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THE LIGHT SENSITIVENESS OF COPPER OXIDE.

By A. H. Pfund.

OF the various substances which experience an increase in conductivity under the influence of light, selenium and stibnite show the effect most markedly. A comparative study of these substances has shown an unmistakable parallelism of behavior and this has pointed toward the conclusion that the mechanism involved in the production of light-sensibility is probably of the same general character. It is needless to state that hardly a start has been made toward explaining the complicated behavior of these substances. With the idea in mind that something might be learned from a study of other light-sensitive substances, yet unknown, a search was begun. The first, new light sensitive substance discovered was cuprous oxide (Cu_2O). While indications of light-sensitiveness were also found in other substances, the following discussion is to be confined to the consideration of cuprous oxide.

Mode of Preparation of Cu_2O.

Cuprous oxide was prepared from a band of pure copper having the following dimensions: $0.75 \times 10 \times 150$ mm. This band was heated in air by means of an electric furnace at a temperature of about 900° C. for 20 hours. At the end of that time, the copper was entirely oxidized but for a short portion near the ends of the band. The entire mass appeared grayish-black and was quite opaque to light. Upon breaking up the original long strip into lengths suitable for making cells, these shorter pieces were dropped into aqua-regia of moderate strength. This was done in order to dissolve off the outer coating of cupric oxide (CuO). The remaining mass of Cu_2O showed a beautiful crystalline structure and marked translucency toward red light even in layers exceeding 1 mm. in thickness. In order to prepare thinner layers several modes of procedure were followed: (1) the original, thick layer was ground down

on an emery-wheel, (2) the thickness was reduced by means of aqua-regia, (3) pieces of oxide were scaled off the ends of the original band. These scales were removed by bending the partially oxidized strip, whereupon they were dropped into aqua-regia to remove the CuO. As a result of this procedure, the scales had a thickness of 0.1 to 0.3 mm. and appeared a brilliant ruby-red in transmitted light.

COPPER OXIDE CELLS.

The types of cells most frequently used are shown in Fig. 1, *A* and *B*. Here *a* represents a strip of tinfoil about 0.5 mm. wide, either straight as in 1*A* or hairpin shaped, as in 1*B*, in close contact with the surface of cuprous oxide. The two electrodes *bb'* consist of flexible tinsel which is held in contact with the Cu_2O by shallow pools of celluloid dissolved in amyl-acetate (albilene). After the acetate has evaporated and the firm celluloid is left, the entire upper surface of the cell receives an opaque, cathodic film of gold. Upon removing the strip of tinfoil the cell is mounted in a glass tube and is then ready for use.

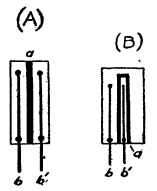

Fig. 1.

In order to study the behavior of such cells at temperatures ranging from +20° to −180° C., the mounting shown in Fig. 2 was used. Here *AA* represents a block of brass which is split—the two halves being separated by a thick layer of mica. A disc of mica *M* is fastened to the brass block and the Cu_2O cell *C* is mounted on the mica. The mica plate and cell are held in place with albilene which, unlike sealing wax, etc., does not release its hold at liquid air temperatures. The two strips of tinsel, coming from the cell, are soldered to the brass block as also are the two wires leading to the outside of the test-tube *T*. A small hole is drilled into the brass block so as to receive the junction of a german-silver-copper thermocouple by means of which the temperature of the system may be determined. A glass or quartz plate covers the end of the testtube and this is finally exhausted and sealed off.

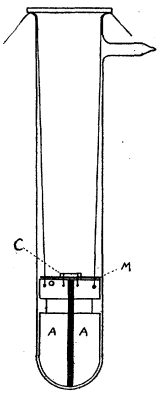

Fig. 2.

The resistance and light-sensitiveness could be made to vary over a wide range—depending upon the design of the cell. One of the best cells thus far made is of the type 1*B*. The width of the bare strip of Cu_2O is about 0.5 mm. and the thickness of layer is 0.8 mm. The resistance at 17° C. for 1 volt is 15,200 ohms in the dark. A 40 watt tungsten lamp at 20 cm. produces an increase in conductivity of about 15 per cent.

