WAVE-LENGTH-SENSIBILITY CURVES OF CERTAIN CRYSTALS OF METALLIC SELENIUM; AND A PARTIAL EXPLANATION OF THE COMPLEXITY OF LIGHT-ACTION IN SELENIUM CELLS.

By L. P. Sieg and F. C. Brown.

IN a recent paper[1] it was shown that there was no apparent characteristic wave-length-sensibility curve for light-sensitive selenium, except when that selenium was made light-sensitive under very definite physical conditions. Some of these conditions have recently been worked out and published by Dieterich[2]. The conclusion seemed advisable if not necessary that the selenium in the selenium cell must be made up of a varying crystal structure, and that in some way the varying characteristics could be explained in terms of the individual crystal units composing the selenium. The recent production by one of us of several crystals of large size[3] has made it possible to obtain further evidence as to the manner in which the individual crystals might explain the variations in mass selenium. In the present work we have studied the wave-length-sensibility curves of a number of crystal forms and have already obtained curves which can explain most of the variations found in selenium. As predicted in our former paper we have found these crystals to have directive axes in the property of light-action as well as in the property of light transmission and crystal structure.

The method for obtaining the wave-length-sensibility curves was in the main the same as that described in our former papers. However for adjusting to equal energy throughout the spectrum the procedure was altered to permit of more rapid working. An aluminium sector disc was calibrated in use with a given Nernst glower, in such a manner that a particular setting of the sector for a corresponding wave-length always allowed the same energy to fall on the thermopile or the crystal as desired. For comparative work with different crystals this method was very satisfactory indeed. From time to time the energy values were checked just prior to each light exposure on the crystal, and as these results

---

[1] Phys. Rev., N.S., Vol. 4, p. 48, 1914.

[2] Phys. Rev., N.S., Vol. 4, p. 467, 1914.

[3] Phys. Rev., N.S., Vol. 4, p. 85, 1914.

checked and because crystals of like character always gave the same sensibility curves under the same conditions, it was certain that no important errors accrued from the method used.

Some of the crystals were not sensitive enough to be used with short periods of illumination. For this reason all crystals were compared for illumination of 30 seconds' duration. Just what differences exist because of varying periods should be investigated in connection with the rates of change as designated in previous papers.

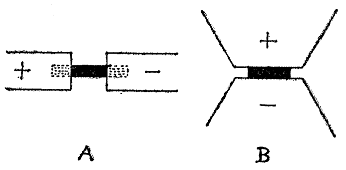

Fig. 1.

The light-sensibility of the crystal was obtained when it was placed between electrodes of the same material as diagrammed in Fig. 1. Both silver and brass electrodes were used at different times, but thus far there does not appear to be any importance to be attached to the material or the structure of the electrodes. In one apparatus, designated *A*, the crystal was pressed against a glass plate by two silver electrodes acting on the ends of the crystal. The illumination could thus be applied to either the front or the back side of crystal, as well as to the edges of the crystal. In the apparatus, *B*, the entire crystal was clamped between brass electrodes. It is to be noted that in the apparatus *A* the light acts directly on the part of the selenium that is not under pressure by the electrodes and that conversely the crystal when placed in apparatus *B* was under pressure at the place of illumination. Further on will be mentioned slight modifications of these methods of clamping. It will appear that the advantages of any one method will depend largely on the shape of the crystal to be used and the crystal face to be illuminated.

COMPARATIVE RESULTS WITH INDIVIDUAL CRYSTALS AND WITH SELENIUM CELLS.

At different times we have shown that light-sensitive selenium is not a simple substance but a complex mechanism and we have taken the view that the complexities arise from more or less elementary constituents. This requires that the atom of selenium can not be the sole unit in the mechanism acted upon. The information that we have thus far is very strong evidence that the variation of the properties of light-sensitive selenium is inherent in the crystals that compose it, that these crystals by virtue of their form, position and location determine the properties of the selenium mass. The reader will we believe become at once sympathetic to this view by a casual observance of the wave-length-sensibility curves in Figs. 2*a* and 2*b*. Fig. 2*a* is taken from our former paper[1] and represents the characteristic curves of various varieties of light-sensitive selenium as found in selenium cells. Fig. 2*b* represents the characteristic sensibility curves of individual crystals, which differ in crystal form or differ as to the direction of the crystallographic axis with regard to the direction of illumination. We do not claim to have exhausted the list of crystals or possible curves that might be obtained with individual crystals. In fact some crystals already discovered have not been investigated because of their insufficiently large size. However the resemblance between the two sets is striking indeed. Both show some curves with a maximum in the ultra-violet, and both show the same range of the maximum in the extreme red. The only lack of agreement is in the fact that we have not yet discovered that crystal which has a distinct maximum in the region of .55 μ, such as found in the typical Dieterich cell. And along with this fact it must be noted that we have examined no crystal which in any position showed a diminishing sensibility at the blue end of the spectrum. In making these comparisons we have made no allowance for the enormous difference in the reflecting power of the selenium in selenium cell from that of the crystal. The former absorbs about 98 per cent. of the light in all parts of the spectrum, while the

