

THE INFRA-RED OPTICAL PROPERTIES OF SOME
SULPHIDES: A BALANCED METHOD OF USING
THE BOLOMETER.

BY IRVING B. CRANDALL.

THE relation between the optical properties of compounds and their chemical properties has been investigated for a number of substances in the visible and ultra-violet regions of the spectrum. Certain organic compounds have also been experimented with in the infra-red spectrum in a systematic manner, but little has been done in this region with classes of inorganic compounds (including minerals) if we except the work of Nichols and his students on the reflection from salts of the alkaline earths,¹ of Clark on the reflection from chromates,² of Morse on the reflection from carbonates,³ of Rubens and Hollnagel on the reststrahlen from salts of the alkalis,⁴ and of Coblentz on the rôle of water in minerals.⁵ Perhaps the field seems unpromising on account of the difficulty of obtaining good pieces of the right dimensions of the solids in question, and polishing their surfaces.

Last year Prof. A. Trowbridge, noting the perfect cleavage in one direction of the minerals molybdenite and stibnite, was led to investigate the optical properties of thin layers of these substances. He used an infra-red spectrograph of moderate resolving power, and obtained approximate values for the extinction modulus $n\chi$ for the two substances. On observing the transmission of very thin cleavage layers of molybdenite there were found broad absorption bands, regularly spaced, beginning at wave-length 5 or 6 μ . The same piece exhibited bands close together in the very short region in the red end of the visible spectrum for which it was transparent. It was not known whether these bands were due to interference in the layer, or simply to ordinary absorption. The object of undertaking the present investigation was to repeat these measurements with apparatus of larger resolving power, and determine, if possible, the refractive indices. In addition, it was planned to experiment with other sulphides, and discover any common optical properties

¹ *Phys. Rev.*, XXVII., 1908, p. 225, and other papers.² *Astro. Jour.*, 35, 1912, p. 48.³ *Astro. Jour.*, 26, 1907, p. 225.⁴ *Sitz. Ber. Preuss. Akad. Wiss., Berlin*, 4, 1910, p. 26.⁵ *Jour. Fr. Inst.*, CLXXII., 1911, p. 309.

that might exist. The position and magnitude of the bands shown by molybdenite were to receive especial consideration, as, if they proved to be due to interference, a way might be found to determine the refractive index that did not depend on the reflecting power. The refractive indices of molybdenite and stibnite were known to be very high¹ so that they should be interesting substances from this point of view alone. Before going further, we may remark that the sulphides are, next to the halogen salts and oxides, the simplest class of binary metallic compounds, and ought to give easily interpreted results.²

A BALANCED METHOD OF USING THE BOLOMETER.

In the work to be hereinafter described the bolometer was used in a manner perhaps unusual, for comparing intensities of radiation in the infra-red spectrum; we therefore proceed to consider the method somewhat in detail.

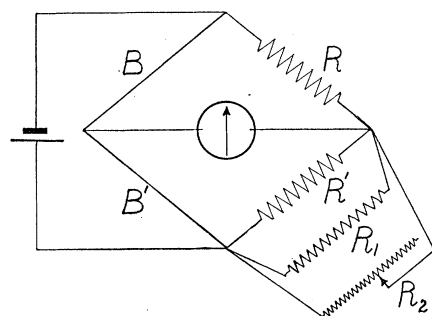


Fig. 1.

A linear bolometer of the usual form was constructed, the dimensions of the two strips forming two arms of the Wheatstone bridge being in width 0.5 mm. and in length 25 mm. These had a resistance of about 4 ohms each. The other two arms of the bridge were coils of manganin wire situated within the bolometer case, and having a resistance of 20 ohms each. The connections are as given in Fig. 1. A current of about 0.08 ampere traversed each arm of the bridge. The radiation is supposed to fall on the strip *B*.

¹ See later references.

² After this work had been completed and prepared for publication, it was found that an important paper dealing with this subject, by J. Koenigsberger and O. Reichenheim (Centralbl. f. Min., 1905, p. 454) had been overlooked. These authors investigated the absorbing powers and electrical conductivities of molybdenite, stibnite, pyrite, galena, and iron sulphide; their work on conductivity furnishes the only data available for these materials, and will be quoted later in the discussion of the present results. On absorption, however, since they did not use spectral dispersion, but only employed screens to obtain comparatively large ranges of radiation—the total radiation in a given region of the spectrum being measured—their results are only approximate. These will be compared with those obtained by the writer for the various materials. Koenigsberger and Reichenheim state that they were usually only able to use small pieces (4×4 mm. in area) of the minerals: in the present work much larger pieces of stibnite and molybdenite were used, and they were also of quite uniform thickness; it must be stated, however, that Koenigsberger and Reichenheim have results for pyrite, which the present author found quite difficult to handle, so that no results are offered here for this material.

The bridge would ordinarily be balanced for zero radiation by shunting one of the arms, say R' , with a more or less constant resistance R_1 , and then, the bolometer strip B being exposed to the radiation, the deflection of the galvanometer deflection taken as directly proportional to the energy received by the strip. The present method, however, consists in balancing the bridge again by adjusting the shunt, and converting readings obtained in this way into relative changes of resistance in B , due to the incident radiation. If we determine the relative changes in the resistance of the strip produced by different quantities of energy falling on it, we have accurately the ratio between the two quantities of energy, if we make the single assumption (fundamental for all bolometric work) that the change in the resistance of the strip is directly proportional to the quantity of energy falling on it. If B were equal to B' and R to R' within very narrow limits, then a resistance of several thousand ohms as R_1 would suffice to balance the bridge; furthermore, a change of 0.1 ohm in R_1 would probably be the smallest convenient amount which would be detected by a good galvanometer, say of 10 ohms resistance and a sensitiveness of 10^{-9} ampere per scale division at a meter distance. In the present case however the strips B and B' were hurriedly made, and only adjusted to within about 1.5 per cent. of each other, so that it became necessary to use R_1 for balancing the bridge for zero radiation, and to add the supplementary resistance R_2 for the purpose of making the adjustments used in measuring the radiation.

