

Anton BERAN*, Josef ZEMANN*

THE OPTICAL CONSTANTS OF HAUERITE IN THE VISIBLE PART OF THE SPECTRUM

A b s t r a c t. Reflectance values for hauerite from Jeziórko, Poland, were measured in air and in oil at $\lambda = 400\text{--}700$ nm, and the results were transformed into the optical constants n , k and α . For the refractive index n a flat maximum resulted at $\lambda = 520$ (10) nm with $n = 2.85(3)$. As to be expected from the deep reddish brown transmission colour in thin splinters, the absorption coefficient k decreases with increasing wavelength, but the slope was found to be less steep than given in the literature.

INTRODUCTION

Hauerite, MnS_2 , and pyrite, FeS_2 , belong to the same structure type. Although they are disulfides of neighbouring transition elements, they show characteristic differences in the atomic bond lengths and in a number of their physical properties. In this context it seems worth mentioning that in hauerite the S-S-distance in the S_2 dumb-bell measures 2.09 Å (Chattopadhyay and von Schnering 1982), while in pyrite it measures 2.15 Å (Stevens et al. 1980), indicating a weaker Me-O bond in hauerite as compared with that in pyrite. This conclusion is supported by the results of Raman work of Vogt et al. (1983) showing that the concept of a S_2 - "molecule" fits the spectra better for MnS_2 , and by IR work of Lutz et al. (1981) leading to a stronger ionicity of the Me-O bond in MnS_2 .

As to the optical properties in visible light, hauerite is characterized by much lower reflectance values R as compared with pyrite (Uytenbogaardt and Burke 1971, Ramdohr 1975, Picot and Johan 1977, 1982) and further by a rather strong decrease of R with increasing wavelength - it becomes transparent for red light in ultrathin slides. The refractive index is given as $n_{\text{Li}} = 2.69$ by Larsen and Berman (1934) and in the near infrared as $n(852 \text{ nm}) = 2.634$ by Bailly (1947, 1948)¹. Quantitative reflectance measurements on hauerite were made at defined wavelengths in air by Vjalsov (1973), by Picot and Johan (1977, 1982), and by Wylie and Ypma (1974). Only the last mentioned authors, however, determined the refractive index n and the absorption coefficient k for several wavelengths.

Because Wylie and Ypma (1974) worked at five wavelengths only and further

* Institut für Mineralogie und Kristallographie, Universität Wien, Dr Karl Lueger-Ring 1, A-1010 Wien, Austria.

¹ Caye and Medenbach (1971) determined $n(589 \text{ nm}) = 2.68$ by an oblique incidence method. As they have neglected absorption, we do not consider this value any further although the error made was not large.

because they used an oblique incidence method that has not found much application among mineralogists, we decided to measure the reflectance of hauerite in air and in oil over the whole range of the visible spectrum in narrow steps of the wavelength by standard "normal incidence" methods, and to transform the results into n , k and α ($k = n \cdot \alpha$) as a contribution to a better knowledge of the optical properties of this mineral.

EXPERIMENTAL

As working material served hauerite from Jeziórko, Poland, where it is found in Miocene sediments. For a description of this occurrence the reader is referred to Osmólski and Plichowski (1978), as to that of a geologically very similar one at Grzybów, Poland, to Hubicka-Ptasińska et al. (1969). Our material was kindly provided by Prof. Dr W. Żabiński, Kraków; it consisted of loose cubes of a few millimeter diameter which were only slightly modified by octahedron faces. As no chemical analysis of the hauerite from Jeziórko seems to exist, we decided to analyse it for the iron content: on the basis of six electron-microprobe point analysis it was determined to 0.09 (5) wt. % Fe. This compares well with the 0.10 wt. % Fe found by wet chemical methods in the hauerite from Grzybów (Hubicka-Ptasińska et al. 1969).

The polished section used for the measurements contained three hauerite grains. It was ground on glass with 15 μm SiC abrasive and finished with 6 μm diamond paste on nylon polishing cloth, with 1 μm diamond paste on "texmet" polishing cloth (Buehler Ltd.), and with 0.25 μm diamond paste on "microcloth" polishing cloth (Buehler Ltd.) by hand. The quality of the polished section seemed to be well suited for our kind of work, and the crystals contained only few inclusions² and regions with the characteristic reddish brown internal reflections. It was, therefore, easy to find a larger number of spots proper to reliable measurements.