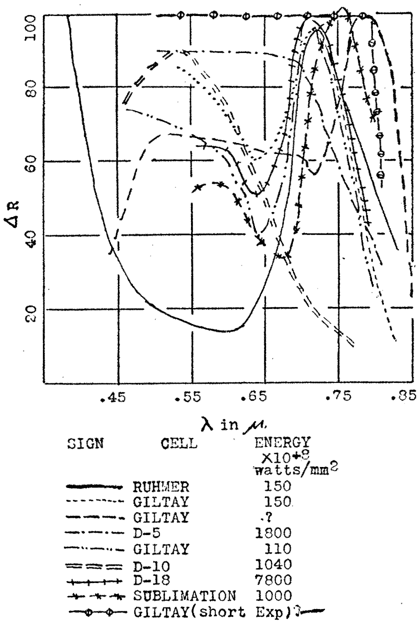

Fig. 2*a*.

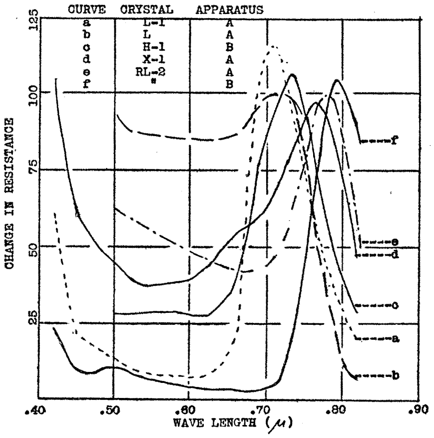

Fig. 2*b*.

---

[1] Loc. cit.

latter probably does not absorb more than 60 to 70 per cent. of the incident light. What may be the consequences of this difference is not certain. It will of course be advisable to measure the absorption constant of the crystals.[1] In as much as the selenium in mass does not show a very great selective absorption and since the shifting of the red maximum is almost identical with the selenium crystals and the selenium mass, it is not expected that the crystals will show much of a variation in reflecting power in this region.

In what ways the crystals give rise to varying sensibility curves will be taken up in the remainder of the paper.

EACH CRYSTALLINE FORM HAS A DISTINCTIVE CHARACTERISTIC CURVE.

Before asserting that each crystalline form of selenium has characteristic photo-electrical properties, it is advisable to know that the character of the curve is not altered by other physical conditions which might vary in the experiments. For example it was determined that the direction of current flow did not alter the sensibility curves when the illumination was on the same part of the crystal. Since it had been shown by one of us[2] that the resistance might vary by a factor of several hundred depending on the pressure on the crystal, there was considerable doubt as to whether the pressure might control the character of the sensibility curves. In fact we mentioned in one of our former papers that a part of the variations in the selenium cells might be accounted for by variations in the pressure on the selenium as it was placed on the cell form. We therefore placed an acicular hexagonal crystal between the electrodes of apparatus *B* and mapped out the sensibility curves when the pressures were of such a magnitude that the conductivity increased by a factor of 50 to 1. The intensity of illumination and other physical conditions were unchanged. The results of the investigation are shown by the two upper curves in Fig. 3. There is no evidence of any change in the position of the maximum or in the ratio of the values of the maximum to the minimum as a result of the change in pressure.

Since Pfund and ourselves had observed an ironing out of the maximum in certain selenium cells by diminished illumination it was thought advisable to see if the sensibility curves underwent any change when the intensity of illumination was varied. We used the same crystal and apparatus just mentioned above. These comparison curves are also

---

[1] Recently a preliminary test was made to determine the reflecting power of these crystals throughout the spectrum. This was found to be practically constant, and probably between 30 and 40 per cent, thus agreeing with the values of Foersterling and Freédericksz (Amer. d. Phys. 43, 1227, 1914) for metallic and amorphous selenium mirrors.

