Physics. — *On the change of the specific heat of tin when becoming supraconductive.* By W. H. KEESOM and J. A. KOK. (Communication N⁰. 221e from the KAMERLINGH ONNES-Laboratory at Leiden).

(Communicated at the meeting of June 25, 1932).

§ 1. *Introduction.* In Comm. N⁰. 219*b* [1]) one of us with VAN DEN ENDE reported on measurements of the specific heat of tin, and concluded that the atomic heat of tin at or near 3.7° K. suffers a rapid change or a jump, so that just below 3.7° K. the atomic heat is larger than just above. The authors remarked further that the coincidence (or nearly so) with the transition point suggests that this rapid change or jump is connected with supraconductivity.

When in measurements, made by one of us and Miss KEESOM [2]) on the specific heat of liquid helium, it had appeared that it was quite feasible to make rather accurate measurements for that substance with heatings of the order of 0.01 of a degree, we resolved to try whether it should be possible to do so too for the much smaller heat capacity of a tin block such as the above-mentioned authors used in their investigation. We hoped thus to be able to discover whether the change in the specific heat of tin has really the character of a jump, and if so, whether this jump coincides with the transition point to supraconductivity.

This paper deals with the results of a series of measurements made with this object in view.

In this series of measurements we did not intend to investigate the influence of a magnetic field, reserving this for a special examination. By chance, however, in a couple of measurements the tin was in such a magnetic field that it disturbed supraconductivity, so that we were able to draw already a preliminary conclusion about the influence of disturbing supraconductivity on the value of the specific heat.

§ 2. *Method.* For the details of the method we refer to Comm. N⁰. 221*d*. The measuring and heating core was the same as that which we used in our measurements on silver [3]). For the calibration of the phosphorbronze thermometer we refer to Comm. N⁰. 219*b*. We used for these measurements a ZERNIKE galvanometer *Zc*, measuring current 0.4 mA. A temperature

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[1]) W. H. KEESOM and J. N. VAN DEN ENDE. Proceedings **35**. 143. 1932. Comm. Leiden No. 219*b*.

[2]) W. H. KEESOM and Miss. A. P. KEESOM. These Proc. **35**. 736. 1932. Comm. Leiden No. 221*d*.

[3]) W. H. KEESOM and J. A. KOK. These Proc. **35**. 301. 1932. Comm. Leiden No. 219*d*.

increase of 0.01 degree corresponded with a deflection of 6.6 cm on the galvanometer scale.

We made for these measurements a new block of tin, of the same degree of purity as that of Comm. N⁰. 219*d*, weight 742.4 g.

In consequence of a very slight untightness of the box [1]) surrounding the tin block the vacuum was not so high as we might have wished. Nevertheless we could derive specific heats with a reasonable degree of accuracy.

§ 3. *Results.* We obtained the results recorded in table I. They are represented in Fig. 1.

