OPTICAL PROPERTIES OF SOME METALLIC SULFIDES.

By E. P. T. Tyndall.

Abstract.

Optical constants of molybdenite (MoS_2) and stibnite (Sb_2S_3) in the visible region, 420 mμ to 740 mμ.—*The reflectivity* of a cleavage surface at 20° incidence was found to range from 0.35 to 0.60 (Figs. 2 and 3). At 45° incidence, the values are the same for MoS_2, but slightly less for Sb_2S_3. When cooled to about − 160° C., MoS_2 shows the selective bands enhanced and shifted toward the violet (Fig. 6), while Sb_2S_3 showed no change. *Transmission of two thin specimens of MoS_2*, 6.3 and 9.6 μ thick, increases rapidly as the infra-red is approached (Fig. 7). From these measurements the extinction modulus $n\kappa$ is computed. Cooling by liquid air was found to shift the transmission curve about 40 $m\mu$ toward the violet. *Indices of refraction and of extinction* were determined by allowing plane polarized light of azimuth 135° to fall on the crystal surface and analyzing the elliptically polarized light reflected. The method and apparatus are described in detail. For MoS_2, n and κ were obtained for light in the direction of the optic axis (Fig. 12). Anomalous dispersion is shown, n having a maximum value at 620 $m\mu$ (5.3) and minima at 595 and 655 $m\mu$. The extinction index lies between 0.2 and 0.4, with two maxima indicating selective absorption bands at 603 and 665 $m\mu$. For Sb_2S_3, two principal indices were obtained for light incident normal to the cleavage plane. Both refractive indices reach maximum values at 510 $m\mu$ (5.5 and 4.8), while both extinction indices increase steadily with decreasing wave-length. Reflectivities computed from these values of n and κ agree in general with those observed directly, but are somewhat higher throughout the middle of the spectrum. In the case of MoS_2 no variation of the optical properties with the age of the surface was observed, but with Sb_2S_3, fresh cleavage surfaces were used as the surface soon changed after exposure to the air. The metallic luster of these sulfides is due to the high refraction, the absorption being considerably lower than for metals.

Reflectivity of cleavage surfaces of pyrite (FeS_2) and of galena (PbS) in the visible region, 420 mμ to 740 mμ, was measured for an incidence of 20 °(Figs. 4 and 5). For 45° incidence, pyrite gives slightly lower values. Cooling with liquid air did not change the results for pyrite; galena was not tried.

CERTAIN of the metallic sulfides in the natural mineral state have very interesting optical properties. These have been studied by Koenigsberger and Reichenheim,[1] Coblentz,[2] Crandall,[3] and Coblentz and Kahler,[4] working in the infra-red region, and by Horn,[5] Drude,[6] and

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[1] J. Koenigsberger, Phys. Zeits., 4, p. 495, 1902–03. J. Koenigsberger and O. Reichenheim, Centralblatt f. Min., p. 454, 1905.

[2] Coblentz, Pub. 65, Carn. Inst., p. 91. Pub. 97, Carn. Inst., pp. 13, 41.

[3] Crandall, Phys. Rev. (2), 2, p. 343.

[4] Coblentz and Kahler, B. S. Sci. Pap. No. 338.

[5] Horn, N. Jahrb. f. Min. Geol. u. Pal. Beil., Bd. 12, p. 269, 1898–99.

[6] D.ude, Ann. d. Phys. u. Chem., 34, p. 489, 1888.

Müller[1] in the visible region of the spectrum. The work in the infra-red has consisted of determinations of spectral reflectivity, spectral transmission, and, in some cases, of the index of refraction from the spacing of the interference bands formed when light is transmitted or reflected by a thin film. In the visible region measurements have been made of the index of refraction and extinction index by studying the nature of the elliptically polarized light reflected from the surface of the crystal when the incident light is plane polarized. These will be referred to in detail later.

The work reported here consists mainly of determinations of the spectral reflectivities and of the indices of refraction and extinction indices of stibnite (Sb_2S_3) and molybdenite (MoS_2). Spectral reflectivities, however, were also obtained for galena (PbS) and pyrite (FeS_2). Previous work has shown that both stibnite and molybdenite have a high index of refraction, high reflectivity, great transparence in the infra-red, and an almost metallic absorption in the visible region of the spectrum. The regular spectral reflection was studied first.

1. Reflection at Room Temperature.

A Lummer-Brodhun spectrophotometer with contrast field was used. The wave-length calibration was made in the usual way with known spectral lines and, for the far red, Hartmann's[2] dispersion formula was used as a check. The arrangement of the apparatus is shown in Fig. 1(*a*).[3] A gas-filled tungsten lamp, *L*, served as a source for both collimators. By means of the lens, *ll′*, light was concentrated on the ground glass screen, *GG′*, in front of the variable slit, *S*. Lens *LL′* served to concentrate the light on the magnesium carbonate block, *BB′*. Either the standard mirror or the specimen being studied was placed at *MM′*. The standard was a small piece of silver-backed plate glass mirror. Its reflectivity was determined in absolute measure by comparison with a freshly prepared, chemically deposited silver surface. The values of the reflectivity of the latter as given in the Smithsonian Physical Tables[4] were assumed.

A determination of reflectivity was made by placing the standard mirror at *MM′*, Fig. 1(*a*), and observing the width of the variable slit, *S*, for a match at each wave-length setting. The standard was then replaced by the specimen and the observations repeated at the same

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[1] Müller, N. Jahrb. f. Min. Geol. u. Pal. Beil., Bd. 17, p. 187, 1903.

[2] J. Hartmann, Astrophys. Jour., 8, p. 218, 1898.

[3] The photometric cube, dispersing prism, and observing telescope are not shown in the figure, but had the usual position relative to the collimators shown.