By connecting this cell to a 2 volt battery and a simple potentiometer, the sensibility is such that exposing the cell to diffuse daylight, too faint to read by, throws the galvanometer spot of light off the scale.

ACCESSORY APPARATUS.

In order to study the effect of monochromatic radiations in the spectral interval 3μ to 0.4μ a Fuess monochromatic illuminator was used. The energy carried by the various bundles of radiation was measured by a two-junction vacuum thermopile[1] whose receiving surface had an area 1×6 mm. The thermopile was connected to a D'Arsonval galvanometer of 15 ohms' resistance and of a working sensibility of 1.5×10^{-9} amp. per mm. deflection for a scale distance of two meters. The sensibility of the thermopile-galvanometer system was such that the total radiation from a candle at 1 meter distance (after passing through the quartz-window of the thermopile) produced a deflection of 400 mm. As in my previous work on selenium, the copper-oxide cell was connected electrically to form part of a simple potentiometer system in which the above-described galvanometer was also employed.

ULTRA-VIOLET MONOCHROMATIC ILLUMINATOR.

The quartz-spectrometer used for studying the ultra-violet region of the spectrum has been in constant use for the past three years with very satisfactory results. As the instrument has not as yet been described, a few words as to its design may not be out of place. The arrangement of the various parts is shown in Fig. 3. Here the light from an iron-arc A is collected by the condensor C and is focused on the primary slit S_1 from which it passes through the collimating lens L_1 thence through the Cornu prism P and is finally focused near the plane of the secondary slit S_2 by means of the lens L_2. The distinctive feature of this design is that the prism, the lens L_2 and the slit S_2 are fixed, hence the monochromatic radiation leaving S_2 always has the same direction and, as a result, any optical system, no matter how complex, may be mounted in a suitable and fixed position behind this slit. The lens L_1 is mounted rigidly on an iron beam B which is pivoted under the center of the first prism-face at x. The slit S_1, the condenser C and the arc A are likewise connected rigidly. The slit and its connections may slide along the beam B but are guided in their motion by a pin which lies under and in line with the slit and which is forced to move in a groove cut into the track T. This track is so inclined to the direction of B that the chromatic aberration of the lenses L_1 and L_2 is counteracted—and as a

[1] Phys. Ztschr., 13, 870, 1912.

result, the spectrum on the slit S_2 is always in focus. To change from one spectral region to another, the arc-condensor-slit combination is shifted bodily along the beam B and the track T. While the chromatic aberration can not be eliminated perfectly by sliding the slit along a straight line, the adjustment is, nevertheless, surprisingly good. In order to fix, properly, the position of the track T a position of the slit is found which allows radiations of the wave-length 3,500 A.U. to pass through S_2 (which is made several millimeters wide and behind which a piece of uranium glass is mounted in close contact). Next S_1 is made very narrow and the lenses L_1 and L_2 are adjusted in such positions that their respective distances from S_1 and S_2 are the same when the spectrum is in sharp focus on the uranium glass. The next step is to shift S_1 into such a position that blue light (λ = 4,500 A.U.) is sharply in focus on S_2. That portion of the track T lying immediately under the engaging pin is now held fixed and a new position of S_1 is found so as to bring λ = 2,700 A.U. to a sharp focus on S_2. If the track be fastened down rigidly in this position it will be found that, upon shifting S_1, only the two spectral regions λ = 4,500 and 2,700 A.U. will be in sharp focus. While a compromise is effected for the other spectral regions, the deviations from perfect focus in the interval λ = 5,500 to 2,400 A.U. are very slight. It is, of course, always possible to improve the apparatus by constructing a properly curved track T, by keeping the prism always at minimum deviation and by keeping the lenses always at equal distances from their respective slits. In view of the fact that such improvements would have added complications to the construction the simpler form of apparatus was constructed.

