CRYSTAL OPTICS OF ABSORBING AND 
GYROTROPIC MEDIA

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Abstract—Optical parameters of various crystals are considered. It is first shown what proper waves
propagate in absorbing and gyrotropic crystals, and then in crystals which possess absorption and
gyrotropy simultaneously. It is also shown that in such crystals proper wave ellipticities are different,
and the waves are non-orthogonal. The solutions of boundary problems are given for crystals with a different
set of optical properties. On the basis of these solutions various methods for determining the optical
parameters are suggested: birefringence, dichroism, proper wave ellipticities, non-orthogonality angle,
circular dichroism, refraction indices and absorption coefficients in strongly absorbing crystals. Some
examples of crystal investigations are given.

1. INTRODUCTION

A. V. Shubnikov attached great attention to the development of crystal optics in the general system
of crystal science, i.e. crystallography. Two of his books [1, 2] specially devoted to this subject, or
more precisely to crystal optics itself as an anisotropic medium, and not at the usage of optical
properties in crystallography (in petrography, for instance) may serve as evidence for the abovesaid.
The two books are a brilliant exposition about the material, especially the properties of transparent
crystals. The absorbing and optically active crystals received considerably less attention and only
from general positions (structure of respective tensor surfaces). Such an approach was to a great
extent justified by the state of knowledge itself in these fields [3, 4] in which, despite the bygone
history of the subject, there still remains many unsolved problems.

At present, the situation has substantially changed thanks to the efforts of many scientists [5–7].
A really general phenomenological theory of absorbing (and not only orthorhombic) crystals has
been worked out, the problem of relation equations, boundary conditions and respective
expressions for electromagnetic energy of the flux vector and density of a light wave in gyrotropic
crystals was elucidated. Also, the general view of the optical activity of crystals has been
established, when the traditional notion about the manifestation of activity as a rotation of the
light wave polarization plane started to be considered as its proper manifestation. The works of
F. I. Fedorov and his disciples made a great contribution to the solution of this problem. The
spectroscopic aspect of the theory of a nature of absorption and activity received its development
[8–10].

Shubnikov was interested, first of all, in the phenomenological aspect of these phenomena, and
we shall try to elucidate the present state of the problem leaning on the Shubnikov's favourite
method: to mark the resemblance and difference between phenomena and things. To do this, we
shall use concrete vivid examples, proceeding from experimental results. In the article, we shall
mainly use the material of investigations carried out by many research workers of the optical
laboratory founded by Shubnikov in the Institute of Crystallography.

2. PROPER WAVES IN CRYSTALS

As it is known, the propagation of electromagnetic waves in vacuum and media is described by
Maxwell's equations [3, 4]. The properties of a medium are defined by the relationships between
the strengths and inductions of fields, i.e. by relation or material equations. Taking into account
the dependence of field inductions $\mathbf{D}$ and $\mathbf{B}$ from spatial dispersion of a medium, the relation
equations may be written in the form [6, 11, 12]:

\[
\mathbf{D} = \varepsilon \mathbf{E} + i\omega \mathbf{H},
\]

\[
\mathbf{B} = \mu \mathbf{H} - i\omega \mathbf{E},
\] (1)
where $\epsilon$ and $\mu$ are the tensors of dielectric constant and magnetic permeability, $\hat{\alpha}$ is the gyration pseudotensor, $\hat{\alpha}^T$ is the transposed pseudotensor (hence forward, we shall omit the prefix "pseudo"). $\hat{\alpha}$ is here written in the covariant form [6].

The crystals of 18 symmetry classes in which tensor $\hat{\alpha}$ differs from zero, are optically active or gyrotrropic [6, 7, 13].

The crystals of the following classes of symmetry may be optically active:

<table>
<thead>
<tr>
<th>Class</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive</td>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axial</td>
<td>2:2</td>
<td>3:2</td>
<td>4:2</td>
<td>6:2</td>
<td>3/4</td>
<td></td>
</tr>
<tr>
<td>Planar</td>
<td>2 m</td>
<td>3 m</td>
<td>4 m</td>
<td>6 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inversional</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 m</td>
<td>4 m</td>
</tr>
</tbody>
</table>

In the general case, tensor $\epsilon$ appears to be complex:

$$\epsilon = \epsilon' + i\epsilon'' = \epsilon' + i\frac{4\pi}{\omega} \sigma,$$

(2)

where $\sigma$ is the conductivity tensor. The crystals in which $\sigma$ differs from zero, are absorbing ones. In crystals of monoclinic and triclinic syngonies the main axes of tensors $\epsilon'$ and $\sigma$ do not coincide and one has to apply the covariant methods for investigating such crystals [5, 14].

If the crystal is an absorbing one, then the gyration tensor is also complex:

$$\hat{\alpha} = \hat{\alpha}' + i\hat{\alpha}''$$

(3)

$\hat{\alpha}'$ describes circular birefringence, $\hat{\alpha}''$ is the circular dichroism.

In order to look into the whole combination of optical properties of such complex crystals, let us carry out the comparative analysis of the properties of only absorbing and only gyrotrropic crystals, and then those of crystals which are, at the same time, absorbing and gyrotrropic.

The study of optical properties of crystals begins with the investigation of proper waves, i.e. the waves which pass through a crystal without changing their polarization. It should be noted that only these waves and their superposition may propagate in a crystal. In transparent non-active crystals of all classes of symmetry (with the exception of cubic ones) two linearly polarized waves orthogonal, one to another, come out to be proper waves. These directions coincide with two extinction positions of a crystal between crossed polarizers. In the general case, the proper waves in optically active and absorbing crystals, are similar and orthogonal, but they are elliptically polarized; in optically active crystals the reversal over the ellipses is an opposite one, while in absorbing crystals it is directed to one side, the major axes of ellipses coincide with the directions of oscillations in the same (but non-active) transparent crystal. If the crystal possesses both the optical activity and absorbance, the proper waves are no longer orthogonal, and their ellipticities are different. Figure 1 illustrates all these cases.