[2] PHYS. REV., N.S., Vol. 4, p. 93; 1914.

shown in Fig. 3. Again there is no apparent change in the curves due to varying intensity. This result is particularly important at this point because it has not been determined if there is a variation of the reflection coefficient in different crystals or along different axes of the same crystal. If there is such a selective variation we have no means of knowing just what is the relative amounts of energy absorbed when we can measure only the incident energy. Unless the selective variation is of some magnitude, we can be reasonably certain that the amount of light absorbed by the crystal does not concern the character of the sensibility curve. Of course electrical theory requires that the reflection constant should vary with the conductivity of the material. But since the resistance of these crystals is so large, it is believed that the reflection due to the free or conducting electrons is small compared to the reflection by the charges in the bound atomic structure. The values of the intensity in Fig. 3 are for the incident energy. The values of the absorbed energy must be many times smaller, but even if the absorbed energy does vary by a factor of fifty the ratios of the absorbed energy surely can not be enough different to make any material error in the conclusions that we have drawn, concerning the independence of light-action and the pressure effect.

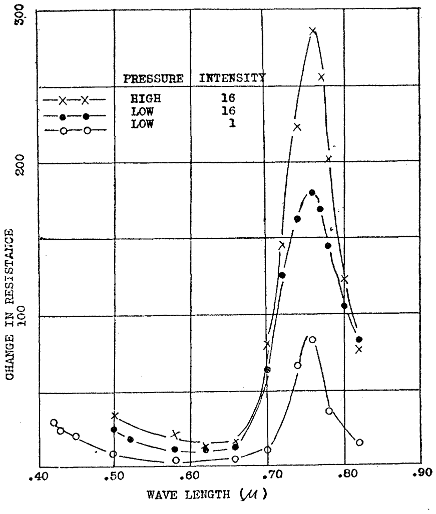

Fig. 3.

It has been shown[1] for selenium cells and also for single crystals that the resistance varies greatly with the electromotive force across the selenium. It is sufficient to mention here that we could not observe any change in the sensibility-curves due to a variation of the resistance by use of varying potential differences between the electrodes.

In the formation of the crystals there were sometimes variations of 20° or 30° in the oven temperature. As nearly as could be discerned such temperature treatment did not alter the sensibility curve of a given crystal form.

Having shown that the preceding conditions did not alter the character

---

[1] Paper by Brown and Stebbins, Phys. Rev., 26, p. 273, 1908 and Brown, Phys. Rev., 33, p. 1, 1911, and other paper not yet published.

of the sensibility curves, we proceeded to investigate the variation of the sensibility curves for the different crystal forms. For this we selected three specimens which were of sufficient size for the purpose. One (*L*–1) was a lamellar crystal[1] with axes perpendicular to the edges. Its size was about 4 × 2 × .2 mm. A second was of the acicular hexagonal form (*H*–2), of size about 10 × .4 × .4 mm., and the third was a combination of crystals that had grown out from a central hexagonal spine. The angles and the form of this are not yet known, but the crystal is probably of the second crystal system. Crystals of the above types are shown in the above articles referred to.

The lamellar crystals were placed in apparatus *A* and illuminated perpendicular to either of the large flat surfaces. In either case the sensibility was that shown by the upper curve in Fig. 4.

The acicular crystals were placed in apparatus *B*. They were illuminated perpendicular to the axis of the crystal. It was apparently immaterial as to which of the six faces were illuminated. The curve for this type showed a sharp maximum in the same place as that for the lamellar crystal (see *H*–2, Fig. 4), but it was very much sharper and its magnitude was relatively much greater than for the lamellar crystal.

The third crystal showed a maximum at wave-length .7 μ, but it was not as sharp as that of the acicular crystal (see *X*–1, Fig. 4). It should be mentioned that all the curves in this paper are drawn each to an arbitrary scale, so that the relative sensibility of each crystal can not be ascertained from the curves. In the crystals just referred to however the sensibility was of the same order of magnitude in each.

THE SAME CRYSTAL GIVES DIFFERENT CURVES WHEN ILLUMINATED ALONG DIFFERENT AXES.

Previously we have shown the crystals to be doubly refracting.[2] Electrical theory requires that any material having directive axes in its optical properties in this way, shall also show directive properties in any phenomena involving electro-optical interactions. Simply stated if a crystal shows electrical phenomena as a result of light acting upon the crystal as a crystal and not as an element, the electrical phenomena should vary when the illumination is along different axes. On the other hand if the light action should be on the atoms without regard to the crystal mechanism it is not conceivable how there could be any difference in the sensibility curves arising from illuminating different sides of the crystal providing the reflecting power is constant.

