WAVE-LENGTH-SENSIBILITY CURVES FOR LIGHT SENSITIVE SELENIUM AND THEIR SIGNIFICANCE.

BY F. C. BROWN AND L. P. SIEG.

IN our last paper[1] we showed that the sensibility curves for one of Giltay's cells was distinct and different from any that had been obtained by other investigators. Since then we have investigated a number of light-sensitive varieties made by Giltay, Ruhmer, Dieterich, and ourselves, and have found the interesting result that selenium as such does not have a characteristic sensibility curve. Such results will be set forth in this paper. Further we shall allude to the fact that the magnitude and position of the maxima of sensibility in the spectrum can be controlled by the treatment of the selenium in the process of making. Incidentally it will be shown that there is an interesting correlation between the change of resistance and intensity of illumination for short exposures no matter what the characteristic curve may be. Lastly we shall indicate the bearing of our results upon the theory of light-action in selenium.

GENERAL CONSIDERATIONS.

The phenomena of light action in selenium are almost unique, and it is for this reason that we should expect any theory of value to incorporate all the diverse phenomena that appear in this element. Of course we shall ultimately wish to explain the conductivity as well as the structure of selenium on the basis of the electron theory. Thus far an analysis reveals that any electron theory that is based on a single type of curve of sensibility is doomed to failure. And as a corollary to this we may say that any electron theory that presupposes only one light sensitive constituent in the selenium is also doomed to failure. For an analysis of exposure and recovery curves for a number of specimens of selenium has revealed that there are at least three components in selenium, at least two of which are acted upon by the light. The results of this paper are quite in agreement with such a complex structure of selenium, although we can not devise the necessary assumptions to determine if the three components are sufficient.

[1] PHYS. REV., N. S., Vol. 2, p. 487, 1903.

Mr. E. O. Dieterich[1] has been led by his researches in this laboratory to believe that the differences in the characteristics of light-sensitive selenium are purely the result of different crystal formations. His argument is very direct and will be presented as soon as his data are completed. Also it may be mentioned that we have produced two new crystal forms of very large size by subliming selenium at the same temperatures at which selenium cells are annealed. This makes it reasonable to assume that these same crystals with perhaps others also are in a more or less stable condition mixed together in light-sensitive selenium.

It is of little avail to select a single sample of selenium made by a particular treatment of the selenium, for the purpose of deducing the nature of light action, because all samples of light-sensitive selenium contain a mixture of certain components, some or all of which may bear direct relations to crystal formations. Any particular pressure, temperature, or time treatment only alters the relative amounts of the components present.

APPARATUS AND METHOD OF MEASUREMENT.

Apparatus.—The general method described in our former paper[2] was followed. The apparatus was improved by the substitution of a Hilger monochromatic illuminator in place of the one by Spindler and Hoyer. In the Hilger apparatus the lenses were 32 mm. or $f/5.6$ in diameter, as compared with the $f/12.7$ of the Spindler and Hoyer apparatus. We were thus able to augment our energy with a given slit width by approximately 5 times. As in the former work the source of light was a Nernst filament kept at practically constant intensity by supplying it with current from storage cells. The filament, while designed for use with 110 volts, was over-volted to about 120 volts, in order to increase the intrinsic brilliancy. The image of the glower was focused upon the first slit of the monochromatic illuminator. In front of this slit was placed a sectored disc, and an optical wedge, either of which, or both could be used to reduce the intensity of the light. The bundle of quasi-homogeneous light coming from the second slit of the illuminator (this slit was kept of the same width as the first one, usually about 0.7 mm.) fell upon a concave silvered mirror. This latter, together with the thermopile, and the selenium cell, was located in a light-tight box. This mirror could be rotated from without, so as to throw the focused image of the slit upon either the thermopile or the selenium. If it was desired to

[1] This work has just been completed and will soon be published.

[2] Loc. cit.

cover the whole cell with diffused light, the cell had merely to be drawn out of focus. Thin glass plates of the same thickness covered the thermopile and the selenium cell.

