

## The Magnetic Properties of the Elements Niobium, Tantalum and Rhenium. Studies in Magnetochemistry II

R. W. ASMUSSEN and H. SOLING

*The Chemical Laboratory B, Technical University of Denmark, Copenhagen, Denmark*

The magnetic susceptibilities of niobium, tantalum and rhenium have been measured at varying temperatures (79° K to 578° K) and at different values of field strength at each temperature. These metals exhibit feeble paramagnetic susceptibilities, which are nearly temperature independent. The  $\chi_g, T$  curves for niobium and tantalum show that  $\chi_g$  decreases slowly and linearly with increasing temperature, the temperature coefficients being  $-0.0003$ , and  $-0.00006$ , respectively. The  $\chi_g, T$  curve for rhenium increases extremely slowly and linearly with the temperature (interpreted as temperature independence). All susceptibilities measured are field strength independent at all the temperatures investigated. As average values for the atomic magnetic susceptibilities for niobium, tantalum and rhenium in the temperature interval 79° K to 578° K may be accepted the values:  $+207 \cdot 10^{-6}$ ,  $+151 \cdot 10^{-6}$  and  $+56 \cdot 10^{-6}$  respectively.

The accuracy of magnetic measurements on metals and alloys is severely limited by the difficulties in preparing samples of the highest degree of purity. Ferromagnetic impurities are easy to detect and correct for on account of the field strength variation of the susceptibility. Paramagnetic contaminations in metals may in some cases be detected and corrected for because of the temperature dependence of the susceptibility. Diamagnetic impurities are difficult to detect because the diamagnetic susceptibility is independent of field strength and temperature variations; these foreign substances must be eliminated by chemical methods.

The measurements here reported have been carried out on spectroscopically pure metals in which the amounts of paramagnetic and diamagnetic impurities are extremely small. Ferromagnetic substances are not present, because the susceptibilities measured are independent of the field strength at all temperatures.

### N i o b i u m

The first magnetic measurements concerning niobium were published in 1910 by Honda<sup>1</sup>. The specimen used was a metal lump ("regulus") obtained from Dr. v. Bolton having the specific gravity 12.7, a value which is very dif-

ferent from that of our sample 8.60. The susceptibility was dependent on the field strength and had at room temperature the value  $1.29 \cdot 10^{-6}$  for  $H \rightarrow \infty$  (gram suscept). The value was not altered by heating to  $450^\circ\text{C}$ . Owen<sup>2</sup> published 2 years later results on a niobium lump from Prof. Freund containing 0.25 % iron and having the specific gravity 12.7 (compare Honda's sample). Owen reports the value  $1.3 \cdot 10^{-6}$  for the susceptibility. The results of Honda and Owen are in agreement but are rather different from recent values, probably a consequence of impurities present in the specimens used by these authors. In 1933, however, de Haas and van Alphen<sup>3</sup> at Leiden measured a spectroscopically pure sample from Brand Hilger containing small traces of iron and tin. The presence of these metals did not influence the result. The gram susceptibilities are at  $289^\circ\text{K}$ ,  $20.4^\circ\text{K}$  and  $14.2^\circ\text{K}$   $2.28 \cdot 10^{-6}$ ,  $2.34 \cdot 10^{-6}$  and  $2.34 \cdot 10^{-6}$  respectively. In 1948 Brauer<sup>4</sup> measured powdered niobium sheet from Siemens having  $\chi_g = 2.15 \cdot 10^{-6}$  ( $18^\circ\text{C}$ ) and another specimen ("sinterpresling" powdered) giving  $\chi_g = 2.20 \cdot 10^{-6}$  ( $18^\circ\text{C}$ ) and  $2.28 \cdot 10^{-6}$  ( $-183^\circ\text{C}$ ). In Fig. 1 our measurements are plotted against temperature ( $^\circ\text{K}$ ). The straight line has been determined by means of the method of least squares and has the form:

$$\chi_g \cdot 10^6 = 2.350 - 0.000353 \cdot T \quad (1)$$

In Fig. 1 we have also plotted the 3 susceptibilities measured at Leiden (●) and the 3 values (○) reported by Brauer. It is significant that these 6 points lie nicely on our susceptibility curve and its extrapolated part. This may be attributed in the main to the high degree of purity of the 4 samples of different origin, used in the 3 laboratories. We also consider this agreement to be a support to our statement that the susceptibilities of our specimen at all temperatures are independent of the field strength (see exptl. part); Brauer *e. g.* used considerable higher field strengths than we (up till 15 350 Ørstedes).

