Physics. — *Measurements of thermo-electric forces of lead and tin down to the temperature of liquid helium.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N⁰. 217c from the Physical Laboratory at Leiden).

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§ 1. *Introduction.* The present investigation forms a continuation of the measurements of thermo-electric forces carried out by the authors in 1929 down to the temperature of liquid hydrogen [1]). The measurements have now been extended to the temperatures of liquid helium [2]) and embrace firstly the supraconductors *Pb* and *Sn*. Communications on measurements concerning some other metals and some binary alloys of *Cu* and *Au* with small concentrations of other elements, especially *Fe, Co* and *Ni* [3]) will soon follow. These measurements, for which we could dispose of a couple of months only, are to be considered as a first exploration with regard to thermo-electric forces of the field covered by the temperatures obtainable with liquid helium.

The thermo-electromotive forces were measured against a certain silver-alloy-wire used as a normal also in our earlier investigation, and the thermo-electric THOMSON-effect of which has earlier been measured by BORELIUS, KEESOM and JOHANSSON [4]) down to the temperature of liquid hydrogen. This wire will in the following paragraphs be referred to as the "normal".

§ 2. *Measuring method and apparatus.* The measuring method was mainly the same as in the previous work. The test-wires had one common junction and were at the other ends connected with leads of copper. The junctions with the leads were held at a constant low temperature T_0. The common junction was first brought to the same temperature T_0, to get the e.m.f. E_0 in the leads, necessary to be known as a correction, and was then raised successively to the temperatures $T_1, T_2, T_3, \ldots\ldots$ and the corresponding thermo-electromotive forces $E_1, E_2, E_3, \ldots\ldots$ were measured. The thermo-electric force per degree was calculated from the combinations

[1]) These Proceedings **33**, 17 and 32, 1930, Comm. Leiden, N⁰. 206a and 206b.

[2]) Measurements of thermo-electric forces at liquid helium temperatures were made for the first time by KAMERLINGH ONNES and HOLST, These Proceedings **17**, 760, 1914, Comm. Leiden N⁰. 142c § 2.

[3]) Viz. of platinum and of alloys of *Cu* with *Fe* down to the temperatures obtainable with liquid helium, of the others down to the temperatures obtainable with liquid hydrogen.

[4]) These Proceedings **31**, 1046, 1928, Comm. Leiden N⁰. 196a.

E_1—E_0, E_2—E_1, E_3—E_2 ......, the corresponding temperature-differences being about 1 to 2 degrees at the lowest and 5 to 10 degrees at the highest temperatures. It may be noted, that this way of combining is slightly different from that used in our earlier work, where E_1, E_2, E_3, ... were always combined with E_0. The present way of calculation somewhat increases the risk of small errors due to inhomogeneities in the test-wires, but gives a more equal distribution of the measured points on the temperature scale.
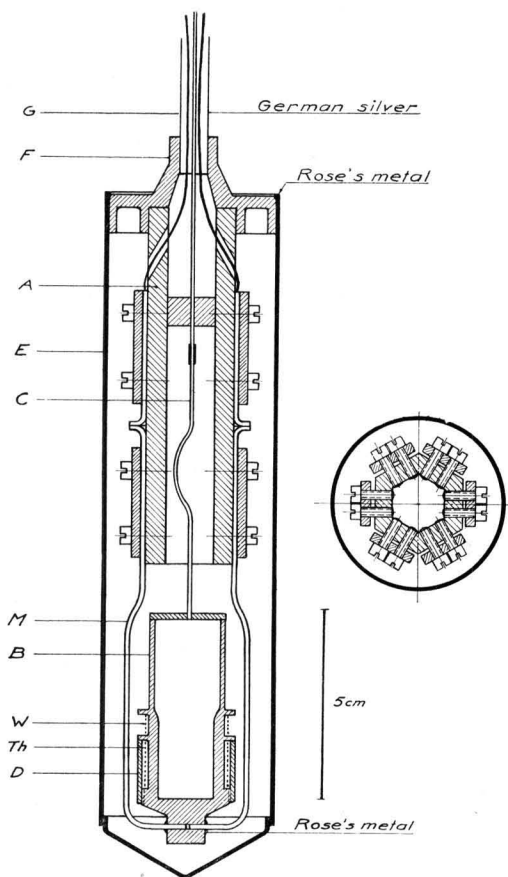

Fig. 1.

The apparatus was similar to the one used in 1929 but was modified with regard to the measurements with liquid helium. The inner parts of the apparatus can be seen in Fig. 1. Four to six of the test wires M (length about 12 cm, thickness 0.75—1 mm) could be applied at the same time. One end was joined to a lead of copper and the junction was fastened to the (hexagonal) copper tube A, which was kept at constant temperature in a cryostat. The wires were electrically insulated from A by means of cigarette paper in such a way that a good thermal contact was obtained.