[4] Smith. Phys. Tab., p. 288 (1920).

wave-lengths, slit S' being kept at 0.2 mm. The ratio of the reflectivity of the specimen to that of the standard was then given by the ratio[1] of the slit-widths in the second case to those in the first. The absolute reflectivity of the specimen was then computed. The use of a variable slit has little to recommend it except convenience of operation and ease of making computations. Its reliability here was checked by transmission measurements made with another Lummer-Brodhun spectrophotometer, for which the variable slit method was known to hold, and with an infra-red spectrophotometer,[2] which used relative galvanometer deflections.

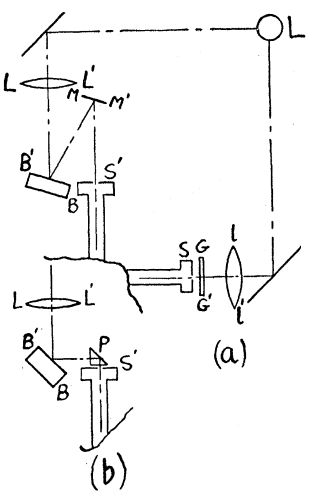

Fig. 1.
Arrangement of apparatus for measuring spectral reflectivity (*a*) at 20° incidence, (*b*) at 45° incidence.

An observer looking through the ocular slit and through the slit S' sees the surface of the carbonate block as imaged in the mirror MM'. In order to secure proper adjustment, that is, to see always the same part of the block in the field, a black, opaque diaphragm, pierced with a small hole, was placed in front of the carbonate. The mirror, MM', was then adjusted until the small spot of light was seen in the center of the field. This adjustment was made at the beginning of every determination, the diaphragm being removed while readings were being taken and then swung back into place at the end of the determination, to make sure that no shift had occurred. The diaphragm was left in place while changing from the standard to the specimen. For specimens which departed considerably from plane surfaces the spot of light, seen through the diaphragm, was irregularly shaped and somewhat spread over the field. It still seemed, however, to locate the best position of MM'. The field, when the diaphragm was removed, was always filled and was quite uniform for the better specimens. Check readings were taken at 550 and 600 mμ with LL' removed, in which case the illumination of BB' was uniform. The angle of incidence was about 20°, which was as

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[1] Actually 0.02 mm. was subtracted from each slit-width before the ratio was computed. See Nichols and Merritt, Phys. Rev., 31, p. 502, 1910; and Karrer and Tyndall, B. S. Sci. Pap. No. 389, pp. 380–382.

[2] The transmission of an amber glass was measured by Dr. J. R. Collins on the infra-red set-up and by the writer on the Lummer-Brodhun instrument, covering the spectral region 720–530 mμ.

near to perpendicular incidence as the arrangement of apparatus would permit.

For measurement of reflection at 45° incidence a small right angle glass prism, *P*, Fig. 1(*b*), was used as a standard. The readings on the specimen were made with it in the position formerly occupied by the hypothenuse face of the prism. The pierced diaphragm was used as before for adjustment. The prism was assumed to have a reflectivity of 0.92 throughout the spectrum. This method was especially convenient for carrying the readings to the extreme red and blue since the light could then be very considerably concentrated on *BB′*.

Molybdenite.—Determinations were made on two specimens of molybdenite, both of which were obtained from Dr. Coblentz, of the Bureau of Standards. Specimen *A* was a thin, flat lamina stuck on plate glass. It had an excellent, plane, mirror-like surface, which must have been at least a year old at the time these measurements were taken. Specimen *B* had a freshly prepared surface, made by splitting some of the material with a razor. It was not so nearly plane as *A*, but the method of making the reflection measurements made this unessential. Each specimen had, of course, a natural cleavage surface, which in this mineral is probably perpendicular[1] to the optic axis. In Curve *A*, Fig. 2, is plotted the average of six determinations from 710–440 mμ, three of these being on specimen *A* at 20° incidence, two on specimen *B* at 20° incidence, and one on specimen *B* at 45° incidence, and the average of three determinations on specimen *A* at 45° incidence covering the spectral regions 690–740 mμ and 480–420 mμ. The agreement between all these different

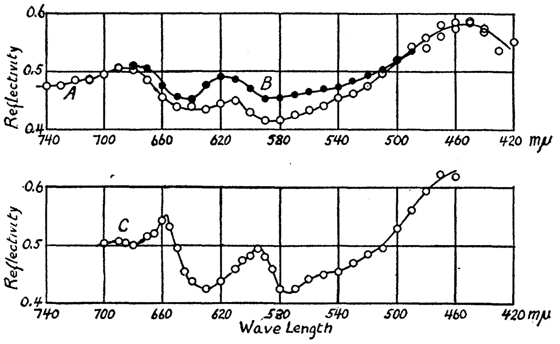

Fig. 2.

Molybdenite: Curve *A*, observed reflectivity room temperature, 20° and 45° incidence; Curve *B*, reflectivity computed from *n* and κ for perpendicular incidence; Curve *C*, observed reflectivity of specimen placed over liquid air, 20° incidence.

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[1] Crandall, loc. cit., pp. 355–6.

determinations was well within experimental errors. It must be noticed that the old surface had the same reflectivity as the new and that there was no appreciable change between reflectivity at 20° and 45° incidence.

Stibnite.—Several samples of Japanese stibnite were very kindly given the writer by Dr. Coblentz. This mineral may be split readily and the natural cleavage surface is almost plane and highly polished. Two specimens were used. Specimen *A* had been split some time before the readings were taken. Specimen *B* was prepared just before the first determination and showed no appreciable change in reflectivity during the period covered by the determinations. Two determinations were made on specimen *B* at 20° incidence. These are plotted in Fig. 3, Curve *A*. One determination of the reflectivity of specimen *B* at 45° incidence was made, covering the region 710–450 mμ, and one covering the regions 680–740 and 500–420 mμ. These are shown by Curve *B*, Fig. 3. The reflectivity at 45° incidence differs slightly from that at 20° incidence. The results for specimen *A* are not given as its reflectivity at 20° incidence was considerably below that for the fresh surface of specimen *B*. Previous work[1] has shown that a stibnite surface alters soon after cleavage. This will be referred to again later.

