

QUANTITATIVE MEASUREMENT OF DICHROISM IN TOURMALINE

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INTRODUCTION

With the Glan¹ spectrophotometer a quantitative comparison of the absorption spectra of one vibration direction of a crystal plate may be made with an unabsorbed spectra from the same source of light. By repeating the observations, after rotating the crystal to the other extinction position, the other vibration direction may be compared with the same source. The ratio of the two intensities for any given wavelength may then be calculated. Two separate slits are used and the intensity of the light through these two slits is equalized before inserting the crystal plate in front of one of the slits. If the light source fluctuates during the course of the observations so as to change the relative illumination of the two slits, the results are in error. Because minerals are apt to show variation in color distribution or because they may contain irregularly distributed inclusions, another source of error is introduced since the slit necessarily covers two different portions of the crystal plate during the course of the experiment.

The Koenigsberger² microphotometer eliminates the first of these two errors because it uses a double image prism of calcite to produce identical images of a single circular aperture. A circular aperture is used instead of a slit to reduce the second type of error because by careful adjustment the same portion of the crystal plate may be used in measuring the absorption in both extinction positions. The microphotometer reduces the error due to unequal color distribution by confining the observations to a very small clear area.

The measurement of dichroism involves a determination of the nature of the difference in color, or the difference in absorption throughout the visible spectrum, between the ϵ and the ω rays. Hence both of the methods mentioned above are indirect methods of measuring dichroism because each vibration is compared to a standard spectrum and the ratio of the intensities calculated through this outside standard. The method described in this paper is a direct method of comparing two

¹ Glan, P., Ueber ein neues Photometer: *Wiedem Ann.*, Band 1, 351-360 (1877).

² Koenigsberger, J., Ueber ein Mikrophotometer zur Messung der Absorption des Lichts: *Zeits. Instrum.*, Band 21, 129-133 (1901). Also, Ueber die Absorption des Lichtes in festen Körpern: *Habilitationsschrift*, Teubner, B. G., 1900, 48 pp. Abst.: *Zeits. Krist.*, 36, 620-623 (1902).

images which are identical except for the direction of polarization and for the difference in intensity, due to unequal absorption. The double refraction of the crystal under observation is used to separate the two images which are formed by light rays which have passed through the same part of the crystal. It is free from errors due to fluctuations in the intensity or spectral characteristics of the light source or in the distribution of light over the entrance slit. The apparatus consists of a monochromator and a one-circle goniometer or spectroscope with a cap-nicol mounted on the eyepiece of the goniometer or spectroscope. The errors in the method are mainly dependent upon the personal equation of the observer when matching visually the intensities of light in the two images.

DESCRIPTION OF METHOD

A prism with the refracting edge perpendicular to the c -axis is ground and polished from a transparent and nearly flawless crystal of light green tourmaline from near Swakopmund, South West Africa.