The other ends of the test-wires were soldered with Rose's metal directly to a small vessel B of copper, the temperature of which could be increased by means of a heating coil W. The vessel itself was a helium thermometer with a volume of 10 cm³ and was also provided with two resistance thermometers Th of platinum and phosphorbronze respectively covered by a radiation screen D. The inner parts of the apparatus were surrounded by a removable vacuumtight copper covering E. In order to improve the thermal contact of the wire with A, hydrogen or helium to a low pressure was brought into the apparatus.

The helium thermometer was connected to a mercury manometer through a capillary C the lower part of which was of contracid. The thermometer was filled with helium to such an amount that the pressure at the normal boiling point of helium was 66 mm Hg. Thus it could be used down to 2° K. The highest temperature for which it was used was 17° K. The helium thermometer was calibrated by measurements of the vapour pressure in the cryostat for two helium pressures and one hydrogen pressure. All measurements with the helium thermometer were performed by phil. nat. docts. A. Bijl.

The wire of the phosphorbronze thermometer was taken from the same spool as the thermometers investigated by Keesom and van den Ende [1]. Its resistance at 0° C was $R_0 = 13.13$ ohm and the course of the ratio $R : R_0$, which was determined at a number of different vapour pressures in the helium cryostat, agreed very nearly with that found by Keesom and van den Ende.

The platinum thermometer (resistance at 0° C 5.7745 ohm) was as a rule calibrated in each measuring series at four temperatures within the range of liquid hydrogen and several times also within the range of liquid oxygen. Any change of the thermometers with the time beyond the limits of the experimental errors was not observed. For the accuracy of the determination of the temperature in the range between liquid hydrogen and liquid oxygen it was fortunate that this thermometer very nearly followed the thermometer Pt-23'-1915, calibrated with great accuracy by Miss van der Horst, Kamerlingh Onnes and Tuyn [2]. As a matter of fact the following interpolation formula was, within the limits of errors, found to be valid

$$\frac{R}{R_0} = \left(\frac{R}{R_0}\right)_{Pt-23'-1915} + \frac{0.008832}{T}.$$

§ 3. *Results for Pb and Sn.* Measurements on *Pb* and *Sn* were of special interest as they ought to show how supraconducting metals behave thermo-electrically below and in the neighbourhood of the critical temperature. The only statement as to the thermo-electric properties of supra-

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[1] These Proceedings **32**, 1171, 1929, Comm. Leiden N⁰. 203c.
[2] Cf. H. Kamerlingh Onnes and W. Tuyn, Comm. Leiden Suppl. N⁰. 58.

conducting metals is an observation of MEISSNER [1]) that a thermo-couple of *Pb* and *Sn* at temperatures where the two metals are supraconducting gives no thermo-electromotive forces above the errors of observation. As however the thermo-electromotive forces for many thermo-couples may be

TABLE I.

Thermoelectric force in microvolt per degree against silveralloy-normal.					
Pb$_{31}$				Sn$_{31}$	
°K	$e \times 10^6$	°K	e	°K	$e \times 10^6$
1.70	0.00 ± 0.01	24.0	1.11	4.83	−0.025
3.00	−0.02 ± 0.02	24.0	1.11	5.17	0.03
3.84	−0.01 ± 0.01	27.2	1.14	5.42	0.04
5.22	0.00	33.4	1.16	7.72	0.10
5.73	−0.01	30.5	1.15	9.09	0.14
5.88	0.01	31.5	1.17	10.1	0.21
8.20	0.17	36.1	1.18	10.6	0.20
9.17	0.30	36.7	1.18	11.3	0.26
9.72	0.36	36.9	1.18	12.5	0.33
9.96	0.42	42.5	1.22	13.3	0.41
9.96	0.44	42.6	1.22	17.3	0.70
11.7	0.72	43.2	1.22	24.0	1.05
11.8	0.74	48.0	1.22	30.3	1.32
16.9	0.97	48.0	1.22	36.7	1.49
17.3	0.98	65.9	1.19	42.7	1.65
17.3	0.99	84.1	1.26	47.2	1.76
21.0	1.09	93.8	1.31	58.9	1.80
22.6	1.09			67.8	1.85
				79.1	1.98
				86.2	1.90
				94.2	1.97
				102.6	2.03
				275.4	2.43

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[1]) W. MEISSNER, Zeitschr. für die ges. Kälteindustrie **34**, 197, 1927.

small at these low temperatures, it does not appear to what extent this result is characteristic for the supraconductors.

Our results for *Pb* and *Sn* are put together in table I. Fig. 2 shows the thermo-electric force per degree below 50° K and Fig. 3 gives the directly measured e.m.f. between 4.236° K and the temperature taken as abscissa, for *Pb*, from measurements on both sides of the critical point.