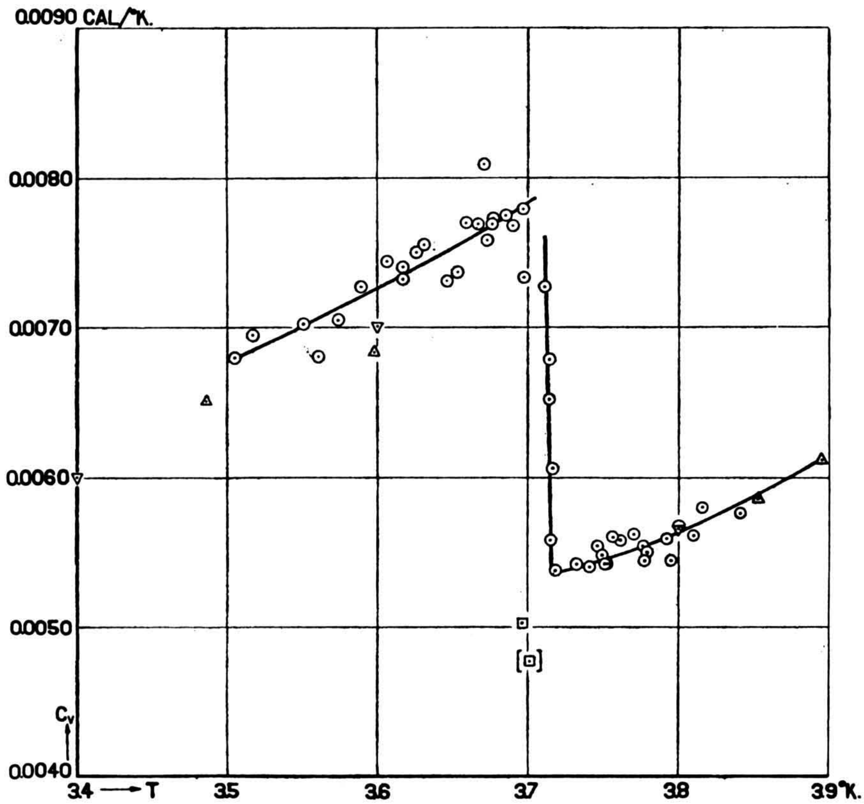

Fig 1

In Fig. 1 4 points measured by KEESOM and VAN DEN ENDE, indicated by △ have been plotted, as well as 3 other points, indicated by ▽ resulting from the smoothed curve they derived from their measurements. It appears that the agreement of our results with theirs is quite satisfactory.

The experiments II *p* and *q*, indicated by ⊡ in Fig. 1, deserve special attention because during them a magnetic field was applied for measurements in a neighbouring cryostat. With regard to the measurements to be made in this neighbour cryostat, our cryostat was partly surrounded by a

[1]) Comp. Comm. No. 219*b*. Fig. 3.

TABLE I.

Atomic heats of tin. Measurements of May 26th, 1932.							
No.	Heat supplied cal	Temperature °K.	Temperature increase °K.	Total heat capacity cal/°K.	Heat capacity core cal/°K.	Atomic heat cal/°K.	Θ
I a	0.000306_3	3.505	0.0069_0	0.0443_9	0.0018_3	0.0068_0	143.3
b	0.000296_8	3.517	0.0065_5	0.0453_2	0.0018_4	0.0069_5	142.7
c	0.000282_4	3.551	0.0061_7	0.0457_7	0.0018_6	0.0070_2	143.6
d	0.000228_6	3.561	0.0051_4	0.0444_7	0.0018_7	0.0068_1	145.6
e	0.000309_3	3.574	0.0067_3	0.0459_6	0.0018_8	0.0070_5	144.4
f	0.000282_4	3.589	0.0059_6	0.0473_8	0.0018_9	0.0072_7	143.5
k	0.000376_6	3.617	0.0079_0	0.0476_7	0.0019_1	0.0073_2	144.2
l	0.000416_9	3.631	0.0084_8	0.0491_6	0.0019_2	0.0075_5	143.3
m	0.000470_7	3.646	0.0098_8	0.0476_4	0.0019_3	0.0073_1	145.5
n	0.000215_2	3.653	0.0044_8	0.0480_4	0.0019_4	0.0073_7	145.4
o	0.000390_0	3.677	0.0077_5	0.0503_2	0.0019_6	0.0077_3	144.0
p	0.000336_2	3.690	0.0067_2	0.0500_3	0.0019_7	0.0076_8	144.8
q	0.000511_0	3.718	0.0143_5	0.0356_1	0.0019_9	0.0053_8	164.4
r	0.000363_1	3.756	0.0098_0	0.0370_5	0.0020_3	0.0056_0	163.8
t	0.000322_8	3.777	0.0089_5	0.0360_7	0.0020_5	0.0054_4	166.4
u	0.000255_5	3.795	0.0070_8	0.0360_9	0.0020_6	0.0054_4	167.2
v	0.000443_8	3.841	0.0116_3	0.0381_6	0.0021_1	0.0057_6	165.9
II a	0.000376_6	3.589	0.0079_5	0.0473_7	0.0018_9	0.0072_7	143.5
b	0.000376_6	3.606	0.0077_8	0.0484_1	0.0019_0	0.0074_4	143.1
c	0.000376_6	3.617	0.0078_1	0.0482_2	0.0019_1	0.0074_0	143.7
d	0.000295_9	3.626	0.0060_6	0.0488_3	0.0019_2	0.0075_0	143.4
e	0.000390_0	3.659	0.0077_0	0.0501_3	0.0019_4	0.0077_0	143.4
f	0.000322_7	3.667	0.0064_5	0.0500_3	0.0019_5	0.0076_9	143.9
g	0.000349_7	3.671	0.0073_0	0.0525_2	0.0019_5	0.0080_9	145.3
h	0.000416_9	3.673	0.0084_5	0.0493_4	0.0019_6	0.0075_8	144.8
i	0.000376_6	3.676	0.0075_2	0.0500_8	0.0019_6	0.0076_9	144.2
j	0.000430_3	3.685	0.0085_3	0.0504_5	0.0019_7	0.0077_5	144.1
k	0.000228_6	3.695	0.0045_1	0.0506_9	0.0019_8	0.0077_9	144.3

