Physics. — *Measurements on Thermo-Electric Forces down to Temperatures Obtainable with Liquid Helium.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N⁰. 217e from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 30, 1932.)

§ 1. *Introduction.* This paper deals with the measurements on thermo-electric forces referred to in Comm. N⁰. 217*d*, of platinum and of some binary alloys of *Cu* with small quantities of *Fe*, which were investigated down to the temperatures obtainable with liquid helium. For the method followed and the apparatus used we refer to §§ 1 and 2 of the paper mentioned.

§ 2. *Results for Pt and an alloy of Pt with Au.* It seems to be rather difficult to get an accurate knowledge of the thermo-electric properties of real pure, not supraconducting metals at the lowest temperatures, as small impurities seem to have a great influence here. Measurements of commercial pure metals will probably only give an approximate orientation. We have tried to get such an orientation by measurements on physically pure *Pt* from HERAEUS in Hanau and on pure *Cu* obtained for spectroscopic purposes from HILGER in London.

The copper contained, however, according to the report of a spectroscopical analysis got from the firm, 0.004 at. % *Fe*, and this impurity was, as will be seen in the next paragraph, sufficient to give thermo-electric properties quite different from those of pure copper.

The platinum gave the values collected in table I and the curve marked Pt_{31} in Fig. 1. The curve crosses the axis at 12° K. and seems to approach the absolute zero point from the negative side of the axis. However, we are not allowed to assume that this should be characteristic of the pure *Pt*. Our earlier measurements on dilute alloys of *Pt* with *Rh* [1]), as well as new measurements on *Pt* with 4.0 at. % *Au* down to the temperature of liquid hydrogen and in fact all our experiences hitherto from the lowest temperatures show, that dilute alloys are thermo-electrically negative against the corresponding pure metal. Thus it is quite possible that the negative values (negative also in the absolute thermo-electric scale) arise from impurities. In fact another sample of physically pure *Pt* from HERAEUS measured in 1929 [2]) and given again in Fig. 1 as Pt_{29} lies more to the positive side.

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

TABLE I.

Thermo-electric force in microvolt per degree for pure and alloyed Pt against silveralloy-normal.					
Pt_{31} (Heraeus)				Pt + 4 at. % Au	
°K.	e	°K.	e	°K.	e
4.15	—0.6	24.0	+2.07	17.4	0.00
5.17	0.81	30.3	3.07	17.4	—0.02
5.42	0.78	36.7	3.88	24.7	+0.54
7.72	0.55	42.7	4.38	31.3	1.06
7.78	0.59	47.2	4.88	38.3	1.58
10.4	0.23	58.9	4.97	45.8	1.98
10.6	0.16	67.9	4.95	50.6	2.06
10.8	0.17	79.0	4.73	62.1	2.15
11.3	0.04	86.2	4.26	68.0	2.14
12.5	+0.07	94.2	4.00	102.0	1.06
13.3	0.27	102.7	3.57	295.0	—7.95
17.3	0.92	275.4	—5.18		

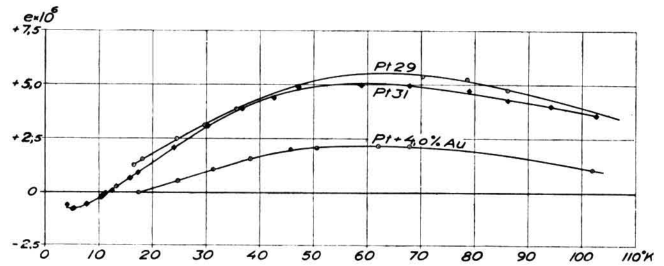

Fig. 1. Thermo-electric force in volt per degree. Against silveralloy normal.

§ 3. *Cu with small quantities of Fe.* The interesting high thermo-electric forces, obtained from our earlier measurements for an alloy of *Cu* with only 0.075 at. % *Fe* at the temperature of liquid hydrogen (Comm. N°. 206*b*), have led to a comprehensive investigation of the thermo-electric forces of copper with small quantities of *Fe* as a function of temperature and concentration and to the use of those dilute alloys for an examination of the way in which the thermo-electric force decreases as the absolute temperature approaches to zero. Besides the wire with 0.075 at. % *Fe*, for which we have got results in good agreement with our earlier measurements, we have measured alloys of *Cu* with 0.004, 0.03, 0.10, 0.30 and 0.87 at. % *Fe*, the four first of them down to the temperature of liquid helium. The alloys were made from a copper from HILGER (containing 0.004 at. % *Fe*) by melting with *Fe* in vacuum. They were carefully homogenised and the homogeneity was controlled by measurements of the electrical resistance in different parts of the sample. The concentrations were obtained by weighing and by the measurements of the electrical resistance. The results of the thermo-electric measurements have been collected in table II and are shown graphically in Fig. 2. In this Figure we also give again the results of earlier measurements (Comm. N⁰. 206*a*) on technically pure *Cu*.