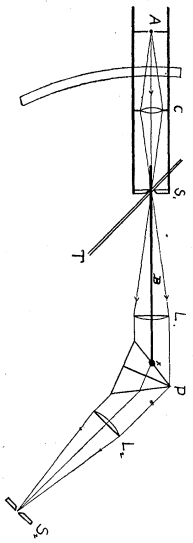

Fig. 3.

The iron-arc used has already been described elsewhere.[1] Suffice it to say that a current no greater than 5 amperes was used and that the upper electrode was positive. Before beginning a series of measurements a bead of iron-oxide, about 7 mm. high, was formed on the lower electrode and a smaller, hemispherical bead was formed on the upper. The arc burned with great steadiness when the two beads were separated by 1.5 to 2.0 mm. Increasing the separation adds but little to the energy radiated in the region of shorter wave-lengths since these come from the regions of the arc very close to the beads. By means of the fluorescence

[1] Astrophysical Journal, 27, p. 296, 1908.

excited on a strip of glass from a broken incandescent lamp bulb, the condensor is adjusted to focus the ultra-violet radiation on the slit S_1. Many tests have shown that energy measurements, taken at intervals during 2 or 3 minutes rarely differ by more than 2 or 3 per cent. if the arc is burning properly. The amount of energy delivered by this spectrometer is large. By mounting the thermopile behind S_2, deflections greater than 500 mm. are obtained in the region $\lambda = 2{,}500$ A.U. with slit-widths no greater than 0.5 mm. It has been found advisable to insert a quartz tank containing a 2 cm. layer of water in front of the slit S_1. A piece of (copper) ruby glass was used as a shutter in the interval 5,500 to 2,900 A.U. and a piece of clear glass was used for the region below 2,900 A.U.

THE VOLTAGE EFFECT.

In order to study the change in conductivity with applied voltage, a Cu_2O cell was connected to a Paul millivoltmeter (used as a galvanometer) and a variable source of potential. The resistance of the millivoltmeter was but 50 ohms which quantity is negligible in comparison with the resistance of the cell. The readings were taken as shortly as possible after closing the circuit in order to avoid the slow creep which sets in when the current is allowed to flow for some time. As soon as a reading had been taken, the circuit was broken and two minutes were allowed to elapse before the process was repeated. The glass tube containing the cell was mounted in a water-bath at 17° C. The results obtained are shown in the following table and in Fig. 4.

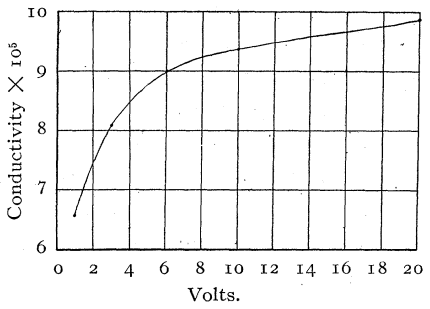

Fig. 4.

E.M.F.	Resistance.	Conductivity.
1 volt.	15,200 ohms.	6.6×10^{-5}
3	12,300	8.1
6	11,100	9.0
10	10,600	9.4
20	10,100	9.9

The fact, that the conductivity increases markedly with the voltage applied, shows that cuprous oxide, like selenium and stibnite, does not obey Ohm's law. That the " voltage effect " is not due to temperature changes has been demonstrated repeatedly.[1]

LIGHT EFFECT *vs.* HEAT EFFECT.