TABLE I. *(Continued).*

No.	Heat supplied cal	Temperature °K.	Temperature increase °K.	Total heat capacity cal/°K.	Heat capacity core cal/°K.	Atomic heat cal/°K.	Θ
ATOMIC HEATS OF TIN. Measurements of May 26th. 1932.							
m	0.000255_5	3.714	0.0059_7	0.0428_0	0.0019_9	0.0065_2	154.0
n	0.000255_5	3.714	0.0057_5	0.0444_3	0.0019_9	0.0067_9	151.9
o	0.000416_9	3.716	0.0106_7	0.0398_7	0.0019_9	0.0060_6	157.8
p[1])	0.000349_7	3.696	0.0104_6	0.0334_3	0.0019_7	0.0050_3	167.0
[q[1])	0.000309_3	3.701	0.0097_3	0.0317_9	0.0019_8	0.0047_7	170.2]
r	0.000430_3	3.698	0.0089_8	0.0479_2	0.0019_9	0.0073_4	147.8
s	0.000430_3	3.711	0.0090_6	0.0474_9	0.0019_9	0.0072_7	148.4
t	0.000416_9	3.732	0.0116_1	0.0359_1	0.0020_1	0.0054_2	164.6
u	0.000390_0	3.746	0.0106_4	0.0366_5	0.0020_2	0.0055_4	164.0
v	0.000443_8	3.751	0.0123_5	0.0359_4	0.0020_2	0.0054_2	165.4
w	0.000416_9	3.749	0.0114_8	0.0363_2	0.0020_2	0.0054_8	164.7
x	0.000376_6	3.752	0.0104_9	0.0359_1	0.0020_2	0.0054_2	165.5
y	0.000416_9	3.761	0.0112_9	0.0369_3	0.0020_3	0.0055_8	164.2
z	0.000403_5	3.770	0.0108_4	0.0372_2	0.0020_4	0.0056_2	164.1
α	0.000430_3	3.776	0.0117_3	0.0366_8	0.0020_5	0.0055_4	165.3
β	0.000322_8	3.779	0.0088_5	0.0364_7	0.0020_5	0.0055_0	165.8
γ	0.000349_7	3.792	0.0094_4	0.0370_4	0.0020_6	0.0055_9	165.4
δ	0.000430_3	3.800	0.0114_7	0.0375_2	0.0020_7	0.0056_7	165.0
ε	0.000376_6	3.810	0.0101_4	0.0371_4	0.0020_8	0.0056_1	166.1
ζ	0.000390_0	3.816	0.0101_7	0.0383_5	0.0020_8	0.0058_0	164.4
η	0.000282_4	3.715	0.0076_6	0.0368_7	0.0019_9	0.0055_8	162.2
ϑ	0.000349_7	3.741	0.0097_8	0.0357_6	0.0020_1	0.0054_0	165.1

magnetic shield. This caused, however, a constant magnetic field which we estimate on account of later measurements to have been about 2 gauss. During the measurements II *p* and *q* the total magnetic field was about 7 gauss. By this the transition point will have been lowered[2]) by an

[1]) Magnetic field on.

[2]) Comp. J. VOOGD. Thesis for the Doctorate, p. 27. Rapports et Communications 6me Congr. Int. du Froid, Buenos Aires 1932. No. 29 § 6.

amount of 0.04 degree, so that the tin in these two experiments was not supraconductive.

A transformation heat at the transition point was not observed.

§ 4. *Conclusions.*

a. It follows from the results plotted in Fig. 1 that between 3.70 and 3.72° K. the atomic heat decreases from a value of 0.0078 to a value of 0.0054.