TABLE II.

Thermo-electric force in microvolt per degree for dilute alloys of Cu with Fe against silveralloy-normal.

Cu + 0.004 at. % Fe				Cu + 0.03 at. % Fe			
°K.	*e*	°K.	*e*	°K.	*e*	°K.	*e*
1.63	1.97	22.6	8.06	1.63	3.76	22.6	14.92
1.73	2.15	24.0	7.98	1.73	4.20	24.0	14.96
1.73	2.17	24.0	8.04	1.73	4.28	24.0	15.05
3.00	3.98	27.2	7.12	3.00	6.95	27.2	14.35
3.84	4.82	30.4	6.44	3.84	8.13	30.4	13.68
5.22	6.34	30.5	6.41	5.22	10.35	30.5	13.74
5.73	6.66	31.5	6.12	5.73	10.71	31.5	13.66
5.88	6.85	36.1	4.95	5.88	10.97	36.1	12.52
6.57	7.06	36.7	4.90	6.57	11.57	36.7	12.40
7.25	7.62	36.9	4.85	7.25	12.04	36.9	12.35
8.20	8.06	42.5	3.65	8.20	13.53	42.5	11.22
9.17	8.61	42.6	3.67	9.17	13.38	42.6	11.27
9.72	8.91	43.3	3.44	9.72	13.65	43.3	10.97
9.96	9.52	48.0	2.61	9.96	14.05	48.0	9.80
11.8	9.23	48.0	2.62	11.8	14.84	48.0	9.87
16.8	8.92	65.9	0.81	16.8	15.02	65.9	6.58
17.3	9.12	84.1	0.30	17.3	15.20	84.1	5.10
17.3	9.16	93.8	0.18	17.3	15.25	93.8	4.56
21.0	8.62			21.0	15.32	275.6	1.62

TABLE II *(Continued)*.

Cu + 0.075 at. % Fe		Cu + 0.10 at. % Fe		Cu + 0 30 at. % Fe		Cu + 0.87 at. % Fe	
°K.	e	°K.	e	°K.	e	°K.	e
17.0	−15.72	2.50	−6.34	2.50	−3.92	17.3	9.78
22.2	15.94	2.62	6.56	2.62	4.18	17.3	9.83
22.7	15.92	3.45	7.88	3.45	5.23	17.4	9.83
26.1	15.60	3.50	7.92	3.50	5.31	17.4	9.83
26.6	15.95	5.30	10.27	5.30	6.95	17.4	9.93
31.2	15.46	7.30	12.09	7.30	8.41	23.9	10.98
34.9	15.00	11.1	14.82	11.1	12.07	23.9	11.10
35.3	14.82	13.3	15.27	13.3	13.10	30.3	11.79
42.5	13.78	17.0	15.75	17.0	13.27	30.4	11.76
52.0	12.18	22.2	16.08	22.2	13 96	36.5	12.15
64.0	10.70	22.7	16.50	22.7	14.40	36.8	12.14
70.5	10.15	26.1	15.76	26.1	14.14	42.5	12.44
85.1	8.72	26.6	15.75	26.6	14.38	42.8	12.37
95 3	7.98	31.2	15.76	31.2	14.53	48.0	12.37
275.8	3.92	34.9	15.32	34.9	14.40	48.0	12.44
		35.3	15.32	35.3	14.54	59.3	12.03
		42.6	14.32	42.5	14.36	62.1	11.98
		52.0	12.97	52.0	14.58	68.0	12.05
		64.0	11.74	64.0	14.37	68.3	11.97
		70.5	10.84	70.5	13.38	77.3	11.98
		85.1	9.74	85.1	12.42	85.9	11.95
		95.3	8.96	95.3	11.80	94.0	12.34
		275.8	4.66	275.8	8.47	102.0	12.04
						102.2	11.95
						275.6	10.55

The results seem to state rather clearly that the thermo-electric force per degree (e) is in the neighbourhood of the absolute zeropoint proportional to the absolute temperature (T). With increasing temperature e first reaches a (negative) maximum and then decreases. With increasing

concentration (c) the maximum is displaced toward higher temperatures.
From the measurements we have also calculated diagrams giving e as