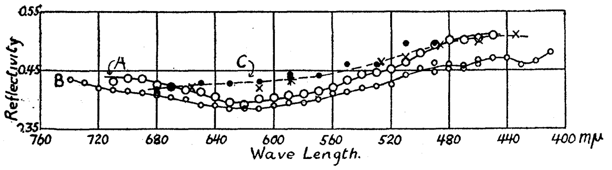

Fig. 3.

Stibnite: Curve *A*, observed reflectivity, 20° incidence; Curve *B*, observed reflectivity, 45° incidence; Curve *C*, reflectivity computed from n_1, κ_1 and n_2, κ_2, ● from writer's values, × from Müller's values.

Galena.—Determinations were made on two specimens, *A* having an old surface, while *B* was split just before making the determination. The results of one determination on specimen *B* at 20° incidence are shown by Curve *A*, Fig. 4. The reflectivity computed from Horn's[2] and Drude's[3] values of the refractive index and extinction index are plotted as solid circles in Fig. 4. This material does not split with a very smooth surface so that the photometric field was rather poor. No determinations were made at 45° incidence. The determinations on specimen *A* are not plotted since the reflectivity was low, this mineral having also undergone a surface change of some kind.

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[1] Drude, loc. cit.

[2] Horn, loc. cit.

[3] Drude, Ann. d. Phys., 36, p. 532, 1889.

Pyrite.—Determinations were made on the reflectivity of one sample of pyrite, which was loaned by Dr. Coblentz. It was in the shape of a parallelopiped with one plane face about 5 x 10 mm. which was used for the observations. No freshly split surface was available, but the surface used was lightly polished with a chamois before using. The results for 20° and 45° incidence are shown in Fig. 5. Curve A is the average of two determinations at 20° incidence and B of three determinations at 45° incidence.

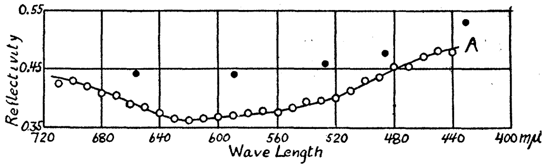

Fig. 4.

Galena: Curve A, observed reflectivity; ● reflectivity computed from n and κ of Horn and Drude.

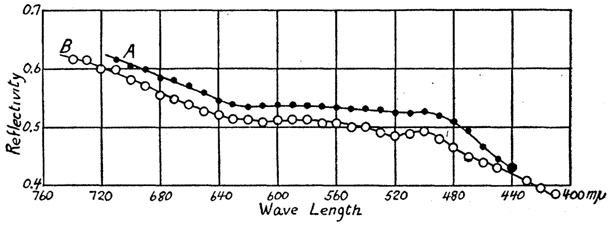

Fig. 5.

Observed reflectivity of pyrite: Curve A, 20° incidence, Curve B, 45° incidence.

2. REFLECTIVITY OF MOLYBDENITE AT LOW TEMPERATURES.

Previous observers[1] have found that the absorption coefficient, index of refraction, and photo-conductivity effect all change for molybdenite at low temperatures. It seemed likely, therefore, that there would be a change in the reflectivity also. To test this a specimen of molybdenite was placed in the position MM', Fig. 1(a), in a clear glass Dewar flask. Readings were taken of the width of slit S throughout the spectrum; then these readings were repeated after liquid air had been poured into the flask, and again repeated after the air had evaporated and the specimen had returned to room temperature. In this manner the reflectivity at low temperatures was compared with that at room temperature, so that the absolute reflectivity for low temperatures could be determined. In Fig. 2, Curve C, is shown the result of one determination, the temperature having been measured, in this case, by means of a thermo-couple

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[1] Crandall, loc. cit. Coblentz and Kahler, loc. cit.

placed adjacent to the specimen. Liquid air was introduced into the Dewar from time to time by means of a paper funnel. The temperature varied from − 155° C. to − 170° C. Several sets of readings were taken at each wave-length setting and at 550 mμ a number of sets were taken, as this served as a sort of a check point and readings were always taken at this point after every five or six sets of readings at other wave-lengths. Several other such determinations were made, all of which were in substantial agreement with this one. In Fig. 6 is plotted a curve of the observed widths of slit *S*, readings being taken at intervals as the specimen warmed up. The approximate temperature is shown on each curve. This shows the shifting of the bands with changing temperature.

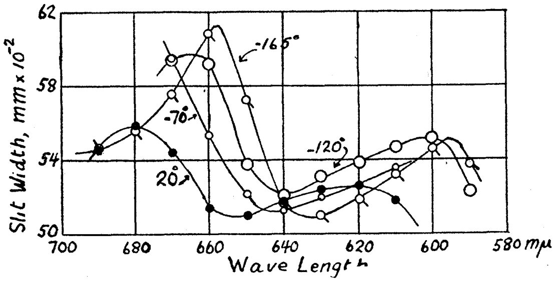

Fig. 6.
Molybdenite: Width of variable slit, *S*, at various temperatures.

Stibnite and pyrite showed no appreciable change in reflectivity at low temperatures. Galena was not tried.

