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1914 Proc. Phys. Soc. London 27 70

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V.—*Note on the Conduction of Electricity at Point Contacts.*

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THE experiments here described were undertaken with a view to clearing up, if possible, one or two questions which suggested themselves during the examination of a number of minerals for "unilateral conductivity."

The subject has already given rise to a considerable literature, but as this has recently been very fully summarised in the "Proceedings" of this Society* references will here be given only to such Papers as bear immediately on the points under discussion.

The present Paper relates purely to the conductivity of "point contacts" when a steady, or slowly varying, E.M.F. is applied, and no attempt will be made to deal with the effect of high-frequency oscillations.

According to the usual practice the results are presented as "characteristic," or volt-ampere curves for the respective contacts. To obtain these curves it has been usual to take readings on amper- and volt-meters, and from them to plot the characteristic on squared paper. Since, however, for the present purpose a large number of curves were required, a form of mirror galvanometer was used by which the characteristic was directly plotted as the path of the spot of light on the screen. The arrangement was of the ordinary rocking mirror type, and need not therefore be described in detail. One coil (of low resistance) was connected as amperemeter, the other as voltmeter. Thus the co-ordinates of the deflection were those of the characteristic curve.

An arrangement of this type is naturally not capable of the same accuracy as dial instruments, but, on the other hand, the curves obtained can be followed continuously, and any sudden change in the conductivity of the crystal contact is immediately indicated by a violent displacement of the spot of light. The time taken to plot one curve is about 15 seconds.

The first part of this note consists of a description of the behaviour of a typical point contact (zincite and tellurium) in terms of which the results for the other pairs can be described.

* P. R. Coursey, "Proc." Lond. Phys. Soc., Feb., 1914.

The second half of the paper deals with the results of a systematic examination of the forty-five contacts which are possible between the ten substances employed. The question to be answered may be put briefly thus: If the behaviour of the contacts between substances A and B and A and C is known, can any rule be found for predicting the behaviour of the third combination B and C? A partial solution of the problem has been attempted by the arrangement of the ten substances in a series.

1. *The Behaviour of a Typical Point Contact (Zincite-Tellurium).*

The use of natural cleavage surfaces is not advisable, as these are frequently coated with a film of altered material. A polished surface of zincite was therefore employed, the fragment being imbedded in fusible metal, and the tellurium was in the form of a polished globule fused on the end of a pin. The pin was inserted in a lever which pressed it down on the zincite surface, different weights being hung on the end of the lever. For other substances which required lighter contacts the lever was replaced by a very light spring. The weights are given in grams at the contact.

The diagram (Fig. 1) shows the types of curve obtained. Under light weights the contact tellurium-zincite was relatively a non-conductor for voltages up to about 5 volts. As the weight increased (100 to 500 grams) the current passing with zincite negative became appreciable, increasing more rapidly than that with zincite positive. Thus the well-known unilateral curve was obtained. This is marked AA' in the figure, and will be referred to as type A throughout this note.

With still further increase in weight the conductivity improved, but experiments in this direction were terminated by the breaking either of the tellurium globule or of the zincite.

Contacts such as galena-tellurium (Fig. 3), which give the A curve under a weight of 1 gram or less, become good conductors under increased weight (10 grams) and their characteristic then resembles that marked BB'; it is not linear, but the asymmetry is greatly reduced. It seems fair to assume that the same effect would be observed with zincite if the material were strong enough to stand the weight required.

An effort was now made to find the limits to which the A curve could be pursued on raising the voltage. It was found that when a certain point was reached (from 1 to 6 volts

according to the contact) the curve terminated in a sudden breakdown of resistance (AB, Fig. 1), and on lowering the voltage the tracing point returned along a much steeper curve, which passed through the origin at an angle corresponding with a resistance of 500 ohms or less, and could be pursued to some distance beyond it (BB'). The voltage at which this breakdown occurred was on an average higher with zincite positive than when it was negative. This curve is marked BB, and will be termed type B. It persists, at any rate for some hours, in most contacts, and it seems clearly due to a definite change of condition due to the breakdown.

