ON CONTACT RECTIFICATION BY METALLIC GERMANIUM

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In a recent note[1] I have called attention to the significance of the phenomena of contact rectification in their bearing upon theories of thermo-electric power and have suggested that because of the relative simplicity of the conditions the study of these phenomena in the case of the elements is especially desirable. Experiments with selenium contacts were described in the September number of these PROCEEDINGS. The search for elements showing rectifying properties has been continued and in the present communication I shall describe the measurements made thus far with metallic germanium.

The high thermo-electric power of germanium;[2] the fact that in Mendeleef's series Ge falls in the same group as Si, which is one of the best rectifying materials known; and the further fact that Ge and Si have the same crystal form, all lead us to expect that germanium contacts will show rectifying properties. This expectation has been confirmed by tests made with a specimen of this rare metal weighing twelve grams which was loaned to me by Professor L. M. Dennis. The rectifying action with Ge is less marked than with many other materials, but the contacts are quite stable and the behavior at different points on the surface is more uniform than in the case of most crystal rectifiers. Except in certain unusual cases mentioned below the resistance of a Ge contact is least for a current flowing into the Ge from the contact point. This is also the direction of the rectified current when an alternating e.m.f. is used. It will be noticed that the direction of rectification is opposite to that found for Se.

In experiments on rectifying contacts it is, of course, necessary to make electrical connection with the sensitive material at two points. In the case of crystal detectors it is customary to mount the crystal in such a way as to make one of the contacts of relatively large area, the tacit assumption being that if the area of contact is sufficiently great the current density will be so small that any rectifying action at this large contact will be negligible. A common procedure is to mount the specimen in melted solder or Wood's metal. With most crystals the matter is simplified by the fact that the rectifying or detecting action is confined to certain sensitive spots, while the greater part of the surface is relatively inactive. With Ge, however, practically all parts of the surface seems to be active, so that it is particularly important that the area of contact with the support should be large. Since it did not seem desirable to use solder or Wood's metal the specimen was clamped between two iron jaws, the latter being covered with several layers of tin foil, or of iron or copper gauze to give a yielding surface and a larger contact area. Until this procedure was adopted erratic results were obtained which are probably to be ascribed to imperfect connection between the specimen and its support.

The resistance of the contacts used was sufficiently low so that the fall of potential through the measuring instrument was appreciable. To simplify the procedure a Weston voltmeter placed in series with the contact was used as an ammeter, with a reversing key so located as to reverse the current through the contact but not through the voltmeter. The reading of this instrument gave at once the correction to be applied to the applied e.m.f. (as measured by a second voltmeter) while the reading divided by the resistance of the instrument gave the current through the contact. The current sensitivity was adjusted to any desired value by means of shunts.

The contacts to be used were made by pressing the rounded end (radius of curvature about 0.5 mm.) of various metal rods against the Ge surface by means of a spring. To avoid disturbances due to vibration the whole apparatus was mounted on a block of wood that was supported by stretched rubber bands. In the case of all the results here recorded contact was made with a part of the Ge surface that had been polished with emery.

Characteristic curves for several typical contacts are shown in figure 1. These were all taken with the Ge surface freshly polished. With the applied e.m.f. less than 3 volts the contacts were stable and the curves could be reproduced. It will be noticed that the asymmetry of the characteristics is not nearly so marked as in the case of Se[1] or of many of the crystals used in crystal detectors.

Contacts at different points on the Ge surface did not give identical characteristics. But the differences were usually not great; and the change resulting from the use of a different metal for the contact point often seemed to be greater than that due to a change in the position of the contact. The curves plotted in figure 1 have been selected as representing in each case the average behavior of contacts with the metal named. The characteristics for Pt and Cu contacts fall so close to that for Fe that they have not been plotted. Al and Zn also gave nearly identical characteristics. In fact all five of these metals were so nearly alike in their behavior that their relative position on the plot is probably not significant.

There can scarcely be any doubt, however, that a real difference exists between the behavior of Bi and Sb. The contacts of these two metals for which characteristics are shown in figure 1 differed greatly in resistance. But although the bismuth contacts almost always had the higher resistance, I do not regard this difference as of great significance, since the resistance of a contact depends so greatly upon the pressure and the area. The bismuth contacts varied in resistance more than in the case of any of the other metals studied and some bismuth contacts had resistances as small as that of the antimony contacts. The most significant difference between the two metals was in the *form* of the characteristic. The antimony characteristic in figure 1, which is typical of all those observed, shows a marked difference between the positive and negative branches, while all of the bismuth characteristics that I have observed have their positive and negative branches nearly alike. In other words antimony gives better rectifying contacts than bismuth.

