

Physics. — *New Super-Conductors.* By EDM. VAN AUBEL, W. J. DE HAAS and J. VOOGD. (Comm. N^o. 193c from the Physical Laboratory at Leiden.)

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§1. *Object of the experiments.*

The behaviour of the electric resistance of compounds of two metals at low temperatures, has not so far been much investigated.

It is known that these compounds at ordinary temperature are sharply distinguished from alloys of the same metals, not in chemical combination, by the extreme values for specific conductivity.

Further, the Röntgen analysis of compounds of two metals has shown that the atoms of the components are arranged regularly in the lattice.

On the basis of these data it seemed to us that it would be of interest to examine the behaviour of the electric resistance at low temperatures.

We wished to pay special attention to compounds in which one of the components belonged to the super-conducting metals.

We examined rods of Cu_3Sb , Ag_3Sb , Ag_3Sn , Cu_3Sn , Bi_5Tl_3 , $SbSn$ and further a rod of probably the compound of Sb and Sn containing 40.21 % Sb in the proportion two Sb to three Sn ¹⁾.

All the rods were prepared by one of us (VAN A.) in the physical laboratory at Ghent.

§ 2. *Resistance measurements between 0° C. and —259° C.*

Although the real object of our investigation was the behaviour of compounds in liquid helium, we determined the resistances over the whole of the above range of temperature. We give the results below, practically without comment.

At each extremity of the rods two wires were soldered on for the resistance measurements. The rods were then placed in open guard-tubes and mounted in the cryostat.

The temperatures were attained by baths of methyl chloride, ethylene, oxygen and hydrogen.

The resistance measurements were made in the usual way with a DIESELHORST thermoforce-free compensation apparatus.

In Table I we give the values for the resistances at 0° C. before and after the measurements. Only in Cu_3Sn does the value seem to have

¹⁾ According to KONSTANTINOW and SMIRNOW the compounds $SbSn$ and Sb_2Sn_3 exist. According to BRONIEWSKI and SLIKOWSKI only the compound Sb_2Sn_3 exists. BRONIEWSKI et SLIKOWSKI, C. R. Paris. 11—6—1928 p. 1615. Revue de métallurgie Paris 6—1928, p. 312.

changed with time. The resistance of Ag_3Sb and of Ag_3Sn changed through a potential wire breaking during the measurements. This had to be repaired, an operation, which slightly shifted the contacts.

TABLE 1.

	Resistance at 0° C. before measurement in liquid Helium	Resistance at 0° after measurement in liquid Helium	Specific resistance $\times 10^3$
Cu_3Sb	0.005150 Ω	0.005146 Ω	0.770
Ag_3Sb	0.020796		
	0.020987	0.020978	1.417
Ag_3Sn	0.003702		
	0.003698	0.003698	0.190
Cu_3Sn	0.000802	0.000826	0.100
Bi_5Tl_3	0.011049	0.011042	0.583
$SbSn$	0.004361	0.004360	0.302
Sb_2Sn_3	0.002575	0.002574	0.250

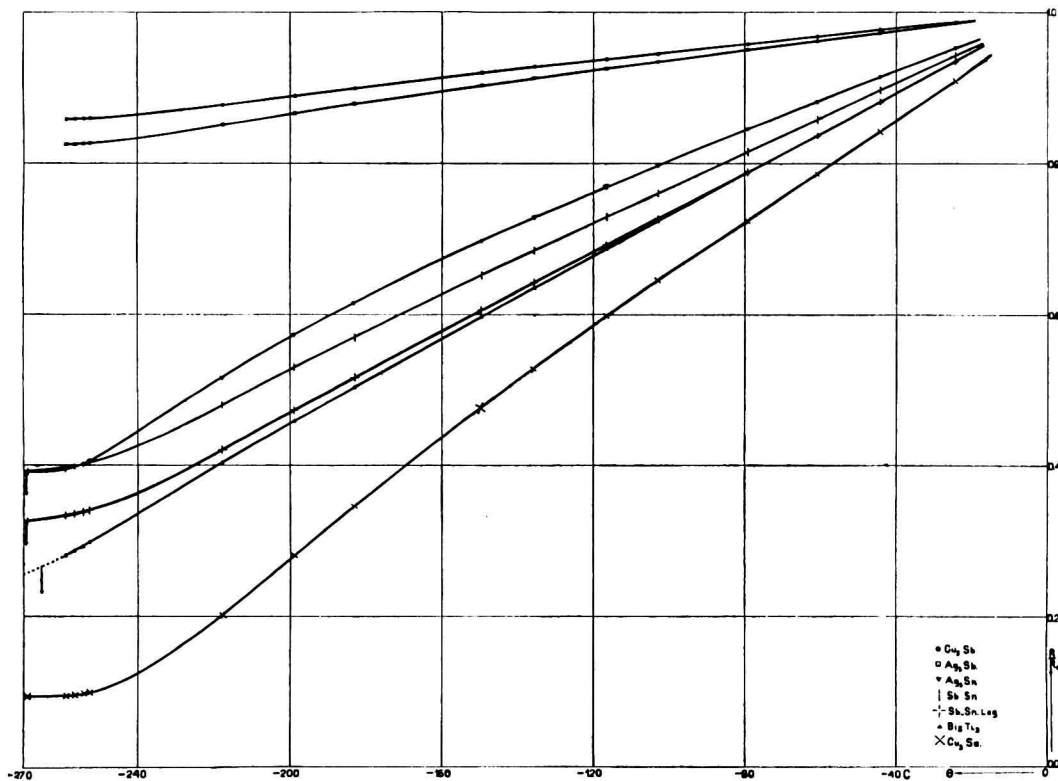


Fig. 1.

