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POLARIZATION IN CARY MODEL 14 INSTRUMENTS AND ITS EFFECT ON TRANSMITTANCE MEASUREMENTS OF ANISOTROPIC MATERIALS

by

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ABSTRACT. In our laboratory Cary Model 14 instruments are used to measure the transmittance of optical components. These instruments have been found to have polarization characteristics that affect the transmittance values of anisotropic or dichroic materials. A study was made to determine the extent of polarization in the instruments and its variation with wavelength. Type HNP'B, HN22, and HR Polaroid polarizers and Polacoat polarizing filters, formula 105 UV, were used to cover the wavelength range from 0.2 to 2.5 μ. A Bausch and Lomb 90-8 hot mirror was used to protect the HR Polaroid polarizers. Data points were obtained every 10, 20, or 50 Å using a Datex digital system. In the ultraviolet the degree of polarization is fairly constant from 3000 to 4000 Å. In the visible the degree of polarization shows some variation with wavelength. In the near infrared the variation of the degree of polarization with wavelength is large, showing sharply defined maxima at approximately 0.77, 0.97, and 1.27 μ. These wavelengths correspond to the calculated positions of the Wood anomalies. The spectral transmittance of optical quality sapphire, a uniaxial crystal, cut at 45°, 60°, and 90° to the c-axis, showed undulations for certain orientations of the privileged directions.

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M. R. Etheridge, Capt., USN .... Commander
H. G. Wilson .... Technical Director (Acting)

FOREWORD

This report describes a study made to determine the degree of polarization in the Cary Model 14 spectrophotometers and its variation with wavelength.

The study was supported by Naval Air Systems Command Task Assignment A 365 333 01/216-1/F001-05-01 and Advanced Research Projects Agency Order No. 585.

This report was reviewed for technical accuracy by H. E. Bennett and F. K. Odencrantz.

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INTRODUCTION

In our laboratory Cary Model 14 spectrophotometers (Cary Instruments, Monrovia, California) are used to measure the transmittance of optical components. These instruments have been found to have polarization characteristics that affect the transmittance values of anisotropic or dichroic materials (Ref. 1). The extent of polarization in the instruments and its variation with wavelength have been determined. Anomalies that can result when the instruments are used to measure the transmittance of anisotropic materials have been demonstrated using sapphire specimens cut at various angles to the c-axis and appropriately oriented in the sample compartment. Sapphire was chosen as an example because it is often used as a substrate for interference filters and as window material.

EXPERIMENTAL

Definition of Degree of Polarization. The kind of polarization has not been determined; the degree of polarization will be treated mathematically as though the beam consists of a mixture of unpolarized light and linearly polarized light. The degree of polarization P is given by the equation

$$P = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} , \qquad (1)$$

where I_{max} and I_{min} refer to the light intensities recorded with the analyzer oriented so that the detector signal indicates maximum or minimum intensity. These orientations of the analyzer are 90^{o} apart. In the Cary 14 instruments these positions of the analyzer correspond to the transmission axis of the analyzer being either horizontal or vertical. The equation may be rewritten in terms of the horizontal, I_H, and vertical, I_V, components of the intensity:

$$P = \frac{I_H - I_V}{I_H + I_V} . \qquad (2)$$

The horizontal component of the intensity may be greater or smaller than the vertical component depending upon the wavelength and the particular instrument. As a consequence P may have negative as well as positive values.

Calculation of Degree of Polarization From Absorbance Values. The degree of polarization can be expressed in terms of absorbance or transmittance. Making the calculations in terms of absorbance eliminates both encoder phasing problems and the necessity to establish a flat baseline. Let A_V and A_H refer to the absorbance of the analyzer measured with the transmission axis oriented vertically and horizontally, respectively. Then

$$A_V - A_H = \log \frac{I_H}{I_V} = \log R \;, \tag{3}$$

where

$$R = \frac{I_H}{I_V} \;.$$

Then

$$P = \frac{R - 1}{R + 1} \;.$$

It should be noted that this calculation of the degree of polarization gives an over-all value for the response of the instrument and not just for the light in the sample beam because some of the elements in the optical train following the specimen may be sensitive to the orientation of the electric field vector $\vec{E}$.

Cary 14 Instruments. Cary 14 spectrophotometers are prism-grating double-beam instruments (Fig. 1). In the ultraviolet and visible regions dispersed radiation is used in the sample compartment. In the near infrared the light path is reversed and the light is dispersed after it passes through the specimen. One of the instruments used, a Cary 14R, has an additional capability in that dispersed radiation may be used in the sample compartment up to 1.8 μ. Phototubes (1P28) are used in the ultraviolet and visible regions; lead sulfide detectors are used in the near-infrared region.

The Cary 14R is equipped with a Datex digital system that digitizes and records the data--both wavelength and absorbance or transmittance--in the form of punched paper tape. The command to read out data may be initiated by incremental change in wavelength, incremental change in transmittance or absorbance, or both. The analog output of the Cary 14 instruments not equipped with digital systems was converted to digital form by transferring the chart from such Cary 14 instruments to the

Cary 14R and manually causing the pen to follow the trace (Ref. 2). The digital system was then used to record both the wavelength and pen position (absorbance or transmittance).

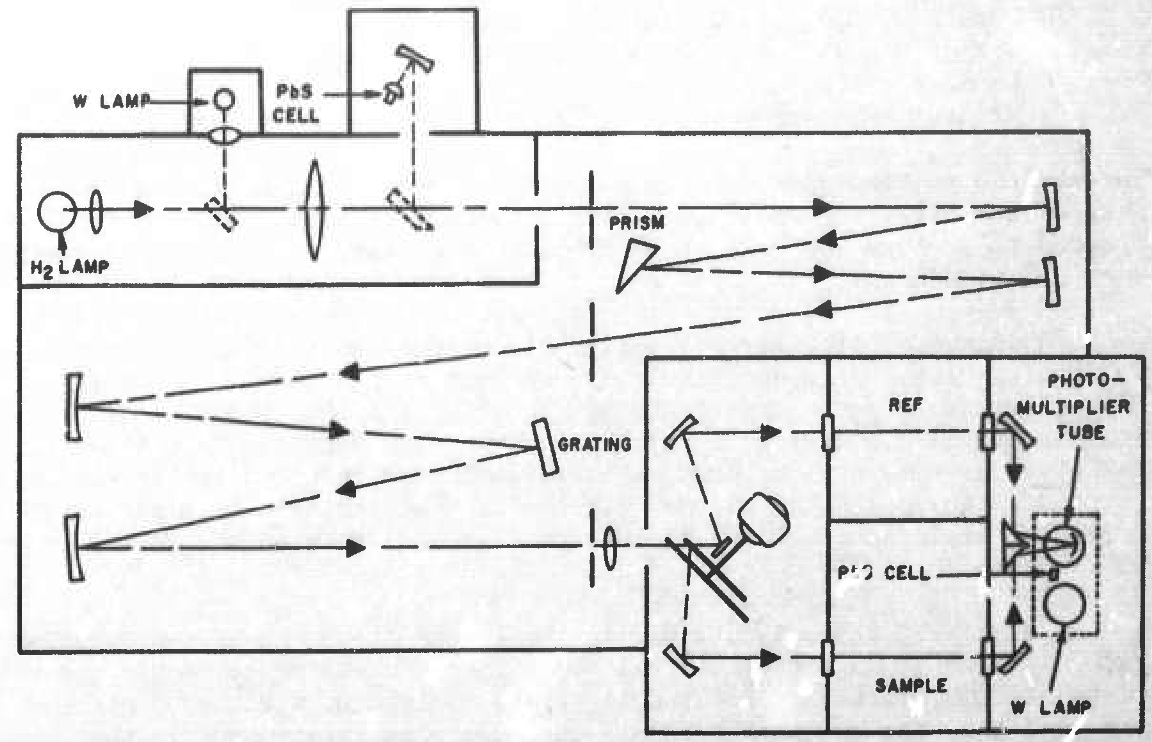

FIG. 1. Optical System of Cary Model 14R Spectrophotometer.

