

## ABSORPTION AND PLEOCHROISM: TWO MUCH-NEGLECTED OPTICAL PROPERTIES OF CRYSTALS\*

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### ABSTRACT

Certain fundamental relationships of absorption and pleochroism are presented to stimulate interest in the quantitative expression of these two properties. The absorption coefficient ( $k$ ) is given preference as the absorption constant, while biabsorption is re-emphasized as a quantitative expression for pleochroism. Methods for the determination of the absorption coefficients are briefly discussed. Two methods for the determination of biabsorption are presented in detail.

### INTRODUCTION

With the polarizing microscope (probably the most widely used tool in mineralogy today), methods have been evolved which make possible the accurate measurement of many optical properties of crystals. However, investigators have overlooked certain other optical properties. Absorption and pleochroism, although they are sometimes mentioned in a qualitative manner, have been almost entirely ignored.

The purpose of this paper is three-fold. First, it is hoped that interest in absorption and pleochroism will be stimulated among mineralogists and petrographers. Secondly, certain constants for the quantitative expression of these two properties are suggested. Lastly, some methods for measuring these properties are described.

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### HISTORY

The absorption of light in crystals was first investigated early in the 19th century, but it did not progress beyond a rule-of-thumb system until much later. Among the earlier investigators was Babinet (1838), who discovered that the greatest absorption in a crystal generally coincided with the direction of greatest refractive index. He found many exceptions to this rule, however. Laspeyres (1880) pointed out the existence of absorption axes (directions of least, intermediate, and greatest absorption). He investigated certain biaxial crystals and found that the

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absorption axes, although subject to the symmetry of the crystal, did not necessarily coincide with the principal directions of the indicatrix. Between 1880 and 1900, Voigt (1885) and Drude (1900) presented the fundamental theories of absorption in crystals. During this same period, notable experimental work confirming these theories was carried out by Voigt (1885), Becquerel (1887), Ramsay (1888), and Ehlers (1898). Shortly afterwards, Pockels (1906) presented an excellent summary of the work up to that time.

The introduction of photoelectric devices restimulated activity in this field during the 1930's. Vogel (1934) investigated absorption in certain crystals colored by chromium (emerald, natural and synthetic ruby, and synthetic spinel). Unfortunately, his absorption data were given in terms of galvanometer readings and served only to determine the wave lengths at which absorption maxima and minima occurred. He did not specify the orientation of his crystals; nor, apparently, did he measure their absorption for any particular direction. Tromnau (1934) studied the optical properties of synthetic spinel colored by various amounts of cobalt. Again absorption data were presented as galvanometer readings. Tromnau's paper is interesting, however, for the refractive index data presented. It is one of the few tabulations of refractive indices that clearly illustrates the change from normal dispersion to the so-called anomalous dispersion in an inorganic isomorphous series.

Berek's many contributions in the field of absorption are summarized in the book by Rinne and Berek (1953).

In the last ten years much work has been done on the study of light absorption in crystals. However, a great deal of this work includes the same objectionable features of some of the earlier studies: especially, inconsistencies in the choice of absorption constants. Some modern investigators still use terms such as "optical density" [Cohen (1956)] and "absorption modulus" [Vultée and Lietz (1956) and Lietz and Münchberg (1956)].

Bloss (1955) presented a study of absorption in the series  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and correlated absorption (optical density and molar absorbance) with composition.

Pleochroism, although included in the titles of many early papers, has been almost completely omitted from any quantitative investigation. Slawson and Thibault (1939) expressed the pleochroism of a tourmaline crystal in terms of the ratio  $I_o/I_e$ . Denning and Mandarino (1955) suggested the term "biabsorption" as a quantitative expression for pleochroism. They defined biabsorption in a uniaxial crystal as the difference between the absorption coefficients for the extraordinary and ordinary rays.

ABSORPTION TERMINOLOGY

*Theory*

If light having an initial intensity of  $I_0$  passes through a medium, the initial intensity is reduced by: 1) scattering, 2) reflection at both surfaces of the medium, and 3) the inherent absorbing power of the medium.

