MAGNETIC PROPERTIES OF THE PALLADIUM METALS AND SOME OF THEIR COMPOUNDS

BY

ALBERT N. GUTHRIE

University of Illinois, Urbana

Many investigators have made susceptibility measurements on palladium but the results are in wide disagreement. The susceptibilities of ruthenium and rhodium are less well determined. It is known that palladium approximately follows the Weiss law, $X = C/(T-\Theta)$; where X is the susceptibility per unit mass, T is the absolute temperature, C is the Curie constant, and Θ is the Curie point. The susceptibilities of both ruthenium and rhodium increase with temperature.

Determination of the magnetic moments of ions of these elements is of considerable importance in testing the spectroscopic method of predicting ionic moments. These determinations can be made by finding the law of variation of susceptibility of compounds of these elements with temperature, provided that this law is the Curie law or the Weiss law. Otherwise there is no theory which allows a calculation of the ionic moments.

The laws of variation of susceptibility with temperature for the metals ruthenium, rhodium, and palladium and for the compounds $RuCl_3$, RuO_2, $RhCl_3$, and Rh_2O_3 have been determined in the hope of contributing more accurate data on the metals than are now available and of furnishing material for calculation of ionic magnetic moments.

DESCRIPTION OF SAMPLES

Samples of the metals, which had been prepared with great care for exact determination of physical and chemical constants, were made available by the Bureau of Standards, Washington, D. C. They were prepared in sponge form by igniting the double salts of ammonia and chlorine. The Bureau states:

> "The content of iron is probably not over one part in a million and may be much less. It is difficult to say whether the traces of iron are alloyed with the metals or are present as ferric oxide. It is possible that there are minute traces of cobalt and nickel in the rhodium, but spectrographic examination did not show any. These elements are less likely to be present in the other metals than in rhodium."

The compounds were prepared with special care by Dr. Streicher of the American Platinum Works, Newark, N. J. His report is as follows:

> "The metals which went into the compounds were 99.9 percent pure and free of base metals. The metal content of the oxides is that theoretically correct for the compound. The metal content of the trichlorides is slightly higher than that theoretically correct. This means there are traces of the dichlorides present in these compounds."

APPARATUS AND EXPERIMENTAL METHOD

The measurements were made by means of an improved Curie balance.[1] In this balance the usual mechanical torsion head was replaced by an electrically operated one. For this purpose a set of Helmholtz coils was employed, the suspension which controlled the balance arm being suspended from the movable coil and this in turn being suspended from a fixed torsion head. By placing the movable coil at right angles to the fixed coils, and controlling the current through the movable coil the proper torque to bring the balance arm back to its zero position, when displaced by the magnetic field, could be applied to the controlling suspension without going near the balance. The deflections of the movable coil were measured by means of a telescope and scale placed at a distance of about one meter. For samples of different susceptibilities suspensions of different torsion constants were used in order to have deflections large enough to reduce the error of reading to a small percentage.

The magnet used was a large Dubois type which gave a field of 6,400 gausses without appreciable heating. Its pole pieces were set at an angle of about 12 degrees with the line joining their centers.

The thermocouple used in measuring the temperatures of the samples was cu-constantan and was used in series with a D'Arsonval galvanometer and a resistance of about 2,000 ohms. The hot junction was mounted in the furnace so as to occupy the same relative position as the sample and the cold junction was kept in a bath of ice and water in a Dewar flask. A deflection of the galvanometer of one mm. corresponded to a temperature change of about 2.5 degrees. The thermocouple was calibrated by means of the boiling points of substances that are well known.

The apparatus was calibrated by making measurements on distilled water the susceptibility of which was taken as -0.749×10^{-6} when measured in air at 20° C. and atmospheric pressure. The water used was

---

[1] P. Curie, Collected Works, p. 232.

doubly distilled, the second time from a solution of $KMnO_4$ in a quartz still. The calibration measurements were repeated at frequent intervals throughout the course of the investigation.

It is estimated that the results are correct (compared to water) to about 1.5 percent.