Polarizers. Several polarizing elements were needed to cover the entire spectral range of the instruments. Polacoat polarizing filters,[1] formula 105 UV, and HNP'B Polaroid polarizers[2] were used in the ultraviolet, HN22 Polaroid in the visible, and HR Polaroid in the near infrared. Exposure of the HR Polaroid to the undispersed energy of the source often resulted in pronounced degradation of the polarizer. This can be avoided by using a Bausch and Lomb 90-8 hot mirror between the source and the HR Polaroid and placing the HR Polaroid at the end of the sample compartment away from the source. The quantity $A_V - A_H$ was determined over the range 0.8 to 1.7 μ both with and without the hot mirror; the determinations agreed with each other within the limits of noise.

[1] Polacoat Incorporated, Cincinnati, Ohio.
[2] Polarizer Division, Polaroid Corporation, Cambridge, Massachusetts.

Sapphire. Sapphire disks[3] were fabricated to the following specifications:

1.00 in. Diameter by 0.100 in. thick
Flat to 20 fringes
Parallel to 0.001 in. per 1 in. diameter
Cut at 0°, 45°, 60°, or 90° to the c-axis (± 5°)
Minimum striae
Without twinning

The angle specified is the angle between the c-axis and the normal to the face of the disk. Several disks of a given cut were examined between crossed polarizers and only those transmitting uniformly across the clear aperture were used.

Specimen and Polarizer Holders. The devices[4] used to mount the polarizing elements or sapphire specimens and to provide for their rotation about the light beams by 90° are shown in Fig. 2. The V-block is similar to the standard cell holder; however, the V-groove is cut deeper to allow for mounts with large apertures. The cylindrical collar can be rotated to any position and then clamped in that position with the set screw. Changing the corner set into one V-groove rotates the filter by 90°.

A polarizing element suitable to the wavelength range being investigated is mounted in the holder and the holder placed in the sample compartment. The collar is rotated to give a maximum or minimum of absorbance and the spectrum is recorded. The holder is rotated 90° in the V-block and the spectrum recorded. Digitized data are recorded every 10, 20, or 50 Å.

RESULTS AND DISCUSSION

The absorption spectra obtained with HN22 and HR Polaroid are shown in Fig. 3 and 4. Computer programs were used to calculate the degree of polarization from the appropriate absorbance data. The first program subtracted one absorbance value from another at a given wavelength; the second one computed the degree of polarization from differences in absorbance. Figures 5-7 show the degree of polarization in the ultraviolet for the three instruments. The data were obtained using Polacoat

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[3] Purchased in 1966 from Crystal Products Department, Linde Division, Union Carbide Corporation, Torrance, California.

[4] The holders are similar to those fabricated by Cary Instruments on special order.

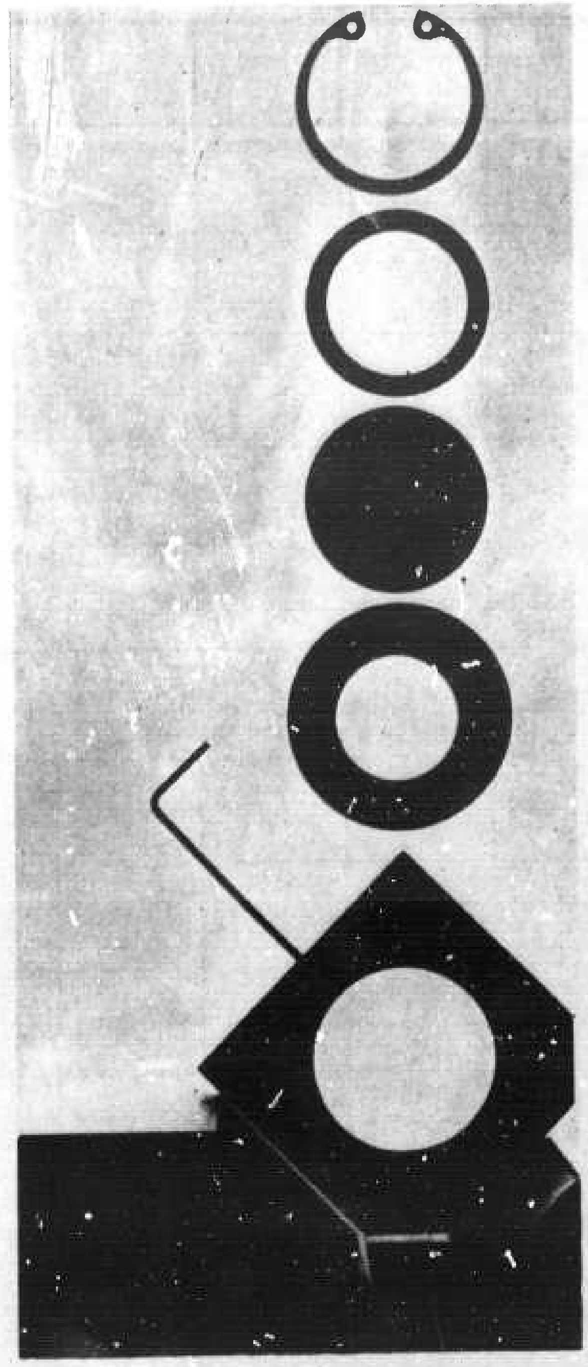


FIG. 2. Specimen and Polarizer Holder.

