Upon the dependency of the specifical resistance of some metals on pressure.*

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1. The dependence of the specifical resistance of the metals on pressure was investigated first by *Chwolson, Tomlinson* and *Lussana* and then by *Lisell,*[1]) *E. Williams,*[2]) *Lafay*[3]) and *Beckmann.*[4]) While the results obtained by the three first mentioned authors are not in concordance, the results of the four later mentioned experimentators show quite a good agreement also relative the numerical values of the coefficients of pressure of the specifical resistance of some metals. They have proved that the specifical resistance of the pure metals is diminished by increasing pressure, the relative diminution being proportional to the pressure. The relative change by increasing pressure of the specifical resistance of the alloys is less than that of the pure components and the change of resistance may be not only negativ as that of the pure metals, but also positiv after passing through zero, as this is shown by manganin. *Williams* observed, that among the pure metals bismuth shows an exceptional behaviour as his specifical resistance increases by increasing pressure.

The older theory of electrons of the conduction of electricity through metals was not able to account for the diminution of the specifical resistance of the pure metals by increasing pressure. By this theory the contrary effect may be rather

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1) Erik Lisell, Inaug. Diss. Upsala, 1902.

2) E. Williams, Phil. Mag. (6) 13, p. 635, 1907.

3) Lafay, Ann. de Chim. et de Phys. (8) 12, p. 289, 1910.

4) Bengt Beckmann, Inaug. Diss. Upsala, 1911.

suggested, because the compression is staying the movement of the electrons by approaching the atoms to each-other.

The measurement of the change by temperature of the specifical resistance of the metals especially at very low temperatures showed an doubtless connection between the specifical resistance and the caracteristical frequency of the metal, which determines the value of the atomic heat in the theory of atomic heat of Debye.[1]) It could be concluded from the experiments for instance (I.), that the specifical resistance of the monoatomic pure metals is proportional at low temperatures to one universal function of $\frac{T}{\beta\nu}$ alone, where T designates the absolute temperature, ν the caracteristical frequency, β being the wellknown constant of the theory of radiation of Planck. And E. Grüneisen[2]) stated the empirical result also (II.), that the specifical resistance divided by the absolute temperature is proportional at low temperatures to the atomic heat, this remarkable result being precisely verified by the experiments. W. Wien[3]) has undertaken to give an explanation of this obvious connection between the specifical resistance and the atomic heat by means of the theory of quanta. He gives for the specifical resistance w the expression:

$$w = \frac{2\,m\,u}{e^2\,N\,l}$$

where e is the charge, m the mass, u the velocity and l the mean free path of the electron, and N their number in a cm^3. The velocity u and the number N are independent of the temperature. Therefore w can only depend on the temperature by means of l. Wien assumes the electrons moving in channels among the atoms. It is evident that an electron can travel along such a channel as more easier as the walls of the channel are smoother and the channel is straighter. Therefore the movability of the electrons shall be greater, when the amplitudo of the oscil-

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1) P. Debye, Ann. d. Phys. (4), 39, p. 789 (1912).
2) E. Grüneisen, Ber. d. Deutschen Phys. Gesp. p. 186 (1913)
3) W. Wien, Sitzungsber. d. Berl. Akad. p. 184 (1913)

lations of the atoms, they are forming the walls of the channel, become smaller. Wien is concluding in this way, that the mean free path of the electrons is inversely proportional to the square of the amplitudo of the oscillating atoms and further, as this amplitudo is increasing with increasing temperature, that the specifical resistance shows the same behaviour i. e. increases with increasing temperature. Putting this ideas in mathematical form he has obtained the following formula:

