The pressure effect in selenium crystals and its relation to the light effect

Ernest Otto Dieterich
State University of Iowa

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THE PRESSURE EFFECT IN SELENIUM CRYSTALS
AND ITS RELATION TO THE LIGHT EFFECT.

By E. O. Dieterich.

A Thesis
submitted to the faculty
of the
Graduate College
of
THE STATE UNIVERSITY OF IOWA
in partial fulfillment of the requirements for the degree
of
Doctor of Philosophy.

June 14, 1916
INTRODUCTION.

The recent discovery by F.C. Brown\textsuperscript{1}) of a method by which large perfect crystals of selenium may be produced has added impetus to the study of the interesting electrical and mechanical properties of this element in the crystalline, so-called metallic, form. As a result of some of these investigations Brown\textsuperscript{2}) has proposed an explanation of the nature of electric conduction in metallic selenium. According to this theory, which is very similar to J.J. Thomsom's doublet theory of electrical conduction in metals, the conductivity of selenium may be altered in two ways; namely, by a change in the rate of emission of conducting electrons from the atoms, or by a change in the rate of recombination of these electrons with the positive residues. The theory was proposed as a result of certain experiments which confirmed the assumptions made. However, the experimental evidence upon which the conclusions were based considered only the effect of light in changing the conductivity of selenium under differing conditions of pressure and voltage. Since then, Mrs. Dieterich\textsuperscript{3}) has shown that the light effect under different conditions of temperature is in agreement with the theory.

The following investigation was undertaken for the purpose of studying the effect of pressure in changing the conductivity of selenium, to test out the theory more completely in that direction, and to correlate the effect of light and pressure. To accomplish this, the recovery of selenium crystals was studied after their equilibrium conductivity had been changed by a variation in the pressure and light intensity to which they were subjected.
THEORETICAL

Assuming that the conductivity of a crystal of selenium at any instant is directly proportional to the number of conducting electrons present at that instant, Brown has shown that the rate of change of conductivity, when the equilibrium conditions have been disturbed, may be expressed by the equation,

\[ \frac{di}{dt} = -\alpha i^2 \quad (1) \]

in which \( i \) represents the equilibrium conductivity of the crystal under fixed conditions of light intensity, temperature, pressure, and potential difference, and \( \alpha \) is called the coefficient of recombination of the conducting electrons with the positive residues.

This equation was tested in the form,

\[ \frac{\Delta i}{\Delta t} = -\alpha i^2, \]

by a series of experiments in which the crystal was allowed to reach its equilibrium value of conductivity in the light; the light was then shut off and \( \frac{\Delta i}{\Delta t} \) determined, \( \Delta t \) being kept very small, .02 sec. The results showed that in varying intensities of light \( \alpha \) remained constant, justifying the assumption made that \( \alpha \) is independent of light intensity, and has the same value in the dark as in the light.

At equilibrium, \( \frac{di}{dt} = 0 \), for the rate of recombination is then exactly equal to the rate of emission of conducting electrons from the atoms. Writing \( q \) for the rate of emission in the dark, and \( \Delta M \) for the increase in the rate caused by the light, we have, in the dark,

1. Loc. cit.
\( \frac{di}{dt} = 0; \text{ and } q = -\alpha i_c^2; \quad (2) \)

where \( i_c \) is the equilibrium conductivity in the dark. At equilibrium in the light,

\( \frac{di}{dt} = 0; \text{ and } M + q = -\alpha i_l^2; \quad (3) \)

in which \( i_l \) is the equilibrium conductivity in the light. When the light is shut off, \( \frac{di}{dt} \) is equal to the difference between the rate of emission and the rate of recombination, or,

\[ \frac{di}{dt} = q + \alpha i_c^2, \]

But \( q = -\alpha i_c^2 \), hence,

\[ \frac{di}{dt} = \alpha i_c^2 - \alpha i_c^2, \]

\[ = \alpha (i_c^2 - i_c^2). \]

If \( \alpha \) be assumed equal to \( \alpha_i \), as experiment shows to be true, then,

\[ \frac{di}{dt} = \alpha (i_c^2 - i_c^2). \quad (4) \]

Also, if \( i_c^2 \) is small compared to \( i_l^2 \), we may write,

\[ \frac{di}{dt} = \alpha i_l^2. \quad (4a) \]

and, determined by experimental methods,

\[ \alpha = \frac{\Delta i/\Delta t \cdot i^2}{i_l}. \]

From (3) we may write,

\[ i_l = \sqrt{\frac{M + q}{\alpha}}. \quad (5) \]

The last equation shows that a change in conductivity may be produced by a change in either \( \alpha \) or \( M \). Since for increased intensity of light over a wide range \( \alpha \) remains constant, the conclusion is reached that \( M \), the rate of emission of conducting electrons, is changed by a variation in light intensity.

The same argument, leading to exactly the same equation
can be applied to a consideration of the change in conductivity produced by pressure. If, with increased pressure, \( \alpha \) remains constant, we may conclude that the effect of pressure is the same as that of light. If, however, \( \alpha \) is found to have different values, at different pressures, in particular, if the values of \( \alpha \) are such that the product, \( \alpha i^2 \), which represents the rate of change of conductivity, decreases with increasing pressure, it may be interpreted as meaning that the rate of emission of electrons is not being altered, but merely that the rate of their recombination is diminished. For, if the rate of emission were increased, more positive residues would be present, increasing the chances for recombination, and, thus increasing \( \alpha i^2 \). The same considerations, of course, apply to other agencies besides pressure.

It shall be the object of this paper to show, from experimental observation, the definite effect of pressure in altering the conductivity of selenium, and in what way the pressure effect differs from the light effect.
EXPERIMENTAL ARRANGEMENTS AND METHOD OF MEASUREMENTS.

The crystals used were some isolated large ones kindly furnished by Professor Brown who had prepared them by sublimation. They were found to be more satisfactory than masses of crystals in the form of plates on account of their lower resistance and greater sensitiveness to changes in pressure and illumination. Some data taken on plates indicates a behavior identical with that of crystals. The crystals were of several different types, described in the paper first referred to, but since the conditions of their formation were not definitely known no attempt was made to find a relation between the observed effects and the conditions of temperature and pressure under which the crystals were formed. The size of the various crystals was about the same in all cases; the surfaces exposed to light and pressure were roughly equal and approximately 5 sq.mm. in area.