For the sake of completeness we give here the numerical calculations relating to a definite set of values for the various resistances used. Several combinations were tried, but the one which seemed best adapted to the sensitiveness of the galvanometer was the following:

$$\begin{aligned} B &= B' \pm 1.5 \text{ per cent.} = \text{ca. } 4 \text{ ohms,} \\ R &= R' = 20 \text{ ohms,} \\ R_1 &= 588 \text{ ohms,} \\ R_2 &= 4,800 \text{ ohms (variable by increments of 0.1).} \end{aligned}$$

Given different changes in R_2 corresponding to different values of the resistance of the arm of the bridge (or different quantities of energy falling on B) we desire the relation between them. If the total resistance of the arm is denoted by R , then

$$\frac{1}{R} = \frac{1}{R'} + \frac{1}{R_1} + \frac{1}{R_2} = \frac{R_1 + R'}{R_1 R'} + \frac{1}{R_2} = a + \frac{1}{R_2}, \quad (1)$$

where $a = (R_1 + R')/(R_1 R')$ is kept constant. Differentiating,

$$dR = \frac{dR_2}{(R_2 a + 1)^2}, \quad (2)$$

which shows at once that dR_2 is quite different for equal changes dR if we consider two changes dR which are the first and last increments in a total change of, say, $100dR$. We must therefore derive a convenient formula for correcting the observed readings dR_2 : one would naturally expect that an additive per cent. correction would be easiest to apply to dR_2 . Since dR_2 is now no longer an infinitesimal, but a considerable fraction of R_2 we must derive the formula rigorously from the beginning. Writing down (1) and increasing R and R_2 by dR and dR_2 respectively, we have

$$R = \frac{R_2}{1 + R_2 a}, \quad (3)$$

$$R + dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a}, \quad (4)$$

whence

$$dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a} - \frac{R_2}{1 + R_2 a}, \quad (5)$$

$$= \frac{dR_2}{(R_2 a + 1)^2 + adR_2(1 + aR_2)}, \quad (6)$$

for which we may write

$$dR = \frac{dR_2}{(R_2 a + 1)^2} (1 - x), \quad (7)$$

in which x denotes the required per cent. correction. Equating the right-hand members of (6) and (7), we find that

$$x = \frac{adR_2}{(1 + aR_2) + adR_2}. \quad (8)$$

As $|adR_2| < |1 + aR_2|$ we note that if dR_2 is negative, x is negative and therefore the correction is additive. To apply the correction, we first calculate

$$a = \frac{R_1 + R'}{R_1 R'} = \frac{1}{R'} \left(1 + \frac{R'}{R_1} \right).$$

Since a is approximately $1/R'$, or $1/20$, x is very nearly independent of a , and this approximate value of a is quite good enough to use in computing x . If we compute x as a function of dR_2 we have the following values which are plotted in Fig. 2.

$$\frac{1}{a} = R' = 20 \text{ ohms. } R_1 = 588 \text{ ohms. } R_2 = 4,800 \text{ ohms.}$$

dR_2	$-x = \frac{-dR_2}{R' + R_2 + dR_2}$
- 100 ohms	+0.021
- 400	0.091
- 800	0.199
-1200	0.331

We can easily read from the curve the proper correction to apply to a given reading; *e. g.*, if dR_2 is 1,200 ohms we add 33 per cent. or multiply by 1.33 to obtain a number directly proportional to the change in resistance of an arm of the bridge. Assuming that the change in resistance is directly proportional to the energy falling on the strip, we then have a number directly proportional to this quantity of energy. Note in passing that, in case R_2 shunted an adjacent arm of the bridge and had to be increased, the correction would be a negative one, and relatively decreasing with increasing dR_2 , *i. e.*, concave to the right instead of to the left.

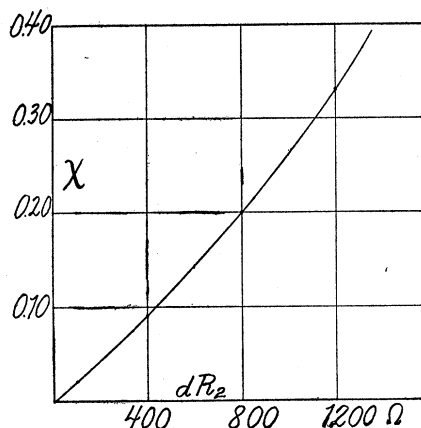


Fig. 2.

The following points in favor of this method of using the bolometer may be noted:

It does not assume that the current through the galvanometer is directly proportional to the change in the resistance of one of the bridge arms.

It is independent of changes in the sensitiveness of the galvanometer, and also of the position of the galvanometer zero, if this varies.

In passing through parts of the spectrum rich in energy, there is no abrupt change in the sensitiveness of the apparatus to radiation, as there would be if successive shunts or series resistances had to be thrown into the galvanometer circuit. In fact the double uncertainty of non-linear galvanometer scale and inaccurate shunts was what led the writer to try this balanced method. The non-linear scale, in particular, is a great disadvantage, which can scarcely be avoided as long as we have to use for measuring radiation galvanometers with small suspended system turning through relatively large angles. For these reasons this method should be peculiarly adaptable to running energy-spectrum curves.

Under favorable conditions as to steadiness of bolometer (using a very tightly enclosed vacuum-bolometer) one could easily read the energy at the maximum of an energy curve to one ten-thousandth part of itself. This condition was realized by the present writer, in the following measurements, as far as quantity of energy and sensitiveness was concerned, but not with regard to steadiness, as the bolometer was air enclosed, and,

in passing through the spectrum, the zero (that is, the value of R_2 necessary to balance for no radiation falling on the strip) was not determined after each reading, but only at intervals over the whole range. It takes time and patience to balance the bridge, but when accurate results are desired, it seems that this method may be valuable, although where the energy curve is flat and the quantity of energy relatively small (say for $\lambda > 10\mu$) it must be said that the deflection method yields about as accurate, and rather more easily obtained results.

