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CRYSTAL RECTIFIERS FOR ELECTRIC CURRENTS AND ELECTRIC OSCILLATIONS.

PART II. CARBORUNDUM, MOLYBDENITE, ANATASE, BROOKITE.

BY GEORGE W. PIERCE.

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Introduction.

Concerning Part I. — Carborundum had been found by General Dunwoody[1] to be capable of acting as a receiver for the electric waves of wireless telegraphy. Having learned of this property of carborundum, the writer thought that a further study of the electrical behavior of this substance would be interesting. In the course of this study, an account of which has been published in the Physical Review[2] for July, 1907, it was discovered that when a piece of carborundum is placed in a clamp between contact electrodes, the hetereogeneous conductor consisting of the carborundum and the electrodes permits the passage of a greater current in one direction than in the reverse direction under the same applied voltage. The device can be used as a rectifier for small alternating currents and oscillations. The phenomenon is very striking. For example, with one specimen under an electromotive force of 30 volts the current in one direction is 4,000 times as great as the current in the opposite direction under the same external voltage.

Although the rectified current is not large (in the case just cited, 3 milliamperes in one direction and .00075 milliampere in the opposite direction) such a rectifier, being constructed entirely of solid parts, possesses sufficient permanence and constancy to permit of many useful applications, where the detection and measurement of small alternating currents is required. As an example of such applications details are given in Part I. of the employment of the rectifier in the construction of an alternating current voltmeter operable with an extremely small consumption of energy.[3]

Questions Arising in Connection with the Phenomenon. — Many questions of theoretical interest arise in connection with the phenomenon. Is the action localized at the surface of contact between the crystal and the metallic electrode? Is the action due to electrolytic polarization? Is the action thermoelectric, conditioned on unequal heating of the two electrode contacts? If the phenomenon is novel, how is it related to the hitherto studied properties of conductors?

In the experiments on carborundum performed by the writer the

[1] Dunwoody, U. S. Patent, No. 837,616, issued December 4, 1906.

[2] Pierce, Phys. Rev., Vol. 25, pp. 31–60, 1907.

[3] G. W. Pierce, U. S. Patent, No 879,061.

investigation of these questions met with limitations on account of the occurrence of the carborundum in discrete masses to which electrodes could not be rigidly attached; so that the conditions at the electrodes could not be widely varied. However, by increasing the pressure of the electrodes against the carborundum beyond a certain limit, and by cathodically platinizing the surfaces of the carborundum at both the contact areas, the rectification though not entirely eliminated was rendered very imperfect; that is to say, the ratio of the strength of the current in one direction to that in the reverse direction approached unity. On the other hand, platinizing one only of the surfaces of contact, while the other surface was left unplatinized, generally rendered the rectification more nearly perfect. This fact indicated that the seat of the action was the area of contact with the electrodes, and that the action at the two contacts were in opposition to each other, so that when the action at one of the contacts was reduced by platinizing, the rectification at the other contact appeared more pronounced.

These characteristics of the phenomenon are consistent with the view that *the rectification is conditioned on the localization of the energy of the circuit at the high resistance boundary between the two different classes of conductors, the crystal and the metallic electrode.*

Now such a localization of energy at the boundary of the two conductors is favorable to the production of electrolytic polarization, if we may have electrolytic polarization in solids, and is also favorable to the production of a thermoelectromotive force, either of which might result in rectification.

Nevertheless, in Part I., a number of experiments are described which were taken to indicate that neither electrolysis nor thermoelectricity plays an important part in the phenomenon.

On the Question of Electrolysis, the following experiment, performed since the publication of Part I., has a bearing.

Experiment Showing Permanence of the Carborundum Rectifier. — In confirmation of the absence of electrolytic polarization, a durability test of the rectifier has later been made as follows: A crystal of carborundum enclosed in a glass tube with a few drops of oil[1] and held between brass electrodes, one of which was under

[1] The oil was put in to prevent accumulation of moisture.

tension of a spiral spring, was kept under almost daily observation [1] from October 23, 1907, until March 18, 1908. During this time more than 1,200 measurements were made of the direct current obtained through the crystal under different direct and alternating voltages. The rectifier was kept in a thermostat and subjected to various long periods of heating and cooling ranging from 0° to 80° C. Notwithstanding the long continued exposure of the crystal to large changes of temperature, and notwithstanding the frequent loading and occasional overloading of the rectifier with current, it was found at the end of the series that the values of the direct current obtained from the crystal under a given applied alternating voltage over a range of current from 4 to 400 microamperes (direct) and a range of voltage between 1.5 and 6 volts (alternating) did not differ from the corresponding values at the beginning of the series by an amount exceeding the limit of accuracy of the experiment, which was about one third of 1 per cent.

This experiment shows that if there is any kind of electrolytic action, it must be of such a character as not to change the nature of the electrodes or of the crystal.

On the Question of a Possible Thermoelectric Origin of the Phenomenon. — It is apparent that the disposition of the carborundum for the best rectification is exactly the most favorable disposition for the development of a thermoelectric voltage at the high resistance contact. This voltage, being always in one direction, by superposition on an alternating current through the crystal, might give rise to a unilateral cycle through the crystal. In Part I., several experiments are described which present evidence adverse to this explanation, and the opinion is expressed that "heat is practically a negligible factor in the process."

However, since it is very important to exclude the possibility of bringing the experiments into consistent relation with thermoelectricity before admitting that we are dealing with a new phenomenon, the question of the applicability of the thermoelectric explanation is taken up anew in the present account.

[1] This series of measurements were carried out by Mr. K. S. Johnson, to whom the writer wishes to express his sincere thanks. The experiment was finally discontinued on account of the accidental melting of the cement holding in the ends of the tube.

Extension of the Experiments to Other Crystals. — Prior to the publication of Part I., the writer had found a number of other crystals showing the rectifying property similar to carborundum. These have now been under investigation for a period of more than a year, and though the work is by no means completed, it is thought that an account of the experiments as far as they have gone may be of interest. The present account deals with the rectifying action of anatase, brookite and molybdenite in contact with a metallic electrode.

Anatase and Brookite.

Anatase. — Anatase, an octahedral crystal of oxide of titanium with the chemical formula TiO_2, was found to rectify quite markedly when placed in a clamp, under a contact pressure of 1 to 3 kilograms. Current-voltage curves[1] of anatase, with a diagram of the disposition of the crystal in the experiment, are given in Fig. 1. The

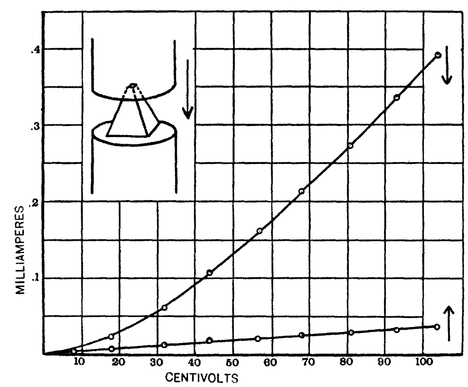


Fig. 1. — Current-voltage curves for anatase, with direct current.

upper curve was obtained when the current was through the crystal in one direction, the lower curve was with the current in the opposite direction, as indicated by the arrows. The contact pressure in this experiment was 2 kilograms. These curves have the same general form as those obtained in the experiments on carborundum. By a

[1] The current-voltage curves were drawn in Part I. with positive coördinates when the current was in one direction and negative coördinates when the current was in the opposite direction. In order to economize space in the present account, both the positive and negative currents are drawn in the same coördinate quadrant. This has the advantage of permitting an easier comparison.

comparison with Part I., it is seen, however, that the anatase gives much larger currents with a small applied voltage than does the carborundum. This characterizes the anatase as a much more sensitive rectifier for small alternating voltages and as a much more sensitive detector for electric waves than is the carborundum.

Brookite. — This is another crystal form of TiO_2, which was found to serve as a rectifier of small alternating currents with about the same sensitiveness as anatase. Although a considerable amount of time was spent in experimenting with anatase and brookite, these substances, occurring, like carborundum, in discrete pieces to which terminals could not be attached, did not serve to throw much light on the phenomenon. Numerical data in regard to them are, therefore, omitted.

MOLYBDENITE.

One of the most sensitive and interesting of the rectifiers thus far investigated makes use of molybdenite as a member.[1] Molybdenite, with the chemical formula MoS_2, is a mineral occurring in nature in the form of tabular hexagonal prisms with eminent cleavage parallel to the base of the prism. The cleavage of the crystal resembles that of mica, and thin sheets of the mineral several square centimeters in area may be scaled off from a large crystal of molybdenite. These sheets have a metallic lustre and look not unlike sheets of lead foil. They can be readily electroplated with copper, so that connecting wires may be soldered to them. This property, together with the thinness of the sheets and the ease with which the thermoelectric property of the substance may be studied, admirably adapts it to the present experiments.