From these data and the dimensions of the rods we determined the specific resistances. The values found are given also in Table 1 (accuracy specific resist 1 %).

In Table 2 the values for the resistance, divided by the resistance at 0° C. are given for the different temperatures. In Fig. 1 the course of the resistances is given graphically.

TABLE 2.

θ	Cu_3Sb	Ag_3Sb	Ag_3Sn	Cu_3Sn	Bi_5Tl_3	$SbSn$	Sb_2Sn_3
-24.48					0.9344		
-24.50				0.9081			
-24.51		0.9851					
-24.52	0.9876					0.9424	
-24.53							0.9333
-24.54			0.9528				
-44.27	0.9771	0.9728	0.9148	0.8417			
-44.28					0.8811	0.8962	0.8808
-60.94	0.9682	0.9621	0.8819				
-60.95				0.7852	0.8364		0.8363
-60.96						0.8571	
-79.29	0.9583				0.7871	0.8149	
-79.31							0.7885
-79.32		0.9501		0.7224			
-79.34			0.8453				
-103.09	0.9460		0.7967	0.6453	0.7229	0.7599	0.7265
-103.10		0.9346					
-116.61	0.9386		0.7686	0.5976	0.6864	0.7286	
-116.62		0.9254					0.6917
-135.72					0.6342		
-135.73				0.5271			
-135.74	0.9277	0.9122	0.7274			0.6840	0.6417
-149.65	0.9195		0.6963				
-149.66		0.9023		0.4750		0.6512	

TABLE 2 (Continued).

θ	Cu_3Sb	Ag_3Sb	Ag_3Sn	Cu_3Sn	Bi_5Tl_3	$SbSn$	Sb_2Sn_3
-149.67					0.5962		0.6052
-183.10	0.8985					0.5699	0.5163
-183.11				0.3456	0.5032		
-183.24		0.8779	0.6150				
-198.93	0.8886	0.8657	0.5729		0.4582		0.4728
-198.94				0.2801		0.5297	
-217.86							0.4199
-217.91	0.8767	0.8504	0.5160				
-217.92						0.4802	
-217.93				0.2019			
-217.94					0.4030		
-252.65				0.0998			
-252.66	0.8596	0.8262	0.4054		0.2978	0.4029	0.3391
-254.38	0.8591	0.8255	0.4015	0.0979	0.2927	0.4007	0.3368
-256.62	0.8587	0.8247	0.3972	0.0961	0.2865	0.3984	0.3344
-258.99	0.8582	0.8242	0.3937	0.0947		0.3964	0.3323
-259.00					0.2804		

§ 3. Graph of Table 2.

Our results show that the resistances of Cu_3Sb and Ag_3Sb depend little upon the temperature. This was to be expected by analogy with MATTHIESEN'S rule on account of the relatively high values of the specific resistance of these substances.

Further we found that the resistance of all the rods decreased less than that of their components.

Finally we wish to draw attention to the fact that all the resistance lines show an inflection point. This phenomenon is known to occur in some simple conductors.

§ 4. Resistance measurements in liquid helium.

For this, the most important part of the investigation, the resistances of Ag_3Sn , Cu_3Sn , Bi_5Tl_3 , $SbSn$ and Sb_2Sn_3 were mounted in the Helium cryostat.

In Tables 3, 4, 5, 6 and 7 the values for R/R_0 at the different temperatures

TABLE 3.

Bi_5Ti_3		
T	P_{helium}	R/R_0
4.2	760	0.0000

TABLE 4.

Sb_2Sn_3		
T	P_{helium}	R/R_0
		170 m.A.
4.20	760	0.3257
4.10	689	0.3196
4.00	622	0.0637
3.95	589	0.0062
3.80	500	0.0000

TABLE 5.

$Sb-Sn$				
T	P_{helium}	R/R_0		
		170 m.A.	85 m.A.	17 m.A.
4.20	760	0.3917		
4.10	689	0.3911		
4.00	622	0.3672		
3.95	589	0.3080	0.2995	0.277
3.80	500	0.0927		
3.75	473	0.0616		
3.73	463	0.0537		
3.65	421	0.0349		
3.55	369	0.0261		

TABLE 6.

