THE ELECTRICAL, THE PHOTO-ELECTRICAL AND THE ELECTRO-MECHANICAL PROPERTIES OF CERTAIN CRYSTALS OF METALLIC SELENIUM, WITH CERTAIN APPLICATIONS TO CRYSTAL STRUCTURE.

By F. C. Brown.

OUR information concerning the structure of the atom has perhaps advanced faster of recent years than has our information about the larger unit which is composed of atoms. The phenomena of radioactivity which are fundamentally independent of crystal structure have in a large measure furnished the data for studies on the atom. In the end the facts about either unit will aid in the understanding of the other unit of matter. Bragg's studies[1] on the reflection of X-rays show the crystal structure to be made up of stationary parts. These parts indicate charges of electricity resting almost in a plane. I wish in this paper to correlate some notions about the atom and the crystal after I have related some experiments with crystals of metallic selenium which point toward a new departure as to the rôle of the conducting electron in matter. These crystals of selenium show many unique properties involving co-related phenomena of electrical, optical and mechanical nature, and it is because of these new phenomena that we have a possible opportunity of arriving at further advances in the electrical view of matter. There will be given reasons however for believing that these related phenomena are merely accentuated in selenium much as the magnetic properties are accentuated in iron.

Action at a Distance by Light.

Recently[2] it was shown that when light illuminated one part of a crystal that there was a consequent change of electrical conductivity throughout the crystal. The electrical effect was observed in one case 10 mm. away from the point of illumination, and the effect was apparently as large as if the illumination fell on a point only 0.5 mm. away. In the latter paper referred to it was shown that this electrical effect could even be transmitted from one crystal to another when the crystals

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[1] W. L. Bragg, Proc. Roy. Soc., *A*, 89, p. 248, and W. H. Bragg, Proc. Roy. Soc., *A*, 89, p. 277, 1914.

[2] Phil. Mag., Ser. VI, vol. 28, p. 497, and Phys. Rev., N. S., vol. 4, pp. 85 and 507, 1914.

were grown together. The essential difference between the direct action and the transmitted action as thus far observed is that the maximum effect for a given energy intensity is produced at longer wavelengths in the latter case. This shifting of the maximum sensibility was observed for 30-second exposures, which duration probably gave very nearly the equilibrium effect for a given intensity.

The action was, so far as could be observed, just as rapid when transmitted to a distance of 10 mm. as when transmitted only 0.5 mm. It thus can not be a mere temperature disturbance. Furthermore the major portion of the recovery after removing the light source was almost instantaneous.

When the crystal examined was illuminated at various points by a narrow beam of light it appeared that the light action was not uniform along the crystal. There were centers of varying sensibility. Thus the crystal has a mechanism of rather large dimensions, which when acted upon at different places produce results differing in magnitude.

The question that first arises is whether the equilibrium conductivity with a given illumination on a crystal represents an altered state of the crystal structure or whether it represents merely a condition in the crystal in which there is a constant liberation and supply of electrons that scatter throughout the crystal; the supposition being that for equilibrium the balance is kept up by the absorption of a similar quantity of electrons.

THE PRESSURE EFFECT IS NOT TRANSMITTED.

It has already been shown[1] that the conductivity of either the acicular or lamellar crystals may be increased several hundred times by the application of mechanical pressure. Also it was demonstrated in the same paper that the absolute change of conductivity by a given intensity of illumination increased proportional to the conductivity in the dark. Apparently the increased pressure on the crystal made it easier for the light to free the electrons. The view that is here being taken is that the greater the pressure the greater is the number of electrons existing in a state of equilibrium almost unstable. When in the dark it is these semi-fixed electrons that are transferred from center to center by electrical potential differences and it is also these that light acts upon and makes free of the atomic structure. Consequently the greater the number of these semi-stable electrons the greater will be the change of conductivity by a given illumination. This is a fairly simple explanation of the increased light-sensitiveness of the crystals when under high pressures. Of course later information may make this explanation purely a conventional one.

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[1] PHYS. REV., Ser. 2, Vol. 4, p. 85, 1914.

