SOLID RECTIFIERS.

BY GREENLEAF W. PICKARD.

In 1874 Ferdinand Braun published an account[1] of his investigations of the asymmetric or unilateral conduction of current by certain of the natural (mineral) metal sulphides. Although this publication is undoubtedly the first important contribution to our knowledge of this subject, Braun's methods of observation, as will be hereinafter shown, were such that concordant results were not obtained, and in consequence a false theory of the phenomenon, based on crystalline structure, resulted.

Braun's principal tests were made upon the mineral tetrahedrite, a compound of copper, antimony and sulphur, having essentially the formula $Cu_8Sb_2S_7$, but with material amounts of other metals replacing a portion of the copper. Tetrahedrite, considered from the crystallographic standpoint, is in the isometric system, and, as is suggested by its name, crystallizes in the tetrahedral group, forming well-defined tetrahedral crystals. It was with such crystals that his principal tests were made, in which the most marked asymmetry was found. The method employed was to include the mineral in circuit with a potentiometer and galvanometer by means of two silver wires with rounded ends pressed firmly in contact with the crystal, and to note the change of galvanometer deflection upon reversal of the current. With the above arrangement, Braun found that certain pairs of contacts gave deflections depending upon the direction of current flow, the ratio of the apparent conductivities corresponding to these deflections being in one experiment as great as seven to twenty. The maximum ratio between positive and negative current conductivities was found when one wire contacted with the base of the tetrahedron, while the other pressed against one of the plane faces near a point of the crystal.

Braun's tentative theory of the action, advanced in the above-mentioned publication, was based upon a supposed thermal expansion of portions of the crystalline structure by the current, this expansion acting in one direction to increase the effective area or number of minute contacting points of one of the metal electrodes with the mineral, and in the other to decrease this contact area. His explanation of the mechanism of this supposed action is by no means clear, being based upon a unilateral heating and cooling (apparently a sort of Peltier effect) of the base and point of each of the minute tetrahedrons comprising the entire crystal. As I shall hereinafter show that whatever may be the true explanation of unilateral conductivity, crystalline structure does not necessarily enter as a factor, it will be unnecessary to consider this hypothesis in further detail.

Braun, however, effectively disposed of any thermoelectric explanation of the phenomenon. In the above-mentioned experiment with tetrahedrite, electromotive forces of as high as eight Bunsen cells (approximately fifteen volts) were employed. While it has been known for a long time that the thermoelectric powers of certain minerals, particularly some of the metal sulphides, were much higher than those of the metals, certain mineral thermo-couples giving ten or fifteen times the electromotive force per degree of the most powerful metal-to-metal couple, yet even this high thermoelectric power falls far short of explaining a marked unilateral conductivity under electromotive forces as high as fifteen volts. While thermoelectric action must be abandoned as explaining this phenomenon, there is, however, a significant relation between high thermoelectric power and unilateral conductivity, which will be considered later.

In answer to certain criticism of the above-mentioned article, Braun, in a later publication, defends his explanation, and gives further reasons for considering the effect as distinct from either thermoelectric or imperfect contact action. In this reply[2] he describes in detail his test of another unilateral conductor, psilomelane, a hydrous oxide of manganese.

The employment of unilateral conductivity for the purpose of rectifying alternating or oscillating currents was not considered by Braun, nor, indeed, does it appear that anyone conceived of the possibility of this until after wireless telegraphy had been in use for a long period of years.

