

INVESTIGATION OF MANIFESTATION OF OPTICAL ACTIVITY IN ANISOTROPIC CRYSTALS

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Abstract

The special features of the manifestation of optical activity in the anisotropic absorbing crystals are described. The influence of optical activity on the characteristics of the transmitted light depending on the wavelength of incident light, temperature, orientation of optical axis and inclination is shown. The results of investigation of the some crystals of different classes of symmetry are given.

Introduction

The phenomenon of optical activity, or gyrotropy, occupies special position among the physical properties of crystals. Systematic investigations of optical activity in the crystals in the directions of optical axis started long time ago, and currently the large number of crystals, which rotate the plane of polarization, are known. However, optical activity and circular dichroism of crystals were experimentally investigated comparatively less and, until now they do not have sufficient utilization. It is connected with the fact that the crystals in all directions, different from the optical axis, possess linear birefringence and linear dichroism; moreover linear effects, as a rule, larger than circular.

In this work main attention to the special features of the manifestation of optical activity during the investigation of crystals in the transmitted light is given. The results of investigation of some crystals obtained in the Institute of Crystallography of the Russian Academy of Sciences are given.

1. Relationships for description of optically active crystals

The effect of optical activity of crystals can be determined by the measurements of azimuth (χ), of ellipticity of the light ($\tan V$), which transmits through an optically active birefringent absorbing plate, as well as the intensity of light (J), which transmits through the system polarizer – sample – analyzer. In many cases, multiple reflections are ignored in analyzing the results of measurements of the parameters of the light transmitted through a crystal plate. Then for sufficiently thick samples oriented in proper axes these expressions take the form [1]:

$$\tan 2\chi = \frac{\cos \Delta \sin 2\alpha \pm \sin 2\gamma \sin \Delta \cos 2\alpha}{\cos 2\gamma \operatorname{sh} \delta + \cos^2 2\gamma \operatorname{ch} \delta \cos 2\alpha + \sin^2 2\gamma \cos \Delta \pm \sin 2\gamma \sin \Delta \sin 2\alpha}, \quad (1)$$

$$\sin 2V = \pm \frac{\sin 2\gamma \operatorname{sh} \delta + \cos 2\gamma [(\operatorname{ch} \delta - \cos \Delta) \sin 2\gamma \cos 2\alpha + \sin \Delta \sin 2\alpha]}{\operatorname{ch} \delta + \cos 2\gamma \operatorname{sh} \delta \cos 2\alpha}, \quad (2)$$

$$J = T \{2 \operatorname{ch} \delta \cos^2(\alpha - \beta) - (\operatorname{ch} \delta - \cos \Delta) \sin 2\beta \sin 2\alpha + 2 \cos 2\gamma \operatorname{sh} \delta \cos(\alpha + \beta) \cos(\alpha - \beta) - \sin^2 2\gamma (\operatorname{ch} \delta - \cos \Delta) \cos 2\beta \cos 2\alpha \pm \sin 2\gamma \sin \Delta \sin 2(\alpha - \beta)\} / 2, \quad (3)$$

where T is the general transmission of plate; α, β are the azimuth of the direction of the greatest transmission of polarizer and analyzer; the complex refractive indices of eigenwaves propagating in the crystal can be represented by the relationship $N_{1,2} = n_{1,2} + i \kappa_{1,2}$, where n_1 and n_2 are the refractive indices, κ_1 and κ_2 are the absorption indices; $\Delta = 2\pi d(n_2 - n_1)/\lambda$, $\delta = 2\pi d(\kappa_2 - \kappa_1)/\lambda$; d is the plate thickness, λ is the wavelength of the incident light; $\sin 2\gamma = 2k/(1 + k^2) = x$, $k = \tan \gamma$ is the ellipticity of the eigenwaves. In (1 – 3), the plus and minus signs refer to the right - and left-handed crystals, respectively.

2. Azimuth and the ellipticity of the light transmitted through an optically active plate

When the light propagates along directions different from the optic axis of optically active nonabsorbing plate the ellipticity of the eigenwaves $k = \pm 1$ (both eigenwaves circularly are polarized). In this case the phase difference Δ is determined only by circular birefringence, i.e. $\Delta = \Delta_c = 2\pi d \Delta n_c / \lambda$, and (1), (2) can be represented in the form:

$$\tan 2\chi = \operatorname{tg}(2\alpha - \Delta_c), \quad \sin 2V = 0. \quad (4)$$

In this case the linearly polarized light, passing through the crystalline plate, remains linearly polarized ($\sin 2V = 0$), but its azimuth of polarization changes to the some angle of Ψ , i.e., the rotation of the polarization plane is observed:

$$\Psi = (\alpha - \chi) = \Delta_c / 2 = \pi d G / \lambda n_o = \pi d \Delta n_c / \lambda = \rho d, \quad (5)$$