It is seen from Fig. 1 and equation (1) that the susceptibility decreases very slowly with increasing temperature. As the niobium sample is spectroscopically pure and most paramagnetic metals are absent, this suggests that this slow decrease with temperature may be attributed to the niobium metal. The following average values valid for the temperature interval  $79^\circ\text{K}$  to  $578^\circ\text{K}$  may be accepted for niobium:

$$\bar{\chi}_g = + 2.225 \cdot 10^{-6} \text{ and } \bar{\chi}_A = + 207 \cdot 10^{-6}$$

#### T a n t a l u m

Honda<sup>1</sup> also studied tantalum using a sheet of the metal from Dr. v. Bolton having the specific gravity 16.6 (our value is 16.7). Honda gives the value  $0.93 \cdot 10^{-6}$  for the gram susceptibility at room temperature decreasing to nearly  $0.7 \cdot 10^{-6}$  at  $800^\circ\text{C}$ . Owen<sup>2</sup> measured a sheet of tantalum from Dr. v. Bolton and reports the value  $0.8 \cdot 10^{-6}$  decreasing slightly with the temperature. The susceptibilities given by Honda and by Owen differ rather much (nearly 15 %). The magnetic properties of tantalum have not received attention since 1910—12.

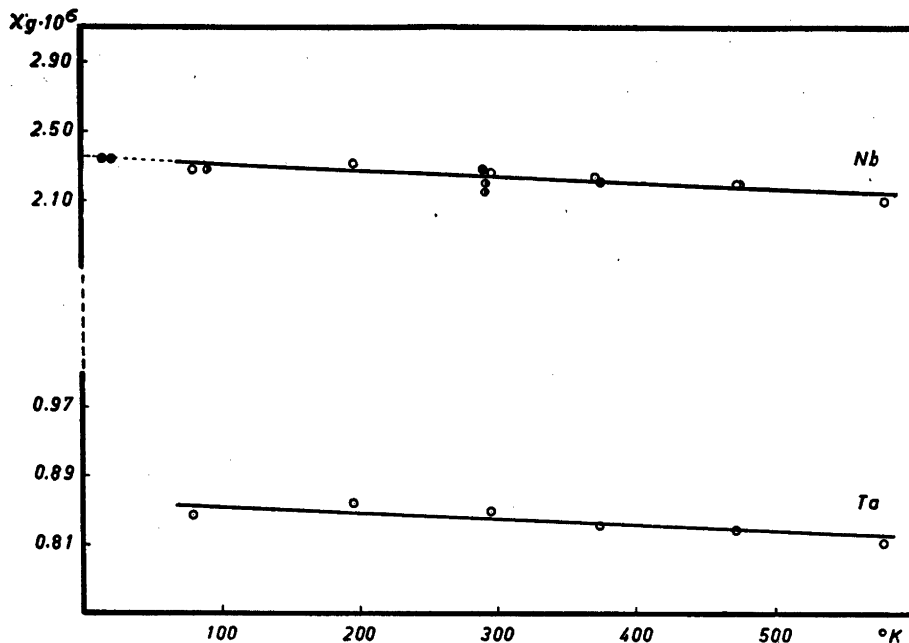


Fig. 1. Temperature dependence of the magnetic gram susceptibilities of niobium and tantalum. Our measurements O, Leiden measurements ●. G. Brauer's results ⊙.

