Physics. — *Measurement of the thermo-electric* THOMSON *effect down to the temperature of liquid hydrogen.* By G. BORELIUS, W. H. KEESOM and C. H. JOHANSSON. (Comm. N⁰. 196*a* from the Physical Laboratory at Leiden.)

(Communicated at the meeting of November 24, 1928).

§ 1. *Introduction.* Earlier measurements of the THOMSON effect down to the temperature of liquid air have given no definite knowledge concerning the temperature dependence of the effect. As however, the knowledge concerning this temperature dependence is of great importance with regard to the electron theory of metals we resolved to proceed to lower temperatures.

The present investigation embraces measurements of two wires of copper and silver, alloyed with small quantities of gold, down to 20° K., and further, measurements of pure copper down to 70° K. The composition of the alloyed wires had to be chosen with respect to the possibility of performing the measurements at the lowest temperatures. The measurement of these wires (of which a sufficient quantity is being retained as thermo-electric normals) however afterwards enable the determination of the THOMSON effect for pure metals or other alloys, which may prove of special interest, by means of measuring the thermo-electric force of these metals against one of the wires investigated here. As a matter of fact, the thermodynamic theory of THOMSON gives the relation

$$\sigma_1 - \sigma_2 = T \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e is the thermo-electric force per degree of two metals with the THOMSON effect σ_1 and σ_2 at the absolute temperature T.

By means of measuring the THOMSON effect of two wires to the temperature of liquid hydrogen, we have further been able by the aid of formula (1) to obtain a control of our measurements of this effect after having measured also the thermo-electric force of a couple formed by these wires.

§ 2. *The measuring method* was on the whole the same as the one used earlier by BORELIUS [1]) and by BORELIUS and GUNNESON [2]). A wire of the metal, which was to be investigated, was so arranged that the ends were kept at a constant temperature. An electric current sent through the

[1]) G. BORELIUS. Ann. d. Phys. (4) **63**, 845, 1920.

[2]) G. BORELIUS and F. GUNNESON. Ann. d. Phys. (4) **65**, 520, 1921.

wire causes a rise in its temperature which is greatest in the middle part of the wire. In one part of the wire the current then goes to a higher temperature, in the other part towards a lower one. The THOMSON effect in the two parts of the wire occasions heat actions of different signs, which change when the direction of the current is changed. The THOMSON effect may be obtained in volt/degree from the formula

$$\sigma = \frac{\lambda}{I} \frac{\tau}{t} \frac{3q}{y} \Phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where y is the distance in cm between a certain point on the wire and its middle point, t the increase in temperature at the point considered caused by the current heat, τ the change in temperature caused by the THOMSON effect at the same point, q the cross section of the wire in cm^2, λ the spec. heat-conductivity in watt/cm degree, I the current intensity in ampères and Φ a correction factor, the value of which at a suitable choice of wire dimensions and current intensity is situated near 1. The mathematical formula of Φ is to be found in the earlier publications referred to.

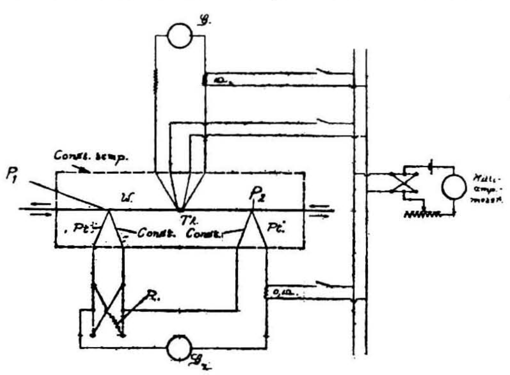

Fig. 1.