In order to convert the measured transmittances  $I'/I_0$  to the correct transmittances  $I/I_0$ , the losses due to scattering and reflection must be accounted for. Losses due to scattering can be ignored if the crystal being investigated is relatively free from inclusions and imperfections. Losses due to reflection can be rectified by applying the well-known Fresnel corrections. The relation between the true intensity  $I$  and the measured intensity  $I'$  is given by

$$I = I' \left( \frac{1}{1 - R} \right)^2 \tag{1}$$

in which  $R$  is the reflecting power. The value of  $R$  may be calculated from the following equation:

$$R = \left( \frac{n - 1}{n + 1} \right)^2 \tag{2}$$

in which  $n$  is the index of refraction of the crystal for the vibration direction being investigated. Substitution of the value of  $R$  in Equation 1 yields

$$I = I' \left[ \frac{(n + 1)^2}{4n} \right]^2 \tag{3}$$

Absorption must be expressed in terms of carefully defined constants. A variety of constants have been employed in the past. All of these constants have been based on the following general equation:

$$I/I_0 = e^{-ab} \tag{4}$$

In this equation,  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the emergent light corrected for reflection losses,  $e$  is the base of the natural logarithms,  $a$  is the absorption constant, and  $b$  is a constant dependent on the conditions of measurement. The value of  $I/I_0$  is determined and the value of  $a$  is then calculated from the equation to yield the desired absorption constant. The numerous absorption constants found in the literature are due to various expansions of the exponent  $b$  in Equation 4.

Table 1 is a compilation of terms which have been used to express absorption. Many of these terms over-simplify the process of absorption; others, although suitable for special applications (i.e., colorimetry) are unsuitable for fundamental absorption studies. A term for the ex-

TABLE 1. VARIOUS TERMS USED TO EXPRESS ABSORPTION

In the equations,  $t$  = optical path length in the medium,  $c$  = concentration of the coloring material,  $M$  = molecular weight of the coloring material,  $\lambda$  = wave length of the light used,  $n$  = refractive index of the medium,  $I_0$  = the intensity of the incident light, and  $I$  = the intensity of the emergent light corrected for reflection losses.

Symbol	Term	Equation
T	Transmission = Transmittancy	$T = I/I_0$
A	Absorption = Absorbancy	$A = 1 - T$
D	Optical density	$D = \log_{10} (I_0/I)$
E	Extinction	$E = \log_{10} (I_0/I)$
K	Extinction coefficient	$K = \frac{\log_{10} (I_0/I)}{t}$
$k$	Specific extinction	$k = \frac{\log_{10} (I_0/I)}{ct}$
$\alpha$	Specific absorption coefficient	$\alpha^{-ct} = I/I_0$
$\epsilon$	Molecular extinction	$\epsilon = \frac{M \log_{10} (I_0/I)}{ct}$
$m$	Absorption modulus	$I/I_0 = e^{-mt}$
$k$	Absorption coefficient	$I/I_0 = e^{-k(4\pi t/\lambda)}$
$X$	Absorption index	$I/I_0 = e^{-X(4\pi t n/\lambda)}$

pression of absorption should be based on the following precepts: 1) an absorption constant, like index of refraction, should be mathematically dimensionless; 2) it should be based on accepted physical theories, thus lending itself to the calculation of special constants for special absorption problems; and 3) it should be easily measurable or easily calculable from an easily measurable quantity.

An expression such as "absorption modulus," because of its dimensions ( $\text{cm}^{-1}$ ), gives the erroneous impression of "absorption per centimeter." But more important: it has very little significance in the concept

of the complex index of refraction for absorbing media. Simply stated, the complex index is a combination of the refractive index and the absorption ( $N = n - ik$ ). Consequently, both properties should be expressed as dimensionless quantities.

In analyzing the terms found in Table 1, it can be seen that two terms meet the first two requirements stated above. In addition, they may both be calculated from easily measurable quantities. These terms are: the "absorption index" ( $X$ ) and the "absorption coefficient" ( $k$ ). They are related by the following equation:

$$k = nX \tag{5}$$

in which  $n$  is the index of refraction.