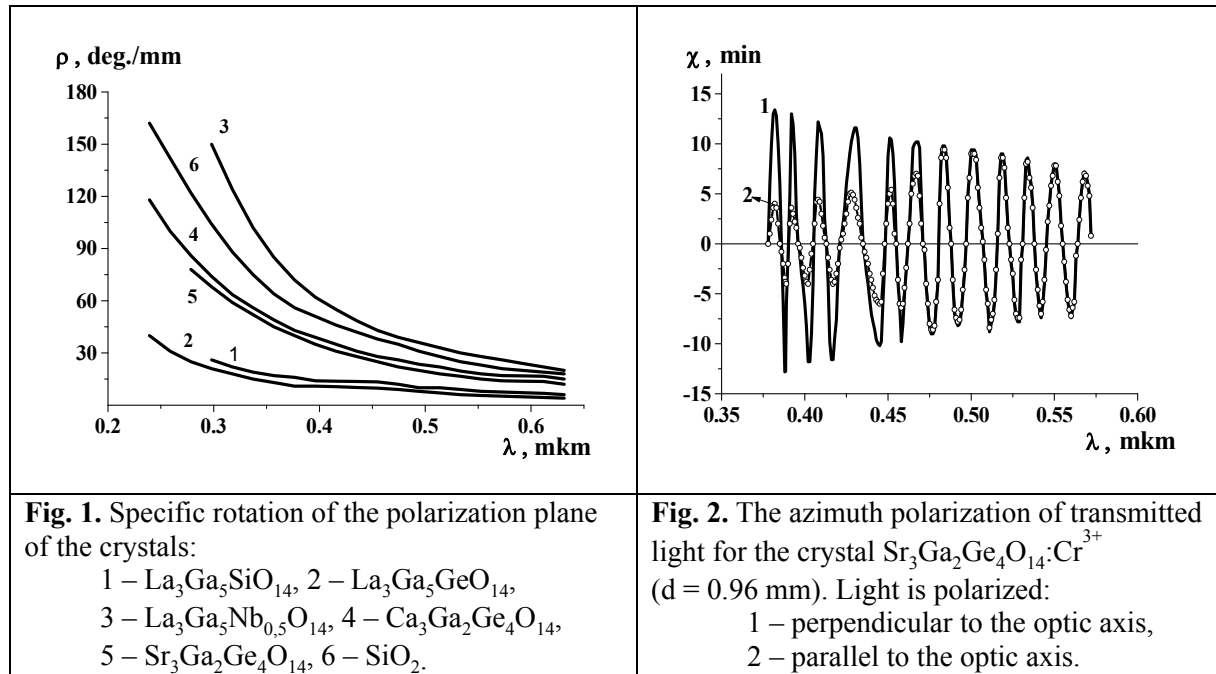
where G is the scalar parameter of gyration, which depends on crystal symmetry, the phase difference for the crystal $\Delta = \Delta_c = 2\rho d$, $\rho = g_{33}\pi/\lambda n_o$ is the specific rotation of the polarization plane ($G = g_{33}$ for uniaxial crystals). For absorbing crystals it is possible to write down:

$$\Psi = (\rho + i \tau) d = \pi d (G' + iG'') / \lambda n_o, \quad (6)$$

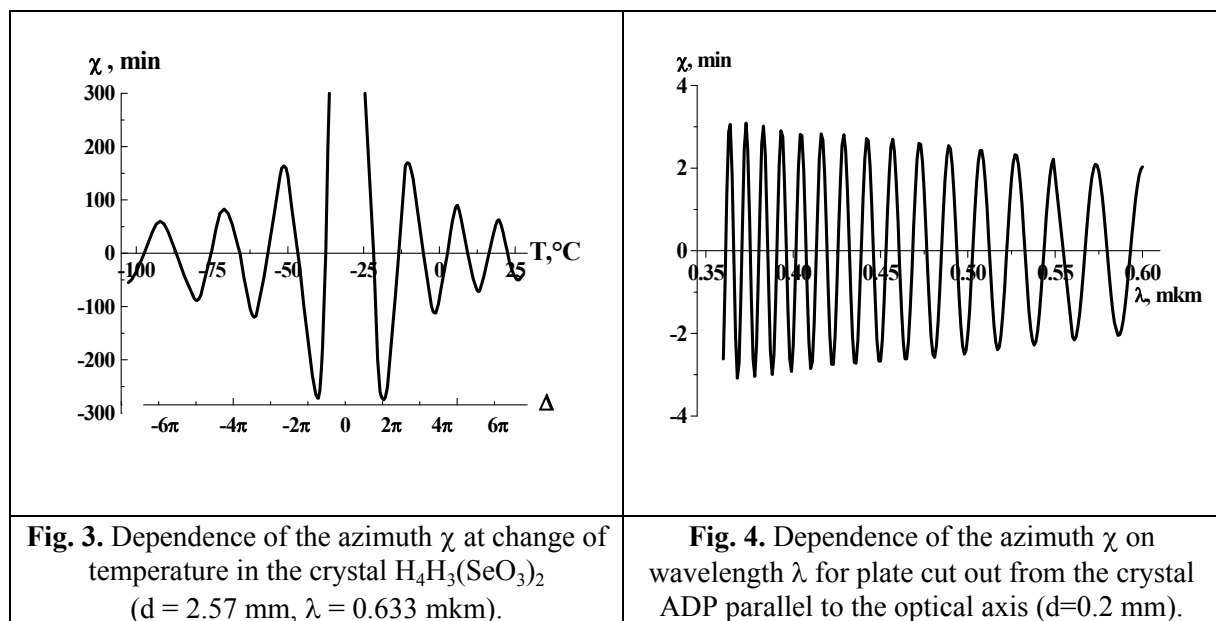
In the directions, different from the optical axis, k is small value and from (1, 2) we have

$$\begin{aligned} \operatorname{tg} 2\chi_{\parallel} &= \pm 2ke^{-\delta} \sin \Delta, & \operatorname{tg} 2\chi_{\perp} &= \pm 2ke^{\delta} \sin \Delta, & (\alpha = 0) \\ \sin 2V_{\parallel} &= \pm 2k(1 - e^{-\delta} \cos \Delta), & \sin 2V_{\perp} &= \pm 2k(1 - e^{\delta} \cos \Delta), & (\alpha = \pi/2). \end{aligned} \quad (7)$$

Examples of investigation of crystals in the directions parallel and perpendicular to optical axis are given in Fig. 1 and Fig. 2 [2].



