APRIL, 1933 REVIEWS OF MODERN PHYSICS VOLUME 5

The Copper-Cuprous-Oxide Rectifier and Photoelectric Cell

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(Received December 17, 1932)

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GENERAL

IN this review are given many data which seem to be especially of practical interest. They are included on account of their theoretical importance and are chosen with the purpose of providing a good background of information for the many workers who have taken an interest in the physics of the rectifier. Many of the experimental results are published here for the first time.*

When cuprous oxide is formed on copper at a high temperature, the junction between the two has certain unique characteristics. It has the now well-known characteristic of asymmetrical resistance at the boundary between cuprous oxide and mother copper, which is made use of in the copper-copper-oxide rectifier[11]; and the more recently discovered light effect, which consists in the production of an e.m.f. at the boundary between the copper and the cuprous oxide when this boundary is illuminated.[14]

Both of these effects are different from the well-known contact phenomena in that they are distributed over an entire boundary area and are sufficiently uniform to enable one to use not only the full area of a single unit, but as many units as desired in parallel. This is the result of the method of production, which is such that the materials which meet at the internal boundary have never been exposed to the atmosphere or to other substances which could cause contamination of the surface with foreign materials. The layer of oxide is not only formed on the copper, but from the copper as well. On one side of the boundary we have copper of high purity, and on the other side, cuprous oxide of similar purity, and neither has been exposed so as to enable the oxygen of the atmosphere or any other reagents to change the condition of the surface. It is probable that under no condition of experimentation with separate surfaces is it possible to get this degree of absence of contamination.

This unique condition exists when the oxide is formed on the copper at a high temperature. When formed at such a temperature and on clean copper, the oxide adheres to the copper so intimately that the copper and the cuprous oxide may be considered one body of matter. If such a disk of copper is bent to loosen the cuprous oxide, it is found that the cuprous-oxide crystals are often more likely to crack in the body of the crystal than they are to crack away from the copper. In addition to clean surfaces, the very close junction between the two materials is undoubtedly important. Of primary importance is also the fact that the condition of formation of the oxide is very nearly the same over the whole surface, so that the type of junction between the two different types of crystals is uniform.

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* These data were obtained in the Research Laboratory of the Union Switch and Signal Company and with the very valuable and gratefully acknowledged cooperation of D. G. Ackerly, C. M. Bouton, C. C. Buchanan, P. H. Dowling, P. H. Geiger, F. H. Nicholson, A. J. Sorensen, C. K. Strobel, and H. L. Taylor.

Discovery

To emphasize at the beginning this difference between the copper-cuprous-oxide junction here under discussion and contacts between separate bodies of different materials, it may be of interest to report how the discovery of the characteristics of the copper-cuprous-oxide junction was made.

In the fall of 1920 the writer was studying the possibility of using light-sensitive cells as relays in certain circuits. It seemed desirable to try to construct a light-sensitive cell with sufficient capacity to control a comparatively large current. It was thought that the best way to do this would be to arrange the light-sensitive material in a thin layer and to apply contacts to the opposite sides of the layer, thus obtaining a short path with large cross section. The plan was to use materials which changed their resistance upon being illuminated, and cuprous oxide suggested itself since it was known to exhibit this internal photoelectric effect.[126] Cuprous oxide is a brittle material; and in order to support it and make contact to it over a considerable area, it was thought best to oxidize a sheet of copper only partly so that the mother copper could serve as a support for the cuprous oxide and at the same time as a contact to one side. With this backing of mother copper it was expected that the unit would be strong enough also to support a contact on the free surface of the oxide without breaking it. Such a unit was prepared by oxidizing a strip of copper about 1 mm thick, 1.6 cm wide, and 12 cm long in an electric furnace at a temperature between 900° and 1000°C. When the strip was removed from the furnace, the unoxidized copper was about one-half the original thickness. One of the ends was bent enough to break the oxide so that it could be removed and so that the mother copper could be used as one of the connections. On the remainder of the strip the black oxide was removed by holding it lightly against an emery wheel, and contact was made to the outer surface by clamping the strip between pieces of Bakelite and laying a piece of lead between the Bakelite and the cuprous oxide on one side. The original strip, after the black oxide was removed and in its present condition, is shown in the photograph of Fig. 1. A reconstructed assembly is shown in Fig. 2.

FIG. 1. Photograph of first rectifier.

When this assembly was connected to a Wheatstone bridge and subjected to illumination in order to determine the effect of light on its resistance, it was found that whether it was illuminated or dark its resistance remained the same. As the experiment progressed, however, it was found that the resistance was sometimes 400 ohms and sometimes 1200 ohms and that this change in resistance bore no relation to the con-

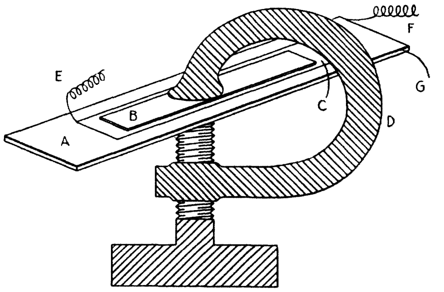

FIG. 2. First rectifier assembly. *A* is oxidized surface of copper strip; *C* is the piece of lead used for contact; *B* is micarta insulation; *E* is the terminal connected to the lead; and *F* is terminal connected to mother copper.

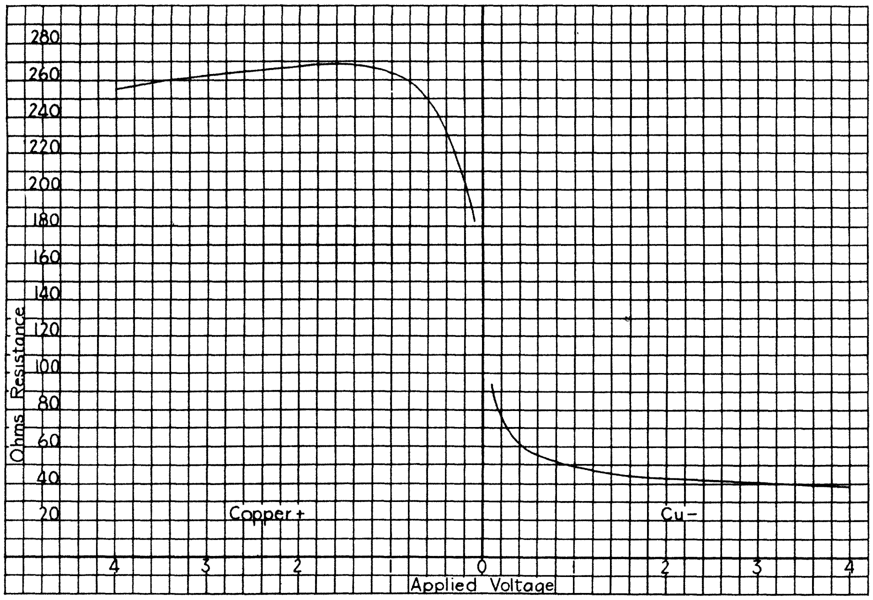

FIG. 3. Resistance voltage characteristic of first rectifier measured in a new assembly 9 years after oxidation. Area of lead, 3.23 sq. cm.

dition of illumination. It was soon discovered that this difference in resistance depended on the polarity of the applied e.m.f. The low resistance was obtained with mother copper negative. The ratio of 3 between the resistances in the two different directions was low and would have been very much higher if a higher voltage had been used on the unit. The voltage was too high to show the photoelectric effect that was found later and was too low to give a very good rectifying effect. The existence of asymmetry, however, showed that the disk could be used as a rectifier and when shortly afterwards a rectifier for small currents was needed, this copper-cuprous-oxide unit was available. After a small amount of development work, the rectification ratio was raised to 10 : 1, then to 50 : 1. Ratios of 50 : 1 or even lower make it possible to build practical rectifiers, and soon a B-battery charger with such disks was designed and built. Fig. 3 shows the voltage resistance characteristic of the original unit in a new assembly made in 1929, nine years after the oxidation.

STRUCTURE

The rectifying characteristic of a single solid body such as this with an extended boundary area between two materials was surprising. Asymmetrical resistances were known, and it is frequently stated in the literature that one substance or another—such as cuprous oxide or galena, for instance—is unidirectionally conducting. As a matter of fact, the writer is not aware that any material in itself has been found to be asymmetrically conducting. If a substance has a certain resistivity in one direction, it has the same resistivity in the opposite direction. Cuprous oxide is like all other substances in this respect, and, of course, copper does not have any asymmetry in its conduction. Arrangements of solids into systems of asymmetrical resistance of useful ratio that were known before the discovery of the cuprous-oxide rectifier all had their asymmetry localized in very small area or "point" contacts between dissimilar substances. The extended area available in copper-oxide rectifiers is the result of the formation of the cuprous oxide at such a high temperature that it can crystallize freely and form a homogeneous crystalline layer of uniform thickness and constitution over the entire surface of a disk of any size.

Analysis of the oxide shows that in practical rectifiers it is to a large extent cuprous oxide. In one rectifier which was carefully analyzed, the base copper was found to be 99.949 percent pure. The copper content in the cuprous oxide was 88.78 percent, which shows that it is nearly pure. Assuming that the remainder of the material is cupric oxide, the cuprous-oxide content is 98.7 percent. Microphotographs taken of etched sections cut at right angles to the surface of the cuprous oxide show that the crystal grains are in the form of columns with their bases resting on the surface of the mother copper. This has recently been shown also by Torres.[81]

Fig. 4 is a microphotograph of such a section through a layer of oxide obtained by oxidizing a strip of copper completely to cuprous oxide. The line of dark spots across the middle of the photograph represents the position where the two layers of oxide met upon completion of the oxidation. The columnar nature of the crystal grains is clearly shown.

When the mother copper of a rectifier is ground away so that there remains only a very thin layer next to the oxide, the copper can be stripped away from the oxide. In order to accomplish this without breaking the oxide, the rectifier was first fastened by means of Canada balsam to a piece of glass with the oxide toward the glass. The copper comes off fairly clean but may have small crystals of cuprous oxide adhering to it. When the two substances are separated, there is revealed a reticulum which is present both on the oxide and on the copper surfaces. Fig. 5 is a microphotograph of such a copper surface, showing the reticulum. Fig. 6 shows the same reticulum as it appears on the corresponding cuprous-oxide surface. It is seen that if they are folded over, they match one another.

Fig. 7 shows a larger field of the same piece of copper. The large area enclosed by the reticulum in the center of the field may be recognized. Fig. 8 shows the same after it has been etched with nitric acid. The acid has removed the reticulum and revealed the copper crystal grains. It is readily seen that they are independent of one another in size and shape.

Fig. 9 shows the oxide surface of Fig. 6 after it has been deeply etched and ground to remove all traces of the reticulum and re-etched to show the outlines of the oxide crystal grains. Although the crystals have changed a little, they can be easily recognized as having the same general outlines as the reticulum.