The reflectance measurements were made with a reflected light microscope Leitz Orthoplan-Pol equipped with a microscope photometer MPV2 (photomultiplier S20, type EMI 9558) and with a Leitz monochromator ($\Delta\lambda = 4 \text{ nm}$). The measurements were made using planachromates $20\times/0.40$ (effective numerical aperture 0.20). The diameter of the measuring area was 0.07 mm. As reflectance standard served SiC, as immersion liquid DIN oil 58884.

When measuring at any one spot repeatedly, the standard deviation of the reflectance was obtained to be about 0.5 rel. %. However, at $\lambda = 589 \text{ nm}$ a spread of 2 rel. % was obtained for the mean values of the reflectances determined at ten different spots which were all excellently suited for measurement and which, according to careful microscopic inspection, were of equal quality. The standard deviation of those the single mean values from their average was, of course, smaller than the spread, namely 0.7 rel. %. For the final measurements at different wavelengths a spot was chosen the preliminary results for which corresponded closely to the average of the ten spots mentioned.

The wavelength was varied from 400 to 700 nm in steps of 20 nm. Further measurements were made at the standard wavelengths of the Commission on Ore Microscopy of the International Mineralogical Association. At every wavelength each ten measurements were made in air and in oil, and were averaged. The results are given in Table 1.

² Microscopic inspection of our polished section showed that the hauerite crystals contained tiny inclusions ($\phi \leq 0.01 \text{ mm}$) of an isotropic mineral with pale yellow reflection colour, evidently pyrite, and inclusions of several minerals with a very low reflectance, probably silicates.

Table 1

Reflectance values for hauerite from Jeziórko (Poland) in air (R) and in oil DIN 58884 (${}^{\text{im}}R$) in %. Standard deviations in air: ~ 0.10 , in oil: ~ 0.05

λ (nm)	R	${}^{\text{im}}R$	λ (nm)	R	${}^{\text{im}}R$	λ (nm)	R	${}^{\text{im}}R$
400	24.9	11.1	540	23.7	10.0	680	20.7	7.8
420	24.7	10.9	560	23.3	9.6	700	20.7	7.8
440	24.6	10.7	580	22.8	9.2			
460	24.5	10.6	600	22.2	8.8	470	24.4	10.6
480	24.4	10.5	620	21.6	8.4	546	23.6	9.8
500	24.3	10.4	640	21.2	8.1	589	22.5	9.0
520	24.1	10.2	660	20.9	7.9	650	21.0	8.0

EVALUATION AND DISCUSSION

Fig. 1 presents our reflectance values for hauerite in air. It gives further the R 's according to Vjalsov (1973), Picot and Johan (1977, 1982) and Wylie and Ypma (1974). The last mentioned authors calculated their R 's from refractive indices n and absorption coefficients k obtained by an oblique incidence method. In addition, for $\lambda = 852 \text{ nm}$ also the R value calculated from the n as given by Bailly (1947, 1948) is plotted; thereby absorption was neglected in accordance with Bailly and as suggested by the decrease of k with increasing wavelength (cf. Fig. 2).

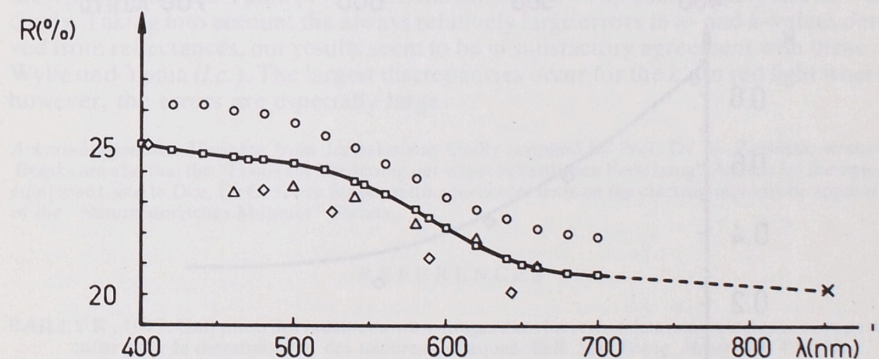


Fig. 1. Reflectance values R for hauerite (in air)

Squares connected by full line: this work; Circles: Picot and Johan (1977, 1982); Triangles: Vjalsov (1973); Rhombs: Wylie and Ypma (1974); Cross: Bailly (1947, 1948)

As the R 's of Picot and Johan (*l.c.*) are up to $\sim 2.5\%$ higher than those of Wylie and Ypma (*l.c.*) although both groups worked on hauerite from Raddusa, Sicily, we decided to check the reflectance of hauerite from this locality. To this end we prepared a polished section containing each one grain of hauerite from Raddusa³ and from Jeziórko by exactly the same procedure as described above. Measurements at $\lambda = 589 \text{ nm}$ gave for both grains the value of Table 1 within our limits of accuracy. This result strongly indicates that the differences in the R 's between Picot and Johan

³ Electronmicroprobe analyses gave for this hauerite 0.08 (5) wt. % Fe, a value practically identical with that for hauerite from Jeziórko.