The experimental arrangements are shown in diagram in Fig. 1. The crystal, $Se$, was placed between platinum electrodes in one arm of a Wheatstone bridge circuit. From the upper electrode, at a point very near the crystal, and passing through a hole in the base of the electrodes a long shanked hook was suspended upon which could be hung varying weights, $W$. A constant weight, $w$, of 500 grams, was rigidly fixed to a rod hinged at $A$ in such a manner that it could be allowed to rest upon the upper electrode or be raised some distance above it. This weight was connected to the shaft of the heavy timing pendulum, $P$, by means of a cord passing over the pulleys $pp$. The pendulum served as a means of raising the weight $w$ at the instant of closing the galvanometer circuit for a desired short interval of time - in nearly all
cases this interval had a value of .04 sec. No inaccuracy was intro-
duced by the use of the cord; this was checked up by placing various
resistances in the arm of the bridge occupied by the crystal and taking
a series of galvanometer readings with the weight \( w \) attached to the
pendulum. The deflections were found to be uniform, both for large
and small values, over a period of time much longer than that necessary
to obtain a set of observations on the crystal. The electrodes and
weights were enclosed in a light tight box (a Freas oven) whose glass
doors were covered with a piece of cardboard having a narrow slit, \( S \),
in front of the electrodes. When it was desired to study the light
effect, light from a Nernst glower at a distance of about 75 cm. from
the electrodes was focused on the crystal and was cut off, by means
of a shutter, \( Sh \), carried on a wooden arm attached to the pendulum
shaft, at the instant the key, \( K_1 \), closing the galvanometer circuit
was tripped.

The method of obtaining the recovery during the first
short interval of time following a change in the equilibrium conditions
was as follows. The crystal was allowed to come to the equilibrium
value of conductivity under the existing conditions and the bridge
adjusted so that the galvanometer read zero. \( K_1 \) was then opened, \( K_2 \)
remaining closed. Immediately thereafter the pendulum was tripped;
as soon as it struck \( K_1 \), closing the galvanometer circuit, it also
changed the equilibrium conditions, either by shutting off the light
or by raising the weight, \( w \), or both. The resulting galvanometer
deflection is a measure of the change of the crystal conductivity
during the time the circuit remains closed. To obtain the change
of resistance of the crystal during this interval a resistance, \( R \),
consisting of an adjustable india ink resistance, was substituted for
the crystal and varied until the resulting galvanometer deflection was the same as that obtained for the crystal. This resistance was then measured in the usual way.

Conditions, other than those producing the desired change of conductivity, were kept constant throughout the series of experiments. The readings were all taken at room temperature, and a constant voltage of 14.2 volts was kept across the crystal. The factors which were varied were light intensity and pressure.

The values of \( W \) used ranged from 500 grams to 4000 grams, so that the pressure on the crystal extended from about 10 \( \text{Kg./cm}^2 \) to about 100 \( \text{Kg./cm}^2 \). At pressures higher than 100 \( \text{Kg./cm}^2 \) the crystals became too unsteady and the sensitiveness too low to obtain reliable readings.
DISCUSSION OF RESULTS.

A large number of crystals of several types were investigated; the data obtained was consistent for all, and the measurements could be satisfactorily duplicated at different times. For purposes of comparison all the results given in the tables below refer to a single specimen, a hexagonal prism about 1 mm. thick and 5 mm. long.

The rate of change of the conductivity of the crystal during the first .04 sec. after the equilibrium conditions had been varied was studied under the following experimental arrangements:

1. The crystal was allowed to come to equilibrium in the dark under pressure $W + w$. The rate of recovery following a change in the pressure due to the removal of the weight, $w$, was determined for different values of $W$.

2. The same procedure was followed as that described in (1), except that the crystal was exposed continuously to light of constant intensity.

The behavior of the crystal under these conditions is shown in Table 1, and in the curves in Figures 2 and 3. In Fig. 2 attention is called to the relation between $W$, which is proportional to the pressure on the crystal in the direction of the current, and the conductivity as shown by the curves $A$ and $A'$. $A$ refers to the crystal in the dark, $A'$ to the crystal under fixed illumination. This straight line relation was found in each case for the range of
Table 1.

<table>
<thead>
<tr>
<th>W in grams</th>
<th>(L_1) - cond. in dark (\text{ohms} \times 10^7)</th>
<th>(L_1) - cond. after exposure (\text{ohms} \times 10^7)</th>
<th>(\alpha L_1^2) (\text{ohms} \times 10^7)</th>
<th>(\alpha L_1) (\times 10^{-7})</th>
<th>(\alpha L_1^2) (\times 10^{-7})</th>
<th>Condition of crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>6.71</td>
<td>4.23</td>
<td>2.48</td>
<td>2.83</td>
<td>127.3</td>
<td>Dark</td>
</tr>
<tr>
<td>1000</td>
<td>8.55</td>
<td>6.91</td>
<td>1.64</td>
<td>1.18</td>
<td>86.2</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>11.86</td>
<td>10.97</td>
<td>.89</td>
<td>.343</td>
<td>48.3</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>15.79</td>
<td>15.00</td>
<td>.79</td>
<td>.172</td>
<td>42.8</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>20.00</td>
<td>12.26</td>
<td>7.74</td>
<td>.737</td>
<td>294.0</td>
<td>Light</td>
</tr>
<tr>
<td>1000</td>
<td>24.90</td>
<td>19.40</td>
<td>5.50</td>
<td>.390</td>
<td>242.0</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>34.10</td>
<td>31.26</td>
<td>2.84</td>
<td>.150</td>
<td>174.0</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>44.00</td>
<td>41.20</td>
<td>2.80</td>
<td>.039</td>
<td>120.0</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.
pressures studied. If the curves are produced back to the conductivity axis they cut this axis at a finite value. That is, at zero pressure the crystal should be conducting. This is consistent with results obtained in previous experiments\(^1\) in which the pressure on the crystals was in the same direction as the current. The so-called selenium cells, constructed as described by Elliott\(^2\), are further evidence that at zero pressure, under definite conditions of temperature, voltage and light intensity, there is a finite conductivity, for in these there is no pressure in the direction of the current, yet the resistance is far from infinite.