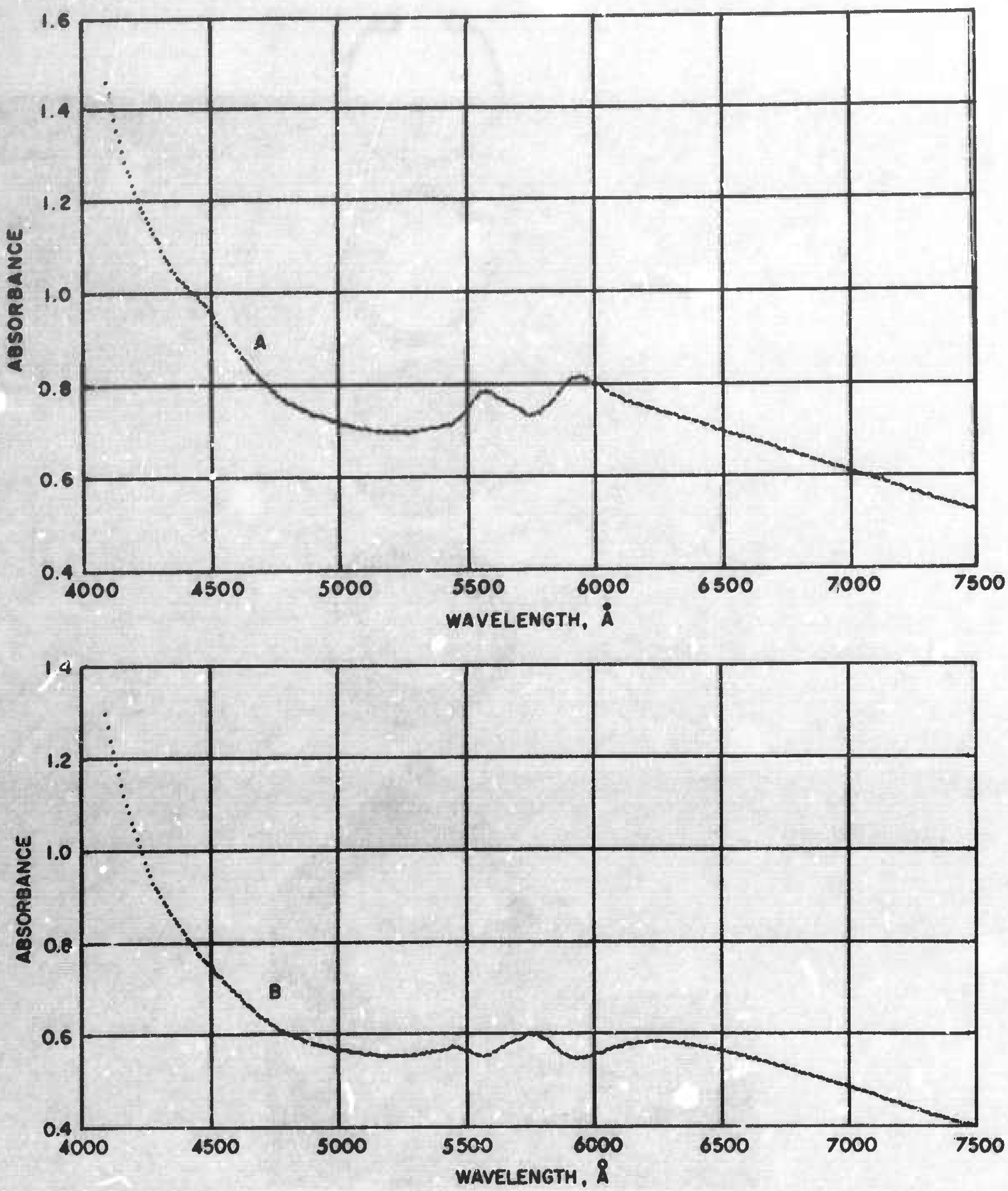
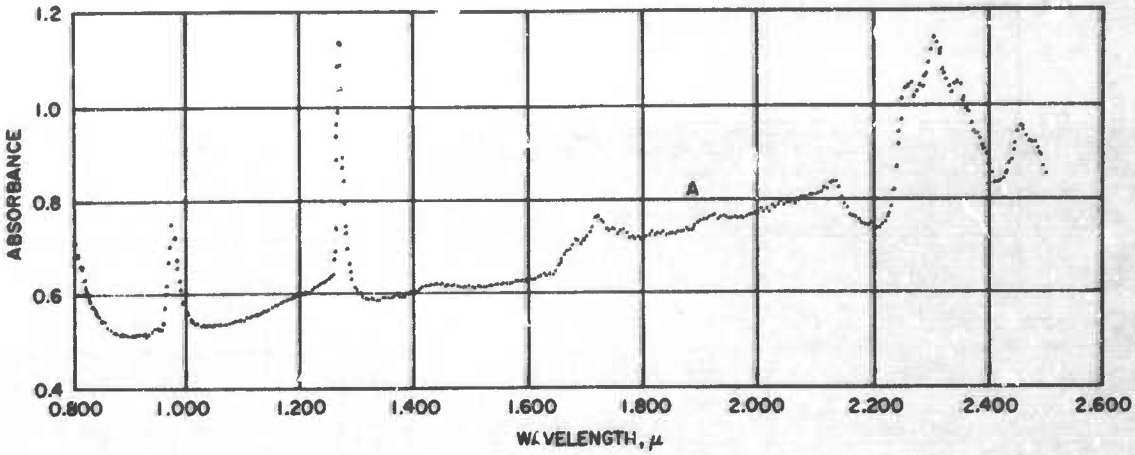


FIG. 3. Absorption Spectra of HN22 Polaroid (Cary 14R). Curve A: Transmission axis vertical. Curve B: Transmission axis horizontal.



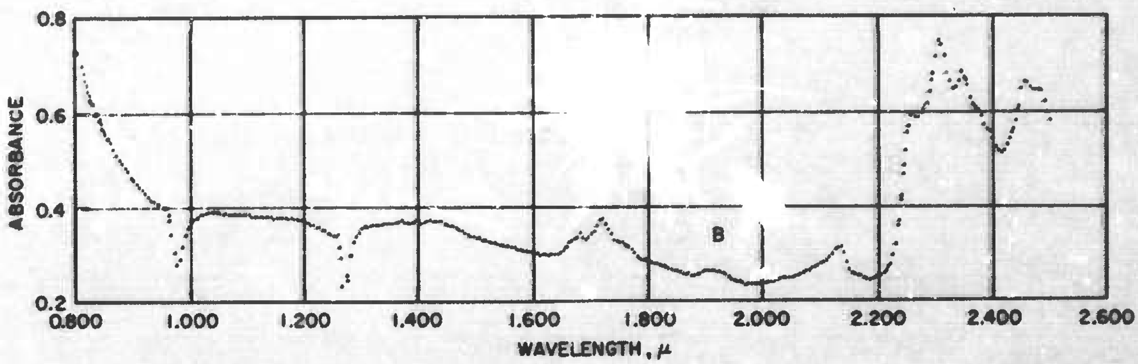


FIG. 4. Absorption Spectra of HR Polaroid (Cary 14R). Curve A: Transmission axis vertical. Curve B: Transmission axis horizontal.

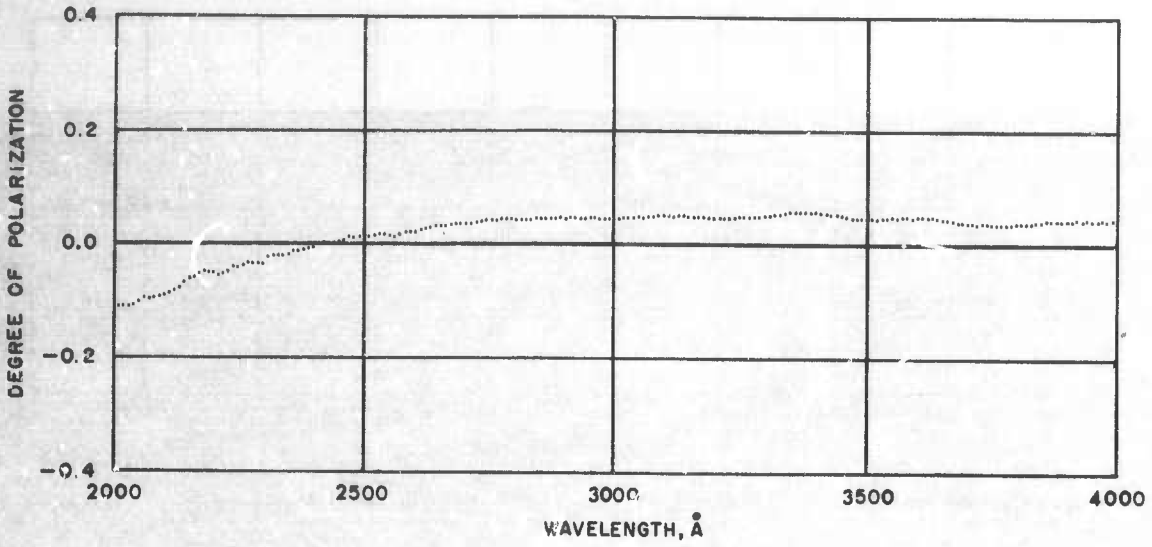


FIG. 5. Degree of Polarization in the Ultraviolet of Cary 14, Ser. No. 65 (Polacoat Filter).