FIG. 1.—THE DIAGRAM REPRESENTS THE TWO TYPES OF CURVE COMMONLY ENCOUNTERED.

The curve marked A A' is the common unilateral curve, B B' is the result of applying excessive voltage, and these are respectively termed types A and B throughout the Paper.

The dotted lines indicate the movement of the spot of light on breakdown and on recovery. The breakdown is sudden, the recovery is relatively slow.

This curve BB in its turn was now examined under increasing voltage. With zincite negative it underwent further alterations, becoming more and more linear in form, with decreasing resistance. If it had been caused by a breakdown of the A curve with zincite positive it generally remained permanent, but if the original breakdown had occurred with zincite negative, a very remarkable recovery could be obtained in the following manner.

If the voltage was raised to a certain point (generally from 1 to 4 volts) with zincite positive and the contact was then allowed to stand, the current could very frequently be seen to diminish more or less rapidly, so that the spot of light returned toward the A curve (point B', Fig. 1). In favourable circumstances the A curve was actually regained and could then be repeated in its original form. If the recovery was partial the resulting curve was of an intermediate character throughout its course, as indicated by the short curves in the figure.

The following table of readings on an amperemeter will give some idea of the progress of such recoveries.

*Contact Copper-zincite, standing after alteration with Zincite Positive. •
(E.M.F., approx. 2.5 volts.)*

Time.	Current.		
	Expt. a.	b.	c.
0	...	...	...
10	215	186	210
20	200	180	202
30	198	179	197
40	194	178	189
50	191	177	184
60	189	173	182
70	184	170	...
80	180	168	...
90	184	168	172
100	182	170	172
Seconds.		Micro-amperes.	

2. Comparison of the Results given by Polished Contacts of Ten Substances taken in Pairs.

Curves of the type described above were obtained in every case,* though not with the same facility, for in some cases the contacts required were extremely light.

The great similarity of the unilateral curves is well known to all who have had occasion to plot curves for various contacts, it is illustrated in the two curves reproduced in Figs. 2 and 3. Since the curves, especially the A type, are strongly unilateral in character, it is possible, for the purposes of classification, to describe the effect by giving the signs + and — respectively

* It will be observed that all these curves are convex toward the axis along which the voltage is measured. The theory recently discussed by Eccles ("Proc." Lond. Phys. Soc., June, 1913) requires for many cases curves which are concave. No such curves were observed in any of the contacts here described.

FIG. 2.—CURVE OF TYPE A FOR THE CONTACT OF BROOKITE WITH GALENA.

The B type does not seem to be obtainable by pressure, as neither brookite nor zincite will withstand the increase of weight which might be expected to yield it. The weight for the curve shown is already 350 grams

FIG. 3.—CURVE OF TYPE A FOR THE CONTACT OF GALENA WITH TELLURIUM.

The similarity of this with Fig. 2 can leave little doubt that the same effect is being observed, although the weight is here of the order of 1 gram. The B type is readily obtained on increasing the weight, or by application of excessive voltage.

The straight line illustrates a direct method of ascertaining the scale; it is the "characteristic" of a 500-ohm voltmeter. The scale of the other figures is approximately that shown here.

None of these curves show irregularities greater than would be expected from the errors of tracing, except where definite breakdown has occurred.

to the two substances in contact; thus, quite arbitrarily, zincite might be called negative to tellurium, tellurium positive to zincite.

When this has been done a table can be prepared, such as that below, in which the sign given in each square describes the curves given by the corresponding mineral in the top line when in contact with the mineral named in the column on the left.

