

Reflecting Powers of Some Metallic Sulphides.

By

Kwan'ichi Asagoe and Naoichi Kumagai.

(Received November 21, 1925)

Certain sulphides of metals in the natural state, having high metallic lustre, have very interesting optical properties. These were studied by Königsberger and Reichenheim, Coblenz, Crandall, and Coblenz and Kahler, working in the infra-red region, and by Horn, Drude and Müller in the visible region¹.

With respect to the reflecting powers, Coblenz² measured them for the sulphides of zinc, iron, lead and antimony in the infra-red region. Recently Tyndal³ investigated the reflecting powers in the visible region of molybdenite, stibnite, galena and iron pyrite by using a Lummer-Brodhun spectrophotometer with contrast field, and compared the reflectivities of the samples with that of a fresh silver mirror deposited chemically, the angle of incidence being about 20°. For the measurements of reflection at incidence of 45°, a small right angled prism of glass was used as a standard. Quite recently, the ultra-violet reflectivities of the four metallic sulphides, molybdenite, stibnite, galena and pyrite have been investigated by Coblenz and Hughes⁴. But we regret we were not able to consult their report.

It is the purpose of our present investigation to study the reflecting powers of some metallic sulphides in the ultra-violet region; the samples employed being iron pyrite, chalcopyrite, zinc-blende, molybdenite, stibnite, argentite and galena.

1 Phys. Rev., (2), **21**, 162 (1923).

2 Bullet. B. S., **2**, 457 (1907).

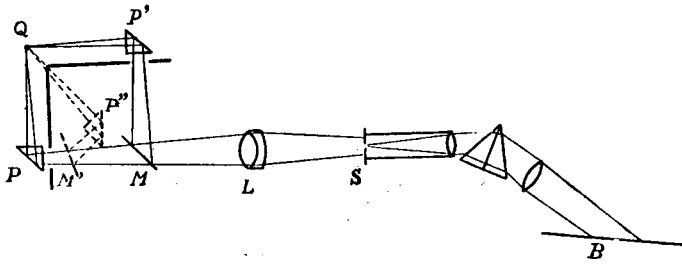
3 Phys. Rev., (2), **21**, 162 (1923).

4 Sci. Pap. B. S., No. **493**, 577 (1924).

METHOD AND APPARATUS.

The apparatus employed in the present experiment is shown diagrammatically in Fig. 1. P and P' are two total reflecting quartz prisms which were cut from one piece of quartz in order to ensure the same optical conditions. Both prisms are of equal size, the length of hypotenuse of the triangular section being 1.3 cm. Each prism was fixed upon a rotatable wooden stand, whose axis of rotation coincided with the vertical line passing through the centre of the hypotenuse face of the prism. Q is a point source of light, and P and P' are each placed at a distance of 15 cm. from Q , the angle PQP' being 90° .

Fig. 1.



As the source of light, the so-called John's electrodes were first tried, but the result was not satisfactory, and after some trials, it was decided to employ a condensed electric spark between tungsten electrodes. The spectrum of the tungsten spark is rich in lines in the ultra-violet, and besides this these electrodes have the advantage of keeping the light source steady and constant for some twenty minutes.

The condensed electric spark was produced by an electric discharge from a condenser of a capacity of about 0.008μ F through an ordinary oscillating circuit consisting of a coil of certain self-induction and the spark gap, the condenser being charged by a Thordarson transformer of 1 k V A giving 15000 volts in the secondary.

The source and the rotatable stands upon which the prisms are attached are so mounted on a small square wooden table that P , P' and Q are in the same horizontal plane which contains the axes of the condensing lens L and the collimator of the spectrograph. The two totally reflected pencils PM and $P'M$ thus obtained are in good symmetry.

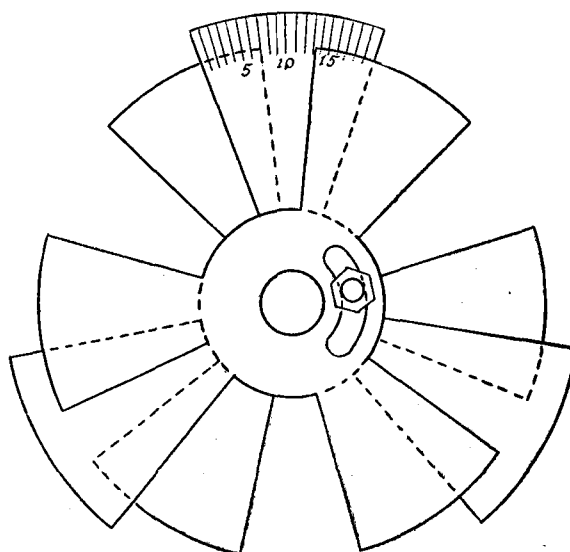
A piece of crystal whose reflecting power is to be measured was crushed into small pieces and from such pieces one having a sharp edge was selected. Such piece of crystal is placed at M in such a position that the surface bisects the angle PQP' and the upper sharp edge of the mirror