The thermopile, of the linear Rubens type, was one of the new series-parallel instruments of Bi with an alloy of Bi and Sn, made by Dr. W. W. Coblentz.[1] Its resistance was 2.25 ohms. The galvanometer used with the thermopile was of the Thomson type, made by Siemens and Halske. With its coils in parallel its resistance was 1.35 ohms. The sensibility depended of course upon the period, and with a period of about 6 sec., which we usually employed, its sensibility was about 5×10^{-10} amp. With this thermopile-galvanometer arrangement, a deflection of 1 mm. was obtained on a scale at a distance of 125 cm. when an incident energy of 4.4×10^{-8} watts/mm.^{2} covered the thermopile strip. This latter determination was made with a calibrated carbon lamp at a distance of 2 meters, in accordance with the instructions in the certificate of the Bureau of Standards. In our experiment the area of the focused image of the slit was only 1/7 the area of the thermopile strip. Hence a deflection of 1 mm. in our actual experiments indicated an energy of 7×4.4 or 30.8×10^{-8} watts/mm.^{2} upon the thermopile, and hence upon the selenium cell.[2]

One other device should be described. This was the arrangement by which we could expose the selenium cell at a certain moment, and then throw in the galvanometer for a certain short time. The same device that opened the shutter from in front of the Nernst glower, operated a trigger that released a pendulum. As this pendulum started moving it removed a shutter, thus exposing the cell. As soon as desirable after this operation (usually at once) a key was thrown by this same pendulum thus connecting a galvanometer in circuit. At a certain time later a second key was tripped, disconnecting the galvanometer. The change of resistance could thus be determined by the galvanometer throw for a short interval and at any reasonable time after the exposure of the selenium. The selenium was placed in one arm of the Wheatstone bridge, in which various E.M.F.'s were used. In some cases long exposures were made, but unless otherwise indicated our curves are for mean exposures of 0.4 seconds. In either the long or short exposures we employed the same galvanometer described in our previous paper.

[1] PHYS. REV., N. S., III., p. 59, 1914.

[2] A correction should be made to the footnote of our previous paper, Vol. II., p. 489. While a deflection of 1 mm. meant an energy of 9.3×10^{-8} watts/mm.^{2}, using the total area of the thermopile, the area of the image of the slit was, in this case, about 1/6 of that of the thermopile strip. Then in our previous experiments 1 mm. deflection corresponded to 6×9.3, or 55.8×10^{-8} watts/mm.^{2} upon the thermopile, and hence upon the selenium. So our present arrangement is approximately twice as sensitive as was the former.

As in our previous work, care was taken to adjust for equal energy throughout the observations for each curve. Possibly equal energy is not the proper basis upon which to compare light actions, but at any rate it is the most definite and fundamental basis upon which to work. While equal energies were obtained as determined by the thermopile, the question might nevertheless be raised as to whether equal values of the energy penetrated and acted upon the selenium. If the selenium were selectively reflecting this would be a serious source of uncertainty. However, in connection with a separate investigation we measured the amount of energy reflected from the surface of the selenium in a typical cell for which we determined the characteristic curve and we found that for each wave-length the total reflected energy was only a little more than one one hundredth of that incident of the selenium. Thus it appears that a selenium cell is a fairly good black body. We shall deal with the optical properties of selenium in a separate paper.

Effect of Varying Slit Width.—As is well known, the beam of light from a monochromatic illuminator is only a quasi-homogeneous beam, and its non-homogeneous character becomes more and more evident as the red end of the spectrum is approached. Any curves for such an apparatus can be corrected with considerable definiteness[1] for the slit width, although the calculation is rather a laborious one. In view of the labor involved in the calculation, it was thought best to try first an experiment to test the extent of the inaccuracy that arises from the use of a finite slit width.

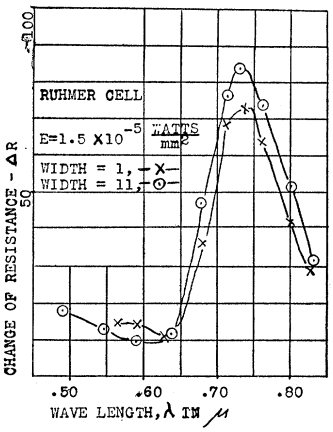

Fig. 1.