The connection diagram, which in several respects differs from the ones earlier used, is seen in Fig. 1. τ and t have been measured with thermo-elements at two symmetrically situated points P_1 and P_2 of the wire W. In the measurement of t the thermo-elements were coupled in series ; in the measurement of τ against each other. In the determination of t the current was alternately closed and opened ; in the determination of τ it was repeatedly reversed. The same galvanometer G_z was used for both determinations, a supersensitive ZERNIKE galvanometer, the sensitivity of which was considerably lowered when the thermo-elements were coupled in series, by the automatic attaching of a big resistance of 2000—10000 ohm. The joint resistance of the galvanometer and the thermo-elements amounted to about 50 ohm. The sensitivity of the galvanometer was estimated in the different cases by sending known currents, measured with a milliampèremeter, through a resistance of 0.1 ohm, which was constantly coupled to the galvanometer circuit. The determination of the temperature of the wire was made by means of a platinum thermometer Th, wound around its middle point.

The experimental arrangement is illustrated by Fig. 2. In order to obtain a constant surrounding temperature, the measuring wire W was attached to a block of copper B, and covered by a radiation screen of copper Sc. The block was cooled by direct contact of the cooling liquids L

which were supplied to a receptacle R of capacity about 0.4 liter by means of a thin electro-plated tube T. The block and the receptacle were sur-

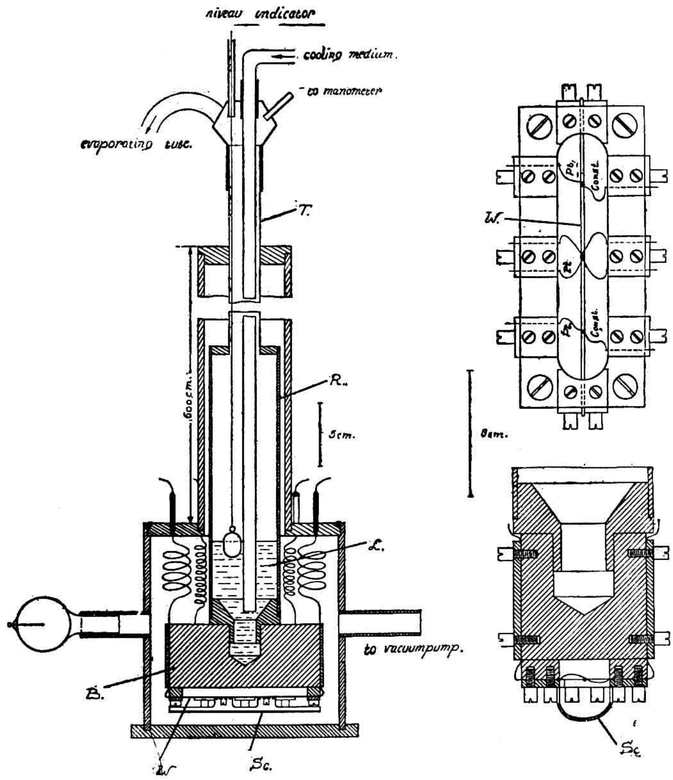

Fig. 2.

rounded by vacuo. At a good vacuum and with one hydrogen filling measurements could be made during about 80 min. The heat capacity of the block — which weighed 3 kg — was enough to enable the temperature, when the cooling medium had evaporated, to rise sufficiently slowly to allow of measurements even during the rise in temperature. The measuring wire and the eight leads (0.25 mm copper wires) to the thermo-elements and to the resistance thermometer were fastened to the block with a good electric insulation, and with the best possible heat conducting contact, for which purpose thin cigarette paper was put to a convenient use as interlining. Further the measuring wires, which were about 1 mm thick, were covered by a thin coating of enamel lacquer which enabled a direct placing of the resistance thermometer and the thermo-elements on the wire, where they were fixed by means of shellac. We are indebted to Mr J. LAGERKVIST, of the Sieverts Kabelverk firm, Stockholm, for rendering kind assistance with the coating of the wires.

The resistance thermometers consisted of 0.05 mm physically pure platinum from the HERAEUS firm. They were wound about 20 times round the measuring wire, their resistance being about 4 ohm at room temperature. Each thermometer was aged, after having been applied on the wire, by successive coolings and heatings with a subsequent calibration in the apparatus at a number of temperatures obtained by means of melting ice, liquid hydrogen, and nitrogen or oxygen, boiling at different pressures.