It is known that the homogeneous waves in absorbing crystals become excited only at normal incidence [5]; we shall consider only this case. One has to bear in mind that the elliptically polarized waves in absorbing crystals originate only in crystals of the lowest syngonies [5]. In optically active crystals the ellipticities of proper waves are not the same and differ one from the other depending on anisotropy of a crystal [6]. In most cases, the difference in ellipticities of crystals may be neglected. Special consideration should be given to crystals of classes 3 · m, 4 · m, 6 · m in which vector $E$ of the usual wave is linearly polarized, while vector $E$ of the unusual wave is elliptically polarized [6].

The ellipticities of proper waves in crystals depend on the direction of the wave normal; they are given in Ref. [6]. If the difference in ellipticities of proper waves is not taken into account, one may use, in most cases, a simpler expression for gyrotrropic crystals [15]:

$$k = \frac{2G}{(n_{02}^2 - n_{01}^2) - \sqrt{(n_{02}^2 - n_{01}^2)^2 + 4G^2}},$$

(4)

where $n_{01}$ and $n_{02}$ are the refraction indices, optical activity not taken into account; $G$ is the scalar parameter of gyration which depends on crystal symmetry and direction of the wave normal [4, 6, 15].
In the works [5, 15] the ellipticities of proper waves in absorbing crystals of the lowest syngonies have been investigated by the covariant method.

When tensor $\epsilon$ can be reduced to a diagonal form in the principal material coordinate system, we have for the ellipticity of proper waves in absorbing crystals [16]:

$$s = \frac{2\gamma_{12}}{(\gamma_{22} - \gamma_{11}) + \sqrt{(\gamma_{22} - \gamma_{11})^2 + 4\gamma_{12}^2}}$$

(5)

where $\gamma_{ij}$ are the components of two-dimensional complex tensor $\epsilon^{-1}$. In optically active absorbing crystals the expressions for ellipticities of proper waves are, in the general case, very cumbersome [6] and cannot be reduced even for crystals of orthorhombic syngony (this is illustrated, in explicit form, in Ref. [17]).
In order to see clearly the nature of ellipticity of proper waves, the calculation results for a crystal of orthorhombic syngony of class 2:2 near the optical axis are given in Fig. 2 [17]. For these calculations we used various values of refraction indices, absorption coefficients and gyration tensor components:

\[
N_1 = 1.64 + i 4.00 \cdot 10^{-3}, \quad \delta_1 = (3.0 \cdot 10^{-5} + i 5 \cdot 10^{-7}) 10^9, \\
N_2 = 1.65 + i 3.94 \cdot 10^{-3}, \quad \delta_2 = (1.5 \cdot 10^{-5} + i 3 \cdot 10^{-7}) 10^9, \\
N_3 = 1.67 + i 4.04 \cdot 10^{-3}, \quad \delta_3 = (4.0 \cdot 10^{-5} + i 2 \cdot 10^{-7}) 10^9,
\]

\( p \) takes on the value \( p + 0, 1 \), whereas the values \( N \) remain unchanged.

Two waves with ellipticity equal to \( \pm k \) propagate in an optically active crystal. Two waves whose ellipticity is \( k = \pm 1 \), i.e. two circularly polarized waves with opposite reversal (Fig. 2) propagate along the optical axis. Only this is accounted for by the propagation plane rotation taking place at the exit from the crystal and in just such a way that the phenomenon of optical activity in quartz crystals was discovered more than 150 years ago.

In the general case, two so-called circular axes are formed in absorbing crystals of the lowest syngonies, instead of each of the optical axes; consequently, the crystal has four circular axes.
Besides the proper waves with circular propagation $s = 1$, one more wave, the so-called Voight wave [18], can propagate in the direction of circular axes. The Voight waves polarization changes with penetration into a crystal from circular to linear in a thin layer of a crystal; then a change up to circular polarization which is a proper one for the given crystal takes place.

The Voight waves are considered in detail in Refs [19–21]. Two waves with ellipticity [Fig. 2(b)] propagate in directions different from circular axes. The isotropic axes may also exist in crystals of the lowest syngonies; a wave of any polarization may propagate along such an axis, as in a uniaxial transparent crystal. Refs [6, 13] give the information as to what optical axes may exist in absorbing crystals and present a general classification of absorbing crystals of the lowest syngonies.

In optically active absorbing crystals the proper waves ellipticity is a rather complicated one and it may possess the same or different signs depending on the relationship between the values characterizing the activity and absorption [Figs 2(c) and (d)].

In the case of an absorbing non-active and transparent active crystals the proper waves are orthogonal. The waves in an absorbing gyrotropic crystal of the lowest syngonies may be, near the optical axis, substantially non-orthogonal [Figs 2(e) and (f)]. The width of the region of substantial non-orthogonality depends on the relationship between the optical activity and dichroism. In the directions far away from the region of optical axes the proper waves remain non-orthogonal not only in biaxial, but also in uniaxial crystals. Their non-orthogonality is less than $1^\circ$ and the waves in these directions may be considered as being orthogonal. Then the principle of superposition is valid for proper waves ellipticity, i.e. proper waves ellipticities in absorbing gyrotropic crystals are equal to

$$k_1 = s + k, \quad k_2 = s - k.$$

The ellipticity values calculated from appropriate formulae (6) are shown in Figs 2 (c) and (d) by dots.

The authors of Refs [22, 23] were the first to draw attention to proper waves non-orthogonality and the principle of ellipticity superposition. In spite of the fact that the nature of proper waves ellipticity is illustrated for crystals of 2:2 class in Fig. 2, the main relationships peculiar to crystals of the lowest syngonies will remain the same.

3. BOUNDARY PROBLEMS IN CRYSTAL OPTICS

The problem concerning the light passing through a crystalline plate can be solved, if one knows the proper waves parameters in crystals and refraction indices. In the general case, the application of covariant calculation methods is the best way of getting the precise solution [5, 6]. In most cases one can also use for this purpose, the approximate expressions for polarizing the passed light by means of the proper waves addition method. It turns out, however, that the passed light polarization is, in the main, defined by anisotropic properties of a crystal, i.e. by birefringence and dichroism as well as by a nature of proper waves polarization. It is shown [24–26] that, in most cases, the light reflections from a crystal boundary exert only a slight influence on the passed light polarization, therefore they may be neglected which simplified the calculations.