$$\frac{1}{l} = C \frac{h}{M \nu v} f \left(\frac{T}{\beta \nu} \right);$$

where C denotes a constant, M the atomic weight, v the atomic volume and h the constant of the theory of radiation of Planck. The specifical resistance shall be then proportional to f $\left(\frac{T}{\beta \nu}\right)$. The experimental results described in (I) Wien's theory accounted for, but the special form of the function f, determined by Wien, gives only in a very rough approximation the dependency of the specifical resistance on the temperature. The explanation of Grüneisen's results, which are more special, is not yet given by means of the theory of quanta. It is all the more remarkable, that Wien's theory is accounting for the dependency of the specifical resistance on pressure, as it was shown by Grüneisen.[8]) The following formula has been deduced by Grüneisen from Wien's theory for the isothermical coefficient of pressure of the specifical resistance:

$$\frac{1}{w} \left(\frac{\partial w}{\partial p} \right)_T = \frac{1}{u} \left(\frac{\partial u}{\partial p} \right)_S - \frac{1}{N} \left(\frac{\partial N}{\partial p} \right)_S +$$
$$+ \varkappa_S - \frac{1}{c_p} \left(\frac{\partial v}{\partial T} \right)_p \left[1 + a_T \, T \right],$$

where p denotes the pressure, $\varkappa_S$ the adiabatic compressibility, Cp the atomic heat and

$$a_T = \frac{1}{w} \left(\frac{\partial w}{\partial T} \right).$$

The first two terms of the right hand side of this equation constitute by the evaluation of Grüneisen only a small amount of the value of the complete right hand side and on the other hand it is

$$\varkappa_S < \frac{1}{c_p}\left(\frac{\partial v}{\partial T}\right)_p.$$

We may conclude therefore from this equation, that the specifical resistance is diminished by increasing pressure. This agrees with the results of the experiments, except the researches of Williams on bismuth. Grüneisen has calculated with this formula the coefficient of pressure of the specifical resistance of several metals and he had published the following table of computed and observed values:

		Al	Ni	Cu	Ag	Cd	Pt	Au	Pb
$-\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T \cdot 10^6$	observed	4,3	1,6	2,2	3,9	10,0	2,0	3,0	15,0
	calculated	4,2	2,0	2,3	3,9	8,5	1,7	3,0	10,5

He neglected the first term on the right hand side of the equation, containing the influence of pressure on the velocity of the electrons, as being very small also by Wien's evaluation and employs only the three other terms for the calculation of

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T.$$

As the dimensions of the wire change by pressure, the observed values of the coefficient of pressure of the specifical resistance shall be corrected by adding $-\frac{1}{3}\varkappa_S$ to them. All the investigated metals are enumerated in the table. (Pb, Al Williams; Pt Lafay; Cu, Ni, Pb, Ag, Pt, Lisell; Au, Cd Beckmann.) The concordance of the observed and calculated values in the cases of Al, Cu, Ag, and Au is as well, that we may consider the above mentioned neglection as justified. But there are also some discrepencies. The values in the table are given for the temperature of the melting ice. The melting-temperatures of Pb and Cd lying not high enough in comparison with this temperature, this may be the probable cause, as Grüneisen observed, of the discrepency of the observed and calculated values in the case of this metals. In the case of Ni the calculated value is greater than the observed. This may be explaned by a little impureness of the wire, this circumstance diminishing the value of $\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T$. But in the case of Pt the observed value being greater than the calculated, this may be nor accounted for bÿ impureness, never by the circumstances mentioned in the case of Pb, for the melting temperature of Pt is one of the highest among the metals. This behaviour of Pt seems also to indicate an inefficiency of the theory. In the view of the exceptional theoretical interest of the value of $\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T$ for Pt I have undertaken a new and careful determination of it and also a new investigation of the exceptional behaviour of Bi. The coefficient of pressure of the specifical resistance of some other wires were determined in connection.