B and B' represent the conductivity at the end of .04 sec. after releasing the pressure. The difference in the ordinates of A and B and of A' and B' divided by the ordinates of A and A', respectively, gives us the pressure sensitiveness of the crystal. A steady decrease, both in the light and in the dark, is noted, indicating that at a high enough pressure the pressure sensitiveness becomes zero.

In Fig. 3 curves A and B show the variation of \(\alpha\) with pressure in the dark and in the light respectively. C and D show the corresponding relations between \(\alpha i^2\) and pressure. \(\alpha\), it is seen, shows a marked decrease with \(w\), this decrease being more rapid in the dark than in the light. Although \(i\), the conductivity, increases to a large extent as \(w\) increases, the product, \(\alpha i^2\), which is equal to \(\frac{di}{dt}\), also decreases and, indeed, at a more rapid rate in the light than in the dark. Now, equation(5) shows that a change in \(i\) may be

produced either by a change in $\alpha$ or in $M+q$, the rate of emission of conducting electrons. These experiments show that part of the change, at least, in conductivity is due to a change in $\alpha$. The decrease in $\alpha$ alone, is not sufficient to warrant the conclusion that the only effect of pressure is to vary the rate of recombination, and not the rate of emission, $M+q$. But, taken in connection with the decrease in $\alpha$, the rate of change of conductivity, we may conclude that such is actually the case, for, if pressure increased the rate of emission of conducting electrons one should expect the rate of recovery, $\alpha i^2$, to increase as the conductivity increased, since, on this view, a greater number of positive residues would be formed thus increasing the probability of recombination.

3. The crystal was allowed to reach equilibrium in the light and the rate of recovery due to a change in the intensity of illumination was determined for different values of $W$. Instead of cutting off the light completely, however, as in previous experiments, it was reduced in intensity by the use of a shutter made of a partly darkened photographic plate. This procedure was adopted in order that the light effect so produced might be compared with the pressure effect produced in a similar manner in cases (1) and (2). The results obtained were identical to those obtained when the light was completely extinguished by means of an opaque shutter, except for numerical magnitude.

The results for this procedure are given in Table 2 and in Fig. 4. $\alpha$ decreases, while $\alpha i^2$ shows an increase with pressure, as shown in curves C and B, respectively. Curve A shows that $\alpha i$ remains constant as the conductivity changes. These
Table 2.

<table>
<thead>
<tr>
<th>W</th>
<th>( \dot{w} ) in light</th>
<th>( \dot{w} ) after removing</th>
<th>(( \dot{w} )) \times 10^7</th>
<th>( \alpha \times 10^7 )</th>
<th>( \alpha )</th>
<th>( \alpha \dot{w}^2 ) \times 10^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>15.36</td>
<td>14.36</td>
<td>1.00</td>
<td>.106</td>
<td>1.62</td>
<td>25.00</td>
</tr>
<tr>
<td>1000</td>
<td>19.20</td>
<td>18.05</td>
<td>1.15</td>
<td>.078</td>
<td>1.50</td>
<td>28.75</td>
</tr>
<tr>
<td>2000</td>
<td>28.47</td>
<td>26.70</td>
<td>1.77</td>
<td>.054</td>
<td>1.50</td>
<td>43.75</td>
</tr>
<tr>
<td>3000</td>
<td>38.15</td>
<td>35.90</td>
<td>2.25</td>
<td>.039</td>
<td>1.47</td>
<td>56.40</td>
</tr>
<tr>
<td>4000</td>
<td>47.35</td>
<td>44.40</td>
<td>2.95</td>
<td>.033</td>
<td>1.57</td>
<td>74.00</td>
</tr>
</tbody>
</table>
results show quite clearly the difference between the action of pressure and of light in changing the conductivity of the crystal. The increase in conductivity of the crystal in the light may be ascribed to two causes, namely, a decrease in the rate of recombination of the conducting electrons with the positive residues as the pressure is increased manifested by the decrease in $\alpha$ with increased pressure, and an increase in the rate of conducting electrons which is indicated in the rise in $\alpha_1^2$. The curves in Fig. 5 which show the variation of the light sensitiveness with pressure are to be compared with the curves in Fig. 2. The latter show that the pressure sensitiveness decreases as the pressure rises, while the former show the constancy of the light sensitiveness at different pressures, at least for the range studied. These results are in complete agreement with those obtained by F. C. Brown\(^1\) in similar experiments.

4. The crystal was allowed to come to equilibrium under a constant pressure in different intensities of light, and the rate of recovery due to shutting off the light was determined. The results are summarized in Table 3, and are of exactly the same nature as those found by F. C. Brown in the paper referred to above. $\alpha$ remains constant, indicating a change in the rate of emission of conducting electrons.

5. The crystal was allowed to come to equilibrium under $W + w$ in the light. $w$ and the light were then simultaneously removed and the rate of recovery determined.

Table 3.

<table>
<thead>
<tr>
<th>Intensity</th>
<th>W in grams</th>
<th>&quot;spread&quot; in inches, ( \times 10^2 )</th>
<th>&quot;fold&quot; in inches, ( \times 10^2 )</th>
<th>( s^2 ) in inches, ( \times 10^2 )</th>
<th>( \Delta s ) in inches, ( \times 10^2 )</th>
<th>( \lambda \times 10^7 )</th>
<th>( L \times 10^7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>32.00</td>
<td>30.73</td>
<td>1.27</td>
<td>.031</td>
<td>31.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>26.10</td>
<td>25.20</td>
<td>.90</td>
<td>.033</td>
<td>22.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>19.74</td>
<td>19.29</td>
<td>.45</td>
<td>.029</td>
<td>11.2</td>
<td></td>
</tr>
</tbody>
</table>
The data obtained is shown in Table 4. The behavior of the crystal in this experiment was interesting. When it was kept in the dark and the conductivity changed by a change in pressure it was found to return to its equilibrium value, after the pressure had been restored, quite rapidly; when light produced the change it required a considerably longer time to return to a constant resistance. After a change in both the light and pressure the equilibrium conditions were reached much more slowly than in either of the two preceding cases — where it was a matter of a few minutes in the case of pressure, and not usually more than a quarter of an hour in the case of light, when both were changed the equilibrium value of the resistance was not reached, at times, for hours. Here, again, the dissimilarity of light and pressure in changing the conductivity of the crystal is evident. \( \alpha \) for light shows a very different value than \( \alpha \) for pressure. Also, \( \alpha_i^2 \), the rate of recovery due to light, plus \( \alpha_P^2 \), the rate of recovery due to pressure is not equal to \( \alpha_{LP}^2 \), the rate of recovery due to the simultaneous change of the light and pressure. If the effects were identical and additive in nature one should expect \( \alpha_i^2 + \alpha_P^2 \) to equal \( \alpha_{LP}^2 \). The fact that such is not the case indicates that the increased pressure influences the stability of the atom in such a way as to make the light more effective in expelling conducting electrons from the atom.
Table 4.