If a crystal is non-active and transparent, then for the azimuth $\chi$ and ellipticity $(b/a = \tan \gamma)$ of the passed light (without an account of reflections in Refs [1, 2] the simple relationships are given depending on phase difference $\Delta$ appearing in a crystalline plate, and on azimuth $\alpha$ of the incident light polarization:

$$\tan 2\chi = \tan 2\alpha \cos \Delta,$$

$$\sin 2\gamma = \sin 2\alpha \sin \Delta,$$

where $\Delta = (2\pi d/\lambda)\Delta n$ and $\Delta n$ is the birefringence in a crystal, $d$ is the plate thickness, $\lambda$ is the length of the incident light wave.

For optically active transparent crystals in which the proper waves ellipticity is equal to $k$, the expressions for the azimuth and ellipticity of the passed light were obtained by different methods

$$k_1 = s + k, \quad k_2 = s - k.$$
and are of the form:

\[
\tan 2x = \frac{\tan 2\chi}{1 + k^2},
\]

\[
\sin 2\gamma = \frac{\sin 2\gamma}{1 + k^2},
\]

If \( k = 1 \) which is in conformity with circularly polarized waves propagation along the optical axis, then:

\[
\tan 2\gamma = \tan(2\chi - \Delta), \quad \sin 2\gamma = 0.
\]

This means that after the passage of linearly polarized light through a crystal, the light goes out also linearly polarized with the polarization plane rotated through an angle \( \chi = \Delta/2 = \rho d \); here, the rotation per length unit or specific rotation is equal to:

\[
\rho = \frac{\pi G}{\lambda d},
\]

where \( G \) is the scalar parameter of gyration [15]. At present, there have been carried out numerous measurements of specific rotation whose values are given in many works, e.g. in Refs [8, 19–31].

Of interest are crystals of classes \( 4 \) and \( 4 \cdot m \) in which, according to symmetry conditions, the optical activity is lacking in the case of light propagating along the optical axes. Crystals AgGaS\(_2\) (class \( 4 \cdot m \)) and crystals CdGa\(_2\)S\(_4\) (class \( 4 \)) having an isotropic point (with birefringence equal to zero) on plates cut out parallel to the optical axis were investigated [32, 33]. The polarization plane rotation was measured for this wave length. The analogous measurements were carried out on some other crystals with an isotropic point.

Among the biaxial planal crystals the polarization plane rotation was observed in the crystal Na\(_2\)ZnGeO\(_4\) (class \( 2 \cdot m \)) [34] in which the optical axis plane is perpendicular to the symmetry plane.

For the absorbing crystals with proper waves ellipticity equal to \( s \), we have for the passed light polarization azimuth [35]:

\[
\tan 2\chi = \frac{\sin 2\alpha \cos \Delta}{\sin 2\gamma} = \frac{2s}{(1 + s^2)} - \frac{4s^2}{(1 - s^2)} \sin 2\alpha \cos \Delta - 2s(1 + s^2) \sin 2\alpha \sin \Delta,
\]

\[
\sin 2\gamma = \frac{\sin 2\gamma}{\sin 2\alpha \cos \Delta} - \frac{4s^2}{(1 - s^2)} \sin 2\alpha \sin \Delta + 2s(1 - s^2) \sin 2\alpha \cos \Delta.
\]

In all the uniaxial crystals and in some directions of biaxial crystals \( s = 0 \) [14], then we obtain from equations (11) and (12):

\[
\tan 2\chi = \frac{\sin 2\alpha \cos \Delta}{e^s \cos^2 \alpha - e^{-s} \sin^2 \alpha},
\]

\[
\sin 2\gamma = \frac{\sin 2\alpha \sin \Delta}{e^s \cos^2 \alpha + e^{-s} \sin^2 \alpha}.
\]

As already mentioned, at \( s = 1 \), the Voight waves can propagate in a crystal. The proper waves ellipticity \( s \) decreases rapidly when moving away from the optical axes and, in most cases, the terms of order \( s^2 \) may be neglected, the expressions (11) and (12) becoming much simpler.
The expressions for the azimuth and ellipticity of the passed light were obtained in Refs [36, 37] for uniaxial absorbing optically active crystals in which the proper waves ellipticity is defined by the activity only. In the case of low-symmetric absorbing optically active crystals the analogous relationships were obtained in Ref. [35] for the orthogonal approximation of proper waves and in Refs [38, 39] with an account of their nonorthogonality.

In the general aspect, they appear to be rather complicated, therefore let us give them only for the orthogonal approximation. Such an approximation holds true for the directions different from the optical axes, then the proper waves ellipticities are small and the terms of order $k_0^2$, $k_1^2$ may be neglected. For the azimuth and ellipticity of the passed light, we have:

\[
\begin{align*}
\tan 2\chi &= \frac{\sin 2\alpha \cos \Delta - 2[(s + k) \cos^2 \alpha + (s - k) \sin^2 \alpha] \sin \Delta}{e^\delta \cos^2 \alpha - e^{-\delta} \sin^2 \alpha + 2k \sin 2\alpha \sin \Delta}, \\
\sin 2\gamma &= \frac{\sin 2\alpha \sin \Delta - 2[(s + k)(e^\delta - \cos \Delta)\cos^2 \alpha + (s - k)(e^{-\delta} - \cos \Delta) \sin^2 \alpha]}{e^\delta \cos^2 \alpha + e^{-\delta} \sin^2 \alpha - 2s \sin 2\alpha \sin \Delta}.
\end{align*}
\]

(15) (16)

In many cases, at small $s$ and $k$, one can use just these expressions when investigating the polarized light passed through a plate cut out from an optically active absorbing crystal.

For the polarization of the incident light polarized in the main plane ($\alpha = 0$) or perpendicularly to it ($\alpha = 90^\circ$) in transparent crystals $k = s = 0$ and $\tan 2\chi = \sin 2\gamma = 0$, i.e. the light goes out linearly polarized without changing the azimuth of the incident light polarization. The situation is different in the case of active absorbing crystals. For the same cases of the incident light polarization we have [35]:

\[
\begin{align*}
\tan 2\chi_1 &= -2(s + k)e^{-\delta} \sin \Delta, \\
\tan 2\chi_\perp &= 2(s - k)e^\delta \sin \Delta, \\
\sin 2\gamma_1 &= -2(s + k)(1 - e^{-\delta} \cos \Delta), \\
\sin 2\gamma_\perp &= -2(s - k)(1 - e^\delta \cos \Delta).
\end{align*}
\]

(17)

The peculiarities of optical activity and absorption in directions different from the optical axis manifest themselves most strikingly. In these particular cases of the incident light polarization, it can be seen that a change in the phase difference will involve the oscillation of the values $\sin \Delta$ and $\cos \Delta$, while $k$ and will change smoothly.