The later investigators who have repeated this work of Braun, notably Pierce[3] and Fleming[4], have considered the possibility of the use of unilateral conductivity as a means of rectification either of alternating or oscillating currents, but with this exception have added little of novelty to the early publications of Braun. It is true that with the greater instrumental equipment available, these experimenters have made far more accurate measurements, and, by extending the range of the investigation, the list of unilateral conductors has been quite materially increased. Little, however, seems to have been accomplished toward the establishment of the conditions of contact necessary to make this phenomenon a definite one as to direction and amount, and the influence of Braun's incorrect crystalline-structure theory of the action has persisted to the present time, as is particularly shown by the title of the above-mentioned publication of Pierce, "Crystal Rectifiers," and by the hypothesis advanced by Fleming, in which the crystalline structure of the unilateral conductor is considered as an electronic valve whose complex molecule allows electrons to leave more freely at some points on its surface and to take them in more freely at others. Fleming states that if these molecules are irregularly arranged, the electrons should be able to move with the same ease in either direction, but considers that if the substance be crystallized, it is possible that all the valves might face one way, thereby facilitating the electron drift in one direction, while offering great opposition to their motion in the opposite direction.

This explanation, while undoubtedly ingenious, certainly more plausible than that of Braun, and in probable accord with the facts as known to Fleming, would hardly have been advanced had he been in possession of complete data as to the conditions governing this action.

The writer's attention was directed to the phenomena of unilateral conductivity some years ago, while investigating the action of a certain type of telephone transmitter. In this instrument, known as the Blake transmitter, a platinum bead is pressed in contact with a polished carbon surface, and a small electromotive force (a single cell of Leclanche battery) is included in a local circuit through this contact. In the normal operation of this transmitter, the platinum bead is in light or microphonic contact with the polished carbon surface, and the local current exhibits the customary irregularities of current flow through imperfect contacts. In an attempt to obtain constant conditions, the writer increased the pressure to such an extent that the contact became sub-

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[1] "On the Conduction of a Current Through Sulpho-Metals." Poggendorff's Annalen, Vol. 153, 1874, p. 550.

[2] Annalen der Physik und Chemie, Vol. 19, 1883, pp. 340-352.

[3] Physical Review, June, 1907.

[4] Cassier's Magazine, Vol. 34, September, 1908, pp. 458-464.

stantially perfect, although still of extremely small area. An accidental reversal of the battery, in a repetition of a series of resistance measurements, disclosed the fact that the transmitter was now unilaterally conducting, although but feebly, the current in one direction being about five per cent greater than that in the other.

The possibility that this action might be the basis of an efficient "wireless" detector, particularly for wireless telephony, was thereafter conceived, and this observation became the starting point of an extended investigation of the action of contacts of small area between dissimilar conductors, resulting in the discovery of a very large number of unilateral conductors capable of forming efficient wireless detectors under certain conditions of structure.

Early in this investigation was discovered the necessity of establishing for the second circuit terminal of the unilateral conductor, a contact not only substantially perfect, but of large area. In the lack of such a contact of large area, the rectification obtained was not only variable as to direction, but was frequently entirely absent, owing to an opposing action at the second contact, which, if of small area, itself acted as an opposing rectifier, thereby reducing or even eliminating the observable rectifying action. Braun, working with two contacts of small area, obtained accidental unilateral conductivity, which was doubtless due to differences in the physical character of the contact surfaces, whereby one contact was occasionally of larger effective area than the other. For example, in his two contacts on the crystal of tetrahedrite, the one on the base, and the other on one of the planes near a point, the former was probably a fracture face made in removing the crystal from its surrounding mineral. This contact might occasionally be of different effective area than the contact on a smooth, even, mirror-like, crystal face, even although the contacting terminals were similarly shaped, and applied with equal pressure. Had Braun employed the method early adopted by the writer to insure contact of large area, which consists in mounting the rectifying conductor in fusible metal, his results would have been of a far more definite character. And not only would they have become definite, but a few tests would have demonstrated that the direction of rectification was always the same for the same conductor, regardless of the position of the contact of small area with respect to the crystal faces or structure. This is clearly shown by the following experiment, which can be made with any asymmetric conductor. The conductor is first shaped into a rough cube, and one of its faces pressed into molten fusible metal, which is allowed to cool and solidify, thereby securing a perfect contact of large area. The remaining five edges of the cube can then be explored with an electrode of small area, with the invariable result that the rectification observed is always in one direction. For example, a crystal of the well-known electric-furnace product, carborundum, or carbon silicide, always acts as an "in" rectifier, the maximum conductivity being for currents entering the crystal through the contact of small area, and the minimum being found for those in the opposite direction, entering through the contact of large area, and leaving through the smaller. For the above reasons, the writer calls the combination of a unilateral conductor with a large and a small-area contact a solid rectifier, in distinction from the well-known electrolytic and gaseous rectifiers.

