An Experimental Study on the Influence of Magnetism and Temperature on the Electrical Resistance of Bismuth and its Alloys with Lead and Tin

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The prime cost of copper is known to be greater than that of iron for equal conductivity; and reckoning on this basis, irrespective of difficulty of fusion, it is stated in the Report of the Lightning-rod Conference to be 50 per cent. dearer. If that were all, then doubtless the small saving in using iron would be more than counterbalanced by the attendant disadvantages of deterioration by rust, and the like. But when the higher fusion-point, the greater capacity for heat, and the lesser density of iron are taken into account, the superiority of iron, for equal total prime cost, becomes so marked as to once more raise the question whether it may not be expedient to return to the original practice of Franklin, and use lightning-rods of iron instead of those of copper.

London, December 12, 1887.

XVIII. *An Experimental Study on the Influence of Magnetism and Temperature on the Electrical Resistance of Bismuth and its Alloys with Lead and Tin.* By EDMOND VON AUBEL, of Liège, Member of the Physical Society of London.*

PRELIMINARY COMMUNICATION.

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MANY physicists have been at work upon the influence of

* Read January 28, 1888.

magnetism on the electrical conductivity of metals. The metals which have already been studied are iron, nickel, cobalt, antimony, tellurium, and especially bismuth.

The above investigations have been carried on principally with the view of discovering an explanation of Hall's phenomenon.

The present memoir is intended to fix the date of publication. Our researches were commenced last May; since then many works have appeared on the question which we were studying, notably the excellent memoirs of Messrs. Goldhammer*, A. von Ettingshausen†, and W. Nernst‡.

Quite recently we saw, in the *Wiener Anzeiger*, 1887, p. 222, that Messrs. von Ettingshausen and Nernst had made a communication to the Academy of Sciences at Vienna, having the title "Ueber das thermische und galvanische Verhalten einiger Wismuth-Zinn-Legirungen im magnetischen Felde." This paper is not yet published, as far as we know; so that we cannot take account of it in what follows.

Our researches are far from being finished. They will be continued as soon as our other occupations will permit.

I. *The Preparation of Rods of Bismuth.*

We have studied bismuth under three molecular states:—

- (1) Melted and cooled slowly,
- (2) Melted and rapidly cooled or tempered,
- (3) Compressed.

Let us examine the preparation of rods of bismuth in these three cases.

1. In order to prepare bismuth wires slowly cooled, capillary glass tubes were procured, to which were joined at both ends, at right angles to the capillary part, glass tubes of fairly large diameter. These capillary tubes were heated in a sand-bath, and some grains of bismuth were introduced into one of the side branches. When the metal was melted, it ran down by its own weight into the capillary tube. The

* We have given in the Bibliography only the list of works relating to bismuth.

† *Vide* the Bibliography.

‡ *Annalen der Physik*, 1887, No. 85.

capillary tubes were then left to cool very slowly ; they were taken from the sand-bath only when it was quite cold. It often happens that, owing to the unequal expansions produced during the cooling of the bismuth and the glass, the tubes are broken ; for this reason we used capillary tubes with very thin walls.

Working in this way, any formation of oxide in the capillary part is entirely avoided ; and this part alone must be used in the experiments.

We think that this way of preparing bismuth wires is much more convenient than the method by exhaustion employed by others*, and which cannot furnish results entirely comparable, because there is no certainty that the melted metal is always cooled under the same conditions. The bismuth rod being thus prepared, the two side branches which are not wanted are taken away.

The electrodes to convey the electric current remain to be fixed. For this purpose one end of the capillary rod of bismuth is heated at the same time as a platinum wire in a Bunsen burner up to the melting-point of bismuth ; then the red-hot platinum wire is plunged into the capillary tube. It is easy to see that a good contact is thus produced.

2. In order to obtain bismuth rods very rapidly cooled or tempered, the melted metal was poured rapidly into a kind of iron trough, cold, and forming a somewhat acute dihedral angle. If the pouring takes place rapidly, by inclining the trough sufficiently to cause the melted bismuth to run down very quickly, rods of bismuth can be obtained sufficiently long and not too thick. This last condition is indispensable, otherwise the bismuth rods will have too small a resistance.

No adherence takes place during this tempering between the iron and the bismuth. Moreover, by taking certain precautions, the surface of the bismuth may also be filed, and a fresh part of the metal be thus exposed.

In this case the electrodes were made of copper wire, soldered to the two ends of the rod of bismuth by means of a fusible alloy.