<table>
<thead>
<tr>
<th>Condition of crystal</th>
<th>$i_1$ in $\text{m} \times 10^7$</th>
<th>$i_2$ in $\text{m} \times 10^7$</th>
<th>$\Delta i$ in $\text{m} \times 10^7$</th>
<th>$\alpha \times 10^7$</th>
<th>$\alpha i_2 \times 10^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light</td>
<td>13.34</td>
<td>12.72</td>
<td>.62</td>
<td>.09</td>
<td>15.4</td>
</tr>
<tr>
<td>Pressure</td>
<td>6.97</td>
<td>7.86</td>
<td>1.11</td>
<td>.34</td>
<td>27.8</td>
</tr>
<tr>
<td>Light and Pressure</td>
<td>20.81</td>
<td>15.58</td>
<td>5.23</td>
<td>.30</td>
<td>131.0</td>
</tr>
</tbody>
</table>
GENERAL CONSIDERATIONS.

The results discussed above all lead to this conclusion—that the effect of pressure in changing the conductivity of selenium is merely to decrease the rate of recombination of the conducting electrons with the positive residues of the atoms from which they were expelled. In no case can the experimental results be interpreted to indicate an increased rate of emission of electrons, for with increasing pressure a decrease in $\alpha$ and in $\alpha_1^2$ was always found. Now, Professor Brown¹ has shown that with an increase in the potential difference across the crystal the value of $\alpha$ due to a change in the light intensity is decreased in a manner exactly similar to that of pressure. In a recent paper by Mrs. Dieterich on the temperature effect on the rate of recombination a decreasing value in $\alpha$ due to light was found with increasing temperature, the behavior being identical with that found in the pressure and voltage effects. The conclusion is obvious—the only agency which changes the conductivity of selenium by causing an increase in the rate of emission of conducting electrons is light; pressure, temperature, and potential difference act in such a manner as to decrease the rate of recombination of conducting electrons and positive residues. This could be explained by assuming that the effect of these agencies is to lower the stability of the atom so that the electrons within the atom itself are less strongly bound, and the

1. Loc. cit.
2. Loc. cit.
attraction between the conducting electrons and the positive residues is materially lessened.

Further, it has been shown above that under zero pressure we should expect, and do, actually, obtain a finite conductivity in selenium. If the action of temperature and potential difference is identical with that of pressure, then we should expect a finite conductivity at 0 Abs., also at zero voltage. On this view, the rate of recombination would rise, with decreasing voltage or temperature, until a further decrease in the magnitude of these quantities would have no effect upon it, and \( i \), the conductivity, would remain constant; i.e., \( \alpha_i q/k \). These conclusions, with respect to voltage and temperature, should be subjected to experimental verification.
SUMMARY

1. The rate of recombination of conducting electrons with the positive residues in selenium crystals has been determined when the change of conductivity of the crystals was produced by a change in pressure on the crystals in the direction of the current, both in the dark and in the light. The rate of recombination so determined decreases with increase of pressure, in both cases, indicating that the action of pressure in increasing the conductivity does not consist in altering the rate of emission of electrons from the atoms.

2. The rate of recombination was measured when the change of conductivity, from equilibrium conditions, was produced by a change of light intensity. This rate was found to remain constant with increasing light intensity, agreeing with the results of previous work, and indicating that the effect of light in increasing the conductivity of selenium consists in altering the rate of emission of conducting electrons.

3. A simultaneous change in pressure and light intensity produces a rate of change of conductivity which is not equal to the sum of the rates of change due to each agency acting alone, indicating that the effects of light and pressure are dissimilar.

4. Evidence was brought forward to show that at zero pressure on the crystal it would still have a finite conductivity; i.e., under fixed conditions of temperature, voltage, and light intensity an equilibrium condition is reached by the crystal in which
conducting electrons are present. It was shown, also, that it is reasonable to expect a finite resistance at zero temperature, and at zero voltage.

5. A consideration of the results obtained in this investigation, together with the data of other observers on the effect of voltage and temperature leads to the conclusion that the conductivity of selenium is increased by a change in the rate of emission of conducting electrons from the atom only under the influence of light; the effect of pressure, temperature, and voltage, on the other hand, is merely a change in the rate of recombination of these conducting electrons with the atomic residues.

6. The results obtained are consistent with the theory that conduction in selenium takes place by means of electrons which are only temporarily free, recombining with the positive residues at a definite rate under fixed conditions of temperature, pressure, voltage and light intensity.

The writer wishes to acknowledge his indebtedness to the staff of the physical laboratory for their continued interest in the problem, especially to Professor Brown and Professor Stewart for numerous helpful suggestions and criticisms, and to Mrs. Kathryn Johnston Dieterich for help in the experimental work.
THE EFFECT OF TEMPERATURE ON THE LIGHT SENSIBILITY CURVES OF DIFFERENT TYPES OF SELENIUM CELLS.

By E. C. Dieterich.

This paper summarizes a study of the wave-length-sensibility curves of three types of selenium cells at temperatures higher than room temperature. The investigation was begun in the early fall of 1914 and some of the results reported at the November meeting of the American Physical Society that year. The experiments, however, were interrupted and it has not been possible to complete the work as originally planned. In the meantime an article describing the effect of low temperatures on the light sensibility curves of selenium and stibnite cells has been published by D. S. Elliott\(^1\) who finds a behavior similar to that described below. It was thought worth while, however, to call attention to these results inasmuch as they were obtained at high temperatures and on cells of entirely different nature than those used by Elliott.