In the present work the question has arisen whether Cu_2O, with its large, negative temperature coefficient of resistance (0.024) owes its increase in conductivity to a heating effect or to a specific action of the light. While all of the experiments on the color-sensibility curves make it highly improbable that we are dealing with a heating-effect, the following crucial experiment was carried out. A cell, similar in design to that shown in Fig. 1*A* was prepared and the central portion was covered with a very thin, non-conducting layer of albilene (celluloid). Upon connecting this cell to the potentiometer system and projecting monochromatic beams of light upon the central strip, a galvanometer deflection of more than 100 mm. was observed. This deflection did not increase upon prolonged illumination, but remained steady. Since the galvanometer required 7 seconds in order to reach its maximum deflection, it is evident that the change in conductivity occasioned by light reached a steady state in an interval of time at least no greater than 7 seconds. That a temperature equilibrium could have been reached in the rather massive piece of Cu_2O seems improbable. Next, the central strip of oxide was painted over with a thin but opaque coating of lamp-black and shellac in alcohol. This produced an absorbing surface which would heat up the cuprous oxide upon exposure to radiation. Electrical conduction through the lamp-black was prevented by the coating of celluloid underneath. As a matter of fact the resistance of the cell was not affected by putting on the layer of lamp-black. Upon exposing the cell to the same radiations as before, no galvanometer deflection as great as 1 mm. was observed. The conclusion to be drawn is that, while there may be a slight effect due to heating, the observed effect is preponderatingly due to a specific action of the light.

COLOR SENSIBILITY CURVES.

The color-sensibility curves were obtained in the usual manner by throwing monochromatic slit-images on the copper-oxide cell and observing the resultant change in conductivity. The energy carried by each monochromatic bundle was made the same by projecting the radiation on the thermopile and varying the intensity so that the same gal-

[1] Luterbacher, Ann. d. Phys., 33, p. 1392, 1910.

vanometer deflection was obtained. A typical curve for a cell, similar in design to that shown in Fig. 1*A* is plotted in Fig. 5. This cell had a thickness of layer of 1.2 mm. and a central, bare strip of Cu_2O 1.5 mm. wide. In all cases the equilibrium change in conductivity was recorded. Curve *A* applies to a temperature of +19° C. while curve *B* applies to a temperature of −127° C. The last-named curve was obtained by lowering the test-tube, containing the cell, into a Dewar flask containing liquid-air. By raising or lowering the liquid-air surface and by plugging up the top of the Dewar flask with cotton-batting, the temperature of the cell could be kept constant to within less than 5° C. for hours.

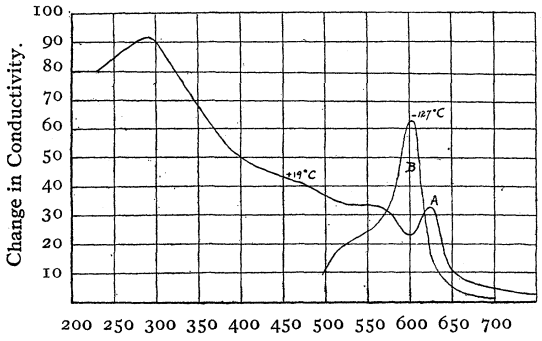

Fig. 5.

It will be noted that the sensibility maximum in curve *B* is shifted toward the shorter wave-lengths, as in the case of selenium and stibnite. The region of greatest sensibility lies far in the ultra-violet near $\lambda = 2800$ A.U. Later on it will be shown that such curves as the above do not represent *the* sensibility curves for cuprous oxide but that they apply only to the cell in question. This will be established by showing that the form of the sensibility curve may be changed by modifying the design of the cell.

Relation between Energy and Conductivity Change.

In order to establish the law which connects the equilibrium change in conductivity (ΔC) with the amount of energy (E) absorbed, a cell was first exposed to a beam of monochromatic radiation which was subsequently cut down to half value by means of a rotating sector. The last column in the following table shows the value of the deflection, obtained by calculation, for half energy on the assumption that the change in conductivity is proportional to the square-root of the energy.

Results were obtained only in the spectral region entirely absorbed by cuprous oxide. From the above table it is evident that, within the limits

Wave-Length.	Deflection for Full Energy (E).	Deflection for Half Energy ($\frac{1}{2}E$).	Calculated Deflection for $\frac{1}{2}E$.
4,820 A.U.	115 mm.	79 mm.	80 mm.
5,220	152	106	108
5,470	175	122.5	122
6,040	118	85	83
6,180	133	91	93

of accuracy of measurement, the law connecting ΔC (which is proportional to the deflections) and E is of the form:

$$\Delta C = KE^{\frac{1}{2}}$$

This same law also applies to selenium and stibnite.