is at the height of the horizontal line passing through the centre of the total reflecting prism. The surface, then, reflects off the lower half of the beam P'M, and letting the upper half of PM pass over the sharp edge, and the two beams combine into a complete pencil, in which, of course, the lower half is less intense than the upper half. This complete pencil is brought into the chamber of the Hilger quartz spectrograph by an achromatic lens L of a fluorite-quartz combination; the mirror being focussed on the slit of the collimator.

Thus, upon the photographic plate B, two parallel horizontally dispersed line spectra of the source are impressed, the upper spectrum being due to the direct light and the lower one to the reflected. In order to determine photographically the reflecting power of the sample for monochromatic rays, the intensity of the direct light should be weakened gradually by means of a rotating sector T placed between the light source and the prism P, the aperture of the sector being varied.

The rotating sector consists of three circular plates of brass, each of which has three angular apertures of 80° at equal angular distances of 40° . Of the three plates, one (rad. = 5.5 cm.) is somewhat larger than the other two (rad. = 5 cm. each). One sector of the former is divided into 20 equal divisions at its periphery. (see Fig. 2.)

Fig. 2.



These three plates, having the larger one in the middle, are clamped through a shaft of steel at their centres, the larger plate being firmly fixed

to the shaft, and the whole aperture can be adjusted by fixing the smaller two properly to the larger one. Thus the total aperture can successively be increased by 6° (1.67% of 2π) to the maximum value of 240° (66.7%).

This sector was driven by a small motor, the number of rotations being varied from 300 to 400 per minute.

Now, according to Schwarzschild, the relation between the blackness of a photographic negative and the time of exposure is given by

$$B = Kt^p \dots\dots\dots (1)$$

provided the exposure be normal; where K is a constant depending on the intensity of light, p is called the Schwarzschild constant and depends upon the kind of photographic plate employed. Other workers have found that within the limit of experimental errors, the index p may be taken as unity.

In our case, if θ is the total aperture of the rotating sector, the true time of exposure of the direct light during the rotation of time t is

$$t' = \theta n / \omega \cdot t \dots\dots\dots (2)',$$

where ω is the angular velocity and n the number of rotations of the sector per unit time. And since

$$\omega / n = 2\pi,$$

(2)' becomes

$$t' = \theta / 2\pi \cdot t \dots\dots\dots (2).$$

The blackness of the spectrum impressed by the direct light is given by

$$B' = at' \dots\dots\dots (3)$$

and that by the reflected light is

$$B = aRt \dots\dots\dots (4),$$

where R is the reflecting power of the mirror and a is a common constant. And if $B = B'$, then

$$Rt = t' = \theta / 2\pi \cdot t.$$

Therefore

$$R = \theta / 2\pi \dots\dots\dots (5),$$

that is, the reflecting power is given by the total aperture of the sector divided by 2π .

To determine the curve of the reflecting power, a comparison of the blackness of the photographic negative in the upper and lower spectra was made by observing the spectral lines through a magnifying glass, and the points where the spectral lines in both spectra had nearly the same blackness were plotted for all sets of spectra. In order to test the correctness of this procedure, the reflecting power of a chemically prepared silver surface was first investigated, the plate thus obtained is reproduced in Fig. 11. Comparing this with the curves shown in Fig. 3, it will be seen that the

result obtained by this method coincides fairly well with those of previous observers. Thus this method is valid. The following experiments, then, were started.

By this arrangement, we can thus measure the reflecting power of the mirror at the angle of incidence of 45° , and also by removing P' to P'' , and M to M' as shown by the dotted lines in Fig. 1, the reflecting power at 20° or at a more acute angle of incidence can be determined.

RESULTS.

The reflecting powers of the seven metallic sulphides, viz., iron pyrite, chalcopyrite, zinc-blende, molybdenite, stibnite, argentite and galena, were determined at the angle of incidence of 45° . The results obtained will be described below.