The results of our measurements are given in Fig. 1. Like the susceptibilities for niobium these may be represented by a straight line having the equation:

$$\chi_g \cdot 10^6 = 0.860 - 0.000068 \cdot T \quad (2)$$

The slope of this line is lesser than that for niobium (1). For reasons given above for niobium one may conclude that this slight decrease with temperature probably is a property of the metal. The average values of the gram susceptibilities and of the atomic susceptibilities in the temperature interval 79° K to 578° K are:

$$\bar{\chi}_g = + 0.83_7 \cdot 10^{-6} \text{ and } \bar{\chi}_A = + 151 \cdot 10^{-6}$$

### R h e n i u m

Six years after the discovery of rhenium Albrecht and Wedekind <sup>5</sup> published the first magnetic measurement on the element. The gram susceptibility was determined to be  $+ 0.046 \cdot 10^{-6}$  at room temperature. 1933—35 Perakis and Capatos <sup>6</sup> studied rhenium samples from Riedel-de Haën, Kahlbaum and Hilger at room temperature and the sample from Kahlbaum also at 0°, -24°, -79° and -180° C. The average value for all samples was  $+ 0.366 \cdot 10^{-6}$ . The susceptibility was practically temperature independent in the interval

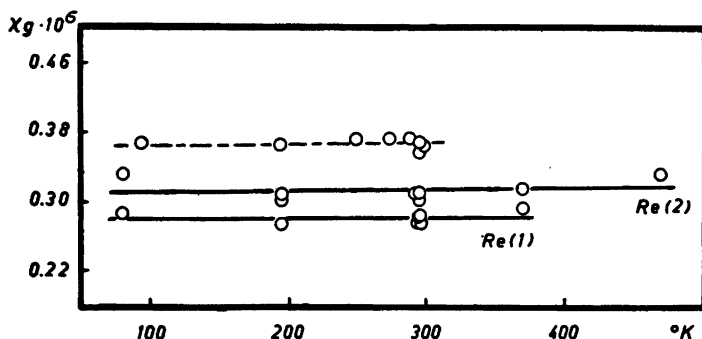


Fig. 2. Temperature dependence of the magnetic gram susceptibility of rhenium. Our measurements given in the two lower curves for the 2 samples Re (1) and Re (2). Results of Perakis and Capatos, upper curve.

93° K to 298° K. In Fig. 2 we give our results for our 2 specimens Re (curve 1) and Re (curve 2) studied in the temperature interval 79° K to 471° K. The diameter of the dots correspond to the experimental error ( $\pm 2\%$ ) in these particular cases. It is possible by means of the method of least squares to fix a straight line through the points for each sample. These lines have the equations:

$$\text{Re (1): } \chi_g \cdot 10^6 = 0.280 + 0.0000075 \cdot T \quad (3)$$

$$\text{Re (2): } \chi_g \cdot 10^6 = 0.310 + 0.000017 \cdot T \quad (4)$$

These equations and the curves in Fig. 2 show that the susceptibilities increase extremely slowly with increasing temperature. For comparison we also plot the values of Perakis and Capatos<sup>6</sup> tabulated in their paper. We have drawn a straight line through these points by judgment (upper curve). The 3 curves demonstrate that the paramagnetic susceptibility of rhenium is independent of the temperature (79° K to 471° K). We are not convinced that the very small positive temperature coefficient is more than apparent. Another question is however: which of the 3 curves (respectively mean susceptibilities) must be preferred? The average values for our samples are  $\bar{\chi}_g = +0.282 \cdot 10^{-6}$  and  $+0.314 \cdot 10^{-6}$ . Perakis and Capatos give  $\bar{\chi}_g = +0.366 \cdot 10^{-6}$ . Our sample Re (1) is spectroscopically pure and free for paramagnetic and most diamagnetic elements (see exptl. part). We have no reason for preferring Re (1) for Re (2) and can not explain why our mean values are 22.9% and 14.2% lower than that of Perakis and Capatos. Only the presence of rather considerable amounts of diamagnetic components in our samples can account for this discrepancy, and this is not probable. The presence of paramagnetic impurities in the specimens of Perakis and Capatos is only possible if these foreign substances have a paramagnetism independent of the temperature. It is well known that the reduction of the perrhenates with hydrogen for preparing metallic rhenium gives samples with higher susceptibilities than those of Perakis and Capatos until the reduction is completed. Schüth and Klemm<sup>7</sup> have measured the susceptibilities of  $\text{Re}_2\text{O}_7$ ,  $\text{ReO}_3$  and  $\text{ReO}_2$ . The gram sus-