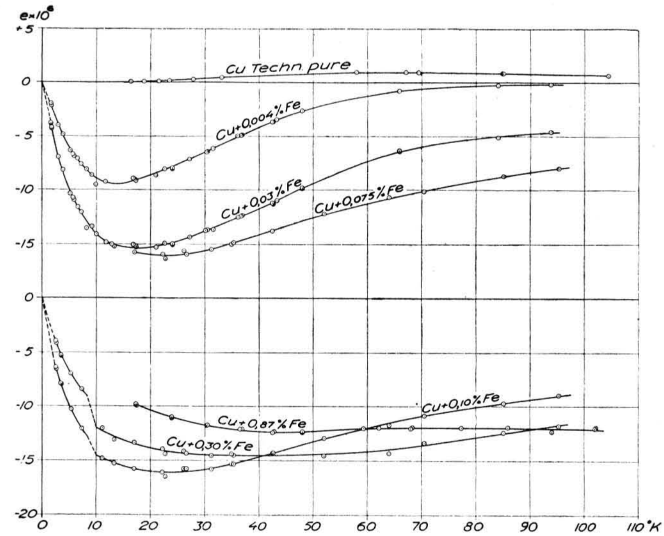

Fig. 2. Thermo-electric force in volt per degree. Against silveralloy normal

a function of c for different constant temperatures. Such isotherms have been put together in Fig. 3. The curves show a striking likeness to the curves in Fig. 2. An analysis of e as a function of T and c looks very interesting and will probably be carried out later on.

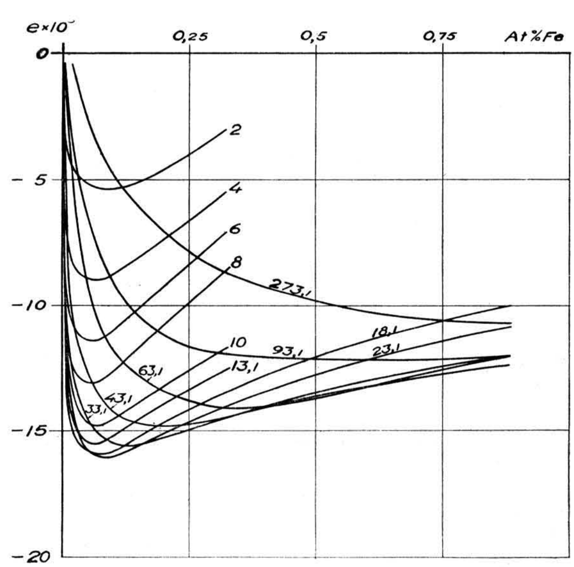

Fig. 3. Thermo-electric force in volt per degree for dilute alloys of *Cu* with *Fe* as a function of the concentration of *Fe*. The numbers give the temperature of the isotherms in the Kelvin-scale. Against silveralloy-normal.

The alloys with 0.1 and 0.3 at. % *Fe* show, between 8 and 10° K., a discontinuity as well in thermo-electromotive force (see Fig. 4) as in the thermo-electric force per degree (see Fig. 2). Possibly the fact that in Fig. 2 for *Cu* with 0.03 and 0.004 at. % *Fe* the points for the temperature range mentioned lie a little beside the curves, is also a sign of traces of such a discontinuity. The discontinuity in the alloys with 0.1 and 0.3 at. % *Fe* was studied by repeated variations of the temperature up and down and was proved to be reversible. For the present the nature of the discontinuity is, however, quite unknown.