ARRANGEMENT AND ADJUSTMENT OF THE OPTICAL APPARATUS.

The infra-red dispersion apparatus consisted of a rock-salt prism of angle $60^\circ 1' 8''$ and faces 11 cm. by 7.5 cm. high, fitted with a Wadsworth mirror, the whole rotating with the 17-inch divided circle of a large spectrometer of the ordinary type. Two concave mirrors of 66 cm. focal length and 7.5 cm. aperture served as collimators, being rigidly mounted on arms of the spectrometer. The bolometer case was held by an independent massive support, as were also the slit and an external mirror (of 7.5 cm. aperture and 33 cm. focus) which was used to bring a real image of the source of light on the slit. When not in use a glass cover jar was fitted over the prism, and sealed with oil in an annular trough around the edge; a drying agent placed within assured a dry atmosphere surrounding the prism. This arrangement has been very satisfactory for a period of time of several months. The whole apparatus, then, does not differ from the ordinary infra-red prism spectrograph except perhaps in point of size.

The width of the bolometer strip has been given as 0.05 cm.; in most of the following work the slit was of the same width, and its length was such that the spectrum covered nearly all of the bolometer strip. In a few cases, however, the proportions of the slit were changed in order to try the transmission of a small specimen. A slit of width 0.05 cm. subtends an angle of 0.00076 radians or 2.7 minutes of arc, if viewed from the telescope mirror. This is equal to an extent in the spectrum of from 0.1μ to 0.5μ , depending on the dispersion. On the average, between 1μ and 7μ the strip may be considered as receiving the energy of a spectral region 0.25μ in extent.

For calibration, the D line was taken as a datum, and a curve was plotted showing the deviation from the position of the D line as a function of λ . The prism angle was carefully measured, and for the dispersion of the rock-salt, Paschen's¹ values were used. From the deviation curve, a scale of wave-lengths and angular rotation from the D line was con-

¹ Ann. d. Physik, 26, 1908, p. 128.

structed by projection on the drawing board. This scale was about 12 inches long for the region from $\lambda = 0.5896\mu$ to $\lambda = 7\mu$. For making the measurements rapidly, advantage was taken of a train of gears which connected the rotating prism-circle with a plate lowering apparatus, which was originally designed so that infra-red holograms could be made by recording the galvanometer deflections on a moving sensitive plate. The graphically constructed scale was of such a length that when fitted to the plate-carrier (the whole apparatus being adjusted to the D line), the scale slid by a fiducial mark giving correct wave-length readings as the spectrum was made to march across the bolometer strip. A test of the scale usually gave the wave-length of the CO_2 absorption band within 0.02 or 0.03 μ of its correct value ($\lambda = 4.38\mu$). Of course settings made with this scale cannot compare for accuracy with those made by means of a calibration curve and a reading microscope, but this would have been very tedious work for these measurements. The various gears between the plate carrier and the rotating circle introduced small errors of lost motion and uneven running which could not be eliminated. Taking into consideration all errors, it is estimated that the absolute position in the spectrum at any setting was known, on the average, to within 0.05 μ , and any setting could be repeated (by turning back, and coming forward again until the same division was under the mark) to about 0.01 μ . Some badly determined points may be noticed among the observations: the steep slopes of the energy curve near the atmospheric absorption bands at 2.1 μ , 2.7 μ , and 4.4 μ were especially troublesome, and inaccuracies due to this cause cannot be avoided unless a setting can be repeated to within a few thousandths of a μ , which was impossible with the method and apparatus used by the writer.

As a source of light, a one-ampere A.C. Nernst filament operated somewhat below full capacity on a storage battery, was found to give the most constant radiation. After being used for some time, the A.C. glower (with leads fused in at each end) seemed to develop a very constant resistance. It may be stated that enclosing the source of radiation in a water jacket proved very effective for disposing of all the energy not thrown into the spectrometer by way of the collimating system.

No limiting diaphragm was used anywhere in the path of the beam. Practically, the prism face acted as such a diaphragm, as the beam from the collimator was so much larger than the prism face that the prism refracted only about 50 or 60 per cent. of the light, that is, the central portion. Since the light from the edges of the mirrors was thus lost, small errors in collimation, introduced by interposing specimens, had practically no effect on the position and intensity of the spectrum.

THE OBSERVATIONS.

In determining the per cent. of light transmitted through, or reflected by a given specimen, settings were made at intervals of about 0.1μ throughout the spectrum, and readings taken with the bridge balanced at each setting—thus obtaining measures of the relative quantities of energy at different wave-lengths. Then the spectrometer was turned back, the specimen interposed, the same settings repeated and the energy determined as before. The ratio was easily computed after the corrections earlier described were applied to the bridge readings.

If natural specimens are used it is hardly practicable to place them in parallel light; they must be placed where the beam is small, *i. e.*, near the slit. All the transmission specimens used by the present writer were placed perpendicular to the beam, and *behind* the slit. It is especially important for specimens of highly refracting material that they be placed, behind rather than in front of the slit, in order that the focus of the image of the energy-source on the slit shall be exactly the same with and without the specimen in place. For reflection the arrangement shown in Fig. 3

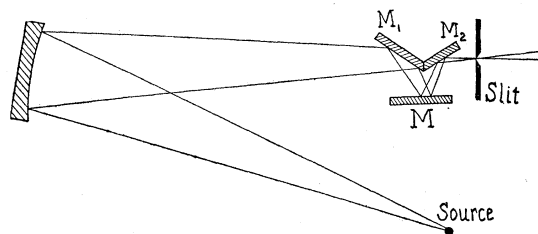


Fig. 3.

was used: the silvered mirrors M_1 and M_2 were fixed, and the mirror M , also silvered, could be removed and a surface of the material to be investigated substituted. The angle of incidence was here about 18° , which was practically normal incidence for materials of high refractive index. The reflecting power of the specimen was easily determined, using Hagen and Rubens'¹ values for the reflecting power of silver to correct the energy observed when mirror M is in place.

THE OPTICAL PROPERTIES OF SOME SULPHIDES.