The anomalous behavior of Bi contacts was more marked when the surface of the Ge was slightly tarnished, as was always the case after heating. Contacts with a tarnished surface always showed a much higher resistance than contacts with a freshly cleaned surface. With

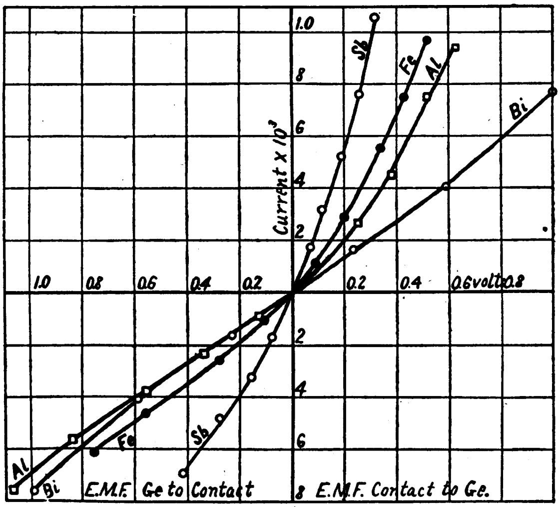

FIGURE 1
Current-voltage characteristics for contacts between *Ge* and *Bi, Al, Fe* and *Sb.*

Bi the two branches of the characteristic were nearly alike, although the current through the contact from Bi to Ge was usually greater than the current for the same e.m.f. reversed. But contacts were frequently found for which the current was greater in the direction Ge to Bi. With an alternating e.m.f., Bi contacts usually gave normal rectification, i.e., the rectified current flowed from Bi to Ge. But many contacts were found which gave no rectification, while a few gave rectification in the opposite sense. In the case of such contacts the direction of the current developed by warming the Bi contact was also reversed, being, in each case, opposite to the rectified current. Some contacts were found which rectified normally for light pressure but in which the rectified current was reversed when the pressure was increased. In these contacts the direction of the thermo-electric effect was normal and was not reversed by pressure.

Selenium contacts sometimes show a similar reversal of rectification. The development of a thermal e.m.f. because of heating at the contact offers a plausible explanation of such reversals. But the magnitude of the reversed effect raises some doubt as to the correctness of this explanation. Further study of these anomalous effects is much to be desired but is made difficult by the instability of the contacts that show such effects.

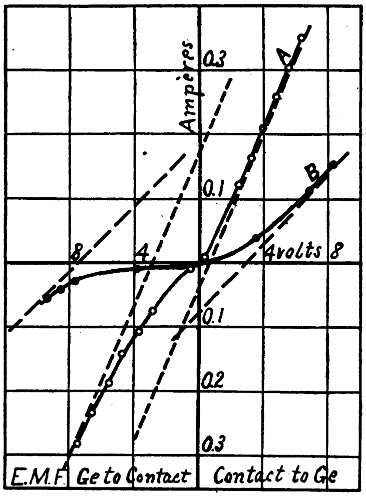

FIGURE 2

A. Contact between *Ge* and *Sb*. B. Contact between *Ge* and steel.

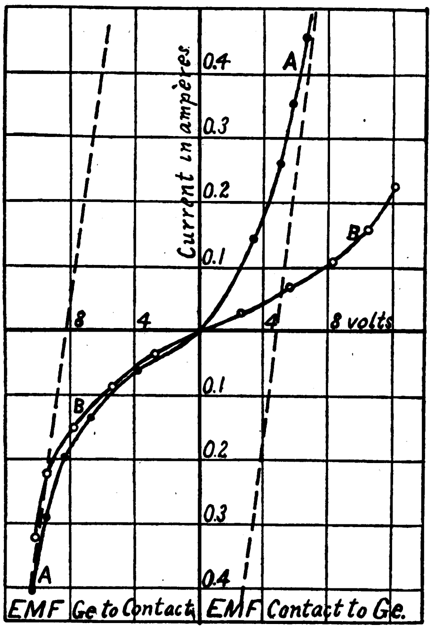

FIGURE 3

Contacts between polished *Ge* and different corners of a broken piece of *Ge*.

It seems probable that the relatively small rectifying action of bismuth contacts and the occasional reversal of the direction of the rectified current and of the thermo-electric effect are connected with the fact that Bi lies much closer to Ge in the thermo-electric series than any of the other metals used. The results thus indicate that the connection between thermo-electric power and rectifying action is extremely close.

With Ge contacts, as in the case of Se contacts, each branch of the characteristic approaches a linear asymptote for large values of the applied e.m.f. In the case of the negative branch this is often not at all obvious, for the contacts are even more likely to break down at high e.m.f's. than are Se contacts and it is rarely possible to follow the negative branch far enough to make sure that it approaches an asymptote. Curves for two unusually stable contacts are shown in figure 2. It will be noticed that the two asymptotes are quite accurately parallel, as was found to be the case with Se contacts. Curve A, of figure 3 also shows parallel asymptotes.