The Molybdenite Rectifier. — The rectifying action of the molybdenite was first obtained with a thin, flat specimen of the mineral held between flat contact electrodes in a clamp of which the two jaws were insulated from one another. With this form of mounting the molybdenite also acts as a receiver for electric waves with or without a battery in the local circuit.

It was soon found, however, that the apparatus was more sensitive

[1] See also G. W. Pierce, "A Simple Method of Measuring the Intensity of Sound," Proc. Am. Acad., Vol. 43, p. 377, February, 1908, in which the molybdenite rectifier was employed.

as a receiver for electric waves and as a rectifier, when one of the contacts between the molybdenite and the electrode had a high resistance. A form of mounting in which this is attained is shown in section in Fig. 2. *T* is a threaded brass post on the top of which is placed a disc of mica *N*. On top of the mica is a thin circular disc of the molybdenite *M* with an area of about 1 square centimeter, leaving a projection of the mica beyond the periphery of the molybdenite. A hollow cap *D*, threaded inside and having a conical hole at the top, is screwed down on the post *T* so as to clamp the molybdenite between the mica disc [1] and the annular shoulder of the cap, with the upper surface of the molybdenite exposed above. At the free surface of the molybdenite contact is made with metallic rod *P*.[2]

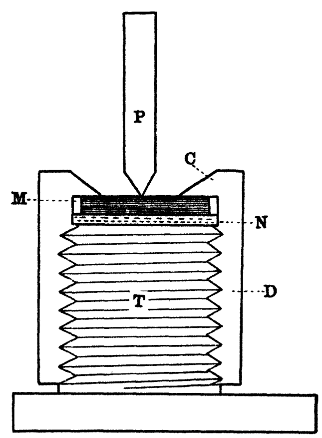


Fig. 2. Holder for molybdenite.

The rod *P* was either supported unadjustibly as in the author's experiments on sound,[3] or it was mounted in a manner to permit of ready adjustment as is shown in Fig. 3. The clamp *K* containing the molybdenite is metallically connected with the binding post *H* (Fig. 3). Another binding post is attached to the metallic block *A*, on top of which is supported a stout spring *B*. Through a hole in *B* provided with a set screw, the rod *P* is allowed to drop down into contact with *K*. The set screw is then tightened against *P*, and the final adjustment is made by the slow-motion screw *S*. The apparatus is connected in circuit by means of the binding posts, so

[1] The purpose of the mica disc under the molybdenite is to confine the current as much as possible to the upper layer of the molybdenite. This was done so as not to complicate the phenomenon by conduction across the laminæ of the substance, and also so that when the detector is immersed in oil in some of the later experiments, the oil shall have free play over the conducting surface and over the contacts, and serve the better to avoid possible changes of temperature of the essential parts of the apparatus.

[2] In the diagrams of Fig. 2 and Fig. 3, the lower end of the rod *P* is shown pointed. It is found, however, that the end of the rod *P* may be blunt or even flat with an area as great as 4 sq. mm. without much loss of sensitiveness of the instrument as a receiver for electric waves or as a rectifier.

[3] Loc. cit.

that the current of the circuit is made to enter the molybdenite through the contact area between P and the molybdenite and to leave by way of the contact between the molybdenite and the cap C, or the reverse. It is found that a larger current flows in one direction

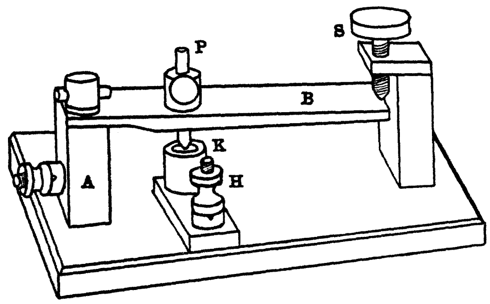


Fig. 3. Mounting of molybden te.

than in the reverse direction for a given applied elecromotive force.

Current-voltage Characteristic of the Molybdenite Rectifier. — A large number of current-voltage curves of the molybdenite rectifier with the form of mounting shown in Fig. 3, have been taken both with direct and alternating applied voltages. Two sets of these curves, with the corresponding tables are here given. In taking the observations of Fig. 4, Table I., the rectifier was submerged in a constant temperature oil-bath. The oil was rapidly stirred and had free access to the surface of the molybdenite and to the point contact between the molybdenite and the copper rod. A steady voltage was applied to the terminals of the rectifier, and the current through the crystal was measured. The voltage was then reversed and the current again measured. The process was repeated with various values of the voltage. These values thus obtained in the oil-bath were found to be the same as the corresponding values when the rectifier was in air at the same temperature. That is, the presence of the oil about the rectifying contact did not materially affect the process.

The values of Table I. are plotted in the curves A and B of Fig. 4. A is the curve obtained when the current was sent from the copper to the molybdenite, B the corresponding curve when the current was sent from the molybdenite to the copper. These curves

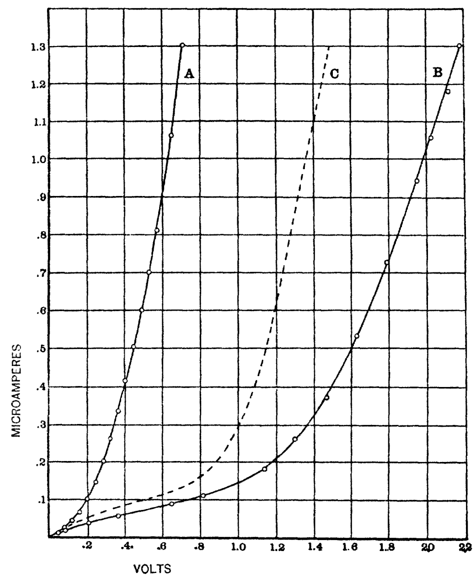


Fig. 4. Current-voltage curves of the molybdenite rectifier. *A*, current from copper to molybdenite; *B*, current from molybdenite to copper; *C*, excess voltage.

Table I.

Current-Voltage Values for the Molybdenite Rectifier.

Current from Copper to Molybdenite.		Current from Molybdenite to Copper.	
Volts.	Microamperes.	Volts.	Microamperes.
.0407	.012	.082	.020
.0815	.025	.203	.038
.122	.043	.363	.058
.163	.068	.651	.090
.203	.102	.815	.114
.244	.147	1.140	.185
.285	.202	1.300	.261
.326	.262	1.465	.375
.363	.337	1.630	.534
.407	.415	1.79	.732
.447	.504	1.96	.947
.488	.600	2.03	1.056
.529	.700	2.12	1.180
.570	.812	2.18	1.306
.651	1.062		
.710	1.306		

resemble those obtained in Part I with carborundum. The molybdenite rectifier is, however, seen to operate with a much smaller resistance than the carborundum rectifier. This makes the molybdenite rectifier applicable to use with smaller voltages than the carborundum, consequently the molybdenite rectifier is a more sensitive detector for electric waves or for small alternating voltages than the carborundum rectifier. In fact, the molybdenite rectifier, with selected specimens of molybdenite, when used as a detector for electric waves, is, so far as the writer can judge, equal in sensitiveness with the most sensitive detectors heretofore employed in wireless telegraphy. Also the molybdenite rectifier, giving comparative large values of direct current for small values of applied alternating voltage, affords a sensitive method of measuring the small alternating voltages arising in telephony and in experiments on sound. Application of the rectifier to the measurement of sound has been made in a paper entitled a "Simple Method of Measuring the Intensity of Sound."[1]

Referring again to Fig. 4, attention is called to the dotted curve *C*. This curve is calculated from the curves *A* and *B* by subtraction of corresponding abscissas. The curve *C*, therefore, represents the excess of voltage required to force the current from the molybdenite to the copper above that required to send an equal current in the opposite direction. The table of values for curve *C* follows as Table II.

TABLE II.

Excess of Voltage to Send Current from MoS_2 to Cu above that to Send Current from Cu to MoS_2.

Microamperes.	Excess Volts.	Microamperes.	Excess Volts.
.05	.18	.70	1.24
.10	.515	.80	1.27
.20	.89	.90	1.32
.30	1.01	1.00	1.36
.40	1.09	1.10	1.40
.50	1.15	1.20	1.45
.60	1.19	1.30	1.48

The current-voltage values for the molybdenite rectifier differ for different specimens and for different adjustments of the same speci-

[1] Pierce, Proc. Am. Acad., Vol. 43, p. 377, February, 1908.

men. The results of another experiment, in which larger values of the current and voltage are employed, are given in Table III. These values were obtained with a specimen mounted somewhat differently from the mounting in Fig. 3, in that, in order to eliminate any possible uncertainty from the use of the clamp holder K (Fig. 3), the tight-contact terminal was soldered to a copper plated area on the molybdenite, and the sheet of molybdenite with its soldered terminal were held down upon a block of wood by means of a mica covering screwed to the block. A hole through the mica covering admitted the contact rod P.