Stibnite.—The observations on stibnite are given in Fig. 4. Two determinations were made of the reflection, and of the transmission of two different thicknesses. The curves are simply a mean, intended to

¹ Ann. d. Physik, 11, 1903.

be as consistent as possible with both sets of observations. This practice was followed with all the observations.¹

Specimens of Japanese stibnite were used with natural, fresh cleavage surfaces. Stibnite crystallizes in the orthorhombic system, and is biaxial if like all known transparent crystals of this class. The cleavage

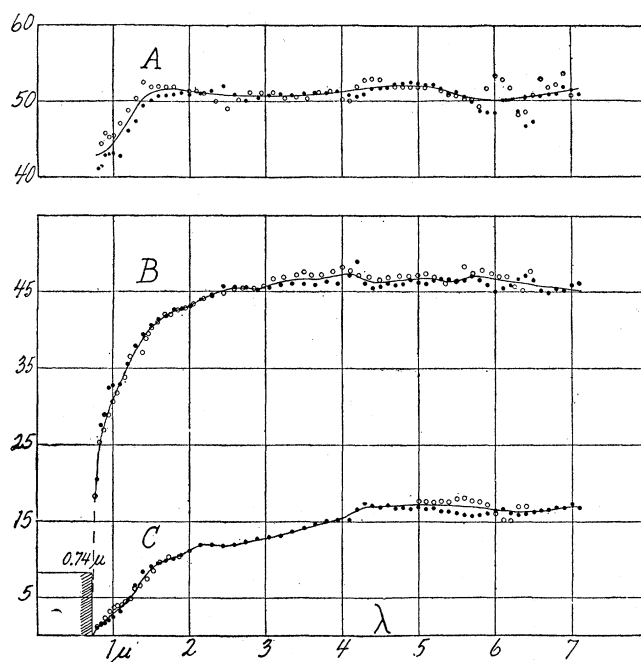


Fig. 4.

Curve A: Per cent. of energy reflected from stibnite.

Curve B: Per cent. transmitted through layer 0.18 cm. thick.

Curve C: Per cent. transmitted through layer 0.73 cm. thick.

is perpendicular to the crystallographic b -axis, so that the path of the light lay along this axis. The bisectrix of the optical axes of crystals of this type may lie along any one of the a , b , c , crystallographic axes, so that the optical constants here determined are for neither pure ordinary or extraordinary rays. They are offered merely as empirical relations which will have to serve for cleavage layers until this substance is more thoroughly investigated.² In Fig. 8 are given the values of the extinction-

¹ Koenigsberger and Reichenheim obtain somewhat lower values for transmission and reflection of stibnite. Coblenz, however (quoted in Wood's Optics, 2d ed., p. 400), obtains a value for transmission very close to that offered here.

² The following experiments by Prof. A. Trowbridge on the double refraction of stibnite may be of interest here:

A collimator system containing a glass lens, a slit, and a concave mirror was set up between

modulus¹ $n\chi$ computed from the observations on the transmission of the two thicknesses by means of the formula

$$n\chi = \lambda\alpha = \frac{\lambda \log J_1/J_2}{4\pi(d_1 - d_2) \log e}$$

in which α = the extinction coefficient,

J_2 = relative transmission of the thin piece,

J_1 = relative transmission of the thick piece,

d_1 = thickness of thick piece, and

d_2 = thickness of thin piece, measured with the micrometer caliper.

In the derivation of this formula the reflection from the first surface and one reflection from the last surface are eliminated. If a specimen acts as a Fabry and Perot interferometer, and by successive internal reflections contributes to the transmitted energy, we can only observe that on account of the thickness the resulting interference bands in the spectrum are so narrow that the bolometer does not resolve them, and only the mean energy is observed. This should be equal to the energy in the first transmitted ray, so that we are justified in placing confidence in the above given formula; furthermore the successive rays due to multiple internal reflections are rapidly extinguished by the increased absorption due to lengthening path in the material.²

The limit of transmission of a piece a fraction of a millimeter thick is at 0.74μ .³

a Nernst filament and a bolometer. In this collimator system were placed an analyzer and a polarizer consisting of transmission plates of mica, with their directions of greatest transmission crossed. Between analyzer and polarizer was placed a layer of stibnite which was rotated. There was no dispersion, total radiation through the glass lens being measured by the bolometer. On the stibnite cleavage surfaces there are striæ parallel to the crystallographic a -axis: it was found that when the layer was turned so that the striæ made an angle of 45° with the plane of polarization of the polarizer, about four times as much energy was transmitted as when the striæ were either perpendicular or parallel to the plane of polarization. This shows either that it is more transparent to a vibration making an angle of 45° with the striæ, or that in that case it gives rise to a circular vibration: either explanation would imply double refraction.

Again, the polarizer was removed, and a prism placed in the collimator system, thus converting it into a dispersion apparatus. The layer of stibnite was put in with its striæ parallel to the slit, and energy spectra observed with the analyzer set at different azimuths. It was found for wave-lengths less than 3μ (for which the glass lens was transparent) that more energy got through when the plane of vibration of the analyzer was parallel to the striæ than when perpendicular. This shows that its extinction coefficient is different for vibrations in different directions, or, that it acts like tourmaline to some degree, and may be used as an analyzer.

¹ We follow the notation of Kayser, *Handbuch*, III., p. 15.

² Koenigsberger and Reichenheim (loc. cit.) derive a more rigorous formula, taking into account the second reflections, but we do not carry the formula this far, for the reasons stated.

³ A piece of stibnite transparent down to 0.7500μ at ordinary temperature became transparent to 0.7200μ on being cooled by immersing in liquid air.