1. Iron Pyrite (FeS_2)

Crystals of iron pyrite have very bright surfaces. But there are many lines on the surfaces parallel to one of its edges. A good optical surface could not be found among the natural crystals. Hence a surface corresponding to a 100 face of the Pentagonal Hemihedry class of the Regular System, was polished with pitch and rouge, and this was examined. The resulting surface had still many pits and scratches, and was inferior to the natural crystal surface in lustre. It was found, however, impossible to remove entirely these imperfections after several attempts of polishing. Therefore, the mirror measured was of the second quality, consequently it was expected beforehand that it might have a poor reflecting power. Curve A in Fig. 4 is for this mirror. The reflectivity of the same sample investigated five days after being polished is shown by Curve B in Fig. 4. This decrease in the reflecting power, especially in the part of shorter wave-lengths, indicates that iron pyrite gradually tarnishes in open air. Curve C in Fig. 4 shows Tyndal's result for a natural crystal surface.

2. Chalcopyrite (CuFeS_2)

The natural surfaces of the crystal were usually tarnished. A piece of the crystal was polished with pitch and rouge. A fairly good plane surface was eventually obtained, but it was very soft. The reflecting power was very poor as shown by the curve in Fig. 5. A slight maximum and minimum are noticed at the wave-lengths about 2500\AA and 3300\AA respectively. One of the photographic plates obtained for this sample is reproduced in Fig. 12.

3. Zinc-blende (ZnS)

A good surface of a crystal was obtained by splitting and this was

used for the experiment without further polishing. The surface corresponded to a 110 face of the Tetrahedral Himihedry class of the Regular System. Between the wave-lengths of 4500\AA and 2300\AA , the reflecting power is nearly constant for about 40 per cent, but the curve makes a sudden depression at 2200\AA .

The sample, after having been kept in a desiccator for four months, was again examined, and the result is shown by Curve B in Fig. 6. This decrease in the reflecting power may probably be due to the change of the surface conditions which arose within these four months. One of the total reflecting prisms, P', was removed to a new position P'', (see Fig. 1.), and this mirror was again investigated at 20° incident angle. Curve C in Fig. 6 shows the result.

4. Molybdenite (MoS_2)

This mineral is very soft. A mirror was prepared by splitting some of the mineral with a sharp knife edge. The surface obtained which was considered to correspond probably to a 0001 face of the Hexagonal System, was free from any visible pits and scratches, but not a perfect plane. The experiment, therefore, was only of qualitative. The result obtained, however, well coincided with the record of Tyndal in the region common to us, as indicated in Fig. 5.

5. Stibnite (Sb_2S_3)

The natural cleavage surface, a 010 face of the Rhombic System, obtained by splitting was an almost perfect plane. This surface is very soft, and even brushing with cotton may produce fine scratches. The reflecting power for the region of wave-lengths larger than 3000\AA , is very good, reaching to 80 per cent. But it begins to decrease gradually and finally diminishes to 30 per cent at 2000\AA . Fig. 9 shows the comparison with the result obtained by Tyndal. The difference between the two curves may probably be due to some differences in the surface conditions of his and our samples.

6. Argentite (Ag_2S)

The sample was obtained from Besbee, in Arizona. This mineral had been tarnished to a dark gray colour. This was filed to a plane and polished with pitch and rouge, giving a bright mirror, but the surface was of the second quality. Several attempts to remove the fine scratches were unsuccessful. The reflecting power of this mirror was very poor as indicated by Fig. 10.

7. Galena (PbS)

A newly split cleavage of a natural crystal has high lustre. But a

perfect plane could not be found among the many pieces obtained by cracking a crystal. However, a crystal face parallel to its 100 surface of the Halohedry class of the Regular System, was polished with pitch and rouge. A highly polished plane surface free from visible imperfections was obtained. But the mirror was very soft, a number of scratches were readily produced on its being rubbed with cotton. The reflecting power for this mirror is shown by Curve A in Fig. 7.

In the ultra-violet region, the reflecting power is rather better than that for visible light, but it seems to decrease suddenly in the region of wave-lengths shorter than 2200\AA . The curve shows a maximum at 2500\AA . The result obtained by Tyndal for a newly split surface is shown by Curve D in Fig. 7. There is good agreement in the two results.