FRONT AND BACK ILLUMINATION.

If electrodes be applied to the upper surface of a disc of selenium and if the lower surface be illuminated, it was shown by Gripenberg[1] that a change in conductivity is produced and that this change is of the same order as that obtained by illuminating the upper surface. Since the selenium was entirely too opaque to permit light from below to penetrate to the electrodes on the upper surface, it is evident that changes in conductivity are also brought about in portions of the selenium not directly illuminated. This phenomenon, which has been termed the "Transmitted Effect" has been studied in great detail by Brown[2] on isolated crystals of selenium. In order to determine whether or not a similar effect was also shown by Cu_2O, many experiments similar to those of Brown and Gripenberg were carried out. Without discussing in detail the ten or more experiments which were carried through, it may be stated that if cuprous oxide shows the effect at all, it is infinitesimal in comparison to that shown by selenium. As a matter of fact, the experimental evidence indicates that, in the case of Cu_2O, the change in conductivity is practically confined to the portion of the material penetrated by the light.

But one experiment will be discussed in this connection. A cell, similar in design to that shown in Fig. 1*A* was mounted in an evacuated glass tube. The disc of Cu_2O was but 0.4 mm. thick and, as a result, showed marked translucency to red light. The tube containing the cell was mounted vertically on a block of wood which could be rotated, between stops, through 180°. In this manner a monochromatic slit-image could first be thrown on that side of the cell bearing the electrodes (front illumination) and then, on the back (back illumination). It goes

[1] Gripenberg, Phys. Ztschr., 15, p. 462, 1914.

[2] Brown, Phil. Mag., 28, p. 497, 1914.

without saying that the light was focused on the bare, central strip of Cu_2O and on the portion immediately behind it. While the various beams were not reduced to equal energies, a water-cell containing cuprammonia was inserted in front of the primary slit so as to cut down the tremendous intensity of the red end of the spectrum. The results are shown, graphically, in Fig. 6.

It is here seen that, for wave-lengths below 6,000 A.U. the change in

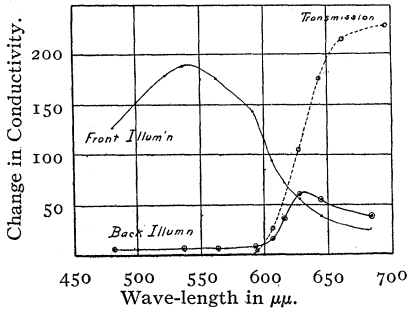

Fig. 6.

conductivity for " back-illumination " is small while for wave-lengths greater than 6400 A.U. the change in conductivity is even greater than in the case of front illumination.[1] If now we consider the transmission of a thin scale of cuprous oxide (as shown by arbitrary numbers in the dotted curve of Fig. 6) we see that the increasing deflections, due to " back-illumination " occur in the spectral region in which the cuprous oxide becomes increasingly transparent. Without carrying through the argument in detail, it would appear that the light from the back gives rise to large changes in conductivity as soon as it is able to penetrate into the region where the current-density is comparatively great. Whether the small, but definite, changes in conductivity, occasioned by the shorter wave-lengths, are in the nature of a true transmitted effect is still an open question.

In this connection is was thought of interest to compare the " front " and " back " illumination curves for selenium and cuprous oxide. A selenium cell, similar to the Cu_2O cell in design and dimensions was prepared. The selenium layer was entirely opaque in the spectral region

[1] Just what this higher value is due to has not been determined. In part, at least, it is due to the fact that the gold electrodes cut off some of the light—furthermore, internal scattering of the light may also contribute toward the effect observed.

Since the scale of Cu_2O was only translucent, no true values for the transmission could be found. The values recorded were obtained by mounting the scale on the first slit of the monochromatic illuminator and measuring by means of the thermopile, the relative amounts of energy for the various wave-lengths. This, of course, yields only a qualitative determination.

studied and the usual sensibility-curve showed a marked maximum at the wave-length 7,000 A.V. The ratio of the change in conductivity brought about by "front" ΔCF and "back" ΔCB illumination is shown in Fig. 7.