No attempt to obtain the refractive index was made except in a very general way from the reflection observations. After 4μ the reflection and absorption curves are practically constant: since the value of $n\chi$ is so very low, we may obtain an approximate value for the refractive index by ignoring $n\chi$ and using the formula for reflecting power

$$R = \left(\frac{n - 1}{n + 1} \right)^2, \quad (9)$$

which, solved for n , gives

$$n = \frac{1}{1 - R} (1 + R \pm \sqrt{4R}). \quad (10)$$

Using the larger root for n we calculate the following values:

λ	n
1.5 μ	6.00
3.0	5.95
5.0	6.16
7.0	5.97

which are given simply as being in the neighborhood of those given by E. C. Müller, namely $n_{\text{red}} = 4.69$ and $n_{\text{blue}} = 5.53$.¹ The outstanding feature is of course the very small dispersion, and the constancy of the extinction coefficient α from about 2μ on, in the infra-red.

On the electromagnetic theory for absorbing bodies the relations²

$$n^2(1 - \chi^2) = \epsilon, \quad (11)$$

$$N^2\chi = \sigma T, \quad (12)$$

should hold, in which ϵ is the dielectric constant, σ the conductivity in absolute electrostatic units, and T the time of one vibration. The writer is unable to find any data for the two electrical constants, but the following table, calculated from the values of n and $n\chi$ may be of some use (we take $n = 6.00$ for these values of λ):

λ	n	$n\chi$	$\sigma = n^2\chi/T$
1.5 μ	6.0	3.35×10^{-5}	4.0×10^{10}
3.0	6.0	5.6×10^{-5}	3.3×10^{10}
5.0	6.0	7.2×10^{-5}	2.6×10^{10}
7.0	6.0	10.0×10^{-5}	2.6×10^{10}

A conductivity of 3×10^{10} electrostatic units is equal to a resistance of 30 ohms per cubic centimeter.

¹ Wood, Physical Optics, 2d ed., p. 400.

² Drude, Lehrbuch d. Optik, 2d ed., p. 341.

Sphalerite.—The observations on this substance, the natural sulphide of zinc, are given in Fig. 5. Sphalerite is isometric (optically isotropic) and all cleavages should give specimens with the same optical properties. The material is marred by a yellow coloring and resinous streaks due to

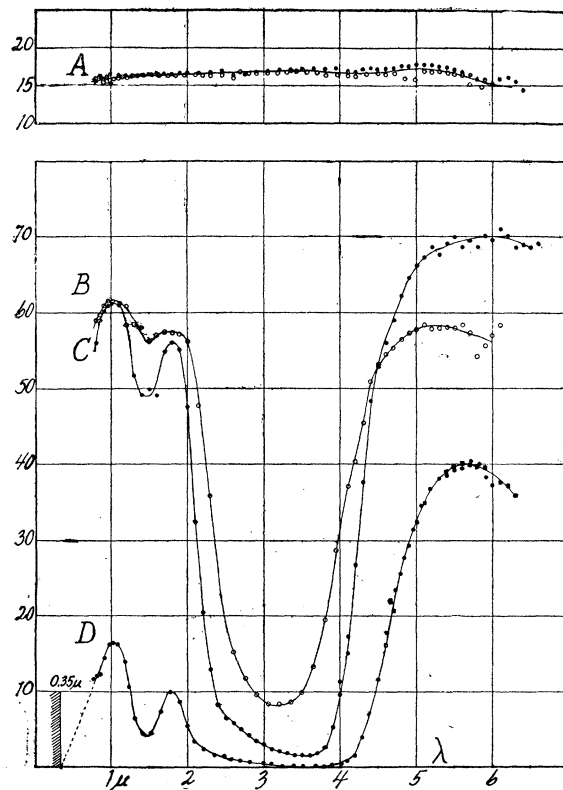


Fig. 5.

Curve A: Per cent. of energy reflected from sphalerite.
 Curve B: Per cent. transmitted through layer 0.067 cm. thick.
 Curve C: Per cent. transmitted through layer 0.253 cm. thick.
 Curve D: Per cent. transmitted through layer 1.68 cm. thick.

the presence of iron and manganese sulphides, which crystallize isomorphous with the sphalerite. With regard to the curves, the crossing of *B* and *C* at $\lambda = 4.5\mu$ may be explained by the fact that *B* is from a very small specimen, which necessitated using a short and wide spectrometer slit in running the curve. *B* is offered simply for its interest near the absorption band at 3.2μ . The fact that *D* is so much lower than *C* for $\lambda < 3\mu$ is probably due to a much greater quantity of the brown impurity in the thick specimen. The values of $n\chi$ computed from curves *C* and *D*

are given in Fig. 8. The limit of transparency of a piece about 0.5 mm. thick was determined by the writer with the aid of an ultra-violet spectrograph and found to be about at 0.35μ . It is practically impossible to determine the refractive index of sphalerite in the infra-red without polishing acute prisms of the material. Experiments made by the writer show that a polish even approaching the perfection of a cleavage surface is out of the question, as the material is comparatively soft; its hardness on the Moh scale being about 3.7. The refractive index is so high ($n_{\text{green}} = 2.4007$, $n_{\text{yellow}} = 2.3692$, $n_{\text{red}} = 2.3417^1$) that natural cleavage prisms (of angle 60°) are of no use, even if they could be obtained of sufficient size.²

The absorption bands determined at 1.5μ and 3.2μ should be characteristic of pure sphalerite. According to numerous analyses, no water of crystallization or of combination is contained in the material.

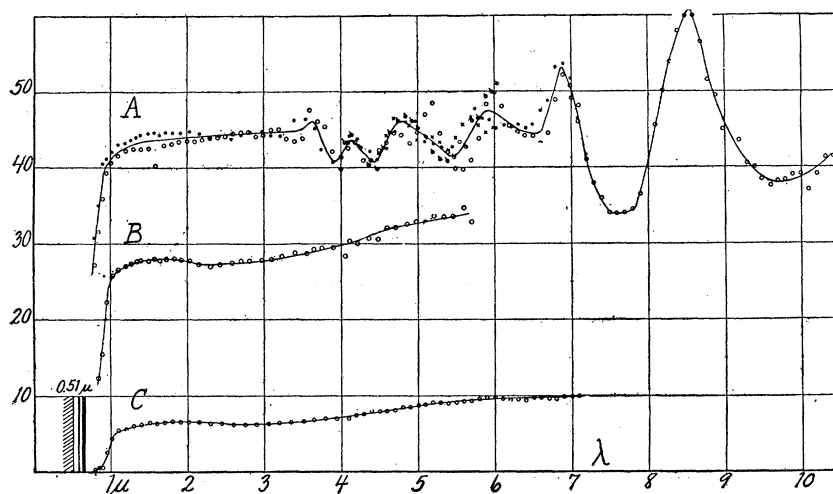


Fig. 6.