The cells used were some prepared by the writer and previously described\(^2\). Three types were studied:

- **Type A**, which shows no maximum in the red whatever;
- **Type C**, in which the maximum in the red is lower than that in the blue;
- **Type D**, in which the maximum in the red is higher than that in the blue.

The permanence of the light sensibility curves of the different types was demonstrated here; those obtained at this time were essentially the same, for the same conditions of temperature, as those obtained when the cell was first completed. Fig. 1 shows these curves for a cell of type A.

To determine the light sensibility curves, the method outlined by Brown and Sieg\(^1\), and previously used, was followed. For obtaining the curves at temperatures higher than room temperature the cell was placed in a small oven which was about one inch square and three inches deep. This oven was constructed of plaster of Paris, wound with Nichrome wire and insulated by means of asbestos packing. It was provided with a small mica window to admit the light. By connecting it to a battery of storage cells a very constant temperature could be maintained. Temperatures were measured by means of a thermometer placed directly behind the cell. At the higher temperatures the cell served as a very sensitive means of indicating variations too small to be detected on the thermometer; the resistance changing to such an extent that the galvanometer deflection amounted to several hundred centimeters. Whenever possible, exposures of 0.5 sec. were taken, for with short exposures the fatigue of the cell is much less than with long exposures. However, at the higher temperatures the sensitiveness of the cells became so low that the short exposures gave galvanometer deflections too small to be read with very great accuracy, so here the exposures were increased in length. For certain types of cells, namely, type A, this change of period of illumination has no effect on the shape of the light sensibility curve, as is shown in Fig. 2, where the time of illumination varies by a factor of 75. For those cells whose

Fig. 2.

A - 16 volts, .4 sec.
B - 16 volts, 30 sec.

λ in μm
light sensibility curve depends upon the period of illumination. A constant period of exposure, 10 sec., was used at all temperatures. At the higher temperatures, to increase the sensibility, higher voltages were also found necessary. It has been shown repeatedly, however, that a change of voltage does not alter the light sensibility curves of selenium.

The behavior of the various types of cells with increasing temperature is shown in Figs. 3, 4, and 5. Fig. 3 represents the curves obtained with a cell of type A. The sensibility in the blue end of the spectrum decreases markedly while in the red it is hardly affected. At the highest temperature reached, however, there is no indication of an appearance of a maximum in the red, as might be expected, perhaps, as a result of the depression in the blue. Unfortunately, while trying to raise the temperature of this cell to somewhere near the melting point of selenium, the selenium melted and the identity of the cell was thereby destroyed.

From the behavior of cells of type A, one would be led to expect that in the case of cells with a maximum in the red, this maximum should be displaced towards the longer wave lengths. This was actually found to be the case. Figs. 4 and 5 show the progressive change of the position of maximum sensibility with increasing temperature. These results are in perfect agreement with Elliott's who finds the maximum shifted towards the shorter wave lengths at the temperature of liquid air.

Fig. 3.
Fig. 4

No. 16

A - 20°C, 2,500,000 Ohms
B - 50°C, 4,000,000 Ohms
C - 90°C, 1,200,000 Ohms

12 volts, 10 mA.
Fig. 5

No. 33

A - 300000 ohms, 22°C
1.5 volts, 10 sec.

B - 30000 ohms, 128°C
15 volts, 10 sec.

λ in µm

Fig. 5
Fig. 6 shows that the characteristic wave-length-sensibility curve at room temperature is not changed by the heat treatment; the maximum returns to the original place. The difference in resistance and sensitiveness before and after heating may probably be due to slow changes taking place in the selenium similar to those exhibited by the freshly manufactured cells.

It is a great pleasure to express my indebtedness to the staff of the physical laboratory for their interest in the work, and to Mrs. Kathryn Johnston Dieterich for her aid in the tedious experimental work.

Physical Laboratory

The State University of Iowa.
Fig. 6

ΔR

λ in μm

No. 33
A - Before heating
B - After heating
NOTES ON THE CONSTRUCTION OF SELENIUM BRIDGES.

E. O. DIETERICH.

The value or effectiveness of a selenium bridge depends upon several factors; namely:

1. The resistance of the bridge.
2. Its permanence, or stability.
3. Its sensitiveness, i.e., the ratio of the resistance of the bridge in the dark to that in the light.
4. The shape of the wave-length-sensibility curve.

This paper summarizes the results of an investigation of the conditions governing the production of selenium bridges of certain types.

In this investigation bridges of the Bidwell type were constructed; that is, two parallel wires were wound spirally around an insulating form, and the spaces between the wires were filled with selenium. In applying the selenium to the form the following method was adopted. The form was first heated to a temperature slightly above that of the melting point of selenium, 217°C., and then the selenium, in stick form, was rubbed over the heated surface. In this way, a thin, uniform layer of selenium was obtained which crystallized immediately, on cooling, to the gray metallic variety, which is conducting and light-sensitive. However, in these experiments, the resistance was, in general, very high, and the sensitiveness low. The samples were, therefore, subjected to an annealing process; i.e., they were kept in an electric oven at a high temperature for some hours. After annealing each sample was immediately transferred to a glass tube which had been carefully dried and which was then securely sealed to prevent the access of moisture and vapors. With these precautions all of the samples were found to be permanent, with respect to light sensitiveness, at least throughout the duration of this investigation, and very steady.

To analyze the bridges the same method of procedure was followed as that described by Doctors Brown and Sieg, and the same apparatus was used. The analysis revealed several new types of wave-length-sensibility curves. It was found that some bridges, instead of showing a maximum sensitiveness to red light, were most sensitive to blue light. In general, two types of curves resulted; those that showed a maximum at wave lengths shorter than 640μμ, and those that had a maximum at
wave lengths greater than 640$\mu\mu$. Those which showed a maximum above 640$\mu\mu$ had a pronounced minimum at 640$\mu\mu$, a broad maximum at the shorter wave lengths, and a sharp maximum at either 700$\mu\mu$, or 720$\mu\mu$. Maxima were found at the following wave lengths in various samples: 440$\mu\mu$, 500$\mu\mu$, 550$\mu\mu$, 700$\mu\mu$, 720$\mu\mu$, and 800$\mu\mu$. The location of the maximum was found to be dependent upon the method of annealing; those samples annealed at temperatures above 190°C. had a maximum in the blue, while those annealed at temperatures below 190°C. showed a maximum in the red.