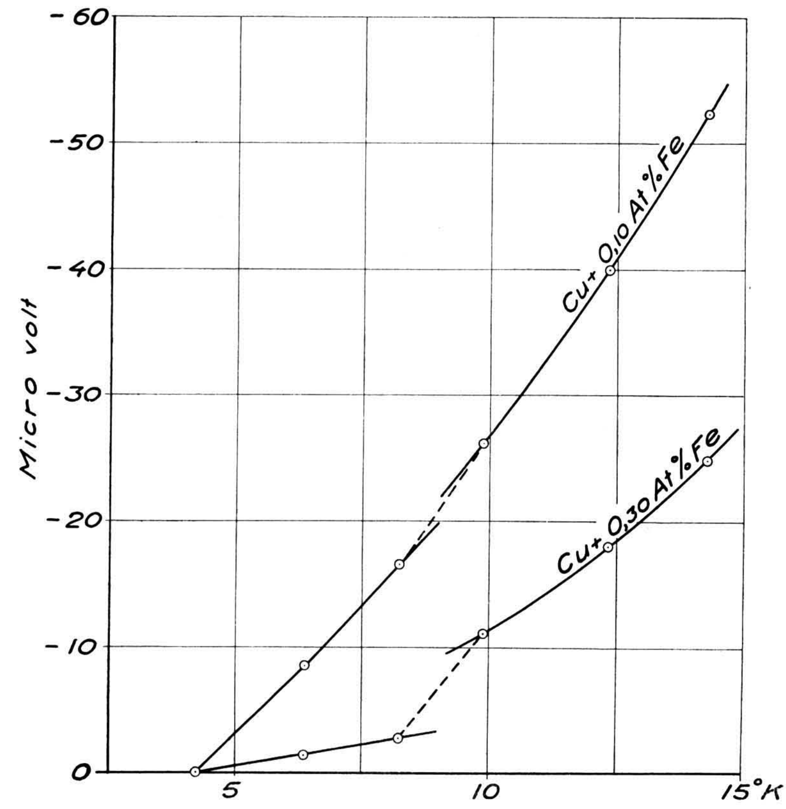

Fig. 4. E. m. f. against *Cu* with 0.004 at. % *Fe*. Cold junction at 4.24° K.

It may be mentioned, that the alloys of *Cu* with *Fe* are highly supersaturated at room temperature and are obtained as homogeneous solid solutions, at the highest concentrations here used, only by rapid cooling from about 800° C. According to TAMMANN and OELSEN [1]) the solubility of *Fe* in *Cu* should be only 10^{-11} at. % *Fe* in the equilibrium state at room temperature (extrapolated value). The supersaturated state is, however,

[1]) G. TAMMANN and W. OELSEN, Z. f. allg. u. anorg. Chem. **186**, 257, 1930.

known as practically stable at all temperatures for concentrations below about 0.1 at. % *Fe*.

§ 4. *Thermo-electric forces per degree at corresponding temperatures.* The tables III and IV give graphically interpolated values of the thermo-electric forces against the normal of the wires dealt with in this paper.

In Table III we added corresponding values for lead and tin and for pure and alloyed silver derived from the results obtained in Comm. N⁰. 217*c* and N⁰. 217*d*.

Above —255° C. the temperatures are the same as those given in the corresponding tables of our earlier papers. The thermo-electric force per degree on the absolute thermo-electric scale is obtained by adding the values of table III of Suppl. N⁰. 69*b*.

TABLE III.

Thermo-electric force in microvolt per degree against silveralloy-normal.							
°K.	°C.	Pb	Sn	Ag_{31}	Ag + 0.91 at. % Au	Pt_{31}	Pt + 4.0 at. % Au
2.0	—271.1	0.00	0.00				
4.0	269.1	0.00	—0.01			—0.73	
6.0	267.1	—0.01	0.05			0.74	
8.0	265.1	0.13	0.11			0.55	
10.0	263.1	0.43	0.19	+0.15		0.27	
13.1	260	0.82	0.39	0.21		+0.23	
18.1	255	1.01	0.75	0.35	—0.16	1.05	+0.03
23.1	250	1.10	1.01	0.49	0.20	1.92	0.42
28.1	245	1.14	1.22	0.63	0.23	2.73	0.82
33.1	240	1.17	1.40	0.71	0.27	3.45	1.20
38.1	235	1.19	1.53	0.73	0.30	4.03	1.55
43.1	230	1.21	1.66	0.71	0.32	4.50	1.85
53.1	220	1.22	1.77	0.60	0.33	4.98	2.12
63.1	210	1.23	1.83	0.49	0.33	5.03	2.15
73.1	200	1.24	1.88	0.41	0.33	4.80	2.05
83.1	190	1.26	1.94	0.34	0.34	4.44	1.81
93.1	180	1.32	1.99	0.29	0.34	4.03	1.45
103.1	170		2.03	0.28	0.35	3.57	1.01
275.6	+ 2.5		2.43	0.21	0.38	—5.18	

TABLE IV.

Thermo-electric force in microvolt per degree against silveralloy-normal.