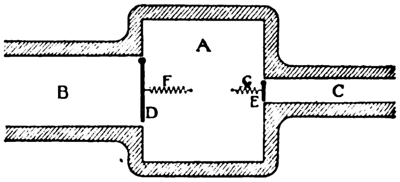

FIG. 1.—HYDRAULIC ANALOGY OF SOLID-RECTIFIER ACTION.

Although no better proof is needed of the independence of the rectifying action and any crystal structure than the simple fact above stated, *i. e.*, the independence of crystal structure and position of the small-area contact, it may be of interest to state that the writer has discovered a number of amorphous rectifying conductors. Among these are varieties of the non-metallic element silicon, and solid solutions of certain metallic oxides (notably zinc oxide), in readily fusible silicates. Optical and other tests have shown the entire absence of regular crystalline structure in these conductors, yet they possess marked rectifying properties, the rectification being always in the same direction for the same conductor.

A clearer conception of the rectifier action may be obtained by considering a hydraulic analogy of the solid rectifier which has been developed by the writer. In Fig. 1 the rectifying solid is represented by a closed vessel A fitted with large and small outlet and inlet pipes B and C, which represent, respectively, the large and small circuit contacts of the rectifying solid. In the vessel A, at the openings of the pipes B and C, are placed swinging valves, D and E. These valves are shown as leaky valves, not completely fitting their respective orifices, the cross-section of the leak around the valve being perhaps ten per cent of the entire cross-section of the orifice in each case. This leak represents the incompleteness of the valve action in the solid rectifier, which does not entirely stop the reverse flow of current. Attached to the valves D and E are retractile springs F and G, which tend to make the valves resist any outward flow of water. It is apparent that a flow of water through the pipe C into the vessel A will not be resisted by the valve E, and as the leak around valve D may be of larger area than the total cross-section of the orifice of pipe C, any amount of water that can enter A through C can leave it by means of this leak, without disturbing valve D, which, though held against a flow outward from A, is powerless to check the small flow that can enter through C. If it is attempted to pass a current of water through the vessel A in the reverse direction, from B to C, valve D and its large leak will offer no opposition, but valve E, with its retractile spring G, opposes effectively all flow save that minute one due to its own leak. If, now, the above device is connected between two water mains which are alternately supplied with pressure, representing the terminals of a circuit across which there is an alternating electromotive force, a rectified current will flow through the vessel A, as a pulsating direct current from C across to B.

While the above analogy is by no means perfect, it is probably as good as the average hydraulic analogy of an electrical action. It illustrates clearly the effect of the large and small contacts in the solid rectifier, particularly as to the indifference of the large contact to the currents rectified by the smaller. It should be clearly borne in mind, however, that in all probability no such structure as shown actually exists in the solid rectifier.

Among the many solid rectifiers discovered by the writer, there are three which have proved of commercial value in wireless communication. These are the silicon[5], perikon[6] and molybdenite[7] detectors,

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[5] United States Patent Nos. 836,531, 877,451, 888,191.

[6] United States Patent No. 886,154 and Trademark No. 70,587.

[7] United States Patent No. 904,222.

constructed, respectively from the unilateral conductors silicon, zinc oxide and molybdenum sulphide. Although these all act as rectifiers, they are not equally efficient as wireless detectors, the best being the zinc oxide or perikon detector.