Fig. 10 shows a part of a line in the reticulum on the copper which has the appearance of a row of bubbles. The borders of some of the copper crystal grains are visible.

This series shows that the outlines of the grains of the copper-oxide crystals are independent of the outlines of the grains of the copper crystals, and that some unusual activity takes place on the surface of the copper at the bound-

FIG. 4. Section of cuprous oxide at right angle to boundary, ×100.

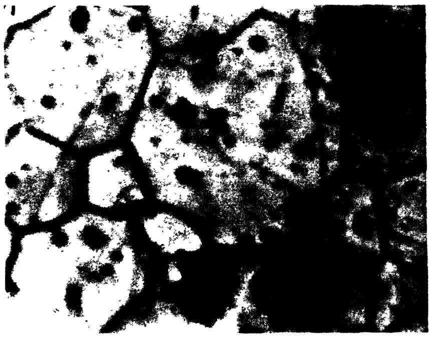

FIG. 5. Surface of copper stripped from oxide, ×500.

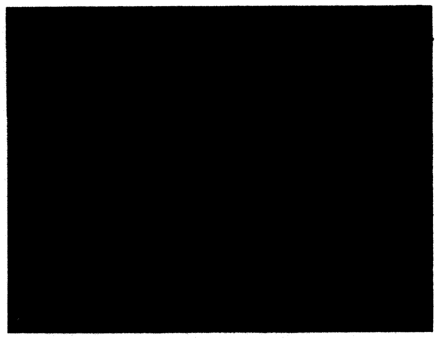

FIG. 6. Surface of oxide opposite copper of Fig. 5, ×500.

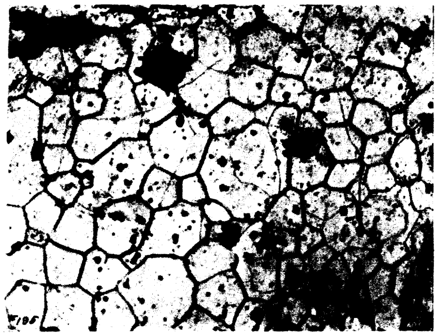

FIG. 7. Same as Fig. 5, ×200.

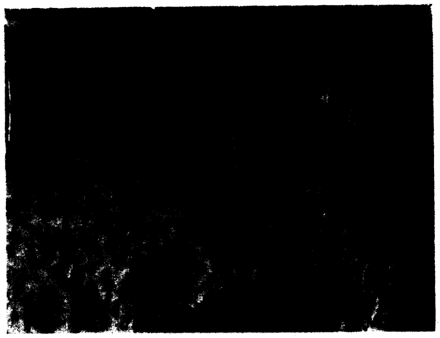

FIG. 8. Same as Fig. 7. Etched to show the outlines of the copper crystal grains, ×200.

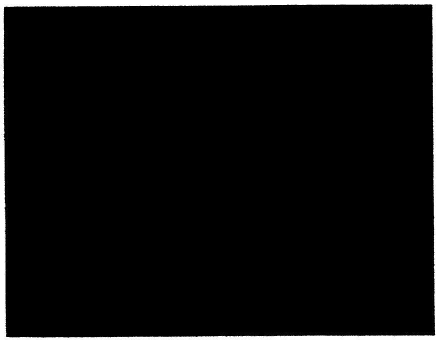

FIG. 9. Cuprous-oxide surface of Fig. 6 showing crystal grains, ×500.

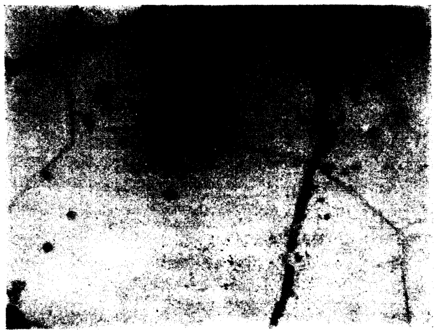

FIG. 10. Part of reticulum on copper, ×1000.

aries of the cuprous-oxide crystals. This may be the result of a freer access of oxygen at these points, or it may be the result of a segregation of impurities resulting from the crystallization of the cuprous oxide. The presence of the reticule was first pointed out by James, Harbord and Law, Metallurgists, of London, England.

HISTORY OF SOLID RECTIFIERS AND SOME GENERAL CONSIDERATIONS

The first rectifiers of the type known as solid rectifiers, which in all cases prior to the cuprous-oxide rectifier consisted of contacts between separate pieces of dissimilar materials, were of the detector type. These rectifiers are known as detectors because they were in all cases used for small currents and almost exclusively for radio detection.

Probably the earliest illustration of such a rectifier is that described by Braun[1] in 1874. Braun, in that paper and in subsequent publications, described his work with various natural crystals. He found that when he inserted such a crystal, with a "point" contact applied, into his circuit, the current passed through the circuit more easily in one direction than in the opposite direction. Schuster[2] found a similar result with tarnished copper wires. He found that he could produce the result in a wire that was originally neutral by burying it for a few minutes in charcoal, so that it is likely that the tarnish which produced his result was a sulphide. In any event, it was very erratic. Braun[3] later suggested the explanation that it might be due to the presence of small amounts of copper oxide on the surface of the wire.

These experiments illustrate the whole field of crystal detection. Practically any "point" contact, e.g., a "cat-whisker" contact, between a conductor and a semiconductor is asymmetric in its conduction. This is true whether the semiconductor is in the form of a crystal of appreciable size or whether it is in the form of a compound formed on a metal by tarnishing or oxidation or other treatment. It is, for instance, true that one can take almost any piece of iron or steel that has been exposed to the air or that has been given any kind of heat treatment, and if one applies to the surface a small wire contact, this contact is unilaterally conducting and may be used as a detector. Sometimes the low resistance will be in one direction and sometimes in the opposite direction, even on the same piece of metal. The direction sometimes varies with the voltage applied. In all these experiments the effect is in the "point" contact. Thompson provided this type of contact on an oxidized piece of copper by shaping the copper in the form of a wheel with a sharp edge and applying a block of metal to the edge. By mounting the disk so that it could be rotated, he made it convenient to hunt for a good spot. Attempts were made by some experimenters to use point contact detectors for larger values of current, but in all cases the "point" was retained.[8] The greater current capacity was obtained by placing more of these rectifiers in parallel.

If the area of contact is increased, the result is the equivalent of putting many of these small point contacts in parallel, and the result is an averaging of the contact resistances; or in some cases, if a very low-resistance spot is included in the area to which contact is made, it may even result in the short-circuiting of the high-resistance contacts; so that for both reasons, as the area is increased, the resistance is decreased and the rectifying action is gradually eliminated. Large-area contacts, therefore, usually have more nearly the same resistance in both directions, although it is very unusual to get exactly the same resistance in the two directions. When a crystal is provided with two contacts, one of which is of considerable area and the other one of which is very small, the large-area contact contributes a very small resistance which is practically symmetrical with reference to direction, and the small-area contact introduces a large resistance which is asymmetrical with reference to direction of flow of the current; so that the resistance of the whole combination is determined by the condition of the small contact. If the small contact is asymmetrical, the whole combination is a small rectifier and may be used as a detector. Even if it were true that the large area had a ratio that was considerable or even equal to the ratio of the small contact, the small contact would still control the rectification, as can be seen from the following illustration.

Let us assume, for instance, that the large-area contact on a crystal has a resistance of 10 ohms in direction A and a resistance of 100 ohms in direction B; and suppose that the small-area contact attached to the same crystal and used in the same circuit has a resistance of 100,000 ohms in direction A and a resistance of 10,000 ohms in direction B: The ratio of currents that may be made to flow through that crystal is approximately 10 : 1, with the greater flow in direction B, in spite of the fact that the contact resistance of the large-area contact is 10 times as great in direction B as it is in direction A. Neglecting the effect of current density, the resistance in direction A is now 100,010 ohms and the resistance in direction B is 10,100 ohms; so that even if the ratio of resistances at the large-area contact were several times as great as the ratio at the small-area contact, the rectification would still be controlled by the small-area contact.

If a very small contact similar to one of the cat's whiskers used in radio detectors is applied to the free surface of the oxide of a copper-oxide rectifier, that point contact has an asymmetry which, on account of its very high resistance compared to the resistance of the rest of the rectifier, controls the rectification; and when the oxide is formed so that the combination constitutes a good copper-oxide rectifier, the rectification produced at such a point contact is nearly always the reverse of the normal rectification of the rectifier. The cuprous oxide on the surface is very uniform in its consistency, so that point contacts applied to such a surface are fairly uniform in their behavior. The dominance of the rectification by the point contact is made more definite by the fact that for the small currents involved, the asymmetry at the junction of a rectifier of considerable area is small. The rectification ratio of the points, however, is low; and as soon as the area is increased even to a very small extent and the current is correspondingly increased, the resistance at the boundary becomes dominant on account of its very much higher ratio, and we then get the normal copper-oxide rectifier behavior. This is an illustration of the principle just described as applying to crystal detectors and explains some of the cases of reverse rectification that have been reported.

Another type of solid rectifier that was known before the advent of the copper-oxide rectifier is the electrolytic rectifier. There are two principal representatives—the Garretson[7] rectifier and the Pawlowski[8] rectifier. It is not necessary to discuss them; but on account of the similarity of the appearance of the assemblies of these electrolytic rectifiers and the copper-oxide rectifiers, it should be said that their rectification is dependent on the presence of a layer of solid electrolyte and that electrolytic forming of the rectifying layer is necessary before these units show any consistency of operation. Two dissimilar substances are placed in contact and not formed one on the other. The rectification takes place in small spots and is not distributed uniformly over the surface. The spots that are active gradually deteriorate and develop a high resistance, so that during the life of such a rectifier assembly the rectification moves from place to place over the surface of contact and eventually a high resistance is developed over the whole surface and the rectified current output drops to a value that is not useful.

METHOD OF MANUFACTURE AND CHARACTERISTICS OF COPPER-OXIDE RECTIFIERS

It has been pointed out that the special characteristics of copper-oxide rectifiers which distinguish them from all other resistances are the result of the special method that is used in the manufacture of the junction between the metal and the compound—namely, the oxidation at high temperature. The oxide melts at 1025°C and the rectifiers are very often oxidized at temperatures as high as 1040°C. In this case the oxide is molten during the formation, with the result that the edges are rounded and the disks that are in contact are fused together.

In oxidizing the disks, it can be arranged to oxidize one or both sides. If both sides of the disk are oxidized, it is necessary, in order to make full use of the oxide, to make contact to both sides of the free oxide surface. If it is desired to oxidize only one side of the copper, this can be accomplished by mounting two disks back to back so that the oxygen has free access to the outer surfaces but not to the adjacent surfaces of the copper. The characteristics of the finished rectifier may be varied over a wide range by the heat treatment that is given the disks after the oxidation. Two types of heat treatment have been and are being used in practical production of the rectifier. The first of these consists in allowing the rectifier to cool in the air after the oxidation. This has the result of producing rectifier disks of high resistance which are able to withstand back e.m.f.'s of high value. The reverse e.m.f. per disk that can be used in the practical application of these disks ranges as high as 30 volts. The forward resistance is also higher than it is with the second process of manufacture which is to be described, so that the current per disk that may be used is less under similar conditions of ventilation. The power output per disk, however, is approximately the same. In one case it is necessary to use more disks in series to rectify a high voltage; in the other case it is necessary to use more disks in parallel to rectify a high current.