In this table, as first drawn, the distribution of the negative signs was at first sight quite arbitrary, but by changing the order of the minerals named it was found that all the negative signs could be brought below the diagonal as in the following table:—

	Zincite.	Brookite.	Molybdenite.	Chromium.	Galena.	Iserite.	Chalcocite.	Copper.	Chalcopyrite.	Tellurium.
Zincite.....										
Brookite	—									
Molybdenite	—	—								
Chromium	—	*	—							
Galena.....	—	—	—	—						
Iserite	—	—	—	—	—					
Chalcocite.....	—	—	—	—	—	—				
Copper	—	—	—	—	—	—	—			
Chalcopyrite.....	—	—	—	—	—	—	—	—		
Tellurium	—	—	—	—	—	—	—	—	—	

From this it is at once evident that the 45 results can be expressed by means of a series of the ten substances, such that the higher member behaves toward the lower as zincite to tellurium.

It should be said that the substances used were selected as typical and uniform in composition. It is most probable that another set of even the same minerals, taken from other localities, would yield a somewhat different series. Further,

* Decisive results were not obtained for this contact.

the effect may be dependent on the orientation of the planes in contact. For these reasons no attempt has been made to give either the locality or the composition of the minerals used; they merely represent certain samples of material.

3. *Conclusions.*

Comparison of these results throws some light on the nature of the effect represented in the unilateral curves.

In the first place (to choose an example which is for the most part established by results published by previous observers) the characteristics given by all the substances here examined, when in contact with zincite under a weight of 1,000 grams, were almost identical in shape. It therefore seems fair to assume that the unilateral effect here obtained is a property of the zincite, and is independent of the physical constants of the other substance used.

The same reasoning may be applied to the contacts of, say, galena with substances standing below it in the table.

Now it is evident that the same substance (*e.g.*, galena) may play one of two distinct parts in a point contact. Toward substances higher in the series, such as zincite, it is in the position which has been called positive. Toward substances below it, such as tellurium, it is negative. What, then, is the condition which determines its behaviour? The answer to this question seems to lie in the fact that, as far as the very rough measurements go, the weight† required to obtain the unilateral curve diminishes progressively along the series, from about 1,000 grams for the zincite contacts to extremely light pressure for the contact of chalcopyrite with tellurium.

This being the case, it is evident that the substances below zincite, when under weights of 1,000 grams, will act alike as good conductors, the resistance of the contacts with zincite being only that of the zincite surface layer in every case.

† It will be noted that weights, not pressures, are here given. In these contacts the softer substance is spread over a certain area on the harder surface. Thus for a given weight the area increases as the substance is softer, but the pressure is correspondingly diminished. If the conductivity of the contact depends jointly on the area and pressure, it will then be roughly independent of the hardness of the substances in contact. The fact that the curves were alike for contacts of zincite with chromium and zincite with molybdenite under 1,000 grams, the area of the latter being about 1 square millimetre, renders it clear that some such assumption is necessary, though the statement that the conductivity is directly proportional to the pressure can only be taken as a rough approximation to the true relationship.

Under lighter weight galena, say, in its turn possesses a high surface resistance which yields a unilateral curve in contact with tellurium.

Many experiments will suggest themselves by which these conclusions could be tested, but it is impossible to discuss them within the limits of this note, of which the chief aim is to present a plea for the examination of the effect on strictly experimental lines. The serial arrangement suggested is advanced as a tentative solution to the question put forward on p. 76. Whether it survives further examination or not it may perhaps serve as a basis for the discussion of the large number of "rectifying" contacts now known.

ABSTRACT.

The Paper deals with the "characteristic" or volt-ampere curves given by various "Point" contacts when the voltage is slowly varied. The curves were plotted by means of a form of rocking mirror galvanometer, which projected the characteristic as the path of a spot of light on the screen, the co-ordinates being respectively proportional to the current and voltage.

The first part describes the behaviour of a typical contact, zincite-tellurium. The well-known unilateral curve is terminated by a sudden breakdown of resistance, after which the contact has a more symmetrical characteristic of lower resistance at the origin. By allowing the contact to stand under a certain voltage with zincite positive it may frequently be restored to the condition of high resistance in which it again yields the unilateral curve.