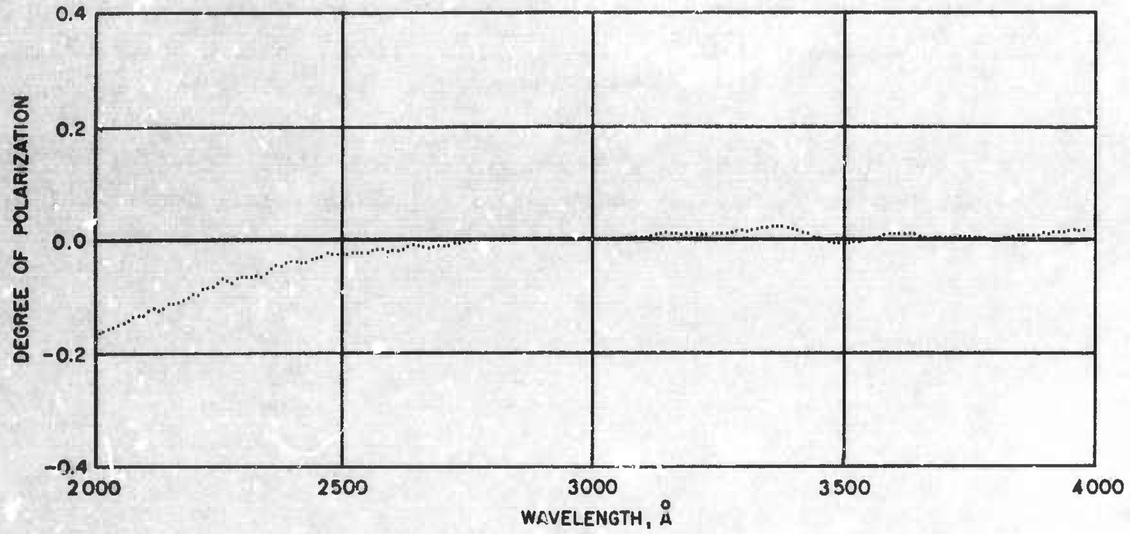


FIG. 6. Degree of Polarization in the Ultraviolet of Cary 14, Ser. No. 244 (Polacoat Filter).

filters; the HNP'B Polaroid is not useable below approximately 2750 Å. Figures 8-10 show the degree of polarization for the visible and Fig. 11-13 for the near infrared. For a given instrument the degree of polarization at wavelengths accessible to more than one mode of operation may vary due to differences in optical components. For example, a difference in the degree of polarization at 4000 Å exists in the Cary 14, Ser. No. 65, between the ultraviolet and visible modes.

Polarizers are not perfect in that they do not extinguish all light regardless of the orientation of electric field vector $\vec{E}$. If the principal transmittances k_1 and k_2 of the polarizers are known, corrections can be made as follows:

$$P_{corrected} = \frac{k_1 + k_2}{k_1 - k_2} P_{uncorrected} \quad . \qquad (4)$$

For HN22 Polaroid k_1 varies from 0.21 to 0.59 while k_2 varies from 0.00001 to 0.000003 for the wavelength range 4000 to 7000 Å (Ref. 3, p. 53). At 4000 Å the correction factor is essentially one:

$$\frac{k_1 + k_2}{k_1 - k_2} = \frac{0.21 + 0.00001}{0.21 - 0.00001} = 1.0001 \quad .$$

In the near infrared the largest correction factor in the range 0.8 to 2.0 μ occurs near 0.95 μ. At 1.0 μ $k_1 = 0.55$ and $k_2 = 0.05$ (Ref. 3, pp. 63 and 64):

$$\frac{k_1 + k_2}{k_1 - k_2} = \frac{0.55 + 0.05}{0.55 - 0.05} = 1.2 \quad .$$

Principal transmittances were not found in the literature for HNP'B Polaroid polarizer and Polacoat filters. All the values shown in the figures are $P_{uncorrected}$. It should be noted that the efficiency of HR Polaroid falls off in the region from 2.3 to 2.5 μ; and therefore, the values for the degree of polarization are not so accurate for the 2.3 to 2.5 μ region as for the rest of the near infrared.

The figures show that there are certain regions within the spectral range of the Cary 14 instruments in which rapid variation of the degree of polarization with wavelength occurs. This is particularly pronounced at about 0.77, 0.97, and 1.27 μ; deviations in the 100% transmittance lines of the instruments have been noted earlier (Ref. 4). The changes in the degree of polarization are due to Wood anomalies (Ref. 5 and 6), which are bands of abnormally high or low intensity in the spectrum of light diffracted by a reflection grating. Their positions correspond to the Rayleigh wavelengths of the 600 line/mm echelette grating used in the Cary 14 instruments.

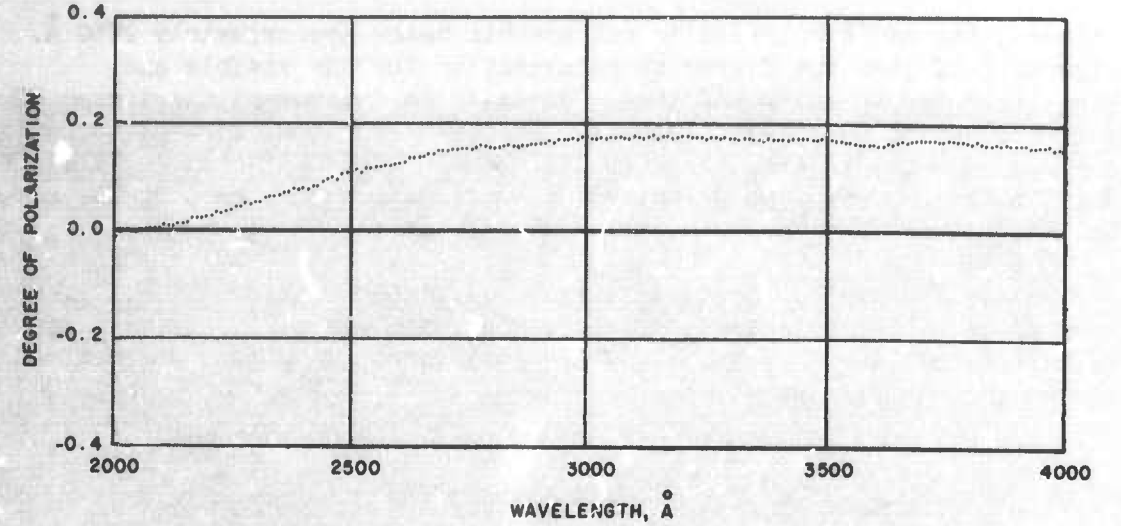


FIG. 7. Degree of Polarization in the Ultraviolet of Cary 14R, Ser. No. 1173 (Polacoat Filter).

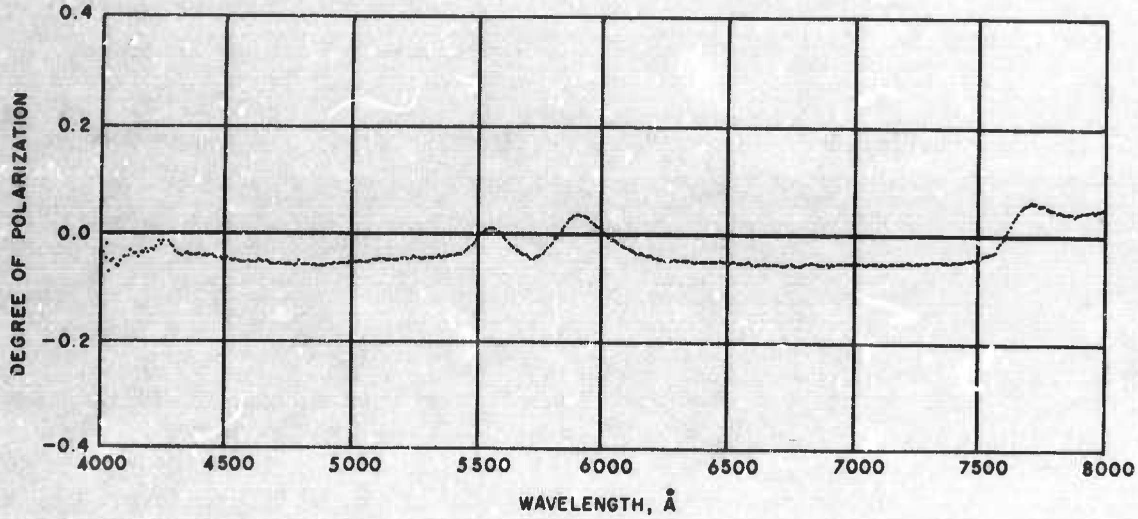


FIG. 8. Degree of Polarization in the Visible of Cary 14, Ser. No. 65.