Molybdenite.

Curve A: Per cent. transmission of a layer 4.2μ thick.

Curve B: Per cent. transmission of a layer 0.0246 cm. thick.

Curve C: Per cent. transmission of a layer 0.0769 cm. thick.

Molybdenite.—This is the most interesting of all the sulphides in its optical properties. Its crystals are hexagonal, with basal cleavage allowing specimens of almost any thinness to be obtained. Hexagonal

¹ Ramsay, Zt. f. Kryst., 12, 1887, p. 218.

² We have no data that will enable us to test the relation $n^2\chi = \sigma T$. Doelter (Sitz. Ber. d. Kais. Akad., Wien, 119, I., 1910, p. 49) states that "zinc sulphide, even when heated to 420° (when it decomposed) showed practically no conductivity."

crystals are doubly refracting, uniaxial with the optic axis along the crystallographic c -axis, that is, perpendicular to the cleavage planes. Therefore in determining the optical constants for light passing along the optic axis, we have to deal only with the ordinary ray, and any constants that we can determine in this way are the true ones for the ordinary ray. The observations for the relative transmission are given in Fig. 6. The wavy character of Curve *A* is very striking and at once suggests interference. That this is interference is proved by the fact that the spacing of the bands varies with the thickness of the specimen. In Fig. 7 Curve *A* gives the energy reflected from a piece slightly thicker;¹ the bands are closer together, as they should be.

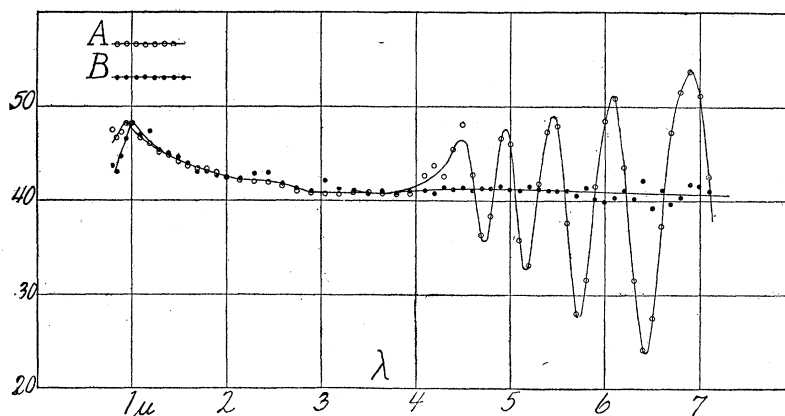


Fig. 7.

Molybdenite.

Curve *A*: Per cent. of energy reflected from a layer 6.6μ thick.Curve *B*: Per cent. of energy reflected from a layer 34μ thick.

Both of these also showed interference in the visible region as will be discussed later. A very thin specimen (about 1μ thick) gave the absorption spectrum shown in the lower left-hand corner of Fig. 6, the limit of transmission being at about 0.51μ . Besides the 3 curves shown in Fig. 6 a fourth might have been given showing the transmission of a piece 34μ thick, but this is omitted, as it is practically identical with Curve *A* except in the matter of interference. The light reflected from this piece is given in Curve *B*, Fig. 7, which is also identical with *A*, Fig. 7, except for the interference. The values of $n\chi$ given in Fig. 8 are computed by the usual method from Curve *A* (using mean values where it oscillates) and Curve *C*, Fig. 6.

¹ Koenigsberger and Reichenheim (op. cit.) give a reflecting power for molybdenite much lower than this.

The determination of the thickness of the very thin pieces of molybdenite is somewhat difficult by ordinary methods. Any method involving pressure is apt to damage the specimen, so that recourse was had to the method of weighing, the specific gravity having been determined and the area of the piece being computed.

To produce a good cleavage surface for reflection, it was necessary to split a thin layer of the material and squeeze it down onto a piece of plate glass by rubbing it lightly with a pad of cotton, thus securing a fairly plane surface and good definition.

We proceed to consider the interference phenomena exhibited by the thin layers of this material. When a thin film is placed in front of the slit of a spectrometer, the positions and the spacing of the resulting interference bands in the spectrum afford a means of finding the dispersion of the material of the film. For a dark band at λ_1 the following relations must hold:

$$2n_1t = (N_1 + \frac{1}{2})\lambda_1;$$

similarly for a dark band at λ_2

$$2n_2t = (N_2 + \frac{1}{2})\lambda_2, \quad (14)$$

in which n is the refractive index, N a certain integer, and t the thickness of the film. For neighboring bands, that is, for two values of λ close together, we assume that dispersion is not an important factor, and consider that the bands occur simply on account of the varying relation between λ and $2nt$; we may then take $n_1 = n_2 = n$ and easily derive the following formula from (13) and (14) by subtraction:

$$N = 2nt \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right), \quad (15)$$

in which $N = N_1 - N_2$, the change in N_1 in passing from λ_1 to λ_2 , and is equal to the number of bands between λ_1 and λ_2 . This may be written

$$n = \frac{N\lambda_1\lambda_2}{2t(\lambda_2 - \lambda_1)}. \quad (16)$$

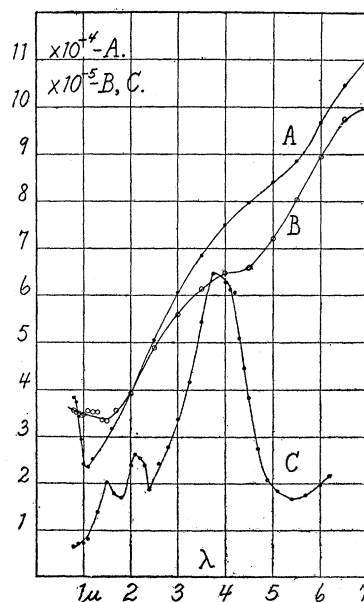


Fig. 8.