The above view was formulated to accord with the experimental result showing the pressure effect not to be transmitted to parts of the crystal not under pressure. The experiments were carried out as shown diagramatically in Fig. 1. The opposite ends, marked (1) and (2), of either a lamellar or an acicular crystal were placed between separate electrodes of brass. This apparatus permitted a number of experiments of varying character to be performed. If end (2) were illuminated the conductivity at end (1) changed almost as much as it did at the illuminated end. If the pressure were increased on end (2) the absolute sensibility to light increased almost proportional to the pressure, but the change of conductivity at (1) by illumination at (2) was not increased by this increase of pressure on end (2). However if the pressure were applied at (1) instead of (2), and the illumination just as above on end (1), then there was an increase in the absolute conductivity at (1).

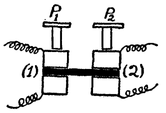

Fig. 1.

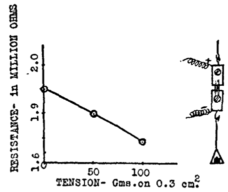

Fig. 2.

The conclusion is that the *pressure effect merely makes it easier for the light to change the conductivity and that the pressure does not act except at the point of application.* As will be pointed out elsewhere these results lead directly to the conclusion that pressure does not increase the conductivity by adding free electrons. And in view of the fact that the increased light-sensitivity due to high pressure is not transmitted we are justified in concluding that light does not produce free electrons in the generally accepted sense. In other words none of the conductivity in these crystals can arise from free electrons such as exist in metals according to the hypothesis of Richardson and Brown.

In the above experiment it was immaterial whether or not a current was flowing across both ends of the crystal simultaneously. A second set of experiments was made, with the same apparatus in such a way that the current flowed all the time through the part of the crystal under study and this same part of the crystal was not under pressure by the electrodes.

The pressure was applied simultaneously on both ends of the crystal. The essential part of the resistance was between the electrodes and this part of the crystal was obviously not under pressure. By varying the pressure on the crystal there was no change in the resistance. The electrodes were separated in different tests by distances ranging from 0.5 to 5 mm. In no case was there evidence that the change of resistance by pressure extended beyond the region under stress. Likewise the light-sensitiveness of the middle portion of the crystal did not increase as a result of the pressure on the ends.

Another related electro-mechanical effect is the change of resistance accompanying a stretching force. For the study of this effect five branch crystals growing out from a central spine such as reproduced in the earlier article were chosen. The opposite ends of these crystals were clamped in brass electrodes as shown in Fig. 2, so that the stress was distributed among the five crystals. The crystals were stretched by adding weights to a pan pulling on one of the electrodes as shown. This experiment was rather difficult because the apparent malleability of the crystals caused them to flatten out, tear and pull out of the clamps and also because the slightest twisting would cause the crystals to weaken and break. However I did succeed in observing that the crystals would withstand a stretching force greater than 10 kgm. per square centimeter. With such stresses there was a decided decrease of resistance as shown in the curve of Fig. 2. When the weights were removed the resistance usually increased again to its previous higher value without stress, thus indicating the crystal to be in equilibrium either with or without the additional forces.

The change of resistance for tensile forces does not seem to be as great as for compression forces as previously related. The interpretation that is to be placed on these results is that stress by stretching brings an increased number of electrons into almost unstable equilibrium and thus increases the current with a given potential difference. The fact that the effect is not so large as by compression forces may arise from an increasing of the distance between some of the semi-stable electrons, when this distance is measured in the direction of current flow.

THE ELECTRICAL CONDUCTIVITY WITH VARYING ELECTRICAL STRESSES.

On the preceding view of the structure of the crystal in which conducting charges are tied up in the atom in a quasi-stable condition, we should expect the number of electrons that could be dragged out of their fixed positions would vary with the electrical forces acting on them, and that only forces acting in the direction of current flow would alter the magnitude of the current. In what way the current should vary with the electrical forces will depend upon a more exact picture than we are yet able to formulate. When a lamellar crystal was under pressures only slightly greater than atmospheric, the resistance varied with increasing potential difference at the electrodes as shown in the lower curve of Fig. 3. The potential was applied in the direction of the current flow for about 20 seconds. For low potentials the change of resistance was almost steady after this time, but for high potentials, above 100 volts, there were signs of unsteadiness if the current were left on too long. Next the pressure was increased so that the conductivity increased twenty times in the dark, and the resistance was then observed to vary as shown by the upper curve in Fig. 3. At first sight one might be inclined to say that the change of resistance with varying electro-motive force is materially less with high pressure on the crystal. But inspection shows that only the percentage change is greater with low pressure. The following table gives the conductivity for some potential differences as deduced from the data graphed in Fig. 3.