Especially clearly optical activity is manifested in the crystals with ε - isotropic birefringence point, when linear birefringence is equal to zero. For example the biaxial crystal $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$ (symmetry class 222) at a specific wavelength and temperature becomes uniaxial, moreover the bisector of the sharp angle of optical axes becomes optical axis [3]. Then at the propagation of light along this direction the rotation of the polarization plane is observed, and in other directions the oscillations of the azimuth of polarization of the transmitted light. These oscillations associated by the simultaneous manifestation of optical activity and birefringence, are observed. In Fig.3 dependence $\chi(T)$ in crystal $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$ is shown. One can see that at $T = -30^\circ\text{C}$ crystal becomes uniaxial, and the rotation of the polarization plane is observed. The oscillations are observed at the directions different from the optical axis.



Similar oscillations, associated with optical activity, are observed during investigation of crystals in the directions different from the optical axis while changing the wavelength of incident light, as shown in Fig. 2. The same dependences $\chi(\alpha)$ are observed in crystal ADP, (symmetry class $\bar{4}2m$), in which the rotation of the polarization plane along the optical axis is impossible and optical activity is manifested only in the directions, different from the optical axis.

Let us give the results of investigating the crystal of benzyl, in which there is ε - isotropic birefringence point [4]. On the plate, cut out in parallel to optical axis one can see the oscillations, analogous to Fig. 2, 3 with exception of region ε - isotropic point at $\lambda=0.4205\text{mkm}$, in which the rotation of the plane of polarization is observed. From the measurements of azimuth χ all values, which characterize the optical activity of this crystal, are calculated. The results of these calculations are given in Fig. 5. The components of the imaginary part of the gyration pseudotensor, which characterize circular dichroism, are given in Fig. 5b.

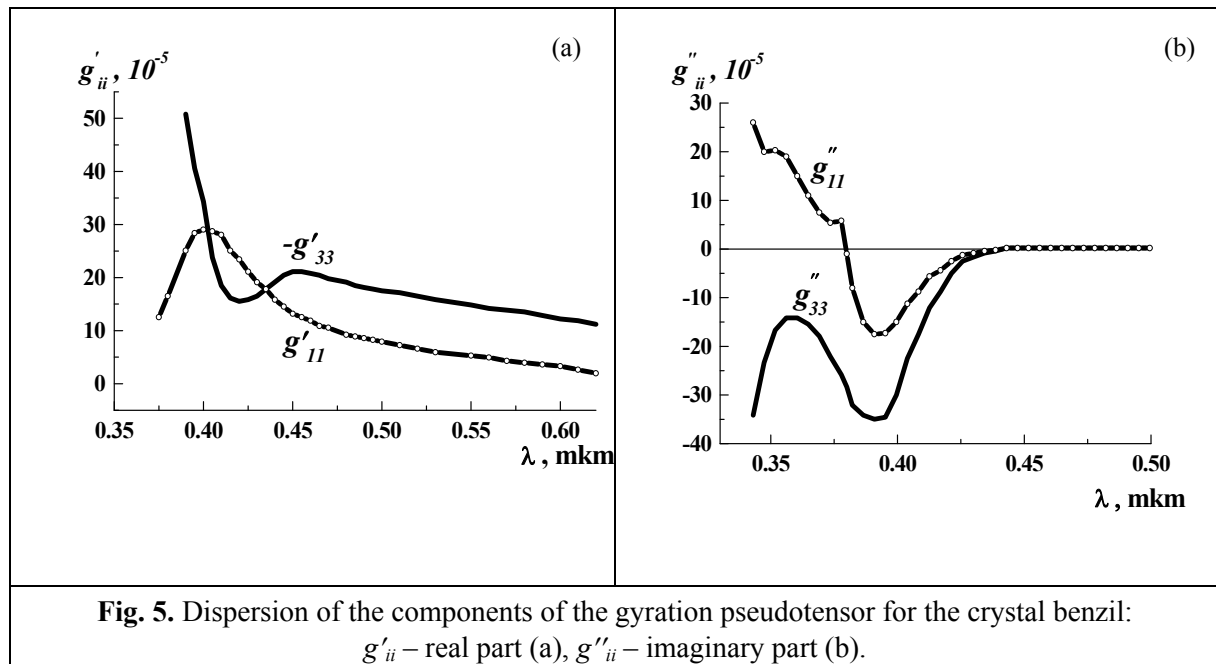
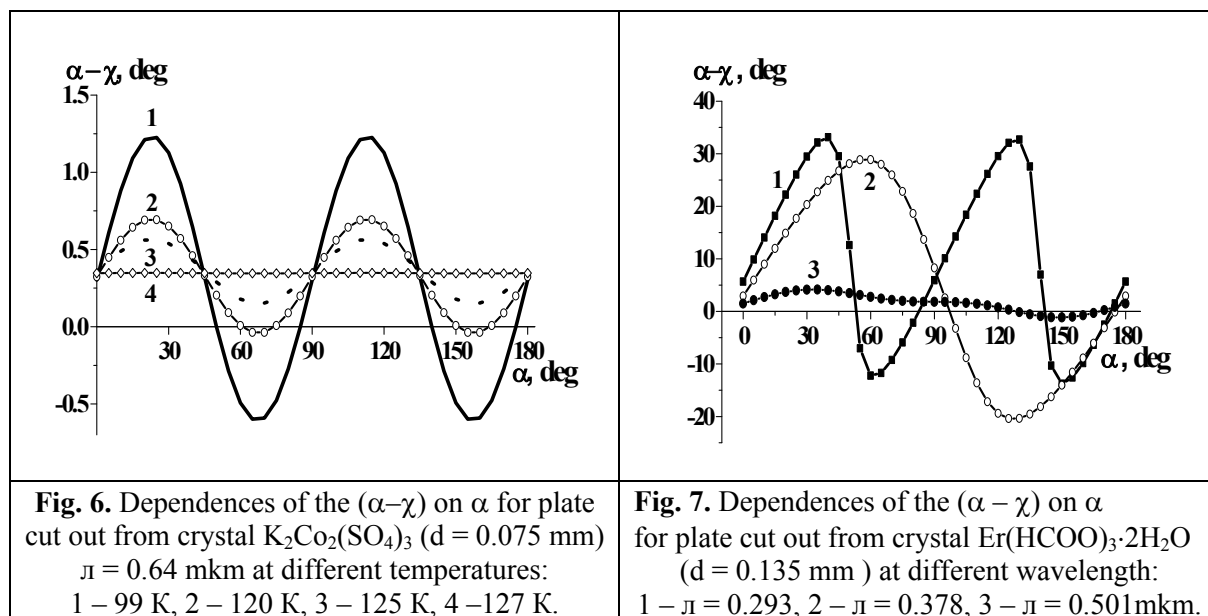