Table III.

Current-Voltage Values for the Molybdenite Rectifier. Larger Currents.

Current from Copper to Molybdenite.		Current from Molybdenite to Copper.	
Volts.	Milliamperes.	Volts.	Milliamperes.
.5	.20	2.0	.02
.6	.50	4.5	.10
.77	1.00	5.27	.25
.84	1.50	7.1	.55
.92	2.00	8.6	1.15
1.07	2.50	10.1	2.20
1.15	3.00		
1.32	4.00		
1.52	5.00		
1.70	6.00		
1.88	7.00		
2.00	8.00		
2.15	9.00		
2.22	10.00		

The values recorded in Table III. are plotted in Fig. 5. By a reference to the curves or to the table it is seen that the rectification at 10 milliamperes is practically perfect; the current from the molybdenite at 2.2 volts is 10 milliamperes, while the current in the opposite direction at the same voltage is about .02 milliampere. This is a larger value of the rectified current, at practically perfect rectification, than I was able to obtain with the carborundum rectifier. It was, therefore, decided to recur to the attempt to obtain an oscillographic record of the phenomenon, as had been attempted with only partial success in the study of carborundum. The result in the present experiment is highly satisfactory.

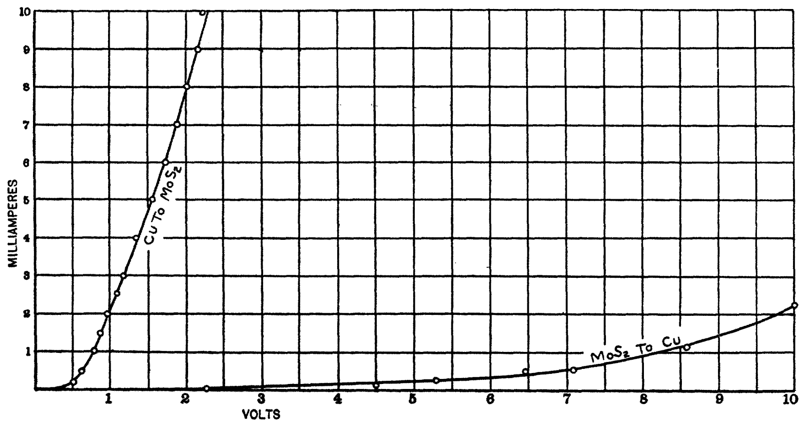


Fig. 5. Current-vocnltage rves of molybdenite recitfier, with large current.

OSCILLOGRAPHIC RECORDS OF RECTIFIED CYCLE.

Method of Obtaining the Oscillograms. — After a prolonged attempt to use an Einthoven galvanometer, which was found to be impracticable on account of the natural period of the "string" of the galvanometer, the Braun's tube oscillograph was employed A sketch of the oscillographic apparatus is given in Fig. 6. The

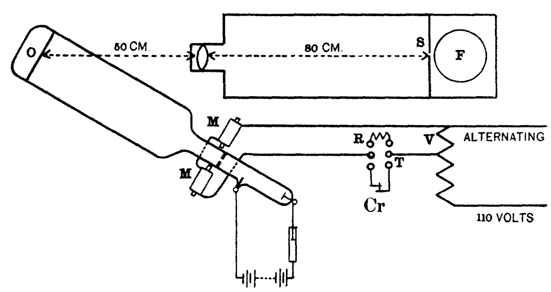


Fig. 6. Oscillographic apparatus.

Braun's tube was filled with hydrogen and was pumped to the vacuum at which it has its highest sensitiveness.[1] The high-potential current through the tube was supplied by Professor Trowbridge's

[1] My thanks are due to Mr. E. L. Chaffee for very carefully pumping out the tube for me, and for other valuable assistance with the oscillographs.

40,000-volt storage battery, which he kindly placed at my disposal. Usually only 20,000 volts of the battery were employed, and this was controlled by means of a running-water rheostat in series with the battery and the tube.

The cathode beam in the tube produced a luminescent spot on the fluorescent screen at *O*. The electromagnets, through which the current to be oscillographed was sent, were placed above and below the Braun's tube at *MM*. Therefore, the deflection of the spot was in a horizontal line perpendicular to the plane of the figure. The photograph of the moving luminescent spot was taken on a sheet of bromide paper carried by a rotating drum *F*, which made 20 revolutions per second about a horizontal axis. This drum was enclosed in a light-tight box at the back of an improvised camera. A horizontal slit *S*, immediately in front of the rotating drum, shut off all luminescence in the tube except that in the line of motion of the spot.

The rotating drum was driven by a synchronous motor operating on the 60-cycle alternating current mains of the laboratory. The alternating current sent through the rectifier and the deflecting magnets was taken from the same supply. The synchronism of the drum with the deflections of the luminescent spot was so perfect that exposures of four minutes could be made, during which time the image of the spot moved over the sensitive paper 4,800 times, without any failure of perfect superposition, and without any appreciable fogging of the paper.

The deflecting electromagnets *MM* had a combined resistance of 436 ohms, and were provided with soft iron cores about 6 millimeters in diameter. With these deflecting coils a direct current of 1.5 milliamperes gave a deflection of 1 cm. on a ground glass put in the place of the sensitive paper at the back of the camera. A calibration for different values of direct current through the coils showed the deflections of the light spot to be proportional to the current, and for the small values of current employed showed no evidence of hysteresis in the iron.

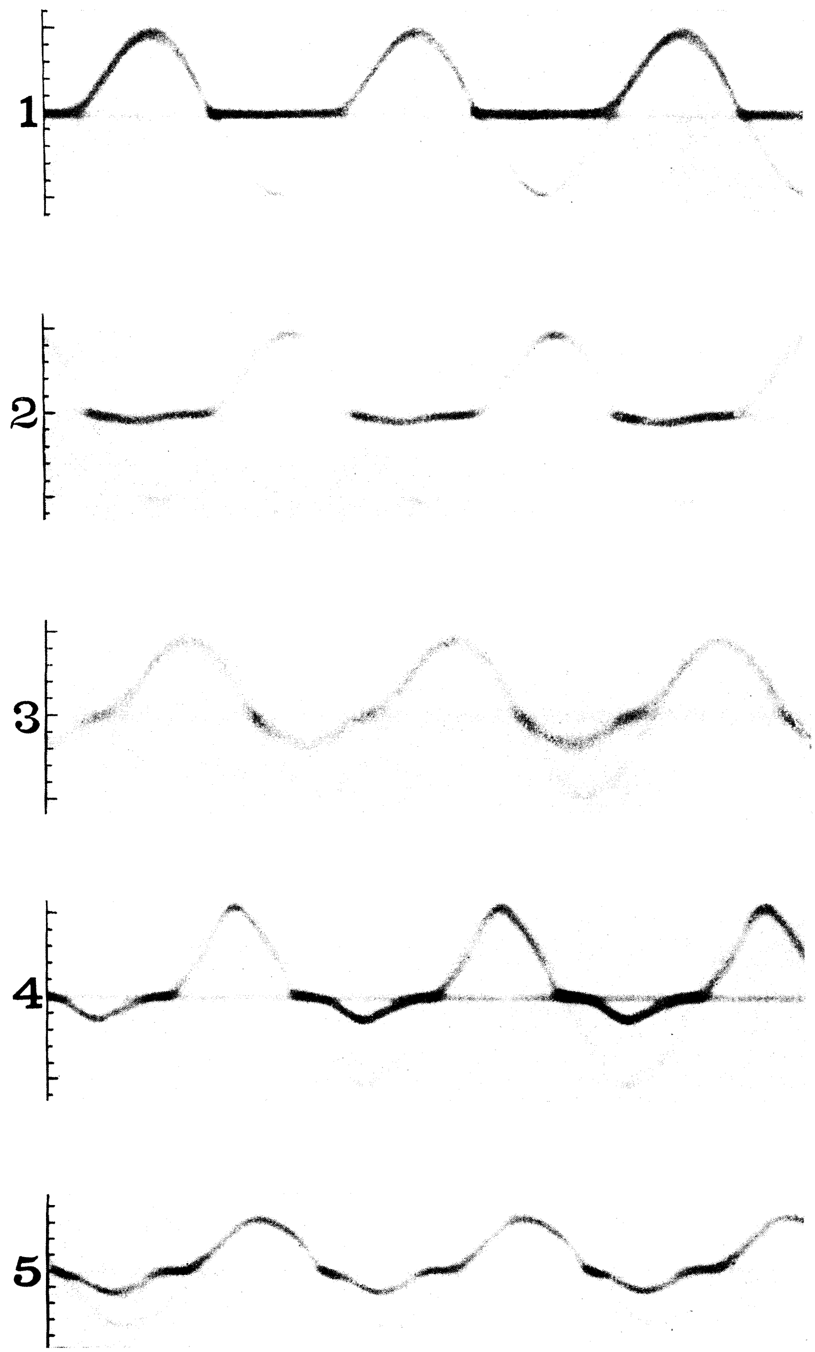
The Oscillographic Records. — Reproductions (reduced to 1/3) of a characteristic set of the oscillographic records obtained are given in Plate I. Oscillograph No. 1 was taken with the molybdenite rectifier adjusted to give practically perfect rectification. No. 2 is with the same rectifier slightly out of adjustment (overloaded), so that the rectification is less perfect. No. 3 is with the same rectifier further out of adjustment. No. 4 is an oscillographic record with the carborundum rectifier. No. 5 is with the rectifier of brookite. In taking No. 2, the rectifier was submerged in oil, to test the effect of cooling, which was found to have no effect.