The second part describes the results obtained on examining the characteristics for the forty-five contacts possible between 10 chosen substances. The conclusion is reached that the results in all cases are similar to those given by zincite-tellurium. No line could be drawn separating "metallic" contacts from those in which one or both conductors were "crystals."

The results obtained are expressed in terms of a series in which the higher member behaves towards the lower as zincite to tellurium.

Series : Zincite, brookite, molybdenite, chromium, galena, inserite, chalcocite, copper, chalcopyrite, tellurium.

In the third part the conclusion is drawn that in a contact yielding the unilateral (high resistance) curve, the resistance lies within the surface of the member standing higher in the series. Rough measurements showed that the weight required in these contacts diminished from about 1,000 grams for zincite to very light contact for the substances lying near tellurium, and it is suggested that this gradation in weight determines the relative positions arrived at for the respective substances.

DISCUSSION.

Mr. DUDDELL thought the author's method of obtaining continuous curves much more satisfactory than the ordinary method, as it gave less chance of the point contacts altering during the experiment, and, further,

the arrangement of the minerals in the table he gave appeared to have some correspondence with their order of sensibility when used as wireless detectors.

Mr. D. OWEN attributed much of the success of the author's experiments to the attention paid to the preparation of polished surfaces of contact. It would be useful if the author would specify the curvatures employed. The two types of characteristic might be accounted for by the greater or less extent to which the electrostatic attraction between the contacts extend, type B occurring when that effect was large. Calculation proved that, assuming a P.D. of only one volt, and a distance apart of 10^{-7} cm. (ten times the molecular distance), the electrostatic pull was of the order of 1,000 gm. wt./mm². It might in some cases be much greater than this.

Mr. P. R. COURSEY thought the main point of interest in the Paper was the table in which the substances were arranged in the order of the effects obtained with them. It would be of considerable use if some connection could be found between the arrangement of the substances in this table and some of their chemical or physical properties, as it should then be possible to extend the present limits of the table to include new substances, and in this way, it may be, to obtain perhaps even more sensitive wireless detectors than were at present available.

The visual method of taking the characteristic was of value for rapid investigation of the behaviour of any particular contact, and in this connection he would ask the author whether in his experiments employing this method he obtained any evidence of a "hysteresis" effect in the contact. A number of experimenters had stated that such an effect does exist, and it should be an easy matter with this arrangement definitely to decide the point for any contact or specimen.

With reference to the jumping of the characteristic from the "A" to the "B" type of curve by the application of excessive voltage, it seemed evident that this must be what happened when a strong "X" was received by a detector; but it does not, however, seem to explain an effect that he had noticed (and others had obtained similar results) when using a zincite-tellurium contact as a detector, that the impact of a strong atmospheric very often does not spoil the reception of signals, but sometimes they are actually stronger after it has passed. This may occur several times in succession, each time the strength of the signals rising somewhat, till finally a steady state seems to set in, in which signals are much louder than it was possible to obtain at first.

The author mentions in the Paper that on no occasion has he obtained characteristic curves *concave* to the volt axis, although Dr. Eccles's theory indicates that such should be possible. On one occasion he had obtained a curve of a particular zincite-bornite contact that was concave to the volt axis on the side with zincite positive, but was convex with the zincite negative, while, moreover, it seemed to be a stable condition as the curve could be repeated (slide shown). It appears, however, to be rather a peculiarity of the specimens employed than a property of the materials, as with other samples he had failed to obtain any such result. It seemed probable, too, that if the voltage limits had been taken higher the curve might have turned and become convex to the volt axis for the higher values.

Prof. FORTESCUE communicated the following: The curves given in Fig. 1 are very interesting. I have repeatedly noticed the same thing with the zincite and galena series of contacts. The breakdown is apparently due to increase of area of the contact, brought about by the increase of mechanical pressure or by the softening, or even fusing, of one of the materials when high voltages are applied. The restoring effect of the reverse current is not so easy to explain; possibly it may be some electrolytic action. I have never found a point which had been rendered conductive by heavy mechanical pressure restored in this way. The

tabulation of the substances given on page 2 can also be carried out from their thermo-electric properties with similar results. Carborundum, however, presents a difficulty, as it can be strongly positive or negative, and is to a large extent independent of the mechanical pressure.