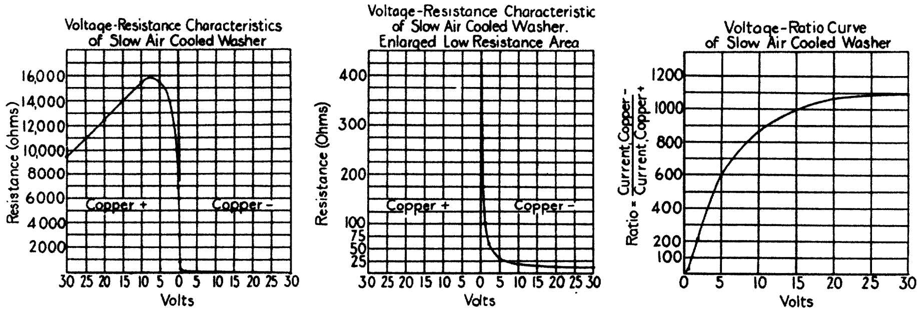

FIG. 11. Resistance voltage characteristic and resistance ratio of air-cooled disk. (Area 10 sq.cm.)

The characteristics of an air-cooled disk are given in Fig. 11, which shows the variations of the resistances in the two directions and of the resistance ratio with impressed voltages. The cooling of this disk was retarded by placing it first in a furnace at 560°C and then allowing it to cool in still air from this temperature.

The characteristics recorded in this section are given for disks the copper-oxide areas of which are practically 10 sq.cm. The area of the lead contact is 8.07 sq.cm. The result is that the readings in the high-resistance direction correspond to 10 sq.cm of boundary and the readings in the low-resistance direction to about 8.07 sq.cm of boundary.

The resistances here shown are high compared to those obtained with water-quenched washers. In general, higher resistances are obtained by slow cooling and lower resistances by rapid cooling from the oxidizing or an intermediate temperature. Any resistance values between these extremes and beyond may be obtained by means of appropriate heat treatment after oxidation. The high-resistance disks that are described here are useful especially in high-voltage rectifiers such as are used for the supply of plate voltages for vacuum tubes.

Water-quenched disks have a greater ratio than the air-cooled disks and a very much lower resistance,[59] so that the forward current that can be carried per unit area is greater than in the other case. On the other hand, the voltage that can be tolerated per disk in the high-resistance direction is so much lower that the power output

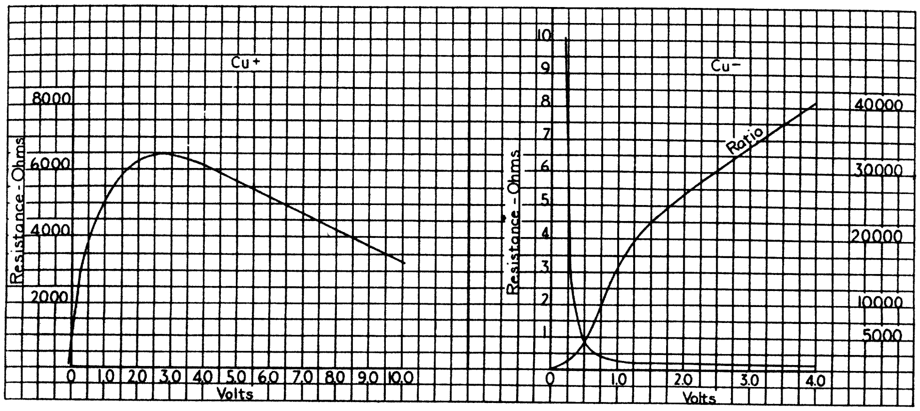

FIG. 12. Resistance voltage characteristics and resistance ratio of water-quenched disk.

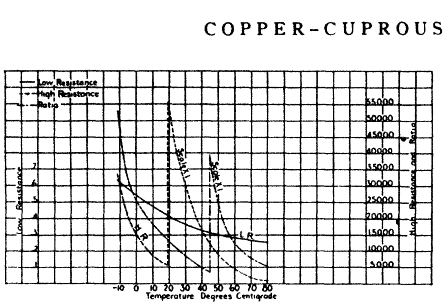

FIG. 13. Variation of resistances at 2 volts and of resistance ratio with temperature. Water-quenched disk.

permissible per disk is approximately the same. The characteristics of one of these disks are shown in Fig. 12. Fig. 13 shows the effect of temperature on the resistances at 2 volts and on their ratio.

Similar data have been published in various articles,[48] but data of the type given here, it is believed, are published for the first time. An attempt has been made in the case of the quenched disk to get more nearly the true characteristics of the boundary layer itself. In data that have been published before this, the resistance in the high-resistance direction has been lower than the resistance here shown. The improved condition is obtained by removing the black oxide with nitric acid instead of the other more usual means. The nitric acid seems to clear up the crystals in such a way as to decrease the conductance in the high-resistance direction, and the result is therefore more nearly the true characteristic of the rectifier itself. The removal of the extra conductance is certainly not complete even in this case, but it is very much more nearly so than is the case with other methods of removing the black oxide. In theoretical studies of the characteristics of the water-quenched rectifiers, it is believed that these are the curves that should be used.

After the oxidation, the cuprous oxide, which constitutes the layer next to the copper, is covered with a layer of cupric oxide. Cupric oxide in this state seems to have a higher resistance than cuprous oxide and is removed in order to lower the forward resistance of the disks. The method of removing the cupric oxide is important in determining the characteristics of a rectifier. On the first unit that was made, the cupric oxide was removed by holding the oxidized surface against an emery wheel. Experiments were made with nitric acid and other solvents; but when production was first begun, the black oxide was removed by means of emery cloth or by sandblasting the surface. Later it was found more practical to remove the black oxide by dissolving it in a solution of sodium cyanide, and that is the common practice at the present time.

Another important item in the process of making the rectifier junction available is the method of making contact to the free surface of the oxide. The first method that was used was to apply a layer of lead, because lead is flexible and flows so that it can be made to fit the surface more nearly than other metals. Even in the case of that material, however, it is difficult to make a uniform, continuous, and low-resistance contact to the free surface; and this is especially important for the current flowing in the forward direction, because lateral flow of this current necessarily introduces a large resistance. In order to correct this lack of continuous contact, finely powdered carbon is rubbed into the surface of the oxide before the application of the lead, and this is now the most popular method of making contact. With time there is some deterioration of this outer contact, which is possibly due to a slight amount of oxidation of the cuprous oxide or to a reaction between the cuprous oxide and the metal that is used for the contact. This interaction between the cuprous oxide and the contact metal can be reduced by using on the lead a metal coating which does not react with cuprous oxide. Tin is being used.

Another method of making a contact consists in the reduction of the cuprous oxide so that a layer of copper is formed on the free surface. This has been used in some practical rectifiers and has the immediate advantage that it does not require pressure for the making of contact. It has the disadvantage, however, that the contact consists of a very thin layer of copper, and even a small amount of corrosion very soon destroys the contact, so that deterioration in this kind of rectifier is very rapid compared to that of a rectifier with the other type of contact. It is not only rapid at the beginning, but continuous, and in a comparatively short time reaches a state in which its forward resistance is too great to be useful.

Many other types of contact have been proposed. The application of suspensions of carbon or of metals has been found satisfactory from some standpoints, and the applications of metals by spraying or sputtering or electroplating have all been tried with more or less promise, but none of these has yet replaced the simple arrangement consisting of carbon and lead.

The circuits in which copper-oxide rectifiers may be used are the same as are used in any type of rectifier both for full-wave and for half-wave rectification. The Graetz bridge is the most popular arrangement for a full-wave copper-oxide rectifier. Such a bridge can be arranged on a single bolt or in any other similar simple construction.

On account of the practical characteristics of the rectifier, it has found application in all the different kinds of circuits in which it is necessary to provide the transformation of alternating to direct current. The possibility of using it at the very high power levels, as well as at those that are very low, depends, as far as current is concerned, on the fact that the current-carrying capacity is additive over any desired area or over many areas in parallel. This is the result of the fact that the impedance for many practical purposes is nearly a pure resistance. As a result of this it is also possible to connect any number of units in series for use at high voltages. Copper-oxide rectifiers have been used for such widely different purposes as battery charging up to 15 kw, smoke and dust precipitation up to 100,000 volts, and in the other extreme, as radio detectors. Practical efficiencies up to 65 percent are obtained, and in the laboratory efficiencies of over 85 percent have been observed.

The boundary area has a capacity the value of which has been variously estimated by different experimenters. Dowling and Place in our laboratory have found a capacity of approximately 0.006 mfd per sq.cm. Their measurements were made by means of a Wheatstone bridge at low frequencies between 60 and 500 cycles per second and at a high frequency of 10^6 cycles per second. The test sample in each case consisted of two disks connected in series opposition, and the capacity obtained was considered the capacity of a single layer. At 10^6 cycles the measurement was also made by substitution in a tuned circuit. No biasing voltages were used. The calculation of capacity was made on the supposition that the sample consisted in a resistance and a capacity in parallel. On this basis it was found that the capacity was independent of voltage up to 10 volts across the pair and that it was independent of frequency up to 10^6 cycles per second.

Schottky and Deutschmann[42] experimented by substituting an equivalent circuit in a bridge and adjusting for a balance between the circuit and a single rectifier disk. Their equivalent circuit consisted in a resistance connected in series with a capacity and another resistance which were connected in parallel. They experimented with different biasing voltages and at different temperatures. The impressed alternating voltage was held constant at 40 mv and the frequency was varied between 800 and 2500 cycles per second. Some of their results are shown as follows: In Fig. 14, the series resistance, R_1; in Fig. 15, the parallel resistance, R_2; and in Fig. 16, the capacity. All are shown at different biasing voltages and the latter two also at different temperatures. At present there seems to be no satisfactory interpretation of the capacity data.

The capacity has the effect of shunting out the high resistance; and unless the resistance in the low-resistance direction is small compared to the capacity reactance, it destroys the rectification. At commercial frequencies the capacity reactance is so large that its effect both on the rectification ratio and on the power factor is entirely negligible. The power factor of the rectifier is then equal to 1. The higher the current density, the lower the forward resistance. The capacity reactance and the resistance are both inversely proportional to the area of the junction between the copper and the oxide. The capacity reactance is also inversely proportional to frequency, but, at least according to one set of data, it is approximately independent of current density. As the frequency is increased, it therefore becomes more and more important to maintain a high current density in order to avoid the effect of capacity. For nearly all purposes it is possible at high current densities to make the resistance so low compared to the capacity impedance that the capacity may be neglected. When it is difficult to operate at such current densities that capacity

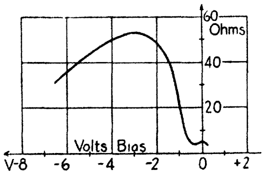

FIG. 14. Schottky and Deutschmann's data on series resistance in rectifier.