In making these records the following steps were taken: The drum carrying the film was set rotating. The high-potential current was started in the tube. The potential V (Fig. 6) and the contact of the rectifier were adjusted so that the deflection of the luminescent spot on the fluorescent screen was wholly or chiefly to one side of the zero position. Exposure of about 2 minutes was then made. This exposure gave the heavy line of the oscillograms. The switch at T was then thrown open, so that the luminescent spot came to its zero position. The exposure in this position was made for a shorter time of about 40 seconds. This traced the light straight line along the center of the picture, and gave the axis of zero current. The switch T was then thrown to the position to put the resistance R in the circuit in place of the crystal. The resistance R had been previously adjusted so that the amplitude of the deflection with R in the circuit should coincide with the amplitude with the crystal in the circuit. With the resistance R in circuit an exposure of about one minute was made, giving the light sinusoida-curve of the picture.

On each picture the three exposures give, therefore, (1) the form of the rectified cycle as a heavy line, (2) the position of the axis of zero current, as a straight line through the figure, and (3) the form and position of the alternating-current cycle when an equivalent resistance R is substituted for the rectifier. The last-named cycle appears in the pictures as a thin-lined sine curve. This curve is in phase with the impressed voltage immediately about the crystal, and is referred to below as the "voltage-phase curve."

In tracing all the curves, the motion of the light spot over the paper is from left to right; the time coördinate is, therefore, the abscissa of the curves and is drawn as usual from left to right.

The scale drawn in ink at the left-hand margin of each picture gives the value of the current; one division being one milliampere.



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Crystal Rectifiers

A tabular description of the conditions under which each of the records was taken is contained in Table IV.

TABLE IV.

Tabular Description of the Oscillographic Records of Plate I.

No.	Material of Rectifier.	Condition.	Maximum Rectified Current in Milli-amperes.	R.M.S. Alternating Volts.	Equivalent Resistance in Ohms.
1	Molybdenite.	Good adjustment.	4.9	3.54	400
2	"	Out of best adjustment. Submerged in oil and overloaded.	4.9	3.54	400
3	"	Out of best adjustment. Overloaded.	4.5		
4	Carborundum, platinized on one side.	Overloaded.	5.4	22.0	6000
5	Brookite	"	3.0	2.22	992

A discussion of the records follows.

Oscillograms 1, 2 and 3, Molybdenite. — The pressure of the copper rod[1] against the molybdenite for good rectification is slight, and is somewhat difficult to attain. Some points of the crystal are more sensitive than others, and the crystal has to be moved around under the copper contact and tried at several different points before the best adjustment can be found. Oscillogram No. 1, Plate I., was taken with a molybdenite rectifier in good adjustment. The rectification in this case is seen to be practically perfect; the cycle through the specimen consists of a nearly sinusoidal curve for one half-period and a practically straight line for the other half-period. The large current flows from the copper to the molybdenite, and the zero current from the molybdenite to the copper.

When the pressure on the contact was increased until a small negative current was permitted to pass, oscillogram No. 2 was obtained. Increasing the pressure still more so as to get a larger negative current gave oscillogram No. 3.

One object in taking these oscillograms, together with the voltage-phase cycle, was to see if there is any evidence of lag of the rectified cycle with respect to the voltage-phase cycle. *No such*

[1] The end of the copper rod in contact with the molybdenite had an area of 4 sq. mm.

lag appears. On the other hand, the rectified cycles *lead* their respective voltage-phase cycles at three positions:

The first of these positions of lead is at the part of the cycle in which the rectified current approaches the zero axis after having traversed the upper half of the curve. This advance, which is so small as to be just perceptible in the oscillograms, amounts to about 1/6000 of a second.

A second, somewhat larger, lead of the rectified cycle ahead of the voltage-phase cycle is at the point of rising from the axis after the rectified current has followed for a half period along the zero axis. The lead here is about 1/1500 of a second.

A third, very significant, lead of the rectified cycle is at the negative maximum, as is seen in the cases of imperfect rectification, oscillograms 2 and 3. Here the lead is a large fraction of a half period.

Oscillogram No. 4, Carborundum. — Oscillogram No. 4, Plate I., was obtained with a carborundum rectifier consisting of a specimen of carborundum, platinized on one side, and held in a clamp under a contact pressure of 3 kg. When sufficient current was sent through the carborundum to give deflections suitable for the oscillogram, the carborundum was overloaded, and permitted current to pass in the negative direction. The carborundum cycle differs from the molybdenite cycle in the absence of lead at the negative maximum and at the point of rising from the zero axis. This anomaly in the case of the carborundum rectifier is seen later to be the effect of its high resistance.

Oscillogram No. 5, Brookite. — The form of the cycle obtained in this case is intermediate between the carborundum cycle and the cycle of oscillogram No. 3. This is consistent with the value of its resistance.

In order to investigate the meaning of the lead of the rectified cycles in the several cases a further examination of the oscillograms is made with the aid of the theory of alternating currents.

Examination of the Oscillograms with the Aid of the Theory of Alternating Currents.

The so-called "voltage-phase cycle" gives the instantaneous values of the current through the deflecting coils and a resistance chosen to make the amplitude of this current the same as the amplitude of one loop of the current through the rectifier, under the same applied voltage. Although the current of the voltage-phase cycle lags behind the externally applied voltage by an amount depending on the relation of the self-inductance of the deflecting coils to the resistance of the circuit, the current is nevertheless in phase with the voltage immediately about the substituted resistance; for the voltage about a resistance is in phase with the current through it. Now by throwing the switch T of Fig. 6 we put the rectifier in the circuit in the place of the resistance. If the rectifier, when current traverses it, introduces into the circuit electromotive forces out of phase with the current through it, we ought to get a shift of phase of the cycle. We can easily see, for example, that if the rectifier contained capacity or inductance, such a shift would occur. Also, if the action of the rectifier were one of electrolytic polarization, the back E.M.F. of polarization would be approximately determined at any part of the cycle by a time integral of the current, and would introduce a shift of phase resembling that introduced by a capacity.[1]

Also, if the action of the rectifier were due to thermoelectricity, we should expect the thermal electromotive forces developed to be of the form

$$\pm a \int i^2 r dt \tag{1}$$

due to the Joulean heat at the high resistance, and of the form

$$\pm b \int i dt \tag{2}$$

due to the Peltier effect at the junctions. To these terms we should have to add also terms taking account of conduction of heat from the junctions. The term for the conduction of heat would be difficult to assign definite values, but they would be functions of the rise of temperature of the junctions, and may be written in the general form

$$F\left(\int i^2 r dt, \quad \int i dt\right). \tag{3}$$

The terms (1), (2) and (3), when put into the differential equation for the current through the circuit and integrated (if possible), would

[1] B. O. Pierce, Newtonian Potential Function, p. 323, Boston, 1902.

give in the result a shift of phase of the current with respect to the voltage-phase cycle.

Let us, therefore, attempt to determine whether there are any phase differences between the rectified cycle and the voltage-phase cycle that are not accounted for by the conditions existing in the oscillographic apparatus. In doing this we shall make use of the current-voltage characteristic of the molybdenite rectifier, as obtained with the current and voltage in the steady state, and recorded in Table III. and Fig. 5. This table of data was obtained with the same molybdenite rectifier in practically the same adjustment as in the oscillograms 1 and 2 of Plate I.