The best way of investigating the optical activity and determining the gyration tensor components is to use these relationships, though the measurements of the passed light intensity are also possible, as it is suggested in Refs [40, 41]. To measure the passed light azimuth it is necessary to place the plate under investigation in the extinction position between crossed polarizers in such devices as a spectropolarimeter or ellipsometer [42–44]. Then, by changing, e.g. the wave length of the incident light or temperature, one can measure the passed light azimuth $\chi$. As an example, Fig. 3(a) gives the values of the dependence of an angle $\chi$ on $\lambda$ for a crystal $La_3Ga_5SiO_{14}$ (symmetry 3:2) cut out parallel to the optical axis [45]. The enveloping curve for an oscillation function is just defined by the proper wave ellipticity $k$. In the given case $k = g_{11}/2\pi \Delta n$; if one knows the birefringence value $\Delta n$ and the mean refraction index of a crystal $\bar{n}$, it is possible to calculate the gyration tensor component $g_{11}$ for a given direction. The other component $g_{33}$ is determined from a change in a polarization plane rotation. Figure 3 (b) shows the dispersion of components $g_{11}$ and $g_{33}$ as well as the birefringence dispersion for a crystal $La_3Ga_5SiO_{14}$. The analogous measurements can be carried out on biaxial crystals, too. The investigation of an ammonium trihydroselinite crystal belonging to symmetry class 2:2 [46] may serve as an example. At some definite relationships between the wave length $\lambda$ and temperature this crystal becomes uniaxial. Figures 4(a) and (b) illustrate the activity manifestation in this crystal when changing the temperature and the wave length. The gyration tensor component is determined, for a given direction, from such measurements as $\lambda = 0.4 \mu m$, $g_{11} = 9.8 \cdot 10^{-5}$, while at $\lambda = 0.7 \mu m$, $g_{11} = 4.5 \cdot 10^{-5}$.

In order to elucidate more clearly the optical activity manifestation in the directions different from that of the optical axis, Shubnikov suggested that the problem of the light passage through two crossed plates of the same thickness cut out from one and the same transparent crystal should be calculated [47]. For these particular cases of the incident light polarization ($\alpha = 0.90^\circ$) we obtain

\[
\begin{align*}
\tan 2\chi &= -4k \sin \Delta, \\
\sin 2\gamma &= 4k(1 - \cos \Delta).
\end{align*}
\]

(18)
As is seen, for the case of crossed plates only the linear birefringence is compensated, whereas the optical activity is not compensated at all. The linear birefringence and optical activity may be compensated simultaneously only if two crossed plates are used, one cut out from the right crystal, the other from the left one. Figure 5 gives the calculated values $\chi(\lambda)$ for quartz plates of different thickness and the experimentally measured dependence $\chi(\lambda)$ for two crossed plates. It is seen that, the oscillation range is really doubled in comparison with one plate [26].

When investigating the polarization of the passed light incident on a plate only the symmetric part of the gyration tensor can be determined, while the antisymmetric part is not being determined. However, in uniaxial crystals $3\cdot m$, $4\cdot m$, $6\cdot m$ the gyration tensor is fully antisymmetric [6, 13]; therefore, the optical activity in these crystals may be investigated only at oblique incidence.

The antisymmetric part of the gyration tensor is encountered in some classes of symmetry. In the general case, the expressions for the amplitudes of reflected and passed waves are rather cumbersome. Let us give expressions only for crystals of planar classes and for the case when the optical axis is located parallel to the interface and perpendicularly to the incidence plane. When the wave incident at an angle $\varphi$ is polarized parallel or perpendicularly to the main plane, we have for the azimuth and ellipticity of a reflected wave, where

$$\tan 2\chi_1 = \tan 2\chi_\perp = 0,$$

\[
\begin{pmatrix}
\begin{array}{c}
\tan 2\alpha \\
\tan 2\beta
\end{array}
\end{pmatrix} = \begin{pmatrix}
\frac{g_{12} n^2 \eta \sin \varphi}{\tilde{n}(\eta_+ + \eta)(\epsilon_0 \eta - n^2 \eta_0)} \\
\frac{g_{13} n^2 \eta \sin \varphi}{\tilde{n}(\eta_+ - \eta)(\epsilon_0 \eta + n^2 \eta_0)}
\end{pmatrix},
\]

\[
\begin{pmatrix}
\begin{array}{c}
\tan 2\beta \\
\tan 2\alpha
\end{array}
\end{pmatrix} = \begin{pmatrix}
\frac{g_{12} n^2 \eta \sin \varphi}{\tilde{n}(\eta_+ - \eta)(\epsilon_0 \eta + n^2 \eta_0)} \\
\frac{g_{13} n^2 \eta \sin \varphi}{\tilde{n}(\eta_+ + \eta)(\epsilon_0 \eta - n^2 \eta_0)}
\end{pmatrix}.
\]

(19)
Fig. 4.(a) Optical activity manifestation in a crystal NH₄H₃(SeO₃)₂ with changing temperature (d = 2.57 mm, λ = 0.633 μm); (b) optical activity manifestation in a crystal NH₄H₃(SeO₃)₂ as the wave length changes (d = 0.92 mm, T = 20°C).

where

\[ \eta = n \cos \varphi, \quad \eta_{0e} = \sqrt{\varepsilon_{0e} - n^2 \sin^2 \varphi}. \]