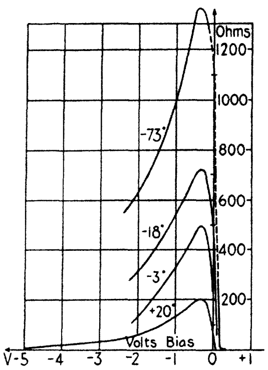

FIG. 15. Parallel resistance at different tempe ratures. (Schottky and Deutschmann).

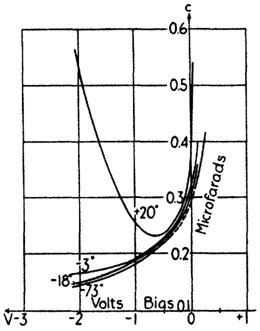

FIG. 16. Capacity at different temperatures. (Schottky and Deutschmann).

is negligible, it is possible to improve the condition of operation, especially at high frequencies, by balancing the capacity of the rectifier with a reactor connected in parallel with it.[84]

The current density that may be used in the rectifier depends largely on the ventilation that can be provided. A current density of 0.07 ampere per sq.cm may be considered normal when no special ventilation is provided. When forced ventilation is provided or any extra precautions are taken to provide large and effective radiating surfaces, the current can be raised to 0.6 ampere per sq.cm or even more without undue heating. Temperatures up to 80°C may be tolerated, but this increases the rate of aging of the rectifier; and when a very long life under high current densities is desired, the temperature should be kept under 40°C.

When a full-wave rectifier is used, the wave form of the rectified current is only very slightly distorted from that of the original alternating current, so that with a resistance load the oscillogram of the rectified current looks just like that of the original alternating current with every other half wave reversed.[14] There is a very slight distortion in these curves because of the fact that the forward resistance of the rectifier is greater at the low voltages than it is at the high voltages, so that the current on the low parts of the wave is a little less than it should be to produce entirely distortionless rectification. When used at high current densities, the distorted part of the curve is such a small fraction of the whole that ordinarily it may be neglected. The fact that it is negligible may be illustrated by the fact that with a rectifier used as a radio detector operating with a high impedance load, the measurable amplitude of the second harmonic introduced was less than 0.5 percent of the fundamental.[84]

The rectifier has a very long, still undetermined life, but there is some aging, especially during the first few months of operation. The change in the forward and the reverse resistances as measured by means of direct current is quite marked; but in an alternating-current circuit with a load and the usual ballast, the effect on the output and on the efficiency of the rectifier is very small. As an example, it may be stated that in certain commercial rectifiers it has been found that while in four years of continuous service the forward resistance at 0.5 volt per disk increased by 150 percent and the reverse resistance at 1.25 volts per disk decreased by about 60 percent, the efficiency in the same period decreased from about 55 percent to about 49 percent. The greater part of the aging takes place during the first few months, and after that the performance is nearly constant.

It must be remembered that the figures given here are only illustrative and that in this respect widely varying results may be obtained, depending on the voltages and other conditions imposed. For instance, as related in the next paragraph, the aging in the low-resistance direction takes place mostly at the outer contact; and since that contact has a greater percentage of the total resistance at the higher voltages than it has at the low voltages, it follows that the percentage increase in resistance in the forward direction is greater at the high than at the low voltages.

The cause of the aging has not been determined. The following experiments show that the greater part of the aging is due to an increase in resistance at the contact to the free surface of the oxide. The method of experimentation was to produce aging in rectifiers under various different conditions and to study them before and after the aging process by determination of the potential drop in various parts of the rectifier when the current was flowing. If a vacuum tube voltmeter is used with probes in the grid circuit, which may be applied to different parts of the rectifier, it is possible to determine the potential drop between the different parts. Apparatus was set up to enable us to apply a probe to the edge of the oxide which could be used, together with the lead contact on one side and the mother copper on the other, to determine the potential drop at the junction between the cuprous oxide and the copper on one side and that at the contact between the cuprous oxide and the lead on the other side. When measurements are made with such an arrangement, it is found that in the high-resistance direction practically all the e.m.f. is used at the boundary between the mother copper and the oxide. In the low-resistance direction, the greater part of the e.m.f. is used at the contact to the free surface of the oxide.

The oxide itself and the junction in the low-resistance direction have very low resistances. As aging progresses, it is found that the most important part of the change consists in an increase in the resistance at the contact between the lead and the oxide. The vacuum-tube voltmeter shows that in an aged rectifier the proportion of the voltage used at this contact is greater than it is in one that has just been made.

Depending on how the aging is accomplished, the resistance in the high-resistance direction at the junction may increase or decrease. If aging is the result of exposure to high temperature without load, the high resistance at the junction increases; if the aging is done at a low temperature without load, the reverse resistance at the junction remains practically constant; while in both cases the forward resistance increases at the contact to the free surface of the oxide. When the aging takes place under load, especially at high voltages per disk, there is sometimes also a decrease in the resistance in the high-resistance direction, so that at high voltages the aging is due to a combination of the two effects—namely, an increase in resistance in the forward direction at the contact to the free surface of the oxide, and a decrease in resistance in the reverse direction at the junction between the oxide and the mother copper. The latter is not great enough to have any important effect on the efficiency of the unit.

Since it is, unfortunately, true that we do not understand either the action of the rectifying junction or the contact to the free surface of the oxide, it is impossible at present to give a satisfactory explanation for the aging of the rectifier. There is the comforting circumstance that the aging follows a nearly asymptotic curve, so that after a few months of aging under normal conditions, the aging is nearly complete and the rectifying performance becomes constant.

The way in which the aging progresses with time suggests that it is due to a process that may be similar to the aging of magnetic iron, for instance, which we imagine to be due possibly to a rearrangement of crystals. When the rectifier is made, there is, of course, a certain amount of strain at the junction between the oxide and the copper, because the coefficients of expansion of the two materials are different, so that during the cooling from the high temperature, the copper contracts more than the oxide. It is possible that the gradual release of this strain may have something to do with the aging in the high-resistance direction. At temperatures below 1030°C, cuprous oxide has a tendency to oxidize to the cupric oxide to some extent, and it may be that a part of the aging which causes the increased resistance in the forward direction is due to an increase in the cupric-oxide content of the oxide layer. (There will be more to say about the resistances of the oxide.) On the other hand, it is also possible that a chemical reaction resulting in the reduction of the oxide and the oxidation of the contact metal may be responsible.

Location of Rectification

Many experiments have been made to determine definitely the seat of the rectification in a copper-oxide rectifier. It has been suggested that the asymmetric resistance was a property of the cuprous oxide itself. This does not seem at all likely, since there is no experimental evidence that the resistance of a homogeneous material is ever different in two opposite directions. Experiments that have been made on separate pieces of oxide detached from the mother copper indicate that the oxide itself has no asymmetry of resistance.

The fact that the material used for the contact to the free surface of the oxide seems to make no difference in the total rectification is an indication at least that this contact has very little if anything to do with the rectifying effect. There is a secondary effect which will be mentioned later.

Since it has been shown also that a change in thickness of the oxide has practically no effect on the current in either direction, these experiments indicate that the rectification must depend on the junction between the mother copper and the oxide, all the other possible locations having been eliminated. Direct experiment by means of a probe and a vacuum-tube voltmeter, similar to the experiment described above and the arrangement of which is shown in Fig. 17, has been used to settle this question definitely. This has been done by Schottky[68] and his collaborators as well as in our own laboratory.

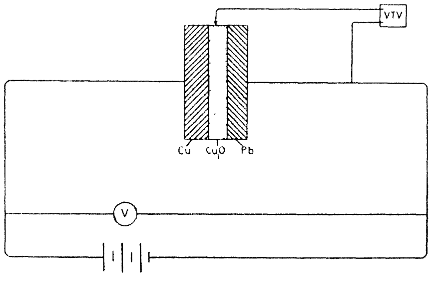

Fig. 17. Determination of the distribution of potential drops in a rectifier.

The feature of the rectifier that is different from the more usual conducting contacts between different materials is not the fact that the current is conducted with very low resistance in one direction, but the fact that the very high resistance is interposed in the opposite direction. The vacuum-tube voltmeter measurements show that this high resistance is practically all located at the junction, or so near to the junction that it has been impossible to separate it experimentally from the junction. Typical data are given in Fig. 18. The voltages represent, roughly, the potential drops at the respective boundaries. The drop in the oxide is included but is small, as shown by other experiments. It may be seen that in the high-resistance direction the drop is principally between the copper and the oxide. In the low-resistance direction the difference is not so great and more of the drop is between the copper and the oxide at low voltages and between the oxide and the lead at the higher voltages.

These experiments, taken together with the fact that the cuprous oxide when separated from the copper does not show rectification and that even the thinnest layer of oxide that can be used still shows the rectification as long as its junction with the mother copper is undisturbed, show conclusively that the rectification is intimately connected with this junction. There are other auxiliary proofs; for instance, there is the effect of a slight bending of the rectifier disk. If the disk is bent by a very small amount and then straightened again, it is found that the rectification is decreased by the decrease of the high resistance and the increase of the low resistance, but principally the former. The unit then becomes a piece of copper oxide with ordinary contacts on both sides and conducts with a fairly low resistance in both directions. The data given in Table I show the effect of such bending even when the bending is so slight that there is no apparent cracking of the oxide.

Table I. *Effect of bending copper-oxide rectifier disk.*

Number of bends	*Currents in Amperes* Forward	Reverse
0	6.5	0.0015
1	0.490	0.042
2	0.450	0.100
3	0.36	0.145
4	0.40	0.15
5	0.325	0.21
6	0.735	0.32
7	Disk shorted	

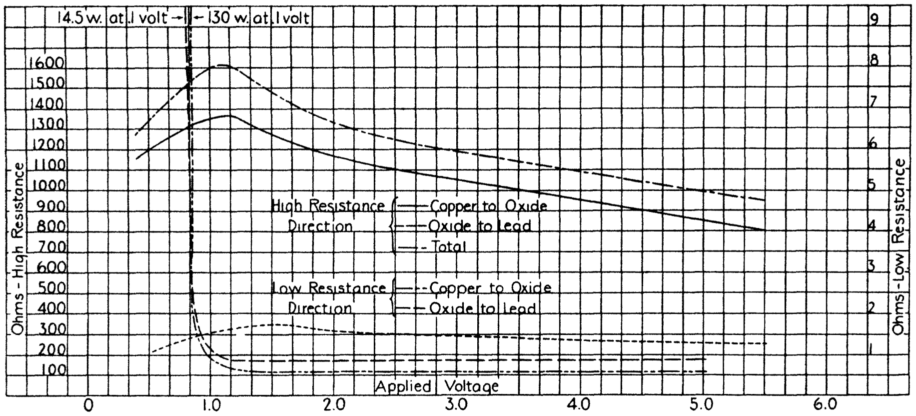

FIG. 18. Voltage distribution in parts of a rectifier.