3. Transmission of Molybdenite.

The spectral transmissions of two thin specimens (from Coblentz) were determined in the red end of the spectrum. To obtain readings to as long a wave-length as 780 mμ it was necessary to rearrange the apparatus somewhat. An image of the lamp filament was focused on the slit, *S′*, and the light was concentrated as much as possible on the ground glass in front of slit *S*. The specimen was placed directly in front of slit *S′*, and since its transmission was in general small it was necessary to use rotating sectored discs of known transmission in front of slit *S*. For the readings with the specimen removed a sector was placed in front of *S′*. Color screens were used in front of the ocular slit to exclude stray light. The thickness of each specimen was measured roughly by pressing it between a cover glass and a piece of plate glass with a spherometer. No. 2 was 9.6 μ and No. 1, 6.3 μ thick. From the difference in thickness and the measured transmission of each specimen it is possible to compute the extinction modulus, $n\kappa$, for this substance. The extinction index may be defined as follows:

$$\kappa = \frac{\lambda}{4\pi d} \log_e \frac{J_1}{J_2},$$

where λ is the wave-length in the material and d is the thickness of material through which the light must pass in order that its intensity may change from J_1 to J_2. The extinction modulus is given by:

$$n\kappa = \frac{\lambda_0}{4\pi d} \log_e \frac{J_1}{J_2},$$

where n is the index of refraction and λ_0 is the wave-length in vacuo. The transmissions of the two specimens are shown by Curves *A* and *B*, Fig. 7. The points indicated by crosses (+) were obtained by Dr. J. R. Collins with an infra-red spectrophotometer. Curve *C*, Fig. 7, shows the transmission of the thinner of the two specimens, No. 1, when placed just above liquid air in a Dewar flask. Curve *D*, Fig. 7, is a plot of the extinction modulus, $n\kappa$, at room temperature, computed from the transmission values as indicated above. The points indicated by ×'s were computed from the transmission measurements made by Dr. Collins.

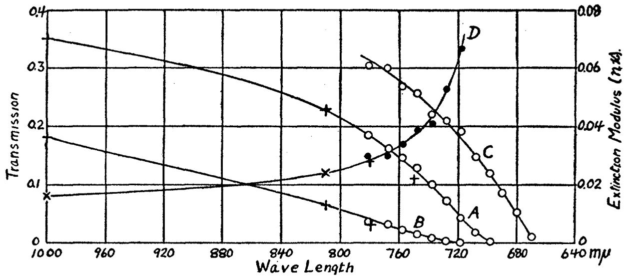

Fig. 7.

Molybdenite: Curve *A*, transmission of specimen No. 1, 6.3 μ thick; Curve *B*, transmission of specimen No. 2, 9.6 μ thick; Curve *C*, transmission of specimen No. 1 placed over liquid air; Curve *D*, computed extinction modulus, $n\kappa$.

4. Determination of n and κ for Molybdenite and Stibnite.

Plane polarized light is in general converted to elliptically polarized light by reflection at a metallic surface. That this is also the case with absorbing crystals has been shown by Drude[1] theoretically and by Horn,[2] Drude,[3] Müller,[4] and others experimentally. If the elliptic vibration is

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[1] Drude, Ann. d. Phys. u. Chem., 32, p. 584, 1887.

[2] Horn, loc. cit.

[3] Drude, Ann. d. Phys. u. Chem., 34, p. 489, 1888.

[4] Müller, loc. cit.

resolved into two components, parallel and perpendicular to the plane of incidence, it is possible to compute the optical constants of the reflecting material in terms of the amplitude ratio and relative phase difference of these two components. For analysis of the elliptically polarized light a Universal Polarimeter was used. This instrument is a modification of the Stokes' analyzer and was devised by Tool.[1] The particular instrument used here is the property of the Bureau of Standards and was very kindly loaned the writer by Dr. C. A. Skinner. It differed from the instrument described by Tool only in having the rotation of the half-shade system read on a fixed circle, instead of relative to the compensator. The set-up is shown diagrammatically in Fig. 8. *C* is the collimator of a Hilger constant deviation spectroscope used as a monochromator. In train with this instrument was placed a large spectrometer in front of whose collimating lens was a nicol prism, *N*. This nicol was adjusted by M'Connel's[2] method so that the incident light vector (electric) made an angle of 135°, counterclockwise, with the incident plane for an observer looking towards the source. The specimen, *ss'*, was mounted over the center of the prism table. The polarimeter was mounted on the other arm of the spectrometer. *cc'* is the mica compensator; *h*, the mica half-shade; and *N'*, the split nicol. The observing telescope, *C''*, could be focused either on the half-shade and nicol dividing lines or else on the image of the first slit on the monochromator. The positions of the compensator and half-shade could be read on two attached circles. Only two complementary[3] settings out of the four possible settings of the compensator were used. These two compensator readings are denoted by C' and C, and the corresponding half-shade settings by N' and N. c and n are defined from the following: $C' - C = c$ and $N' - N = c - n$. To obtain the effective order of the half-shade, observations were made with plane polarized light, collimator C' and telescope C'' being in line. Tuckerman[4] has shown that in this case:

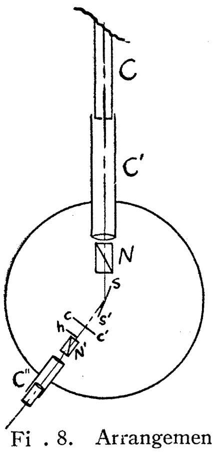

Fig. 8. Arrangement of apparatus for study of elliptically polarized light reflected from a crystal surface.

$$\tan 2\eta = \frac{\sin (n - c) \sin (n + c)}{\sin c},$$

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[1] Tool, Phys. Rev. (1), 31, p. 1, 1910. Tuckerman, Univ. Neb. Studies (9), pp. 194–203, 1909.

[2] M'Connel, Phil. Mag. (5), 19, p.317, 1885.

[3] Tool, loc. cit., footnote, p. 11.

[4] Tuckerman, loc. cit., p. 198, equ. (76).

where 2η is the average effective order of the half-shade. This varied from 1° 10′ at 680 mμ to 1° 35′ at 490 mμ. The method is rather inaccurate but serves well enough since only $\cos 2\eta$ enters into the computation of the elliptic vibration to be analyzed. From this calibration the average sums of the N readings and of the C readings with plane polarized light were also obtained. These quantities, $N_p' + N_p$ and $C_p' + C_p$, were required later to determine γ, the azimuth with respect to the incident vibration of the major axis of the elliptic vibration.