Fig. 1 represents the results of this experiment. The two curves are clearly indicated in the figure, the one for a very narrow slit with (about .14 mm. on both the collimating and focusing telescope) and the other for the unusual slit width of about 1.5 mm. The slit width was thus varied by about a factor of eleven. By means of the rotating sector the energy intensity was lessened to correspond to that of the narrow slit, thus giving the same change of conductivity in the selenium at wave-length $\lambda = .64\ \mu$. There is no special significance to be attached to the slight variation of the magnitude of the maximum. It merely indicates that there are small outstanding errors that nullify any necessity for

[1] Paschen, Ann. d. Phys., 60, 712, 1897.

making slit width corrections. Having justified the use of such a wide slit width, we believe ourselves perfectly secure in our results which were usually obtained with slit widths of 7 mm. This gave us a maximum of energy with a negligible error from spectral impurity.

Effect of the Order of Exposure.—Thinking that the shape of the curves might vary slightly with the order of exposure to the light of varying periodicity, an experiment was tried the results of which are shown in Fig. 2. First a curve was taken for a Ruhmer cell by the usual procedure, *i. e.*, by measuring the sensibility at the shortest wave-length first and then proceeding step by step to the reading for the longest wave-length. Then this procedure was exactly reversed by taking the sensibility for the longest wave-length first and going backward. We concluded from these curves and a number of other cases where it was advisable to check readings that the order of exposure made no material difference. However, a little greater reliability was attached to the first order of exposure. The curves given in this paper are substantially correct. After readjusting our apparatus and replacing some of the cells, we were able to duplicate results with surprising accuracy.

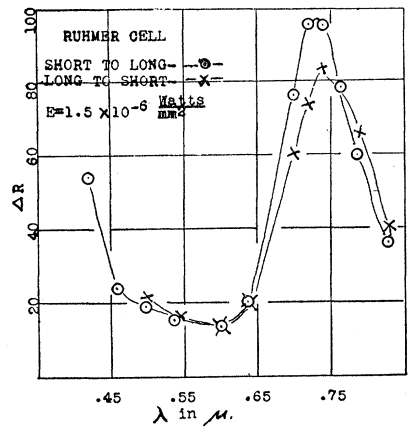

Fig. 2.

THE CHARACTER OF THE SENSIBILITY CURVES.

General.—When this work was begun it was believed that sensibility-wave-length curves obtained by using short exposures should for all varieties of selenium show the same characteristics, providing that the rapid changes in selenium always arise from a common light-action on one component of the selenium. Or conversely it was believed that the sensibility curves should be complex, providing that the rapid changes in the selenium by light arise from action on two or more components of the selenium with widely varying rates. It is the converse view that naturally suggests itself following the analysis made by one of the authors.[1]

Fig. 3 shows the various types of sensibility curves which we have obtained with different samples of selenium, and we do not claim to have exhausted the list. The observed changes of resistance recorded on each

[1] PHYS. REV., 33, p. 403, 1911.

curve were taken for exposures of equal intensity, wherever we found that the form of the curve was materially affected by change of energy. The scales for each curve are however arbitrarily chosen, so that the maximum ordinate of each curve lies at about the value 100. Thus the curves serve a purpose resembling a spectrum analysis of an element. The intensity of the lines can be compared with the lines of the same spectrum in order to establish the character of the unknown. In spectrum analysis the amount and the temperature of the element producing the spectrum are matters of secondary importance. Just so the curves in Fig. 3 are characteristic curves, but they neglect to bring out the absolute or even the relative sensibility of the different samples of selenium. The chart accompanying the curves gives the names of the types of cells used and also the energy intensity that resulted in the indicated curves. However it is rather unusual for the character of the curves to change with varying intensity such as had been previously observed both by Pfund[1] and ourselves.[2] Only two of the curves in Fig. 3 showed such a variation. In some instances tests showed the character to be only imperceptibly changed by intensity variations of the ratio of 50 to 1. Furthermore we found that the character of the curves was not necessarily much affected by the duration of exposure. Only two of the eight samples, whose curves we are discussing, showed such large variations. This also is new.