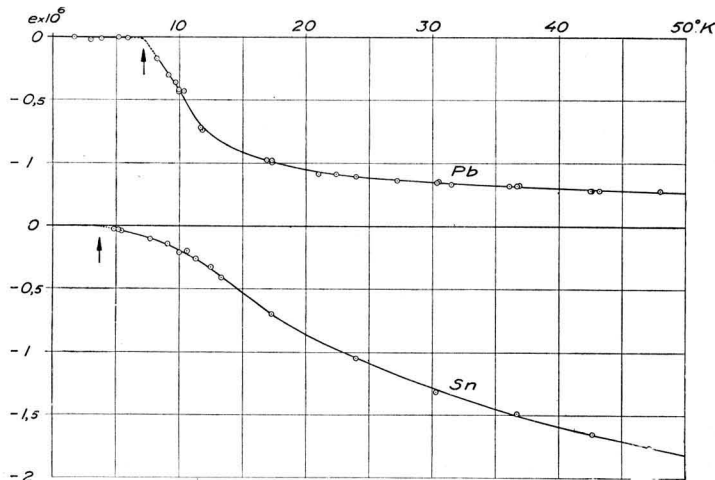Before we discuss these results we might point out, that we have, from

Fig. 2.

Thermo-electric force in volt per degree for Pb_{31} and Sn_{31}.
Against silveralloy-normal.

measurements of different alloys in combination with *Pb*, found that the additivity law for the thermo-electric force is valid also for the metals in the supraconducting state.
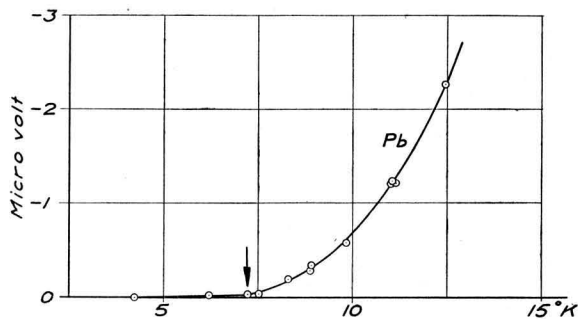

Fig. 3.

E. m. f. for Pb_{31} against silveralloy-normal. Cold junction 4,236° K.

Further is to be mentioned that the fact that our normal has an exceedingly small thermo-electric force against *Pb* in the supraconducting state may be looked upon as a mere chance, other alloys having given big thermo-electric forces against *Pb* at the same temperatures.

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The behaviour of Pb at the critical point is seen from the measurements against the normal. It appears that the thermo-electric force per degree (e) is continuous at the critical point, but that there is a rapid change in the derivative de/dT and thus also in the difference of the THOMSON-effects (σ) calculated from the THOMSON-formula

$$\sigma_{Pb} - \sigma_{norm.} = T \frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As no such change is found at this temperature in the curves for other metals in combination with the normal, it is obvious that the rapid change is in the THOMSON-heat of Pb.

To make clear the behaviour of Sn at the critical point we suitably discuss the thermo-electric forces of the combination Sn—Pb (which are nearly the same as for the combination of Sn with the normal). Our measurements reach down to the critical point, but because of an unfavorable incident we got no measurements below this point. At lower temperatures the couple Sn—Pb was, as mentioned, investigated by MEISSNER, who states the thermo-electric force to be zero though without any indication as to the accuracy of his measurements. As we have, however, by approaching the critical point from above, found the thermo-electric force per degree to approach to zero with an approximation of a couple of hundredths of a microvolt per degree, we think we are justified in accepting from this and from MEISSNER's statement that the thermo-electric force is really zero below the critical point.

In this case the curve for Sn in Fig. 2 below the critical point must nearly follow the axis and so it appears that there is a rapid change in de/dT and σ for Sn also.

As to the THOMSON-effect we first conclude, that the difference

$$\sigma_{Sn} - \sigma_{Pb} = T \frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

calculated from the thermo-electric force per degree (e) of the couple Sn—Pb is zero, when both metals are in the supraconducting state. As the temperature rises this difference first gets a rapid change to the negative side of about 0.1 microvolt per degree at the critical point of Sn and then a new rapid change to the positive side of about 1 microvolt per degree at the critical point of Pb. The THOMSON-effects thus have quite different values for Sn and Pb above the critical points and common values at all temperatures below the critical point of Sn. As such common values should be very surprising less they were zero, and as the NERNST theorem predicts the THOMSON-effect to be zero at the absolute zeropoint it seems to be little doubt, that the THOMSON-effect does in fact at the critical temperatures rapidly fall from finite values to zero. Whether this fall is abrupt, as seems probable, or continuous in a small interval of temperature, must be left to further investigations.

Summary.

Thermo-electric forces per degree were measured, for lead down to 1.7° K, for tin down to 4.8° K, in both cases against a silver-alloy wire.

The authors conclude from those measurements that the thermo-electric force per degree for a couple supraconducting lead-silveralloy is small. From their measurements on the combination lead-tin together with MEISSNER's statement they admit that the thermo-electric force for supraconducting lead-supraconducting tin is zero.

For both metals there is a rapid change in de/dT and hence in the THOMSON-heat at the temperatures where the metals become superconductive. The authors conclude that the THOMSON-effect at the critical temperature rapidly falls from finite values to zero.