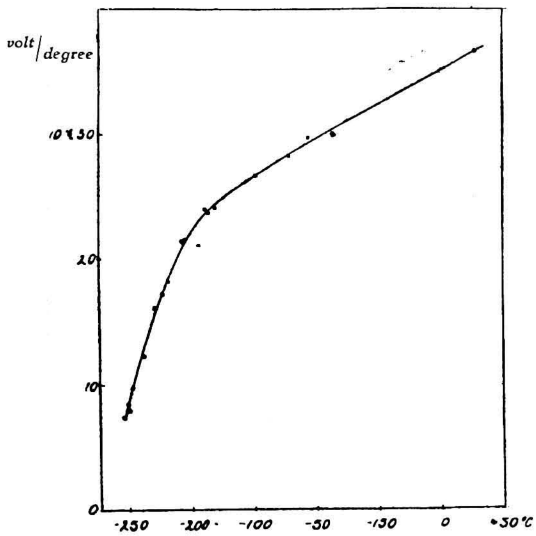

Fig. 3.

The thermo-elements consisted of 0.05 mm platinum and constantan wires. Fig. 3 represents the thermo-electric force per degree for one of these thermo-elements, determined by means of comparison with the resistance thermometer. It is not necessary, in order to estimate the THOMSON heat according to formula (2) to know the thermo-electric force very accurately, as this term only comprises the ratio between the quantities τ and t, measured by one and the same thermo-element. As however the temperature differences τ and t are situated at somewhat varying mean temperatures, the ratio between them must not be considered equal to the ratio between the measured thermo-electric forces, but a slight correction must be introduced for the relative change in the thermo-electric force between these mean temperatures. This correction was considerable only at the lowest temperatures and amounted, in the worst case, to 12 per cent.

The correction factor Φ in formula (2) is introduced on account of the resistance of the measuring wire changing with the temperature, and the external heat conductivity. As in the worst cases Φ deviated from 1 with only —2.5 and + 1.8 per cent respectively, it was quite sufficient to use the temperature coefficient from earlier measurements of the resistance and to estimate the radiation from the black-coated surface of the wire as 87 per cent of black body radiation.

Formula (2) further comprises the specific heat conductivity. For the wires investigated at liquid hydrogen temperatures this was determined at two temperatures according to LEES' method. One end of a piece of the wire was fastened to the copper block while a known amount of heat was supplied electrically to the other end. The decrease in temperature in the wire was then measured by means of two resistance thermometers, at a distance of about 6 cm. The results of the heat conductivity measurements are given in Table I. These values have been noted down together with values of other authors in T/λ, T-diagrams figs 4 and 5 (full curves). They very much resemble resistance-temperature-diagrams, and are especially well suitable for a graphical determination of λ. The curves obtained for λ have

TABLE I.

Heat conductivity.					
Copperalloy			Silveralloy		
T °K	λ $\frac{\text{Watt}}{\text{cm. degree}}$	$\frac{T}{\lambda}$	T °K	λ $\frac{\text{Watt}}{\text{cm. degree}}$	$\frac{T}{\lambda}$
18.8	1.44	13.0	18.9	2.79	6.77
78.9	2.87	27.5	93.4	4.22	22.15

also been traced in the figures mentioned (broken curves). For the technically pure copper wire examined by ourselves only as far as to the

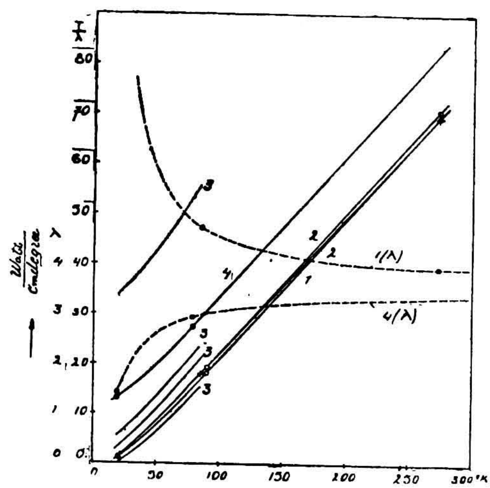

Fig. 4.