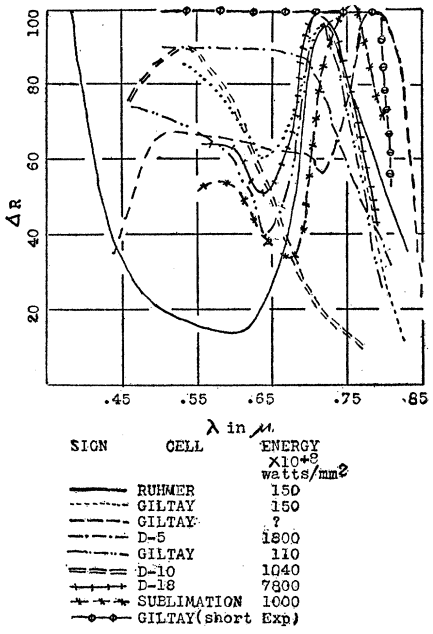

Fig. 3.

It is obvious that there is no characteristic curve to be found by the method of procedure that we followed. A Ruhmer cell in vacuum indicated a maximum in the ultra-violet too far out for us to locate, and another maximum at .72 μ. This selenium had a broad minimum extending from .55 μ to .62 μ. Recently Mr. Dieterich has succeeded in producing two samples of selenium with a maximum near the ultra-

[1] PHYS. REV., 34, p. 370, 1912.

[2] Loc. cit.

violet. But with these exceptions all samples which have come to our notice decrease more or less precipitously in their sensibility back of .5μ. Many specimens have the indicated maxima at about .7 μ, but this maximum wanders all along to .8 μ, and in the typical Dietrich cell, as indicated in our paper by the letter *D*, this maximum dwindles or disappears altogether. Stated briefly the maximum that so frequently appears in the red, may be controlled both as to its location and its magnitude even to its disappearance. One cell has shown considerable sensibility out as far as .85 μ. Similarly as regards the minimum, which usually occurred about .64 μ. In the Ruhmer cell it occurred back as far as .6 μ and in the selenium whose crystals were deposited by sublimation in a high vacuum, it occurred at .68 μ and in one other cell at even longer wave-lengths. In one of Giltay's cells and also in one of Mr. Dieterich's cells, the fourth and ninth curves respectively in the chart, the minimum did not appear at all. At about .55 μ there was usually a broad maximum but it is observed that this region may contain a broad minimum as well.

Without any further work the conclusion seems obvious that light produces more than one action in the selenium, or in other words there is more than one component or kind of selenium if you please existent simultaneously in the selenium cell.

The Giltay and Dieterich Types.—While it is true that both Giltay and Dieterich do make cells of widely varying character, it is nevertheless true that all of Giltay's cells of which we have any knowledge have a pronounced maximum at .69 μ or beyond and a more or less well-defined one in the region of .55 μ. On the other hand Dieterich's samples usually have a very pronounced maximum about .55 μ, and a controllable maximum in the red which may be entirely eliminated by the method of making. This so called Dieterich type is shown by curve *D*, Fig. 4, where the energy intensity was 6.6×10^{-6} watts per mm.^{2} For greater or less illumination intensity, the character of the curve was as far as we could determine identical to this one. In the same figure, the curves G_1 and G_1' are for a typical Giltay cell, where the intensity of illumination varied by a factor of 20 to 1. It is common for the Giltay cells to maintain the same character unaltered for widely varying intensities, just as these curves indicate.