The temperature interval within which this change of the specific heat occurs can be more closely limited by considering the points II*k* and I*q*. As a matter of fact the final temperature in II*k* was 3.699° K., the initial temperature in I*q* 3.711° K. Considering the fact that we may conclude from the results of these experiments that the change in the specific heat must occur between these temperatures, the temperature interval mentioned must be smaller than 0.012 degree.

b. Comparing the temperatures mentioned under *a* with those at which the metal passes into the supraconductive state [1]), we conclude that the change of the specific heat observed coincides with an accuracy of about 0.01 degree with the transition to the supraconductive state.

In drawing this conclusion we have considered that our tin block was in a constant magnetic field of about 2 gauss (cf. § 3). This would have lowered the supraconductive transition point by about 0.015 degree. This may, however, have been approximately compensated by the effect of mechanical tensions that have arisen in the polycrystalline block during cooling. For these reasons a greater accuracy than 0.01 degree cannot be warranted.

c. The conclusion that the change of the specific heat is connected with the phenomenon of supraconductivity is corroborated by the fact, as shown by the measurements II*p* and *q*, that the larger value of the specific heat is not found if supraconductivity is impeded by the presence of a magnetic field.

d. Whether the change of the specific heat occurs abruptly at a definite temperature or in a small temperature interval will, no doubt, depend on the question whether the transition to supraconductivity occurs at a definite temperature or in a small temperature interval. Though we must leave the final conclusion on this point to further experimental investigation, we think it probable that in the case of a single crystal of pure metal the specific heat undergoes a jump at the supraconductive transition point.

e. Transition to the supraconductive state is not connected with a transformation heat.

We gladly record our thanks to Miss A. P. KEESOM, phil. nat. cand., for her help with the measurements.

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1) Comp. J. VOOGD. Thesis for the Doctorate Leiden. 1931. p. 24. Fig. 4.

Summary.

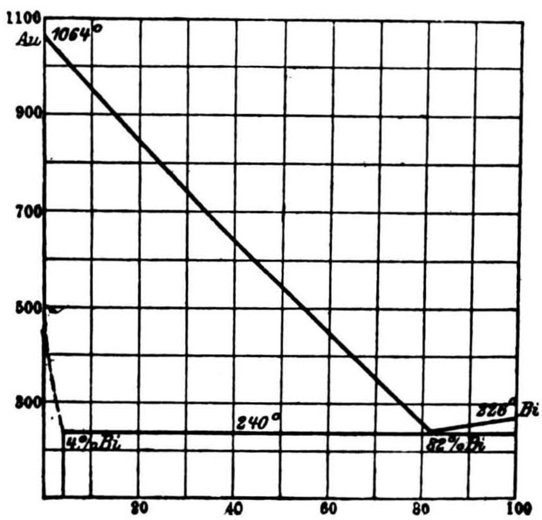
Specific heats of tin were measured between 3.5 and 3.9° K., with heatings of the order of 0.01 degree. Between 3.70 and 3.72° K. the atomic heat decreases from a value of 0.0078 to a value of 0.0054. This change coincides with the transition of the supraconductive to the non-supraconductive state. A magnetic field that impedes the occurrence of supraconductivity prevents also the change in specific heat. Transition to the supraconductive state is not connected with a transformation heat.

Physics. — *The supraconductivity of gold-bismuth.* By W. J. DE HAAS and T. JURRIAANSE. (Communication N⁰. 220*e* from the KAMERLINGH ONNES Laboratory Leiden.)

(Communicated at the meeting of June 25, 1932).

W. J. DE HAAS, E. VAN AUBEL and J. VOOGD found, that the eutectic of the two non-supraconductive metals, gold and bismuth, becomes supraconducting at 1.84° K.

As is evident from the melting diagram of VOGEL [1]), this system consists of two phases viz. a solid solution with the gold lattice in which maximally 4 % Bi is solved and the pure bismuth; fig. 1.



From these measurements the conclusion was drawn, that the supraconductivity was due to the gold phase [2]). To explain this behaviour of the gold-phase we may start from three hypotheses:

1) Zs. f. Anorg. u. allgem. Chem. **50**, 147, 1906.
2) Comm. Leiden No. 197*c*. These Proc. XXXII, p. 724.