PLEOCHROISM IN SYNTHETIC RUBY*

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ABSTRACT

A generally applicable method of quantitatively determining pleochroism of weakly absorbing crystals by the use of spheres is described. Sections of surfaces representing biabsorption ($K_{\epsilon'} - K_\omega$ against wave normal are given. The use of biabsorption as an optical constant is suggested.

Pleochroism is a much neglected optical property of crystals. A few quantitative studies have been made on selected sections of certain crystals. Most of the published data have been obtained from selected plane crystal sections.

The earlier work on pleochroism was performed by European investigators. Babinet (1838) found that, with many exceptions, the greatest absorption in a crystal is along the direction of greatest refractive index. Laspeyres (1879–80) was the first to recognize the existence of "absorption axes," which he defined as the directions of greatest, least, and intermediate absorption in a crystal. He also found that an absorption surface in biaxial crystals is oriented, with respect to symmetry, in a manner similar to the orientation of the indicatrix, but that it does not necessarily coincide with the latter. Voigt (1885) supported this latter finding, as did Becquerel (1887). Ramsay (1887–88) in a study of cylinders and plates of epidote concluded that the absorption axes in plane (010) in monoclinic crystals were not mutually perpendicular. This implies that absorption is nonellipsoidal. Ehlers (1897–98) reported mutually perpendicular absorption axes, inclined with respect to the principal vibration directions, in certain monoclinic crystals. Johannsen (1916) shows absorption surfaces for three uniaxial substances without reference to the color of light used. He also gives a bibliography of the earlier work relating to the absorption of light in crystals. Slawson and Thibault (1939) quantitatively determined the pleochroism of a tourmaline crystal throughout the visible spectrum, for a propagation direction perpendicular to the optic axis.

Because of some uncertainty of the quantitative aspects of pleochroism, particularly whether it is an ellipsoidal property, and because of some ambiguity concerning the use of the terms absorption surface and absorption axes in weakly absorbing crystals (crystals that transmit

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appreciable light in fairly thick sections), a quantitative study was made of the pleochroism of synthetic ruby.

In order to develop easily a three dimensional surface a sphere made by Linde Air Products was used. Synthetic ruby was chosen for investigation because of the ease of obtaining such spheres.

Since pleochroism is the relative absorption with respect to direction, the absolute absorption need not be measured. The method employed consisted of measuring the relative intensity of light in two vibration directions associated with selected wave normals.

The ruby sphere (which was actually slightly biaxial) was mounted and carefully centered on a spindle so that it could be rotated about a normal to its *c*-axis. Selected monochromatic or nearly monochromatic light sources were used. The light source was imaged on the sphere. A lens focused an image of the illuminated sphere on a small adjustable slit. A Wollaston double image prism next to the slit served to produce separate adjacent images of the slit. This permitted the direct comparison of the ordinary and extraordinary light as in an ordinary dichroscope. These double images were examined by means of a microscope fitted with a rotating analyzing prism. Wave normals, rather than the slightly different ray directions, are more useful in such measurements, for while in general the extraordinary ray is deviated from the direction of perpendicularly incident light, the extraordinary wave normal is not. Since the incident light cannot be made perfectly parallel, and since the surface of the crystal used was spherical, the wave normals were not strictly parallel. The dimensions of the apparatus and the location and size of apertures were such that within the crystal the maximum angular deviation of wave normals from the desired direction did not exceed 6°. A schematic diagram of the apparatus is shown in Fig. 1.

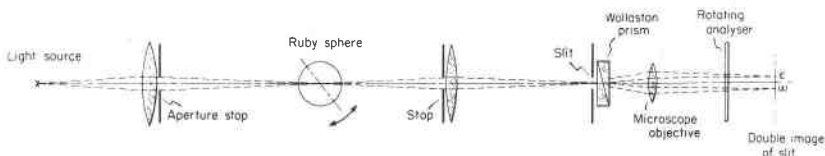For a particular wave length of light, and for given wave normal

FIG. 1. Schematic diagram of apparatus.

directions in the crystal, the two adjacent slit images may be made of equal brightness by rotating the analyzer so that the line of demarcation between the two halves of the field practically disappears. If the angle through which the analyzer must be rotated from the extraordinary virbration direction of the ruby toward the ordinary is θ, then the in-

tensity ratio is

$$\frac{I_\omega}{I_{\epsilon'}} = \cot^2 \theta. \tag{1}$$

If I_0 is the intensity of the incident light, then the transmitted intensities are

$$I_\omega = I_0 e^{(-4\pi/\lambda_0)K\omega t} \tag{2}$$

and

$$I_{\epsilon'} = I_0 e^{(-4\pi/\lambda_0)K\epsilon' t} \tag{3}$$

for the ordinary and extraordinary vibrations respectively. K is the absorption coefficient (Berek, 1937), λ_0 the wave length in air and t the thickness.