The method of computing the amplitude ratio and phase difference from the polarimeter readings may be understood by referring to Fig. 9. The x and y axes are chosen in and perpendicular to the plane of incidence, respectively, and perpendicular to the direction of propagation of the light, the positive x axis being horizontal and towards the observer's right. The ellipse to be analyzed has major axis $2a$ and minor axis $2b$, the former making an angle, γ, with the incident vibration,[1] OD (electric vector), and an angle, α, with the incident plane. B is the amplitude of the component y vibration and A of the x vibration. ω is defined as $\tan^{-1} b/a$ and θ' is defined as $\tan^{-1} B/A$. δ is the relative phase difference between the x and y components. Then the following relations hold true:

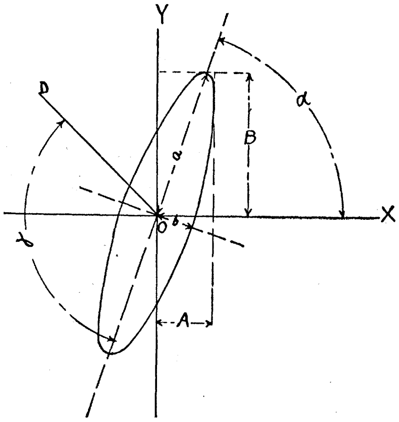

Fig. 9.
Typical elliptic vibration.

$$2\gamma = (N' + N) - (N_p' + N_p) = (C' + C) - (C_p' + C_p),$$ [2]

$$2\alpha = 2\gamma - 90°,$$ [2]

$$\cos 2\omega = \frac{\sin n}{\sin c} \cos 2\eta.$$ [3]

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[1] γ is really the angle between the major axis of the ellipse and the electric vector of a plane polarized vibration which would give the same N and C readings with the polarimeter in position for observations on the crystal that were given when the polarimeter was in line with the collimator, the observations actually being made on the incident vibration.

[2] Tool, loc. cit., p. 11.

[3] This formula, which is more exact than the infinite series for determining the ellipticity given by Tuckerman (loc. cit., equations 82 and 83, p. 201), has been deduced by him since the publication of the above. The writer believes that this deduction has not been published yet. The formula was given the writer by Dr. Tool.

$$\cos 2\theta' = \cos 2\omega \cos 2\alpha,^{1}$$

$$\sin \delta = \pm \frac{\sin 2\omega}{\sin 2\theta'}.^{2}$$

To show more fully the method of computation a sample computation is given in Table I.

TABLE I.

Typical Computation to Obtain Amplitude Ratio and Relative Phase Difference.
Molybdenite. $\lambda = 589.3$ mμ. Angle of Incidence = 76°.

Constants.	Polarimeter Readings.
$\log \cos 2\eta = 9.99987$	$N' = 283.23°$
$N_p' + N_p = 297.31°$	$N = 270.36°$
$C_p' + C_p = 195.21°$	$C' = 89.50°$
	$C = 362.08°$

Whence:

$$2\gamma = N' + N - (N_p' + N_p) = 553.59 - 297.31 = 256.28$$
$$2\gamma = C' + C - (C_p' + C_p) = 451.58 - 195.21 = 256.37$$
$$\text{Average,} \quad 256.32°$$

$$2\alpha = 2\gamma - 90° = 166.32 = 166°\ 19'$$
$$N' - N = c - n = 12.87°$$
$$C' - C = c = -272.58°$$
$$n = -285.43°$$

$$\frac{\sin n}{\sin c} \cos 2\eta = \cos 2\omega \qquad 2\omega = 15°\ 18'$$

$$\tan \theta' = \frac{B}{A} \qquad \cos 2\theta' = \cos 2\omega \cos 2\alpha$$

$$\cos 2\theta' = \cos (15°\ 18') \cos (166°\ 19')$$
$$\cos 2\theta' = -\cos (20°\ 25')$$
$$2\theta' = 159°\ 35'$$
$$2\theta = 180° - 2\theta' = 20°\ 25'$$
$$\tan \theta = \rho = 0.180$$

$$\sin \delta = + \frac{\sin 2\omega}{\sin 2\theta'} = \frac{\sin 15°\ 18'}{\sin 159°\ 35'}$$

Therefore

$$\delta = 49°\ 9'$$
$$\Delta = \pi - \delta = \pi - (49°\ 9').$$

Both Drude and Müller[3] have given in full detail the necessary formulæ for computing the optical constants of absorbing, rhombic crystals from the amplitude ratio and phase difference of the two component vibrations

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[1] Müller u. Pouillet, Lehrb. d. Phys., II., p. 887, equ. 10.

[2] Müller u. Pouillet, Lehrb. d. Phys., II., p. 887, equ. 9.

[3] The general relations for absorbing crystals are developed by Drude (Ann. d. Phys. u. Chem., 32, p. 584, 1887) and applied to stibnite specifically (Ann. d. Phys. u. Chem., 34, p. 489, 1888). Müller gives (loc. cit.) a good summary of Drude's methods and results.

in and perpendicular to the plane of incidence, respectively. These will be summarized here. Referring again to Fig. 9,

$$A/B = \rho = \tan \theta, \qquad \text{where} \qquad \theta = \frac{\pi}{2} - \theta'.$$

Let $\Delta = \pi - \delta$.[1] Then $r = \rho e^{i\Delta}$, where $i = \sqrt{-1}$.

$$R = \frac{1 + r}{1 - r} = x + iy.$$

Then

$$x = \frac{\cos 2\theta}{1 - \sin 2\theta \cos \Delta} \qquad \text{and} \qquad y = \frac{\sin 2\theta \sin \Delta}{1 - \sin 2\theta \cos \Delta}.$$