Let us derive first the numerical equation for the "voltage-phase" curve. In the case of oscillogram No. 1, an ohmic resistance of 400 ohms was in series with the deflecting coils, which had a resistance of 436 ohms, making a total resistance of 836 ohms. Let the inductance of the coils be L. The value of L can be calculated from the voltage and current of the cycle. The R.M.S. voltage impressed on the circuit was 3.54 volts; the maximum voltage was therefore 5.00 volts. The maximum current taken from oscillogram No. 1 was 4.9×10^{-3} amperes, whence we have

$$4.9 \times 10^{-3} = \frac{5.0}{\sqrt{836^2 + L^2\omega^2}}.$$

Therefore

$$L\omega = 584, \tag{1}$$

$$\tan^{-1}\frac{L\omega}{836} = \varphi_1 = 35^\circ, \tag{2}$$

and the equation for the current i_1 of the voltage-phase cycle becomes

$$i_1 = \frac{5.0}{\sqrt{836^2 + 584^2}} \sin(\omega t - 35^\circ). \tag{3}$$

From this equation the values obtained in Table V. were computed, and from these values three half-periods of the voltage-phase cycle are plotted as the sinusoidal curve S of Fig. 7.

The computations when the rectifier is put in place of the 400

TABLE V.

The Voltage-Phase Cycle.

ωt Degrees.	Current in Milliamperes.	ωt Degrees.	Current in Milliamperes.
35	0	135	4.82
55	1.67	155	4.23
75	3.14	175	3.14
95	4.23	195	1.67
115	4.82	215	0
125	4.90		

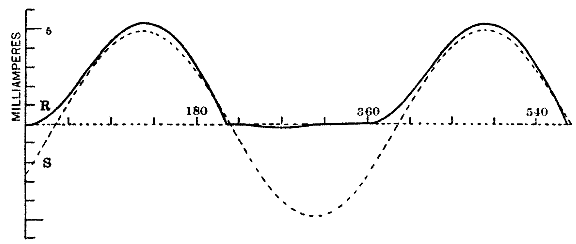

Fig. 7. Rectified cycle computed from the current-voltage values of Fig. 5.

ohm resistance can be made only approximately. The differential equation for the current i_2 through the circuit in this case is

$$E \sin \omega t - e_r = R_c i_2 + L \frac{di_2}{dt}, \tag{4}$$

in which e_r is the drop of voltage about the rectifier, E is 5.0 volts, and R_c the resistance of the deflecting coils = 436 ohms. The drop in voltage e_r about the rectifier is a function of the current. This function is the equation of the current-voltage curve of Fig. 5. It is difficult to obtain an exact analytical expression for this function. But for values of current between 1 and 6 milliamperes, when the current is from copper to molybdenite, e_r is approximately a linear function of the current, with the equation

$$e_r = q + ri, \text{ in which } q = .60 \text{ volt}, r = 183 \text{ ohms}. \tag{5}$$

With this approximation, equation (4) becomes

$$E \sin \omega t - q = (r + R_c) i_2 + L \frac{di_2}{dt}. \tag{6}$$

Integration of this equation gives

$$(7)\quad i_2 = \frac{E}{\sqrt{(r+R_c)^2 + L^2\omega^2}} \sin\left(\omega t - \tan^{-1}\frac{L\omega}{r+R_c}\right) + ce^{-\frac{(R_c+r)t}{L}} - \frac{q}{R_c+r},$$

in which c is a constant of integration. If we substitute known values in this equation; namely,

$$(8)\quad \begin{aligned} r + R_c &= 183 + 436 = 619, \\ L\omega &= 584, \\ E &= 5.0, \\ q &= .60, \end{aligned}$$

we have

$$(9)\quad i_2 = 5.87 \times 10^{-3} \sin(\omega t - 43^\circ.3) + ce^{-1.06\omega t} - .97 \times 10^{-3}.$$

For the determination of the constant c we have the relation $i_2 = 0$ when $E \sin \omega t = q$. This gives $c = 5.1$.

From equation (9), values for the current in the upper loop of the rectified cycle for various values of ωt were computed, and are given in Table VI.

TABLE VI.

Computed Values of the Rectified Cycle. Upper Loop.

ωt Degrees.	Current in Milliamperes.	ωt Degrees.	Current in Milliamperes.
0	0	130	5.26
20	.32	140	5.20
40	1.17	160	4.50
60	2.45	180	3.15
80	3.61	200	1.40
100	4.75	213	0
120	5.21		

The lower loop of the rectified cycle was obtained in a similar manner. In this case the drop in potential about the rectifier was obtained from the curve of current from molybdenite to copper of Fig. 5. The equation to this curve, within the limits employed in the calculations, is approximately

(10) $e_r = q_1 + r_1 i_3$, in which $q_1 = 3.8$ volts, and $r_1 = 6470$ ohms.

These values substituted in an equation of the form of equation (7) give, since the exponential term was found to be negligible,

$$(11) \qquad -i_3 = .72 \times 10^{-3} \sin(\omega t - 4.8) - .55 \times 10^{-3}.$$

Computations from this equation give the values of current recorded in Table VII.

Table VII.

Computed Values of the Rectified Cycle. Lower Loop.

ωt Degrees.	Current in Milliamperes.	ωt Degrees.	Current in Milliamperes.
220	0.00	280	.16
240	.07	300	.07
260	.16	320	.00
270	.17		

The computed values of Tables VI. and VII. are plotted as the continuous curve R of Fig. 7, along with the voltage-phase curve which is the dotted sine curve S.

The data used in the computations are entirely independent of the oscillograms, except that the amplitude of the voltage-phase cycle was taken from oscillogram No. 1 or No. 2, and this value was used in determining the self-inductance of the circuit.

The agreement of the diagram of Fig. 7 with the oscillograms No. 1 and 2 of Plate I. is very striking, as regards both the form and the absolute value of the curves. The agreement with oscillogram No. 2 is a little better than with No. 1, and is within the limit of error of the measurement of the photograph. No departure in amplitude or in phase exists between the rectified cycle and the voltage-phase cycle that is not accounted for by the inductance and resistance of the oscillographic apparatus or by the current-voltage curves of the rectifier with steady currents.

This means that if there are any terms, contingent upon heating or other effects which involves an intergal of a function of the current with respect to the time, this integral attains its final value in a time within the limit of error of measuring the oscillograms, which is about 1/6000 second. This time corresponds to 3.5°, and is about 1 mm. on the original photographs.

It might seem that the approximation made as to the analytical expression for the steady current-voltage curve would not warrant the accuracy here claimed; but if we draw the straight line through the points for which the current is 1 and 6 milliamperes, this line will depart from the observed values only for values of i below 1 milliampere, where the departure will have the following values:

i Millamperes.	Departure. Volts.	Departure in Degrees.
.5	.1	.6
.2	.15	1.7
.1	.3	3.4

In the negative loop of the rectified cycle the departure of the approximation from the observed current-voltage curve is still smaller. However, apart from the specific assumption as to the analytical function representing the current-voltage characteristic of the rectifier under the action of a steady current, the theoretical discussion given above permits a ready qualitative understanding of the lead that occurs in certain parts of the rectified cycle, which may be summarized as follows:

1. The case of the advance of the rectified cycle on rising from the axis of no current is seen to be due largely to the fact that after a dormant half-period the current in the circuit follows the ordinary exponential "building-up" curve for a time before coming into coincidence with the sine curve. This building-up curve starts from the axis with zero lag and is, therefore, in advance of the sine curve. To this effect is to be added the effect due to an apparently higher resistance of the rectifier for small currents than for large currents. This apparently higher resistance brings the building-up curve a little nearer to the sine curve.

2. The slightly quicker descent of the rectified cycle on approaching the axis after having traversed the upper half of the curve is also due to this apparently higher resistance of the rectifier when traversed by smaller currents.

3. The very significant lead of the negative maximum ahead of the corresponding voltage-phase maximum is explicable on the assumption that the rectifier has a much higher resistance in the negative direction than in the positive direction. We have seen above that the angle of lag of the voltage-phase cycle behind the impressed

voltage, determined by the inductance and resistance of the circuit, is

$$\tan^{-1} \tfrac{584}{836} = 35^\circ,$$

while in the negative direction in order to bring the voltage-phase curve to the same amplitude as the negative maximum of the rectified cycle there would be required a resistance of at least 6,470 plus 436 = 6,906 ohms, whence the angle of lag in this case would be

$$\tan^{-1} \tfrac{584}{6906} = 4.8^\circ.$$

Therefore the angle of lead of the rectified cycle ahead of the voltage-phase cycle, determined as the difference of these two angles of lag, is 30.2°. This value agrees with oscillogram No. 2.