2. The employed wire was wound up in very loose spirals on an ebonit whin and this was placed in the cylindrical hole of an iron-vessel of very thick walls entirely filled up with lenseed-oil. One end of the wire was soldered to the insulated cable leading through the lid of the iron-vessel and the other end dived in the mercury unto the bottom of the vessel. The required pressure was furnished by one compressor of the *Société Genevoise* and measured by one manometer of *Schäffer and Budenberg*. To obtain a sufficient sensibility of the resistance-measurements I have increased the resistance of the wire of the Hartmann & Braun Wheatstonebridge to the hundredfold of its original value, by adding resistances to his two ends from resistance-boxes of precision of Hartmann & Braun. The resistances required on the two ends of the Wheatstone-bridge-wire were determined by the postulate to have the position of zero in the wire itself. The measurements were made with stationar-current and employing a Deprez-galvanometer of Hartmann & Braun as zero-instrument, the sensibility of which was: 1 mm. deviation on a scaledistance of 1 m. by the current of 10^{-9} Ampére. Considering now the facts, that the coefficient of temperature of the specifical resistance is much greater, for example in the case of Pt about two thousandfold greater than the coefficient of pressure of the specifical resistance and that

the time required for one set of measurements is 8 to 10 hours, we see that the greatest care must be taken to eliminate during this time the disturbing influences of the changes of temperature. For this purpose the iron-vessel was dipped in a water-bath, and this was covered on each side with a wollen wall of a thickness of 10 cms. and then it was wholly surrounded by a big doublewalled tin-vessel containing about third a cubicmeter of water and having a wall-distance of about 10 cms. The whole apparatus was kept in an entirely dark room and the measurements were made on clouded summernights. When the wire was placed in the iron-vessel, the apparatus was left for some days, to allow the differences of temperature to equate themselves. By this precautions I reached, that the mean change of temperature in the inner water-bath during a whole set of measurements happened to be only $\frac{1}{100}{}^{0}$ C. The temperature of the inner water-bath was measured close by the iron-vessel with a Beckmann-thermometer passing through the different walls.

One hour after the compression or expansion in the iron-vessel the changes of temperature of the oil caused by them were equated and the temperature read off on the Beckmann-thermometer could be identified with the temperature of the wire. This is proved by the fact, that the résistance of the wire on a constant pressure of 1 atmosphère was a linear function of this temperature. Notwithstanding I was waiting after each compression for two hours before measuring the resistance of the compressed wire and reading off at the same time the manometer also. The data of the manometer had been controlled with the aid of a manganin-wire. The resistance r of a manganin-wire is increasing by pressure and the value obtained by Lisell for $\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T = +23 \times 10^{-6}$ and Williams observed $\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T = +22{\cdot}2 . 10^{-6}$.

The value of the coefficient of temperature of the manganin-wire-resistance being only a small amount, about $\frac{1}{100}$ of the value of the same coefficient for the pure metals, the changes by pressure of a manganin-resistance may be well employed for pressure-measurements. Lisell has proposed first the construction of manganin-wire-manometers for the measurements of high pressures. The coefficient of pressure of the manganin-wire, I employed, was $\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T = + 22{\cdot}2 \times 10^{-6}$ and the differences of pressures calculated by this value and read off on the Schäffer and Budenberg-manometer were less than $\pm$ 2%. A regular deviation of the data of the manometer, resulting from elastic hysteresis therefore could not be observed.

3. The Pt-wire of a thickness of 0·2 mm. employed to the measurements was purchased from *A. Kahlbaum.* His resistance was $r = 7{\cdot}9177$ Ohm at a temperature of 16·026° C. The results obtained are as follows:

Δr Ohm	p Atm.	t_B	$-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$
—0·0043	306	16·026	1·78
—0·0086	606	"	1·79
—0·0125	837	"	1·88
			1·82
—0·0045	306	16·265	1·85
—0·0086	601	"	1·80
—0·0125	843	"	1·89
			1·84

The third column contains the temperature at the beginning of the observations. The values of Δr in the first set are reduced to this temperature by means of the data of the Beckmann-thermometer, while in the second set the temperature was kept entirely constant. The value for $-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$ my observations lead to, agrees well with thus determined by the former observators. This is shown by the following little table:

Lisell 1902	1·83
Lafay 1909	1·86
Pogány 1920	1·83.