Curve A: $n\lambda$ for molybdenite.

Curve B: $n\lambda$ for stibnite.

Curve C: $n\lambda$ for sphalerite.

The formula is only approximate on account of the real variation of n with λ , but it will be seen that if n varies slowly it should hold over short ranges; moreover, if n should vary rapidly and *increase* as λ *decreases* the bands will naturally come close together, so that we might even use it in this case, if we take only one or two bands as an interval.

We give the following data on the position of interference minima for films of various thicknesses. The infra-red observations are from Curve A, Fig. 7, and Curve A, Fig. 6. The observations in the visible region were made with the aid of a Hilger wave-length spectrometer and are means of several settings. The bands should of course be regularly spaced from the visible on into the infra-red region; since however the width of the bolometer strip was such that in the region from $2\text{--}3\mu$ it covered an extent of about 0.5μ in the spectrum, the bands are so closely spaced that they cannot be resolved.

Thickness.....	Transmission.		Reflection.
	(1) 4.2μ .	(2) 2.2μ .	(3) 6.6μ .
Positions of interference minima . . .	0.7141 μ 0.7208 0.7286 0.7361 0.7453 0.7555 0.7658 0.7759 3.45 3.95 4.45 5.40 6.45 7.65 9.80	0.7001 μ 0.7101 0.7228 0.7379 0.7557 0.7751 	4.75 5.18 5.75 6.45 7.38

Applying the formula successively to the visible readings in set (1) taking two fringes as the interval, and to set (2), taking 1 fringe at a time, and taking for λ the mean of λ_1 and λ_2 , we compute the following:

λ	n Set (1).	n Set (2).	λ	n Set (1).	n Set (2).
0.7050		11.3	0.7453	6.84	
0.7164		9.17	0.7468		7.12
0.7208	8.54		0.7555	6.63	
0.7286	8.25		0.7654		6.87
0.7304		8.02	0.7658	6.85	
0.7361	7.74				

Assuming that n is practically constant between $\lambda = 3.5\mu$ and 10μ , as reflection and transmission curves are horizontal here, and calculating a mean value of n , using the first and last only of the infra-red observations, we have

$$\begin{aligned}\text{From set (1), } n &= 4.2 \\ \text{From set (3), } n &= \underline{4.04} \\ \text{Mean } \dots\dots\dots &4.1\end{aligned}$$

In order to utilize the single readings we observe that the difference in optical length of path which gives rise to the interference is for the transmission piece (1) $2nt$ or about 34.4μ and for the reflection piece 54.3μ . For transmission the path difference should be equal to an odd number of half wave-lengths, and for reflection, an even number (taking into account the phase change of $\lambda/2$ of the directly reflected ray) in order to produce a minimum. By trial the following numbers are found to satisfy this condition approximately, and on assuming that they do exactly, the retardation $2nt$ can be calculated for a given value of λ and hence a value of n_λ found, $2t$ being known.

Set (1) Transmission.				Set (3) Reflection.			
λ	Number, N .	$N\lambda = 2nt$.	$\therefore n$.	λ	Number, N .	$N\lambda = 2nt$.	$\therefore n$.
3.45	9.5	32.8	3.9	4.75	11	52.3	3.98
3.95	8.5	33.5	4.0	5.18	10	51.8	3.95
4.45	7.5	33.4	4.0	5.75	9	51.8	3.95
5.40	6.5	35.1	4.2	6.45	8	51.6	3.93
6.45	5.5	35.4	4.2	7.38	7	51.6	3.93
7.65	4.5	34.4	4.1				
9.80	3.5	34.3	4.1				

We now have approximate values for n over a short range of the visible and a considerable region of the infra-red. The dispersion is given in Fig. 9, Curve *A*; a larger scale is used for the values in the visible region. In drawing the curve more weight is given to the values from set (3) on account of the very accurate spacing of the interference bands in the reflection-specimen. The transmission specimen is undoubtedly of slightly varying thickness, which accounts for the relatively poor determination of the interference bands observed. By weighing, of course, only a mean thickness is determined. With regard to the accuracy of the method, it should give good results under favorable conditions: that is, with a perfect Fabry and Perot interferometer in front of the infinitely narrow slit of a perfect spectrometer. At any rate, allowing for the unevenness of films, wide slits, etc., which are unavoidable with these

specimens, the values of n should be correct within 5 or 10 per cent. From the reflection curve, taking the limiting value of 41 per cent. reflected light, and using formula (10), we compute $n = 4.5$ which is not far from the value obtained by means of the interference observations.

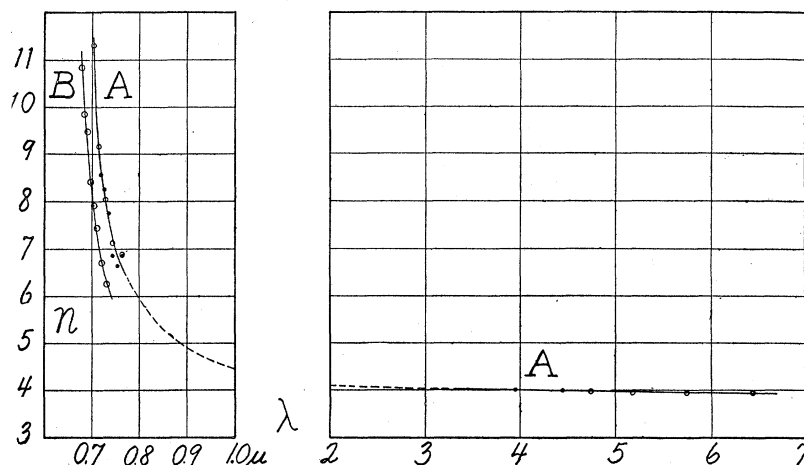


Fig. 9.