Fig. 5. Dispersion of the components of the gyration pseudotensor for the crystal benzyl: g'_{ii} – real part (a), g''_{ii} – imaginary part (b).

In many cases dependences $\tan 2(\alpha - \chi) = f(\alpha)$ are the most informative. By basing on these dependences it is possible to calculate the parameters, which characterize optical activity. For example let us give the results of investigation of the cubic crystal $\text{K}_2\text{CO}_3(\text{SO}_4)_3$ [5], which at change of temperature in the region of phase transition with $T_c = 126\text{ K}$ passes into the improper ferroelectric phase and from the cubic crystal it becomes birefringent (Fig.6).

One can see that prior to the phase transition the dependence $(\alpha - \chi) = f(\alpha)$ remains constant (Fig. 6, curve 4), as must be in the cubic crystal. In process of temperature decrease the crystal becomes anisotropic and the swing of oscillations $(\alpha - \chi)$ increases. That indicates increase of the linear birefringence.



The investigation of biaxial crystals even in the direction of optical axis is a complex problem. The plate can be cut out perpendicularly to optical axis only for one wavelength of incident light it occurs because of the optical axis dispersion. Therefore in contrast to the uniaxial crystals it is necessary to measure always dependences $\text{tg}[2(\chi - \alpha)] = f(\alpha)$, from which then it is possible to calculate the parameters of optical activity. An example of such measurements is given in Fig. 7 for biaxial crystal $Er(HCOO)_3 \cdot 2H_2O$ (symmetry class 222). From such measurements with the help of relationship (1) the components of the gyration pseudotensor of this crystal were calculated, and the rotation of the polarization plane was determined [6]. There are some peculiarities for determination of the components of the gyration pseudotensor in the biaxial crystals. Such peculiarities depend on the symmetry of crystal. It is necessary to conduct measurements in several differently oriented samples not only at normal, but also at inclined incidence of light on the crystal.

3. Intensity of the light transmitted through the polarizer – sample – analyzer system

Optical activity is manifested also during investigation of the intensity of the light transmitted through the polarizer – sample – analyzer system. In this case the polarizer and analyzer can be oriented in different ways. Depending on the rotation of the sample on angle of α (this is identical to synchronous turning of polarizer and analyzer) it is possible to observe dependences $J(\alpha)$, from which it is possible to calculate the anisotropic optical parameters, such as birefringence, dichroism and the parameters of optical activity [1].

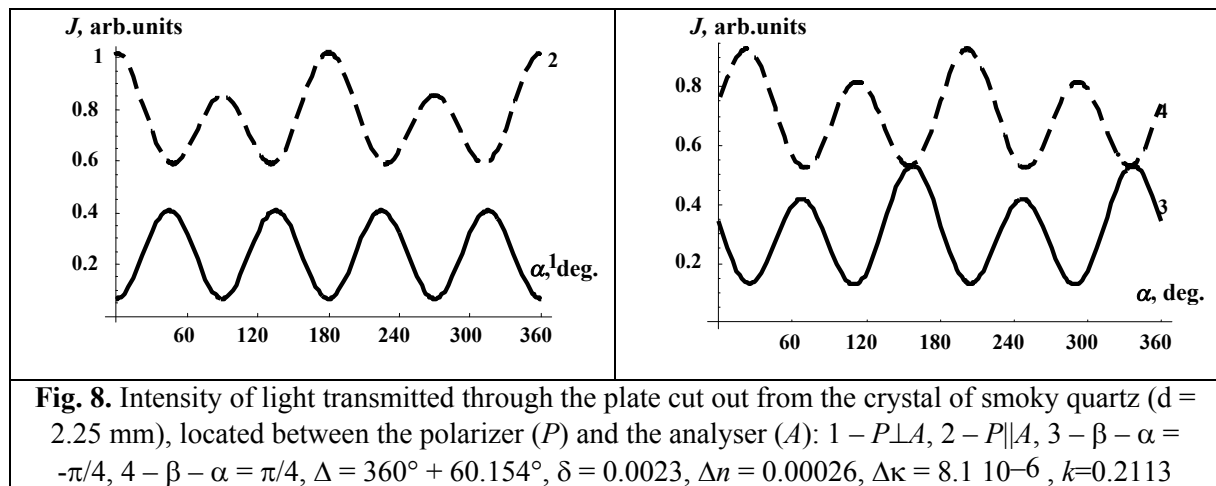
Formula (3) can be rewritten in another way in the form of the section of Fourier series:

$$I = T(a + b_1 \cos 2\alpha + b_2 \sin 2\alpha + c_1 \cos 4\alpha + c_2 \sin 4\alpha), \quad (8)$$

where coefficients a_i , b_i , c_i depending on the mutual orientation of polarizer (P) and analyzer (A) are written differently.

$P \perp A (\beta - \alpha = \pi/2)$	$P \parallel A (\beta = \alpha)$	$\beta - \alpha = -\pi/4$	$\beta - \alpha = \pi/4$
$a_{\perp} = (1 + x^2) (\text{ch}\delta - \cos\Delta),$ $b_1^{\perp} = b_2^{\perp} = 0,$ $c_1^{\perp} = -(1 - x^2) (\text{ch}\delta - \cos\Delta),$ $c_2^{\perp} = 0.$	$a_{\parallel} = 4\text{ch}\delta - (1 + x^2)(\text{ch}\delta - \cos\Delta)$ $b_1^{\parallel} = 4 \sqrt{1 - x^2} \text{sh}\delta,$ $b_2^{\parallel} = 0,$ $c_1^{\parallel} = (1 - x^2) (\text{ch}\delta - \cos\Delta),$ $c_2^{\parallel} = 0.$	$a^- = 2(\text{ch}\delta - x \sin\Delta),$ $b_1^- = b_2^- = 2 \sqrt{1 - x^2} \text{sh}\delta,$ $c_1^- = 0,$ $c_2^- = (1 - x^2) (\text{ch}\delta - \cos\Delta).$	$a^+ = 2(\text{ch}\delta + x \sin\Delta),$ $b_{1,2}^+ = \pm 2 \sqrt{1 - x^2} \text{sh}\delta,$ $c_1^+ = 0,$ $c_2^+ = -(1 - x^2) (\text{ch}\delta - \cos\Delta),$

Dependences $J(\alpha) = f(\alpha)$ for all these cases are given in Fig.8.



The intensity measurements can be conducted on a spectrophotometer, with attached special extension module in order to rotate the polarizer and analyzer with the specific step. In result the Fourier coefficients are calculated. It is necessary to keep in mind that the sample can be located arbitrarily; therefore it is necessary to consider that always $b_1^2 + b_2^2 = b^2$, $c_1^2 + c_2^2 = c^2$. Knowing Fourier coefficients, all anisotropic optical parameters can be calculated from the relationships:

$$x^2 = \sin^2 2\gamma = \frac{4k^2}{(1+k^2)^2} = \frac{a_{\perp} - c_{\perp}}{a_{\perp} + c_{\perp}}, \quad (9)$$

$$e^{2\delta} = \frac{a_{\parallel} \cos^2 2\gamma + b_{\parallel} \cos 2\gamma + c_{\parallel} (1 + \sin^2 2\gamma)}{a_{\parallel} \cos^2 2\gamma - b_{\parallel} \cos 2\gamma + c_{\parallel} (1 + \sin^2 2\gamma)}, \quad (10)$$

$$\cos \Delta = \frac{a_{\parallel} \cos^2 2\gamma - c_{\parallel} (3 - \sin^2 2\gamma)}{\sqrt{[a_{\parallel} \cos^2 2\gamma + c_{\parallel} (1 + \sin^2 2\gamma)]^2 - b_{\parallel}^2 \cos^2 2\gamma}}, \quad (11)$$

It is possible to also calculate Δ and δ from the relationship:

$$\cos \Delta = \frac{a_{\parallel} - a_{\perp} - 2c_{\perp}}{a_{\parallel} + a_{\perp}} \text{ch} \delta, \quad \tanh \delta = \frac{b_{\parallel} \sqrt{1 - x^2} (a_{\perp} + b_{\perp})}{2(a_{\parallel} + a_{\perp})c_{\parallel}}. \quad (12)$$

If $(\beta - \alpha) = \pm \pi/4$, then for the transparent crystals it is possible to determine Δ and x from the relationships:

$$x^2 = \frac{(a^+ - c^+) + (a^- - c^-) - 2\sqrt{(a^+ - c^+)(a^- - c^-)}}{(a^+ + c^+) + (a^- + c^-) - 2\sqrt{(a^+ - c^+)(a^- - c^-)}},$$

$$\cos \Delta = \frac{-(c^+ + c^-) + 2\sqrt{(a^+ - c^+)(a^- - c^-)}}{(a^+ + a^-)} \quad (13)$$