As with zinc-blende, this sample was also examined again four months after the first experiment. Fig. 7, Curve B and C show the results, for 45° and 20° incident angles respectively.

DISCUSSION OF RESULTS.

1. A certain similarity was found to exist in the curves for galena, zinc-blende and chalcopyrite, i. e., they all show a maximum reflection in the neighbourhood of a wave-length of about 2500\AA . That this phenomenon is not due to some peculiarity of the method can be easily recognized by the fact that the other substances examined by the same procedure did not show this phenomenon. It may, therefore, be considered that this phenomenon is a genuine property of the samples.

2. Galena showed the highest reflecting power of all the substances examined, in the region from 3500\AA to 2200\AA . An optical surface of this mineral may be readily prepared by ordinary polishing with pitch and rouge, but the surface gradually tarnishes in air. The advantage of its use in optical instruments requiring the reflection of light of short wave-lengths is obvious. But from a practical point of view, this desideratum can not be realized, for this mirror surface is very soft, even brushing with cotton may produce a number of fine scratches.

3. Metallic sulphides are generally photoelectric active substances. One of the purposes of our experiments with these substances was to examine whether there existed some relation between the photoelectric activities and the reflecting powers, or not. The results obtained, however, do not suggest that any definite relations existed between them.

4. The reflecting powers of the samples examined are generally very poor and have a tendency to sudden decrease in the region of the spectrum of wave-lengths shorter than 2200\AA . But whether this fact is true or not

is yet undetermined. Because, such photographic plates as the Orthoprocess plates employed in our experiment decrease remarkably their photographic sensibility for the extreme ultra-violet light, and hence the validity of the Schwartzschild law in this region is quite doubtful. Therefore, in order to determine accurately the reflecting powers of the samples in this region, it would be necessary to use the Schumann plates or ordinary plates bathed in a fluorescent oil.

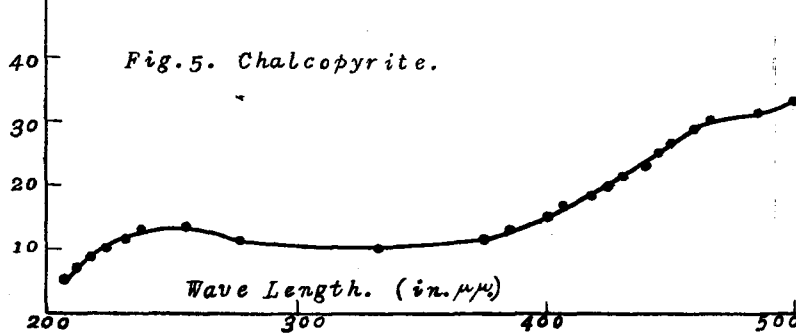
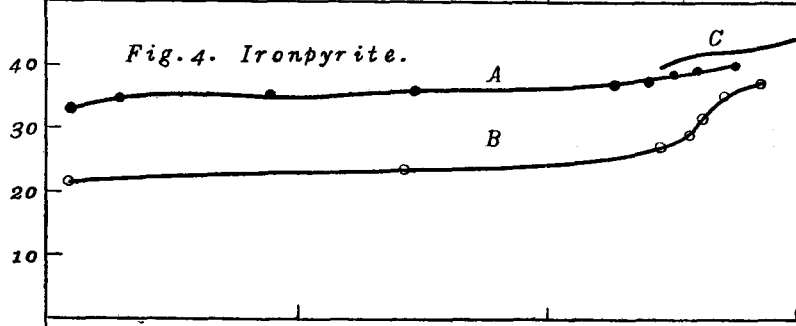
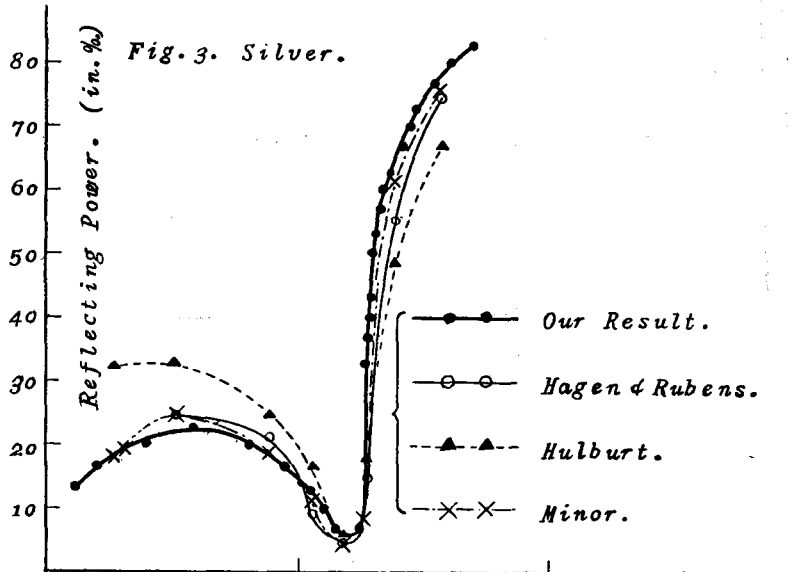
SUMMARY.