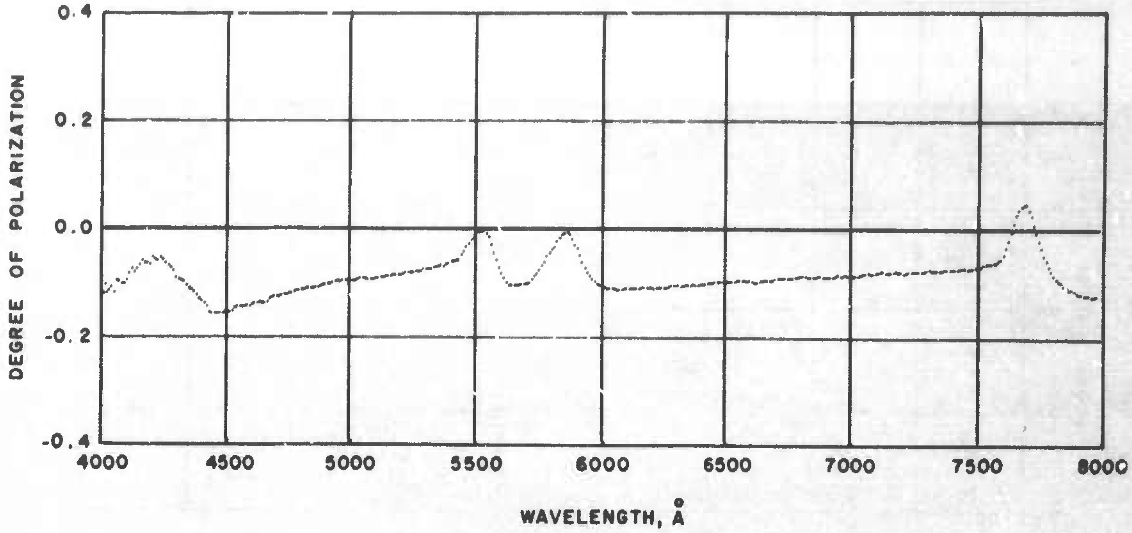


FIG. 9. Degree of Polarization in the Visible of Cary 14, Ser. No. 244.

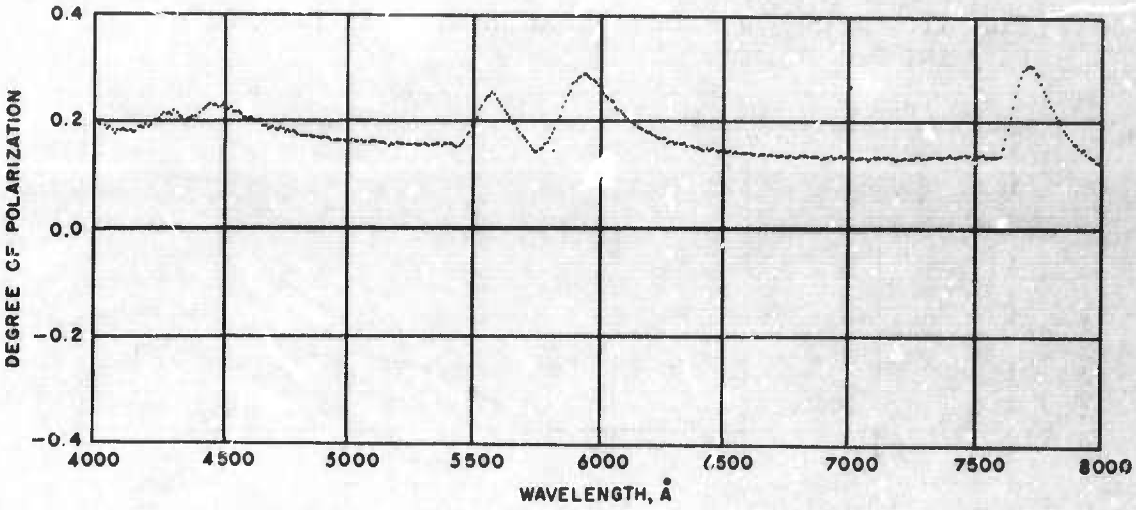


FIG. 10. Degree of Polarization in the Visible of Cary 14R, Ser. No. 1173.

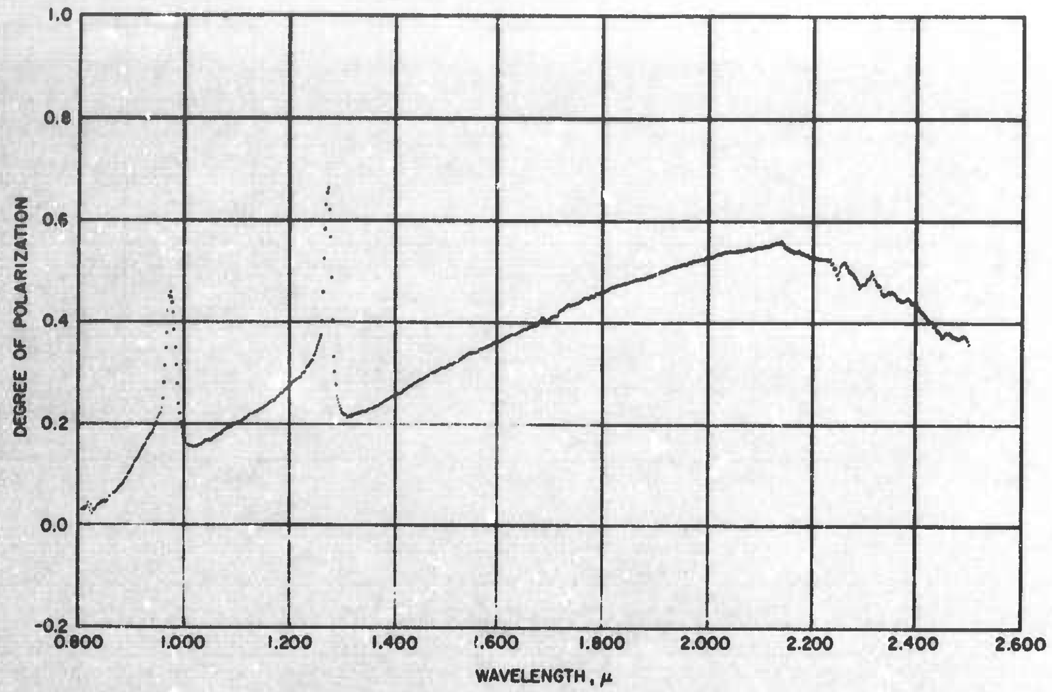


FIG. 11. Degree of Polarization in the Near Infrared of Cary 14, Ser. No. 65.