The two characteristics shown in figure 3 are for contacts between polished Ge and two different corners of a broken piece of the same metal. While curve A shows as great a difference between its two branches as either of the curves in figure 1, curve B is nearly symmetrical. The fact that the characteristic is curved indicates, however, that for either direction of current there is a marked deviation from Ohm's law. The non-linear character of the characteristics is probably in all cases more significant than the fact that the two branches are usually unlike.

Bidwell[2] has found that the thermo-electric power of Ge against Pt reverses sign at about 300°C. Since the direction of the rectified current in contact detectors is usually opposite to the current produced by heating it seemed of interest to study the behavior of Ge contacts at temperatures above the reversal point, the expectation being that the rectification would also be reversed. The specimen was therefore placed in a furnace and characteristics were determined at different temperatures as the furnace was heated and then allowed to cool. A copper-advance thermo-element was used in measuring the temperature; since no special precautions were taken to secure high accuracy errors of as much as 10°C. are not unlikely. A series of characteristics determined in this way is shown in figure 4.

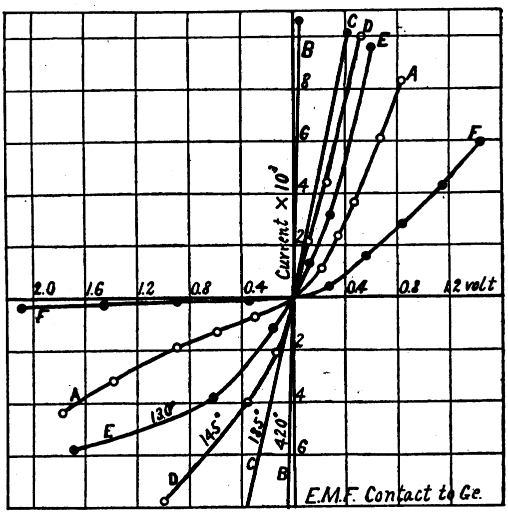

FIGURE 4

Characteristics for a *Ge-Fe* contract at different temperatures. A before heating. F after cooling.

It will be noticed that the resistance of the contact is greatly reduced at high temperatures. At 400°C. the resistance, which was of the order 200 ohms at ordinary temperatures, had fallen to about 5 ohms. For temperatures up to 200°C. the resistance was least for the direction contact to Ge—i.e., when electrons passed out of the Ge at the contact. But the asymmetry of the characteristic became less as the temperature was raised. At 185°C. some difference was still observable, the resistance being 39 ohms in one direction and 45 ohms in the other. But at 220°C. when the resistance had fallen to 5 ohms, and for higher temperatures, no difference between the two directions could be detected. In the hope that rectifying action might be detected by a more sensitive measuring instrument the voltmeter was replaced by a galvanometer and an alternating e.m.f. of about 1 volt was used. At temperatures above 200°C., the galvanometer deflections were small and erratic; if any rectification occurred it was so small as to be entirely masked by the uncertainties of measurement. But upon cooling below 200°C., the rectifying action increased with great rapidity; a change of 10° in the temperature of the contact caused the galvanometer deflection to increase from 1 division or less to more than 150.

The resistance of the contact after cooling was always considerably greater, and the asymmetry of the characteristic more marked, than before heating. A difference between the original and final characteristic such as is shown in figure 4 in curves A and F was found in all cases. There can be no doubt that this change was due to the formation of a film, presumably of the oxide, on the Ge. The presence of such a film was indicated by the fact that the polished Ge surface usually showed a slightly tarnished appearance after heating. Although too thin to show interference colors this film was of extremely high resistance. When the contact point was pressed only lightly against such a film-covered surface—e.g., by its own weight—the resistance was often as great as ten megohms. Upon using more pressure or by rubbing the contact point back and forth the resistance was greatly reduced, and by repolishing the Ge surface the conditions before heating were restored. The rapid diminution in the resistance of the contact as the temperature is raised is what would be expected if the film consisted of an oxide of germanium. The results therefore support the view[3] that the presence of a high resistance film is an important and possibly an essential factor in determining the behavior of contact rectifiers.

[1] Merritt, E. *Proc. Nat. Acad. Sci.*, **11**, 572, 1925.

[2] Bidwell, C. C. *Physic Rev.*, **19**, 447, 1922.

[3] Indications that a film separates the two surfaces in a rectifying contact have been found by numerous observers. Perhaps the most direct evidence of the importance of such a film is to be found in the papers of Goddard and Flowers here referred to: Goddard, R. H., *Physic Rev.*, **34**, p. 423, 1912, and Flowers, A. E., *Ibid.*, **29**, 445, 1909.