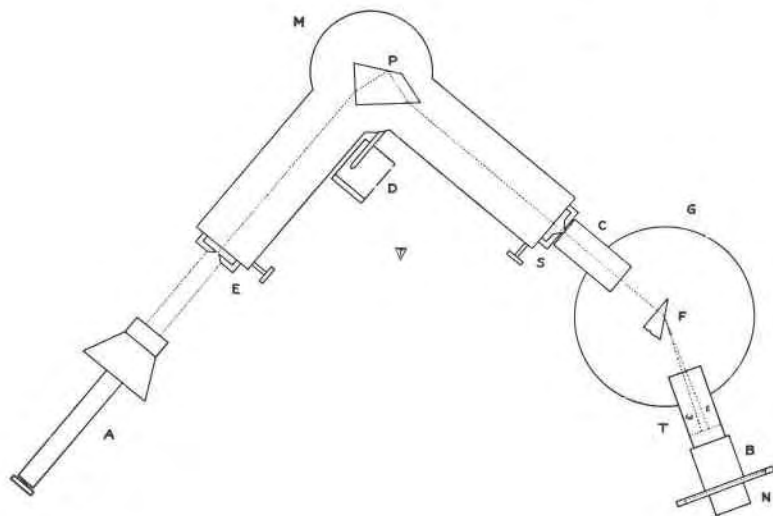


FIG. 1. Arrangement of apparatus for measurement of dichroism. *A*, arc-light; *M*, monochromator; *E*, entrance slit; *P*, constant-deviation prism; *D*, wave-length drum; *S*, exit slit; *C*, collimator; *G*, goniometer; *F*, dichroic mineral prism; *T*, telescope; *B*, collar; *N*, cap-nicol.

One surface of the wedge was crystallographically a prism face of the crystal which was slightly ground and polished to remove minor surface imperfections. This face was blocked off by opaque paper except for a narrow slit parallel to the refracting edge through which the light rays entered the crystal. The prism angle of this wedge was ground to about 32° , a convenient angle which would separate the ordinary and extra-

ordinary rays to such an extent that the separate images of the entrance slit formed by these rays would appear side by side in the telescope of the goniometer, but would be separated by only a narrow interval.

The prism was mounted upon a one-circle goniometer with the refracting edge vertical. The Websky signal slit on the front of the collimating tube was removed and a Fuess-Wülfing monochromator mounted in front of the collimating tube so that the exit slit of the monochromator could serve as the entrance slit of the collimator (Fig. 1). The telescope was then focused upon the exit slit of the monochromator which served as a signal. The prism was adjusted as in the determination of the indices of refraction by the method of perpendicular incidence with the natural prism face of the crystal perpendicular to the beam of light emerging from the collimator. That portion of the beam which fell upon the small slit made in the opaque paper covering the prism face of the crystal was transmitted through the crystal normal to the prism face and upon emerging from the crystal separated into two beams, one vibrating in a vertical plane, and the other vibrating horizontally. When seen through the telescope these two beams formed images of the exit slit of the monochromator which appeared side by side in the field of the telescope and were polarized at right angles to each other. A simply constructed collar of brass was designed to fit around the telescope of the goniometer. This accessory was rigidly attached to the telescope, but contained a bed perpendicular to the telescope axis which allowed the rotation of a cap-nicol of the same design as used with the polarizing microscope. The nicol carried a graduated circle, while the flange of the brass collar bore but a single mark.

When the vibration direction of the cap-nicol was parallel to the vibration direction of the image formed by the ordinary ray, that image was transmitted by the cap-nicol, but the image formed by the extraordinary ray was completely extinguished. On rotating the cap-nicol the ordinary image decreased in intensity while the extraordinary image increased in intensity. These two images, upon continued rotation of the nicol, finally became equal in intensity and from the angle of rotation of the cap-nicol a ratio expressing the relative intensities of the two transmitted rays was calculated.

If we let AE represent the amplitude of the vibration of the extraordinary ray for any given wave length, AO equal the amplitude of the ordinary ray, and AP , the vibration direction of the nicol at the position of equal illumination, then from Fig. 2:

$$\begin{aligned} AP &= AO \cos \alpha \\ AP &= AE \sin \alpha, \text{ or} \\ AO \cos \alpha &= AE \sin \alpha \end{aligned}$$

in which α is the angle of rotation of the cap-nicol from the position of complete transmission of the ordinary ray and extinction of the extraordinary ray. Then,

$$AO = \frac{\sin \alpha}{\cos \alpha} = \tan \alpha.$$

It must be remembered that this value represents the amplitude of the ordinary ray when the extraordinary ray is unity and, since the intensity is proportional to the square of the amplitude, the visual intensity of the ordinary ray would be equal to $\tan^2 \alpha$. Changing to a percentage basis, $100 \tan^2 \alpha$ is the per cent transmission of the ω ray when that of the ϵ ray is 100%.