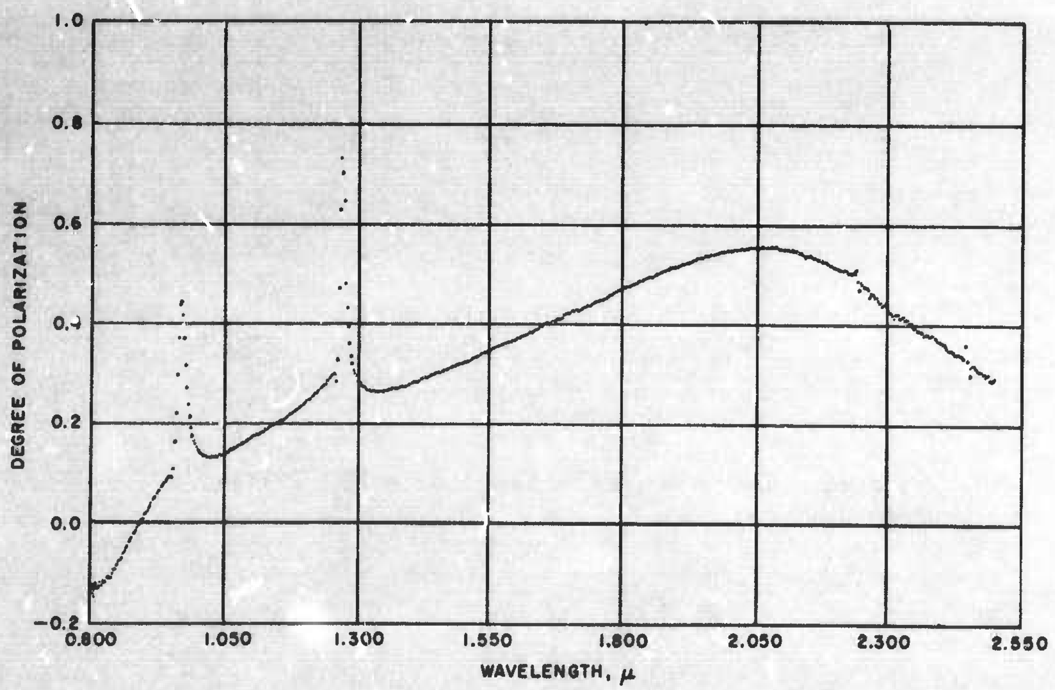


FIG. 12. Degree of Polarization in the Near Infrared of Cary 14, Ser. No. 244.

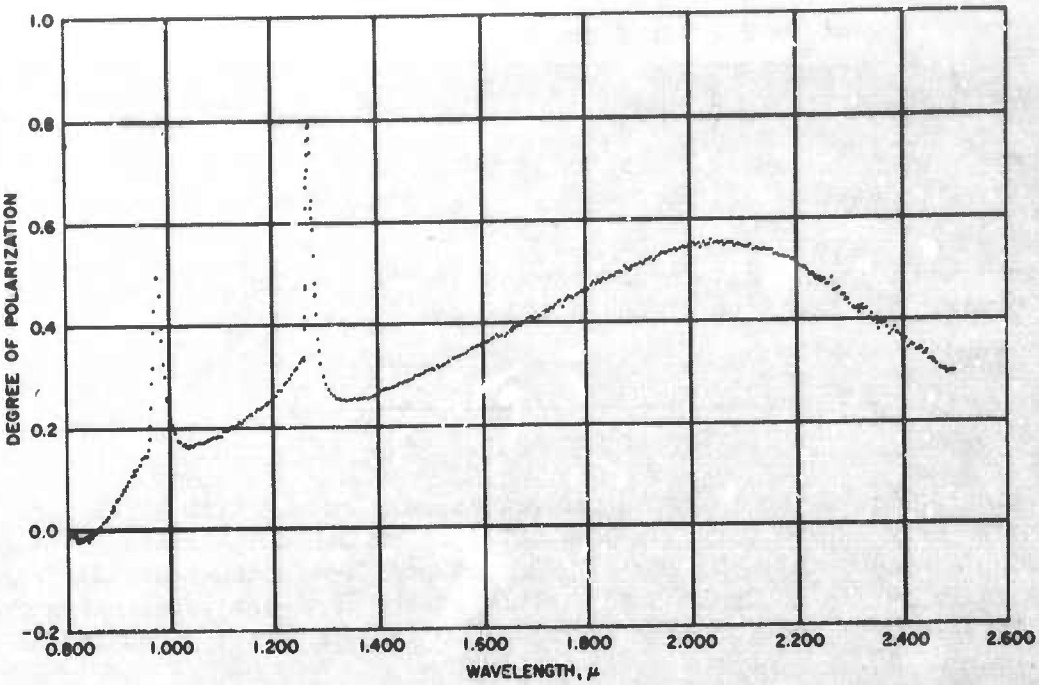


FIG. 13. Degree of Polarization in the Near Infrared of Cary 14R, Ser. No. 1173.

Wood anomalies may be separated into two groups depending upon the orientation of the electric field vector $\vec{E}$. The S-anomalies occur for light polarized with the $\vec{E}$ perpendicular to the rulings of the grating; the P-anomalies occur for light having $\vec{E}$ parallel to the rulings. In a theoretical treatment of gratings Rayleigh found mathematical singularities occurring at wavelengths of the diffracted light for which light of the same wavelength is diffracted in another order at such an angle as to graze the surface of the grating. These particular wavelengths are known as Rayleigh wavelengths. As the singularities occur only for $\vec{E}$ perpendicular to the rulings they account only for S-anomalies on the basis of Rayleigh's theory. The P-anomalies occur with deeply ruled grating. Their positions are sometimes given by the equation that predicts the position of S-anomalies (Ref. 5). A theory proposed by Hessel and Oliner appears to account for both S- and P-anomalies (Ref. 7).

The Rayleigh wavelengths,[5] λ_R, for a particular grating may be calculated by solving the grating equations for the two orders involved (see Fig. 14):

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[5] This development follows that of Stewart and Gallaway (Ref. 6).

$$n\lambda_R = 2\ a \sin \phi \cos \alpha\ , \tag{5}$$

$$(n + k)\ \lambda_R = a\ (\sin \phi_i + 1) \text{ for grazing positive orders}\ , \tag{6}$$

$$-k'\ \lambda_R = a\ (\sin \phi_i - 1) \text{ for grazing negative orders}\ , \tag{7}$$

where k and k' are positive integers, a is the grating spacing, and n is the order. The solution of Eq. 5 and 6 for λ_R is

$$\lambda_R = \frac{2a}{n + 2k} \frac{1 \pm [2\sqrt{nk + k^2}/(n + 2k)] \sin \alpha}{1 + [n \tan \alpha/(n + 2k)]^2}\ . \tag{8}$$

Solution of Eq. 5 and 7 for λ_R yields the same result with k replaced by k'. The Cary 14 and Cary 14R have 600 line/mm echelette gratings used in such a manner that the angle, 2 α, between the incident and diffracted rays is $16^\circ 30'$.[6] In Table 1 are tabulated the Rayleigh wavelengths for the first-order spectrum (n = 1) for a 600 line/mm grating mounted so that $\alpha = 8^\circ 15'$.

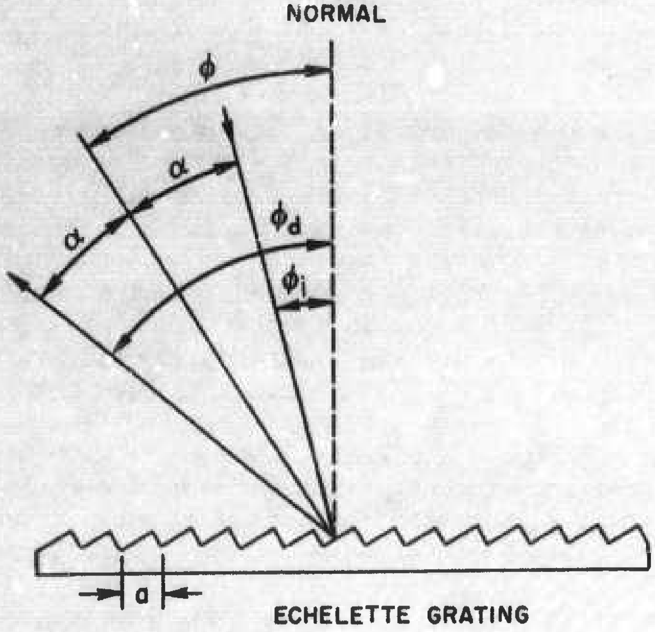

FIG. 14. Schematic of Diffraction of Light by a Grating.