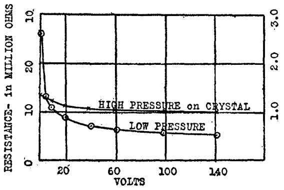

Fig. 3.

Difference of Potential.	Conductivity in Dark.	
	With Low Pressure.	With High Pressure.
1.4 volts	3.84×10^{-8}	75.2×10^{-8}
10 volts	9.17×10^{-8}	83.3×10^{-8}
41 volts	14.3×10^{-8}	96.1×10^{-8}
100 volts	18.2×10^{-8}	98.0×10^{-8}
143 volts	19.6×10^{-8}	100×10^{-8}
Extreme variation in absolute specific conductivity	16×10^{-8}	25×10^{-8}

It is observed that the extreme variation of conductivity for the potentials used was somewhat greater with the crystal under high pressure than under low pressure. This merely signifies that the saturation current was not nearly reached by increasing the conductivity by a factor of twenty. The increased pressure probably makes the electrons free to leave the atomic structure with lower potentials. The instability of the electrons is increased by either mechanical pressure or electrical stresses.

Light-sensitiveness with Different Potentials.—If light produces free electrons and the electrical stress merely pulls electrons out of the atomic structures in the line of conduction, we should expect that the conductivity by illumination would be increased by the same amount regardless of the potentials across the crystal. This is on the supposition that the conductivity increases proportional to the increase in the number of conducting electrons, and that the stability of the fixed electrons in no wise determines how many are to be freed by light.

The following table gives the results that were obtained to check the validity of the above, when the crystal was illuminated with light of constant intensity until equilibrium was reached.

Potential Fall Across Crystal.	Resistance.		Ratio of $\frac{\text{C in Dark}}{\text{C in Light}}$.
	In Dark.	Illuminated.	
1.4 volts	1.30×10^6	$.82\times10^6$	
	1.20 "	.80 "	
	1.20 "	.79 "	
	1.20 "	.79 "	
	1.20 "		1.53±.03
60 volts	$.475\times10^6$	$.299\times10^6$	
	.475 "	.310 "	
	.49 "	.323 "	
	.492 "	.325 "	
	.495 "	.330 "	1.53±.02

It is observed that the percentage increase of conductivity is the same regardless of what the initial conductivity may be as influenced by the potential fall across the crystal. But this means that the absolute increase of conductivity is nearly three times greater with the higher voltage. Therefore the presumptions mentioned above are not true. The exactness of the ratio of the increase of conductivity would favor the view that the light renders a constant number of electrons in a quasi-stable equilibrium, and that the apparent increased sensibility by using higher potentials is merely the result of a pulling out of a greater number of semi-stable electrons.

It should be noted that the constancy of the light-sensibility ratio above shown for electrical potentials is identical to the result noted in my previous paper[1] where the percentage increase of conductivity by illumination remained constant for varying pressures. No doubt the two sets of results have an analogous explanation and this leads to the suggestion that electrical stresses and mechanical pressures alter the equilibrium of the crystal structure in identical ways.

The Non-transmissibility of the Electrical Potential Effect.—If the above identity exists we should expect that the effect of high potentials should alter the conductivity only on that part of the crystal in the immediate field the same as found for the pressure effect. Two experiments were carried out in a fairly satisfactory manner to answer this question.

In the first experiment one end of an acicular crystal was placed

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[1] Loc. cit.

between electrodes differing in potential by 1.4 volts. The exterior circuit was closed through a galvanometer as shown in Fig. 4. The deflection of the galvanometer was noted. Then a potential difference of 100 volts was applied across the opposite end (*B*) of the crystal. This high potential changed the conductivity of end (*B*) by about a factor of five, but there could not be detected the slightest change of conductivity at the end *A*, as result of the potential effect, even when the opposite sets of electrodes were approached within one millimeter of each other. It should also be noted that there was no permanent potential generated at (*A*) by the application of the high potential at (*B*). Such a potential would have been indicated by the galvanometer.

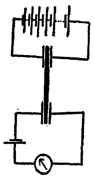

Fig. 4.

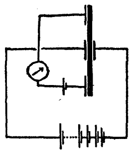

Fig. 5.