Drude's theory introduces three complex constants, α, β, and γ, in the direction of the vertical, brachy, and macro axes, respectively. These three constants may be interpreted on the basis of the electromagnetic theory as follows:[2]

$$\alpha = \frac{c^2}{\eta_1}, \qquad \beta = \frac{c^2}{\eta_2}, \qquad \text{and} \qquad \gamma = \frac{c^2}{\eta_3},$$

c being the velocity of light in vacuo and η_1, η_2, η_3 being three complex constants analogous to the three principal dielectric constants in transparent crystals. For stibnite the three constants α, β and γ are different. As Drude has shown, α and β may be found to a first approximation if two sets of observations are made on the crystal, (1) with the vertical axis perpendicular to the plane of incidence and the brachy axis parallel to the plane of incidence, (2) with the vertical axis parallel to the plane of incidence and the brachy axis perpendicular to the plane of incidence. The macro axis is perpendicular to the plane of incidence in each case, since it is perpendicular to the cleavage surface. For these two positions the above quantities are given the subscripts 1 and 2, respectively. If φ is the angle of incidence we have:

$$R_1 + R_2 = (\sqrt{\alpha} + \sqrt{\beta}) \frac{\sin^2 \varphi}{\cos \varphi}$$

and

$$R_1 - R_2 = (\sqrt{\beta} - \sqrt{\alpha}) \frac{1 + \cos^2 \varphi}{\cos \varphi}.$$

If we set

$$\sqrt{\alpha} + \sqrt{\beta} = A + iB = \frac{\cos \varphi}{\sin^2 \varphi} [(x_1 + x_2) + i(y_1 + y_2)]$$

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[1] Drude's formulæ are developed for an incident vibration of azimuth 45°. To develop the results by means of his formulæ it is necessary to use $\Delta = \pi - \delta$. Müller also does this for his results where the azimuth of the incident vibration was not 45°.

[2] Winkelmann, Handb. d. Phys., Vol. 6, p. 1286, or Drude, Theory of Optics (tr. by Mann and Millikan), p. 369, equ. 31, where $a_0^2 = \alpha$, $b_0^2 = \beta$, $c_0^2 = \gamma$.

and

$$\sqrt{\beta} - \sqrt{\alpha} = C + iD = \frac{\cos\varphi}{1 + \cos^2\varphi}[(x_1 - x_2) + i(y_1 - y_2)],$$

then

$$\beta = b + ib' = \frac{(A + C)^2 - (B + D)^2}{4} + \tfrac{1}{2}i(A + C)(B + D),$$

$$\alpha = a + ia' = \frac{(A - C)^2 - (B - D)^2}{4} + \tfrac{1}{2}i(A - C)(B - D).$$

Light incident perpendicularly on the cleavage surface is broken into two waves, traveling in the direction of the macro axis in the crystal, the waves being plane polarized with their planes of polarization mutually perpendicular. Associated with each of these waves is an index of refraction and extinction index. n_1 and κ_1 are obtained from α and n_2 and κ_2 from β, either Drude's or Müller's formulæ being applicable, though the latter are somewhat more convenient for computation. Müller defines angles χ and ϵ such that

$$\tan\chi = \frac{a'}{a} \quad \text{and} \quad \tan\epsilon = \frac{b'}{b}\cdot$$

Then

$$\kappa_1 = \tan\frac{\chi}{2} \quad \text{and} \quad \kappa_2 = \tan\frac{\epsilon}{2},$$

$$n_1^2 = \frac{\sin 2\frac{\chi}{2}\cos^3\frac{\chi}{2}}{a'} \quad \text{and} \quad n_2^2 = \frac{2\sin\frac{\epsilon}{2}\cos^3\frac{\epsilon}{2}}{b'}\cdot$$

For molybdenite α and β were assumed equal[1] since the crystal axes in the cleavage plane are of the same length for this mineral. Only one value of the extinction index and index of refraction is found for molybdenite, namely, that corresponding to light propagated in the direction of the optic axis (*i.e.*, normal to the cleavage plane).

Stibnite.—The results of the observations on this mineral are shown in Table II. and by the curves in Fig. 10. The observations were made on a fresh cleavage surface for each of the two positions of the crystal, the last readings being taken not more than two hours after the crystal was split. Drude and Müller have both investigated the effect of a surface film which forms soon after the surface is exposed to air. Müller concludes that observations taken in the course of a day would be sufficiently accurate for computing the optical constants. In the table,

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[1] This is the case of a uniaxial crystal, the reflecting surface being perpendicular to the optic axis. See case I, Drude, Ann. d. Phys., 32, p. 618.

TABLE II.

Stibnite, Angle of Incidence = 74°.

Wave-length.	$\alpha = a + ia'$.		$\beta = b + ib'$.	
	a.	a'.	b.	b'.
680 mμ......	.0455	.00346	.0463	.00750
670	.0450	.00375	.0457	.00874
650	.0451	.00447	.0433	.0117
630	.0418	.00552	.0442	.0143
610	.0402	.00510	.0438	.0146
589.3	.0366	.00728	.0441	.0144
589.3	.0365	.00867	.0431	.0170
589.3	.0378	.01005	.0433	.0174
570	.0370	.0102	.0423	.0178
550	.0320	.0116	.0386	.0182
530	.0290	.0141	.0376	.0197
510	.0254	.0155	.0336	.0221
490	.0235	.0195	.0308	.0241
480	.0222	.0218	.0252	.0236

By E. C. Müller.