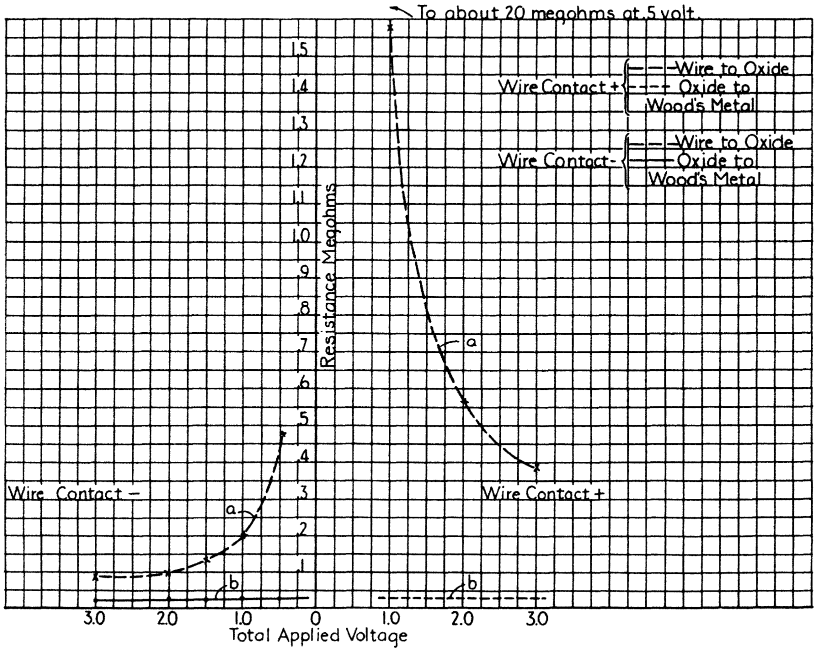

FIG. 19. Voltage resistance characteristics of contacts between metals and semiconductors. (a) Small contact; (b) Larger contact.

The presence of the very high resistance in the high-resistance direction at the boundary produces at the outer free surface a condition that assists the rectification and that may be considered a sort of pseudo-rectification at the contact to the free surface of the oxide. As has been pointed out, a contact between a metal and a semiconductor is very sensitive to variations in voltage. Its resistance is very high at low voltages and becomes progressively lower as the voltage is increased. In the high-resistance direction, therefore, since the current that flows through the contact is very small, the voltage is low at the outer contact, practically all the e.m.f. being concentrated at the junction. The resistance of the front contact is then many times as great as it is when the current flows in the forward direction. This is clearly shown in Fig. 18. The presence of the rectifying boundary at the junction with the mother copper, therefore, has the effect of making an auxiliary rectifier out of the front contact which would not have been there except for the existence of the asymmetry at the boundary. This general characteristic of contacts between metals and semiconductors is illustrated for a large and a small contact in Fig. 19, which represents the analysis of the resistances in a copper-oxide crystal detector consisting of a piece of cuprous oxide removed from a rectifier disk and mounted in Wood's metal and provided with a fine wire for the rectifying contact. The wire contact represents a small-area or "point" contact, the Wood's metal a large-area contact.

CHARACTERISTICS OF CUPROUS OXIDE

Partly as a result of the interest aroused by the discovery of the copper-copper-oxide rectifier, a great deal of study has recently been devoted to the characteristics of cuprous oxide. As mentioned above, it has been credited with having asymmetric conduction, which, experiments have shown, does not exist. Tests have been made by Engelhard and Cudden,[134] by Schottky and Deutschmann,[42] and in our laboratory, all with the same results. Experiments have shown also that when the oxide is prepared as it is in rectifiers, it does not have the voltage effect sometimes attributed to it. Its resistivity is independent of potential gradient over a wide range of applied voltages.

Some very interesting characteristics have been announced by O. von Auwers.[131] He states that the resistance of cuprous oxide depends on the pressure of the ambient gas. As the air or hydrogen pressure is reduced, the resistance also is reduced. With the reduction of oxygen pressure, resistance increases. Nitrogen and neon seem to have no definite effect. As the dissolved gases are removed, the resistance increases by hundreds of percent, which seems to be contradictory to the result as far as external pressure is concerned. The author states also that cuprous oxide has a transformation range at about 56°C, above which the red oxide becomes opaque. This appearance of opacity also depends on the removal of gases. The more thoroughly the dissolved gases are removed, the less pronounced is the decrease in transparency. The same author states that the coefficient of expansion of cuprous oxide also varies with temperature in such a way that up to 56°C there is practically no expansion. It is less even than in the case of quartz. Above 56° it contracts, and when it is cooled it contracts still further.

Gudden and Mönch[136] have tried to find the appearance of opacity referred to by Auwers and have failed. They experimented both with natural and with artificially produced oxide, and in no case did they find the change in transparency, and they found no relation between transparency and electrical conductivity. They come to the conclusion that there is no relation between the two.

The conductance in cuprous oxide seems to be purely electronic. Various experimenters have found that the resistance that is obtained when the material is thoroughly degassed so that there is no excess of oxygen present is very high compared to the resistances that are actually encountered in rectifiers. Le Blanc and Sachse[132] working with compressed powders found for cupric oxide a conductivity at 20°C of 6.4×10^{-4} $\text{ohm}^{-1}\ \text{cm}^{-1}$ and for cuprous oxide a conductivity of 3×10^{-9} $\text{ohm}^{-1}\ \text{cm}^{-1}$. They also find an enormous decrease in resistance in the presence of oxygen. Gudden[135] likewise quotes from Engelhard resistivities for cuprous oxide varying from 10^2 to 10^6 ohm-cm. K. Bädeker[125] in 1907 published data on resistances of various semiconductors, among them cuprous oxide, which he found to have a resistivity of 40 ohm-cm, and cupric oxide, which he found to have a resistivity of 400 ohm-cm. These figures are more nearly like the values of resistance that are actually encountered in a copper-oxide rectifier. The resistance of the rectifier in the low-resistance direction shows that the resistivity of the cuprous oxide cannot be more than of the order of 100 ohm-cm. In the curve shown in Fig. 12 the resistance of the rectifier disk in the low-resistance direction at 4 volts is 1.411 ohms per sq.cm, which shows that even if we assume that all the resistance of the rectifier is in the oxide, the resistivity of the oxide, which was about 0.0076 cm thick, could not be over 185 ohm-cm. The conclusion reached by the various investigators who have studied the question is that the low resistivity of the cuprous oxide in this form is due to the presence of an excess of oxygen. This has further been interpreted by some as being due to the presence of cupric oxide, which does not seem reasonable since the cupric oxide has never been reported to have a resistivity of less than 400 ohm-cm. It seems likely, therefore, that this effect is a type of secondary effect due to the presence of the oxygen, which may influence the conductivity in a way that will be referred to again.

Dubar[112] has made a chemical and microscopic study of the oxide in the conducting and in the nonconducting states. The nonconducting state was obtained by reducing the conducting oxide in the presence of hydrogen. Chemical analysis showed no difference between the two. The oxygen content indicated less than 1.5 percent cupric oxide. In the conducting state microscopic study revealed the presence of a number of small opaque crystals distributed through the oxide. In the semiconducting and nonconducting states these were absent, and instead there were observed throughout the oxide the presence of vacuoles. X-ray analysis showed no difference in the crystal structures of the conducting, the semiconducting, and the insulating varieties and failed to show the presence of any cupric oxide.

Another interesting characteristic of cuprous oxide which has a special bearing on its use in a rectifier is the fact that as a semiconductor it behaves against metal contacts applied to its surface in a very uniform way. This consistency of performance of the cuprous oxide of a rectifier is believed to be due to the fact that it is produced from practically pure copper and that the crystallization has taken place in a consistent way, the crystals all growing from one and the same side and all growing at the same temperature and under the same conditions generally.

Vogt[130] has studied the conductivity and the Hall effect in cuprous oxide from −70°C to +75°C. Assuming that there are no boundary resistances, he calculated the electron concentration and found that throughout this range it varied in accordance with the equation $n=n_0e^{-q/kt}$. The energy of ionization of the electrons for the particular specimen of cuprous oxide lay between 0.28 and 0.35 electron-volt. Gudden[129] discusses these experiments and points out that they are the same electrons that may be set free either by illumination or by thermal agitation. The calculation indicates that the conductance in darkness is explained by saying that only one in every 10^4 cuprous-oxide molecules contributes an electron. The result is not consistent from sample to sample, and it is concluded that these special molecules that are able to contribute an electron are in some way influenced by the presence of a foreign material, possibly excess oxygen. That seems consistent with the experiments referred to above. The "dark" conductance of cuprous oxide is thus explained as being due to free electrons which are liberated only on account of the presence of a very small amount of foreign material. Gudden suggests that possibly perfectly pure cuprous oxide would have infinite resistance.

Dünwald and Wagner[139] have investigated the conductivity of cuprous oxide between 800°C and 1000°C and find that it is definitely related to the oxygen pressure: conductivity = constant $\times$ (oxygen pressure)$^{1/7}$. Wagner[71] favors the idea that the conductance in cuprous oxide is "Defektleitung." The presence of excess oxygen removes electrons from some of the copper atoms, producing an electron deficiency in some parts of the lattice. Conduction of electric current then takes place as a result of the loss of electrons by normal copper atoms and the taking up of electrons by copper atoms that are deficient. This leads to a positive Hall constant, which is not consistent with experiment. Dünwald and

Wagner report that thermoelectric experiments at 1000°C indicate that cuprous oxide of low resistance has fewer free electrons than cuprous oxide of high resistance. The results seem contradictory, but the conditions under which the two sets of experiments were performed are so different that more work will be necessary to show the true correlation.

Finally should be mentioned other interesting and related data published by Auwers.[128] He summarizes his results as follows: The Hall effect in cuprous oxide is very great. The influence of illumination on the Hall effect is very small. The resistance change in a magnetic field is very small. The effect of illumination on this resistance change is very great. The conclusion is that cuprous oxide is a semiconductor with a considerable internal photoelectric effect.

THEORY

Many attempts have been made to explain the action of the copper-oxide rectifier. The theories that have been proposed may be classified in terms of the phenomena and ideas on which they are based as follows:

(1) Thermoelectricity.
(2) Electrolytic action.
(3) A geometrical arrangement of parts which gives, in effect, the juxtaposition of point and plane.
(4) Assumption of the presence in crystal lattice of occasional atoms with a deficiency of electrons.
(5) The difference in work functions across the boundary in opposite directions.
(6) The assumption of the existence of an insulating layer between the mother copper and the cuprous oxide.
(7) Assumption of a physical separation between oxide and mother copper with associated cold electron emission.
(8) Assumption of the presence of an electron atmosphere in the cuprous oxide.
(9) Combinations in various ways of the last five.