In Fig. 2 are shown the characteristic voltage-conductance curves of these three detectors, when in their most sensitive state as wireless detectors. These curves were obtained by placing the detector in a wireless receiving circuit, adjusting until the maximum response was obtained to a distant sending station, and then interpolating a galvanometer, potentiometer, battery and reversing switch in the detector circuit. By varying the magnitude and direction of the electromotive force over a wide range, the relation between voltage and current was obtained, and from this the apparent conductance determined. The rectifying conductors were in all cases set in fusible metal, to insure a perfect contact of large area for the nonrectifying terminal, while the contact of small area, or rectifying terminal, consisted of a rounded brass point on both silicon and molybdenite, and a fragment of chalcopyrite, or copper-iron sulphide, for the perikon or zinc-oxide detector.

By varying the adjustment, it was found possible to produce much higher ratios between the "in" and "out" conductances than those shown in the curves, but with such adjustments the efficiency as a wireless detector was found to be materially reduced, probably owing to the fact that the highest ratios were obtained by such minute effective contact areas that the resistance of the detector became too high for the maximum efficiency in the wireless circuit. It will be noted that the maximum slope, or change in conductance, is confined to a range of but a few tenths of a volt. The conductances are given in microhms, or reciprocal megohms; thus, for example, the conductance of the perikon detector at zero voltage is forty microhms, which corresponds to a resistance of 25,000 ohms, or one-fortieth megohm.

In the course of the writer's investigations it was discovered that in all solid-rectifier detectors investigated, the action is materially improved by the use of a small electromotive force in the detector circuit, this being so poled as to send current through the rectifier in the direction of the rectified current, its magnitude being such as to bring the conductance of the detector to the steepest part of the curve. For example, in the case of the perikon detector, the best electromotive force is about one-tenth volt, so poled as to cause a circuit flow into the rectifying conductor through the contact of small area. The curve for silicon indicates that with this detector the best electromotive force is about two-tenths volt, in the opposite direction to that employed with perikon, and this is closely checked by experiment.

The writer frankly confesses that he has no satisfactory explanation of the phenomena of rectification in solid conductors. In his early work he adopted the thermoelectric hypotheses for public explanation, not that it was satisfactory even then, but because it was at least understandable and fulfilled many of the conditions. Curiously enough, all of the rectifying conductors possess high thermoelectric power, as well as high specific resistance (at least in comparison with any of the metallic conductors) and high thermal conductivity. There is undoubtedly a connection between high specific resistance and thermoelectric power. Liebenow[8] gives the following formula for thermoelectric power:

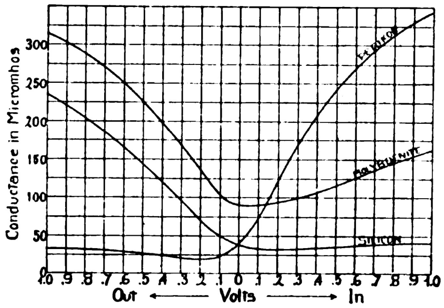

FIG. 2.—CHARACTERISTIC CURVES OF VARIOUS SOLID RECTIFIERS.

$$dE = \pm 2.04 \sqrt{\frac{RL}{T}}\, dt,$$

where E = electromotive force.
R = specific electrical resistance.
L = specific thermal conductiivty.
T = absolute temperature.

It is apparent from this formula that high thermoelectric powers would not be expected in metallic conductors, for the reason that in all metals low specific thermal conductivity is associated with high specific resistance, *i. e.*, thermal and electrical conductivities vary together. As above stated, all the rectifying conductors fulfill the conditions demanded by this formula for high thermoelectric power.

In the early rectifying conductors examined by the writer the thermoelectric currents were in the same direction as the rectified current. This seemed to support the thermoelectric theory of the action, but later a number of rectifying conductors, such as, for example, impure silicon, were found to have the thermoelectric current in the opposite direction to the rectified current, and when tested as detectors the resultant current was found to be in the reverse direction from that produced by heating the junction, thereby proving that the action could not be thermoelectric. Austin has independently, although later than the writer, discovered this opposition of thermoelectric and rectification action in the case of impure (commercial) silicon. It is a fact, however, that out of several hundred solid rectifiers investigated by the writer but three have been found with the thermoelectric action in opposition to the rectified current.

