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THE CRYSTAL FORMS OF METALLIC SELENIUM AND SOME OF THEIR PHYSICAL PROPERTIES.

By F. C. Brown.

WHETHER light-sensitive selenium is made up of homogeneous crystal structure or of complex units is of importance in explaining the nature of light action in selenium. Thus the author has been led into a study of the crystal forms of metallic selenium, which study has been particularly fruitful in that new crystal forms of very large size have been isolated. These crystals are of such a size that the optical and photoelectric properties of individual crystals can be studied. Thus we are able to eliminate some of possible causes of complexity in selenium, such as polymorphic crystal mixtures, unknown condition of crystal contacts, irregular placing of the crystals, and impurities. The fact that these new crystal forms are light-sensitive opens up a large field of investigation of which this paper is only preliminary.

Muthman[1] described only one crystal form of metallic selenium of the hexagonal rhombohedral system. These crystals were produced by the sublimation of the vapor of selenium in air and were never larger than 0.2 × 0.5 mm.

Saunders[2] also describes only one form. His conclusions were based upon the changes in volume accompanying temperature changes, as determined by dilatometric measurements. The difficulty with Saunders's method is that different crystal forms having identical or only slightly varying density could not be detected.

Marc[3] following the experiments of Uljanin[4] who observed two distinct crystallographic structures under the microscope, and following his own

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[1] Zeit. f. Kryst., 17, 356, 1890.

[2] "The Allotropic Forms of Selenium," Journ. of Phys. Chem., Vol. 4, p. 423, 1900.

[3] Die Physikalische Chemischen Eigenschaften des Metallisches Selens, Verlag von Voss, 1909.

[4] Wied. Ann., 34, p. 241, 1888.

experiments on selenium cells, was led to believe in the existence of several forms of metallic selenium, which through the action of light underwent polymorphic transformations. By the investigations of the heat changes, the electrical conductivity and a microscopic investigation of the surface he was able to detect with certainty the existence of two polymorphic forms. The one form was crystallized by heating the selenium at lower temperatures in the neighborhood of 100°. It was essentially non conducting and was designated form *A*. At temperatures of 205° to 215° this selenium went over into selenium *B*, which was found to be quite conducting. A microscopic investigation showed the form *B* to be of uniformly round mounds, while that crystallized at 200° contained long crystals. The crystals observed however were only of the size of about 0.004 mm. Marc's results which led him to believe in the existence of two forms *A* and *B* and which led him to believe in the dynamic equilibrium of these forms, were not sufficient to convince him that there could not be other forms. One of the phases producing equilibrium he regarded as a vapor phase, thus giving only one solid form for two phases.

Recently White[1] did some very excellent work with selenium blocks crystallized at 200°. He found the interesting result that a greater change of conductivity was produced when the incident light was in the direction of flow of the current than when the illumination and electric current directions were at right angles to each other. He concluded that in the selenium block the highest resistance is at the electrode contacts and also that the greatest change of conductivity by illumination takes place at the electrodes. However in interpreting his results he did not consider the change of conductivity arising from increased potential gradient when the blocks were illuminated at the contact surfaces. He also observed a number of phenomena such as has been observed in the so-called selenium cells.[2] This work of White further suggests the advisability of obtaining single isolated crystals of selenium in which the physical conditions, may be known and controlled.

THE PRODUCTION OF ISOLATED CRYSTALS.

The new crystal forms that are the subject of discussion were in all cases produced by the sublimation of the vapor, either in a high vacuum or at atmospheric pressure. The vitreous selenium which it was desired to transform into crystals was placed in one end of a glass tube of 35 mm. inside diameter and of 30 to 60 cm. length. This glass tube fitted snugly

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

[2] Unquestionably the term "selenium bridge" as he suggests is a better term than "selenium cells."

into a cylindrical electrical oven of 30 cm. length, of which one end was closed. Near the open end of the oven there was a rather large temperature gradient whether the tube was evacuated or not. All the selenium that deposited in any form was usually within a distance of less than 7 cm. along the tube. A current of about six amperes in the oven was sufficient to heat the selenium to be transformed to about 270°. The selenium was kept at this temperature for a period varying between one day and one week. But there was no temperature regulator and consequently there was considerable variation in the temperature during the day, with either the dynamo or the storage battery as a source of current. The selenium was allowed to sublime on the walls of the glass tube, on a thermometer bulb, or on a form with wire electrodes for a light-sensitive selenium bridge. It was hoped that the thermometer would register the temperature at which the crystals formed on it, but the temperature gradient was so large that no reliance was placed in the readings.