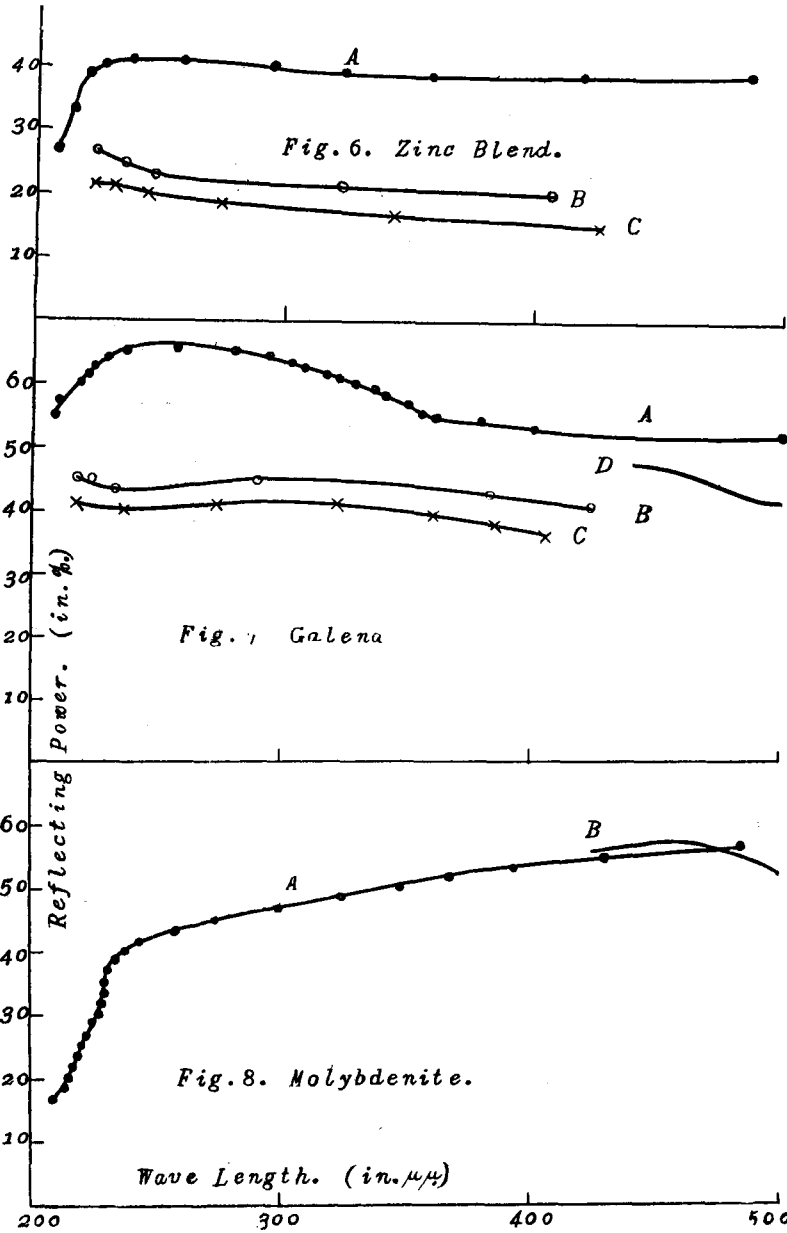
1. A simple method of measuring the reflecting power of metallic mirror was devised. By examining the reflectivity of a chemically deposited silver mirror, it was found that this method gave fairly accurate result.

2. The reflecting powers of the metallic sulphides, — iron pyrite, chalcopyrite, zinc-blende, molybdenite, stibnite, argentite and galena, — were investigated in the region from 5000\AA to about 2200\AA , the angle of incidence being 45° . The results were shown by curves. Galena and stibnite were found to have considerably high reflecting powers for the ultra-violet light.