Although the writer has no entirely satisfactory theory of the action in a rectifying conductor, he advances the following:

As an extremely perfect contact of small area is one of the requisite conditions for the manifestation of the rectifying property, it is evident that the current flow in the rectifying conductor must be extremely constricted in the immediate neighborhood of this small contact. Such extreme constriction of current path in material where the conduction is not metallic may lead to electronic impoverishment of either the positive or negative electrons, according as the conductor is an "in" or "out" rectifier, thereby making the passage of either "in" or "out" currents difficult, the conductor and contact of small area then acting as a rectifier. The improvement noted when a small electromotive force of the proper amount and direction is employed in the detector circuit may perhaps be due to the further electronic impoverishment created by such a current.

Aside from their utility as wireless detectors, solid rectifiers afford the best means of measurement of extremely small alternating currents, such, for example, as those existing in wireless receiving circuits energized from very distant sources. The writer has found that with the perikon detector any received signal capable of giving an appreciable sound in the telephone receiver will give a measurable deflection of a galvanometer in the same circuit.

Owing to the fact that commercial wireless receiving circuits are rarely free from

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[8] Wiedemann's Annalen, Vol. 68, p. 316.

[9] Bulletin of the Bureau of Standards, Vol. 5, August, 1908, pp. 133-147.

irregular, though minute, extraneous disturbances other than the currents under measurement, an extremely sensitive galvanometer is not always desirable. The writer uses for such measurements a 2,000-ohm D'Arsonval galvanometer, giving at one metre distance a millimetre scale deflection for 2×10^{-9} ampere. This not only gives measurable deflections on all signals of readable intensity, but may be readily calibrated on low-frequency (sixty-cycle) alternating current by the use of a potentiometer adapted to alternating currents.

For measurements on circuits free from such disturbances a much more sensitive galvanometer may be used. With this it is possible to measure received signals that are entirely inaudible in the most sensitive telephone receivers. It is also possible to do this on low-frequency circuits. In a series of measurements made by the writer on the attenuation of 750-cycle alternating current on artificial telephone circuits, measurements were found possible when a sensitive telephone receiver in series with the detector was absolutely silent.

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Selective Emission of Incandescent Lamps.

The February meeting of the New York Section of the Illuminating Engineering Society was held on February 11 in the Engineering Societies Building, the small attendance being in a measure offset by the number of prominent men present.

A paper, entitled "Selective Emission of Incandescent Lamps as Determined by New Photometric Methods," by E. P. Hyde, F. E. Cady and G. W. Middlekauff, was read by the first named, and this abstruse subject was presented in such a manner as to be readily understood by all. That the subject is of great importance may be seen from the introduction presented by the authors, viz.:

"The recent development of high efficiency metallic - filament lamps has aroused new interest in the measurement of the high temperatures of glowing metals, and has raised the question as to whether the high efficiencies are due primarily to the high temperatures at which the filaments operate, or to a selective radiation, where by selective radiation is meant that the distribution of the energy in the spectrum of the radiating body at a given temperature is different from that of a black body at the same temperature."

The authors investigated seven kinds of filaments by the method which was first outlined by Holborn in his original description of the Holborn pyrometer, and which was subsequently applied by Drs. Waidner and Burgess in their recent work, "Preliminary Measurements on Temperature and Selective Radiation of Incandescent Lamps," and the results of the investigation are given in Tables I, II, and III.

TABLE I.—AVERAGE VALUES OBTAINED ON LAMPS OF EACH TYPE AT VOLTAGES CORRESPONDING TO A "COLOR MATCH" WITH THE STANDARD LAMP AT 75 VOLTS.

Types of Filament.	Red Black-Body Tempera-tures.	Relative Per Cent Change Cp. for 1% Change in Watts.	Lumens per Watt.
Untreated carbon.	1420 C.	1.00	1.00
Helion	1405	1.00	0.97
Treated carbon...	1395	0.97	1.06
Gem	1400	0.98	1.05
Tantalum	1340	0.83	1.28
Tungsten	1345	0.79	1.49
Osmium	1390	0.80	1.85

TABLE II.—AVERAGE VALUES OBTAINED ON LAMPS OF EACH TYPE AT VOLTAGES CORRESPONDING TO A "COLOR MATCH" WITH THE STANDARD LAMP AT 100 VOLTS.