The result may be stated in a general way as follows. The largest crystals in every case were formed at the highest temperature at which the selenium sublimed in the closed tube. This temperature is believed to be above 210°. It should have been ascertained more accurately, but the effort was rather discouraging because of the absence of automatic temperature control. These crystals became smaller as the cooler portion of the tube was approached, until about 3 cm. back of the largest crystals there was a continuous sheath of selenium of a silver luster surrounding the inner wall of the tube. On some occasions the hotter edge of this sheath was fringed with small well-developed rhombohedral-hexagonal crystals (see Fig. 1) such as described by Muthman[1]. Back of this silver-like sheath was sometimes discerned a rather black sheath which also had a metallic luster. Further along the tube at temperatures perhaps below 100° was usually a very thin deposit of red amorphous selenium. I was rather surprised to find so small an amount of selenium deposited in the red amorphous form, and so large a quantity in the metallic forms. I was also surprised in some cases to find so large a fraction of the selenium as one fifth of the total to be deposited in the form of large crystals. This is rather a sufficient argument against any view that might presuppose impurities to form the large crystals. The selenium that was placed in the tube to be sublimated was Merck's purified selenium.

Invariably the largest crystals were formed at the highest temperature, but it is not clear what determined the form they should take. The photograph in Fig. 2 shows distinctly varying formations that occurred

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[1] Loc. cit.

in two separate tubes. The acicular crystals were sometimes 11 mm. long and not more than 0.2 mm. in any other dimension. Usually they developed a number together in a cactus-like growth, with from 3 to 20 spines starting from a common center. These spines or needles were quite stiff and tough, rough handling and even dropping very rarely injuring them. The needles of any given cluster were usually very much alike in size and appearance. They always had a metallic luster by reflected light. If fully developed there were six surfaces. And yet some entire clusters apparently developed with any number of surfaces less than six. Under the microscope these crystals seemed the least transparent of any that were produced.

The crystals of the second type shown in Fig. 2 were large flat crystals with parallel surfaces usually less than 0.3 mm. apart. The length of one of these crystals indicated in the photograph was 9 mm., and for the greater part of the length the width was about 2 mm. These crystals frequently began growth by the addition of longer and longer crystals to the side of the last crystal laid down. This accounts for the triangular point frequently seen on these large crystals. Sometimes these flat crystals were nearly square and again diamond shaped. Frequently the flat would develop in places as a rolling surface and also be distorted at the edges. But in any given run with fixed resistance coils in series with the oven heater, there was an unmistakable resemblance between all the crystals formed in a given vicinity of the tube. The largest crystals of this form appeared in a tube in which the air pressure had been reduced to less than 0.01 mm. previous to the sealing off of the tube.

The crystal groups to the left in Fig. 3 are also typical of those that were formed in one tube. They were as long as 4 mm. and as wide as 0.8 mm. They were the result of uniform twinning in such a manner that an open or closed V-shaped gauge was formed by each spine.

Yet another interesting formation that appeared once was a large number of very flexible sheets, sometimes 4 mm. long and as wide as .6 mm. They developed largely one in a place. As they waved about freely by slight air currents, they much resembled a miniature aluminium leaf as used in an electroscope. The thickness of one of these was of the order of 0.01 mm. The other forms described above showed no such flexibility at all. The relative dimensions of two of these crystals may be estimated from the reproduced photograph in Fig. 5. The length of the longest is about 3 mm.

The crystals that formed at the edge of the metallic sheath were only occasionally like those described by Muthman. Fig. 3 shows a photograph of a much larger formation, some as large as 4 mm. which appeared

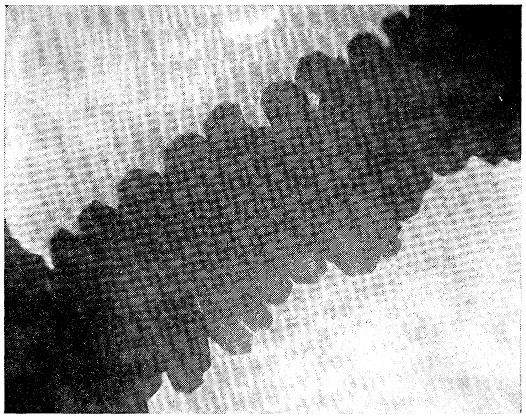

Fig. 1.

Magnified hexagonal crystals, natural size of single crystals not over 0.1 mm. in width.

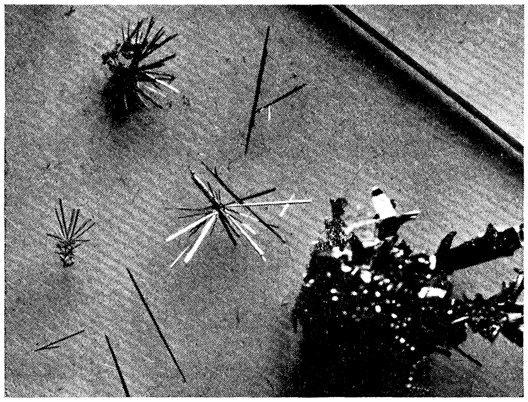

Fig. 2.

(*a*) Groups of acicular crystals to the left. Natural size of longest ones about 11 mm. (*b*) Growth of lamellar crystals in lower right-hand corner, the largest of which as seen in the figure was about 9.0 × 2 × 0.4 mm.