(*l.c.*), Wylie and Ypma (*l.c.*) and ourselves essentially do not reflect real differences in the optical properties, but rather systematic errors in at least two of the three sets of data. This is, of course, only one more example for the general experience that experimental reflectance values are very dependent of the finishing of the polished section, the measuring device, the method used, etc. As the chemical variation of hauerite is generally only minor, also the material used by Vjalsov (*l.c.*) has probably optical constants very similar to those of the other specimens.

Three items seem to support our hopes that the new reflectance data presented here are fairly reliable: (a) the conversion of our R 's and mR 's into k 's never leads to complex values (vide infra), (b) our R 's can smoothly be extrapolated to the calculated R -value for $\lambda = 852$ nm (Fig. 1), and (c) our R 's do not lie outside of the range of the other authors. By presenting these arguments we do, of course, not claim that our values are definitely superior to the other three sets.

The omission of a comparison between the reflectance values discussed here with the diffuse reflectance curve of Vaughan (1971) seem to be allowed because

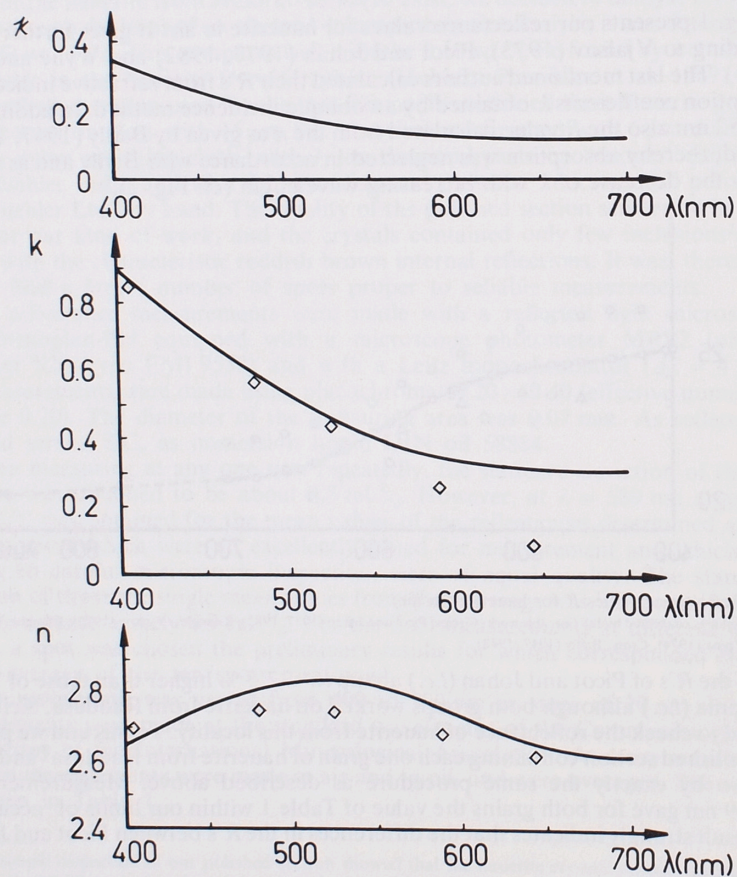


Fig. 2. Optical constants of hauerite
Full lines: this work; Rhombs: Wylie and Ypma (1974)

the physical basis of his method is considerably different from that of the papers dealt with here.

Refractive indices n and absorption coefficients k were calculated from our R 's and mR 's using the formulas of Koenigsberger (1914). Thereby allowance was made for the dispersion of the refractive index of the immersion oil — e.g., $\lambda = 400$ nm: $n = 1.537$, $\lambda = 589$ nm: $n = 1.515$, $\lambda = 700$ nm: $n = 1.510$, all at 23°C (Patzelt 1975).