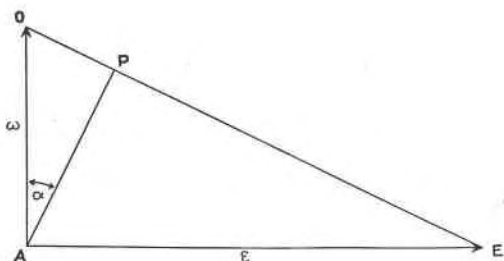


FIG. 2. Diagrammatic derivation of formula for transmission of ω -ray compared to ϵ -ray.

The relative intensity of the ordinary ray with respect to the extraordinary ray of the tourmaline was compared for twenty different wave lengths of the spectrum. The accuracy of the determination of the position of equal brightness of the two images involves considerable in the way of a personal factor. Different individuals have different degrees of acuity of perception of relative brightness. The ability of the observer to repeat his readings of the angle of rotation increases rapidly with experience and training, and drops off sharply with fatigue or eye strain. The absolute intensity of the image is also an important factor in matching intensities. The greatest difficulty is experienced when the images are too bright, so it is desirable to regulate the intensity of the light source so that the images are moderately weak in absolute brightness. In order to minimize the personal equation a series of twenty readings were taken at each wave length. The position of equal illumination was determined by alternately approaching this position by rotating the nicol clockwise and then counterclockwise toward the position of equal illumination.

From these successive readings the average visual intensity of the

ω ray was calculated, together with the average deviation of the mean for the readings at each wave length. These values are given in Table 1. The values given in the second column represent on a percentage basis the visual intensity of the ω ray compared to that of the ϵ ray when the intensity of the ϵ ray is taken as unity. The third column gives the average deviations. In Fig. 3 these values are shown diagrammatically.

TABLE 1.

Wave-length $\mu\mu$	Per cent Transmission ω ray	A.D.	Wave-length $\mu\mu$	Per cent Transmission ω ray	A.D.
427.5	2.71	.04	538	10.24	.10
445	3.60	.05	545	10.77	.09
465	5.20	.05	567	12.01	.10
480	6.77	.07	585	11.59	.10
489	7.85	.06	600	9.66	.08
495	8.76	.10	615	7.88	.07
502	9.76	.09	630	6.45	.09
510	10.02	.06	650	5.24	.06
520	9.60	.08	670	4.45	.07
530	9.64	.08	685	3.99	.06

The curve thus plotted shows a slight change in trend between 500 and 550 $\mu\mu$, and it is important to determine whether this is due to experimental error, or is a characteristic of the material studied. The percentage deviation in this region averages .88%, but for a margin of safety this might wisely be increased to 1.50%. Using this latter figure, there appear on Fig. 3 two additional curves in the region of 500 to 550 $\mu\mu$ representing the probable limits of error in both directions. This indicates that the change in trend is beyond the limits of experimental error.

The light was transmitted through a small portion of the wedge of the tourmaline crystal. The average thickness of this small area of the wedge, 1.35 mm. \pm .01 mm., was determined by measuring the distance of the center of the small slit made in the opaque paper from the refracting edge of the crystal and multiplying that value by the tangent of the refracting angle. Because the image in the telescope is produced by all rays transmitted through the crystal, its intensity is proportional to the average thickness of that portion of the crystal through which the light passes.

The curve does not represent a comparison between the spectrum of

the ω ray and the spectrum of white light, but a quantitative visual comparison of the spectrum of the ω ray with that of the ϵ ray when the ϵ ray is taken as unity. It may also be interpreted as a measure of the ability of this crystal to produce polarized light by absorption. At only