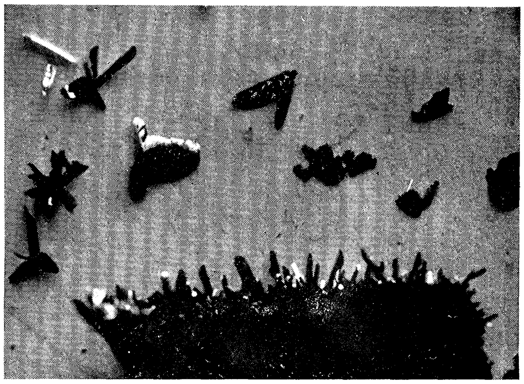

Fig. 3.

The lower part of the photograph shows the growth of single and twinned crystals of maximum length about 4 mm. at the edge of a crystal mass of finer grain. The scattered crystals are of the same formation.

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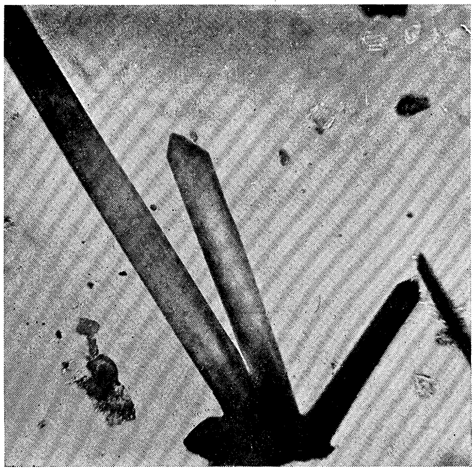

Fig. 4.

The above crystals are the same form as those shown in Fig. 3, but were photographed by transmitted light with a magnification of about 100 times.

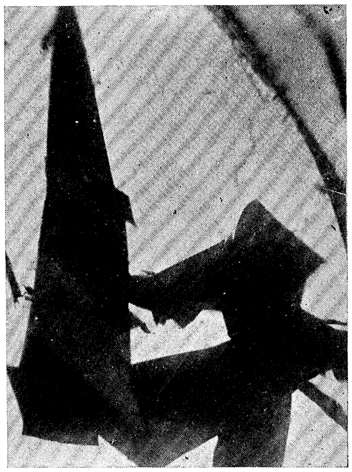

Fig. 6.

Lamellar crystals of gradually increasing width. Magnification about 100. Note the striations making an angle of about 35° with the edge.

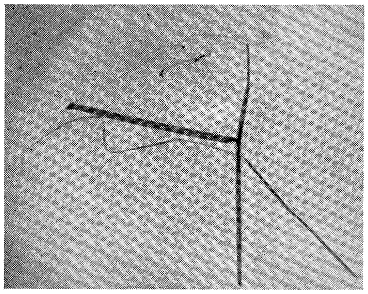

Fig. 5.

Two crystals of flexible lamellar type. The longest of the above was about 4 mm. long. The width and thickness may be estimated from the reproduction.

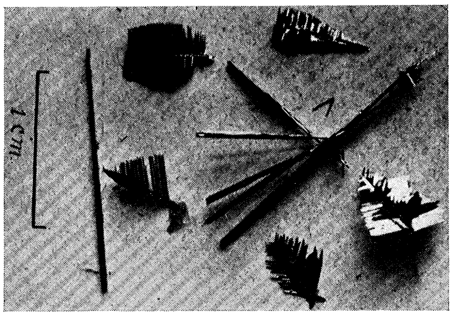

Fig. 9.

Crystals of metallic selenium by sublimation. Acicular hexagonal and acicular with side branches. Side branches perpendicular to stem are hexagonal. Those leaving at angle of 60° are lamellar plates showing parallel extinction.

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under similar circumstances. Some of the same crystals were magnified much more and photographed by transmitted light as seen in Fig. 4.

The manner in which some of the semi-flexible lamellæ developed is shown by the photograph (transmitted light) in Fig. 6. The striations can be seen running across the surface at about an angle of 35°. With the aid of polarized light these striations become much more marked. They indicate the way in which the large sheet lamella are sometimes built up.

Yet other crystal forms of small dimensions that appeared under the microscope are shown in Fig. 7. The largest of these was about .05 mm. All of these were observed many times. However they were too small for a study of their electrical properties.

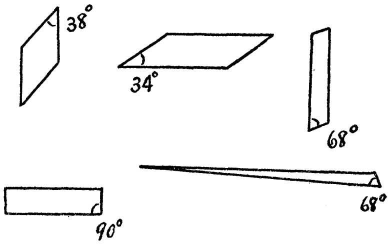

Fig. 7.

Unfortunately all the large crystal forms that I have described were formed at high temperatures. When we have obtained a satisfactory temperature regulator, we shall endeavor to obtain large-sized crystals at about 150°. No doubt more constant and better defined temperatures will produce more regular and larger crystals of the types that I have described, and perhaps new ones.

It is probable that all the crystals belong to the third crystal system, but before this can be decided definitely I believe that it will be at least advisable to obtain more large crystal forms, in order to determine accurately the angles between the faces.