For the wave passed through a plate, we have, for the same cases of the incident light polarization \([\Delta = (2\pi d/\lambda)(\eta_e - \eta_0)]\)

\[
\tan 2\chi_i = \frac{2g_{12} \eta_e \sin \varphi (\varepsilon_{0e} \eta_e + n^2 \eta_0) \sin \Delta}{\tilde{m}_{0e} \varepsilon_{0e} (\eta_e + \eta_0)^2},
\]

\[
\tan 2\chi_{e} = \frac{2g_{12} \eta_0 \sin \varphi (\eta_0 + \eta_e \varepsilon_{0e} + n^2 \eta_0) \sin \Delta}{\tilde{m}_{0e} (\varepsilon_{0e} \eta_e + n^2 \eta_0)^2},
\]

\[
\begin{align*}
\left( \frac{b}{a} \right) &= \frac{g_{12} \sin \varphi [n^2 \eta_0 (\eta_e + \eta) - n \varepsilon_{0e} (\varepsilon_{0e} \eta_e + n^2 \eta_0) \cos \Delta]}{\tilde{m}_{0e} \varepsilon_{0e} (\eta_e + \eta_0)^2}, \\
\left( \frac{b}{a} \right) &= \frac{g_{12} \sin \varphi [n^2 \eta_0 (\eta_e + \eta) - n \varepsilon_{0e} (\varepsilon_{0e} \eta_e + n^2 \eta_0) \cos \Delta]}{\tilde{m}_{0e} (\varepsilon_{0e} \eta_e + n^2 \eta_0)^2}. 
\end{align*}
\]

In the same cases of the incident light polarization the wave is elliptically polarized in contrast to a non-active crystal, the ellipticity values as well as the azimuth being proportional to \(g_{12} \sin \varphi\).

On the basis of an analysis of the obtained expressions a method was suggested for determining the antisymmetric part of a gyration tensor from an investigation of the polarization azimuth of
the passed light or from a measurement of the ellipticity of the light reflected from a plate placed in immersion medium with the refraction index close to that of a crystal [41].

The works [49, 50] have recently appeared describing the optical activity in crystals CdS with symmetry 3·m in an exciton absorption band.

It thus follows that, when investigating crystals at normal incidence and carrying on the measurements on a spectropolarimeter one can determine, by an oscillation method, the symmetric part of a gyration tensor; the investigations in reflected light make it possible to determine the antisymmetric part.

4. THE DETERMINATION OF OPTICAL PARAMETERS OF CRYSTALS

Anisotropic media are characterized by complex tensors of dielectric constant and gyration. One of the important problems in crystal optics is to find the components of these tensors. The whole complex of problems for determining the refraction indices has been for a long time available for transparent crystals [51]; various handbooks contain the optical constants for such crystals [52-55]. In slightly absorbing crystals the refraction indices are determined as in transparent crystals, whereas various spectrophotometric methods are to be used for determining the absorption coefficients [56, 57]. In gyrotropic absorbing crystals the determination of optical constants is a more complicated problem as compared with ordinary crystals. For practical work, one has to know not only the refraction indices, absorption coefficients and gyration tensor components, but also the values of dichroism birefringence and proper wave ellipticities. Various methods have been worked out for determining the optical parameters; it should be noted that the values of birefringence and dichroism are not determined simultaneously, although in many cases the determination of optical parameters from one experiment may prove desirable. The authors of Ref [40, 41] suggest that the birefringence and optical activity should be determined from light intensity measurements in transparent crystals. We have proposed a method of simultaneous

Fig. 5. (a) Theoretically calculated dependence of the passed light azimuth on wave length \( \lambda \) for plates cut out from the right quartz. \( a--d = 1 \text{ mm}; b--d = 0.1 \text{ mm}; c--experimentally obtained dependence of the passed light azimuth \( \chi \) on wave length \( \lambda \) for two crossed plates from right quartz (\( d = 1.5 \text{ mm} \)).
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determination of optical parameters from the passed light azimuth \( \chi \) measurements depending on the incident light azimuth \( \alpha \) [36, 38]. We show in these works that the dependences

\[
\tan 2(\alpha - \chi) = \frac{a_4 \tan^4 \alpha + a_3 \tan^3 \alpha + a_2 \tan^2 \alpha + a_1 \tan \alpha + a_0}{b_4 \tan^4 \alpha + b_3 \tan^3 \alpha + b_2 \tan^2 \alpha + b_1 \tan \alpha + b_0}
\]  

(21)

proved most informative; here \( a_i, b_i \) depends on birefringence \( \Delta n \), dichroism \( \Delta N \), proper wave ellipticities \( k_1 \) and \( k_2 \) and non-orthogonality angle \( \beta \). In the general aspect, expression (21) is rather complicated, but in directions different from the optical axis, when it is possible to use the proper wave orthogonal approximation, we obtain from expression (21):

\[
\tan 2(\alpha - \chi) = \frac{(1 - \cos \Delta) \sin 2\alpha \cos 2\alpha + 2k \sin \Delta \sin 2\alpha + 2s \cos 2\alpha \sin \Delta}{\cos^2 2\alpha + \sin^2 2\alpha \cos \Delta \sin 2\alpha \cos 2\alpha + 2s \sin 2\alpha \sin \Delta},
\]  

(22)

where

\[
\Delta = \frac{2\pi d}{\lambda} \Delta n, \quad \delta = \frac{2\pi d}{\lambda} \Delta N.
\]

The dependence \( (\alpha - \chi) = f(\alpha) \) possesses the oscillating character and four extremal values, when changing \( \alpha \) from 0 up to 180°, as is shown in Fig. 6. The extremal values of function are linked by the following relationships:

\[
M_i = \tan 2(\alpha - \chi)_i, \\
M_1 + M_2 + M_3 - M_4 = 4m_1, \quad M_1 + M_2 + M_3 + M_4 = 4km_2, \\
M_1 + M_2 - M_3 - M_4 = 4\delta m_3, \quad M_1 - M_2 - M_3 + M_4 = 4sm_4,
\]  

(23)

where

\[
m_1 = \frac{1 - \cos \Delta}{2\sqrt{\cos \Delta}}, \quad m_2 = \frac{\sin \Delta(1 + \cos \Delta)}{\cos \Delta}, \\
m_3 = \frac{(1 + \cos \Delta)^{3/2}}{4\cos \Delta}, \quad m_4 = \frac{\sin \Delta(1 + \cos \Delta)^{3/2}}{2(\cos \Delta)^{3/2}}.
\]  

(24)