Let now designe w the specifical resistance, and $\varkappa$ the compressibility. Then it is:

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T = \frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T - \frac{1}{3}\varkappa .$$

We have therefore for Pt:

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T = -1{\cdot}84 \times 10^{-6} - 0{\cdot}13 \times 10^{-6} = -1{\cdot}97 \times 10^{-6},$$

that is a value greater than the value calculated with Grüneisen's formula, the difference being about 15%.

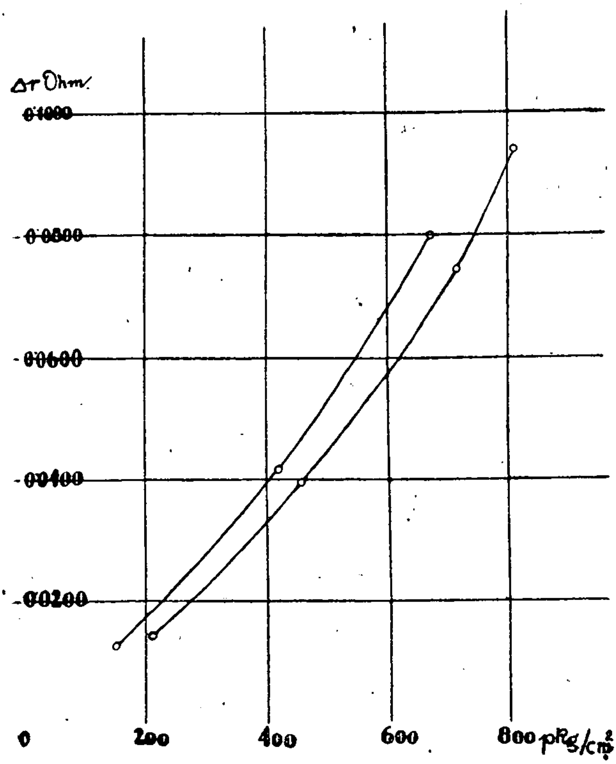
5. §. Measurements were made also on so called hair-wires of Pt and Pd supplied from Hartmann & Braun. Their diameter was 0·0206 mm. and their material contained 99% of pure Pt or Pd. The values of the coefficient of temperature of the resistance, diminished by this impurity of 1%, were for the Pt and Pd-hair-wire respectively 0·0021 and 0·0028, while the values of the same coefficients for the pure metals are respectively 0·0037[1]) and 0·0035.

The resistance of the Pt-hair-wire was 71·9226 Ohm at a temperature of 23·515° C. The results obtained by this wire are as follows:

	Δr Ohm	p Atm.	t_B	$-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$
I.	—0·0125 —0·0424 —0·0798	150 420 675	23·575 „ „	1·64
II.	—0·0145 —0·0398 —0·0743 —0·0942	210 453 716 810	23·427 „ „ „	1·61
III.	—0·0345 —0·0840	362 870	24·230 „	1·32 1·34
IV.	—0·0278 —0·0659	360 706	24·367 „	1·30

[1]) Lafay l. c.

The time elapsed between the first and second and between the third and fourth sets of observations was one day, while between the second and third sets it was an interwal of 8 days. As it is shown by the figure the resistance is not a linear function



of the pressure. The forth column of the table therefore contains only the mean values of the coefficient of pressure. The coefficient of pressure of the resistance diminished after repeated compressions. The same effect has been observed by Lafay.

The resistance of the Pd-wire was 86·2314 Ohm at 24·840° C. The following results had been obtained:

Δr Ohm	p Atm.	t^B	$-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$
—0·0440 —0·0902 —0·1073	290 600 700	24·840 „ „	1·75 1·73 1·98
			1·82
—0·0360 —0·0740 —9·1050 —0·1347	250 516 687 887	24·010 „ „ „	1·68 1·70 2·06 1·73
			1·79
—0·0300 —0·0670 —0·1025 —0·1310 —0·1410	226 487 687 903 960	23·498 „ „ „ „	1·54 1·65 2·06 1·53 2·04
			1·76

As the compressibility of alloys may be calculated by the rate of mixture of the alloy, the compressibility of these wires containing 99% of Pt or Pd can hardly differ from the compressibility of pure Pt and Pd respectively. We may use therefore the compressibilities of the pure metals for the correction of the observed values of the coefficient of pressure of the resistance. The corrected values are thus $-1{\cdot}43 \times 10^{-6}$ for the Pt-hair-wire and $-1{\cdot}95 \times 10^{-6}$ for the Pd-hair-wire, while for the pure metals it is respectively $-1{\cdot}97 \times 10^{-6}$ and $-2{\cdot}46 \times 10^{-6}$.[1]) The impurity of 1% in the material of the wires lowered also the values of the coefficient of pressure of their specifical resistance.