A satisfactory theory of the action of a copper-oxide rectifier must explain the following facts:

(1) The very high resistance in the high-resistance direction.
(2) As the voltages decrease and approach zero, the resistances in the two directions approach the same value. However, contrary to statements that have frequently been made in the literature, the resistances are never exactly equal and there is some rectification even at the lowest voltages.
(3) The resistance in the high-resistance direction has a maximum which is very pronounced and falls between 0.75 volt and 1.5 volts.
(4) Beyond this maximum the high resistance decreases practically linearly.
(5) The resistance in the low-resistance direction decreases very rapidly according to a nearly exponential law as the voltage is increased.
(6) There is a very considerable electrostatic capacity at the junction between the copper and the cuprous oxide.
(7) Except for this capacity, the impedance in both directions is pure resistance.
(8) The rectifier is instantaneous in its action.
(9) Intimately associated with the rectifying action and probably also involved in its explanation is the fact that the rectifier produces an e.m.f. when the junction between the copper and the cuprous oxide is illuminated.

There are many other secondary phenomena which have to be taken into account in judging a theory, but these are the principal and fundamental characteristics.

(1) Thermoelectric theories are based on the idea that the heat generated at the junction produces an e.m.f. that opposes the current in the high-resistance direction and assists it in the low-resistance direction. Copper oxide against copper has a very high thermoelectromotive force, but unfortunately for the theory, it is in the wrong direction. Experiments have shown, too, that the existence and the value of the thermal e.m.f. are independent of the existence of the rectifying characteristic at the boundary. A rectifier which had been bent enough to destroy its rectifying action had not changed in thermoelectric characteristics.

(2) Electrolytic theories are represented principally by one that has been proposed by Pelabon. Pelabon's theory has in it several ideas which seem to be assumed on a rather vague foundation. In the first place, Pelabon[62] states that cupric oxide has a very much lower resistivity than cuprous oxide. This seems to be contrary to fact for the conditions in which the oxides exist in the rectifiers. The only pieces of evidence on which we can base this statement are Bädeker's results referred to above and the fact that the very thin layer of cupric oxide which exists on the oxide when it has just been formed has such a high resistance that for practical purposes it must be removed from a rec-

tifier. In the condition in which it exists there, it seems to have a very much higher resistivity than cuprous oxide.

In the second place, he states that the cupric oxide extends between the crystal grains of the cuprous oxide and that the conductance in the oxide is to be credited almost altogether to the cupric oxide. This seems to be unbelievable on account of the fact that the cuprous-oxide layer has a very clear red color by transmitted light and does not show the presence of any large amount of cupric oxide. The chemical analysis also shows that the oxide is 98.7 percent cuprous oxide. The amount of cupric oxide present, therefore, seems to be so small that it would have to be in a superconductive state in order to explain the transmission of the current through the oxide layer.

In the third place, it is stated that the action of the cupric oxide is electrolytic and that when the current flows in one direction, oxygen is liberated and sets up a very high resistance; and that when it flows in the opposite direction, copper is liberated, which allows the current to flow. Such electrolytic action would necessarily be accompanied by the phenomenon known as "forming," and it is very well known that that phenomenon is not present in copper-oxide rectifiers. It is believed, therefore, that the electrolytic theory based on conductance in cupric oxide may be set aside as unsatisfactory.

(3) The theories which are based on arrangement of parts approximating a point and plane seem to be taken entirely from imagination. Nothing in the microphotographs has any appearance that seems to justify this suggestion.

A theory which has in it something similar to this but which is based on a different point of view is one of the theories expounded by Schottky and collaborators.[68] In experimenting with contacts to the free surface of the oxide they found that the rectification was better when the areas were very small or when the contacts were broken up into very small point contacts, and they concluded that possibly the rectification was due to a large number of small contacts and that the oxide and the copper at the junction were separated from one another except for these very small points at which they joined. A more recent experiment, in which Waibel and Schottky[82] have determined the thermal conductance across the junction, has led them to the conclusion that this theory is untenable, since the thermal conductance across the junction is too high to allow of the existence of anything less than a practically continuous contact.

(4) A theory proposed by Carl Wagner[71] is based on the "Defektleitung" described above. Rectification is thought to be due to the condition that electrons going from oxide into copper (high-resistance direction) must be taken from the normal copper atom in the lattice. A saturation condition is therefore to be expected. Electrons passing in the opposite direction must be absorbed by the electron-deficient copper atoms in the oxide and near the boundary. This explanation seems improbable at least for the one reason that no saturation has been observed in the high-resistance direction.

(5) One of the first theories that were proposed was based on Schottky's detector theory. The existence of a work function at the boundary of a material makes it possible, if the work functions are different or if the potential humps are different in shape at the boundaries of two materials in contact, to show that there should be a difference in conductance across the boundary in the two opposite directions. Schottky has made use of this to explain detector action, and others have attempted to use it in connection with copper-oxide rectifiers. It is a very tempting picture but seems to fail on account of the fact that the work functions of copper and of cuprous oxide are too nearly the same. For that reason, I believe, Schottky[42] does not consider it seriously in connection with copper-oxide rectifiers.

(6) The theories that postulate an insulating layer between the copper and the cuprous oxide are illustrated by that proposed by Slepian[27] and are probably prompted by the existence of the very considerable capacity that has been observed to be a characteristic of the rectifier. Dr. Slepian's theory may be stated as follows: He attempts to classify thermionic rectifiers and solid, and even electrolytic, rectifiers under one head as thin film rectifiers. By "thin film" he means not necessarily a film that is thin geometrically, but one that contains a small number of atoms, so that it corresponds to a thin film from the standpoint of the material involved. As

a first illustration of a thin film rectifier, he mentions the thermionic tubes, and he discusses in turn crystal detectors, electrolytic rectifiers, the solid electrolytic rectifier of Pawlowski, and finally, the copper-oxide rectifier. In this explanation it is necessary in all cases to postulate an insulating, or at least a very high-resistance, film. In the case of a copper-oxide rectifier it is assumed that at the junction between the copper and the cuprous oxide the cuprous-oxide crystals are deformed on account of their attachment to the copper. This is based on the erroneous assumption that the outlines of the crystals at the boundary are the same for the two materials. It is assumed then that the result of this strained condition is that there exists at the boundary a very thin layer of exceedingly high resistance and that electrons are emitted more readily from the copper than from the oxide. The copper, therefore, becomes the cathode.

This theory seems more reasonable than it did at first in view of some of the recent work on the characteristics of cuprous oxide. As has been pointed out, it has been found that cuprous oxide, when it is devoid of excess oxygen, has very high resistance—so high, in fact, that it is practically in the class of insulators. It can easily be imagined that very near the surface of the copper the oxygen is very dilute because of its power to combine with copper. The oxygen in the layer very near the copper combines chemically with the copper and in that way provides a layer of cuprous oxide which is oxygen-free and therefore of high resistance. This theory, proposed by Waibel and Schottky,[82] is, to the writer's mind, the first satisfactory suggestion of a reasonable theory for the existence of an insulating layer which could possibly be the cause of the rectification. When that is admitted, however, it is difficult to see how the condition can be maintained during the life of the rectifier except on the assumption that even at room temperatures the copper at the boundary continues to function as an absorber of oxygen.

The authors just mentioned have made some exceedingly interesting and significant experiments in which it has been shown that a contact made by evaporating gold or silver and letting it condense on a surface of cuprous oxide is not asymmetric unless the cuprous-oxide surface has first been bombarded by atoms or electrons, or has been treated electrolytically. After such treatment rectification ratios as high as 20 : 1 at 2 volts were obtained. The bombardment seems to produce a rectifying layer which may be gradually removed by solution and it may be reformed by repeating the original treatment. The following table shows the effect of the progressive removal of the layer in terms of the relative rectification produced by the remainder in each case.

Table II.

Thickness of layer removed ($\times 10^{-6}$ cm)	Relative rectification (percent)
0	100
1.2	30
2.5	12
4.6	1

This layer may possibly be the result of the removal of free oxygen by the bombardment and may therefore be similar to the layer next to the mother copper.

(7) Frenkel,[45] Frenkel and Joffe,[75] and van Geel[61] have been very much impressed with the possibility of explaining rectification in terms of cold electron emission and the existence of a separating space between the oxide and the mother copper. If their basic assumption is accepted, the theory seems to have some promise, but it is difficult to believe that the oxide is really separate from the copper over any considerable portion of the area at the boundary. Another difficulty lies in the fact that the differences in contact potentials seem too small to account for the rectification. The facts to which reference has been made in connection with the mechanical structure of the rectifier, especially the close adherence of the oxide to the copper, indicate that the contact at the junction is continuous and very intimate. The experiment of Schottky in which he determined the thermal conductance across the boundary contradicts this theory. It seems likely that it would be difficult also to show in terms of the cold-electron-emission theory why the resistance in the high-resistance direction should have a maximum at a voltage as large as approximately 1 volt.

(8) The present writer has made an attempt along different lines[12] in that less weight has been placed on the work function and a different picture of the condition that exists at the junction has been proposed. It is assumed that the junction between the copper and the cuprous oxide is the most intimate possible. The cuprous oxide is formed on the mother copper and adheres very closely to it. The writer assumes that while the passage from copper to cuprous oxide at the junction is abrupt, the last atom of copper may be in such a position that it may be considered a part of a cuprous-oxide crystal or a part of a copper crystal. If this kind of contact between the two materials is postulated, it is seen at once that the work functions of the two materials must merge into one, so that the energy lost by an electron in passing from copper into oxide is simply equal to the difference between the two work functions. Schottky and Deutschmann[42] report the work of Barton on cuprous oxide and that of Goetz on copper. They find the energy of electron emission for these materials to be 4.8 electron-volts and 4.4 electron-volts, respectively. The difference is small enough to result in a great amount of diffusion across the boundary even at room temperature.

We can further assume that the number of free electrons in copper is vastly greater than it is in cuprous oxide. If we assume equal mobility for the electrons and that the number of free electrons is proportional to the conductivity in both cases, the number of electrons per cc in copper is 10^7 times as great as in cuprous oxide. Since a large percentage of the electrons in copper have a greater kinetic energy than is necessary to pass the boundary between the copper and the cuprous oxide (this number is further increased by the degenerate state of the electrons in the copper), there will necessarily be a lively diffusion of electrons across this boundary, which diffusion will establish a condition of kinetic equilibrium when the condition is reached in which the number of electrons that cross the boundary in one direction is equal to the number that cross the boundary in the opposite direction. Equilibrium will be established between the diffusion or evaporation of electrons out of the copper on one side and the diffusion in the opposite direction plus losses due to conduction on the other side.