At measurement of the sample, which is cut out perpendicular to the optical ($x = \pm 1$), one can obtain that $J(\alpha) = \text{const}$. In this case of $c_{\perp} = c_{\parallel} = b_{\perp} = b_{\parallel} = 0$, the phase difference Δ is determined by circular birefringence, and value δ is determined by circular dichroism (linear birefringence and linear dichroism are equal to zero). Values Δ and δ are determined:

$$\cos \Delta = \frac{a_{\parallel} - a_{\perp}}{a_{\parallel} + a_{\perp}} \text{ch} \delta, \quad \text{ch} \delta = \frac{(a_{\parallel} + a_{\perp})(a^+ + a^-)}{\sqrt{2[(a_{\perp} a^+ - a_{\parallel} a^-)^2 + (a_{\perp} a^- - a_{\parallel} a^+)^2]}}. \quad (14)$$

4. Manifestation of optical activity at the inclination of plate.

Relationships (1 - 3) can be used during investigation of dependence $\chi(\phi)$, $\tan V(\phi)$, $J(\phi)$, where ϕ is the angle of inclination of plate around the axis, in parallel to its surface. Let us consider the case, when polarizer and analyzer are crossed ($\beta - \alpha = \pi/2$), and the investigated transparent optically active plate is located between them. Then at $\alpha = 0$ relationship (1 - 3) can be represented in the form:

$$\text{tg} 2\chi = [\pm \sin 2\gamma \sin \Delta] / [1 - 2 \sin^2 \gamma \sin^2(\Delta/2)], \quad (15)$$

$$\sin 2V = \pm \sin 4\gamma \sin^2(\Delta/2), \quad (16)$$

$$J = T \sin^2 2\gamma \sin^2(\Delta/2) \quad (17)$$

One can see that these dependences are proportional to the ellipticity of eigenwaves ($\sin 2\gamma = 2k/(1 + k^2)$) associated with optical activity. In the inactive crystals right sides of (15) - (17) become zero, i.e., crystal is located in the position of extinction. It is obvious that in the optically active crystals dependences (15) - (17) oscillate when the phase difference Δ changes. Usually these changes are associated by a change in the wavelength of incident light. Sometimes these changes are associated with the external influence, for example the application of electrical or magnetic field or with a change of the temperature.

Let us look how these dependences change with the inclination of plate (Fig.9) [7]. In this case changes of phase difference Δ due to a change in the birefringence, value $\sin^2(\Delta/2)$, $\sin \Delta$ oscillate, while values $\sin 2\gamma$, $\sin 4\gamma$, $\sin^2 2\gamma$, associated by optical activity, change smoothly and they envelope (dotted lines in Fig. 9) the corresponding oscillatory dependences.

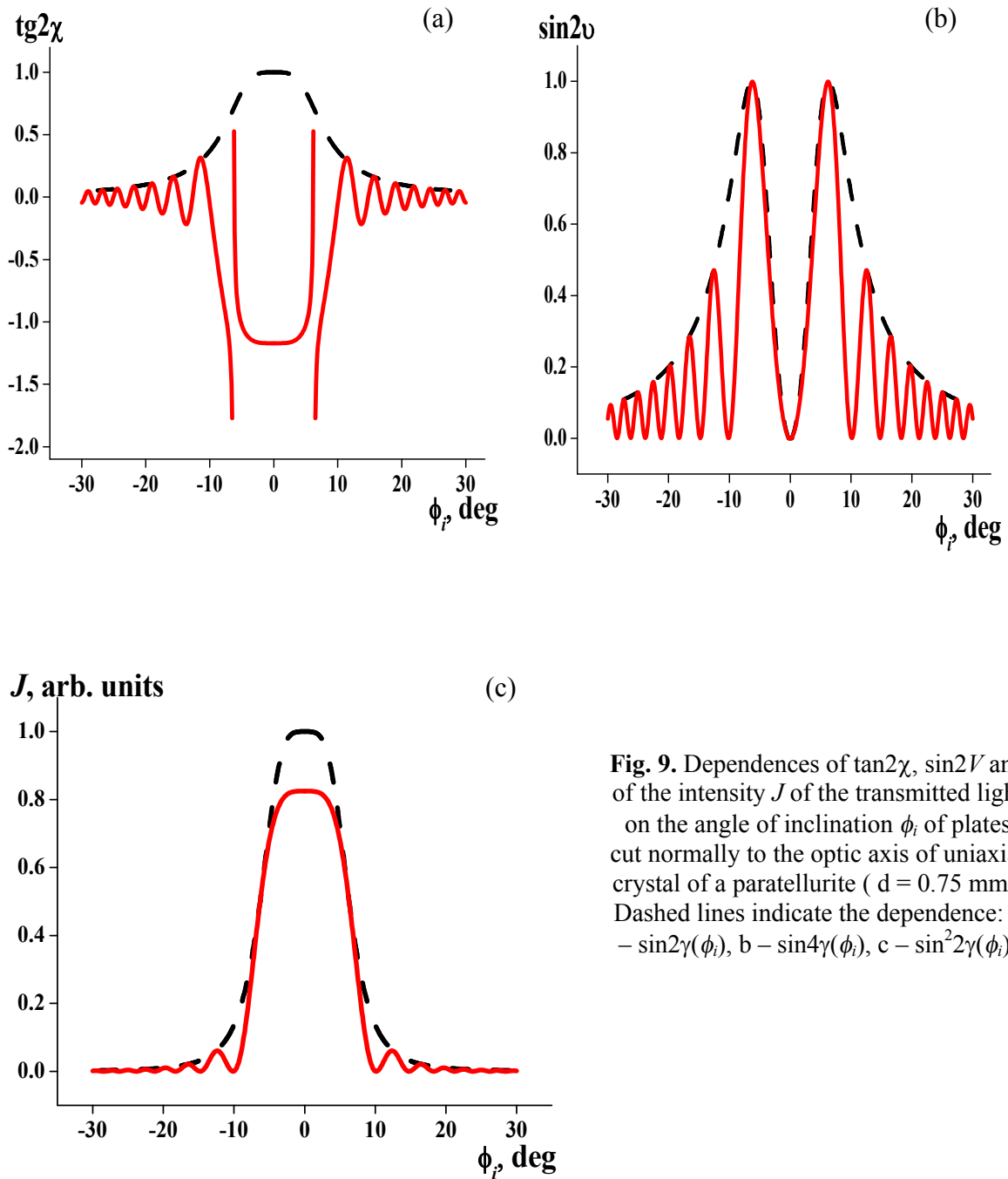
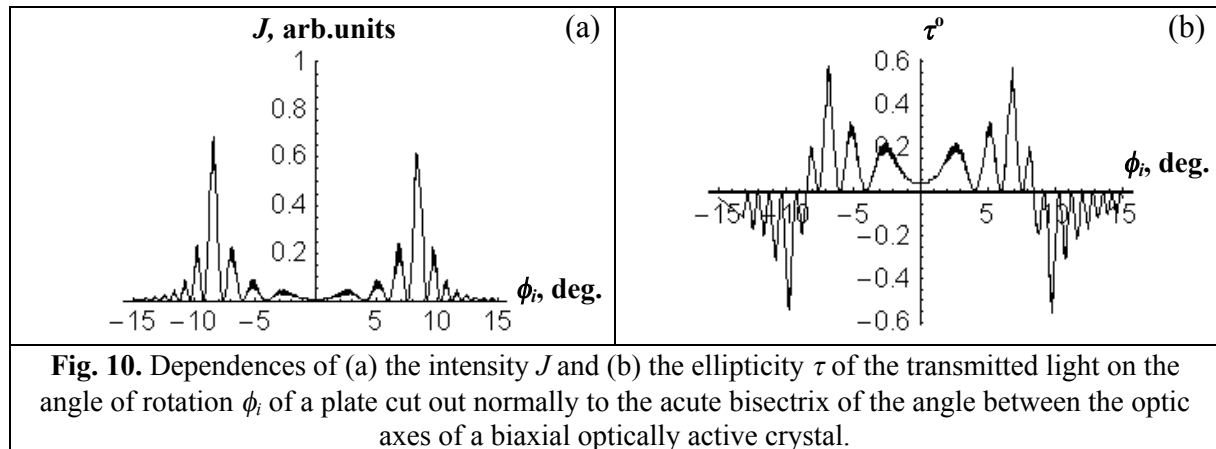