	a_{11}.	a_{12}.	a_{21}.	a_{22}.
656	.0451	.0049	.0480	.0117
610	.0409	.0086	.0501	.0183
589	.0365	.0092	.0472	.0183
527	.0285	.0141	.0406	.0218
510	.0253	.0170	.0386	.0241
486	.0202	.0195	.0350	.0273
460	.0164	.0242	.0312	.0310
434	.0116	.0295	.0274	.0348

however, one may note three sets of readings taken at wave-length 589.3 mμ. These were taken at the beginning, middle, and end of the determinations, respectively. While the values of neither of the indices of refraction are much affected by the changes in α and β, there is considerable change in the extinction indices. Only by using a fresh cleavage surface for each wave-length setting could this difficulty be obviated, and there was not available enough material to make this practicable. In Table II., also, Müller's values of α and β are quoted for comparison. The values of the indices of refraction and extinction indices are plotted in Fig. 10, Müller's points being shown by solid circles (●) and crossed circles (⊕). The agreement on the whole is good. The reflectivity of a substance may be computed from the usual formula

$$R = \frac{(n-1)^2 + \overline{n\kappa}^2}{(n+1)^2 + \overline{n\kappa}^2}.$$

This was done separately for the two values of n and κ. The mean of the two computed reflectivities should be the reflectivity for natural light. These mean values of the reflectivity at perpendicular incidence are plotted in Fig. 3, Curve C, for comparison with the directly observed reflectivity, values computed from Müller's values of the optical constants being indicated by ×'s.

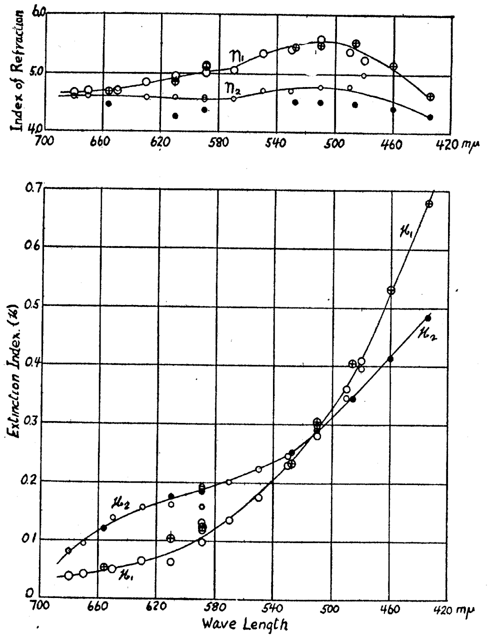

Fig. 10.
Refractive indices and extinction indices for stibnite; ● and ⊕, Müller's values.

Molybdenite.—Two determinations were made on molybdenite, one at 70° 10′ incidence and one at 76° incidence. The specimen used throughout was made by splitting one of the samples previously obtained from Dr. Coblentz. It showed no measurable change during the determinations. Some samples of Australian molybdenite obtained from R. M. Wilke, Palo Alto, Calif., on which a few readings were taken, seemed to have a somewhat higher extinction index but practically the same index of refraction. The molybdenite surface obtained by cleavage is not plane and the images of the slit seen in the telescope were spread more or less, although the field was quite uniform when the telescope was focused on the dividing lines. This made it rather difficult to set the specimen exactly at some particular angle of incidence. For this reason the specimen was set as well as possible at the desired angle and then left in position throughout any one determination. The agreement of the results taken at the two different angles of incidence shows that no considerable error could have arisen from this difficulty. The intensity of the light was also reduced considerably by the lack of a plane surface and it was therefore not possible to carry the readings very far towards the ends of the visible spectrum, although an arc light with its image focused on the slit of the monochromator was used as a source.

The results are shown in Table III. and Figs. 11 and 12. Fig. 11 is a plot of the values of ρ and δ for wave-length 589.3 mμ at different angles of incidence. The principal angle of incidence as read from the curve

Table III.

Molybdenite.

Wave-length.	$\varphi = 70° 10'$.		$\varphi = 76°$.		Average *a*.	Average *a'*.
	a.	*a'*.	*a*.	*a'*.		
680 mμ			.0269	.0093	.0269	.0093
670	.0270	.0136	.0273	.0155	.0272	.0145
660	.0311	.0171	.0309	.0184	.0315	.0179
660	.0319	.0178	.0320	.0185		
650	.0344	.0153	.0367	.0160	.0362	.0157
650	.0359	.0160	.0376	.0154		
640	.0353	.0140	.0351	.0145	.0352	.0143
630	.0320	.0132	.0328	.0141	.0324	.01365
620	.0289	.0143	.0306	.0157	.0294	.0152
620	.0294	.0151				
610	.0294	.0192	.0295	.0198	.0294	.01945
600	.0315	.0228	.0310	.0228	.0312	.0228
589.3	.0347	.0210	.0354	.0216	.0356	.0211
589.3	.0348	.0189				
589.3	.0359	.0209	.0362	.0214		
589.3	.0360	.0211				
589.3	.0353	.0211				
589.3	.0352	.0213				
589.3	.0348	.0209				
589.3	.0362	.0210				
580	.0356	.0190	.0356	.0201	.0356	.01955
570	.0346	.0173	.0353	.0194	.03495	.0184
560	.0339	.0178	.0339	.0181	.0339	.0179
550	.0333	.0167	.0330	.0179	.03315	.0173
540	.0318	.0165	.0324	.0175	.0321	.0170
530	.0301	.0164	.0308	.0174	.0305	.0170
530			.0309	.0178		
520	.0285	.0157	.0289	.0176	.0285	.0165
520	.0276	.0153	.0290	.0175		
510	.0267	.0162			.0267	.0162
500	.0230	.0163	.0241	.0170	.0235	.0166
490			.0208	.0181	.0207	.0181

is 78.6°. In Table III. are given the values of the constants *a* and *a'* from the two determinations already referred to. The readings at 589.3 mμ, which were taken at intervals throughout the two determinations, show how little change there is in the surface, quite unlike the change experienced by the stibnite. *n* and *κ* are plotted in Fig. 12, while in Fig. 2 the computed reflectivity is plotted (Curve *B*) for comparison with the observed.