The great disparity in the form of the two curves is apparent. In selenium we have a true "transmitted effect" which, instead of being greatest in the deep red where selenium is known to be the most trans-

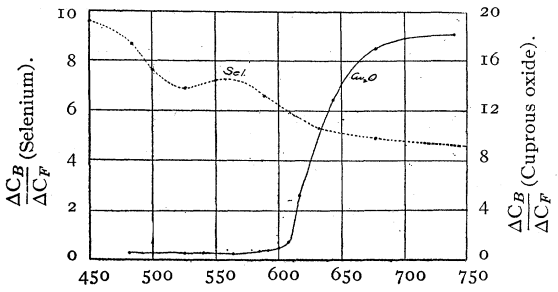

Fig. 7.

parent, is really the greatest in the violet. While these results were obtained with discs of selenium and cuprous oxide consisting of a conglomerate of small crystals, it would be premature to state that the "transmitted effect" does not exist in isolated crystals of Cu_2O. Recently the writer has found that such crystals (cuprite) may be obtained —therefore the above-mentioned uncertainty will be removed shortly. At any rate it has been established that cuprous-oxide, in the form used, shows no definite "transmitted effect" and in this one respect, differs decidedly from selenium.

SENSIBILITY CURVES FOR CELLS OF DIFFERENT DESIGN.

If the change in conductivity is confined to the illuminated portion of cuprous oxide, then, by varying the design of the cell, different sensibility curves ought to result: This inference was tested by constructing two cells out of a single strip of Cu_2O. This strip had the dimensions 1.2 × 5 × 12 mm. In Fig. 8 (*a*) the two gold electrodes *A* and *B* are separated by a bare strip of Cu_2O about 0.75 mm. wide on the flat side of the strip while *A* and *C* are two identical electrodes on opposite sides of the strip. The electrode *B* is about 0.75 mm. wide. Upon connecting the electrodes *A* and *B* to a source of potential, the variation of current-

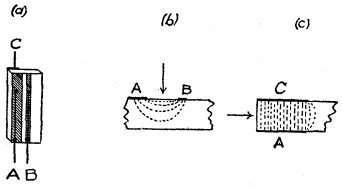

Fig. 8.

density (lines of flow) through the mass of material underneath is shown diagrammatically in Fig. 8(*b*). Here, the region of greatest current-density lies very near the surface, whereas, if the electrodes *A* and *C* be used, the current-density will be practically constant as shown in Fig. 8 (*c*). (Fig. 8 (*b*) and (*c*) are much magnified.) If a beam of red light be allowed to fall on these two cells, cell (*c*) ought to be, relatively, the more sensitive since the light penetrates almost the entire current-carrying layer before being absorbed. On the other hand, cell (*b*) ought to be the less sensitive since but little energy is absorbed in the region of greatest current-density. It is evident that exactly the reverse ought to be true for blue light which is absorbed very near the surface. When these two cells were tested for their sensibility-curves it was found that, while they had almost the same resistance, cell (*b*) was considerably the more sensitive. The actual sensibility curves are shown in Fig. 9, where curve I. applies to cell (*b*) and curve II. to cell (*c*).

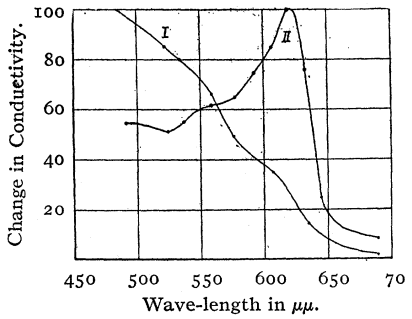

Fig. 9.