* See notably the memoir of Leduc, *Journal de Physique* [2], iii. p. 363.

3. The compressed bismuth which we used in our experiments was given to us by Prof. Spring. Having been prepared in a drawplate*, it was absolutely cylindrical.

The electrodes were formed, as in the case of the tempered bismuth, of copper wires soldered to the bismuth with a fusible alloy.

The molecular arrangement in this compressed bismuth is very remarkable. A fracture normal to the axis of the cylinder presents a radial structure. We shall see later on the curious results that this sample has given us.

The alloys have only been studied under two states :—

- (1) Melted and very slowly cooled,
- (2) Tempered.

Rods of these alloys have been prepared in the same way as those of bismuth.

II. *Alloys.*

To obtain the alloys, two sandstone crucibles are used. Bismuth is put into one, tin or lead into the other. These metals have previously been weighed. When the bismuth is melted it is kept liquid, being warmed gently to avoid too much oxidation; it is then poured upon the other metal, which is also liquid. The contents of the crucible are then poured into the other, and this decanting is repeated several times. We have worked in this way in order to obtain alloys in which the proportion of tin or lead should be given almost exactly by the weight, and to avoid having to make analyses of the alloys in order to know their approximate composition.

III. *Analyses of the different Specimens of Bismuth studied.*

We have measured the resistance of several specimens of bismuth. They came from the manufactory of chemical products of Messrs. Monheim at Aix-la-Chapelle, Trommsdorff at Erfurt, and Schering at Berlin. Mr. Monheim's bismuth

* *Annales de la Société Géologique de Belgique*, t. xi. p. cxxxiv (1884).

is commercially pure metal. We have three different specimens from the firm of Trommsdorff, which we shall call, for brevity, "Trommsdorff I.," "Trommsdorff II.," and "absolutely pure Trommsdorff."

The two first, as well as the bismuth from the Schering factory, are products referred to as very pure in the catalogue of manufacturers.

The "absolutely pure Trommsdorff" bismuth, of which the cost was far higher than that of the others, has been specially prepared for us in the Erfurt manufactory.

As to the compressed bismuth, it has been obtained by means of the commercial metal. Prof. Spring dissolves this metal in HNO_3 , precipitates it by pouring the solution into a large quantity of water, filters, and washes it. He then redissolves the basic nitrate, precipitates a second time, calcines, and reduces in a current of pure hydrogen.

We give all these directions, so that it may be possible for physicists to repeat our experiments, and in order to show how little confidence ought to be placed in certain determinations which have been made on the physical constants of bismuth.

M. A. Classen, Professor of Analytical Chemistry at the Upper Technical School at Aix-la-Chapelle, was so kind as to undertake to make qualitative analyses of various specimens for us. We wish again to thank him here for the indispensable assistance which he has given to our work.

Results of the qualitative analyses :—

Bismuth.	Impurities.
Monheim . . .	<i>Copper*</i> , <i>lead</i> , iron.
Trommsdorff I. .	<i>Iron</i> , copper.
Trommsdorff II. .	<i>Lead</i> , copper, nickel.
Absolutely pure Trommsdorff . }	<i>Lead</i> , copper (traces), iron, carbon.
Schering . . .	Copper, <i>lead</i> ?, nickel.

It is very difficult to prepare pure bismuth. Even the method indicated above for preparing the metal which has

* The metals whose names are in italic are those which were found in considerable quantities in the bismuth analysed.

been compressed, does not yield a pure product. A small quantity of lead and copper is always precipitated with the bismuth; and it is only by repeating this operation several times that the metal can be obtained very pure.

M. A. Classen is occupied at the present time in preparing for us pure bismuth, which is to be used in our later researches.

It results from all this that the various specimens of so-called pure bismuth are very different from a chemical point of view. Their points of fusion and their specific weights have been likewise determined; they vary very sensibly from one sample to another.

IV. *Measurement of Electrical Resistances.*

The threads of bismuth were placed in a water-bath, which was heated all along its length by a linear gas-burner, forming a series of small flames: a thermometer indicated the temperature.

The whole was placed between the poles of a Ruhmkorff's electromagnet of large size, worked by an Otto gas-engine and a dynamo-electric machine of Siemens and Halske*.

The intensity of the electric current in the spirals of the electromagnet was sensibly 28 amperes during the whole course of the experiments.

The ordinary poles of the electromagnet were replaced by large flat poles, made of thick iron circular plates, each one having a thickness of 15 millimetres and a diameter of 150 millimetres. In this way the magnetic field was made more uniform.