ceptibility for  $\text{Re}_2\text{O}_7$  is  $-0.08 \cdot 10^{-6}$  at 2 050 Ørstedes and  $-0.05 \cdot 10^{-6}$  at 3 640 Ørstedes, the decrease is nearly 37 %. The gram susceptibilities of  $\text{ReO}_3$  is at 2 050 Ørstedes  $+0.16 \cdot 10^{-6}$  and at 3 640 Ørstedes  $+0.13 \cdot 10^{-6}$ ; the decrease is nearly 19 %. The oxide  $\text{ReO}_2$  gives  $+0.2 \cdot 10^{-6}$  independent of the field strength. Both these oxides have metallic character and their susceptibilities seem to be temperature independent. We do not consider these oxides to be present in our samples, because they do not show any significant field strength dependence at the values 2 657, 3 346, 3 822 and 4 194 Ørstedes at all temperatures measured (see Table 1). We also state that our samples were measured and kept in evacuated, sealed off measuring tubes (gas pressure  $10^{-4}$ — $10^{-5}$  mm Hg).

We give the average value of all our measurements of the susceptibilities of Re (1) and Re (2) as our accepted value for the susceptibility for rhenium metal in the temperature interval  $79^\circ\text{K}$  to  $471^\circ\text{K}$ :

$$\bar{\chi}_g = +0.29_g \cdot 10^{-6}, \quad \bar{\chi}_A = +56 \cdot 10^{-6}$$

The susceptibility  $+0.046 \cdot 10^{-6}$  given by Albrecht and Wedekind<sup>5</sup> received some attention because this value does not lie between the susceptibilities of the neighbour elements wolfram and osmium having the values  $+0.33 \cdot 10^{-6}$  and  $+0.074 \cdot 10^{-6}$  respectively; compare, however, our determination:  $+0.30 \cdot 10^{-6}$ .

## EXPERIMENTAL

### 1. The metal samples used for the measurements

*Niobium.* This metal was prepared by The Fansteel Corp. of North Chicago in very high purity for use as a spectroscopic standard. It contained 99.99 % Nb. A spectroscopic examination has proved that the sensitive lines of Si, Fe, Ti, Al and Cu were only faintly visible. The lines of the elements Ag, Ca, Co, Cr, K, Li, Mg, Mn, Mo, Na, Pb, Sb, Sn, Ta, V, W, Zn and Zr were not observed. The metal contained a trace of Ni ( $<0.01\%$ ), which however had no influence upon the measurements (field strength dependence of the magnetic susceptibility). The specific gravity was determined to 8.60 (Landolt-Börnstein's tables give 8.60). The shape of the specimen was cylindrical (diameter 4.71 mm and length 10.01 cm).

*Tantalum* originated from the firm above mentioned. The metal contained more than 99.98 % tantalum. The spectrographic analysis has shown that the sensitive lines of Nb, Mg, Si and Cu were faintly visible. The elements Ag, Al, Ca, Co, Cr, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, Ti, V, Zn and Zr were not present. The specific gravity was determined to be 16.7 (Landolt-Börnstein's tables give 16.6). The cylindrical rod had the dimensions: diameter 4.48 mm and length 9.77 cm.

*Rhenium.* Two rhenium samples of different origin were used for the magnetic measurements.

*Re (1)* was prepared by Johnson, Matthew and Co., London for use as a standard in spectrographic analysis. The sensitive lines of Ca, Mg and Cu were faintly visible and the lines of Al, Si and Fe were only very faintly visible. The elements Ag, Ca, Cr, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, Ti, V, Zn and Zr were not detected.