The Effect of Varying Electrical Intensity.—Since it has seemed advisable to regard the selenium as in a state of equilibrium under the action of a number of forces, it is reasonable to expect that an alteration of any one of these forces might alter the form of the sensibility curve. We have yet to test this point particularly for the varying temperature conditions. An examination of the voltage effect shows that the char-

acter of the curve is only slightly altered, while the sensibility is uniformly and materially altered in magnitude. The curve in Fig. 5 indicated by circles shows the characteristic curve of cell D7 for an intensity of 0.1×10^{-5} watts per mm.^{2}, when exposed for 30 seconds. There was a potential difference of 3.5 volts across the selenium. Next this was changed to 0.5 volts and the intensity altered till it produced the same change of resistance at .45 μ as was produced with less intensity and

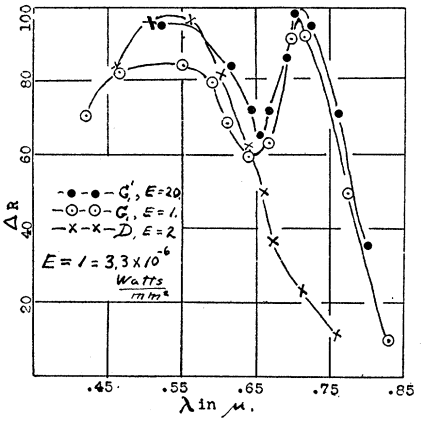

Fig. 4.

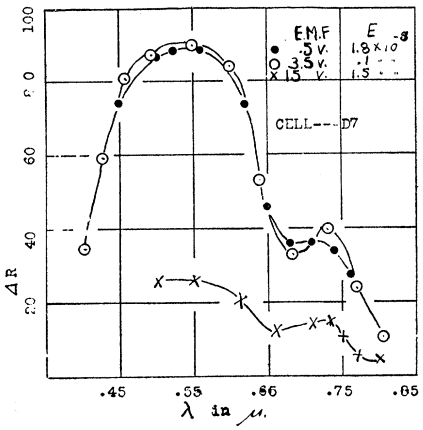

Fig. 5.

greater potential. With this intensity which was 18 times greater the curve indicated by solid dots was obtained. It is to be noted that altering the intensity by a factor of 18 to 1 had the same effect as altering the potential by a factor 7 to 1. However it must also be noted that while the deflections were nearly identical for the sake of comparison, that the absolute change of resistance was only about one seventh in the second case of what it was in the former.

It may be estimated that a change of potential of the order of 50 to 1 will so balance the selenium in this cell that the same absolute change of resistance would be produced when the intensity of illumination is varied by a ratio of 18 to 1. The conclusion is that for this cell the alteration of the electric intensity alters the character of the curve only slightly, but that it makes a large difference in the absolute change of resistance by light. This last point has also been verified in former papers. The lower curve in the figure is for short exposures, and with 15 volts across the selenium. Thus changing the duration of exposure, the electrical intensity and the light intensity does not alter the character of the curves to any definite and marked degree in this particular cell.

The Maxima are Inherent in the Selenium.—Since the well-known

experiments of Pfund and Berndt no one has questioned that at least a great part if not all the light sensitiveness of selenium is in the selenium structure itself and not because of some impurity or selenium compound. Yet when different samples show such widely varying characteristics, the question may well be raised again as to whether impurities do not play an important rôle in prescribing the characteristics. Mr. Dieterich is obtaining a large amount of evidence to prove that impurities are of very secondary importance if they enter at all. One point that may be mentioned is illustrated in Fig. 6. He took a Giltay cell marked "normal G" and subjected it to purely physical treatment, after which the characteristic curves were of the form indicated by curves E_1 and E_{10}, where the illumination intensity varied by a factor of ten. By this treatment which he will relate in detail, the Giltay cell was transformed into a Dieterich cell. It is also worthy of note that the character of the curves was unchanged by a variation of the intensity by a factor of ten. As has been previously pointed out, the selenium components seem to be put in a dynamic equilibrium in the process of making the cell under the action of a number of forces such as heat, and pressure treatment, and further, these components are maintained in equilibrium under a number of forces such as pressure, temperature, illumination, absorbed materials, electrical stress and the crystal formation itself.