In this connection it is interesting to notice that a lead of this negative maximum in the case of the carborundum oscillogram does not appear. The explanation of this is easily obtained if one substitutes for the resistance values of the molybdenite the corresponding values for the circuit containing the carborundum rectifier. The equivalent resistance of the carborundum in its positive loop is 6,000 ohms, so that the angle of lag of the voltage-phase cycle with this resistance in it is only 5.6°, while in the negative direction the equivalent resistance of the carborundum is about 20,000 ohms, giving an angle of lag in the neighborhood of 1°. The difference between these two angles of lag, which would give the phase difference between the carborundum cycle and the corresponding voltage-phase cycle would be a quantity just perceptible on the oscillogram, as was verified in the original protographs.

In conclusion of this discussion of the oscillograms, I should say that we have not been able to detect in the photographs any evidence of a thermoelectric or other integrative action of the rectifier.

Thermoelectric Properties of Molybdenite.

In the present section an account is given of the investigation of the thermoelectromotive force of molybdenite against copper, and a determination of the temperature coefficient of resistance of molybdenite. Apart from their possible bearing on the action of the rectifier, these properties of molybdenite are of interest in themselves.

Thermoelectromotive Force. — Five specimens were mounted for the study of the thermoelectromotive force of molybdenite against copper. These specimens are referred to as *A*, *B*, *C*, *D*, *E*. The method of mounting the specimen *E* is shown in

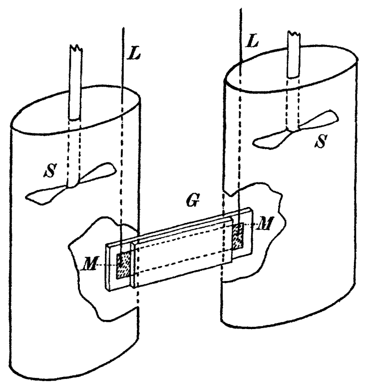

Fig. 8. Apparatus for determining thermoelectromotive force of molybdenite against copper.

Fig. 8. A thin sheet of molybdenite .1 or .2 mm. thick, 2 cm. wide, and 8 cm. long, was cemented between two glass microscope

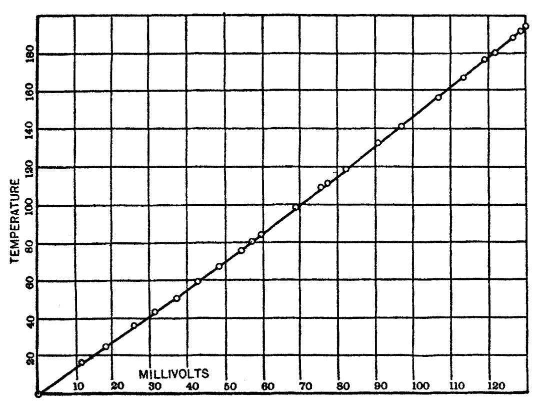

Fig. 9. Thermoelectromotive force of copper-molybdenite couple *E* for various temperatures of hot junction. Temperature of cold junction 0° C.

s des *G* with a cement made of water glass and calcium carbonate.[1] The molybdenite was then copper-plated over a small area at each

[1] Otto Reichenheim suggests the use of such a cement in Inaugural Dissertation, Freiburg, 1906.

of the exposed ends *MM*, and to these copper-plated areas were soldered copper wires, .2 mm. in diameter, so as to form thermal junctions with the molybdenite. The thermal junctions and the ends of the glass mounting were inserted into two brass vessels for containing the temperature baths of oil. The joints between the brass vessel and the glass mounting were made tight with the cement of water glass and calcium carbonate. The oil-baths were provided with stirrers driven by a motor. One of the baths was kept at 0° C., and the other bath was given various temperatures between 0° and 200° C. The resulting thermoelectromotive force was measured by means of a potentiometer to which the copper wires *LL* led. The results are recorded in Table VIII., and plotted in the curve of Fig. 9.

Table VIII.

Thermoelectromotive Force of the Copper-Molybdenite Couple, "E" the Cold Junction being kept at Zero.

Temperature of Hot Junction.	E.M.F. in Millivolts.	Temperature of Hot Junction.	E.M.F. in Millivolts.	Temperature of Hot Junction.	E.M.F. in Millivolts.
10.1	− 7.5	59.2	−42.5	133.2	− 90.7
14.3	−10.7	67.4	−48.6	141.9	− 96.9
16.2	−11.5	70.8	−51.2	156.8	−106.8
18.7	−13.8	76.0	−54.1	166.9	−113.2
21.5	−16.0	80.8	−57.2	176.8	−119.0
24.1	−17.6	99.2	−68.4	179.0	−120.0
25.6	−18.5	109.3	−75.2	180.9	−121.5
33.1	−24.6	111.6	−77.2	188.5	−126.2
36.2	−25.9	116.3	−79.2	192.7	−128.7
41.9	−31.5	118.7	−83.2	195.0	−130.0
51.1	−36.7				

The negative sign before the E.M.F. in Table VIII. indicates that this specimen of molybdenite is thermoelectrically *negative* with respect to copper; that is to say, the current at the hot junction flows from the molybdenite to copper.

A slightly different form of mounting was employed for specimens *A*, *B*, *C* and *D*. These specimens, which were cut from two different large crystals of molybdenite, were each 1 cm. wide, 5 cm. long and from .5 to 1 mm. thick, and were mounted in corks. Each cork 4.5 cm. long, was split lengthwise, and one of the longitudinal half-corks was grooved out to contain the molybdenite. The two half-corks with the molybdenite between were put together again and cemented with plaster of Paris, so as to leave 2 or 3 mm. of molybdenite protruding from each end of the cork. These small areas were then copper-plated, and copper wires .2 mm. thick were soldered to the copper-plated areas, so as to form thermal junctions. The four corks containing the specimens *A*, *B*, *C* and *D* were inserted in round holes in two copper vessels for containing the temperature baths of oil, so that the junction at one end of each specimen should be in the hot bath, while the junction at the other end was in the cold bath. The cold bath was kept at 20°C.; the hot bath was given various temperatures between 20° and 100° C. The thermoelectromotive force of each couple was measured on a potentiometer. The results for *A*, *B*, *C* and *D* are contained in Table IX., and are plotted in Fig. 10. For comparison a part of the curve obtained for *E* is also plotted in Fig. 10.

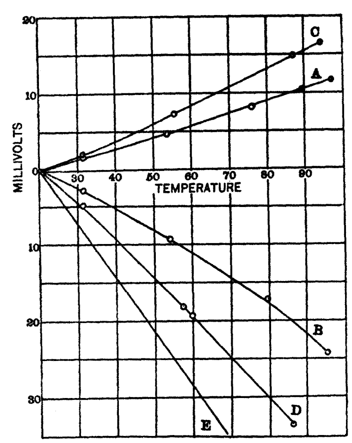

Fig. 10. Thermoelectromotive force of five copper-molybdenite couples, for various temperatures of hot junction. Temperature of cold junction 20° C.

Some of the specimens (*B*, *D* and *E*) are thermoelectrically negative with respect to copper, while the other specimens (*A* and *C*) are thermoelectrically positive with respect to copper. The thermoelectromotive force per degree differs largely with the different specimens, as may be seen by a reference to Table X., which con-

TABLE IX.

Molybdenite-Copper Junctions A, B, C, D. The Cold Junction was at 20° C. The Hot Junction was at Temperature T° C. The Thermoelectromotive Force V is in Millivolts.

Junction *A*.		Junction *B*.		Junction *C*.		Junction *D*.	
T	*V*	*T*	*V*	*T*	*V*	*T*	*V*
31.9	1.45	31.6	− 2.70	31.7	2.01	31.6	− 4.81
53.5	4.63	54.1	− 9.21	55.2	7.20	57.5	−17.9
76.6	8.21	80.0	−17.1			59.8	−19.4
89.4	10.4	87.4	−20.0	87.2	14.9	86.7	−33.7
97.1	11.5	95.3	−24.2	94.4	16.6		

tains the thermoelectromotive force per degree of the different specimens of molybdenite against copper, and against lead (obtained from the known value of the lead-copper junction). For comparison, Table X. also gives the thermoelectromotive power of some other remarkable thermoelectric elements.

TABLE X.

Substance.	Thermoelectromotive Force in Microvolts per Degree Centigrade, at 20° C.		Authority.
	Against Copper.	Against Lead.	
Molybdenite A.	110	113	Present experiment.
B.	−230	−227	" "
C.	175	178	" "
D.	−415	−413	" "
E.	−720	−717	" "
Silicon.		−400	Frances G. Wick.[1]
Bismuth.		− 89	Matthiessen.[2]
Antimony.		26	"
Tellurium.		502	"
Selenium.		807	"

The comparison shows that these specimens of molybdenite have very large thermoelectromotive force against copper or against lead. The specimens *D* and *E* were found to be at the extreme negative end of the thermoelectric series.

The great variability among the specimens studied may be due to an admixture of small quantities of some other substance with

[1] PHYS. REV., Vol. 25, p. 390.