Equations (2) and (3) may be combined as

$$\frac{\lambda_0}{4\pi} \ln \left(\frac{I_\omega}{I_{\epsilon'}} \right) = t(K_{\epsilon'} - K_\omega) \cdot \tag{4}$$

Equation (4) is analogous to the well-known relationship between retardation, thickness and birefringence. For this reason it is proposed that $(K_{\epsilon'} - K_\omega)$ be called biabsorption. Biabsorption, like birefringence, is dimensionless and is independent of the thickness of the crystal. Unless a particular wave normal direction is specified, the term biabsorption should refer to the maximum or principal value $(K_\epsilon - K_\omega)$ as in the case of birefringence. The value for intermediate directions $(K_{\epsilon'} - K_\omega)$ may lie between the maximum and zero. A surface useful in visualizing the quantitative aspects of pleochroism can be constructed by plotting biabsorption against wave normal direction for a particular wave length. The biabsorption for a given wave length in air and for a selected wave normal direction may be determined from the measured θ and t.

$$(K_{\epsilon'} - K_\omega) = \frac{\lambda_0 \ln \cot^2 \theta}{4\pi t} \cdot \tag{5}$$

Several light sources were used to provide suitable approximately monochromatic light. A ribbon filament incandescent lamp was employed with a single layer interference filter to provide 486 mμ, and with a Wratten A and wedge interference filter for 620 mμ. An arc lamp and Wratten 87 filter furnished radiation of about 800 mμ which was observed with an infrared image converter tube. A sodium lamp supplied 589 mμ light. A mercury 546 mμ source could not be used because of the relatively strong absorption band of the synthetic ruby in that portion of the spectrum.

The diameter of the sphere used was 9.52 mm. For each wave length two settings were made for the θ values, after a few preliminary trials to
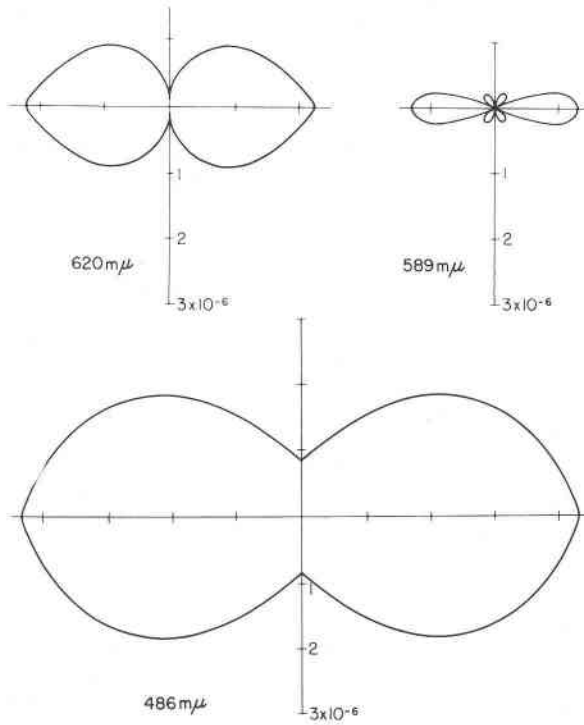
FIG. 2. Biabsorption curves for synthetic ruby. c-axis vertical.

gain experience in matching the two halves of the field. Such readings were obtained for successive wave normal directions which made an angle ρ with the c-axis of the crystal sphere. The results of the measure-

TABLE 1. (FOUR QUADRANTS AVERAGED)

ρ	486 mμ $(K_{\epsilon'} - K_\omega)$	σ	589 mμ $(K_{\epsilon'} - K_\omega)$	σ	620 mμ $(K_{\epsilon'} - K_\omega)$	σ
0	-0.86 $\times 10^{-6}$	0.2 $\times 10^{-6}$	-0.04 $\times 10^{-6}$	0.05 $\times 10^{-6}$	-0.07 $\times 10^{-6}$	0.1 $\times 10^{-6}$
10	-1.02	0.3	-0.17	0.1	-0.06	0.1
20	-1.32	0.3	-0.17	0.1	-0.11	0.2
30	-1.69	0.1	-0.24	0.1	-0.80	0.1
40	-2.25	0.2	-0.24	0.1	-1.13	0.2
50	-2.85	0.2	-0.20	0.1	-1.36	0.1
60	-3.37	0.2	0.00	0.1	-1.56	0.1
70	-3.77	0.2	$+0.28$	0.2	-1.75	0.1
80	-4.09	0.3	$+1.17$	0.4	-1.97	0.1
90	-4.32	0.3	$+1.80$	0.4	-2.27	0.1

ments of four quadrants were combined to yield the curves of Fig. 2. The average values of the absorption coefficients are tabulated in Table 1. The measurements were made in the plane of the optic axes.

