$ for the sample in which the light propagates at an angle $\phi = 15^\circ40'$ to the optic axis. For the other sample we have found $p + a = 2.8 \times 10^{-5}$.

At this point of the interpretation the linear birefringence, the linear dichroism, the value of $\delta Y$ and the value of $p + a$ are all known. Therefore, it is possible to calculate $2k'_1 - (p - a)$ from the fitting parameter $C_{21}$. It is known that the optical activity changes sign at

$$\lambda = 503 \text{ nm}$$

for light propagating along the optic axis. Therefore, we have taken values of $p - a$ such that $2k'_1 + p - a \approx 0$ at this wavelength. In figure 6 we show the values of $k'_1$ that were obtained in this way.

The discontinuities in the figures arise at those wavelengths at which $\sin(\Delta/2) = 0$. The first reason for this is that the assumptions made in deriving the HAUP intensity formula are not valid when $\Delta$ equals an integer multiple of $2\pi$ (Kremers and Meekes 1995). Secondly, it is very difficult to subtract exactly the correct contributions $28Y \cos(\Delta/2)$ and $E(p + a) \cot(\Delta/2)$ from the fitting parameter $C_{21}$. Therefore, terms can remain in $k'_1$ that behave as $(\sin(\Delta/2))^{-1}$ and $(\sin(\Delta/2))^{-2}$. These terms are singular whenever $\Delta/2$ is equal to an integer multiple of $\pi$. The observed discontinuities are, therefore, not sample properties. We have to conclude that the results of the HAUP method must be evaluated very carefully in regions in which $\sin(\Delta/2)$ is close to zero.

From $k'_1$ the circular birefringence $n_t - n_l$ is calculated in the following way:

$$n_t - n_l = \frac{\lambda}{\pi} \Delta k'_1.$$  \hspace{1cm} (33)

The circular birefringence of the sample with an orientation of $\phi = 15^\circ40'$ to the optic axis is given in figure 7. This could have been done in the same way for the other sample. The obtained circular birefringence is then, approximately, of the same magnitude. Nevertheless, the determination of the circular birefringence in directions perpendicular to the optic axis is more difficult, because the linear birefringence is very large there. As a result, $k'_1$ becomes very small for this direction, so that it is difficult to measure it. Moreover, it is not easy to make the sample so thin that the number of times that $\Delta/2$ becomes equal to an integer multiple of $\pi$ is limited. In this case, the thickness was only 0.10 mm, but, still, six discontinuities are observed in the measured wavelength interval (see figure 6). The circular birefringence of figure 7 has, except for the discontinuities, a wavelength-dependence
The onset of a second circular dichroism peak is observed at a wavelength for the sample in which the light propagates at an angle $\phi = 15^\circ40'$ with respect to the optic axis. The structure within this peak is probably caused by the fact that there is a wavelength there for $X_0$ to measure. The sensitivity can be reduced to a certain position. It is, therefore, reasonable to assume effects. It has been explained by Kremers and Meekes (1995) that this sensitivity is, approximately, equal to $10^{-5}$ rad for the measurement of $\delta Y$ error. The actual orientation of the polarizer can differ from its supposed position due to, for example, mechanical inaccuracies in the driver system. The optical effects that are expected to be present in the crystal. The HAUP intensity formula can be given in a unified form in terms of these eigenpolarizations. It can then be used to measure the complex ellipticities of an arbitrary sample. On the other hand, it is possible to translate the unified HAUP intensity formula directly into the corresponding expression in terms of the Jones parameters. Then, one can measure the magnitude of the optical effects that are expected to be present in the sample.

The presence or absence of optical effects can give information about the breaking of spatial-inversion symmetry (such as in incommensurately modulated crystals), of time-reversal symmetry (such as, in high-$T_c$ superconductors), of both (such as in magneto-electrics). In all cases, there is great interest in this information, but the optical effects that might occur are expected to be very small. Therefore, it is important to have an idea of the sensitivity of HAUP for such effects. It has been explained by Kremers and Meekes (1995) that this sensitivity is, approximately, equal to the accuracy with which polarizers can be set at a certain position. It is, therefore, reasonable to assume a sensitivity of $1 \times 10^{-5}$ rad for the measurement of the ellipticity angles $k_1$, $k_2$, $k_3$ and $k_4$. It must be noted, though, that the sensitivity can be reduced to a large extent if the reciprocal linear birefringence and the sample thickness are such that the value of $\Delta/2$ is close to an integer multiple of $\pi$.

Often, an interesting optical effect is found from the ellipticity angles by multiplying with the magnitude of the reciprocal linear birefringence, see equations (24).