Curve A: Dispersion of molybdenite at ordinary temperature.

Curve B: Dispersion at temperature of liquid air.

The relation $n^2\chi = \sigma T$ may be tested for this substance. Calculating $\sigma = n^2\chi/T$ for several values of λ for which we have n , we find:

λ	n	$n\chi$	$\sigma = n^2\chi/T$
0.80μ	6.00	3.9×10^{-4}	8.60×10^{11}
3.0	4.02	6.1×10^{-4}	2.45×10^{11}
4.0	4.0	7.5×10^{-4}	2.25×10^{11}
5.0	3.98	8.4×10^{-4}	2.00×10^{11}
6.0	3.94	9.7×10^{-4}	1.91×10^{11}
7.0	3.90	11.0×10^{-4}	1.85×10^{11}

A conductivity of 2×10^{11} electrostatic units is equal to a resistance of 4.5 ohms per c.c. Prof. A. Trowbridge, of Princeton, and Prof. G. W. Pierce, of Harvard, have made determinations of the specific resistance of this material which are, respectively, 3 ohms and 6 ohms per c.c.¹ at ordinary temperature (ca. 17° C.).

Through the courtesy of Professor Trowbridge the writer is enabled to

¹ Koenigsberger and Reichenheim (op. cit.) give for the resistance of molybdenite 3.06 ohms at 17° C. in the direction of the C-axis (the direction of light propagation in the present work). They also find that the conductivity increases rapidly with rising temperature. Pierce's data for the resistance of a molybdenite rectifier (PHYS. REV., 28, 1909, p. 151) exhibit this effect in a very striking manner.

communicate the following details regarding the optical properties of molybdenite at low temperatures:

A piece 4 or 5 μ thick which was transparent down to 0.7020 μ became transparent to 0.6660 μ at the temperature of boiling liquid air (-190°C.).¹

A piece 4.1 μ in thickness was kept immersed in liquid air and the interference bands in the visible region found with the aid of a concave grating to lie at the wave-lengths

0.7430 μ	0.7130	0.6911	0.6750]
0.7320	0.7053	0.6854	0.6720
0.7220	0.6977	0.6795	

The writer is unable to find data on the coefficient of expansion of molybdenite, but neglecting the effect of expansion on the thickness of the film, we compute, using formula 16, taking two bands at a time, the following values of the index:

λ	n
0.6757 μ	14.8
0.6802	10.85
0.6853	9.86
0.6915	9.48
0.6982	8.40
0.7054	7.92
0.7136	7.44
0.7225	6.70
0.7325	6.24

This dispersion is plotted in Fig. 9, Curve *B*. The refractive index cannot possibly be independent of the temperature unless the coefficient of expansion is in the neighborhood of 0.001, which would be very high, say from 3 to 5 times as great as that of metals. The general facts set forth here agree very well with what Pulfrich found for glasses—namely, as the temperature fell, the ultra-violet absorption band moved toward the ultra-violet end of the spectrum, and the dispersion was decreased.

Other Sulphides.—Some other sulphides were ground into thin plates and tested qualitatively for transparency in the region $1\mu < \lambda < 6\mu$. It was difficult to produce thin layers of any accuracy and polish, but as the materials seemed to be opaque, no further attention was given them. The results are given in this table:

Material.	Thickness of Layer.	
Covellite, CuS,	about 0.2 mm.	} Opaque, $\lambda < 6\mu$.
Chalcocite, Cu ₂ S,	about 0.5 mm.	
Galenite, PbS,	about 0.5 mm.	
Bismuthinite, Bi ₂ S ₃ ,	about 0.2 mm.	Opaque in visible. Sample too small for infra-red work.

None of these specimens became transparent when cooled in liquid air.

¹ Koenigsberger and Reichenheim established the fact that the transmission of total radiation by this substance was at 110° only 62 per cent. of the value at 40° . With regard to the

Koenigsberger and Reichenheim offer data on the reflecting power and transmission of pyrite, iron sulphide, and marcassite. They could not obtain similar films of galenite.

CONCLUSION.

While we have given approximate values for the refractive indices of stibnite and molybdenite, it is greatly to be desired that more accurate measures be made of these constants in the infra-red region. It is possible that very acute prisms of these materials could be filed out, and used in connection with a small spectrometer of short focal length. A prism of 1 or 2 mm. base would probably let through enough energy (where the energy spectrum is rich) to permit measurements by the method of minimum deviation.

A good determination of the electrical constants—conductivity and dielectric constant—is also necessary if much is to be done with these minerals.¹

In molybdenite and stibnite we have two substances which in the near infra-red region have properties very much like those of ordinary transparent bodies in the visible—with the additional features of high refractive index and continued transparency for an indefinite distance with increasing wave-length. A two-term dispersion formula was applied to the dispersion curve of molybdenite, with the result that no solution for an absorption band in the distant infra-red could be obtained. Perhaps a method will be found for measuring the refractive index of the extraordinary ray in molybdenite, and determining the three refractive indices of stibnite. These results would be of great interest from a theoretical point of view.

A film of molybdenite a few microns thick offers possibilities with light of wave-length about 20μ for an investigation of the optical behavior of the film when twice its thickness is optically less than one wave-length.

The writer is under obligation to Prof. Augustus Trowbridge for suggesting this work, and for help and criticism throughout its progress. Prof. A. H. Phillips, of Princeton, has very kindly placed at the disposal of the writer his knowledge of mineralogy and crystallography and furnished an unusual crystal of sphalerite for this work.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.

relation between conductivity and optical properties, it is well known that many oxides, sulphides, and other minerals which are poor conductors at ordinary temperatures become much more conducting when heated. For quartz and some other oxides, Doelter (op. cit.) found enormous decreases in resistance for specimens heated to 1300°C .

¹ Koenigsberger and Reichenheim give the conductivity of molybdenite (and its variation with temperature) in both crystallographic directions. They also give the conductivities of some of the other sulphides, but not of stibnite.