Fig. 9. Dependences of $\tan 2\chi$, $\sin 2V$ and of the intensity J of the transmitted light on the angle of inclination ϕ_i of plates cut normally to the optic axis of uniaxial crystal of a paratellurite ($d = 0.75$ mm). Dashed lines indicate the dependence: a – $\sin 2\gamma(\phi_i)$, b – $\sin 4\gamma(\phi_i)$, c – $\sin^2 2\gamma(\phi_i)$.

Relationships (15 – 17) hold for biaxial crystals. In this respect, we examine crystals belonging to the orthorhombic crystal system (class symmetry 222) when the plate is cut normally to the acute bisectrix of the angle formed by the optic axes and it is located between the crossed polarizer and analyzer [8].

If the principal plane of the plate coincides with the direction of transmission of the polarizer ($\alpha = 0^\circ, 90^\circ$), the regularity characteristic of uniaxial crystals for directions close to the optic axis should be valid for each optic axis of the biaxial crystal (Fig. 10).



It is clear, that for calculation of parameters of optical activity of biaxial crystals it is necessary to consider correctly the value of birefringence and scalar parameter of gyration. In crystals of this crystal system, the rotation of the polarization plane along the optic axes is identical and, hence, the intensities of the transmitted light along the optic axes are equal to each other. In the crystals belonging to monoclinic or triclinic systems, the rotation of the polarization plane along both optic axes is unequal and can even be opposite in sign. Consequently, the dependences of the intensity, ellipticity, and azimuth for a plate cut out normally to the acute bisector of the angle between the optic axes of this crystal, unlike an orthorhombic crystal, appear to be asymmetric in shape and a number of variants exists depending on the optical parameters of the crystal.