Considering the 95% confidence region of our average R 's and mR 's, the errors of the n 's are estimated to be ± 0.03 in the whole range of wavelengths, those of the k 's also to be ± 0.03 in the violet, but to increase to ± 0.17 in the far red. This estimation is based on the calculation of a greater number of n 's and k 's with different combinations of errors in the R 's and mR 's. Weakly indefinite values for k were obtained only in the far red, and only when combining there a positive error in R with a negative one in mR , the worst possible combination of errors. The systematic errors of the R 's and mR 's caused by the quality of the surface, the measuring device, the error in the reflectance values of the standard, etc. are very hard to estimate (cf. Piller and von Gehlen 1964, Embrey and Criddle 1978). We think that they should be in any case as large as our standard deviations given above.

Fig. 2 gives our values for n and k of hauerite as a function of the wavelength, together with the values of Wylie and Ypma (1974). It further gives our α values ($k = n \cdot \alpha$).

A remarkable feature of our results is a flat, but highly probably real, maximum in the curve of the refractive index at $\lambda = 520(10)$ nm with $n = 2.85(3)$. In the plot of the n 's of Wylie and Ypma (1974) this maximum shows up considerably less convincingly. Taking into account the always relatively large errors in n - and k -values derived from reflectances, our results seem to be in satisfactory agreement with those of Wylie and Ypma (*l.c.*). The largest discrepancies occur for the k 's in red light where, however, the errors are especially large.

Acknowledgements. Hauerite from Jeziórko was kindly supplied by Prof. Dr W. Żabiński, Kraków. Thanks are also due the "Fonds zur Förderung der wissenschaftlichen Forschung" Austria for the optical equipment, and to Doz. Dr G. Kurat for permitting measurements on the electronmicroprobe apparatus of the "Naturhistorisches Museum" Vienna.

REFERENCES

- BAILLY R., 1947: Utilisation des radiations infra-rouges dans les recherches minéralogiques et en particulier pour la détermination des minéraux opaques. *Bull. Soc. Franç. Miner.* 70, 49–152.
 BAILLY R., 1948: Infrared light for mineral determination. *Amer. Mineralogist* 33, 519–531.
 CAYE R., MEDENBACH K., 1971: Die Bestimmung des Brechungsindex transparenter Minerale durch die Messung ihres Reflexionsvermögens. *Leitz-Mitt. f. Wiss.u. Technik* 5, 155–158.
 CHATTOPADHAY T., SCHNERING H.G. von, 1982: Electron density distribution in MnS_2 and SiP_2 with pyrite structure. VII. Intern. Conf. Solid Compounds of Transition Elements (Grenoble). Abstract No. 187.
 EMBREY P.G., CRIDDLE A.J., 1978: Error problems in the two-media method of deriving the optical constants n and k from measured reflectances. *Amer. Miner.* 63, 853–862.
 HUBICKA-PTASIŃSKA M., NIEĆ M., ŻABIŃSKI W., 1969: Hauerite from Grzybów (Poland). *Bull. Acad. Polon. Sci., Sér. géol. géogr.* 17, 97–101.
 KOENIGSBERGER J., 1914: Über Messungen des Reflexionsvermögens und Bestimmung der optischen Konstanten. *Ann. Physik* 43, 1205–1222.
 LARSEN E.S., BERMAN H., 1934: The microscopic determination of the nonopaque minerals. *U.S. Dept. Interior, Geol. Survey Bull.* 848.
 LUTZ H.D., KLICHE G., HAEÜSSLER H., 1981: Lattice vibration spectra. XXIV. Far-infrared reflection spectra, optical and dielectric constants, and effective charges of the pyrite type compounds FeS_2 , MnS_2 , $MnSe_2$, and $MnTe_2$. *Z. Naturforschung* 36a, 184–190.
 OSMÓLSKI T., PILICHOWSKI E., 1978: Hauerit oraz problemy koncentracji manganu w ilach ba-