In order to measure the resistances, Thomson's method was employed, and a Siemens's *dead-beat* galvanometer, with the magnet in the form of a bell, was used.

In order to avoid heating the thread of bismuth by the passage of the current, one Grove cell only was used, and, by the aid of a see-saw commutator, the current was not allowed

* The electromagnet was set in such a direction as to have no influence on the galvanometer.

to pass in the bismuth for a longer time than was necessary for the observations.

The deviations of the galvanometer-mirror were observed in a telescope furnished with a graduated scale, the distance between each division being two millimetres, and placed at a distance of more than seven metres from the mirror. One can judge of the sensitiveness of the method. We have also employed Kirchhoff's method of measuring resistances, preserving all the other arrangements. A great number of rods of bismuth and its alloys have been tried ; in the following tables we only give the values obtained for a sample of each kind.

In our experiments we did not obtain directly the resistance of the thread of bismuth, because in Thomson's method the wires for conveying the current were not fixed directly to this metal, but to the copper or platinum conductors which served as electrodes. It was necessary therefore to deduct the resistances of these copper or platinum conductors, in order to obtain values relating only to the bismuth. In the case of the wires slowly cooled, we have subtracted the values obtained directly, as the resistance of the platinum conductors exterior to the wire of bismuth, because this latter metal adheres very easily to platinum, and the section of the rod of bismuth is very great when compared with that of the thread of platinum.

V. Results of Electrical Measurements.

The values of W are the electrical resistances in Siemens's units ; the values of W_m are the electrical resistances in the same units under the action of a magnet.

(a) <i>Rods of Bismuth slowly cooled.</i>			
	Temp.	W.	W _m .
Trommsdorff bismuth, absolutely pure.....	17.2	0.4100	0.4120
	42.7	0.4050	0.4070
	70.8	0.3953	0.3966
Trommsdorff bismuth I.	20.4	0.1000	0.1010
	42.4	0.1092	0.1099
	69.9	0.1210	0.1217
Monheim bismuth	18.6	1.1295	1.1455
	41.2	1.0425	1.0525
	72.2	0.9375	0.9435
Schering bismuth.....	18.2	0.2522	0.2572
	43.5	0.2652	0.2662
	71	0.2789	0.2789
Trommsdorff bismuth II.	20.4	0.1661	0.1671
	43	0.1713	
	73	0.1811	0.1821
(b) <i>Rods of Bismuth tempered.</i>			
Trommsdorff bismuth, absolutely pure.....	15.2	0.1788	0.1790
	40.7	0.1805	
	69.7	0.1812	0.1812
Monheim bismuth	18.4	0.0934	0.0940
	43	0.0932	0.0937
	70	0.0909	0.0911
Trommsdorff bismuth II.	16.2	0.0784	0.0789
	40.8	0.0774	0.0777
	74.2	0.0765	0.0770
Schering bismuth	20.2	0.1239	0.1254
	42	0.1239	0.1249
	72.4	0.1244	0.1249
Trommsdorff bismuth I.	18.2	0.0510	0.0515
	41.6	0.0512	0.0517
	71.4	0.0541	0.0545
(c) <i>Alloys with Tin.</i>			
(1) <i>Rods slowly cooled.</i>			
Absolutely pure Tromms- dorff bismuth.	19	0.3364	0.3374
	42.8	0.3444	0.3454
	71.6	0.3475	0.3475
0.39 gr. tin to 100 gr. Bi.	19.6	0.3966	0.3976
	45.2	0.4066	0.4066
	70.6	0.4166	0.4166
Trommsdorff bismuth I.	19.6	0.3643	0.3663
	41.2	0.3733	0.3743
	69.8	0.3803	0.3813
0.40 gr. tin to 100 gr. Bi.	19.8	0.3643	0.3663
	41.2	0.3733	0.3743
	69.8	0.3803	0.3813
Schering bismuth.	19.8	0.3643	0.3663
	41.2	0.3733	0.3743
	69.8	0.3803	0.3813
0.40 gr. tin to 100 gr. Bi.	19.8	0.3643	0.3663
	41.2	0.3733	0.3743
	69.8	0.3803	0.3813
Trommsdorff bismuth II.	21	0.5133	0.5183
	42.6	0.5258	0.5288
	71.8	0.5343	0.5363
0.46 gr. tin to 100 gr. Bi.	21	0.5133	0.5183
	42.6	0.5258	0.5288
	71.8	0.5343	0.5363

Table (continued).