*Re (2)* was prepared in this laboratory from purified potassium perrhenate. The salt was reduced in hydrogen at  $400^\circ\text{C}$ . Potassium hydroxide was removed by extraction with water; drying in oxygenfree nitrogen. Re (1) and Re (2) were measured as powders.

## 2. Magnetic measurements

The magnetic susceptibilities were measured at the four field strengths 782, 1 500, 2 138 and 2 657 Ørstedes (Nb and Ta). The rhenium samples were measured at 2 657, 3 346, 3 822 and 4 194 Ørstedes. The dependence upon temperature was studied in the temperature interval 79° K to 578° K. The higher temperatures were produced by means of a small electric tube-furnace with bifilar wiring. A copper-constantan thermoelement placed in a defined position between the sample and the protection tube indicated the temperature (constant force). The magnetic force was determined by weighing (micro-balance, Gouy's method).

The results of the magnetic measurements are given in Figs. 1 and 2. The field strength dependence was investigated at each temperature applied. The susceptibilities were constant in the interval 782–2 657 Ørstedes for niobium and tantalum, and in the interval 2 657–4 194 Ørstedes for rhenium. The measurements arbitrarily selected for Table 1 exemplify this constancy.

The determinations of the susceptibilities of the rhenium samples at all temperatures and field strengths were carried out with 4 and 3 independent packings in the measuring tube for Re(1) and Re(2) respectively.

Table 1. Magnetic gram susceptibilities at different temperatures and field strengths.

H(Ørstedes)	Niobium		Tantalum		Rhenium (1)				
	Temp. °K	79	472	79	472	Temp. °K	79	295	371
782		2.27 <sub>3</sub>	2.23 <sub>3</sub>	0.84 <sub>3</sub>	0.81 <sub>7</sub>	2 657	0.29 <sub>3</sub>	0.28 <sub>3</sub>	0.29 <sub>3</sub>
1 500		2.27 <sub>5</sub>	2.17 <sub>6</sub>	0.84 <sub>1</sub>	0.82 <sub>5</sub>	3 346	0.29 <sub>5</sub>	0.28 <sub>5</sub>	0.29 <sub>5</sub>
2 138		2.28 <sub>1</sub>	2.18 <sub>5</sub>	0.84 <sub>3</sub>	0.83 <sub>3</sub>	3 822	0.28 <sub>5</sub>	0.28 <sub>5</sub>	0.29 <sub>4</sub>
2 657				0.84 <sub>3</sub>	0.83 <sub>1</sub>	4 194	0.27 <sub>5</sub>	0.28 <sub>5</sub>	0.29 <sub>2</sub>
Mean value		2.28	2.20	0.84 <sub>5</sub>	0.82 <sub>7</sub>	Mean value	0.28 <sub>7</sub>	0.28 <sub>5</sub>	0.29 <sub>4</sub>

The results plotted in Figs. 1 and 2 are mean values calculated as in the table. We have not determined the susceptibilities at  $H \rightarrow \infty$  by extrapolation of the  $\chi_g, H^{-1}$  curves to the zero value of  $H^{-1}$ , because our measurements do not indicate any significant variation of  $\chi_g$  in the field strength interval applied.

## REFERENCES

1. Honda, K. *Ann. Physik* [4] 32 (1910) 1027.
2. Owen, M. *Ann. Physik* [4] 37 (1912) 657.
3. de Haas, W. J. and van Alphen, P. M. *Koninkl. Akad. v. Wetenschap. Amsterdam* 36 (1933) 263.
4. Brauer, G. *Z. anorg. Chem.* 256 (1948) 10.
5. Albrecht, W. H. and Wedekind, E. *Naturwissenschaften* 19 (1931) 20.
6. Perakis, N. and Capatos, L. *Compt. rend.* 196 (1933) 611; 198 (1934) 1905. *J. phys. radium* [7] 6 (1935) 462.
7. Schüth, W. and Klemm, W. *Z. anorg. Chem.* 220 (1934) 193.

Received January 23, 1954.