Naturally the question arises as to why selenium crystallizes in so many forms at so nearly the same temperatures. I wish to proclaim a most profound ignorance as to this question. However there is strong indication that the partial pressure of the vapor of selenium and the temperature gradient in the tube at the place of formation are the prime factors. For example I have noted repeatedly that the thin lamellar form appeared when the oven temperature was low, where the amorphous selenium was placed for sublimation. Without doubt the conditions for formation of the crystals should be studied more carefully.

A photograph of some interesting crystals formed at atmospheric pressure is shown in Fig. 9.

The Property of Double Refraction.

All the forms of metallic selenium that have thus far been observed display a distinctly metallic appearance by reflected light. The surfaces were nearly always quite plane and consequently, as the photographs show, the crystals appeared very light or very dark depending on the position of the surface angle with regard to the direction of maximum illumination. It is to be observed in Figs. 2 and 3 that the diffuse light is much less than that from the white paper which served as a background. Even the fine-grained crystal masses formed at lower temperatures and shown in Fig. 3 show a distinct black with contrasting white specks here and there. Likewise all the crystal forms except the acicular ones transmit light even through great thicknesses, and it is interesting to note that wherever the crystal transmits light it displays the property of double refraction. When examined under crossed nicols the transmitted light is most frequently some tinge of deep red, but various formations and thicknesses of crystal show the transmitted light to be distinctly a blue, yellow, orange, green or even white. The fully developed rhombohedral hexagonal crystals in Fig. 1 show a deep ox-blood red under crossed nicols. The transmitted light seems to appear as a body color in the crystal. This may be due to a deviation or scattering of the light inside the crystal. In a lamellar crystal such as shown in Fig. 6, several variations of color are observable at different places. The striations become particularly distinct under crossed nicols by the variation of color and color density.

The elementary crystal forms and the position in which they show extinction of light under crossed nicols are shown approximately correct in Fig. 8. The nicol prisms are placed as shown by the arrows. The dark positions are those of light extinction and the light positions those in which the light was readily transmitted, in some color or other. The crystal *a* is for one having acute angles of about 35°. Crystal *c* is obviously the multiplication of *a*. Crystal *b* is one having 68° angles. Its axis obviously runs lengthwise of the crystals. In *d* is a distinctly right-angled lamellar form, also with optic axis running lengthwise of the crystal. The crystal *e* which is also representative of a large number that were observed, showed the optic axis to run parallel to the very short edge. The acute angle here was about 68°. Thus this crystal may be regarded as built up of a large number of *b* crystals of gradually increasing length. It happens that all the crystals represented in Fig. 8 were

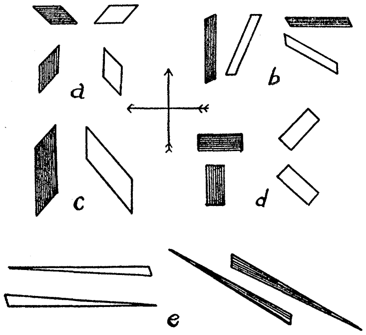

Fig. 8.

drawn under the same magnification, but they might have been chosen in widely varying sizes. It appears contrary to first expectation that the crystal in Fig. 6 for example is not built up of units of *e*, but rather of units of the crystal *b*. Under crossed nicols it shows extinction parallel to the striations. The crystal in Fig. 5 when viewed flatwise shows extinction parallel to the length of the crystal, indicating the optic axis to be lengthwise of the crystal. This long and flexible crystal may therefore be regarded as built up of the crystals of type *d*, in Fig. 8. The crystals in Fig. 1 show extinction parallel to the long crystallographic axis.

It may be of passing interest to deviate from the topic of this paper to note that the glittering red plates of the red crystalline variety of selenium show double refraction and also that they are not at all metallic in appearance, nor do they show electrical conductance even under very high pressures.

Some time ago the depth of penetration of light into selenium[1] was deduced to be greater than 0.014 mm. This result is very much larger than that of other observers. Pfund,[2] for example, found the depth to be about 10^{-6} cm. White[3] on the other hand believed his selenium blocks indicated a greater penetration than any result indicated above. It seems that the depth of penetration should and does vary with the size, character and positions of the crystals. I have observed a large amount of light transmitted through a lamellar crystal such as shown in Fig. 2 of thickness as great as 0.3 mm. This transmitted light was a deep red and was deviated from its path on emergence through a large angle, perhaps 40°. Thus in a mixture of small crystals adjacent to each other the path might be devious indeed. There is no reason to believe that the light or the light action might not travel several millimeters in a well-formed crystal. Evidence will be mentioned later which indicates that the total number of electrons liberated does not vary greatly whatever may be the deviations of the light.

The Effect of Pressure.

The pressure effect on selenium was discovered in 1905[4] showing a very large increase of conductivity for increased pressure up to 1,000 atmospheres. Montèn[5] extended the study independently up to 3,000 atmospheres and observed conductivity changes more than a hundred-

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[1] Phys. Rev., 34, p. 201, 1912.

[2] Phys. Rev., 28, p. 324, 1909.

[3] Loc. cit.

[4] Phys. Rev., Vol. 20, p. 185, 1905.