When this condition of equilibrium has been established, there will be a rather dense electron atmosphere in the oxide layer near the copper. The density of this electron atmosphere decreases gradually as the distance from the copper boundary is increased.

If such a condition is established, it must be attributed to the very close and uniform junction between the copper and the cuprous oxide. In order to allow the diffusion of electrons across the boundary to take place uniformly over a large area without serious loss on account of conductance across the boundary in the opposite direction, it is necessary that the condition for evaporation must be very nearly the same over the whole surface. The contact on the free surface of the oxide is not a contact of this kind but is more like an ordinary electrical contact in which the condition of the contact varies from point to point. This variable condition, as has been pointed out before, results in what we ordinarily recognize as a good electrical contact; and although we do not understand its performance, it does not have any very decided asymmetry or other peculiar characteristics.

In going farther with the discussion of the behavior of this electron atmosphere in producing asymmetry, it is necessary to consider the nature of the asymmetry as it is found to exist experimentally. The resistance in the low-resistance direction decreases approximately exponentially as the voltage is increased. As the e.m.f. approaches zero, this resistance in the low-resistance direction approaches a certain value which is the same as the value approached by the high resistance when its e.m.f. is gradually reduced toward zero. As the e.m.f. in the high-resistance direction is increased from zero, the resistance increases up to a maximum at some value between 0.75 volt and 1.5 volts; and as the e.m.f. is further increased, the resistance slowly decreases.

The important question to answer in connection with the copper-oxide rectifier as far as theory is concerned is not to explain the conductance in the low-resistance direction, since that seems to be more or less what one would expect with good contacts. The difficult question is to explain how the high resistance is developed when the current is made to flow from the copper to the oxide through the boundary.

If one considers the electron atmosphere in the oxide, which has been described above, an explanation seems possible and the plausibility of the explanation can be made to appear by referring it to a characteristic curve, illustrations of which are shown in Figs. 11 and 12. Let us consider first the current in the forward direction. In the condition of equilibrium there are only a few electrons in the copper that have a sufficiently high kinetic energy to be able to mount the hump of negative charge encountered just outside the boundary of the copper and the oxide. If an external e.m.f. is applied then to carry electrons in this direction, as long as the e.m.f. has a low value there are only a few electrons that can be given a sufficient amount of assistance to enable them to pass over the hump. This is represented by the high resistance at low e.m.f.'s. As the e.m.f. is increased, the number of electrons that can pass over the hump becomes greater and greater; and as this number increases, the measured resistance decreases.

If we consider the current flow in the high-resistance direction and begin again with a very low e.m.f., we have to begin with the same condition—namely, that there are very few electrons that can be carried over the hump. As the e.m.f. is increased, the electrons are driven toward the copper and the outer slope of the hump becomes steeper, making it more difficult for electrons to pass; and the hump may also increase in height on account of the added electrons from the side of the free surface of the oxide. This has the effect of increasing the resistance with increasing voltage up to a certain value of resistance, which we find experimentally is between 0.75 volt and 1.5 volts. This e.m.f. also has the effect of driving the electrons back into the copper and so of reducing the hump; and beyond the voltage just mentioned, this effect becomes predominant and the resistance in the high-resistance direction decreases, although in this case the decrease is slow and nearly linear.

The principal argument that has moved others to postulate an insulating layer as being present in the copper-oxide rectifier is the fact that the rectifier has electrostatic capacity. The proposed theory seems to explain this condition without requiring the presence of an insulating layer or a condenser consisting of two conducting plates separated by an insulator. It seems likely that the condition that has just been described might manifest itself as a sort of pseudo-capacity. When the current flows in the low-resistance direction, it carries away some of the electrons which constitute the electron atmosphere; and when the current flows in the high-resistance direction, these electrons are returned, and up to a certain point the electron atmosphere is reestablished. We have, then, storage of electric charge which depends on voltage and which therefore behaves, at least from this standpoint, like a condenser. The electrostatic capacity simulated by this change in density of charge may be calculated, and it may be shown that a very small change in electron concentration is sufficient to explain the capacity.

By means of the equations describing electron emission that were developed by Bartlett,[57] we have constructed a curve for the current in the low-resistance direction and find that it has the same general shape as the curves that are obtained in practice. Attempts to apply the formula to current in the high-resistance direction have not been successful. Gentry[13] has suggested that if the electron atmosphere is important, the current should vary with the 3/2 power of the voltage. The results obtained by substitution of published data in the formula seem to check it satisfactorily but are hardly conclusive.

(9) It seems likely that the explanation will develop into a combination of some of the five theories that have been last mentioned. The insulating layer certainly is tempting from the standpoint of capacity. At the same time, it is very difficult to accept even the high-resistance cuprous oxide as an insulating layer in this case because when a rectifier disk is allowed to stand for some time at room temperature, this high resistance increases. That may, of course, be due to secondary effects; but if it is real, it would seem to be just the reverse of what one would expect unless the oxygen that is left in the cuprous oxide is bound in the crystal lattice so that it can not diffuse. That seems unlikely. The electron atmosphere seems promising on account of its simple explanation of the presence of

capacity and on account of the fact that it seems to check with the experimental result that at low voltages the resistance is nearly the same in both directions. If the existence of an insulating layer can be established, it might be profitable to think of it as the location of a space charge.

Van Geel[61] has proposed a combination of Schottky's detector theory with the idea of a high-resistance layer in which exists very high potential gradients, a condition very similar to that considered under cold emission. He also takes into account the effect of space charge. The principal feature of the theory is the cold electron emission, and the author concludes that a difference between the contacting materials, even if it exists only in the "inner" work function, is sufficient to account for rectification. One of the conclusions from his theory is that the only temperature effect should be due to the variation in resistance of the oxide itself. This seems unlikely, since the resistance of the oxide is certainly too small to have any appreciable effect on the current in the high-resistance direction, and in this direction the effect of temperature is the greatest.

No one of the theories thus far proposed is entirely satisfactory. All that seems definitely established is that the phenomenon is electronic and that it depends on the difference in the ease with which the electrons can cross the boundary from mother copper to copper oxide and *vice versa*.

COPPER-OXIDE PHOTOELECTRIC CELLS

During some experiments in which a copper-oxide rectifier was used with an instrument to read a very small alternating current, it was found that the readings were erratic. The present writer discovered that this erratic behavior of the rectifier was due to its condition of illumination and that it had a photoelectric sensitiveness which reduced the output of the rectifier when it was illuminated.[14] Later study in cooperation with P. H. Geiger showed that this effect was due to an e.m.f. which opposed the flow of current through the rectifier disks in the low-resistance direction. More recent study by A. J. Sorensen has proven that this effect, as it was then observed, was produced at the junction between the oxide and the mother copper. Auwers and Kerschbaum[91] conclude that the effect on the rectification of small currents is due to the addition of the photoelectric current in the high-resistance direction and its subtraction in the low-resistance direction. At a later date, B. Lange[88] announced a copper-oxide photoelectric cell in which the action of the light to produce an e.m.f. was present also at the contact between the oxide and a thin layer of copper that was sputtered on the front surface of the oxide of a rectifier disk. The former type of cell we shall call the "back-wall" cell, and the latter type the "front-wall" cell, in accordance with the usage that is developing in Germany and the translation used by Nix.[117] Schottky and his coworkers and Lange have done a great deal of work on the characteristics of these cells.

In the original type of cell it was necessary in some way to give the light an opportunity to strike the oxide and get to the junction between the oxide and the mother copper as freely as possible, and these photoelectric cells were therefore made with a front contact which took the form of a grid.[85, 86] The grid was first made by coiling a lead wire and placing it on the surface of the oxide with openings between the coils so as to allow the light to pass. Later constructions have consisted in coating the outer surface with copper or other metal either by sputtering or by reduction of the oxide and then removing a part of the coating so as to form a grid of any desired fineness. The reduction of the cuprous-oxide surface can be accomplished either electrolytically or by immersing the hot disk as it comes from the furnace in oil or in a solution of alcohol.

The first photoelectric cells of this type were simple copper-oxide rectifiers in which the light was allowed to strike the edge of the disk. The output that was obtained from these first disks was of the order of 15 or 20 microamperes through a 150-ohm meter when the disk was illuminated with an intensity of 2000 lux. Lange[88] reports 10^{-8} ampere per lux for a back-wall cell of 2 sq.cm area and 5×10^{-8} ampere per lux per sq.cm for a front-wall cell. E. D. Wilson[124] has recently announced that he has obtained a watt of output from a square meter of back-wall cell, and for a cell 6.45 sq.cm in area he reports 10^{-4} ampere per lumen. Lange[102] reports 25×10^{-6}

volt per lux for a back-wall cell and 15×10^{-6} volt per lux for a front-wall cell.

The photoelectric cell is very quick in its operation. Some of the earlier cells were tried at voice frequencies and were found to respond quite satisfactorily. Duhme[100] has found that at 6000 cycles per second there is no apparent lag.

The spectral-sensitivity curve of these cells depends on the method of construction. In the back-wall cell the effect appears at the short-wave-length limit of about 570 millimicrons. The maximum comes at about 630 millimicrons, after which it drops off gradually to the long-wave-length limit of 1.4 microns. The short-wave-length limit of this curve shifts with temperature in accordance with the transmission of cuprous oxide, which is, of course, the determining factor. These results are shown in Fig. 20, which is reproduced from Lange.[103]

In the front-wall cells the spectral sensitivity extends farther into the visible part of the spectrum, and here again it depends on the transparency of the medium through which the light has to travel, which in this case is a film of metal such as copper, silver or gold.

Lange and others have also determined the effect of temperature on the sensitivity of a copper-oxide photoelectric cell. In a back-wall cell Lange has found a maximum of voltage at about −140°C and a maximum of current at approximately −60°C. His data are given in the curves of Fig. 21 reproduced from his article. From the same article is taken Fig. 22, which shows the effect of temperature on the performance of a front-wall cell. In our laboratory have been obtained certain data which apparently contradict these results. Using the complete spectrum of radiation from a 15-watt lamp on a back-wall cell gave the results shown in Table III.

The fact that the current is independent of temperature may be interesting. The experiment reported by Teichmann[108] makes one wonder how much of the effect may have been caused by thermal e.m.f. s. Lange's experiment[103] seems to be free of that criticism, and the difference in results probably depends on the arrangement of the electrode on the free surface of the oxide.

The effect of externally impressed e.m.f. has been shown by Schottky.[106] Illustrations of his data are given in Fig. 23 reproduced from his article. Both curves were taken at −183°C, the full-line curve with a good rectifying contact, the dotted line with a very poor rectifying contact.

TABLE III.

Temperature (°C)	Photo e.m.f.	Current ($\times 10^{-6}$ amp.)	Resistance (ohms)
−45	0.150	0.6	400,000
−18	0.068	0.6	
24	0.008	0.5	12,000

Schottky, by considering the photoelectric cell as a source of e.m.f. located in the area that is illuminated and the remainder of the cell as a shunt resistance which shunts the external load, has shown that the source of electrons in the back-wall cells is at the boundary between the copper and the cuprous oxide. In our laboratory Sorensen obtained the same result by a special construction of cell in which he eliminated all the other possible sources of electrons one by one and showed in that way directly that they must originate at or very near the boundary.