Types of Filament.	Red Black-Body Tempera-tures.	Relative Per Cent Change Cp. for 1% Change in Watts.	Lumens per Watt.
Untreated carbon.	1680 C.	0.86	3.85
Helion	1650	0.85	3.85
Treated carbon...	1645	0.84	4.15
Gem	1650	0.84	4.0
Tantalum	1570	0.72	4.35
Tungsten	1555	0.71	5.25
Osmium	1610	0.69	5.9

TABLE III.—AVERAGE VALUES OBTAINED ON LAMPS OF EACH TYPE AT VOLTAGES CORRESPONDING TO A "COLOR MATCH" WITH THE STANDARD LAMP AT 125 VOLTS.

Types of Filament.	Red Black-Body Tempera-tures.	Relative Per Cent Change Cp. for 1% Change in Watts.	Lumens per Watt.
Untreated carbon.	1890 C.	0.76	9.0
Helion	1850	0.75	9.2
Treated carbon...	1855	0.74	9.5
Gem	1855	0.76	9.4
Tantalum	1765	0.65	10.0
Tungsten	1740	0.67	11.5
Osmium	1800	0.65	12.5

Thus, from the data given in column 4, it will be noted that when these various types of filaments have the same distribution of energy in the visible spectrum, the lumens per watt range from unity to 1.85.

If there were no relative selectivity, the lumens per watt would be unity for every type. There is marked evidence, therefore, that there is considerable selectivity among the different types of filaments, and it is quite interesting to note the order in which the filaments arrange themselves. A higher value of lumens per watt, as, for example, the value of 1.85 for the osmium lamp, as compared with 1.00 for the untreated carbon filament, indicates that when the osmium filament has the same distribution of energy in the visible spectrum as the untreated carbon filament, the energy curve of the osmium lamp drops off considerably in the infra-red as compared with the energy curve of the untreated carbon. In other words, the osmium radiates selectively in favor of shorter wave-lengths, that is, in favor of the visible spectrum, and is, therefore, a more efficient luminous radiator than an untreated carbon filament.

The authors have been unable to determine the true temperature at which a color match with a black body can be obtained with any material except platinum, and, therefore, they are unable to state as to what extent the higher efficiency of the metallic filaments is due to selective radiation, although the results would indicate that in the case of osmium from thirty to forty per cent of the increased efficiency over a carbon-filament lamp is due to selective radiation.

The paper was discussed by Professor Ganz, Dr. A. H. Elliott, Wilson S. Howell and P. S. Millar.

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The Mexican Northern Power Company.

The Mexican Northern Power Company is a new Canadian enterprise recently organized with a capital stock of $10,000,000 and an authorized bond issue of $7,500,000. The company has secured valuable franchises from the government of Mexico for the utilization of water-powers in the northern portion of the Mexican Republic. The powers granted are very broad, embracing the use of water for irrigation purposes as well as for power and light. The franchises are perpetual in their tenure, and carry exemption from taxation for a term of years. Bonds amounting to $5,000,000, recently offered for subscription by the Canadian Electric Syndicate, of Montreal, have been largely over-subscribed. G. F. Greenwood, C. E., late managing director of the Havana Electric Power Company, is the president of the new concern; E. B. Greenshields, director of the Bank of Montreal, is vice-president, and Frank Thompson, secretary. The company expects to develop up to 30,000 horsepower, there being, it is stated, a market for more than twice this amount of power. The consulting engineer of the company is W. F. Tye, C. E., late chief engineer of the Canadian Pacific Railway, and he will have associated with him James Dix Schuyler, C. E., who is at present a member of the Panama Canal Commission, and an eminent authority on hydraulic construction. W.