[5] Arkiv för Matematik, Astronomi och Fysik, Bd. 4, No. 31, p. 1, 1908

fold. About the same time a study of the light sensitiveness under varying hydraulic pressures[1] very decidedly indicated that the pressure produced a genuine change in the selenium and did not alter the contact resistances. This argument was based on the presumption that no part of the light action was of a nature of alteration of contact resistances. A recent consideration of the similarity of certain physical properties in light-sensitive selenium and crystal contacts[2] has led the author to intimate that the early presumption referred to above might be wrong. White's recent work[3] with selenium blocks showed the largest change of resistance by light to take place at the electrodes.

A study of a single crystal, in contact with plane electrodes, under varying pressure should reveal important information as to the seat of the pressure effect in ordinary light sensitive selenium as well as in the individual crystal. This pressure effect was easily studied by placing the crystal between two surfaces as shown in Fig. 10. The pressure was increased by merely adding weights. This pressure was applied in the direction of the flow of current. The curves in Fig. 11 show the remarkable variation of the conductivity of a single lamellar crystal such as shown in Fig. 2 with change in pressure. The lower curve is the conductivity in the dark and the upper one is for the conductivity in the light. In the dark the conductivity increases about 120 times for an increase of pressure of 180 atmospheres. The crosses on the curves show the conductivity values both in the light and in the dark as the pressure was released. Thus it appears that the selenium crystal attains a given equilibrium under a given pressure. Under higher pressures the con-

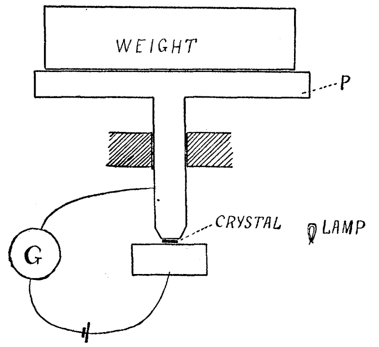

Fig. 10.

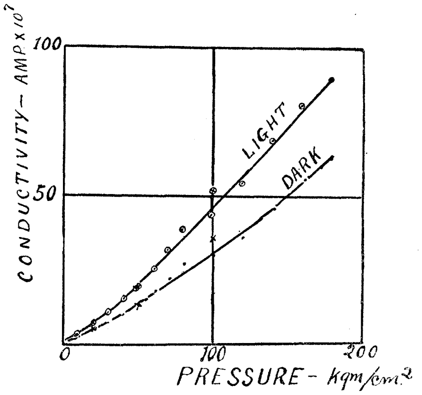

Fig. 11.

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[1] See paper by Brown and Stebbins, PHYS. REV., 26, p. 273, 1908.

[2] PHYS. REV., N. S., Vol. 1, p. 245, 1912, and Proc. Iowa Acad., 1913.

[3] Loc. cit.

ductivity was unsteady, so that thus far the action of higher pressures is uncertain. However I succeeded in increasing the conductivity of one crystal about a million times by pressure. Under these conditions it was not light sensitive. The fact that there was only a slight hysteresis as illustrated by the fact that the points on the curves shown were not taken in exactly regular order, is strong evidence that the pressure effect is in the selenium crystal and not at the electrode contacts.

THE VARIATION OF THE LIGHT-SENSITIVENESS WITH PRESSURE.

Experimental Results.—With the apparatus shown in Fig. 10 it was easy to determine the light-sensitiveness with different pressures. The interesting result followed that the light action increased with increase of pressure. In the following table is given the conductivity (*c*) in the dark, which prevailed under the varying pressures recorded in the upper curve of Fig. 11, and also the proportional change of conductivity, $\Delta C/C$, produced by constant illumination. The conductivity is indicated in terms of divisions deflection of the galvanometer, *G*. It is observed that the conductivity in the dark varied by a factor of 124. Within this large range, the light-action as measured by the change of conductivity is directly proportional to the conductivity in the dark. It may be concluded for pressures up to 180 atmospheres, that the percentage increase of conductivity by a given illumination is constant. This result leads to a remarkable interpretation as to the nature of light action.

C.	$\Delta C/C$.
.5	.6
2.0	.5
4.5	.45
7.4	.42
10	.44
13	.42
17.8	.40
21.6	.43
28.5	.46
35	.50
46.5	.46
55	.45
62	.43

Interpretation of Result $\Delta C/C$ = Constant.—First it will be seen that the resistance exists in the selenium itself and not at electrode contacts. For suppose the light to produce a change of resistance ΔR in the selenium. Then the proportional decrease of resistance by the light, $\Delta R/(Rs + Rc)$, would get constantly greater inversely proportional to the change of resistance, where Rs and Rc are the resistances of the selenium and the contacts respectively. This result would follow whether the light action were at the contacts or in the selenium itself. For pressures of only a few grams the above ratio was sometimes observed to increase with increase of pressure, but with pressures of 50 gm. or more the ratio of $\Delta C/C$ (or $\Delta R/R$) was constant as shown in the preceding table. It is concluded therefore that contact resistances are of very secondary or negligible consequence in connection with the ordinary light-electric phenomena in selenium crystals. This result is quite consistent with other experiments to be published later.