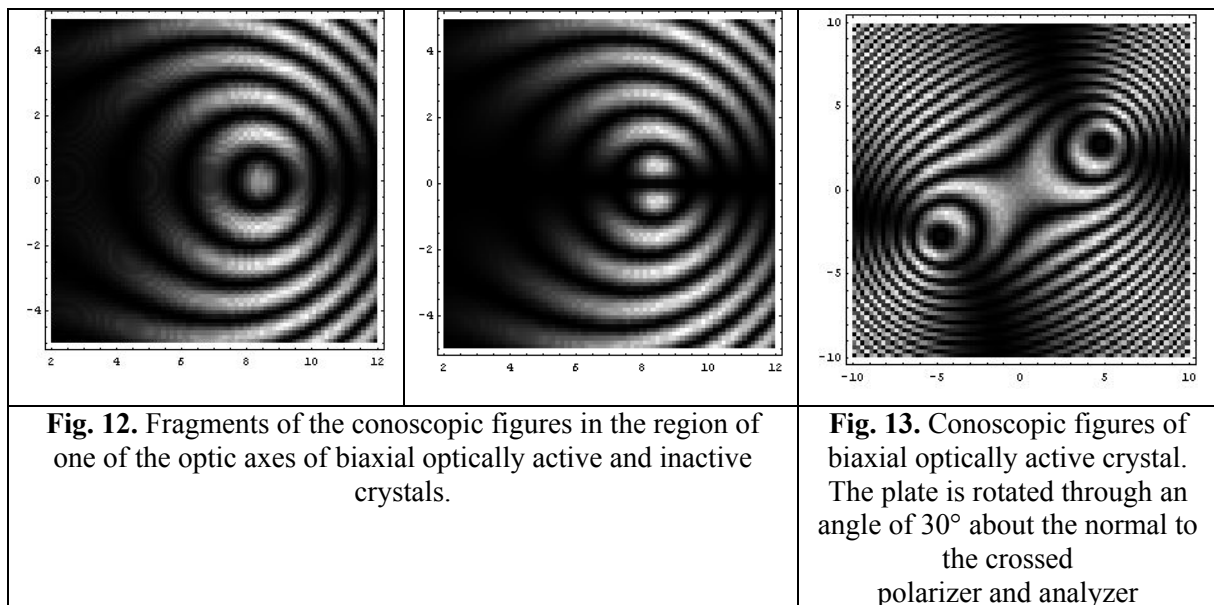
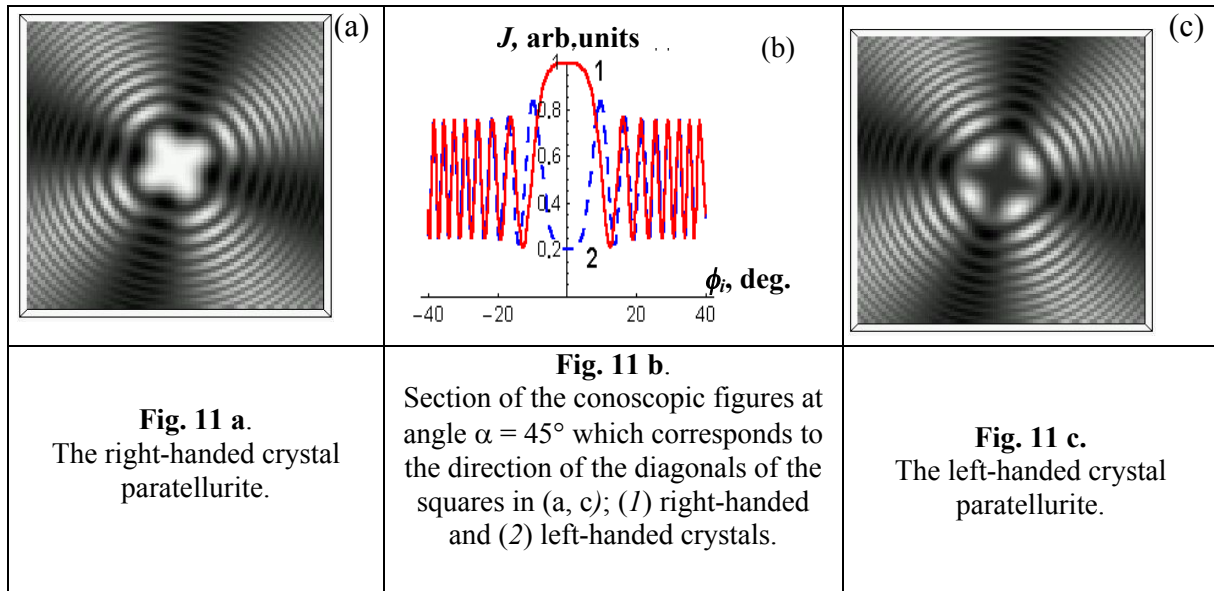
5. Description of conoscopic figures of the optically active crystals

The conoscopic figures can be described and can be calculated by using of the formulas for the intensity (3) of the transmitted light in case when the optical activity plate is located between polarizer and analyzer [7, 8].

Fig. 11 shows the conoscopic pictures, modelled with the application of a program, comprised with the aid of the system of computer mathematics - the integrated package "Mathematica-4.1" [9] on the basis of relationship (3). Fig. 11b depicts the dependence of the intensity of light, transmitted through the right and left-handed uniaxial crystal, which corresponds to the section of conoscopic pictures (Fig. 11a, c) at angle of 45° .

As in the case of uniaxial crystals, the conoscopic figures for biaxial crystals can be described by relationship (3). It can be seen from Fig12 that the difference between the optically active and inactive crystals is especially noticeable along the optic axis.

For an optically active crystal, the light intensity at the center of the conoscopic figure differs from zero, because the crystal rotates the polarization plane in this direction. Similar differences are clearly seen in the case when the plate is rotated through a certain angle between the crossed polarizer and analyzer (Fig. 13).



Conclusion

The expressions, which describe the influence of the optical activity on the measured results of the azimuth and ellipticity of transmitted light, are presented. The expressions determining the intensity of the light transmitted through the polarizer – optically active sample – analyzer system are considered. The conoscopic figures of optically active crystals are described and the differences between the optically active and inactive crystals are established with the use of the formulas for the intensity of the transmitted light. A technique is proposed for determining the parameters of the optical activity from experimental data on the intensity and azimuth of the transmitted light.

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