[2] Everett, Units and Physical Constants.

the molybdenite, or it may be due to structural differences from point to point of the crystal. I have not yet investigated the question of the cause of the variability of the phenomenon. The differences in the specimens could not have arisen from the copper-plating or from the heat employed in soldering the junctions, because the specimens *A*, *B*, *C* and *D* were tested before the copper-plating and soldering were done, and by means of the preliminary test were classified as positive, negative, positive and negative respectively; which agrees with the determination after soldering.

The preliminary test was made by touching the specimens with two copper wires connected to a galvanometer, one of the wires being slightly warmer than the other. This preliminary test proved very interesting in that it shows that one may find all over many of the pieces cut from a crystal of molybdenite points where the substance is thermoelectrically positive and other points where it is thermoelectrically negative. These positive and negative points sometimes lie so near together that with a fine-pointed exploring electrode connected to a galvanometer and warmed by heat conducted from the hand one may find the deflections of the galvanometer reversed from large positive values to large negative values on making the slightest possible motion of the pointer over the crystal.

Explorations of this kind failed to show any definite orientation of the thermoelectric quality with respect to the crystallographic axes.

The existence of small thermoelectrically positive and negative patches in a piece of the molybdenite may indicate that the thermoelectromotive force measured by attaching wires to the specimen is too low on account of the inclusion under the electrodes of both positive and negative areas which would partially neutralize the thermoelectric action against another electrode. It may be, therefore, that the contact electrode as it is employed in the use of the molybdenite as a rectifier would be subjected to much larger thermoelectromotive forces than those revealed in the soldered connection experiments.

It may be said in passing that the specimens *D* and *E*, with the soldered connections, still showed the phenomenon of rectification when used with alternating currents, even when the two junctions of the copper with the molybdenite were in oil-baths at the same temperature as the room and the oil in the baths was vigorously stirred with motor-driven stirrers. The rectification in this case was, however, very imperfect.

Temperature Coefficient of Resistance. — Another interesting thermal property of the molybdenite is its temperature coefficient of resistance. A preliminary report on this coefficient is here given. Two specimens of the molybdenite were made into the form of resistance thermometers, by depositing heavy copper-plated areas near the two ends of thin pieces of the molybdenite and soldering thin copper strips to the copper plate. For insulation a thin strip of mica was placed over the molybdenite, and one of the copper leads was bent back over the mica so that both leads ran away parallel with the mica insulation between. The whole conductor was then placed between two mica strips and inserted in a flattened brass tube. The tube was then mashed tight together so as to securely clamp the molybdenite and its leads. The end of the tube adjacent to the molybdenite was soldered up. The leads were brought out at the other end of the tube and connected to binding posts insulated by a hard rubber head from the tube.

The two molybdenite resistances thus mounted are called No. 50 and No. 51. The dimensions of the molybdenite used in No. 50 were not recorded. The molybdenite in No. 51 was .65 cm. wide by .7 cm. long; the thickness was about .3 mm.

The resistances of these two conductors were measured at various temperatures with the aid of a Wheatstone bridge. They showed no evidence of rectification. In making the measurements it was necessary to keep the current small so as to avoid electrical heating of the conductors. With successive heatings and coolings the resistance of the molybdenite showed small progressive changes, which, however, after some months, almost disappeared. When the resistance of the two specimens of molybdenite had settled down to a practically steady condition, the values plotted in Fig. 11 were obtained. The curves marked "50" and "51" give the resistance of No. 50 and No. 51 respectively. The ordinates for these curves are at the left margin of the diagram, and are in ohms. The curves "*C* 50" and "*C* 51" are for the reciprocals of the resistance of No. 50 and No. 51 respectively. The ordinates for these curves are at the right hand margin of the diagram.

Each of the specimens has a large negative temperature coefficient of resistance. With No. 50, for example, the resistance at 93.1° C., is 229 ohms; at 0° C., the resistance is 561 ohms; at – 76°, the resistance is 3,051 ohms; and at the temperature of liquid air, the

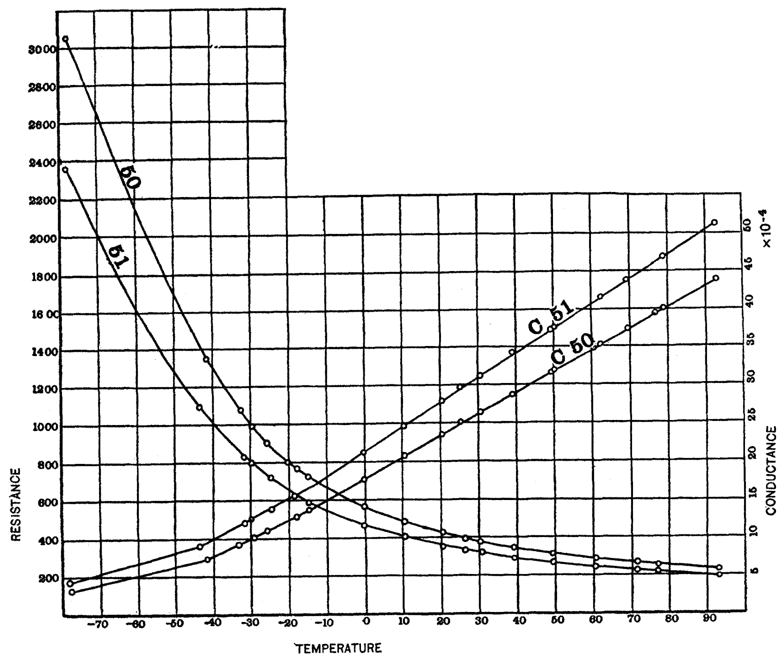

Fig. 11. Effect of temperature on electrical resistance of molybdenite.

resistance of this specimen was found to be over 6,000,000 ohms. This last value is not plotted on the curves.

It is interesting to note that *between – 15° and 93° the temperature-conductance curve of each of the specimens is a straight line.*

At 0° C. the resistance of each of the specimens decreases about 1.53 per cent. per degree centigrade increase of temperature. At 20° the decrease of resistance per degree increase of temperature is 1.19 per cent.

A previous determination of the resistance of molybdenite has been made by Otto Reichenheim.[1] He did not solder on his con-

[1] Otto Reichenheim, Inaugural Dissertation, Freiburg, 1906.

nections but led the current into the specimen through contact electrodes and found that the resistance depended on the contact pressure. His data are, therefore, not comparable with mine, but I find that one of his specimens,[1] measured parallel to the direction of cleavage, gives the conductance a linear function of the temperature between 19.5° and 92.5° C. with a slope not very different from that obtained in the present experiments.

The large thermoeletromotive force of the molybdenite against the common metals, together with its large negative temperature coefficient of resistance, lends plausibility to the hypothesis that the rectification is due to thermoelectricity. For if we pass an electric current through the rectifier and the current begins to make its way through a small area at the contact, this small area is heated and decreases in resistance so that the greater part of the current flows through this particular small area, heating it still more, while the portions of the contact through which the current has not started remain cool and continue to offer a high resistance. The effect of this action is to confine the heating to an extremely small area, which is the condition necessary for the extremely rapid and efficient action of the rectifier. That there is, however, strong evidence against this explanation of the phenomenon is, I think, made clear in the succeeding experiments.

Experimental Facts Adverse to the Thermoelectric Explanation of the Phenomenon of Rectification.

The Thermoelectric Effect Opposite to the Rectification. — A number of experiments with different specimens of molybdenite were made, in which the rectification and the thermoelectric effect could be simultaneously studied. A diagram of the arrangement of apparatus is given in Fig. 12. The specimen of molybdenite is shown at *M* and was held down upon a wooden base by a spring clip. One end of each specimen, which were easily interchangeable in the apparatus, was electroplated with copper at *S*. To this copperplated area a copper lead was soldered. A copper rod *C*, supported as in Fig. 3, was brought into contact with the part of the molybdenite distant from the soldered junction. The molybdenite and the contact

[1] Described as *Stab II.*, p. 27 of the Dissertation.

were put in an electric circuit containing a microammeter or galvanometer at *A* and a source of variable alternating potential at *V*. The alternating potential *V* could be applied or omitted by closing or opening the switch at *T*. A small heating coil was wound on the rod *C*, and another similar heating coil *E* was wound on a second copper rod, placed immediately below the contact of *C* with *M*.

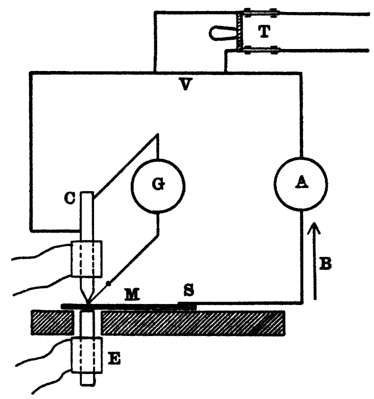

Fig. 12. Apparatus for comparison of rectified current with thermal current.