The constancy of the ratio of $\Delta C/C$ could be explained if it were possible that the increased amount of the conducting component produced by pressure were the only component that could still further be acted upon by light. But this seems so unreasonable, and it is certainly inconsistent with the results obtained by the author in his various works on selenium cells.

The only reasonable interpretation, it seems, must be worked out somewhat along the following line. Suppose a number of isolated conducting centers throughout the crystal and that this number is a function of the pressure. Generally such an insulated center would not conduct at all, but as the pressure becomes greater a large number of these centers would come within each other's confines, thus increasing the conductivity of the crystal. If the number of centers is small, the conductivity should increase as the number of centers. If a given illumination produces a definite number of new centers, then these new centers should bridge over gaps between old centers approximately proportional to the number of gaps filled, which should vary as the number of old centers or circuits. Of course if the selenium should have a very large number of gaps already completed without the light action, then the light would not have the opportunity of completing a circuit so frequently for every center acted upon. In agreement with this notion I found that when pressures, sufficient to increase the conductivity a million fold were applied that the light sensitiveness diminished to practically zero. It may be convenient to modify this explanation later to satisfy the electron theory of conduction. However it may be mentioned that as a result of further experiments with these crystals Dr. Sieg and myself are compelled to revise the electron theory of electrical conduction. These experiments will be described later.

THE ACTION OF LIGHT.

Essentially in the Body of the Crystal.—In view of White's[1] experiments with selenium blocks in which he observed the greatest change of conductivity at the electrode contacts, it seemed advisable to try the same experiment with a single crystal. This time one of the lamellar crystals of about 4 mm. length was chosen. The ends were clamped to silver electrodes as shown in Fig. 12, leaving about 2 mm. between. A movable

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[1] Loc. cit.

slit of 0.1 mm. width was placed about 1 cm. in front of the crystal in the path of a parallel beam of light from an arc lamp. The slit was moved along in front of the selenium by a screw attachment. The conductivity was read when the illumination was on the contacts and at various positions between. The result showed the change of conductivity by constant illumination to be almost unvarying throughout the distance between the electrodes and to be slightly less when illuminated at the contacts. This result seems to lead unmistakably to the conclusion that in the crystal studied, light action is essentially a genuine action throughout the selenium crystal. The action was not a surface action, as evidenced by the fact that if the light impinged on the back side of the crystal the effect was unaltered.

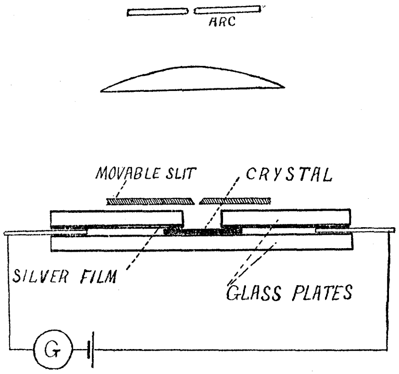

Fig. 12.

The Action of Light Spreads Inside of the Crystal.—With the arrangement shown in Fig. 12 the slit was adjusted midway between the two electrodes. Then the slit width was widened .05 mm. on each side at a step, the idea being that if each fraction of the light altered the part of the selenium in its path, that the change of conductivity would be in direct proportion to the width of the beam. This should follow from the fact that the parts of the selenium crystal were resistances in series. However the following is typical of the results obtained.

Slit Width Mm.	Convectivity.	Slit Width Mm.	Convectivity.
0	40	.4	101
.1	72	.5	109
.2	81	.6	118
.3	92	.7	126

This indicates that the first unit of light that falls on the selenium by diffused light in the selenium crystal or some sympathetic mechanism acts to either side of the path or throughout the crystal. Ever after that as the path is widened there is only the action of the selenium in the path or its equivalent. The first unit of light produces an excess of conductivity of 22 units, which can only be ascribed to a spreading action inside of the crystal or its equivalent. The above argument presupposes that not all the light absorbed in the selenium can go toward altering the conductivity, or further that the absolute alteration of the value of conductivity decreases with increased illumination.

The Variation of the Conductivity Change with the Light Intensity.—In the previous part of the paper, it was noted that the change in conductivity by a given illumination was proportional to the conductivity in the dark. This may be written in the form $dC/dI = k \cdot C$, providing that for very small illumination intensities the constant k should remain unchanged. By the integration of the above equation is obtained the value of the conductivity for any intensity, as $C = C_0 e^{kI}$, where C_0 is the conductivity in the dark.

I have not yet had the time to check this equation with more direct experiment.

ACTION OF TEMPERATURE.