The thermical dilatation of alloys may also be calculated from the rate of mixture of the alloys, the coefficient of thermical

[1]) B. Beckmann Ann. d. Phys. 1915. Bd. 46 p 498.

dilatation of the hair-wires is therefore nearly the same as that of the pure metals. With these values and with the observed coefficients of temperature of the resistance of the hair-wires we may calculate by Grüneisen's formula the coefficient of pressure of the resistance of the hair-wires. The following table shows the calculated and observed values:

	$-\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T \times 10^{-6}$	
	calculated	observed
Pt	1·70	1·97
Pd	2·09	2·46
99% Pt	1·21	1·43
99% Pd	1·83	1·95

The observed values are in each case greater.

5. §. The next wire measured on was of Ni. I disposed of a greater amount of it, so that a quantitative analysis of the material was possible. Mr. Dyonis Kőszegi, assistant in the chemical Institute of this University, who has had the kindness to carry out the analysis, had found the following rates of mixture:

Ni	99·01 %
Co	0·54 „
Cu	0·23 „
Fe	0·09 „
Si	0·05 „
	99·92 %.

The wire made use of had a resistance of 15·2562 Ohm at a temperature of 16·970° C and the coefficient of temperature of his resistance was 0·00493. The measurements lead to the following results:

Δr Ohm	p Atm.	t_B	$-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$
—0·0070	296	16·905	1·55
—0·0168	686	„	1·64
—0·0106	796	„	1·66
			1·62
—0·0060	250	15·706	1·58
—0·0123	486	„	1·75
—0·0167	673	„	1·54
			1·62

The coefficient of pressure of the specifical resistance of the wire, computed by the aid of the compressibility of pure Ni, $\varkappa = 0{\cdot}56 \times 10^{-6}$, was found to be:

$$-1{\cdot}81 \times 10^{-6}.$$

Lisell obtained for the same coefficient $-1{\cdot}60 \times 10^{-6}$ and Grüneisen's formula gives $-2{\cdot}00 \times 10^{-6}$. Grüneisen suppose, that Lisell's Ni-wire was probably impure and this impureness may account for the difference between the value observed by Lisell and calculated by his formula.'

This is confirmed by the present investigations showing, that the absolute value of the coefficient of pressure of the specifical resistance for pure Ni must be greater than $1{\cdot}81 \times 10^{-6}$. The difference between the values calculated by Grüneisen and observed by myself is such, as it may be entirely accounted for[1]) by the impureness of the material I made use of.

6. §. Measurements were made at last on a bismuth-wire. The wire of electrolytical bismuth of a diameter of 0·1 mm. was supplied by Hartmann & Braun. His resistance was 168·8610 Ohm at a temperature of 19° C and the coefficient of temperature of his specifical resistance was 0·0039. The results obtained are as follows:

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[1]) See the results obtained on the Pt-hair-wire.

Δr Ohm	p Atm.	t_B	$-\frac{1}{r}\left(\frac{\partial r}{\partial p}\right)_T \times 10^{-6}$
0·7159	294	19·010	14·3
1·5337	583	„	16·7
1·8983	727	„	14·9
			15·3
0·7676	310	20·020	14·5
1·5836	543	„	14·4
2·0723	832	„	15·2
			13·7

The value obtained for the coefficient of pressure of the resistance of bismuth is thus $+15{\cdot}0 \times 10^{-6}$, E. Williams observed $+19{\cdot}6 \times 10^{-6}$.