An auxiliary thermal junction, formed by a small constantan wire attached to the lower end of the copper rod *C* was connected to a second galvanometer shown at *G*, for use in a later experiment.

The copper rods *C* or *D* could be heated by the surrounding coils, and the thermal current in the circuit through the molybdenite or the circuit through the constantan could be read on the galvanometers *A* or *G*. Also the rectified current obtained by applying the alternating voltage *V* could be read on the galvonometer *A*. When the thermal current or the rectified current through *A* is in the direction of the arrow *B* the molybdenite, following the usage in thermoelectricity, is said to be *positive*. When the current in *A* is in the direction opposite to the arrow *B*, the molybdenite is said to be *negative*.

The results obtained with a number of specimens of molybdenite when heat was applied *above*, and when heat was applied *below* and when the *alternating voltage* was applied are contained in Table XI.

TABLE XI.

Sign of Molybdenite, when Heated Above or Below and when Subjected to Alternating Voltage.

Specimen No.	Heated Above.	Heated Below.	Under Alt. Voltage.
75	+	—	—
81	+	—	—
Turned over.	+	—	—
93	—	+	+
Another point.	—	—	+
"	—	—	+
Turned over.	—	—	+
78	+	+	+
Another point.	+	—	—
"	+	+	—
94	—	—	+
Another point.	—	+	+
"	—	+	+

From this table it appears that the thermoelectric voltage *when the junction is heated by heat conducted from above*, in twelve out of the thirteen cases tried, is opposite to the direct voltage obtained when an alternating current is passed through the junction. *When the heat is conducted to the junction from below, through the molybdenite*, the thermoelectromotive force in four cases is opposite to the rectified voltage and in nine cases is in the same direction as the rectified voltage. In only one case, one point of no. 78, is the rectified voltage in the same direction as the thermal voltage both when the junction is heated from above and when it is heated from below.

In all of these cases the heat was applied in the neighborhood of the same junction and there was no opportunity for heat to get to the other junction by conduction, on account of the great distance of the other junction from the source of heat. To make this the more certain this distant junction was in some cases submerged in an oil-bath.

So far as I have been able to learn, this phenomenon of the reversal of the thermoelectromotive force at a junction, conditioned on whether the heat is conducted to the junction through one element of the junction or the other element of the junction is novel. It may be explained by the assumption of another thermal junction of opposite sign in the molybdenite itself below and in the immediate neighborhood of the copper-molybdenite junction. This assumption is plausible because it has been shown above that the molybdenite with which these experiments were performed is thermoelectrically an extremely heterogeneous substance. On the other hand, the phenomenon may also be explained on the theory that the direction of the thermoelectromotive force is determined by the direction of the flow of heat.

Whatever the explanation of the dependence of the sign of the thermoelectromotive force on the manner of applying heat, it is seen that the thermoelectromotive force is usually opposite in sign [1] to the electromotive force produced by sending an alternating current through the junction.

By applying the heat from above and at the same time applying the alternating voltage one can make the thermal current and the rectified current neutralize each other. The opposition of the sign of the rectified current and the thermal current renders the thermoelectric explanation of the phenomenon of rectification highly improbable.

Effort to Detect Heating of the Contact of the Rectifier. — With the aid of the auxiliary thermal junction of copper-constantan placed at the contact of the copper with the molybdenite, as shown in Fig. 12, an effort was made to detect heating of the copper-molybdenite junction by the alternating current which was being rectified. When the rectified current was 118 microamperes, the heating shown by the copper-constantan junction did not exceed .01° C. When on the other hand, as a control experiment, heat was applied to the copper-molybdenite junction from below so as to be conducted through the molybdenite and through the copper-molybdenite junction to the copper-constantan junction, the heating shown by the auxiliary copper-constantan junction was 11.4° C., while the thermal current from the copper-molybdenite junction was only .2 micro-

[1] In a series of experiments with silicon-steel, carbon-steel and tellurium-aluminum, L. W. Austin has found that the rectified current generally flows in opposite direction to that produced by heating the junction. In his experiments (Bulletin of the Bureau of Standards, Vol. 5, No. 1, August, 1908) the heat was applied by a soldering iron brought into contact with the low resistance metal, and therefore corresponds to heat conducted from *above* in these experiments.

ampere. In both the case of the rectified current and the case of the application of heat from below the heat had to be conducted from the point of rectification to the auxiliary junction. Therefore, with a rise of temperature of the auxiliary junction 1,100 times as great as the rise shown during the rectification, the thermal current in the copper-molybdenite circuit was 1/500 of the rectified current; that is to say the rectified current, for a rise of temperature of 1/100 of a degree of the auxiliary junction (being approximately a linear function of the temperature) was less than 1/500,000 of the rectified current from an alternating current producing the same rise of temperature.

From this experiment, also, it seems to the writer that the hypothesis that the action of the rectifier takes place through the intermediation of thermoelectricity is improbable.

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Experiments are still in progress.

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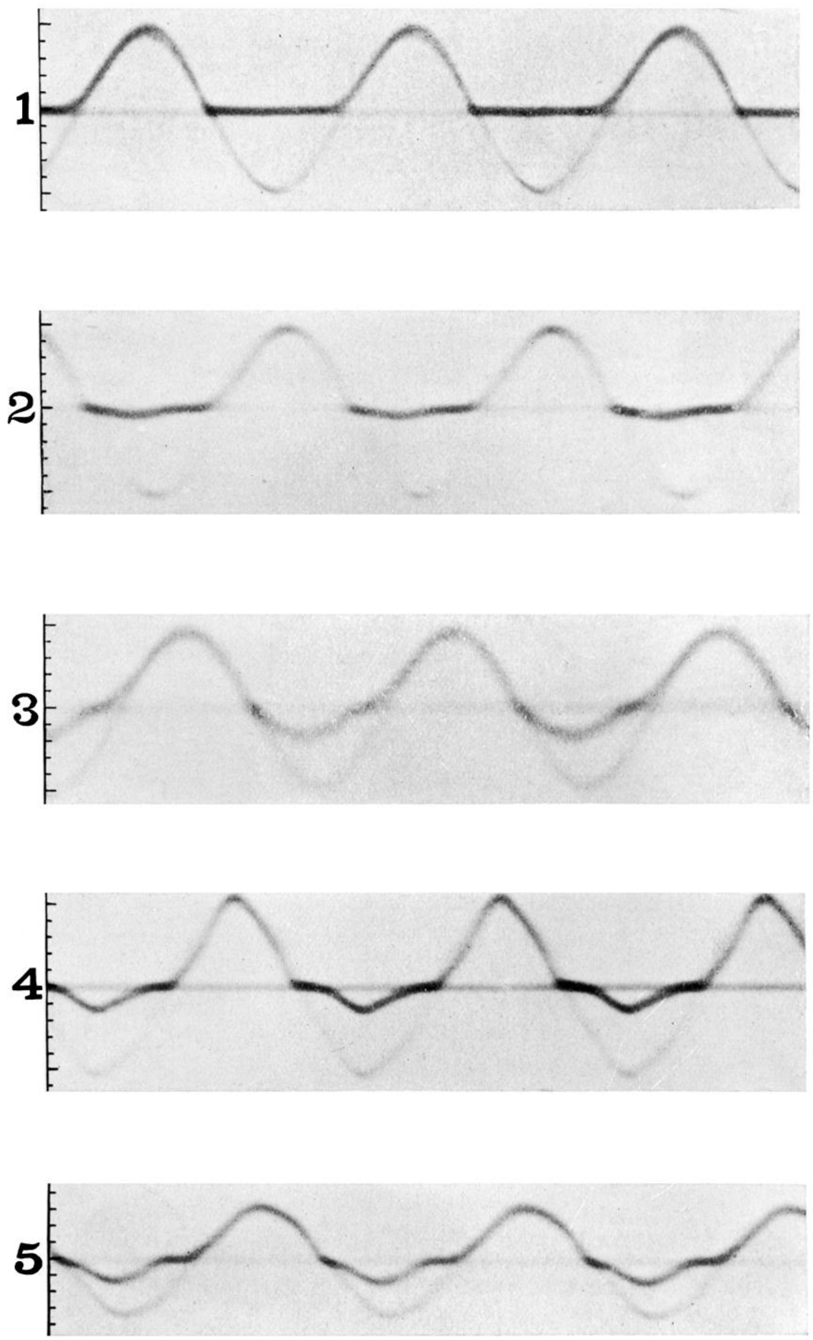

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Crystal Rectifiers