One can estimate the optical parameters proceeding from these relationships. From the first equation of system (23) we find \( m_1 \) and determine the phase difference \( \Delta \). It should be taken into

\[
\text{Fig. 6. Dependence } (\alpha - \chi) = f(\alpha) \text{ for a plate from a crystal with different parameters: } \Delta = 22.92^\circ; \\
1-\delta = 0, k = 0, s = 0; 2-\delta = 0, k = 0.1, s = 0; 3-\delta = 0.1, k = 0, s = 0; 4-\delta = 0, k = 0, s = 0.1; \\
5-\delta = 0.1, k = 0, s = 0.1; 6-\delta = 0.1, k = 0.1, 1, s = 0.1.
\]
consideration that $\Delta = \Delta_0 + 2\pi l$; therefore, only $\Delta_0$ can be determined in this way. To determine
the number $l$ one has to carry out some additional measurements or measurements on thin plates
in which $l = 0$ and $\Delta = \Delta_0$. If we know $\Delta$, we can calculate from expression (24) $m_1$, $m_2$, $m_3$
and determine from expressions (23) the values $k$, $\delta$ and $\gamma$. The period of function $(\alpha - \chi) = f(\alpha)$ is equal
to 90° for transparent crystals and to 180° for absorbing ones. For some relationships $\Delta$ and $\delta$
the function $(\alpha - \chi) = f(\alpha)$ may have not four, but only two extremal values. In the general case, the
determination of optical parameters involves a computation of dependences (21) using the program
of minimization of a function of many variables.

On the basis of the analysis performed we propose a polarization method for determining the
optical parameters. To do this, one has to place the plate under investigation between crossed
polarizers and an analyzer in a polarization device such as a spectropolarimeter or ellipsometer.
Then, the angle $\chi$ of the major axis of the passed light polarization is measured for various values
of the incident light azimuth $\alpha$. Using relationships (21), we can solve the task on a computer, or
approximately from relationships (23). As a result, we calculate the values of optical parameters
$\Delta$, $\delta$, $k_1$, $k_2$, $\beta$ in crystals of any symmetry possessing the optical activity and absorption. We applied
this method for investigating the yttrium, erbium and holmium formiate dihydrate crystals [58–60].
The most characteristic dependences $(\alpha - \chi) = f(\alpha)$ obtained for plates Y(HCOO)$_3$·2H$_2$O,
Ho(HCOO)$_3$·2H$_2$O cut out perpendicularly to the optical axis are given for some wave lengths in
Fig. 7. A legend for each figure contains the computed values $\Delta$, $\delta$, $k_1$, $k_2$.

As the result of computations, the non-orthogonality angle $\beta$ proved to be smaller than 1.5°,
even in the strongest absorption bands, despite the fact that the measurements were made near the
optical axis; this fact does not exert any substantial influence on the determination of optical
parameters.

The polarization method proves convenient when investigating crystals at various external
effects, such as application of electric and magnetic fields, a change in temperature and some others.
For example, we carried out investigation on langbeinite crystals K$_2$Co$_2$(SO$_4$)$_3$ in the temperature
range including the phase transition temperature 126 K [63]. To carry out the measurements, a
specimen 0.075 mm thick, oriented perpendicularly to the second-order axis was used. The
polarization dependences were obtained at temperatures 127 K (cubic phase), 125, 120, 99 K
(low-symmetric phase) both in the transparence $(\lambda = 0.35; 0.45; 0.64 \mu m)$ and absorption
$(\lambda = 0.501, 0.549 \mu m)$ ranges (Fig. 8). It is seen from the figure that at the phase transition
temperature 126 K the oscillations appear whose amplitude increases with decreasing temperature;

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{(a) Dependence $(\alpha - \chi) = f(\alpha)$ for a plate from a crystal Y(HCOO)$_3$·2H$_2$O ($d = 0.062$ mm) at wave
lengths and calculated values of phase difference $\Delta$ and proper wave ellipticities $k$: $1-\lambda = 0.297 \mu m$,
$\Delta = 35.90^\circ$, $k = 0.094$; $2-\lambda = 0.313 \mu m$, $\Delta = 22.20^\circ$, $k = 0.124$; $3-\lambda = 0.366 \mu m$, $\Delta = 10.77^\circ$, $k = 0.206$;
$4-\lambda = 0.436 \mu m$, $\Delta = 5.4^\circ$, $k = 0.299$; $5-\lambda = 0.577 \mu m$, $\Delta = 1.76^\circ$, $k = 0.499$. (b) Dependence $(\alpha - \chi) = f(\alpha)$ for a plate from a crystal Ho(HCOO)$_3$·2H$_2$O ($d = 0.076$ mm) at wave
lengths $\lambda$ and calculated values $\Delta$, $\delta$, $k_1$, $k_2$: $1-\lambda = 0.278 \mu m$, $\Delta = -95.307^\circ$, $\delta = 0.0023$, $k_1 = 0.0497$, $k_2 = 0.0336$; $2-\lambda = 0.344 \mu m$,
$\Delta = -23.818^\circ$, $\delta = 0.0297$, $k_1 = 0.1259$, $k_2 = 0.1073$; $3-\lambda = 0.449 \mu m$, $\Delta = -17.148^\circ$, $\delta = 0.3488$,
$k_1 = 0.1078$, $k_2 = 0.072$; $4-\lambda = 0.590 \mu m$, $\Delta = -2.540^\circ$, $\delta = 0.0051$, $k_1 = 0.3493$, $k_2 = 0.3493$.}
\end{figure}
this is explained by the appearance of the linear birefringence at a phase transition and its temperature dependence. The proper wave ellipticity values change at a phase transition from values close to unit which corresponds to a cubic crystal, to the values \( k \approx 0.01 \). Two waves with different ellipticity propagate in the absorption region; this gives evidence for a large contribution of absorption to the total ellipticity. For a given crystal orientation the linear birefringence changes abruptly from the value of order \((1-10) \cdot 10^{-7}\) to the value of order \((4.1-5.4) \cdot 10^{-4}\). The circular birefringence does not change at a phase transition within the limits of an experiment accuracy, but it possesses a marked dispersion. The crystals can be investigated in this way at some other external effects. The authors of Refs [61, 62] propose another method for determining the optical parameters from the investigation of the dependence \( X = f(\chi) \) and carry on the measurements of orthoferrites in a magnetic field.