For most of the data, eight measurements were averaged. The standard deviations were determined from the angular readings. The computed standard deviation, σ of each value of biabsorption, is also given.

An unexpected result of the measurements is the fact that the biabsorption for light of 486 mμ parallel to the c-axis is not zero. Careful optical alignment, adjustment, and repetition of readings did not remove this apparent anomaly.

It may be that the actual biaxial nature of the crystal, probably the result of internal stress, may contribute to this condition. It must be admitted, however, that one would not expect such a condition to have so large an effect on the absorption coefficient. The curves for the other wave lengths of light do not show a significant departure of the biabsorption from zero for light propagated parallel to the c-axis.

The curve for sodium light shows weak pleochroism ($O > E$ or negative biabsorption) for values of ρ from 0 to 60°. The curve passes through zero at $\rho = 60°$. From 60° to 90° the absorption scheme is reversed ($O < E$ or positive biabsorption). The change of sign of biabsorption cannot, in the authors' opinion, be attributed to experimental error. For yellow light travelling parallel to the c-axis, the biabsorption is practically zero (that is, there is no pleochroism exhibited) within experimental error.

For red light, about 620 mμ, the biabsorption is negative for all values. Along the c-axis the value is again practically zero.

In the near infra-red, approximately 800 mμ, the biabsorption is zero in the c-axis direction and is small (negative) for all other directions. The maximum observed value is -0.84×10^{-6}. The readings obtained were too widely scattered to justify plotting a curve. It was found difficult to match accurately the brightness of the two fields observed in the image converter (snooperscope) tube.

In a uniaxial substance, such as the ruby, the K_ω is independent of direction within the crystal. That this is true was demonstrated by comparing the intensity of the ordinary rays from the crystal with linearly polarized light passed around the crystal and into the Wollaston prism so that a setting of the analyzer could be made to balance the field.

For comparison Fig. 3 shows a curve of birefringence. The value of ($\epsilon' - \omega$) is plotted for the assumed indices $\omega = 1.772$, $\epsilon = 1.763$. The well-known equation of this curve is ($\epsilon' - \omega$) $= (\epsilon - \omega) \sin^2 \rho$ which is very close to the more accurate relation

$$\left(\frac{1}{\omega^2} - \frac{1}{\epsilon'^2}\right) = \left(\frac{1}{\omega^2} \cdot \frac{1}{\epsilon^2}\right) \sin^2 \rho.$$

When a suitable constant (ω) is added to the radius vectors of this curve an ellipse is produced (inverse to a meridian section of the indicatrix) which represents the variation of ϵ' with respect to wave normal direction.

If a similar constant (K_ω) is added to the biabsorption curves, then the curve which results represents the variation of $K_{\epsilon'}$ with respect to wave normal direction.

Since for most of the visible spectrum the absorption coefficient, K, for the ruby used is of the order of 5×10^{-5} (this value was not measured accurately) it is practical to consider the indicatrix as an ellipsoid. The complex index ($n-ik$), in which i is $\sqrt{-1}$, is practically equal to n.

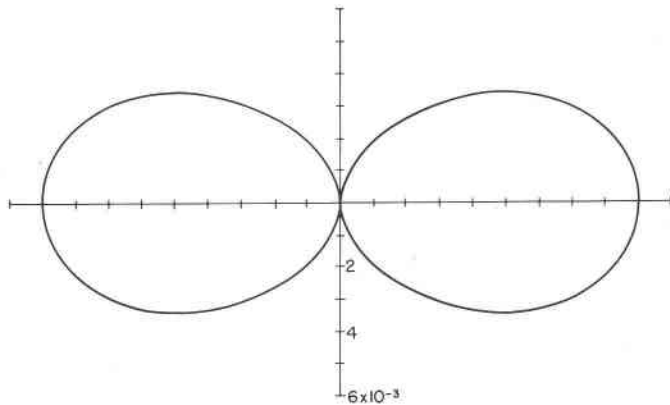Because of recent developments, the study of minor impurities of

FIG. 3. Birefringence with respect to wave normal direction for synthetic ruby. c-axis vertical.

crystals has assumed increasingly greater importance. For this reason it is thought that for some series of weakly absorbing compounds biabsorption for a specified wave normal direction and for selected wave lengths might be a useful optical constant. The value of biabsorption could be determined from thin sections by methods analogous to those used for the determination of bireflection of strongly absorbing crystals.

The writers are indebted to the Linde Air Products Company, who furnished the synthetic ruby sphere for the investigation.

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