(c) <i>Alloys with Tin</i> (cont.).			
(2) Rods tempered.			
	Temp.	W,	W _m .
Trommsdorff bismuth, {	18.6	0.2133	0.2136
absolutely pure. {	41.6	0.2173	0.2178
0.39 gr. tin to 100 gr. Bi. {	70.4	0.2213	0.2213
Schering bismuth. {	16.6	0.2100	0.2105
0.40 gr. tin to 100 gr. Bi. {	41.8	0.2145	0.2150
	73.9	0.2148	0.2150
Trommsdorff bismuth I. {	20.4	0.1443	0.1443
0.46 gr. tin to 100 gr. Bi. {	42.8	0.1478	0.1478
	69.6	0.1498	0.1498
Trommsdorff bismuth II. {	24.5	0.1529	0.1534
0.46 gr. tin to 100 gr. Bi. {	40.6	0.1554	0.1561
	77.8	0.1574	0.1574
(d) <i>Alloys with Lead</i> .			
(1) Rods slowly cooled.			
Trommsdorff bismuth, {	18.8	0.4925	0.4945
absolutely pure. {	44.7	0.4995	0.5015
0.52 gr. Pb to 100 gr. Bi. {	68.9	0.5015	0.5035
Trommsdorff bismuth I. {	21	0.2713	0.2743
0.54 gr. Pb to 100 gr. Bi. {	43.4	0.2778	0.2788
	71.6	0.2878	0.2888
Schering bismuth. {	18.8	0.2631	0.2656
0.49 gr. Pb to 100 gr. Bi. {	44.8	0.2611	0.2632
	67.4	0.2620	0.2630
Trommsdorff bismuth II. {	15.4	0.3923	0.3963
0.60 gr. Pb to 100 gr. Bi. {	43	0.3878	0.3913
	69.8	0.3848	0.3871
(2) Rods tempered.			
Trommsdorff bismuth, {	18.2	0.1690	0.1700
absolutely pure. {	42.4	0.1725	0.1730
0.52 gr. Pb to 100 gr. Bi. {	70.4	0.1735	0.1735
Trommsdorff bismuth I. {	17.4	0.0937	0.0947
0.54 gr. Pb to 100 gr. Bi. {	41.6	0.0929	0.0934
	71	0.0914	0.0919
Schering bismuth. {	18.8	0.1478	0.1493
0.49 gr. Pb to 100 gr. Bi. {	44.4	0.1458	0.1468
	70.2	0.1439	0.1449
Trommsdorff bismuth II. {	22.2	0.1056	0.1066
0.60 gr. Pb to 100 gr. Bi. {	43.6	0.1056	0.1061
	72.2	0.1031	0.1031

Table (*continued*).

(e) <i>Compressed Bismuth.</i> (From Prof. Spring.)			
	Temp.	W.	W _m .
Compressed bismuth ... {	16·8	0·1148	0·1157
	42·4	0·1140	0·1145
	76	0·1150	0·1153
The same compressed bismuth, melted, cooled very slowly in a sand-bath, and then operated upon again. {	16·2	0·1861	0·1871
	42·3	0·2051	0·2053
	71·7	0·2263	0·2263

VI. *Inferences drawn from the preceding Tables.*

1. *The Influence of Temperature.*—If the preceding results be examined, it is easy to see at once that the different samples of bismuth examined behave quite differently. Some of them give an increased resistance, and others, which is remarkable, a diminished resistance, when the temperature rises. This last fact, noticed for the first time by M. Righi, is not due, according to this physicist, to the presence of arsenic as an impurity in the bismuth, but ought to be attributed to the tin, which, even in very small quantities, is able to produce this result.

A number of experiments have been made by us to discover the reason of this diminution of resistance. We studied first alloys of bismuth and tin, in which the latter metal was present in comparatively large quantities. On examining Table (c), it will be seen that these alloys always give an increase of resistance with the temperature, while the bismuth which enters into their composition produces a diminution of resistance for a rise of temperature. Besides, the chemical analysis has shown us that not one of our samples of bismuth contains any tin as an impurity. It is then sufficiently demonstrated that it is not the metal that is the cause of the observed anomaly*. A glance at the results of the chemical analyses and at the electrical measurements will equally prove

* See also the memoir of Mr. W. Nernst (*Annalen der Physik*, 1887, p. 783), which has appeared during the course of our researches.

that the reason for the fact ought not to be looked for in the presence, as impurities, either of arsenic or of iron.