Dieterich[1] has recently shown that the character of the wave-length sensibility curves can to a large degree be controlled by the heat treatment of the selenium during annealing, particularly by the temperature at which the selenium was heated. For example, he found that the annealing at about 200° produced a pronounced maximum in the red end of the spectrum, while if the annealing were about 150°, there was a relatively high maximum about .55 μ. Unfortunately I have not thus far been fortunate in producing large crystals by sublimation at both the above temperatures. Therefore we were not able to investigate individual crystals as to the character of the sensibility curves. However the next best step was taken. A selenium cell form (soapstone frame with parallel platinum wires for electrodes) was placed in a highly evacuated tube in which the selenium was to be sublimated. It was so situated lengthwise of the tube that at the end of higher temperature large crystals of the lamellar type formed in considerable abundance with smaller ones nearby the electrodes. About a centimeter further along the frame where the temperature was perhaps 200° was deposited an even finer crystalline structure of unknown texture. After remaining in the tube several days, almost the entire framework revealed in the presence of intense illumination a large number of glittering crystal faces, resembling in a striking manner the appearance of freshly fallen snow in bright sunlight. Except for the crystal faces in the selenium that were at just the right angle to the observer the background was relatively dark.

By the apparatus recently described by Brown and Sieg[2] we obtained the sensibility curve for the crystal masses at two places in this selenium bridge. For the crystal mass supposedly sublimated at the higher temperature, the upper curve in Fig. 13 was obtained, while for the selenium deposited at the lower temperature the lower curve in the figure was

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[1] PHYS. REV., N.S., June, 1914.

[2] PHYS. REV., N.S., 2, p. 487.

obtained. Thus, contrary to Mr. Dieterich's result referred to, the red maximum appears in the crystals formed from the higher temperature. However it must be noted that this maximum is not in the same position as the maximum which Mr. Dieterich obtained at lower temperature. The cause of the shifting of the maximum will be searched for by the investigation of separate crystals.

General Considerations.

The present status of the theory of light sensitive selenium points towards a separtion of the complex elements along three lines, the light sensitiveness inherent in a given crystal structure, the varying action because of varying refraction, scattering and penetration, and the minor alterations due to the indirect action of the light on the contacts. In view of White's work it seems that contact resistances play a greater part in selenium blocks than in selenium crystals. Whether varying pressure will alter the character of the curves, will depend perhaps on the likeness or unlikeness of the light action for different parts of the spectrum. This point is under investigation at the present time. Also an attempt is being made to locate what characteristics of sensibility curves are seated essentially in individual crystal forms.

This much at least is settled: that the entire action of light in certain crystals at least is in the body of the selenium and not located either at the electrodes or at the surface layer.

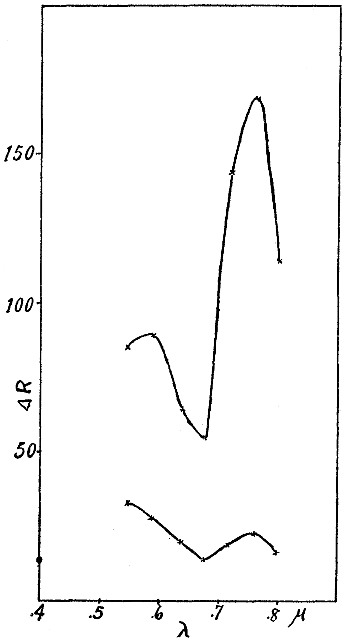

Fig. 13.

Perhaps in the so-called selenium cells the varying temperature action as well as the varying pressure and light action are involved in connection with contact resistances. By placing high pressures, a few atmospheres, on a single crystal of selenium we should be able to eliminate this contact resistance and thereby arrive at the true temperature coefficient of a pure form of selenium and also the true light sensitiveness at various temperatures.

The action of light seems to be in centers inside the crystals and does not necessarily involve the existence of more than one complete crystalline form. These centers inside the crystal resemble the so-called active centers in zinc sulphide as described by Rutherford.[1]

The specific conductivity of the crystals tested varied between 200 ohms and 10^7 ohms depending on the pressure applied. Judging from the conductivity, it would seem that the selenium in White's selenium blocks existed under an internal strain as a result of crystallization in a rigid form. If so we should expect different stress inside the blocks from what it was near the surface. Possibly some such basis might account for the increased photoelectric properties at the electrode contacts.

SUMMARY.

1. A large number of new crystals of metallic selenium have been formed, some of which are of very large size.
2. All of these forms except one are very transparent selectively to light, a large amount of light penetrating to a greater depth than 0.2 mm.
3. All the forms tested are conducting, showing a specific conductivity varying between 200 and 10^7.
4. All the crystal forms but one have been observed to be doubly refracting.
5. All the crystal forms increase in conductivity when illuminated.
6. The action of light is in the selenium itself and not at the contacts.
7. Mechanical pressure produces a genuine change in the selenium which may alter the conductivity more than a thousand times.
8. The absolute change of conductivity in one crystal by constant illumination was proportional to the conductivity in the dark, when that conductivity was altered by pressures between 1 and 180 atmospheres.
9. The temperature at which the crystals sublimate in mass has been shown to influence the character of the wave-length sensibility curves.
10. It has been shown that the production of individual crystals of metallic selenium of large size opens up a large field of investigation, which promises to be free from some of the possible complexities in selenium cells.

In conclusion I desire to thank Mr. M. H. Teeuwen for his assistance in designing and constructing apparatus, Mr. Scott Walker for assistance in taking observations, and Professor G. F. Kay, of the Geology Department, for the use of apparatus and also for his kind and generous help in the crystal studies.

