On the Conduction of Current Through Sulfur Metals

by Ferdinand Braun

In the 9th issue of these Annals (Vol. 153) there is a work by Herwig: "Some observations about the behavior of iron and steel rods in the galvanic current", according to which these bodies, depending on the direction, intensity and duration of the current, oppose various resistances.The changes generally vary between 1/300 and 1/20000 of the full value.This work causes me to relate something of similar experiences which I have made with other bodies, but which I have not yet been able to follow to the extent that I would be able to pronounce the true reason for it simply and precisely. I therefore of course regard the following publication as a simple presentation of observations, which were probably obtained under very complicated conditions, reserving the more exact experimental analysis for myself.

With a large number of natural and artificial sulphides, and very different pieces, both crystals of as perfect formation as I could obtain, and solid pieces, I found that their resistance varied with the direction, intensity, and duration of the current. The differences are up to 30 % of the whole value.

The current, usually from a large Bunsenian element, passed through a zigzag. shaped 0.6 mm thick nickel silver wire (of 3.7 S.E. resistance), which was passed through seven mercury cups of cork distributed on it. Branch current was taken from these mercury cups, which flowed through the sulfur metal and the current-measuring device (a strongly damping Wiedemann bussole with mostly 0.22 S.E. resistance). The difficulty of these experiments lies in reliable contacts. I used mercury contact, strongly pressed against copper, platinum and silver wires finally in one piece an already existing socket with thick nickel silver brackets, which were pressed through screws. Hittorf[1] found this latter type of socket to be the best.

I have to mention that I have found no thermoelectric excitation or polarization remotely capable of detecting the phenomena. I tested this by turning over a seesaw which interrupted the first current and still had to move 2 to 3 mm at fairly high speed to switch the sulphurous metal into the circuit of a second multiplier of suitable sensitivity (resistance).

With a number of natural sulphurous metals: chalcopyrite, pyrite, galena, sallow ore, I generally found that the current intensity differed according to the direction of the current, that this difference increased with increasing current intensity, and that when the current was kept closed, the intensity for that direction which gave less resistance increased, for the opposite one decreased. Care was always taken to ensure that the contacts lay as firmly as possible and were therefore attached to a common board with the specimen to be examined. The devices which had to be switched were on another table.

I refrain from citing several series here, and will only choose, for the sake of example, one obtained from a prismatic piece of cast chalcopyrite. It was set in German silver and had a resistance of almost 2 S.E. at a length of approx. 70 mm, a width of 20 mm and a thickness of only 15 mm. With increasing and decreasing current intensity (due to changing electromotive force) it was compared with metallic resistance.

Table I

Electric Force	Current Intensity	
	chalcopyrite	metallic resistor
—	15.8	17.0
—	64.2	63.8
—	75.3[2]	75.3[2]
—	110.7	114.0
—	117 declining rapidly	126.5
—	119	178
1 Bunsen	159	230

2

[1] Hittorf. Pogg. Ann. Vol. 84, p. 81.

[2] The met. resistance was chosen so that these two current intensities were equal.

The difference in the intensity of the current, depending on the direction of the current, I have observed in many experiments, both with strong and weak electromotive forces, with initial deflections as with constant deflections, and always with the same qualitative result when I am sure of myself : that with a low current intensity one direction offers greater resistance, with increasing intensity both directions behave in the same way and that they then exchange their roles.s

Table I I

	Current direction I		Current direction II	
	first pointer deflection	constant deflection	second pointer deflection	constant deflection
—	10.0	7.8	9.0	5.7
—	43.0	32.0	47	38.2
—	61	45 falls to 39	63	45 increases to 49
—	89	59	105	85
—	155	115 falls to 106	204	163 increases to 167
—	—	106	—	166
1 Bunsen	—	120	—	230

The next task will be to create simpler experimental conditions if possible. But it does not seem feasible, and I emphasize this, to explain the phenomena by sources of error, which are clearly recognized from our present experimental point of view. Imperfect contact does not suffice to explain it, for it cannot be supposed that in the rapid succession of measurements the contact should always have improved and deteriorated in the same period as the current reversal. In fact, if one deliberately makes insecure contacts, as I did by pressing a large number of copper and zinc sheets into a glass tube between two thick wires, I also got differences when the current was changed, but these were arbitrary changed, or went so that if the current intensity was falling, it would fall even more if the current suddenly reversed.