The resistance of the bridges, also, was found to vary with the procedure adopted in annealing, in a manner previously described by Ries$^2$, who, however, gave this phase of the subject but a very brief consideration. With very few exceptions, the samples annealed at a temperature near the melting point of selenium had a low resistance. Some of those that were annealed at 180°C. or 190°C. were given a short preliminary heating at 210-215°C. It was found that those so treated also had a low resistance, while others made at the same time but not given this preliminary heat treatment had a resistance much higher, in some cases, ten to fifteen times as great.

With regard to the conditions governing the sensitiveness of the bridges much cannot be said at this time, except that the sensitiveness also seems to be dependent solely upon the method of annealing. Two samples, much more sensitive than the rest resulted, and, as far as is known to the author, the only difference in making was in the temperature control during the annealing process. These samples, however, did not retain their high sensitiveness, nor has it been possible to duplicate them.

A more complete discussion of the results of this investigation is in preparation, and is soon to be published in the Physical Review.

The writer wishes to acknowledge his indebtedness to Doctor Brown and to Doctor Sieg for the use of their apparatus and for their many helpful suggestions.

BIBLIOGRAPHY.


THE PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA, IOWA CITY.
THE INFLUENCE OF ANNEALING ON THE CHARACTERISTICS OF LIGHT-SENSITIVE SELLENIUM.

BY E. O. DIETERICH.

AN extension, by Brown and Sieg,1 of the work of Pfund in analyzing selenium cells by means of the spectrum revealed the fact that, classified according to their wave-length sensibility curves, a great number of different types of selenium cells were possible. Previous investigations by Pfund,2 Stebbins,3 Brown and Sieg,4 and Nicholson5 pointed to the conclusion that a typical wave-length sensibility curve existed which was essentially the same for all selenium cells, for, in all cases recorded, a maximum in the red end of the spectrum was found. The cells investigated were, in general, made by either Giltay or Ruhmer. The process of making these is a trade secret, but it is quite likely that the same method of crystallization is followed in all the cells of either one of the above types. Pfund, in his earlier experiments, used some cells of his own construction; these, too, were all crystallized in the same manner.

In some later experiments by Brown and Sieg, cells prepared by the author were used. Sensibility curves were obtained which differed widely, some showing a maximum in the red, some having hardly any sensiveness in the red but a maximum in the blue. An analysis of the data covering the method of construction of these revealed the fact that the crystallization of the selenium took place under different conditions in the different samples. This immediately suggested the possibility that a better knowledge of the conditions governing the construction of light sensitive selenium cells might be of assistance in explaining the action of light sensitive selenium. With this purpose in view, the investigation summarized in this paper was carried out.

This paper will describe the method followed in making the cells, and will show that the resistance and the shape of the wave-length sensibility curves of selenium cells can be controlled by varying the process of annealing. A simple explanation for the different types resulting will also be offered.

METHOD OF MAKING.

The cells, of which about 40 were constructed for this investigation, were all of the Bidwell type, i.e., two parallel wires were wound spirally around an insulating form and the spaces between the wires filled with selenium.

The selenium used was some in stick form from Merck. No steps were taken to further purify it, since it is, according to other observers, quite pure. Moreover, Pfund\(^1\) has shown that the presence of metallic selenides does not affect the shape of the wave-length sensibility curve. In a few samples made, rather impure selenium was used, and the cells resulting were not as satisfactory as those made with selenium from Merck. The resistance of these was, in general, very high, and they were sluggish in action although they had essentially the same characteristics as those made from the purer element. Marc\(^2\) has observed that impure selenium crystallizes less completely in a given time than pure selenium. To this fact the unsatisfactory action of the samples made with impure selenium is ascribed.

As insulating material soapstone was used. At first, glazed porcelain was tried, but it proved unsatisfactory on account of the difficulty of working into forms. The advantages of the talc over the porcelain are evident. It is just as efficient as an insulator, besides being much softer, and, therefore, capable of being easily machined.

Several kinds of wire were tried as electrodes, copper, nickel, platinum, German silver, and Advance wire. Again although selenides are formed during the crystallization process, due to the high temperature, the shape of the wave-length sensibility curve will not be changed, although the sensitiveness and the resistance of the cell will be affected. These points are to be verified in some later work. Copper, German silver and Advance wires have this disadvantage that, at the temperature of annealing, a film of oxide covering the wire is readily formed. This so materially increases the resistance of the cell as to make it practically useless for investigation except with very sensitive apparatus. Nickel wire is much less easily oxidized and proved as satisfactory as platinum wire, besides being less expensive, and was used in all except the first few cells.

The size of the sensitive surface was about 1 × 3 cm., except in the first few cells which were larger. The distance between the electrodes was a little less than 1 mm.

In applying the selenium to the form the following method was

\(^1\) Phil. Mag., VII, p. 26, 1904.
\(^2\) Marc, Die Physikalisch-Chemischen Eigenschaften des metallischen Selens, 1907.
adopted as being the most satisfactory. The form was heated, on a hot plate, to a temperature just above the melting point of selenium, 217° C., and then the selenium, in stick form, was rubbed over the heated surface immediately on removing from the hot plate. As is well known, with this treatment, the selenium at once changes, on solidification, to the gray metallic variety and is conducting and light sensitive. By this method smooth, thin films of selenium were obtained. However, in all cases in which the samples were tested out immediately on making, the resistance was found to be very high, of the order of 10⁸ ohms, and the sensitiveness, even under intense illumination, in no case greater than 5 to 1. (By sensitiveness is meant the ratio of the resistance of the cell in the dark to that in the light.) Upon making, therefore, the cells were “annealed,” the process taking place in an electric oven whose temperature could be quite accurately controlled. It is in this “annealing” process, which consists merely in keeping the cells for some time at a high temperature, or in gradually changing the temperature, that the changes which impart different characteristics to the cells take place. This will be described in greater detail in a later section since it is varied from cell to cell.