In this paper the nomenclature of Berek (1953) is used. Absorption is expressed in terms of the absorption coefficient  $k$ . Consequently, only equations dealing with  $k$  are presented here. The basic equation relating the absorption coefficient to the intensities of the incident and emergent light is as follows:

$$I/I_0 = e^{-4\pi tk/\lambda} \tag{6}$$

In this equation,  $k$  is the absorption coefficient,  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the transmitted light corrected for reflection losses,  $t$  is the path length in the absorbing medium,  $e$  is the base of the natural logarithms, and  $\lambda$  is the wave length of the light used.

If a plate of a uniaxial crystal cut parallel to the  $c$ -axis is used for the specimen, the absorption coefficients for the ordinary and extraordinary rays are derived from the following equations:

$$I_\omega/I_0 = e^{-4\pi tk_\omega/\lambda} \tag{7}$$

$$I_\epsilon/I_0 = e^{-4\pi tk_\epsilon/\lambda} \tag{8}$$

in which  $I_\omega$  is the intensity of the transmitted ordinary ray, corrected for reflection losses; and  $I_\epsilon$  is the same for the extraordinary ray. If the specimen is mounted in the usual type of petrographic thin-section, the measured intensities must also be corrected for the reflection losses due to the glass and balsam. The absorption coefficients for the ordinary and extraordinary rays are

$$k_\omega = -\frac{\lambda \ln (I_\omega/I_0)}{4\pi t} \tag{9}$$

$$k_\epsilon = -\frac{\lambda \ln (I_\epsilon/I_0)}{4\pi t} \tag{10}$$

In like manner, similar equations can be derived for  $k_\alpha$ ,  $k_\beta$ , and  $k_\gamma$  for biaxial crystals.

These absorption coefficients are independent of thickness and can

be used to calculate any of the special absorption constants previously mentioned.

### *Methods of Measurement*

All absorption measurements, regardless of the constant desired, require a measurement of the ratio  $I/I_0$ . In some methods of measurement this quantity is measured directly (that is,  $I'/I_0$  is measured, and then corrected for reflection losses to  $I/I_0$ ). However, in many methods, a function of this quantity is measured instead. There are three common spectrophotometric methods of measuring  $I/I_0$  or some function thereof: visual, electronic, and photographic.

Typical instruments for all three types of measurement are fully described by Gibb (1942), Mellon et al. (1950), Judd (1952), Brode (1943), and the Committee on Colorimetry of the Optical Society of America (1953). These references also include comprehensive bibliographies of the literature on spectrophotometry.

The choice of the instrument to be used in absorption work usually depends on the instrument available. For this reason, descriptions of individual instruments will not be presented here.

## PLEOCHROISM TERMINOLOGY

### *Theory*

Although the study of absorption in crystals has been complicated by the use of many different constants, few attempts have been made to apply a quantitative term for the expression of pleochroism. The use of the ratio  $I_\omega/I_\epsilon$  has been suggested (for uniaxial crystals), but this has the objectionable feature of being dependent on the thickness of the sample. Since pleochroism is the difference between the extraordinary absorption and the ordinary absorption in a uniaxial crystal, the quantity  $k_\epsilon - k_\omega$  could be used to express pleochroism quantitatively. This quantity, like the individual absorption coefficients, is independent of thickness. It follows, then, that pleochroism can be calculated from the values of  $k_\epsilon$  and  $k_\omega$ . This method of calculating pleochroism is analogous to the method of calculating birefringence from the indices of refraction. By using various compensators, birefringence can be measured directly without recourse to the values of the refractive indices; similarly, pleochroism can be measured directly.