$\frac{T}{\lambda}$ (and λ) for copper.

1. R. SCHOTT, technically pure,
2. W. MEISSNER[1]), very pure,
3. GRÜNEISEN and GOENS[2]), pure and alloyed,
4. Copper with 0.37 at. $^0/_0$ Au.

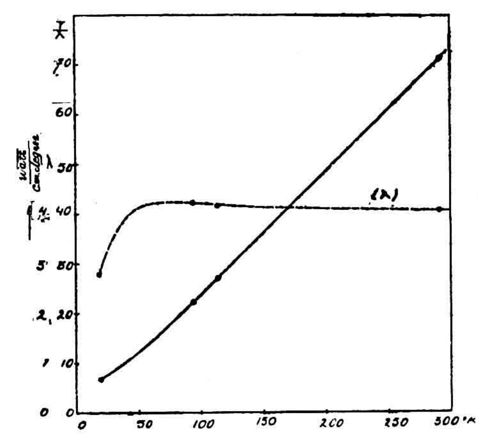

Fig. 5.

$\frac{T}{\lambda}$ (and λ) for silver.

—•— silver with 0.37 at. $^0/_0$ Au

—○— CH. H. LEES[3]), 99.9 weight $^0/_0$ Ag.

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[1]) W. MEISSNER. Ann. d. Phys. (4) **47**, p. 1001, 1915.

[2]) E. GRÜNEISEN and E. GOENS. Zs. f. Phys. **44**, p. 615, 1927.

[3]) CH. H. LEES. Phil. Trans. A **208**, p. 381, 1908.

temperature of liquid air, the values obtained by SCHOTT [1]) for similar substances have been applied.

In reality formula (2) presupposes that λ is independent of the temperature, which applies approximately for pure metals at higher temperatures. At lower temperatures, however, the heat conductivity of pure metals increases with decreasing temperature so considerably that formula (2) may scarcely be applied with a sufficient degree of approximation. Further, the temperature change t decreases with the increase in heat conductivity and the simultaneous decrease in the resistance. This makes the measuring of pure metals at the lowest temperatures too uncertain. We have therefore used pure copper only down to the temperature of liquid nitrogen, for the lower temperatures using as measuring wire copper and silver wires respectively, alloyed with gold.

Our purpose was to add so much gold that it would make λ as little as possible dependent upon the temperature, which we calculated to attain by the addition in both cases of 0.37 atomic per cent of gold. Probably on account of another impurity present at the same time, the influence of the admixture was greater than we had anticipated, and the heat conductivity of the investigated wires decreased to an inappropriate degree at the lowest temperatures. A contributing factor for the copper wire may moreover have been the fact that it was investigated in a hard-drawn condition.

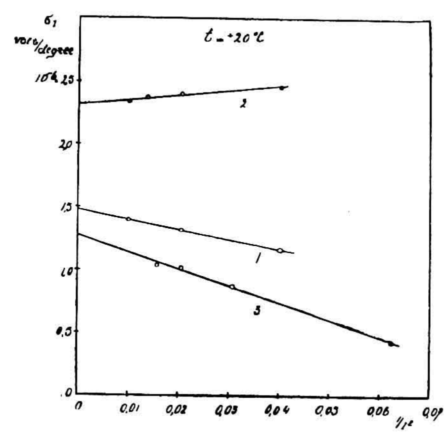

Fig. 6.
1. copper.
2. copperalloy.
3. silveralloy.

A very inconvenient source of error at all measurements of the THOMSON effect is the PELTIER influence caused by slight inhomogeneities in the wire. These PELTIER influences were also clearly evidenced in our measurements by the fact that the apparent THOMSON effect directly calculated according to formula (2), in general was dependent on the current intensity I. It is difficult to decide whether this influence emanates from inhomogeneities in the original wire or from differences between the fastened and the free parts of the wire. As this source of error is predominating, the actual THOMSON effect σ may however be calculated from the apparent one σ_I according to the formula

$$\sigma = \sigma_I + const. \frac{1}{I^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which, the constant being unknown, presupposes measurements with at least two current intensities at the same temperature.