[6] Personal communication from Cary Instruments.

TABLE 1. Rayleigh Wavelengths in the First-Order Spectrum

k	λ_R, Å	Grazing order
1	12585	+2
	9586	-1
2	7598	+3
	5725	-2
3	5436	+4
	4084	-3
4	4231	+5
	3175	-4

Two types of measurements were made in order to show the effect of the inherent polarization of the instruments upon the measured transmittance of sapphire. A piece of sapphire cut at 90° to the c-axis (c-axis lying in the face of the specimen) was placed perpendicular to the light beam in the Cary 14 and rotated about the beam in 5° increments at $\lambda = 1.27\ \mu$; the results are shown in Fig. 15. Figures 16 and 17 show the recorded spectral transmittance of sapphire cut at various angles to the c-axis and oriented with the privileged directions at 45° to the vertical (with the exception of the 0°-cut piece). The undulations, or fringes, are especially pronounced in the case of the 90°-cut specimens. Curves for 60°-cut specimens are of particular interest because the 60° cut is the one commonly used.

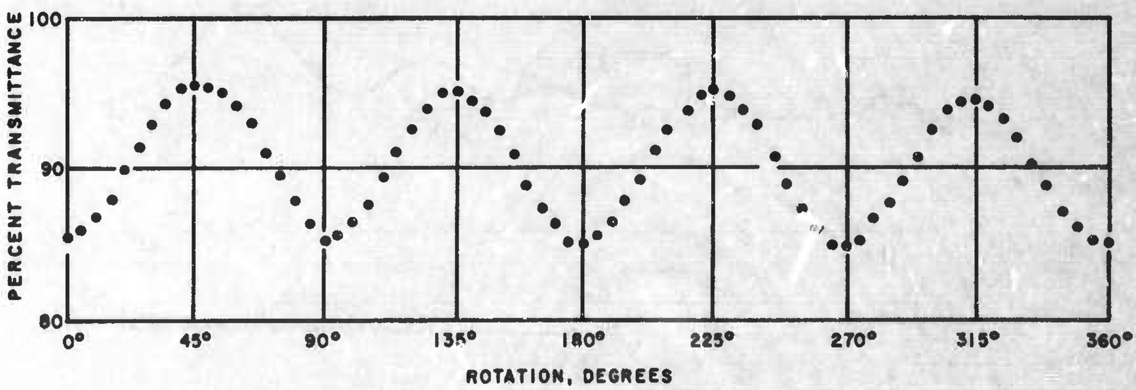

FIG. 15. Percent Transmittance vs. Rotation of 90°-cut Sapphire at 1.27 μ.

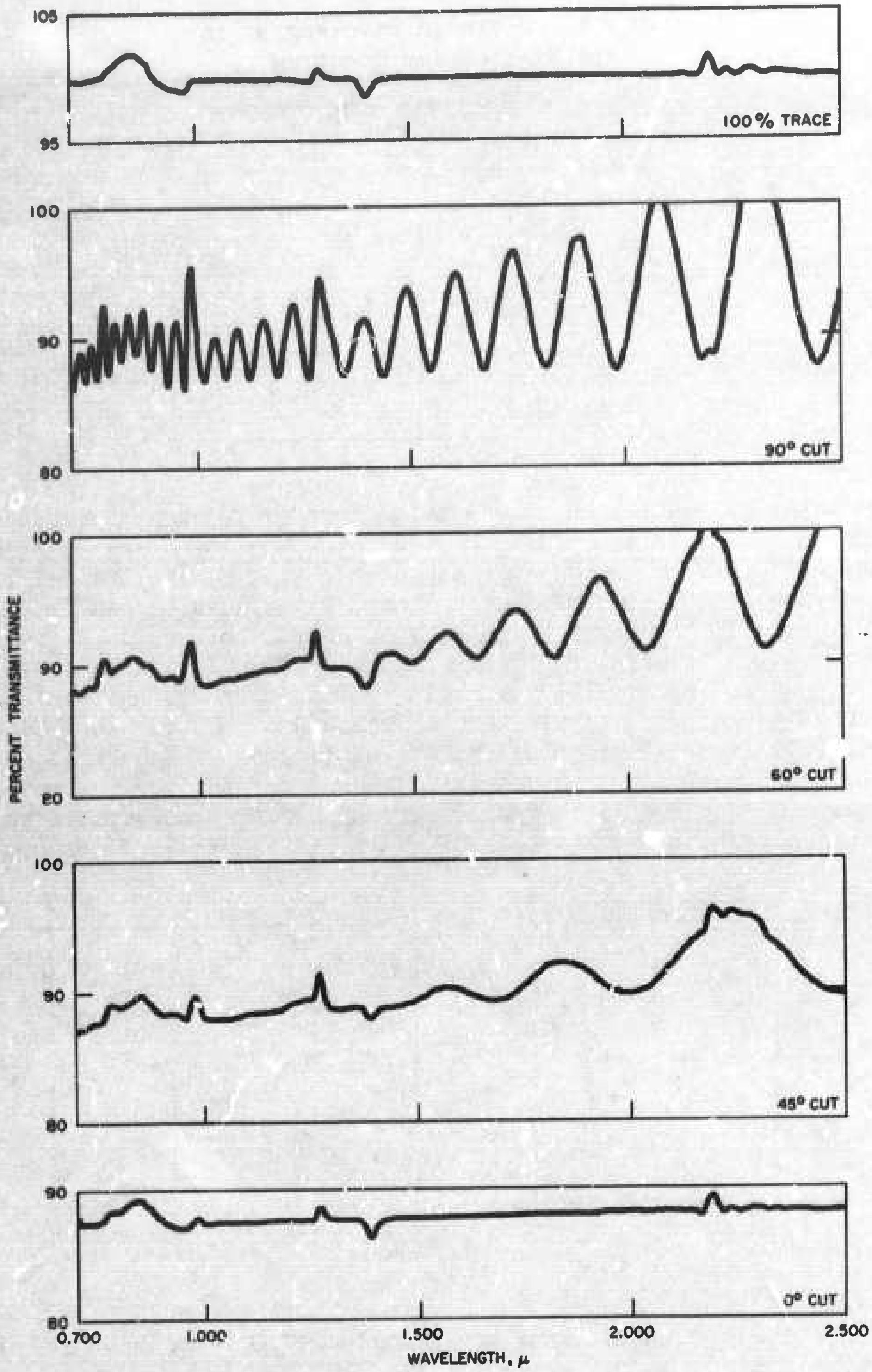

FIG. 16. Spectral Transmittance of Sapphire cut at 0°, 45°, 60°, and 90° to the c-axis; Privileged Direction at 45° to Vertical (Cary 14, Ser. No. 65).