For the simultaneous determination of optical parameters, one should investigate the intensity of light passed through a plate placed between arbitrarily oriented polarizers. 

Shubnikov gives in his books [1, 2] an expression for the intensity for a transparent optically non-active crystal

\[
I = I_0 \left[ \cos^2(\alpha - \theta) - \sin 2\alpha \sin 2\eta \sin \left( \frac{\Delta}{2} \right) \right],
\]

where \( \alpha \) and \( \theta \) are the azimuth of the oscillation directions of vector D in a polarizer and analyzer, respectively. In Ref. [64] an expression was obtained for the intensity of light passed through an
absorbing optically active uniaxial crystal. For directions different from the optical axis, when the circular effects are weak, we have

\[ I = I_0 e^{-\zeta} \left( e^{\delta} \cos^2 \alpha \cos^2 \theta + e^{-\delta} \sin^2 \alpha \sin^2 \theta + \frac{1}{2} \sin 2\alpha \sin 2\theta \cos \Delta + k \sin 2(\alpha - \theta) \sin \Delta \right. \\
\left. + \sin \beta \left[ e^{-\delta} \sin \alpha \sin \theta - e^{\delta} \cos \alpha \cos \theta + \cos(\alpha + \theta) \cos \Delta \sin(\alpha - \theta) \right] \right), \] (26)

where \( \zeta = (2n\pi/\lambda)(N_1 + N_2) \), \( \beta \) is the proper wave non-orthogonal angle. In comparison with expression (25), some terms appeared in expression (26) containing \( e^{\pm \delta} \) and proper wave ellipticity.

Using relationship (26) and carrying on the measurements of light intensity depending on the rotation of a plate placed between arbitrarily oriented polarizers, one can suggest a method for determining the optical parameters [65]. If the polarizers are parallel, then \( \alpha = \theta \); here the maximum \( I_1 \), \( I_3 \) and minimum \( I_2 \) values of function \( I(\alpha) \) are determined by values \( \Delta \) and \( \delta \) as shown in Fig. 9a. [The optical activity does not manifest itself depending on \( I(\alpha) \), if the polarizers are arranged in such a way and the values \( k \) are small.]

To determine the values \( \Delta \) and \( \delta \) we obtain

\[ e^{2\delta} = \frac{I_1}{I_3}, \quad \cos \Delta = a e^\delta \pm \sqrt{(a e^{2\delta} - 1)(a - 1)}, \] (27)

where \( a = I_2/I_1 \). At some relationships between \( \Delta \) and \( \delta \) the dependence \( I(\alpha) \) may have only one minimum value. In this case, it is possible to determine the value \( I(\alpha) \) at \( \alpha = 45^\circ \). Then

\[ e^{2\delta} = \frac{I_1}{I_2}, \quad \cos \Delta = 2b e^\delta - \frac{e^\delta + e^{-\delta}}{2}, \] (28)

where

\[ b = \frac{I_{45}}{I_1}. \]

Fig. 9. (a) Dependence of light intensity \( I(\alpha) \) on a plate rotation angle \( \alpha \) at different values \( \delta \). \( \Delta = 40^\circ \), \( k = 0 \). Up—polarizers are parallel; down—polarizers are crossed. (b) Light intensity dependence \( I(\alpha) \) on the polarizer rotation angle \( \alpha \). \( \Delta = 40^\circ \), \( \alpha = 45^\circ \), \( k = 0 \). (c) Dependence \( I(\alpha) \) at different values \( k \), \( \Delta = 40^\circ \), \( \delta = 0 \). (d) Experimental dependence \( I(\alpha) e^{-\delta} \) for a plate from ruby. \( \Delta n = 8.5 \cdot 10^{-3}, \Delta N = 9.46 \cdot 10^{-5} \).
If $\theta = \alpha = 90^\circ$ (polarizers are crossed), it is possible to determine by an analogous method the values $\Delta$ and $\delta$ from the dependence $I(\alpha)$.

If we locate the polarizers at an arbitrary angle with respect one to the other and rotate the plate, we shall determine all of the optical parameters.

The optical parameters $\Delta$ and $\delta$ for a non-active crystal can be determined, if we locate a plate at an angle of $45^\circ$ to the polarizer, rotate the analyzer and investigate the dependence $I(\theta)$ [Fig. 9(b)]. In this case

$$e^{2\delta} = \frac{I_1}{I_2}, \quad \cos \Delta = (c - 0.5)(e^{\delta} + e^{-\delta}),$$

where $c = I_4/I_1 + I_2$, $I_1$ and $I_2$ are the extremal values of function $I(\theta)$.

The dichroism values can be determined, if $\delta$ is measured without an analyzer. Then

$$I = I_0 e^{-\delta}(e^{-\delta} \cos^2 \alpha + e^{\delta} \sin^2 \alpha)$$

and the specimen birefringence exerts no influence whatever.

In an optically active transparent crystal (with an account of all terms relative to $k$) we have:

$$I = I_0 \frac{1 + k^4}{(1 + k^4)^2} \left\{ \cos^2(\alpha - \theta) - \sin 2\alpha \sin 2\theta \sin^2 \frac{\Delta}{2} \right\}$$

$$+ \frac{k(1 + k^4)}{1 + k^4} \sin 2(\alpha - \theta) \sin \Delta + \frac{k^2}{1 + k^4} \left[ 2(\cos^2 \alpha \sin^2 \theta + \sin^2 \alpha \cos^2 \theta) + \right.$$

$$\left. + (\cos 2(\alpha - \theta) + \cos 2\alpha \cos 2\theta) \cos \Delta \right\}. \quad (31)$$

At $\alpha = \theta$ the value of dependence $I(\alpha)$ is larger relative to $I(\alpha)$, when $k = 0$; therefore the value $\Delta$ can be determined as for a transparent non-active crystal. At $k = 1$, comes out to be a straight line instead of an oscillating dependence $I(\alpha)$; this is in conformity with the value $I = I_0 \cos^2 \Delta/2$, when $\Delta$ depends on the circular birefringence value. The circular birefringence and consequently, the specific rotation can be determined if we place a plate between polarizers, and change the incident light wave length [66].