[1]) R. SCHOTT. Verh. D. phys. Ges. **18**, 27, 1916.

Accordingly, within each temperature range measurements have been made with at least two different intensities of current. In several cases more than two intensities have been used whereby within the limits of the accidental errors formula (3) was found to be confirmed. Fig. 6 gives examples of these measurements.

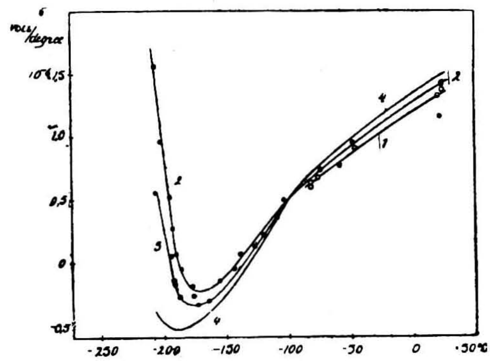

Fig. 7.

THOMSON-effect of copper.
1. 7 amp. 3. 14 amp.
2. 10 „ 4. corrected (to $\frac{1}{I^2} = 0$).

§ 3. *The results.* The direct results of the measurements are given in Table II and Figs 7—9. As temperature at which the measured THOMSON effect refers is taken the mean value of the temperatures of the resistance thermometer with a current and without current in the measuring wire.

The THOMSON effects, graphically determined according to formula (3), are compiled in Table III and Fig. 10.

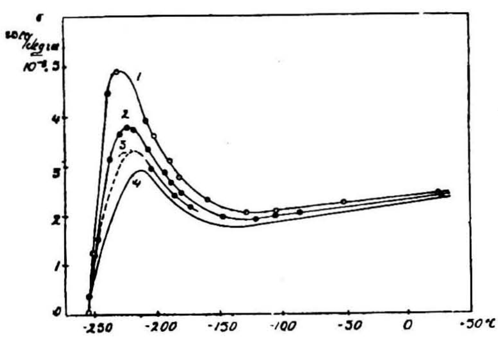

Fig. 8.

THOMSON-effect of copperalloy.
1. 7 amp. 3. 14 amp.
2. 10 „ 4. corrected.

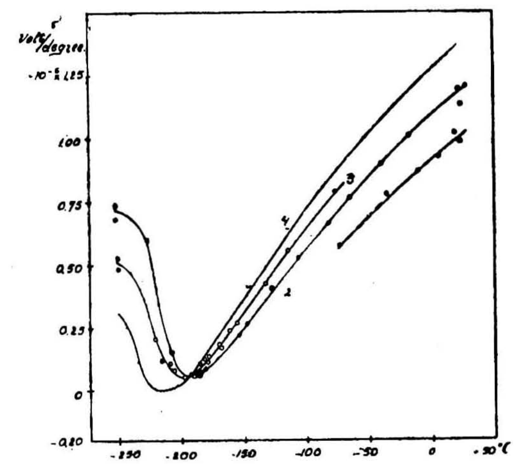

Fig. 9.

THOMSON-effect of silveralloy.
1. 7 amp. 3. 14 amp.
2. 10 „ 4. corrected.

§ 4. *Measurements of thermo-electric forces.* In order to check our measurements of the THOMSON effect with the aid of formula (1) as well as to enable certain conclusions concerning the THOMSON effects at still lower temperatures, we have further measured the thermo-electromotive forces of couples formed by the wires investigated. One of the junctions was accordingly kept at 0° C., the other at varying temperatures, two within

TABLE II.