°K.	°C.	Cu + 0.004 at. % Fe	Cu + 0.03 at. % Fe	Cu + 0.075 at. % Fe	Cu + 0.10 at. % Fe	Cu + 0.30 at. % Fe	Cu + 0.87 at. % Fe
2.0	−271.1	−2.6	−4.85		−5.35	−3.35	
4.0	269.1	5.05	8.65		8.75	5.85	
6.0	267.1	6.9	11.1		11.0	7.55	
8.0	265.1	8.05	12.8		12.6	9.0	
10.0	263.1	8.95	14.1		14.55	12.0	
13.1	260	9.55	15.0		15.2	12.8	
18.1	255	8.95	15.4	−15.85	15.85	13.65	−10.05
23.1	250	8.0	14.95	16.05	16.1	14.2	10.9
28.1	245	6.9	14.15	15.8	15.95	14.4	11.6
33.1	240	5.75	13.15	15.2	15.5	14.6	12.05
38.1	235	4.6	12.1	14.4	14.95	14.55	12.3
43.1	230	3.5	11.05	13.6	14.25	14.55	12.4
53.1	220	1.9	8.7	12.1	12.85	14.4	12.25
63.1	210	1.0	6.75	10.9	11.7	14.05	12.05
73.1	200	0.5	5.7	9.8	10.65	13.4	12.0
83.1	190	0.3	5.05	8.9	9.85	12.65	12.0
93.1	180	0.2	4.7	8.1	9.15	11.9	12.05
103.1	170						12.15
273.1	±0		1.66	3.98	4.72	8.52	10.57

§ 5. *Thermo-couples for temperature measurements at low temperatures.* From this and the preceding paper (Comm. N⁰. 217*d*) one may conclude that the dilute alloys of *Au* with *Co* or *Fe* and of *Cu* with *Fe* may be used as sensible thermo-couples for temperature measurements at low temperatures. The gold-alloys are to be preferred as they are not supersaturated at room temperature and hence are obtained in the homogeneous state without rapid cooling. As a promising couple we may propose a combination of a dilute alloy of *Au* with *Co*, say one with about 1 at. % *Co*, and a dilute *Ag Au*-alloy with about 1 at. % *Au*. As will be seen from Figs. 1, 5 and 6 and Tables I and III of Comm. N⁰. 217*d* this couple will have high values of the thermo-electric force per degree (*e*) for all temperatures from the icepoint down to the lowest temperature of liquid hydrogen. So it will give in microvolt per degree: at $\pm 0^\circ$ C. about 37, at -180° C. about 34, at -220° C. about 28, at -250° C. about 17, and at -255° C. about 14. Also at the temperature of liquid helium high values of e may be expected if they diminish with the temperature in the same way in the system *Au-Co* as in the system *Cu-Fe*. As to the proposed silver-alloy it appears from the diagram of the absolute thermo-electric force (Fig. 2 of Comm. N°. 217*d*), that it may be expected to give rather small thermo-electric variations of its own and thus lead to a smooth e, T-curve. *Ag* is to be preferred to *Cu* or *Au* as it is easier to get it free from traces of *Fe*, and alloyed *Ag* is to be preferred to the pure metal also for the reason that the thermal conductivity does not increase to unsuitable high values at the lowest temperatures. Of course special measurements are necessary to find the most suitable concentrations and to confirm the expectations as to the usefulness of the thermo-couple also in the liquid helium temperatures.

We are glad to record our thanks to the NOBEL-committee for physics, who supported our researches by a subvention.

Summary.

Thermo-electric forces against a silveralloy-normal were measured down to the temperatures which are obtainable with liquid helium, for *Pt* and for alloys of *Cu* with small quantities of *Fe*.

For the last-mentioned alloys the thermo-electric force per degree near absolute zero is proportional to T. At increasing temperatures e reaches a maximum, after which e decreases. With increasing concentration of *Fe* this maximum is displaced towards higher temperatures.

As a sensitive thermo-element for the temperature range of liquid hydrogen and liquid helium the authors recommend the combination *Au* with about 1 at. % *Co* against *Ag* with about 1 at. % *Au*.

Astronomy. — *Mittlere Lichtkurven von langperiodischen Veränderlichen.* VI. *R Cygni.* Von A. A. NIJLAND.

(Communicated at the meeting of January 30, 1932.)

Instrumente: *S* und *R*. Die Beobachtungen wurden alle auf *R* reduziert: die Reduktion $R-S$ beträgt $-0^m.34$. Spektrum Se (*Harv. Ann.* 79 S. 187).

Gesamtzahl der hier zu besprechenden Beobachtungen 729 (2416826 bis 2426648).

Karte: HAGEN, *Atlas Stell. var. Series III.*

Der Stern *B* kommt mit den Helligkeiten $6^m.48$, $6^m.39$ in *Harv. Ann.* 74 vor. Die Stufenskala bezieht sich auf die Grösse $10^m.0$; der Stufenwert