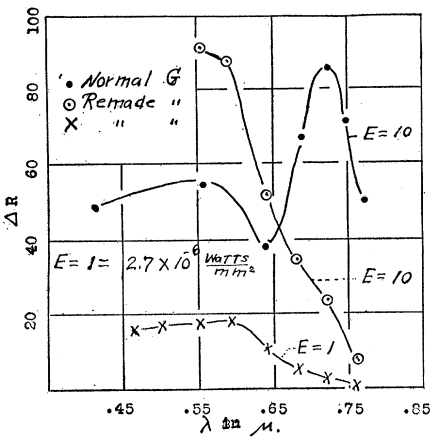

Fig. 6.

That the characteristics of any given specimen are inherent in the selenium itself is yet further verified by the fact that the maximum in the red can be put in or eliminated at will by the heat treatment. And it is expected that the exact conditions will soon be discovered which determine the presence or absence of the maxima in the shorter wavelengths of the visible spectrum and even in the ultra violet. The curves in Fig. 7 are taken from Mr. Dieterich's samples. The remarkable difference in these curves arose solely from the difference in heat treatment during the process of making. In fact he can predict almost without failure what will be the character of a given sample of light-sensitive selenium. It should be noted that the intensity of illumination was the same for all curves in Fig. 7.

The Variation of the Sensibility.—Generally the light sensibility of selenium is regarded as a function of the amount of selenium that has been transferred from the amorphous to the crystalline state. And yet it seems perfectly futile to attempt to explain the enormous variations in sensibility on this basis. The variations so greatly outnumber the possible combinations. Mr. Dietrich has been able to vary the sensibility over a very wide range without altering the character of the sensibility curve, but there seem to be a number of factors entering into the exact control, only a part of which he is aware of. Nevertheless

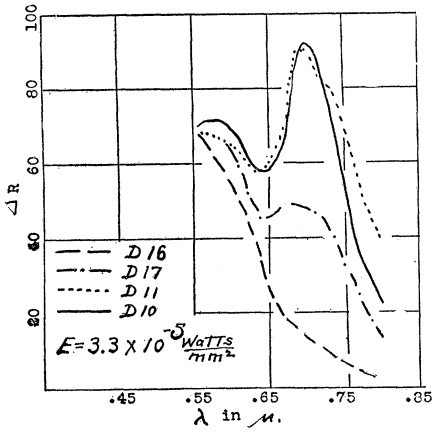

Fig. 7.

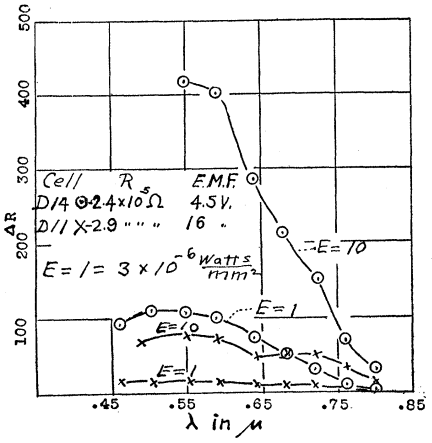

Fig. 8.

he has produced a low resistance cell which shows an effective sensibility at .59 μ about ten times greater than that of any Giltay cell in our possession. Its character is shown by the curve $D14$, Fig. 8, for two intensities varying by ten to one. And again starting with a sample of the same amorphous selenium and proceeding differently with the treatment he produced a cell $D11$ which had about the same specific resistance in the dark and only a slightly different characteristic curve, but its sensibility as can be learned from the curves was only about one twentieth of that of cell $D14$. In making this deduction an allowance must be made for the lower voltage used with cell $D14$.

THE VARIATION OF SENSIBILITY WITH INTENSITY OF ILLUMINATION.