Mr. C. W. Kayser* has shown that expansion on solidification has not taken place when bismuth is combined with 10 per cent. of lead.

For this reason we have examined also the alloys of bismuth and lead, which have furnished us with very interesting results†, recorded in Table (d), but which do not in any way explain the diminution of resistance when the temperature rises.

Some influence might still be attributed to the capillary glass tube in which the wire of bismuth is placed. On heating, the glass and bismuth expand differently, and mutually impede each other in their movements. We have therefore successively studied a rod of bismuth cast in a capillary tube, and the same rod after having broken the glass (with precautions) in such a way as not to alter the metallic wire; no change was observed in the direction of these phenomena. Besides, the rods of tempered bismuth were not prepared in glass tubes, and yet some of these present the same peculiarity.

We likewise assured ourselves that there was no relation between the abnormal electrical phenomenon and the points of fusion or specific gravities of the different kinds of bismuth‡.

2. *Influence of Magnetism.*—On the whole the influence of magnetism on the resistance of bismuth has been more feeble than that which has been announced by M. Righi§. Magnetism always produces an increase of resistance; its influence diminishes when the temperature rises, and is more feeble in the alloys than in the bismuth itself.

* *Berichte der deutsch. chem. Gesellsch. Berlin*, 1869, p. 309.

† M. Leduc had already studied the conductivity of the alloys of lead and bismuth (*Journal de Physique* [2], v. p. 116), but from another point of view.

‡ Mr. C. L. Weber has made known, in 1886 (*Annalen der Physik* xxvii. p. 145), some very curious results on the influence of temperature on the electrical conductivity of the alloys of Rose, Wood, and Lipowitz; but this work has no immediate connexion with our study.

§ Mr. Goldhammer (*l. c.*) has also found the influence of magnetism more feeble than that indicated by M. Righi.

3. *Study of Compressed Bismuth.*—The resistance of compressed bismuth hardly varies with the temperature; from $16^{\circ}\cdot 8$ to $42^{\circ}\cdot 4$ there was a slight diminution; then an increase up to 76° , also very small.

After these first experiments, we took away the two ends of the threads of compressed bismuth, on which was the fusible alloy. With the rest we prepared a rod of bismuth slowly cooled by the method indicated above.

Measurements of the electrical resistances of this bismuth, in this state, gave a fairly large increase of resistance when the temperature rose.

There is, then, a notable difference, with regard to the molecular structure, between bismuth prepared in a drawplate and that which, having been melted, has been allowed to cool slowly. One may conceive in this latter case that the crystals take up their own positions during the cooling, whilst the metal prepared in a drawplate is formed of parallel fibres of bismuth.

More complete electrical researches might make clear this important question of molecular physics. One might especially compare bismuth, compressed in an ordinary compressor, with that prepared in a drawplate.

VII. *Conclusions.*

To sum up, the diminution of electrical resistance observed in certain kinds of bismuth and in some alloys with lead cannot as yet be explained. The molecular structure, which we have modified by tempering and compression, has a great influence on the action of the temperature.

We hope that our further researches will lead us to an explanation of the anomalies which we have pointed out.

In the course of this paper we have never mentioned the name of Prof. Ad. Wüllner, our learned and venerated master; we might well have done so at each step. We are glad to be able here to express our thanks to him for the facilities which he has procured for us for undertaking our researches.

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Technique Supérieure d'Aix-la-Chapelle.
November 1887.

NOTE.

M. G. P. Grimaldi has recently * studied the influence of magnetism on the thermoelectric properties of bismuth. He denotes by ϵ the thermoelectric electromotive force of the bismuth-copper couple, when it is out of the magnetic field; by ϵ' the electromotive force of the same couple in the magnetic field; and takes for a measure of the phenomenon the quantity $\delta = \frac{\epsilon - \epsilon'}{\epsilon}$.

This physicist finds that δ is positive for commercial bismuth and negative for pure bismuth.

One ought, perhaps, to compare this result with those we have obtained relative to the influence of temperature on the electrical resistance of different kinds of bismuth.—EDM. VON AUBEL.

* *Journal de Physique*, Dec. 1887, p. 569. This paper is a *résumé* written by the author of a preliminary note presented to the R. Accademia dei Lincei (Feb. 7, 1886) and of a memoir presented in June 1886 to the Società di Scienza naturali ed economiche di Palermo.

See also *Beiblätter zu den Annalen der Physik*, 1887, no. 6, p. 472.