Schottky,[89, 90, 106] Duhme[90, 100] and others have established the following facts:

> (1) The short-circuit current is directly proportional to the intensity of illumination. (Perucca and Deaglio[105] have shown that under certain conditions it is just as appropriate to say that the voltage is proportional to the illumination. The difference is probably due to the arrangement of the electrodes.)
>
> (2) The flow of electrons is in all cases across the illuminated boundary from oxide to metal—that is, in the direction of high resistance.

Theoretical discussion of the photoelectric cell is in a very much more satisfactory state than that of the copper-oxide rectifier. All the theories connect the photoelectric e.m.f. produced in this cell in some way with the inner photoelectric effect of the oxide, which was described by Pfund.[126] The stop-layer, or barrier-layer, photoelectric effect is similar to the external photoelectric effect in that the electrons are emitted from the body of the oxide. Just as the inner photoelectric effect and the external photoelectric effect are related through the work function, so the inner photoelectric effect and the effect in the stop-layer photoelectric cells are related

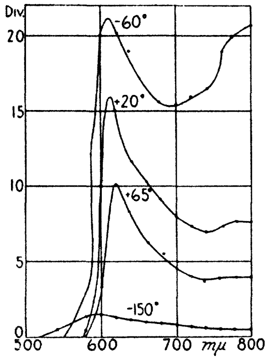

FIG. 20. Spectral sensitivity curve for back-wall cell and effect of temperature. (Lange.)

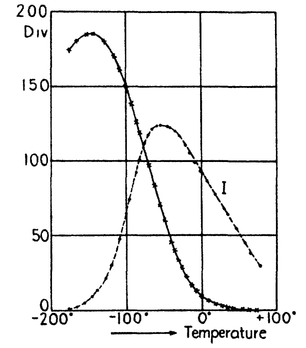

FIG. 21. Effect of temperature on photoelectric effect. Back-wall cell. (Lange.)

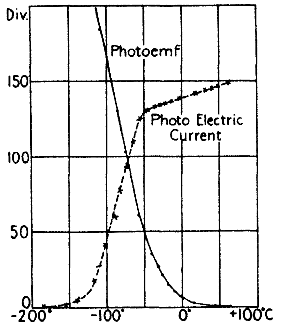

FIG. 22. Effect of temperature on photoelectric effect. Front-wall cell. (Lange.)

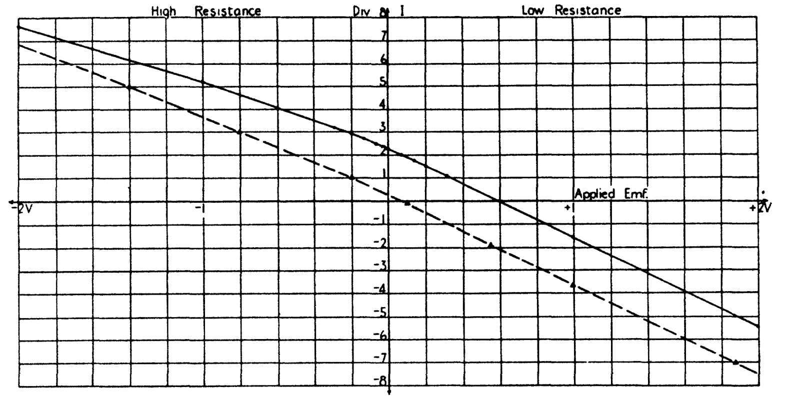

FIG. 23. Effect of external e.m.f. on photoelectric current. Back-wall cell. (Schottky.)

through the energy required to expel an electron from the oxide and into the copper or other metal. The long wave-length limit for the inner photoelectric effect, as calculated by Kurtschatow and his coworkers[114] from the data of Vogt,[130] is 4.1 microns; the long wave-length limit for the stop-layer photoelectric effect is about 1.4 microns.[88, 102] The difference between the two, corresponding to about 0.58 electron-volt, probably represents the energy required to project an electron out of the oxide and into the copper.

Schottky[106] has pointed out that the relation between the current and the absorbed light energy depends on several factors. In order to contribute to the current, the light must be absorbed at a position so near to the boundary that the liberated electrons can move across into the metal. The current for a given illumination then depends on the portion of the light absorbed near the boundary and on the ratio between the number of light quanta absorbed and the number of electrons liberated. Schottky reports measurements by Waibel which show that in a front-wall cell in which the front contact is a sputtered gold film, the maximum yield is at 500 millimicrons, where the number of electrons contributing to the current is about 25 percent of the number of quanta absorbed. In other cases this figure is as high as 50 percent, corresponding to nearly a coulomb per calorie. In such a cell one expects and finds that the effectiveness of light of a given wave-length depends on the rate at which it is absorbed. The higher the absorption coefficient, the nearer the boundary is the origin of the liberated electrons.

It is concluded that electrons that are liberated at least as far as 1 micron away from the boundary still contribute to the current. This means that the electrons must be able to live through a considerable number of collisions and still retain enough energy to pass through the boundary. From this Schottky concludes that the electrons here involved not only are related to but are identical with those involved in the inner photoelectric effect. Schottky[123] and his collaborators have found that the inner photoelectric effect in cuprous oxide is entirely negligible when the oxide is of the conducting variety. They have found, also, that the stop-layer photoelectric effect is absent with contacts that do not rectify, so that it may be concluded that the stop-layer photoelectric effect is a characteristic that is present only with rectifying contacts. If the electrons which are responsible for the inner photoelectric effect are identical with those that are responsible for the stop-layer photoelectric effect, this would be another bit of evidence for the conclusion that there must be a high resistance layer at the boundary.

Recently, E. Rupp[118] has studied the effect of a magnetic field on the photoelectric e.m.f. produced at the stop layer. He has found that the photoelectric current drops off at a rate that is proportional to the square of the applied magnetic field, provided the field is parallel with the plane of the stop layer. This reduction in current is independent of the wave-length of the incident light. He has found that this rate of reduction is practically the same as the rate of increase in the resistance of the cuprous oxide when placed in a magnetic field. The difference is of the order of 10 percent. He concludes that the photoelectrons and the electrons that conduct the current in the cuprous oxide are transported in the same way, and it may be concluded also that the energy given to the electrons by the incident light serves only to set them free.

Of great interest in this connection are the "forced photoelectric currents" just announced by Schottky.[123] He states that by the use of an auxiliary voltage it is possible to increase the photoelectric current to 1000 times that represented by the electrons ordinarily liberated by the incident light.

Whatever becomes the final explanation of the copper-oxide rectifier and its accompanying photoelectric effect, it seems possible now that it will involve the high-resistance layer, which seems to be in the process of being verified experimentally. Even on this basis, all the details of the theories of both phenomena remain to be worked out.

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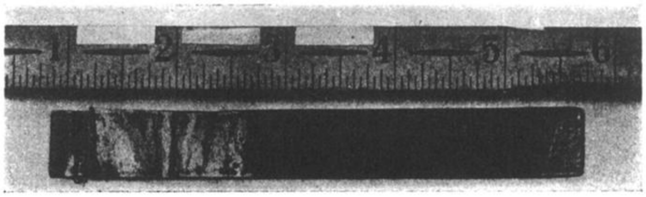

FIG. 1. Photograph of first rectifier.

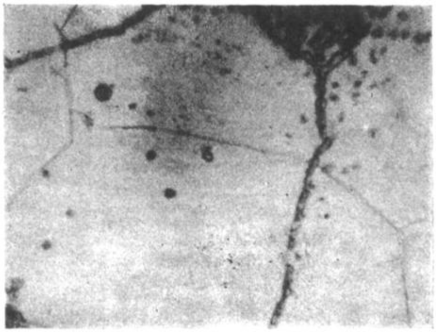

FIG. 10. Part of reticulum on copper, ×1000.

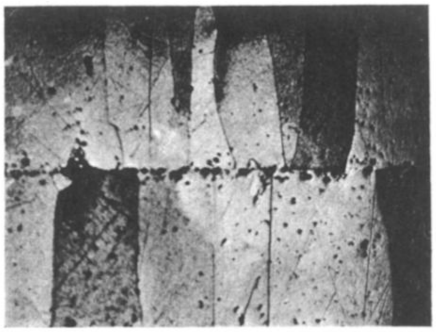

FIG. 4. Section of cuprous oxide at right angle to boundary, ×100.

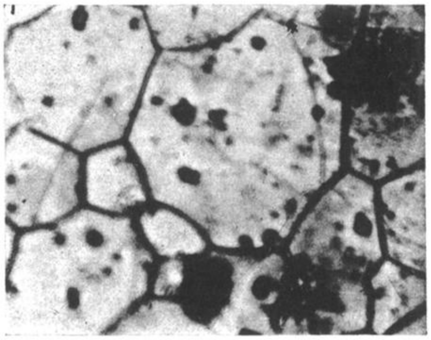

FIG. 5. Surface of copper stripped from oxide, ×500.

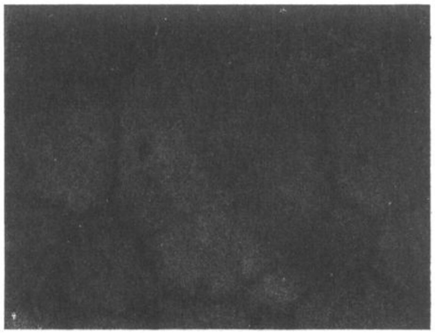

FIG. 6. Surface of oxide opposite copper of Fig. 5, ×500.

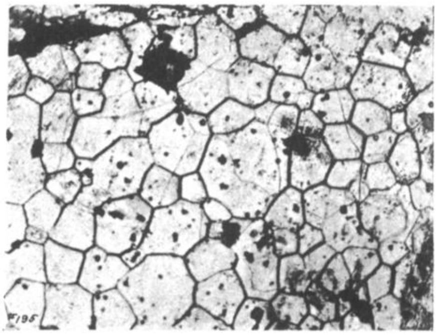

FIG. 7. Same as Fig. 5, ×200.

FIG. 8. Same as Fig. 7. Etched to show the outlines of the copper crystal grains, ×200.

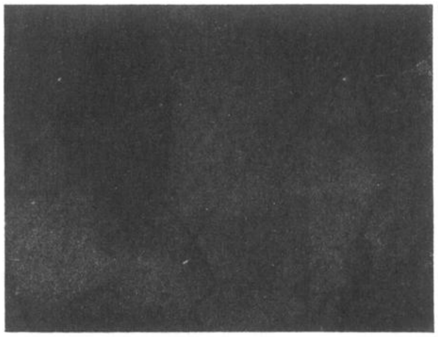

FIG. 9. Cuprous-oxide surface of Fig. 6 showing crystal grains, ×500.