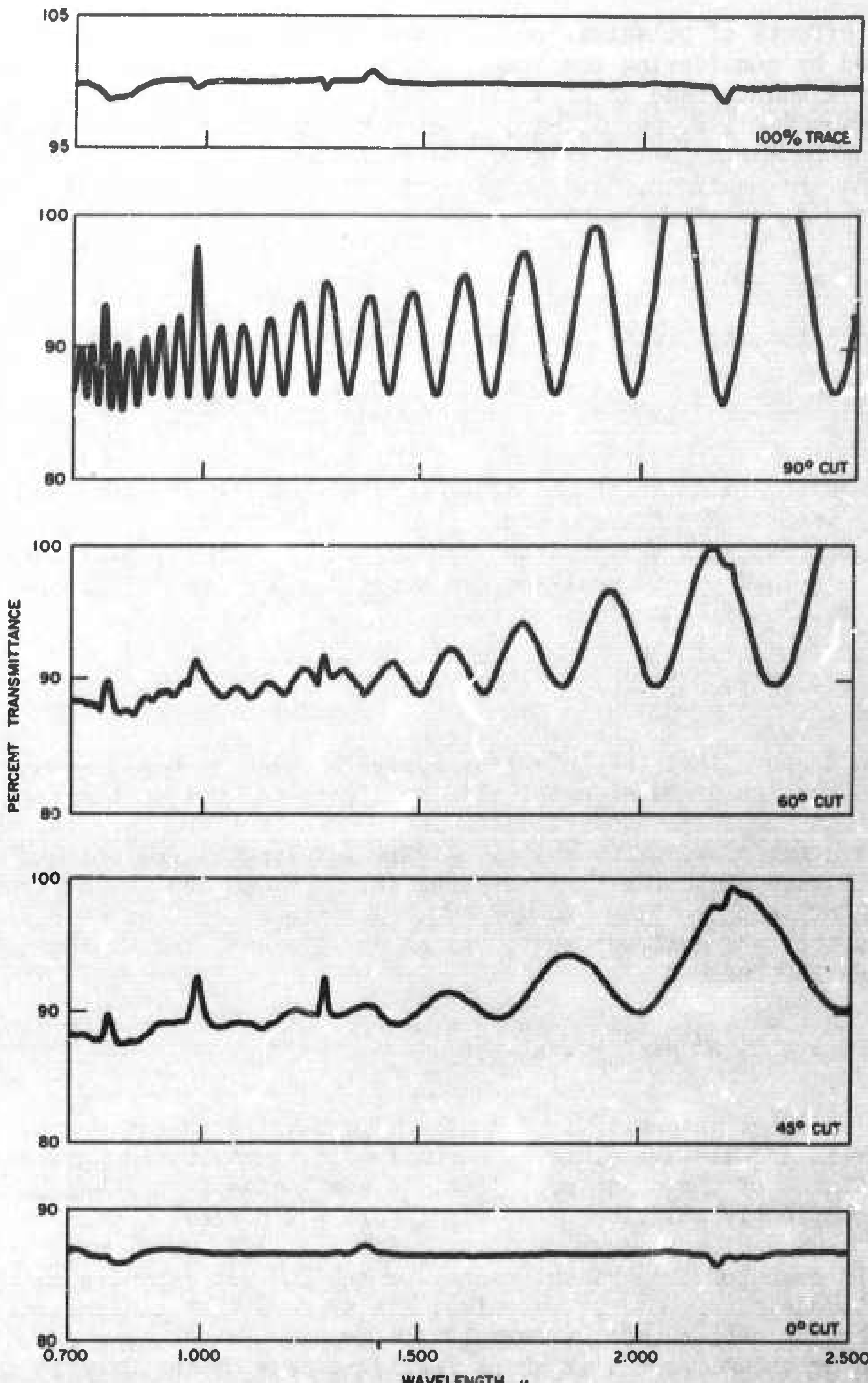

FIG. 17. Spectral Transmittance of Sapphire cut at 0°, 45°, 60°, and 90° to the c-axis; Privileged Direction at 45° to Vertical (Cary 14R, Ser. No. 1173).

The effects of polarization upon the transmittance measurements are explained by considering the transmission of light incident normally on a set of elements made up of a polarizer, a 90°-cut sapphire disk, and an analyzer (Ref. 8, pp. 385-86). Let α be the angle between the optic axis and the transmission axis of the polarizer and β be the analogous angle for the analyzer. If the electric field vector $\vec{E}$ incident on the sapphire disk is given by

$$E = a \cos \omega t,$$

then the intensity transmitted by the analyzer is

$$I = a^2 \cos^2 (\alpha - \beta) - a^2 \sin 2\alpha \sin 2\beta \sin^2 \frac{\epsilon}{2} ,$$

where ϵ is the relative phase difference between the ordinary and extraordinary waves. For fixed α and β the intensity varies as a function of wavelength because ϵ varies with wavelength. For the special case in which the polarizer and analyzer are crossed and $\beta = 45^\circ$ the expression for the intensity becomes

$$I = a^2 \sin^2 \frac{\epsilon}{2} . \tag{9}$$

Equation 9 shows that the intensity varies between zero and a maximum of a^2 as a function of wavelength. If the light incident on the sapphire disk is not completely polarized as is the case for the Cary 14, the minima are not of zero intensity. At the wavelengths for which the disk is a full-wave plate the transmittance is a minimum and is the transmittance of sapphire (Fig. 16 and 17). For the special case in which the polarizer and analyzer are parallel and $\beta = 45^\circ$, the expression for the intensity becomes

$$I = a^2 - a^2 \sin^2 \frac{\epsilon}{2} = a^2 \cos^2 \frac{\epsilon}{2} .$$

In this case the intensity is a maximum for wavelengths at which the sapphire is a full-wave plate. The maxima of transmittance give the transmittance of the sapphire. If the light incident on the sapphire is not completely polarized, the minima are not of zero intensity.

The troughs of the transmittance for the 90°-cut sapphire match the transmittance of the 0°-cut sapphire. This shows that the polarizing and analyzing actions of the Cary 14 are crossed in the near infrared. Rotation of the 90°-cut disk about the light beam of the Cary 14 to bring a privileged direction into coincidence with the plane of vibration of the polarized light of the instrument removes the fringes. This allows measurement of the transmittance of the sapphire. The transmittance of the 45°- and 60°-cut sapphire disks gives the transmittance of sapphire if the privileged directions are brought into coincidence with the plane of vibration of the incident polarized light.

Figure 15 shows the variation of the transmittance at 1.27 μ as a function of the angle between the optic axis and the plane of vibration of the partially polarized light. Since the polarizing and analyzing actions of the Cary 14 are crossed, the applicable expression for the intensity is

$$I = a^2 \sin^2 2\beta \sin^2 \frac{\epsilon}{2} + \text{constant} .$$

Since ϵ is now a constant, the intensity varies upon rotation of the disk as $\sin^2 2\beta$. The minima are not of zero intensity because the light in the instrument is not completely polarized. The expected four minima and four maxima for a complete revolution of the disk about the light beam show clearly in Fig. 15.

CONCLUSIONS

Rapid changes in polarization with wavelength occur at approximately the same wavelength in all three instruments. The degree of polarization at any given wavelength varies from instrument to instrument. The inherent polarization of the instruments causes the measured transmittance of sapphire to depend upon the orientation of the c-axis of the crystal. Fringes caused by polarization effects may be eliminated by proper orientation of the sapphire specimens thus allowing the transmittance of the specimens to be measured.

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13. ABSTRACT

In our laboratory Cary Model 14 instruments are used to measure the transmittance of optical components. These instruments have been found to have polarization characteristics that affect the transmittance values of anisotropic or dichroic materials. A study was made to determine the extent of polarization in the instruments and its variation with wavelength. Type HNP'B, HN22, and HR Polaroid polarizers and Polacoat polarizing filters, formula 105 UV, were used to cover the wavelength range from 0.2 to 2.5 µ. A Bausch and Lomb 90-8 hot mirror was used to protect the HR Polaroid polarizers. Data points were obtained every 10, 20, or 50 Å using a Datex digital system. In the ultraviolet the degree of polarization is fairly constant from 3000 to 4000 Å. In the visible the degree of polarization shows some variation with wavelength. In the near infrared the variation of the degree of polarization with wavelength is large, showing sharply defined maxima at approximately 0.77, 0.97, and 1.27 µ. These wavelengths correspond to the calculated positions of the Wood anomalies. The spectral transmittance of optical quality sapphire, a uniaxial crystal, cut at 45°, 60°, and 90° to the c-axis, showed undulations for certain orientations of the privileged directions.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Polarization Spectrophotometer Transmittance of anisotropic materials						

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