---

[1] For further information about these crystals see papers by Brown, PHYS. REV., loc. cit., and by Brown and Sieg, Phil. Mag. (6), Vol. 28, p. 497. 1914.

[2] Brown, loc. cit.

Several crystals were investigated as to the conductivity change when illuminated along different axes. The best specimen was a lamellar crystal 4 × 2 × 0.2 mm. The large surfaces were rectangular and approximately parallel. We were not able to determine the angles of the edge faces.

When the illumination was directed on either of the large faces as shown by the arrow, marked 1 (Fig. 5), the sensibility began to increase rapidly at wave-length .66 μ and held a broad maximum with the mean position at .74 μ. At λ = .80 μ there was a very large sensibility. By illuminating either of the short edges of the crystal the sensibility had just started to rise at λ = .74 μ, the position where with side illumination the maximum occurred. In this instance the maximum was very sharp and located at .79 μ. In the infra red beyond wave-length .82 μ this edge of the crystal was more sensitive relatively to the minimum than was the flat surface at its maximum. When either of the longer edges was illuminated as shown by arrow 3, the maximum was at .76 μ. Thus a single crystal may have its maximum shifted at least five wave-lengths by changing the side of the crystal that is illuminated. We carefully observed that the direction of current flow made no difference in these experiments.

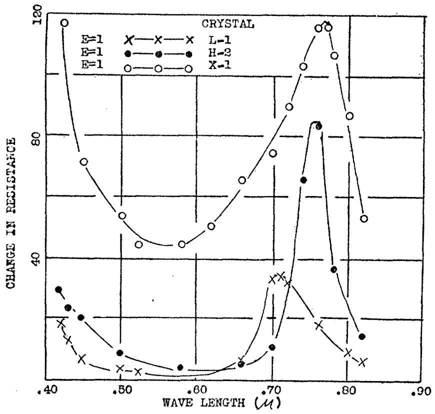

Fig. 4.

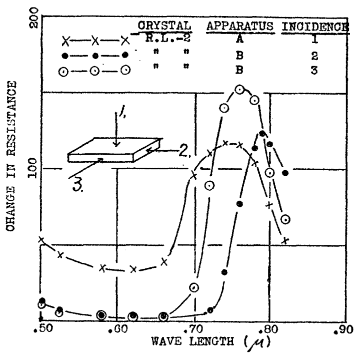

Fig. 5.

It is altogether improbable that the variation of the selective absorption plays an important rôle in giving these different sensibility curves. If so the results are consitent with the idea that the light acts upon the crystal structure rather than upon the atoms. However this mode of explanation of the shifting of the maximum can be sidestepped perhaps if we wish, by attributing the shift toward the longer wave-lengths to transmitted action as will be explained in the last section of this paper.

THE ACTION OF POLARIZED LIGHT.

We have made some observations on the action of polarized light, the significance of which is satisfying only in a general way. The experiments were called forth after we had investigated the effect of varying the angle of incidence on a lamellar crystal. By such variations of the angle of incidence, sensibility curves were obtained for different angles as indicated in Fig. 6. For an angle of about 60° there was a decided change in the character of the curve but for angles larger or smaller the curve form was almost unchanged. It was thought that this might be about the angle of maximum polarization, and that consequently only one component of the light might enter the crystal at this angle.

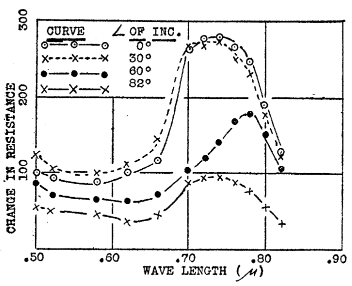

Fig. 6.

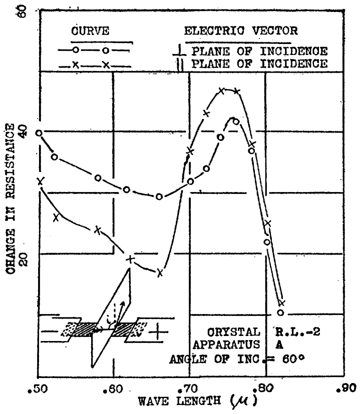

Fig. 7.