Quite recently Nicholson[1] has made a very able mathematical analysis of certain phenomena in selenium on the basis of one electron theory. Without discussing the reasonableness of his assumptions, it may be of interest to test some of his deduced equations over a wider range than

[1] PHYS. REV., N. S., Vol. 3, p. 1, 1914.

was done in his work. He used only two varieties of selenium and he was only prepared to take exposures as short as 12.5 seconds. In applying his results to his theory he presumed that an exposure of such duration was equivalent in its effect to an instantaneous exposure. We are inclined to doubt this presumption. Our results should have the advantage that comes from a study of a larger number of varieties of selenium and also the advantage of exposures of 0.4 second duration, which more nearly approximate instantaneous effects.

The most critical test of Nicholson's theory perhaps lies in the derived relation between the change of conductivity and the intensity of illumination. This relation is expressed by the equation,

$$d = D \cdot I^{\beta},$$

where d is the change of conductivity, I is the intensity, and D and β are constants. According to Nicholson's theory β should have the value $\beta = 1/2$ for instantaneous exposures in the shorter wave lengths and $\beta = 1$ for the red and infra red, and $\beta = 1/2$ for unlimited exposures throughout the spectrum. The above equation was originally set up as an empirical equation by Pfund.[1] We find justification for the use of the equation when used as an empirical one and applied to any given cell, but we can not see that the simple assumptions regarding absorption, reflection and resonance as given in Nicholson's paper, are sufficient to

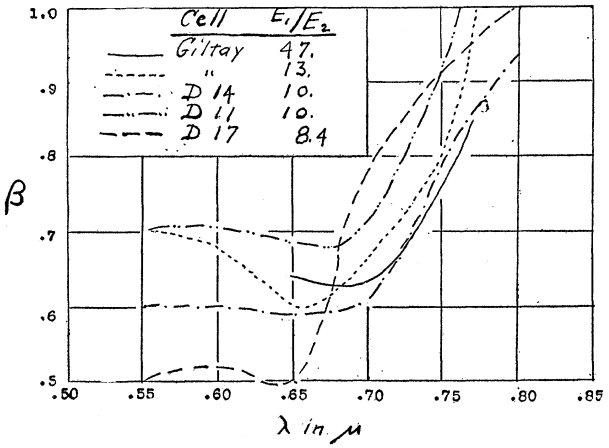

Fig. 9.

explain the varying values of β in the different samples of selenium, nor the variations in a given sample. It must be remembered that the constant β occurs as an exponent, and consequently small deviations in its

[1] PHYS. REV., Vol. 34, p. 370, 1912.

value are of relatively greater importance than relative errors in a multiplying or additive constant.

The manner in which β varies for exposures of 0.4 second for a number of different samples of selenium is shown in Fig. 9. It is rather interesting that cells which gave such widely varying characteristic curves (see Figs. 3, 7, and 8) should show such a general likeness in the variation of the constant β, for the different periodicities of light. It is observed then that β varies in a general way between .5 and 1 for short exposures.

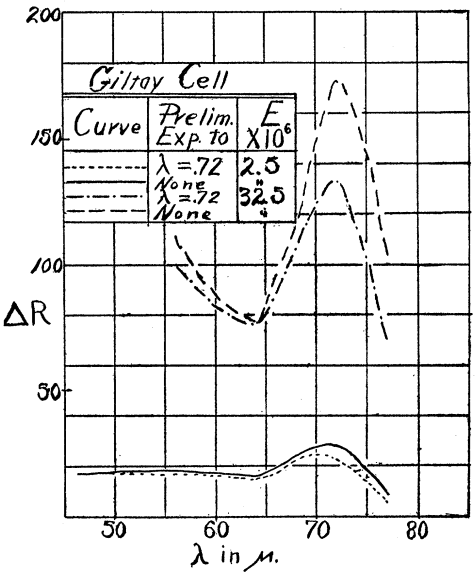

Fig. 10.