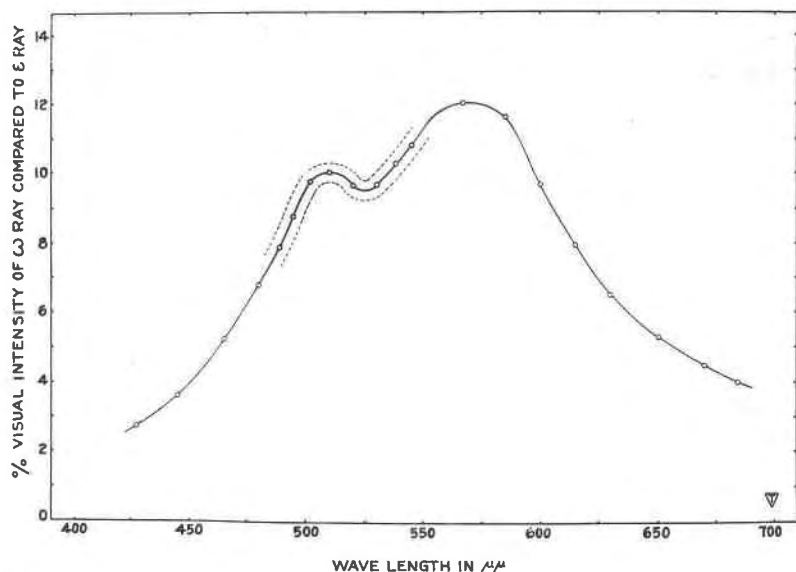


FIG. 3. Curve showing nature of dichroism in tourmaline from Swakopmund, S. W. Africa.

a few points in the middle of the spectrum does the percentage of the unabsorbed ω ray reach ten per cent of the total light transmitted. In other words, a plate of tourmaline 1.35 mm. thick cut from this crystal parallel to the c -axis would produce light by transmission which would be over 90% plane polarized.

MEASUREMENT OF DISPERSION

From the same prism used for the determination of dichroism, the indices of refraction for various wave-lengths were measured by the method of perpendicular incidence. Table 2 gives the average of two determinations, the prism having been reoriented on the goniometer for the second set of readings. The values for the indices of refraction of the ϵ ray between 440 and 656 $\mu\mu$, and for the ω ray between 478 and 632 $\mu\mu$ are probably accurate to within $\pm .0003$. As the limits of visibility are approached in either direction the precision becomes less, due to increasing weakness of the signal. The first and last figures for the indices of

refraction in each column of Table 2 are probably accurate to within $\pm .0005$. The dispersion of the ϵ ray between 440 and 671 $\mu\mu$ is about .0130, that of the ω ray between the same interval about .0137, and the dispersion of the double refraction about .001.

TABLE 2.

Wave-length $\mu\mu$	Indices of refraction		Wave-length $\mu\mu$	Indices of refraction	
	ϵ	ω		ϵ	ω
695	1.6205	—	486	1.6290	1.6500
671	1.6208	1.6410	478	1.6296	1.6507
656	1.6211	1.6414	470	1.6307	1.6515
632	1.6218	1.6420	460	1.6316	1.6524
610	1.6225	1.6426	450	1.6324	1.6534
589	1.6232	1.6436	440	1.6338	1.6547
570	1.6238	1.6445	434	1.6345	—
550	1.6248	1.6455	420	1.6361	—
535	1.6259	1.6463	410	1.6376	—
515	1.6270	1.6483	405	1.6382	—
500	1.6279	1.6491			

CONCLUSIONS

The method of quantitatively measuring dichroism which was used is simpler than those described in the literature and, except for the easily constructed brass collar, calls for the use of no equipment which is not commonly available in mineralogical laboratories. The simplicity of the method allows it to be used for a laboratory experiment for teaching purposes.

Absorption spectra have long been used for determining the chemical characteristics of gases and liquids. With solids the width of the absorption bands makes impossible the same degree of accuracy that can be obtained with liquids and gases. In the case of colored glasses the position of these bands is dependent upon the qualitative chemical composition of the glass, and the width upon the percentage composition of the absorbing element and upon the thickness. At some time in the future it is hoped that the dichroic character of the absorption in certain crystals may be correlated with the composition of the crystals.