THE PHYSICAL LABORATORY,
THE UNIVERSITY OF IOWA,
April 11, 1914.

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[1] Proc. Roy. Soc., *A*, 83, p. 561, 1910.

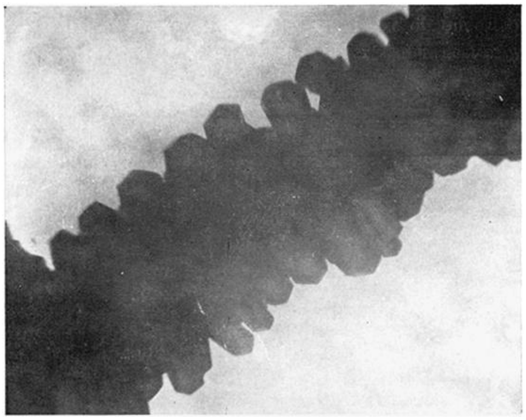

Fig. 1.

Magnified hexagonal crystals, natural size of single crystals not over 0.1 mm. in width.

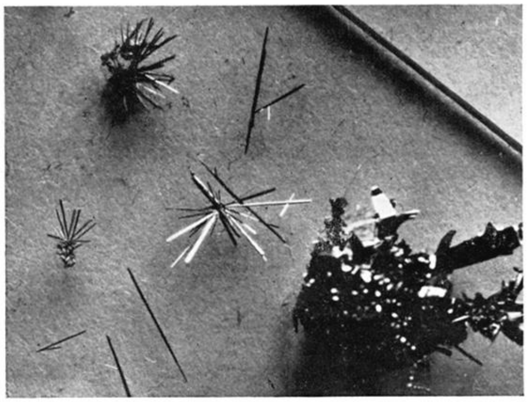

Fig. 2.

(*a*) Groups of acicular crystals to the left. Natural size of longest ones about 11 mm. (*b*) Growth of lamellar crystals in lower right-hand corner, the largest of which as seen in the figure was about 9.0 × 2 × 0.4 mm.

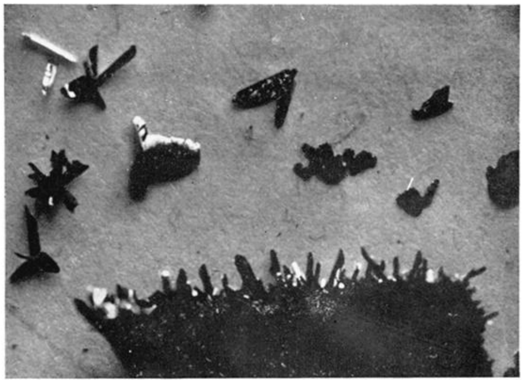

Fig. 3.

The lower part of the photograph shows the growth of single and twinned crystals of maximum length about 4 mm. at the edge of a crystal mass of finer grain. The scattered crystals are of the same formation.

Fig. 4.

The above crystals are the same form as those shown in Fig. 3, but were photographed by transmitted light with a magnification of about 100 times.

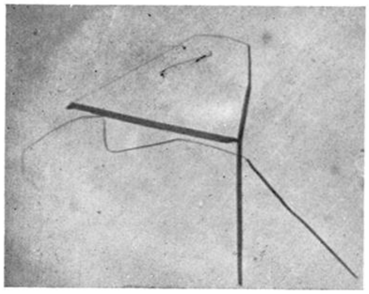

Fig. 5.

Two crystals of flexible lamellar type. The longest of the above was about 4 mm. long. The width and thickness may be estimated from the reproduction.

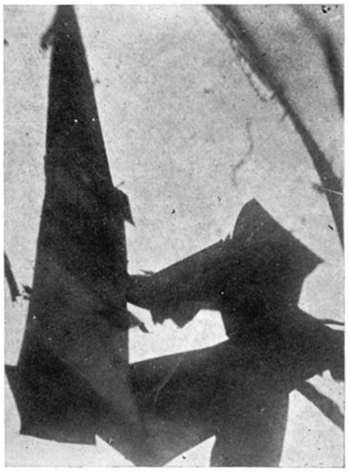

Fig. 6.

Lamellar crystals of gradually increasing width. Magnification about 100. Note the striations making an angle of about 35° with the edge.

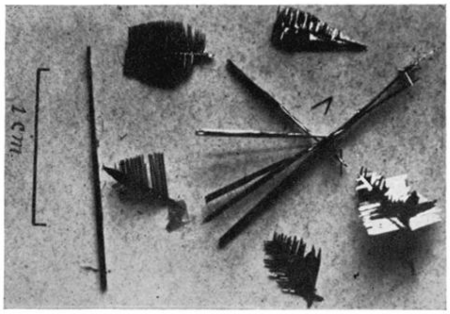

Fig. 9.

Crystals of metallic selenium by sublimation. Acicular hexagonal and acicular with side branches. Side branches perpendicular to stem are hexagonal. Those leaving at angle of 60° are lamellar plates showing parallel extinction.