The equation for  $k_\epsilon - k_\omega$  can be derived from Equations 7 and 8 for the ordinary and extraordinary rays. Division of the ordinary equation (Eq. 7) by the extraordinary equation (Eq. 8) yields

$$I_\omega/I_\epsilon = e^{(4\pi t/\lambda)(k_\epsilon - k_\omega)} \quad (11)$$

Solution for  $k_\epsilon - k_\omega$  yields

$$k_\epsilon - k_\omega = \frac{\frac{\lambda \ln (I_\omega/I_\epsilon)}{4\pi}}{t} \quad (12)$$

The similarity of this equation to that for birefringence ( $n_\epsilon - n_\omega = \Gamma/t$ ) led to the expression of  $k_\epsilon - k_\omega$  as *biabsorption*. Calculation of biabsorption can be accomplished by measuring the ratio  $I_\omega/I_\epsilon$  directly. Just as in the measurement of  $I/I_0$ , reflection corrections must be applied to the measured value  $I_\omega'/I_\epsilon'$ . If the birefringence is relatively small, the correction is negligible. For specimens in ordinary thin-sections, no correction is necessary for reflection losses due to the glass slide, balsam, and cover glass.

#### METHODS OF MEASUREMENTS

There are two generally applicable methods of measuring  $I_\omega/I_\epsilon$  directly. One method uses a standard retardation compensator and a rotatable analyzer. The other method depends on visually matching the brightness of two images formed by a double-image plate.

##### *Double-Image Method*

This method employs a double-image plate above or below a pleochroic plate so oriented that the vibration directions of the crystal plate are parallel to the vibration directions of the double-image plate. The double-image plate may be a Wollaston plate, Rochon plate, or simply a calcite cleavage plate. When monochromatic light is passed through both plates and observed by means of a suitable optical system, two images are seen. The light forming both images is linearly polarized such that the vibration direction of one image is normal to the vibration direction of the other image. Thus, one image represents the intensity of the light transmitted by the ordinary ray of the pleochroic crystal and the other image represents the intensity of the light transmitted by the extraordinary ray. A linear polar placed between the plates and the eye can be rotated until the two images have the same brightness. Figure 1 shows the relations of the amplitudes of the two transmitted rays. OA is the amplitude of the ordinary ray and OB is the amplitude of the extraordinary ray. When the polar is rotated to a position such that its vibration direction is OP, the two images have the same brightness. If angle AOP is designated as  $\alpha$ ,

$$\frac{OA}{OB} = \tan \alpha = \frac{A_\omega}{A_\epsilon} \quad (13)$$

Squaring both sides of this equation produces

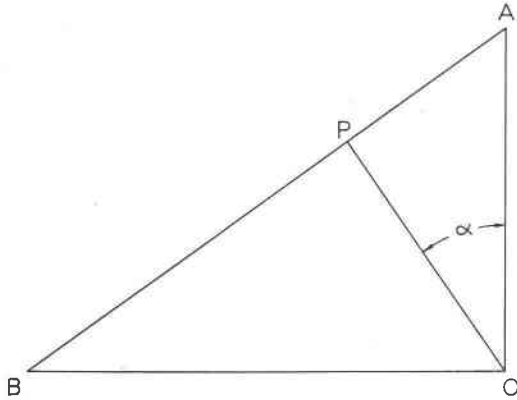


FIG. 1. Relationship between the amplitudes of the transmitted rays of a pleochroic crystal plate.

$$I_{\omega}/I_{\epsilon} = \tan^2 \alpha \quad (14)$$

Thus the ratio of  $I_{\omega}$  to  $I_{\epsilon}$  can be measured directly. Very often the two images have different brightnesses before the pleochroic plate is placed in the system. If such is the case, the ratio between these two incident intensities must be determined and applied as a correction to the measured value of  $I_{\omega}/I_{\epsilon}$ . This correction is determined by rotating the polar to a position of equal brightness when the pleochroic plate is out of the system. If this angle is designated as  $\beta$ , the equation for  $I_{\omega}/I_{\epsilon}$  becomes:

$$I_{\omega}/I_{\epsilon} = \tan^2 \alpha \cot^2 \beta \quad (15)$$

When a calcite cleavage plate is used as a double-image plate, the value of  $\cot^2 \beta$  may vary considerably from unity due to the extreme difference between the refractive indices. The use of a Wollaston or Rochon plate greatly reduces the correction.

The double-image method was used to determine biabsorption in synthetic ruby and the resulting data will be presented in a later paper.