- denu zapadliska przedkarpackiego. (Hauerite and problems of manganese concentrations in Badenian clays of the Carpathian Foredeep.) *Arch. Miner.* 34, 5–18.
- PATZELT W., 1975: Leitz-Immersionssolnash DIN 58884. Leitz, Mitt. Labor Anwendung Mikro, Nr. 81.
- PICOT P., JOHAN Z., 1977: Atlas des Minéraux Métalliques. Paris: Mémoire B.R.G.M. No. 90.
- PICOT P., JOHAN Z., 1982: Atlas of the Ore Minerals. (Transl.: J. Guilloux, Revisor: D.H. Watkinson.) Orleans and Amsterdam: B.R.G.M. and Elsevier.
- PILLER H., GEHLEN K. von, 1964: On errors of reflectivity measurements and of calculations of refractive index n and absorption coefficient k . *Amer. Miner.* 49, 867–882.
- RAMDOHR P., 1975: Die Erzminerale und ihre Verwachsungen. Berlin: Akademie-Verlag.
- STEVENS E.D., LUCIA, M.L. DE, COPPENS P., 1980: Experimental observation of the effect of crystal field splitting on the electron density distribution of iron pyrite. *Inorg. Chem.* 19, 813–820.
- UYTENBOGAARDT W., BURKE E.A.J., 1971: Tables for Microscopic Identification of Ore Minerals. Amsterdam–London–New York: Elsevier.
- VAUGHAN D.J., 1971: Aspects of Structure and Bonding in the Iron Sulfides and Related Minerals. D. Phil. Thesis, Univ. of Oxford. (Zited after Vaughan D.J., Craig J.R., 1978: Mineral Chemistry of Metal Sulfides, Cambridge: University Press, esp. p. 113).
- VJALSOV L.N., 1973: Spektri Otrasczenija Rudnich Mineralov. Moscow: Akad. Nauk SSSR. (Zited after Ramdohr P., 1975: Die Erzminerale und ihre Verwachsungen. Berlin: Akademie-Verlag, esp. „Tabellen neuer Reflexionswerte“ p. 14).
- VOGT H., CHATTOPADHYAY T., STOLZ H.J., 1983: Complete first-order Raman spectra of the pyrite structure compounds FeS_2 , MnS_2 and SiP_2 . *J. Phys. Chem. Solids* 44, 869–873.
- WYLIE A.G., YPMA P.J.M., 1974: Determination of optical parameters – n and k – of absorbing minerals with the microscope: I. Isotropic minerals. *Econ. Geology* 69, 1300–1327.

Anton BERAN, Josef ZEMANN

STAŁE OPTYCZNE HAUERYTU W ŚWIETLE WIDZIALNYM

Streszczenie

Pomierzono zdolność refleksyjną hauerytu z Jeziórka (Polska) w powietrzu i w imersji przy długościach fali 400–700 nm. Na podstawie uzyskanych wyników obliczono stałe optyczne n , k i κ . Dla współczynnika załamania n występuje przy $\lambda = 520(10)$ nm spłaszczone maksimum z wartością $n = 2,85$ (3). Jak można było oczekiwać na podstawie intensywnej czerwono-brunatnej barwy, jaką wykazują okruchy hauerytu w świetle przechodzącym, współczynnik absorpcji k maleje ze wzrostem długości fali, lecz nachylenie odpowiedniej krzywej jest mniejsze, niż wynika to z danych z literatury.

OBJAŚNIENIA FIGUR

Fig. 1. Zdolność refleksyjna R hauerytu (w powietrzu)

Kwadraciki połączone linią ciągłą: dane z tej pracy; kółka: Picot, Johan (1977, 1982); trójkąty: Vjalsov (1973); romby: Wylie, Ypma (1974); krzyżyk: Bailly (1947, 1948)

Fig. 2. Stałe optyczne hauerytu

Linie pełne: ta praca; romby: Wylie, Ypma (1974)

Anton BERAN, Йозеф ЗЕМАНН

ОПТИЧЕСКИЕ КОНСТАНТЫ ГАУЕРИТА В ВИДИМОМ СВЕТЕ

Резюме

Измерялась отражательная способность гауерита из Езюрка (Польша) в воздухе и в иммерсионной среде при длине волны 400–700 нм. На основании полученных результатов были вычислены оптические константы n , k и κ . Для коэффициента преломления n наблюдается при $\lambda = 520/10/n$ м сплюснутый максимум с величиной $n = 2,85$ (3). Как можно было ожидать на основании густо красно-бурого цвета осколков гауерита в проходящем свете, коэффициент адсорбции k уменьшается с ростом длины волны, но наклон соответствующей кривой меньше, чем это следует из литературных данных.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Отражательная способность R гауерита (в воздухе).

Квадратики, соединенные непрерывной линией: данные из настоящей работы; кружочки: Пикот, Йохан (1977, 1982); треугольники: Вяльсов (1973); ромбы: Уили, Илма (1974); крестик: Байли (1947, 1948)

Фиг. 2. Оптические константы гауерита.

Непрерывная линия: настоящая работа; ромбы: Уили, Илма (1974)