The second experiment was designed to detect any effect by an electrical stress acting at right angles to the current flow. The high potential was applied across the middle of the acicular crystal as shown in Fig. 5. The conductivity was being measured by a current flowing lengthwise of the crystal. However a strip of mica on one of the middle electrodes prevented the flow of a current by the high potential of 200 volts.

The result of this experiment was also negative. These two experiments show that a selenium crystal may change its resistance along one axis without altering the resistance along a perpendicular axis. This result is explicable on the view that free electrons are not the current bearers in non-illuminated selenium.

It may be that the piezo-electric effect, as exhibited for example in quartz where a number of electrons are freed by pressure, bears a certain resemblance to the effect described above. The quartz perhaps does not show a corresponding change of resistance because of its extreme insulating properties.

Conclusions.

It has been shown, (1) when a selenium crystal is illuminated at certain points that the conductivity of the entire crystal is increased, (2) that when pressure is applied to the crystal only that part of the crystal under pressure is altered, (3) that electrical forces alter the conductivity only of that part directly under the forces and further that the influence is exerted only in the direction of the electrical force.

The direct conclusion is that light action has to do with an essentially different mechanism than electrical stresses or mechanical stresses. Starting with the above fundamental facts and correlating the other facts mentioned in the paper, I have attempted to formulate certain notions about the structure of the crystal.

This notion premises that a crystal when in the dark has no free electrons in the ordinary sense such as was found to exist in certain metals by the hypothesis and experimental work of Richardson and Brown.[1] True a crystal conducts electricity when in the dark, but this conductivity is small compared with that of the metals. The elementary notion of the crystal is merely a structure composed of positive and negative charges in equilibrium with each other. But this equilibrium is for a large number of the electrons at least in a very low degree of stability. The electrons would be held in equilibrium by the positive forces essentially, but certain of them while necessary to the complete atomic structure, would nevertheless leave the centers (*i. e.*, perhaps atoms) when under small stresses. So long as an electron remains outside an atom requiring one or more electrons, this electron would behave as the traditional free electron. Thus whatever makes free electrons would increase the conductivity.

The hypothesis is that the conductivity in the dark does not arise from the free electrons, except those that have not had time to adjust themselves following an internal disturbance, but from electrons that are pulled from one atom to the neighboring atom and so on by the electrical forces across the crystal. The following is evidence for this view; first it was noted that for very small electromotive forces the resistance was almost infinite and for increasing potentials up to a certain limit the resistance decreased very rapidly. Secondly, it was noted that very large potential differences acting at right angles to the current flow did not alter the magnitude of the current.

The pressure effect is readily explicable on the basis that no free electrons exist in the crystal when in the dark. Pressure may increase the conductivity many hundred fold, but it will not influence the resistance outside the part of the crystal pressed upon. It would seem then that mechanical pressure merely pushes the electrical charges, associated with neighboring atoms, into a less stable equilibrium, perhaps closer proximity, so that a given electrical stress can pull more electrons from one atom to the next.

We are now in a position to assert something concerning the nature of light-action, based on the fundamental property of transmitted action.

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[1] Phil. Mag., Ser. VI, 16, p. 353, 1908.

By some mechanism the light can, no doubt because of its electromagnetic properties, lower the degree of stability of many or all of the electrons throughout the crystal. These same electrons may have their degree of stability yet further lowered by mechanical pressure. The lower the average stability of the electrons the greater will be the current with a given potential difference. With a greater potential difference the same light intensity would therefore seem to produce a greater change of conductivity. The electrons after removal from their fixed positions may behave, until reunited in the structure, somewhat as the traditional electron.

The action of light is not local. The electrons are made less stable or temporarily free by an indirect mechanism operating everywhere in the crystal. The effect is almost uniform at all points. It travels too fast to be a temperature transmission and the maximum sensibility for the transmitted action is in the visible spectrum. The transmission is at least analogous to that of a mechanical vibration, although only certain parts of the crystal may take part in its operation.

The reader will observe that aside from the experimental work the essential new thought in this paper is a new hypothesis to explain the nature of electrical conduction in certain crystals. This hypothesis bears some resemblance to the accepted theory of electrolytic conduction, the distinctive feature being that only electrons move from one center to the next in the chain of centers between electrodes. This view requires that the crystal shall have fixed electrons in its structure but no permanently free electrons.

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