#### *Compensator-Analyzer Method*

In general, when a non-pleochroic, optically anisotropic crystal plate is placed between crossed linear polars such that the vibration directions of the crystal are at  $45^\circ$  to those of the polars, elliptically polarized light is produced. The axes of the resultant ellipse are parallel to the vibration directions of the crystal plate and their ratio is a function of the phase-difference between the two rays transmitted by the crystal. The solid curve in Fig. 2 represents the trace of the elliptically polarized light pro-



duced by a crystal plate whose two rays were subjected to a phase-difference of thirty degrees ( $\lambda/6$  linear path difference).

If the crystal is pleochroic, an entirely different ellipse is traced by the resultant elliptically polarized light. Not only is the ratio of the axes of the ellipse changed, but the axes are inclined to the vibration directions of the crystal. The dotted curve in Fig. 2 is the trace of the resultant elliptically polarized light from a pleochroic crystal whose two rays are subjected to the same phase-difference as before (thirty degrees).

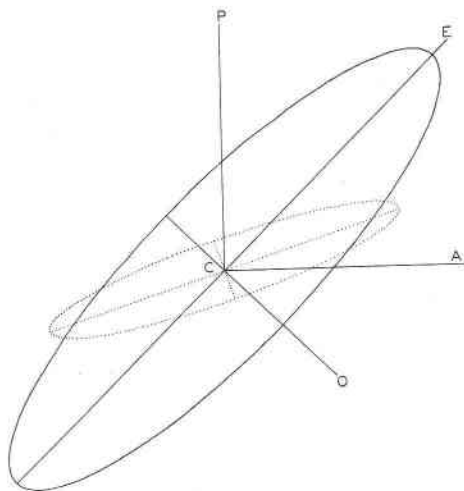


FIG. 2. Traces of the elliptically polarized light produced from crystal plates with a phase-difference of thirty degrees. Solid curve, non-pleochroic crystal; dotted curve, pleochroic crystal.

The angle through which this second ellipse has been rotated is a function of the ratio of the intensities of the ordinary and extraordinary rays. Measurement of this angle makes possible the calculation of  $I_o/I_e$  and, subsequently,  $k_e - k_o$ . The problem is very similar to the determination of bireflection discussed by Berek (1953) and Hallimond (1953).

In order to develop the mathematical relations upon which this method is based, the dotted ellipse of Fig. 2 has been redrawn in Fig. 3. The vibration directions of the polarizer and analyzer are represented by CP and CA, respectively. CO is the ordinary vibration direction of the crystal and CE is the extraordinary vibration direction.  $CO_0$  and  $CE_0$  are the components of the incident light resolved along the ordinary and extraordinary vibration directions of the crystal, respectively.  $CO_1$  is the amplitude of the transmitted ordinary ray and  $CE_1$  is the amplitude of

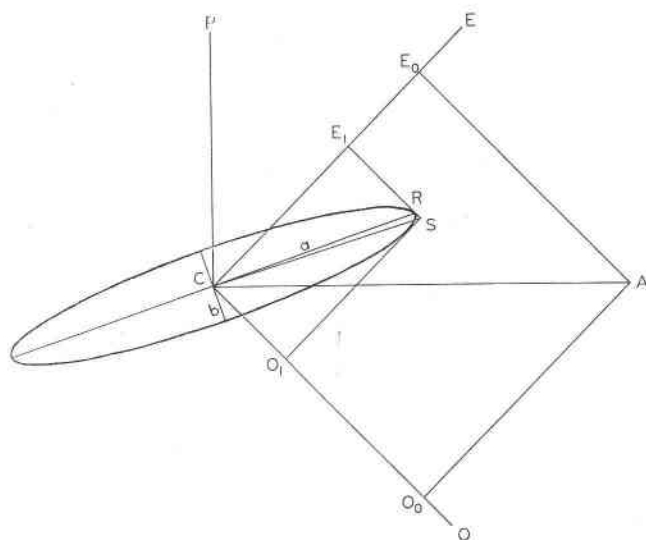


FIG. 3. Geometrical relationships of the elliptically polarized light produced by a pleochroic crystal plate.

the transmitted extraordinary ray. It can be seen that  $CO_1/CE_1$  equals the square root of  $I_\omega/I_\epsilon$ . Because  $CO_1/CE_1 = \tan ECS$ , it is necessary to determine the value of angle ECS.