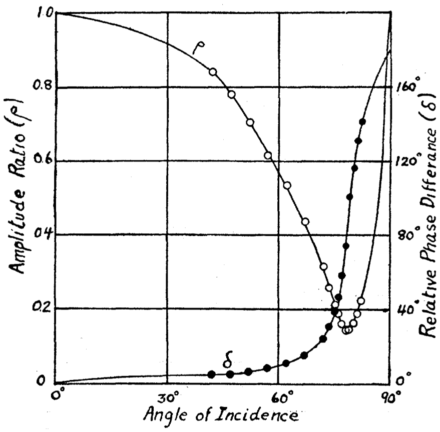

Fig. 11.
Molybdenite: Amplitude ratio (ρ) and phase difference (δ) of the two components of the elliptic vibration for various angles of incidence.

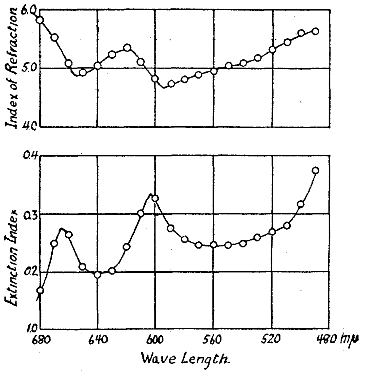

Fig. 12.
Refractive index and extinction index for molybdenite.

5. Discussion of Results.

The reflectivities of the four metallic sulfides are quite similar, being of the same order of magnitude, though the selectivity, on which the surface color depends, differs for pyrite from the other three, each of which has a maximum in the blue and in the red. The reflection measurements on stibnite and molybdenite reported here are in good agreement, where they overlap with the previous measurements made by Coblentz and Crandall, as reference to their work will show. The values of the extinction indices for stibnite agree well with the values obtained by Drude and Müller. For molybdenite one may compare the directly measured values of the extinction modulus, $n\kappa$, plotted in Fig. 7, with the values obtained by Crandall. At 0.8 μ Crandall gives $n\kappa = 3.9 \times 10^{-4}$ while at 0.81 μ the writer computes 2.4×10^{-2} from the measurements made by Dr. Collins. The difficulty here is probably in the measurement of thickness. Crandall states that two specimens of 4.2 μ and 34 μ thickness, respectively, have identical transmission; and the transmission of either of them (at 1.0 μ) is the same as a specimen 7.0 μ thick reported by Coblentz. The writer's 9.6 μ specimen has a slightly lower transmission (at 1.0 μ) than the three mentioned above, while his 6.3 μ specimen has a lower transmission than a 246 μ specimen also reported by Crandall. There is then no quantitative agreement though the general trend of the curves shows a rapidly decreasing absorption as one goes toward the infra-red. The writer's values of $n\kappa$ obtained by the polarized light measurements unfortunately could not be extended far enough to overlap with the directly measured quantities. The nearest approach is given by $n\kappa = 1.0$ at 680 mμ and $n\kappa = 0.067$ at 718.2 mμ. However, it is just in the region between these two points that the transmission seems to change most rapidly with wave-length.

The indices of refraction of stibnite may be compared with the values obtained by Drude and Müller. The agreement here is especially good for n_1 but not so good for n_2, which is rather hard to understand, since κ_1 and κ_2 agree well and the values of all four of these quantities are computed from the same experimental data. Very little new is brought out about the dispersion and absorption of stibnite that has not been already reported by Müller, though it seemed worth while to get the extra points to fill in his curves. The measurements on stibnite were also of value in testing out the instrument.

The index of refraction and absorption index of molybdenite, so far as the writer knows, have never been obtained before throughout the visible spectrum. In the curve for the latter there are two maxima, at about 600 mμ and 660 mμ. These correspond, as far as one can tell, with the two absorption bands observed by Crandall in a piece of molybdenite 1.0 μ thick. Molybdenite shows anomalous dispersion, the index of refraction having a maximum and two minima in the region measured. The change in the reflectivity at low temperatures is doubtless due mainly to a change in the index of refraction and only slightly to the change in absorption. The change in the index of refraction at low temperatures has been observed by Trowbridge in the neighborhood of 0.7 μ. However, all of his values, both at room temperature and liquid air temperature, seem too high, agreeing neither with Crandall's computations nor Coblentz's. For instance, he has at 0.7 μ an index of refraction of 11.00. Neglecting the effect of absorption this would give a reflectivity of 70 per cent. at liquid air temperature. No such high reflectivity in molybdenite has been found.

The change in the reflecting power of molybdenite at low temperatures, the writer believes, has not been reported on before. The shift of the bands is toward the shorter wave-lengths, which is the direction of shift for absorption bands and for the photo-conductivity effect.

Molybdenite and stibnite have been compared by various observers to metals in their properties. Possibly in their two most outstanding features, high reflectivity and great opacity, they are alike, but one should notice that the high reflectivity of both these crystals is due rather to a very high index of refraction than to great absorption. Indeed the latter is only of the order of one fourth the absorption for silver.

Coblentz and Kahler have observed the transformation of plane polarized light to elliptically polarized light by reflection at a molybdenite surface, and a stibnite surface using the spectral region 1.0 μ to 4.0 μ. This should of course be true for any absorbing crystal according to Drude's theory. The relation between incident angle and the amplitude ratio and phase difference for the light reflected by molybdenite, as shown by the curves of Fig. 11, is similar to the same quantities observed for stibnite by Drude. Since the reflected light is plane polarized at grazing and perpendicular incidence, the curves for ρ and δ have been completed. Both stibnite and molybdenite produce elliptically polarized light under the conditions used here, in which the light vector rotates clockwise for an observer looking toward the source.

In conclusion the writer wishes to express his thanks to Dr. Coblentz for the mineral samples, to Dr. Skinner for the loan of the instrument and to Dr. Tool for a set of instructions on the use and calibration of the instrument which proved invaluable. Acknowledgment is also made to Professor R. C. Gibbs for aid and helpful suggestions given during the course of the investigation.

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