3. Four months after the first experiment zinc-blende and galena were again examined for 45° and 20° incident angles. The results show that a decrease occurred in the reflecting power, which might apparently be due to the tarnishing of the surface during that period.

In conclusion, we wish to express our hearty thanks to Professor M. Kimura for his kind guidance.





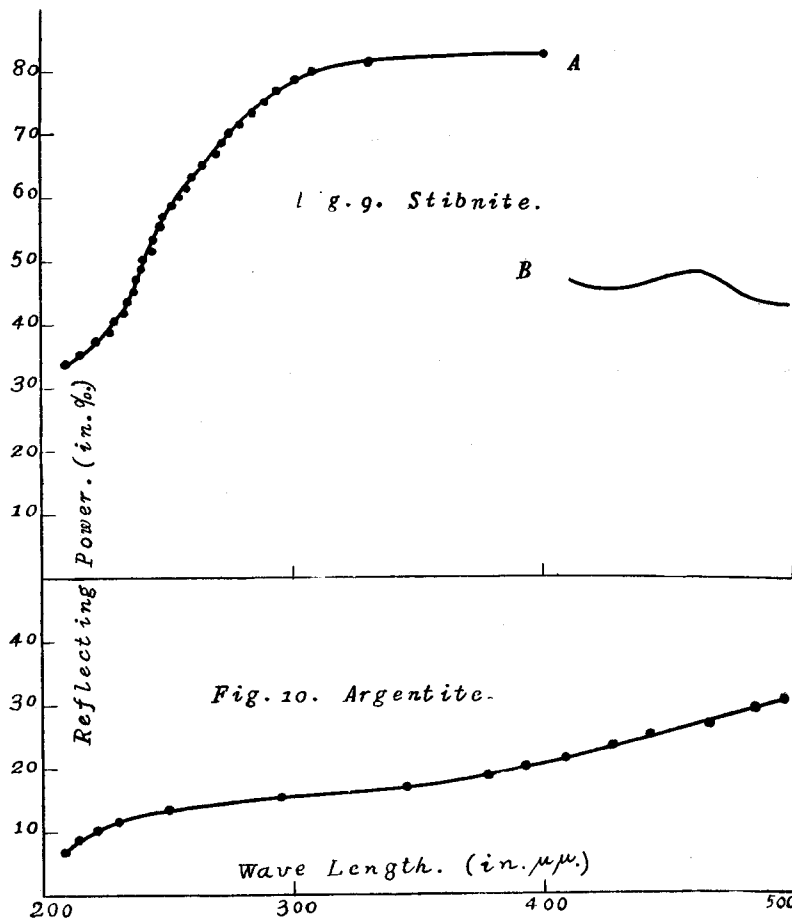


Fig. 11. Silver.

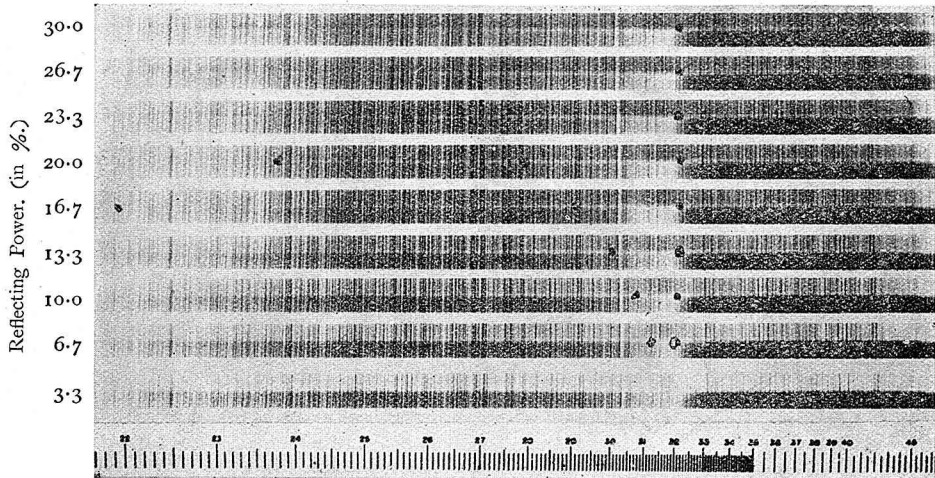


Fig. 12. Chalcopyrite.