The relationships between angle ECS, angle ECR, and  $\Delta$  are given by the following equations from Hallimond (1953). Proofs of these equations are given by Schuster and Nicholson (1924).

$$\tan 2 ECS = \frac{\tan 2 ECR}{\cos \Delta} \quad (16)$$

$$\tan \Delta = \frac{\tan 2(\tan^{-1} b/a)}{\sin 2 ECR} \quad (17)$$

Angle ECR is the angle between the extraordinary vibration direction of the crystal and the major axis of the ellipse.  $\Delta$  is the angular phase-difference between the ordinary and extraordinary rays.

From Equations 16 and 17, it can be seen that measurements of  $b/a$  and angle ECR are necessary for the determination of  $I_\omega/I_\epsilon$ .

Procedures for the measurement of both of these quantities are described by Hallimond. The measurement requires a microscope so constructed that the analyzer may be rotated. In addition, an accessory slot must be provided at  $45^\circ$  to the analyzer vibration direction and must rotate with the analyzer.

If a compensator is placed in the accessory slot, the crystal plate can be compensated only when the vibration directions of the compensator

are parallel to the axes of the ellipse. Thus, in the case of a non-pleochroic crystal, the elliptically polarized light can be resolved into linearly polarized light by adjusting the compensator when the vibration directions of the compensator are parallel to the vibration directions of the crystal plate. In the case of a pleochroic crystal plate, however, the axes of the ellipse are not parallel to the vibration directions of the crystal. Therefore, the compensator and analyzer must be rotated until the vibration directions of the compensator are parallel to the axes of the ellipse. This angle of rotation is equal to the angle ACR which is equal to  $45^\circ$ -ECR.

Many compensators yield values of retardation in terms of linear path-difference,  $\Gamma$ . The angular phase-difference at  $45^\circ$  to the ellipse is designated  $\phi$ . The relation between  $\phi$  and  $\Gamma$  is

$$\phi = \frac{2\pi\Gamma}{\lambda} \tag{18}$$

in which  $\lambda$  is the wave length of the light employed.  $\phi$  is related to the quantity  $b/a$  as follows:

$$\phi = 2(\tan^{-1} b/a) \tag{19}$$

From Equations 16 and 17 it follows that

$$\tan 2 \text{ ECS} = \frac{\tan 2(45^\circ - \text{ACR})}{\cos \Delta} \tag{20}$$

$$\tan \Delta = \frac{\tan \phi}{\sin 2(45^\circ - \text{ACR})} \tag{21}$$

Substitution of the measured values of ACR and  $\phi$  in the preceding equations yields a solution for the value of ECS. The value of  $I_\omega/I_\epsilon$  is determined from the following equation:

$$I_\omega/I_\epsilon = \tan^2 \text{ ECS}$$

Biabsorption can then be calculated in the usual manner from the value of  $I_\omega/I_\epsilon$ .

The compensator-analyzer method is subject to one serious limitation: it can only be used for substances that show appreciable pleochroism in relatively thin plates (more specifically, in plates of relatively low retardation). The double-image method, however, can be used on plates of relatively high retardation.

#### COMMENTS

It can be seen, from the foregoing discussion of measurement methods, that rather expensive equipment is necessary for the determination of absorption coefficients. Unless a suitable spectrophotometer is available to interested workers, it is doubtful whether the absorption coefficient

will become a commonly noted constant in mineralogical literature. However, the measurement of biabsorption requires very little equipment not already present in most mineralogical or petrographic laboratories.

The emphasis in this paper has been on uniaxial crystals. However, these same methods, with appropriate changes in equations, may also be applied to biaxial crystals. It is proposed that  $k_\alpha$ ,  $k_\beta$ , and  $k_\gamma$  refer to the absorption associated with the directions of the refractive indices  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively. *It should be noted that  $k_\alpha < k_\beta < k_\gamma$  will not necessarily hold true.*

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