Copper	
t °C.	$\sigma_I \,.\, 10^6$
7 amp.	
− 193	+ 0.876
81.5	0.594
76.5	0.607
58.5	0.767
46.5	0.903
+ 20.5	1.320
22	1.160
24	1.374
10 amp.	
− 206.5	+ 1.56
202.5	0.961
195.3	0.520
193	0.272
190	0.061
186	− 0.057
180	− 0.269
177	− 0.189
155.5	− 0.155
139	+ 0.062
120.5	0.216
104	0.498
81.5	0.628
74	0.736
48	0.948
+ 23.5	1.427
23.5	1.410
14 amp.	
− 206.3	+ 0.558
194.5	0.050
192.5	− 0.148
191.5	− 0.181
187.5	− 0.280
173	− 0.341
164.5	− 0.312
144	− 0.055
127.5	+ 0.125
109	0.357

Copperalloy	
t °C.	$\sigma_I \,.\, 10^6$
7 amp.	
− 255.2	+ 0.037
251.7	1.25
238.9	4.47
230.3	4.90
208.5	3.93
202	3.62
189.5	3.12
182	2.79
159.5	2.32
129	2.05
105	2.08
51	2.24
+ 25	2.43
10 amp	
− 254.2	+ 0.36
250.0	1.20
237.3	3.15
229.2	3.66
223.7	3.79
218.6	3.74
207	3.35
193.5	2.89
188.5	2.68
180.5	2.47
173.5	2.18
147.5	1.97
121	1.91
105.5	1.97
86	2.03
+ 27.5	2.38
14 amp.	
− 251.1	+ 0.79
247.0	1.53
204.5	2.96
186	2.42

Silveralloy	
t °C.	$\sigma_I \,.\, 10^6$
7 amp.	
− 73.5	+ 0.578
36	0.780
10.5	0.867
+ 19	1.02
22.5	0.988
23.5	0.986
10 amp.	
− 252	+ 0.682
252	0.739
227	0.601
208	0.151
192.5	0.062
188.5	0.071
187.5	0.061
185.5	0.058
185	0.071
181	0.085
154	0.220
147.5	0.265
128	0.410
106.5	0.526
81.5	0.663
65	0.766
40	0.899
18	1.009
+ 21.5	1.193
23.5	1.133
28	1.204
14 amp.	
− 250.6	+ 0.530
250.0	0.485
221	0.206
216	0.119
209.5	0.109
206	0.080
198	0.051
190.5	0.054
186	0.106
182	0.124
181	0.112
179.5	0.112
178.5	0.137
170	0.187
168.5	0.171
162	0.241
156	0.270
133	0.426
115	0.559
77	0.790

TABLE III.

T °K	Copper		Copperalloy		Silveralloy	
	$\sigma.10^6$	$\sigma/T.10^8$	$\sigma.10^6$	$\sigma/T.10^8$	$\sigma.10^6$	$\sigma/T.10^8$
20	—	—	+ 0.44	+ 2.20	+ 0.31	+ 1.55
30	—	—	1.39	4.63	0.24	0.80
40	—	—	2.17	5.43	0.10	0.25
50	—	—	2.84	5.68	— 0.02	— 0.04
60	—	—	2.96	4.93	— 0.02	— 0.03
70	— 0.26	— 0.37	2.71	3.87	+ 0.02	+ 0.03
80	— 0.46	— 0.57_5	2.45	3.06	0.08	0.10
90	— 0.49	— 0.54_5	2.20	2.45	0.14	0.15_5
100	— 0.45	— 0.45	2.00	2.00	0.21	0.21
110	— 0.37	— 0.33_5	1.85	1.68	0.28	0.25_5
120	— 0.26	— 0.21_5	1.75	1.46	0.36	0.30
130	— 0.12	— 0.09	1.71	1.31_5	0.43	0.33
140	+ 0.02	+ 0.01_5	1.73	1.23_5	0.50	0.36
150	0.16	0.10_5	1.77	1.18	0.57	0.38
160	0.32	0.20	1.80	1.12_5	0.63	0.39_5
170	0.47	0.25_5	1.84	1.08	0.70	0.41
180	0.59	0.33	1.88	1.04_5	0.76	0.42_5
200	0.80	0.40	1.95	0.97_5	0.87	0.43_5
220	0.96	0.43_5	2.03	0.92	0.98	0.44_5
240	1.10	0.46	2.11	0.88	1.08	0.45
260	1.24	0.47_5	2.18	0.84	1.18	0.45_5
280	1.38	0.49	2.26	0.81	1.28	0.45_5
300	1.52	0.50_5	2.33	0.78	1.38	0.46

the range of liquid hydrogen, two within the range of liquid nitrogen, and one at room temperature. In these measurements we have also included lead, which is often used as thermo-electric normal. The results are collected in Table IV. A positive sign indicates that the thermo-electric current in the junction which is kept at 0° proceeds towards the copper alloy.