5. Discussion and conclusions

In this paper we have shown that the HAUP method can be applied to a wide variety of crystals of any symmetry. The method allows precise separation of small optical effects (even non-reciprocal ones) from relatively large reciprocal linear birefringence and reciprocal linear dichroism, but also from systematic errors. The latter must always be taken into account for accurate measurements. The small optical effects have been shown to be responsible for the (complex) ellipticities of the eigenpolarizations that can propagate in the crystal. The HAUP intensity formula can be given in a unified form in terms of these eigenpolarizations.
and (25). In the case of NiSO₄ · 6H₂O, for example, the linear birefringence is of the order of 10⁻⁷ rad. The (maximum) sensitivity for the small optical effects will, therefore, be 10⁻⁷ rad. This agrees with the estimated sensitivity for the circular dichroism that was plotted in figure 8.

We believe that, with the sensitivity, HAUP must be regarded as a powerful instrument in crystal optics and can be applied to investigate many interesting problems.

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Appendix A. The expansions of the terms

\[ P_i \Delta A_j^* \pm \rho_k \Delta A_j^* \text{ up to third order in } \Theta, \Lambda, p \text{ and } a \]

\[ P_1 \Delta A_j^* + P_2 \Delta A_j^* = \left[ \frac{i(p + a) - \frac{1}{5}i(p + a)^3}{e_{\Delta \Theta}(p + a)} + (\Lambda - \Theta)[1 + \frac{1}{2}(p - a)^2 + \Lambda \Theta]\right] \]

\[ - \left( \Lambda^2 + \Theta^2 \right) \frac{1}{5}(p + a) \left( \Lambda^2 - \Theta^2 \right) + \left( \Lambda^3 - \Theta^3 \right) \frac{1}{6}(p + a)^3 + \Theta(4) \]

\[ P_1 \Delta A_j^* - P_2 \Delta A_j^* = \left[ \frac{i(p - a) + \frac{1}{5}i(p - a)^3}{e_{\Delta \Theta}(p + a)} + (\Lambda + \Theta)[1 - \frac{1}{2}(p - a)^2 + (\Lambda + \Theta)] \right] \]

\[ - \left( \Lambda^2 + \Theta^2 \right) \frac{1}{5}(p - a) \left( \Lambda^2 - \Theta^2 \right) + \left( \Lambda^3 + \Theta^3 \right) \frac{1}{6}(p - a)^3 + \Theta(4) \]

\[ P_1 \Delta A_j^* + P_2 \Delta A_j^* = \left[ \frac{1}{2}(p + a)^2 + (\Lambda - \Theta)[i(p + a)] \right] \]

\[ + \Theta(1) + \left( \Lambda^2 + \Theta^2 \right) \frac{1}{6}(p + a)^3 + \Theta(4) \]

\[ P_1 \Delta A_j^* + P_2 \Delta A_j^* = \left[ \frac{1}{2}(p + a)^2 + (\Lambda + \Theta)[-i(p - a)] \right] \]

\[ + \Theta(-1) + \left( \Lambda^2 + \Theta^2 \right) \frac{1}{6}(p - a)^3 + \Theta(4). \]

Appendix B. The unified HAUP intensity formula for \( \Theta \) read with respect to an eigenpolarization

\[ \Gamma / \Gamma_0 = (1 + Y^2) \mathbf{C}_{\text{EP}}^{\text{e}} \left( \begin{array}{c} 1 \\ \Theta \end{array} \right) \]

where

\[ \mathbf{C}_{\text{EP}}^{\text{e}} = \cos \Delta \left( -2(k''_e - k''_o) + \sin \Delta \left( 2(k''_e - k''_o) - 2p \right) \right) + e^\Delta \left( 2(k''_e - k''_o) + 2\Delta Y \right) \]

\[ + \sin \Delta \left( -2(p + a) \left( k''_e - k''_o \right) - 2p \delta Y + 2\Delta Y \left( k''_e - k''_o \right) \right) \]

\[ + e^\Delta \left( a^2 + (k''_e - k''_o) \delta Y + (\delta Y)^2 \right) + e^{-\Delta} \left( p^2 \right) \]

All other elements of \( \mathbf{C}_{\text{EP}}^{\text{e}} \) are zero.

References

Agranovich V M and Ginzburg V L 1984 Crystal Optics with Spatial Dispersion, and Excitons (Berlin: Springer)
Hornreich R M and Shtrikman S 1968 Phys. Rev. 171 1065
Kitazawa Y 1990 Phys. Rev. Lett. 65 1275
Laughlin R B 1988a Science 242 525
O’Dell T H 1970 The Electrodynamics of Magneto-electric Media (Amsterdam: North-Holland)
Pisarev R V, Krchevstov B B and Pavlov V V 1991 Phase Transitions 37 63
Uesu Y and Kobayashi J 1985 Ferroelectrics 64 115
Underwood N, Slack F G and Nelson E B 1938 Phys. Rev. 54 355