In all these cases, the simplest way of determining the optical parameters is to use the extremal values of function $I(\alpha)$. A more accurate determination will involve calculations with the aid of a computer. In Fig. 9(a) the experimental dependences $I(\alpha)$ for a ruby sample are given as an example. From these data we obtain the value $\Delta n = 8.5 \cdot 10^{-3}$ for birefringence, and $\Delta N = 9.46 \cdot 10^{-5}$ for dichroism.

In such a way, the investigation of functional relationships $(\alpha - \chi) = f(\alpha)$ or $I = f(\alpha)$ makes possible the determination of optical parameters. The real part of a gyration tensor can be calculated from proper wave ellipticity values. As already mentioned, in optically active absorbing crystals tensor $\tilde{\delta}$ is a complex value. The imaginary part of a gyration tensor $\tilde{\delta}^{11}$ describes the phenomenon of circular dichroism. In the simplest case, when the light propagates in an anisotropic crystal or along the optical axis of a uniaxial crystal, this leads to the fact that two circularly polarized waves are absorbed in a different way. In the general case, the elliptical waves are absorbed differently in directions different from the optical axis direction.

For circular dichroism measurements special devices (dichrographs) have been created which have different design [67].

The circular dichroism was first measured in 1847 by Hiedinger on amethyst crystals. Ever since, a rich experimental material for circular dichroism studies in solutions has been accumulated. This method is one of the important methods of investigation in stereochemistry and biology [68]. The systematic study of this phenomenon in crystals has recently begun [8]. A spectroscopic aspect of this phenomenon has been studied in detail in works of such a type. But we shall not dwell on this in our article, and shall confine ourselves, as before, to a phenomenological consideration. To date, biaxial and uniaxial crystals have not been practically investigated in directions different from the optical axis.
In Ref. [69] an expression was obtained for a signal recorded by a dichrograph, when the light
passes through a sample cut out from a low-symmetric absorbing gyrotropic crystal:

\[ D_1 = \frac{(P_1(1+P_1)e^\delta - P_1(1+P_2)e^{-\delta} - (1-P_1P_2)\sin\beta \sin\Delta + (P_1-P_2)(1-P_1P_2)\cos\Delta \cos\beta)}{(1+P_1)(1+P_2)\cosh\delta - [(1+P_1P_2)^2\sin^2\beta + (P_1-P_2)^2]\cos\Delta}, \]

(32)

where \( \beta \) is the proper wave non-orthogonality angle, and \( P_1, P_2 \) are the values proportional to
proper wave ellipticities.

For uniaxial crystals, when wave ellipticities may be considered as being identical, this expression
becomes much simpler:

\[ D_1 = \frac{\left(\frac{2k}{1+k^2}\sinh\delta - \frac{1-k^2}{1+k^2}\sin\beta \sin\Delta\right)\cos\beta}{\cosh\delta - \sin^2\beta \cos\Delta}. \]

(33)

In the case of isotropically gyrotropic medium or during the light propagation along the uniaxial
crystal axis:

\[ D_1 = \tanh\delta \approx \delta = \frac{2\pi d}{\lambda} \hat{a}_b, \]

(34)

---

Fig. 10. (a) Passed light azimuth dependence on a wave length for a plate from benzyl \((d = 0.425 \text{ mm})\).
Light polarization: \( \bigcirc \) perpendicular to the optical axis; \( \Delta \)—parallel to the optical axis. (b) Dispersion
of benzyl gyration tensor components: 1—\( g_{11} \); 2—\( g_{33} \). (c) Benzyl circular dichroism: 1—\( \Delta g_{11} \); 2—\( \Delta g_{33} \).
\(\delta\) being a measure of circular dichroism; just to the investigation of this case an overwhelming majority of works is devoted.

In Ref. [69] it is shown how one can measure the circular dichroism in uniaxial and biaxial crystals, using the relationships obtained. The measurements in a direction different from that of an optical axis prove especially simple, if a crystal possesses weak birefringence or has an isotropic point. Such measurements have been carried out, e.g. on benzyl crystals with an isotropic point at \(\lambda = 0.4206 \mu m\) [70]. The values of circular dichroism along the axis or perpendicularly to it are given for benzyl in Fig. 10. The same figure presents the values \(\chi(\lambda)\) for two directions of the incident light polarization as well as the calculated values of gyration tensor components. The measurements of circular dichroism in biaxial crystals were made on erbium and holmium formiate dihydrate crystals [70].

Up till now, the problem of studies of crystals in passing light has been considered. But strongly absorbing crystals can be investigated only in reflected light. The authors of Refs [5, 72, 73] propose theoretical methods for determining the absorbing crystal parameters. The experimental investigation of low-symmetric absorbing crystals have not practically been carried out. At present, the methods for investigating only uniaxial strongly absorbing crystals have been worked out and applied. In Ref. [74] an ellipsometric method for studying such crystals is suggested, the data processing has been performed using the obtained computations. In such measurements the “transitional layer” which is always present on the surface exerts influence on the accuracy. This layer should be taken into account when more accurate measurements are required.

Let us give several examples of absorbing uniaxial crystals taken from Ref [74]:

<table>
<thead>
<tr>
<th>Crystal</th>
<th>No</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tourmaline</td>
<td>1.667 + i 0.027</td>
<td>1.697 + i 0.014</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>3.36 + i 1.410</td>
<td>2.25 + i 0.37</td>
</tr>
<tr>
<td>Stibium</td>
<td>2.986 + i 5.412</td>
<td>4.01 + i 5.259</td>
</tr>
</tbody>
</table>

At present, the achievements in the field of ellipsometry and computation technique open up the possibilities of the investigation of strongly absorbing low-symmetric crystals.

5. CONCLUSION

In such a way, since the publication of Shubnikov’s books [1, 2], many new results have been obtained in crystal optics of absorbing and gyrotropic crystals which have substantially changed these chapters of optics of anisotropic media both in theoretica and experimental and methodical aspects.

At the same time, there have appeared and developed new fields of crystal optics such as non-linear optics, investigations of the action effects, crystal optics of liquid crystals. Crystal optics is no longer an auxilliary part of crystallography, but has become a large and important part of solid state physics.

The work published in Ref. [75] formed the basis of the present article.

REFERENCES

Absorbing and gyrotropic media