After lying for a long time (several months) this tube behaved perfectly normally, even when I put little or much distilled water between the sheets. Likewise, when I let the wires lean arbitrarily against the most diverse metallic conductive objects, the behavior was always normal. If one wants to explain the observations by a peculiarity of the contacts (transition resistance), we have so far had no investigations on this. However, I would not consider it absolutely impossible that very thin layers of gas cause the anomaly and that at ordinary temperatures these layers already show the conditions of unipolar conduction of electricity, which easily can be shown to such a striking extent at higher temperatures. – The phenomena are certainly not directly caused by thermoelectric excitation. Because first of all, thermoelectric forces of 1/3 Bunsen and above would have to be assumed, and moreover, according to the theory and the sum of all experiences, the thermoelectric force is proportional to the first power of the current intensity, so that a thermocouple shows no difference in resistance when the direction of the current changes, provided that this is not the case significant permanent excitations have remained. In fact, the apparent resistance of a 64-element thermopile was independent of the direction of the current; on the other hand, a seesaw, which connected the sulphurous metal to a multiplier immediately after it had been turned over, as already mentioned, gave no possible reason. the mirror down to exactly the same part of the scale as to which it fell in the first deflection, going beyond the resting position, if instead of Kieses a metallic resistance e equivalent to it was connected.

Up to now I have not been able to recognize a connection between the directions in which different conductivity or a maximum difference of the same takes place with the crystallographic data of three sulfur metals, although there often seemed to be indications. I only want to mention one more experiment, less because I believe it provides information about this than because it shows that errors, at least in external contact, cannot cause the phenomena. Among the crystals which I examined, I found a piece shiny fahlore of exceedingly great resistance. The tetrahedrons of these were fairly exposed, and occupied large areas. The current of 8 Grove's elements was passed through the crystal and measured on a Wiedemann bussole, the windings of which, together having a resistance of 6000 S.E., were as close as possible to the mirror. Two 2 mm thick silver wires, carefully rounded and smoothed at the ends, which were pressed as firmly as possible to the crystal, conducted the current in and out. If one wire was perpendicular to the horizontally laid tetrahedron surface near the apex and the other near the base of the same surface, the bussole gave a 27^{sc} deflection, independent of the direction of the current. If the latter wire was then braced against the base of the tetrahedron, the anomalous behavior occurred immediately. In one direction the 8 elements gave 17^{sc} deflection, which gradually fell to 14^{sc}, in the other 27^{sc}, which rose rapidly to 35^{sc} and from there slowly to 40^{sc}. With such immense resistance, which also remained when the contact points for the wires were freshly scraped clean, the phenomenon can no longer be ascribed to a defective contact. Other ferrous fahlores (e.g., a matte-surfaced mercury ferrous ore) have had conducting abilities at least several million times better.

It might be possible that the phenomena mentioned can be explained in the following way. If one thinks of small crystals, for example tetrahedrons, embedded in a matrix of a different nature and if they are oriented in such a way that on the whole there are more tips on one side than bases, then the following will happen when current flows through: If the current from the matrix enters the bases of the tetrahedron, then there will be cooling at the base, warming at the top. The quantities of heat lost and produced are equal to each other, but are distributed over different masses; the base will contract more than any of the other three surfaces will expand. The tetrahedron no longer remains similar and, above all, deviates from the form it assumes when the direction of the current is reversed. In the first direction the tip would be sharper, in the second it would be flatter. It is thus conceivable that in one direction the contacts are improved, i.e. the number of points of contact with the surrounding matrix increases, while the other directions of current are reduced. This change can, on the whole, be proportional to the resulting thermal expansion, i.e. proportional to the first power of the intensity.

Further, the matrix and embedded crystals are heated by the current; if this takes place in the two media in different ways, the individual parts shift against each other and there is again a change in contact, which can be proportional to the square of the current intensity. If one sums everything up, then the entire resistance set can be set equal to a function of the form

$$w + c \cdot J + k \cdot J^2$$

where w means true resistance, c and k constants, J the current intensity. With different signs of c and k, this function can obviously be less than or equal to w and greater than w (compare Table II).

If this explanation is correct, i.e. if the differences are due to contact changes, then these also show up in the same way with longer current passage (at least within certain limits), i.e. the resistance must increase for the current direction which has a greater resistance, and for the opposite direction it must increase he fall–quite in accordance with experience.

That with larger current intensities in the interior of some of the brittle sulphurous metals, e.g. galena, contact changes occur, is beyond doubt, since the current intensity then sometimes changes abruptly. But such minerals can be ruled out. But I think such changes are also possible in more solid, not completely homogeneous masses. The only thing that strikes me as surprising is that the anomalies also occur with small intensities and the first deflections. In any case, this consideration points to the possibility of sources of error, which must first be completely eliminated before one can devote oneself to the more interesting conception, which arises immediately when looking at the phenomena, that one is dealing with a kind of direction of the conducting molecule and a certain electrical after-effect.

Leipzig, November 23, 1874.

Translation of:
Ferdinand Braun: “Ueber die Stromleitung durch Schwefelmetalle”,
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English translation by Peter Russer, 25 April 2023

Translator’s note:

- Bunsen was a unit of voltage commonly used in Germany at the end of the 19th century. 1 Bunsen corresponded to about 1.9 volts.
- In 1860, Werner Siemens described a resistance standard consisting of a column of mercury 1m long and 1mm^2 in cross-section at a temperature of 0°C. The resistance of this standard was referred to as the “Siemens Unit” (S.E.) and equaled approximately 0.94 Ω.