We therefore tried first light polarized in the plane of incidence and then at right angles to this plane. For all angles of incidence except 60° there was no change in the character of the sensibility curve, but at about this angle the effect of light polarized in opposite planes was quite different. When the electric vector (see Fig. 7) of the light was perpendicular to the plane of incidence the sensibility curve was much like that shown for the same angle shown in Fig. 6. But when the electric vector was parallel to the planes of incidence the maximum was relatively much broader and higher than in the previous case.

A part of the difference between the location of the maximum in Figs. 6 and 7 may have arisen from the fact that we had no accurate means of setting the angles.

We are concluding from our experiments first that our Hilger monochromator partially polarizes the light that passes through it and secondly that under certain conditions a given intensity of illumination may produce different results depending on its state of polarization.

THE DIRECT AND THE TRANSMITTED ACTION OF LIGHT.

Recently we have shown[1] that the seat of light action in selenium crystals is distributed throughout the crystal, and that light may alter the conductivity of a crystal 10 mm. or more away from the point of impingement. At that time we had not succeeded in determining whether this action could be transmitted from one crystal to another. Now we have gone further and found not only that the action of light can be transmitted from one crystal to another, but we have also mapped out the sensibility curve for such indirect action and compared it with the direct action, where the light falls on the part of the selenium between the electrodes.

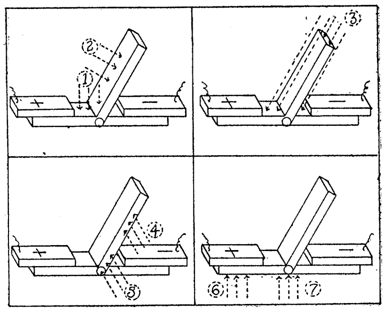

Fig. 8.

We chose for this work a lamellar crystal to the middle portion of which was grown another crystal. This crystal and the apparatus *A* are shown in a very highly conventionalized way in Fig. 8. The dotted arrows show the portions that were illuminated. Wherever any or most of the light fell upon the part of the crystal carrying the current it was called direct action as indicated by the change of conductivity of the crystal. Contrarily if the light impinged on any part of the crystal that did not carry the current, the light effect was designated as transmitted light action.

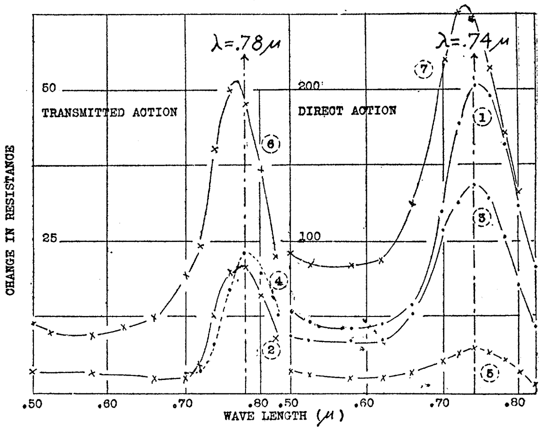

Fig. 9.

In Fig. 9 are shown the sensibility curves, on one side for the trans-

---

[1] Phil. Mag., Ser. 6, Vol. 28, p. 497, 1914 and Phys. Rev. n. s., Vol. 4, p. 85.

mitted action of light and on the right side for the direct action of light. It may be seen that in positions (1), (3), (5) and (7) Fig. 8 the light acts directly on the part of the selenium that directly takes part in the conductivity. The corresponding curves in Fig. 9 show the maximum in all cases to be at about .74 μ. But when the conductivity is altered by transmitted action as by the impingement of the light at positions (2), (4) and (6) the maximum is shifted to = .78 μ. Also it should be noted that in the transmitted action the ratio of the maximum to the minimum is of the order of 5 to 1 while in the direct action this ratio is only about half as great. Thus the position and the relative magnitude of the maximum depend on whether the light impinges directly on the part of the crystal that conducts or whether the change of conduction takes place at a distance from the point of impingement. Of course it is impossible to say what constitutes direct action or to separate entirely the two actions in the so-called direct action. This latter difficulty arises partly from the fact that a part of the light is always absorbed near the surface and does not penetrate all the conducting selenium even in the most favorable condition. Thus if we could obtain and isolate the direct action completely we might find the maximum at considerably shorter wave-lengths than we have indicated.

In this connection an interesting experiment that suggests itself is to see if the thickness of the selenium in the selenium cell determines the position of maximum sensibility. Thus the selenium blocks studied by White[1] should show a maximum far out in the red, because most of the change of conductivity by light in these blocks must be an indirect or transmitted action.

---

[1] Phil. Mag., Ser. VI, Vol. 27, p. 370, 1914.