The AUTHOR, in reply, said that it seemed likely that some correspondence would exist between the order of the substances in the table and the behaviour of the contacts as detectors. If the conclusion of Pierce is accepted, that the characteristic is still followed under high frequencies, the point of best sensitiveness for weak signals should lie near the maximum curvature. The discussion of this question is scarcely possible within the limits of the present note. The ease of adjustment is an important factor in practice; it seems dependent on two conditions: (1) The breakdown may supervene before the bend in the A curve is reached. This is especially true of the metals. (2) The weight permissible for a given contact pair lies between a lower value, for which both surfaces are poor conductors, and an upper limit at which they conduct yielding a relatively symmetrical curve. The further apart the bodies are in the series the greater is the range of weight over which they give the A curve, and the greater, therefore, is the ease of adjustment.

He had not so far been able to connect this series with one derived from other physical properties. Hysteresis, such as was described by Pierce, was observed. This, however, he would assign to alteration and recovery. If the breakdown in Fig. 1 is made less marked, the curve becomes extremely similar to the hysteresis curve. In some experiments the change was so slight that even with the mirror the step was not obviously discontinuous. The action of an X on the detector can scarcely be predicted from the change in the characteristic alone. It would be interesting to see the nature of the characteristics immediately before and after such an alteration. If the X was strongly damped the first impulse might tend either to breakdown or to recovery. The curve shown by Mr. Coursey was extremely interesting. He had traced several curves for zincite-bornite, but had not encountered this form.

The curvature of the surfaces appeared to be immaterial. The form of the area of contact would apparently be that of a small element of the harder surface. Provided the radius of curvature were not comparable with the diameter of contact, the area would be virtually plane; for this reason no special shape beyond that of a blunt point was attempted. Different considerations might, of course, apply to the use of splintered points of mineral. The electrostatic attraction does not seem to offer of itself any possibility of a unilateral effect, since the force on interchanging + and - signs would be the same. Some unilateral property would still be required. In the case of zincite the area in most cases was nearer 0.01 sq. mm. than 1.0. This would require a higher potential gradient, of the order 10^9 volts per centimetre. As the dielectric strength of mica is only 2×10^6 volts per centimetre, the strain in the intervening space would be considerable. If the electrostatic pull were the direct cause of conductivity in the B curve, the curves A and B should be tangential at the origin, for here the pull has a negligible effect on the natural resistance of the contact. As far as could be seen, the two curves cut at a finite angle. Possibly the mechanical breakdown of some film might be assumed, but the high weights in zincite contacts offered difficulties.

The recovery of the contact was undoubtedly one of the most difficult features of these curves. It seemed impossible to conceive a mechanical change which would be reversible to such an extent. The writer felt that the published thermo-electric data which he had encountered were too few and conflicting to permit a comparison with any degree of certainty. The behaviour of such a mineral as pyrite, which exists in two widely different thermo-electric forms, should yield interesting information.

The very high weights required by carborundum would suggest that it

should behave in the same way as zincite, possibly lying beyond it in the table. A very good unilateral curve was published by Pierce,* and this curve has the high current with carborundum negative, "current (in the crystal) toward the platinised surface," as would be expected. The difficulty with carborundum may arise in some cases from the incomplete contact with the fusible metal, and also from the possibility that many of the curves under light pressures were very probably of the B type. Like cassiterite,† carborundum‡ appeared to be a colourless substance, owing its colour and possibly its conductivity to dissolved matter. The variations in the electrical properties of such bodies were probably very great.

* G. W. Pierce, *THE ELECTRICIAN*, December, 1907, p. 375.

† Th. Liebisch, "Sitzungsber. d. K. Preuss. Akad. d. Wiss.," 1911, 414.

‡ "Zeit für Kryst.," L., 33.