In general, all the samples received the same treatment after annealing. They were allowed to come to a temperature of 170° C. while in the oven, then removed and placed in small glass tubes which had been thoroughly cleaned and dried. They were then sealed to prevent the access of moisture and other vapors, and allowed to come to room temperature. Usually they were allowed to rest for 24 hours before being investigated, being kept in a light-tight box in the meanwhile. With these precautions, all the samples were found to be permanent, with respect to light sensitiveness, at least throughout this investigation.

At first, the method generally described for crystallizing the selenium namely, heating it for a few minutes at about 180° C., was followed. The first cell made in this way had a high sensibility but was not permanent. The next few samples were not at all satisfactory, so the method was abandoned. Instead, the cells were annealed at higher temperatures and a longer time was taken for the process. By this method samples were obtained which were quite satisfactory in respect to sensitiveness.

**Characteristics of the Cells.**

The cells were investigated with respect to resistance, sensitiveness, shape of wave-length sensibility curve and permanence.
Resistance.

The resistance of the cells was measured by means of a Wheatstone bridge. Since the resistance varies with the voltage impressed upon it, the same E.M.F., 16 volts, was used throughout.

Here the observations of Ries in regard to the variation of resistance with annealing were verified. Thus Ries records two samples which were heated at different temperatures, and shows that the higher the temperature to which the cell was heated the lower was its resistance. His method differs from that employed in this investigation, however, in that he subjected the individual cells to a series of temperature changes, alternately heating and cooling each cell, and measuring its resistance and sensitiveness while it was at room temperature. In these experiments each cell was subjected to a high temperature but once, but the results were the same as those obtained by Ries. The following table gives some typical data.

**Table I.**

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<thead>
<tr>
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<tbody>
<tr>
<td>23</td>
<td>210-200° C.</td>
<td>6</td>
<td>233,000</td>
</tr>
<tr>
<td>22</td>
<td>210° C.</td>
<td>4</td>
<td>358,000</td>
</tr>
<tr>
<td>28</td>
<td>210° C.</td>
<td>5</td>
<td>490,000</td>
</tr>
<tr>
<td>16</td>
<td>180° C.</td>
<td>3½</td>
<td>1,400,000</td>
</tr>
<tr>
<td>15</td>
<td>190° C.</td>
<td>2</td>
<td>3,690,000</td>
</tr>
</tbody>
</table>

From the above table the influence of annealing on the resistance of the cells can be clearly seen, namely, that the higher the temperature of annealing and the longer the time, the lower is the resistance.

It was further found that if the cells were heated for a short time only at a high temperature and the annealing carried on to completion at a lower temperature the resistance of the cells was materially reduced. This fact is shown in Table II. Thus, cells No. 18 and 19 were given

**Table II.**

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>18</td>
<td>210° C.</td>
<td>½</td>
<td>976,000</td>
</tr>
<tr>
<td>19</td>
<td>180° C.</td>
<td>9</td>
<td>40,000,000</td>
</tr>
<tr>
<td>19</td>
<td>180° C.</td>
<td>9</td>
<td>40,000,000</td>
</tr>
<tr>
<td>20</td>
<td>210° C.</td>
<td>½</td>
<td>250,900</td>
</tr>
<tr>
<td>21</td>
<td>180° C.</td>
<td>14</td>
<td>9,500,000</td>
</tr>
</tbody>
</table>

1 Ries, *Das elektrische Verhalten des Kristallinischen Selens gegen Wärme und Licht*, 1902.
exactly the same treatment except that cell No. 18 was given a preliminary heating of half an hour at 210° C. The resistance of No. 18 is seen to be less than 1/40 that of No. 19. The same is true of No. 20 and 21.

The resistance of the freshly made cells was, in general, low, but increased gradually, reaching a constant value in a few weeks after making. This gradual, permanent increase is no doubt due to the contraction of the selenium and its consequent tearing away from the electrodes. The resistance of the various samples ranged from 12,000 ohms to 42,000,000 ohms.

**Light-Sensitiveness.**

With regard to the effect of annealing on the sensitiveness of the cells not much can be said as a result of these experiments. Two cells of remarkably high sensitiveness were obtained, but this was not permanent, the sensitiveness decreasing to about 1/5 of the original value in less than one month. That phase of the subject is under investigation at the present time, nothing definite having been discovered thus far, however. The sensitiveness of the samples, with the exception of the two mentioned above, varied between 5/1 and 20/1, using a 16 c.p. light at a distance of 30 cm. as a source of illumination.

**The Wave-Length Sensibility Curves.**

In order to determine the wave-length sensibility curves, the same method of procedure as outlined by Brown and Sieg was followed and the same apparatus was used. Three periods of exposure of the cell to light were used; .4 sec., 10 sec., and 30 sec., the time of exposure depending upon the resistance of the cell. The range, in general, was from 460 μμ to 800 μμ, since at values lower than 460 μμ the energy of the source was not great enough to measure very accurately. The exposure always took place in the order from short to long wave-lengths, since Brown and Sieg have shown that the order of exposure does not affect the shape of the curve. The slit width and other factors were kept constant throughout the investigation.

It was found that, except in a few cases, the shape of the wave-length sensibility curve did not change, whether the intensity of the incident light were high or low, or whether the time of exposure were long or short. This is shown by the curves for cell No. 10 in Fig. 1. Here the wave-lengths are plotted as abscissae, and the change in resistance, which is proportional to the deflection of the galvanometer, as ordinates.

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1 Loc. cit.
It is seen from Fig. 1 that the curves for cells of the type represented by No. 10 do not change in their essential characteristics when the energy of the incident light is varied by as great a factor as 50, nor when the time of exposure changes from .4 sec. to 30 sec. Whenever possible, therefore, on account of the sensitiveness of the apparatus, the exposures were made for .4 sec. Cell 17, Fig. 1, represents the type in which a change in the energy of the incident light changes the shape of the curve. These are the typical curves obtained by other observers for the Giltay type of cells.