It is here apparent that the two curves, obtained from the same material are markedly different and that they differ in the predicted manner. The question here arises as to whether or not the sensibility maximum in the red (near λ = 6,200 A.U.) is really indicative of a high intrinsic light-sensibility of the cuprous oxide. In terms of electron-theory, the " intrinsic-light-sensibility " involves the idea of the number of electrons made available for carrying the current per second, per unit cube, per watt of absorbed energy. The energy is supposed to be absorbed uniformly, *i. e.*, each small element of volume of the unit cube is to absorb the same amount of energy per second. In actual experiment it would be necessary to work with films of the light-sensitive material so thin as to be transparent to all wave-lengths. This would make possible a measurement of the absorbed energy and would fulfill to a fair degree of approximation the condition of uniform current density and light-absorption, imposed on the experiment.

DISCUSSION.

Several years ago the writer suggested the idea that light-sensibility might be due to resonance in consequence of which the number of electrons, made available for carrying the current, was increased. The large amount of work since then carried out by Brown[1] and his co-workers, Nicholson,[2] Elliott,[3] Ries[4] and the writer[5] goes to show that the above suggestion well serves the purpose of a working hypothesis. That the final theory will be established on an electronic basis, seems certain. Without discussing the various points which have been established definitely for the other light sensitive substances, the contribution of the present work to the theory will be taken up briefly. According to the "free-electron" theory of Drude and Riecke, the light-sensibility of cuprous oxide would be explained as an actual liberation of electrons which, subsequently, float about freely between the molecules. As diffusion of electrons from the regions of higher concentration is bound to set in, it would follow that the conductivity of the entire mass of material would eventually be increased even though only a small portion of the surface be illuminated. This means that the "transmitted effect" would necessarily exist. On the "doublet" theory of J. J. Thomson, the effect of light would be to decrease the stability of electrons to such an extent that they might be drawn out of their original "doublet" system into the adjacent one. It is here assumed that the potential applied serves merely to orient the doublets—the actual transference of electrons from one doublet to the next is due to the electric field between doublets. According to this view the region of increased conductivity ought to be confined to the region illuminated and hence, a "transmitted" effect ought not to exist. The fact that a true "transmitted" effect is not shown by copper-oxide goes to show that the results obtained are best accounted for on the basis of the "doublet" theory of metallic conduction.

Similar considerations have been brought forth by Brown who has shown that the "voltage" and "pressure" effects in selenium are not transmitted. In selenium, however, the evidence gained from a study of light-sensibility is not clear-cut since matters are complicated by the "transmitted" effect. The true nature of this effect has not as yet been established. In the case of cuprous oxide conditions are much simplified for it has been shown that, qualitatively at least, the behavior of the

[1] PHYS. REV., 5, p. 395, 1915.
[2] PHYS. REV., 3, p. 1, 1914.
[3] PHYS. REV., 5, p. 53.
[4] Ann. d. Phys., 36, p. 1055, 1911.
[5] PHYS. REV., 34, p. 370, 1912.

substance can be accounted for on the assumption that there is no true transmitted effect.

SUMMARY.

The results of the foregoing work may be stated briefly as follows:

1. A convenient monochromatic illuminator for the ultra-violet has been described.

2. It has been proved that cuprous oxide is light-sensitive and that the effect is not due to heat.

3. The failure of Ohm's law for Cu_2O has been demonstrated.

4. The region of greatest light-sensibility lies in the ultra-violet near $\lambda = 2{,}800$ A.U.

5. Lowering the temperature from 19° C. to −127° C. causes a shift of the red sensibility maximum toward shorter wave-lengths.

6. The equilibrium change in conductivity of Cu_2O is proportional to the square-root of the light-energy absorbed per unit time.

7. "Front" and "back" illumination produces effects in cuprous oxide which are entirely different from those produced in selenium.

8. The change in conductivity in cuprous oxide is limited to the portions penetrated by radiation.

9. The absence of a true "transmitted" effect in cuprous oxide shows that this effect is not essential to light-sensibility.

10. With the same material, the light-sensibility curve of cuprous oxide may be changed markedly by modifying the design of the cell.

11. The results obtained are most readily explained on the basis of Thomson's "doublet" theory of metallic conduction.

JOHNS HOPKINS UNIVERSITY,
November, 1915.