Ag_3Sn				
T	P_{helium}	R/R_0		
		147 m.A.	37 m.A.	10 m.A.
4.22	775	0.3865	0.3864	
3.42	311	0.3857		
3.00	165	0.3492		0.336
2.52	64	0.2838		0.250
1.99	17.5	0.2230		0.178
1.36	2.3	0.1668		0.111

TABLE 7.

Cu_3Sn					
Date	T	P_{helium}	R/R_0		
			140 m.A.	80 m.A.	14 m.A.
29—11—'27	4.20	760	0.095 ⁰		
..	3.80	500	0.094 ⁹		
..	3.55	369	0.094 ⁹		
..	2.89	136	0.095 ²		0.09 ⁹
20—1—'28	1.80	10.0		0.093	0.09 ¹
..	1.54	5.6		0.093	0.09 ⁴
..	1.31	1.9		0.092	0.09 ⁰

are given. In the regions of rapid decrease of resistance OHM's law becomes invalid on account of the sensitivity of the resistance to current. Where this was the case we have usually made measurements with various strengths of current. As value for the resistance, in these cases the quotient of potential difference and strength of current is taken as usual. The results are seen in Fig. 2.

§ 5. We found, accordingly, that in the resistances of Bi_5Tl_3 , $SbSn$ and Sb_2Sn_3 the phenomenon of supra-conductivity is developed. *It is very*

surprising that the rod of $\text{Bi}_5\text{-Tl}_3$ becomes super-conducting even above the boiling point of helium.

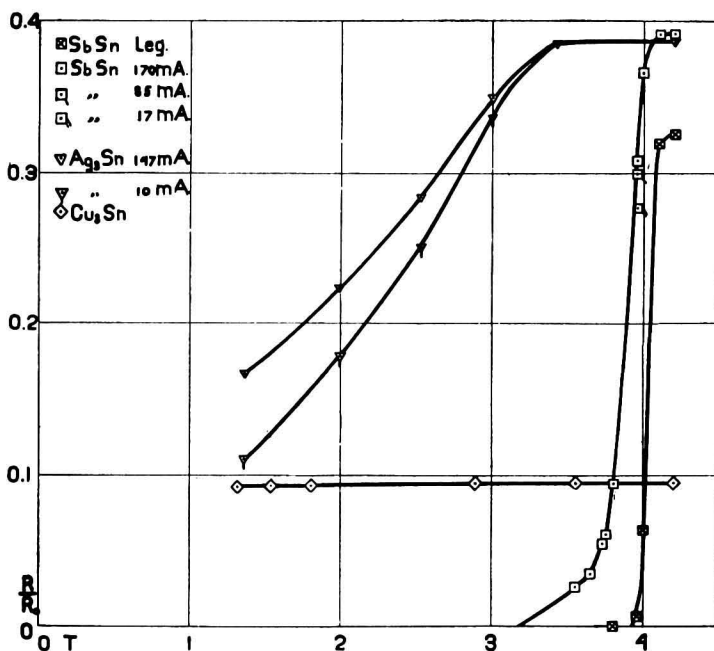


Fig. 2. 1)

Thallium only becomes super-conducting at 2.47°K . and bismuth retains its full resistance certainly down to 1.5°K .

We thus find an enormous elevation in the transition point. We might suspect this to be due to an impurity of lead, of which the metals used for the compounds certainly contained a slight amount. As, however, this amount is not sufficient in either metal to make the resistance disappear above $4^\circ.2 \text{K}$. 2) we do not think it probable that the high transition point of Bi_5Tl_3 is due to this.

The behaviour of SbSn and of Sb_2Sn_3 are in support of this.

Here also the fall of resistance begins at higher temperatures than with pure tin ($3^\circ.8 \text{K}$). The tin used ("Kahlbaum") is very pure.

As the antimony-rich Sb-Sn becomes superconducting at a lower temperature than the antimony-poorer Sb_2Sn_3 , it is impossible to assume an influence of possible lead impurity in the antimony upon the shifting of the transition point.

Thus we see that in these three substances super-conductivity is more easily induced than in their super-conducting components.

This peculiarity in two super-conducting components had already been

1) \square Sb Sn leg. in Fig. 2 should be after BRONIEWSKI and SLIKOWSKI Sb_2Sn_3 .

2) Bi en Tl from KAHLEBAUM from which the preparation was made have been examined on a former occasion.

observed by KAMERLINGH ONNES with an amalgamated tin-foil. That it is not a general rule, however, is proved by the course followed by the resistance in Ag_3Sn and Cu_3Sn .

With Ag_3Sn there was a relatively large fall of the resistance and a great sensitivity to current. It is possible that these phenomena were brought about by an excess of tin in the rod. In that case pure Ag_3Sn would be able to retain its residual resistance down to the lowest temperatures.

This question must be decided by further experiments, but at any rate it is certain that at the temperatures investigated, this tin-rich compound did not become super-conducting.

With Cu_3Sn this fact was even more clearly demonstrated. Here the residual resistance remains constant down to the lowest temperature, and the metal behaves like a normal non-super-conductor.

In conclusion we have great pleasure in thanking Mr. W. H. CAPEL for his assistance in the observations and the calculations.