By means of combining again and again two neighbouring temperatures the thermo-electric forces per degree were calculated. They are given in Table V.

These values may be used as a control of the measurements of the

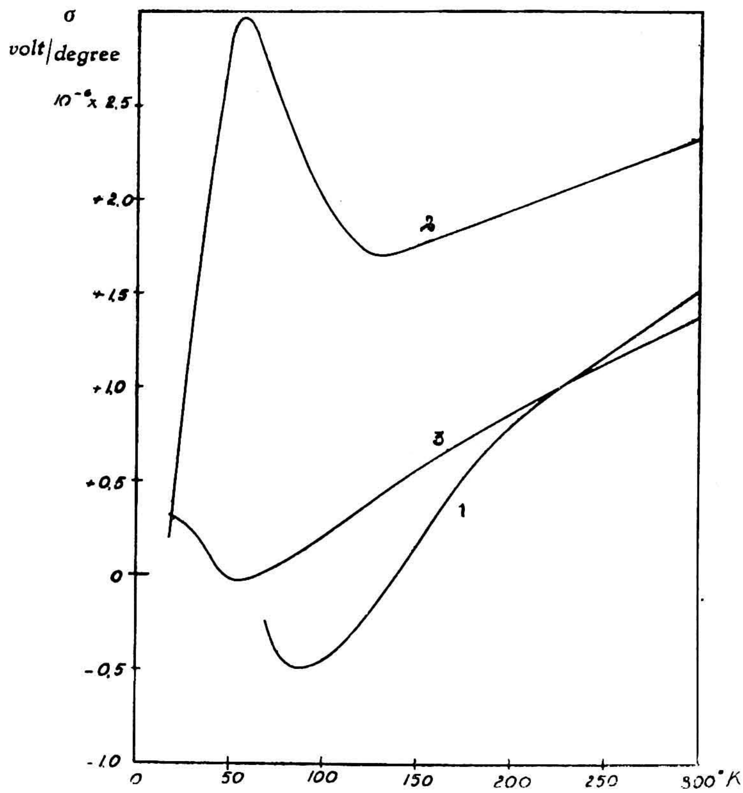

Fig. 10. THOMSON-effect.
1. copper. 2. copperalloy. 3. silveralloy.

TABLE IV.

E. M. F. against copperalloy (microvolt)			
°K	Silveralloy	Copper	Lead
14.22	— 435.95	— 581.9	— 26.1
20.36	— 406.85	— 552.5	— 3.1
63.63	— 234.8	— 350.05	+ 121.1
77.58	— 199.1	— 301.35	+ 139.4
273.09	0	0	0
288.29	+ 5.7	+ 13.16	— 32.0

TABLE V.

Thermo-electric Force per degree against copperalloy (microvolt/degree)			
°K	Silveralloy	Copper	Lead
17.3	+ 4.74	+ 4.80	+ 3.75
70.6	+ 2.56	+ 3.49	+ 1.31
280.7	+ 0.37	+ 0.87	− 2.11

THOMSON effects. As a matter of fact, according to formula (1) the change in thermo-electric force between two temperatures T' and T'' is

$$e'' - e' = \int_{T'}^{T''} \left(\frac{\sigma_1}{T} - \frac{\sigma_2}{T} \right) dT \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The values of this integral were obtained by means of drawing a σ/T, T-diagram (Fig. 11), based on the σ-values obtained, and a graphical integration of the areas, denoted as A, B and C. A comparison between these values of the integral and the corresponding differences in thermo-electric force obtained in Table V gives the results in Table VI.

The deviations from equation (4) are entirely within the limits of the accidental errors; hence this control gives no reason to assume the presence of any methodical or systematic errors in the measurements of the THOMSON effect.