An attempt was made to discern whether any change in the light sensibility curve would result if before each wave length-deflection reading was taken, there was made a preliminary exposure to a fixed quantity of energy from a beam of light of a given wave length. Nicholson made exposure tests similar

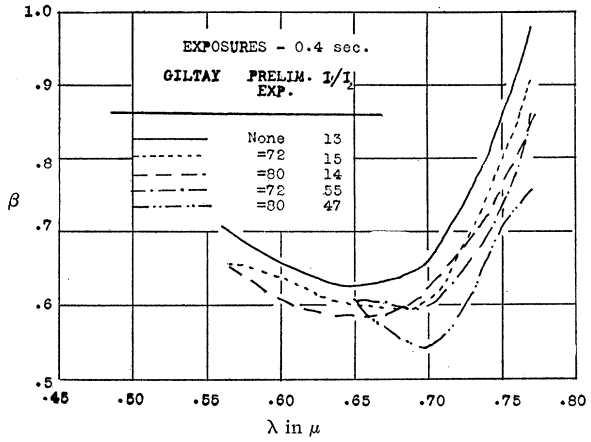

Fig. 11.

to this except that instead of making the additional exposure a preliminary one he left a steady exposure on the cell while he was

running a curve. In both cases the effect is much the same, and has the tendency to blot out the effects due to slow changes of resistance accompanying light-action. The effect of the preliminary exposure was slightly to iron out the maximum. However, the curves relating β and λ are not materially altered by the preliminary exposures. The first of these two results is shown in Fig. 10, connecting the change of resistance and wave-length; and the second point covering the variation of β and λ is shown in Fig. 11.

CONCLUSIONS.

The analysis made some time ago on the basis of the rates of change in the selenium, showed the structure of the selenium to be complex, consisting of three components in the specimens studied. Now we have made an analysis on an entirely different basis, that of the character of the sensibility curves, and our analysis reveals again a structure at least as complex as that revealed formerly by other samples of selenium. We are not yet able, however, in the latter analysis to set up a simple set of postulates whereby we can subject our analysis to a mathematical test as was done formerly. As far as can be seen our analysis requires at least two separate light actions in the selenium.

No doubt the action of light in any of the components is of such a nature that electrons are made free when one component changes to another, because the former analysis into several varieties of light sensitive selenium required that electrons be made free but in no case did it require the recombination of electrons. Knowing that the structure of light sensitive selenium is complex, and knowing what we do about the nature of this complexity we should now perhaps be in a position to apply the electron theory to an explanation of the phenomena.

We have isolated a number of new crystal forms of selenium by sublimation of selenium in a high vacuum. The conditions which determine what kind of crystals will form must be very definite, for we have had very large crystals of different forms grow up within a millimeter distance of each other where the temperature and pressure could not have varied greatly. In free unhampered space some of these crystals have a length of more than ten millimeters. We know of four formations of crystal selenium that are doubly refracting when formed in a vacuum. Whether the crystals in the selenium cell are doubly refracting we are not quite sure, and yet one cell made by the formation of crystals directly from the vapor state must have contained some doubly refracting crystals. The point that we wish to make here is that crystals which are directive in their structure towards light should also be directive in their electrical

properties and if these crystals are instrumental in the conduction they should alter the conductivity differently depending upon their positions. If so we must in explaining the light sensitiveness of selenium allow for the formation of crystals either with axes pointed promiscuously or in consistently varying directions. Add to this a mixture of crystals in more or less stable equilibrium as to form and position and we have we believe a basis on which all the light electric properties of selenium may be worked out.

Previous results on the effect of abrasion[1] and on the pressure effect on the electrical conductivity indicated in a very marked degree that the slow changes accompanying light-action were the result of crystal changes. There was doubt concerning the seat of the rapid changes. It was conceded that perhaps light might expel electrons from the atoms in the transformation of one component to another. If in this present work we had found a single or slightly varying position of maximum spectral sensibility, we might have been justified in concluding with Pfund and others that the primary thing is the liberation of electrons from atoms of selenium. But if there is one significant conclusion that can be accepted as a result of the variation of the sensibility curves, it is that light does not act on the atoms as units. Rather a larger unit, no doubt of the order of a crystal unit, is the seat of the disturbance by light action. We are compelled to recognize crystal boundaries when dealing with the flow of electrons in selenium, possibly also in other elements. Otherwise there is no apparent basis for the unification of our knowledge.

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[1] Phys. Zeits., Nov. 15, 1912.