A wide variety of types of sensibility curves resulted, maxima being obtained at points not previously recorded. Fig. 2 shows the location of some of the most pronounced maxima developed in this investigation. These curves are not plotted to the same scale and, hence, do not show the relative sensibility of the cells; neither do they represent all the
types possible to obtain. At the following wave lengths definite maxima were found: 440 μμ, 500 μμ, 550 μμ, 700 μμ, 720 μμ and 800 μμ.

From Fig. 2 it is seen that the cells can be divided, in general, into two groups, viz., those that have their maximum sensibility at wave-lengths greater than 640 μμ, and those in which the maximum occurs at wave-lengths shorter than 640 μμ. In no case was a maximum found at 640 μμ, nor has the author been able to find one recorded at this point.

One type of cell represented by No. 19, Fig. 2, has two maxima, both of about the same magnitude and very sharply defined, one in the violet at 440 μμ, and one at 700 μμ or 720 μμ. This type is obtained when, after applying the selenium to the form in the manner previously described, it is heated for about 10 hours at 180° C.

Fig. 3 shows the effect of a variation in the temperature of annealing on the shape of the wave-length sensibility curve. This set of curves is typical of a large number obtained when the conditions of temperatures were the same as those indicated here.

![Graphs showing wave-length sensibility curves for different types of cells.](image)

Fig. 3.

(A), Fig. 3, represents the type of curve obtained, when the cell, immediately after making, is subjected to a temperature of 210° C. for
some time, in this case, 4 hours. This type shows a maximum about 500 \( \mu \)u, and very little sensitiveness above 640 \( \mu \)u.

(B), Fig. 3, represents the type resulting when the cell on making is subjected for a short time to a temperature of 210° C., in this case 1 hour, the temperature then allowed to fall to 200° C. and kept constant at this point for 4 hours. Here is seen a change in the shape of the curve and a hint of a maximum in the red.

(C), Fig. 3, represents the type obtained when the cell is heated at 210° C. for 30 min., the temperature allowed to fall to 190° C. and kept constant there for 6 hours.

(D), Fig. 3, represents the type resulting when the cell was heated for 30 min. at 210° C. and then at an average temperature of 170° C.

The control of the maximum in the red end of the spectrum is clearly shown by the curves in Fig. 3. As the temperature of annealing becomes lower, the maximum in the red becomes, relative to that in the blue, gradually higher, until in the type (D) it exceeds that in the blue.

In each case described above the preliminary heating at 210° C. was given in order to lower the resistance of the cell, as was seen to be the case earlier in this paper. This was done in order to increase the accuracy of the measurements, for the apparatus for obtaining the curves is more sensitive and, hence, more accurate, the lower the resistance of the cell measured.

The most obvious explanation of the variation found in the different types of cells, in the light of recent work on selenium, rests on the probable difference in the crystals composing the various types. As we have seen, a rough classification into two general types can be made, those most sensitive to red light and those most sensitive to blue. Recently Professor Brown\(^1\) has succeeded in producing several new forms of selenium crystals of the gray metallic variety by sublimation. A cell made by depositing one variety of these on a form was found to have a maximum at 780 \( \mu \)u. It is not improbable that the maximum sensitiveness of a cell composed of crystals of another variety should lie in the blue end of the spectrum.

In some recent investigations, the results of which have not yet been published, Drs. Brown and Sieg have found the maximum sensitiveness of a single crystal of a certain variety to be in the red end of the spectrum. In another variety two maxima were found, one in the long wave-length and one in the ultra-violet. Moreover, the location of the maximum is found to be dependent upon such factors as the angle of incidence and the intensity of the exciting light, the face of the crystal illuminated, etc.

\(^{1}\) *Phys. Rev.*, Series 2, IV, p. 85, 1914.
The explanation of the different types of cells on this basis, then, is simple. A cell, such as is represented by (A), Fig. 3, may be assumed to contain crystals which are sensitive to a great extent only to blue light, and few or none at all of those sensitive to red light. In other words, the temperature at which this type is annealed is too high to allow the formation of crystals sensitive to red light. Another type, (C), for instance, might be thought of as containing a mixture of the two varieties, the amount of the "red" crystals present not being sufficient to overcome the effect of the "blue" crystals. The type represented by cell No. 19, Fig. 2, can be explained on the same basis, i.e., composed of crystals having maxima both in the red and in the ultra violet, and in which the point of maximum sensibility has been shifted towards the visible spectrum, due to a variation in some one or more of the conditions governing the formation of the crystals. The occurrence of maxima separated by only a few wave-lengths can be explained by assuming a difference in the orientation of the crystals in the various cells, so that in different cells different crystal faces are exposed. Or, the light transmitted through the surface layer may suffer changes, by reflection from the crystal surfaces, causing an effect different from that it would have were it direct. This effect might be manifested by a shift in the maximum.

If the above conclusions are correct, the problem of the explanation of the light sensitiveness of selenium reduces to an explanation of the changes taking place in the single crystal under the influence of light and other agencies.

Fig. 4.
Permanence of the Characteristics.

It is evident that no definite statement as to the permanence of the characteristics of the various types can be made at the present time, since the time elapsed is hardly long enough to warrant that. Fig. 4 shows the characteristic curves of two cells taken at different time intervals, under as nearly the same conditions as possible. It is seen that they are the same in the essentials, the slight differences can be attributed to experimental errors.

Summary.

In this paper has been shown:
1. That the resistance of selenium cells depends to a great degree upon the treatment to which they have been subjected while annealing them.
2. That the location of the maximum in the wave-length sensibility curve can be controlled by a variation in the conditions under which the selenium in the cell is crystallized. It was shown that the temperature variations play the most important part.
3. That the various types of cells produced in this investigation can be explained by assuming the presence of various kinds of crystals, or different positions of the same kind of crystals in the cells. The temperature at which one kind is formed may not be favorable for the formation of another kind, hence, the production of the different types of cells.

In conclusion, I wish to acknowledge my indebtedness to the staff of the department of physics for their interest in the problem, especially to Professors Brown and Sieg for the use of their apparatus, and for their many helpful suggestions, and to Messrs. Scott Walker and Paul Helmick who so ably assisted me in much of the experimental work.

The Physical Laboratory,
State University of Iowa.