§ 5. The measurements give no sufficient evidence as to the manner in which the THOMSON effect varies with temperature in the proximity of the absolute zero point, neither concerning the question whether σ will there approach to 0 [1]). Also because of the theory given by SOMMERFELD [2]), we think measurements at the temperatures, obtainable with liquid helium, very desirable.

If, according to NERNST [3]) lim $e = 0$ for $T \rightarrow 0$, comparatively great values for $\frac{\sigma_1 - \sigma_2}{T}$ would be expected for the thermocouple silveralloy-copperalloy at temperatures lower than those used in these measurements. From $e = 4.74 \times 10^{-6}$ at $T = 17.3$ (see Table IV) follows according to equation (4) for the mean value between $T = 0$ and $T = 17.3$: $\frac{\sigma_1}{T} - \frac{\sigma_2}{T} = \frac{4.74 \times 10^{-6}}{17.3} = 27 \times 10^{-8}$ volt/degree², whereas the greatest

1) W. H. KEESOM. These Proc. **16**, 1913, p. 236. Comm. Leiden Suppl. N⁰. 30*b*.
2) A. SOMMERFELD. ZS. f. phys. **47**, 43, 1928.
3) W. NERNST. Theoretische Chemie 1913, p. 753.

value of this difference within the range of these measurements amounts to 5.4×10^{-8} volt/degree^2 (at 50° K.). The fact, that even at the liquid-

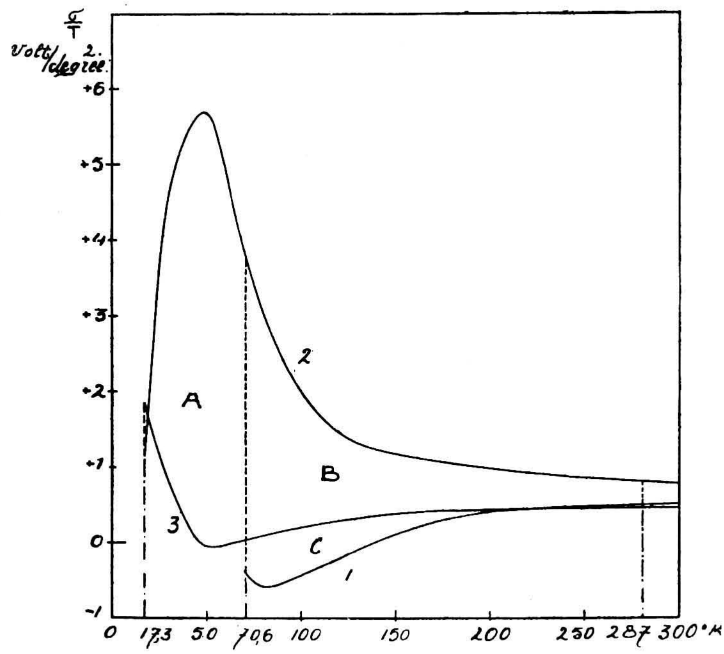

Fig. 11.

1. copper. 2. copperalloy. 3. silveralloy.

TABLE VI.

Differences in Thermo-electric Force per Degree calculated from THOMSON-effect and direct observed				
Microvolt per degree				
°K		$e'' - e' = \int_{T'}^{T''} \frac{\sigma_1 - \sigma_2}{T} dT$	$e'' - e'$ observ.	Diff.
T'	T''			
Silveralloy against Copperalloy				
17.3	70.6	— 2.24	— 2.18	— 0.06
70.6	280.7	— 2.01	— 2.19	+ 0.18
Copper against Copperalloy				
70.6	280.7	— 2.53	— 2.62	+ 0.09

helium temperatures still comparatively great values for σ/T appear, follows also from the measurements concerning thermo-electric forces at that temperature by KAMERLINGH ONNES and HOLST [1]).

We are glad to render our thanks to the NOBEL-committee for physics, which supported this research by a subsidy.

[1]) H. KAMERLINGH ONNES and G. HOLST. These Proceedings **17**, 1914, p. 760. Comm. Leiden N^0. 142c.