RESULTS OF MEASUREMENTS

The Metals. When examined from field strengths of 1,400 to 6,400 gausses, rhodium was the only metal which showed a systematic variation of susceptibility with field strength. Its susceptibility varied from 1.60×10^{-6} at 1,420 gausses to 1.20×10^{-6} at 6,390 gausses along an approximately hyperbolic curve. This variation was assumed to be due to a ferromagnetic impurity and the method devised by Owen[2] was used to calculate the susceptibility of rhodium from these measurements.

The result of the measurements on the metals are given in Table I.

TABLE I

METALS

Temperature °K	Susceptibility $\times 10^6$		
	Pd	Rh*	Ru
298	5.15	1.08	0.427
333	4.79	1.09	.431
373		1.11	
380	4.39		.435
423		1.12	
433	4.03		.443
473		1.13	
480	3.73		.452
523	3.52	1.15	.457
573	3.27	1.16	.466
623	3.05	1.17	.475
673	2.85	1.18	.487
723	2.66	1.19	.496

*Calculated from the measurements by the method of Owen.

The Compounds. The susceptibilities of the oxides were measured up to 400°C. without any indication of decomposition. The chlorides could be heated to only 175°C. No indication of ferromagnetic impuri-

---

[2] Owen, Ann. der Phys. (4) 37: 657 (1912).

ties was found in any sample. The results for the oxides are given in Table II and those for the chlorides in Table III.

TABLE II

OXIDES

Temperature °K	Susceptibility × 10^6	
	RuO_2	Rh_2O_3
296	1.21	0.408
333		0.409
373	1.28	0.410
423	1.31	0.403
473	1.36	0.403
523	1.40	0.402
573	1.43	0.401
623	1.46	0.398
673	1.49	0.397

TABLE III

CHLORIDES

Temperature °K	Susceptibility × 10^6	
	$RuCl_3$	$RhCl_3$
296	7.21	0.00
323	6.64	0.00
348	6.16	0.00
373	5.77	0.00
398	5.44	0.00
423	5.18	0.00
448	4.91	0.00

The Metals. The susceptibilities for ruthenium and rhodium are found to increase with temperature in good agreement with previous results.[3] There is no theory of magnetic properties to account for this behavior. Palladium is found to follow the Weiss law, but the constants of the law change at a temperature of about 200°C. Between 25°C. and 200°C. the equation is:

$$X = \frac{2430}{T + 173} \, . \, 10^{-6}$$

and between 200°C. and 450°C. it is:

$$X = \left[\frac{3040}{T + 225} - 0.54 \right] . \, 10^{-6}$$

The first equation gives an elementary magnetic moment of 7.2 Weiss magnetons per mole, while the second gives 8 Weiss magnetons per mole. These results are in good agreement with those of a number of earlier investigators.[4]

---

[3] Honda, Ann. der Phys. (4) 32:1027 (1910).
Owen, Ann. der Phys. (4) 37:657 (1912).

[4] Foex, Ann. de Physique, 16:230 (1921).
Onnes and Oosterhuis, Proc. Roy. Acad. Sci. Amsterdam. 15:322 (1912).

The fact that calculations of magnetic moments for palladium give a whole number of Weiss magnetons has been used in support of the Weiss theory of the magneton. It appears that calculations have always been made from measurements above 200°C.

The Compounds. A comparison of ionic magnetic moments of these elements determined from susceptibility measurements on the compounds with those predicted spectroscopically is pertinent.[5] The susceptibility of RuO_2 was found to increase with temperature. Rh_2O_3 and $RhCl_3$ showed constant susceptibilities, that of the latter being zero within the limits of the apparatus. The susceptibility of $RuCl_3$ decreased with increasing temperature according to the Weiss law:

$$X = \frac{2360}{T + 38} \cdot 10^{-6}$$

These results give, for the magnetic moment of the ion Ru''', 9.85 Weiss magnetons. Cabrera and Duperier[6], from measurements on $RuCl_3$, have found for Ru''' the moment 12.9 Weiss magnetons and the spectroscopically predicted moment is 29.4. From measurements on IrO_2, Mr. L. T. Bourland (1930) has found for the moment of Ir'''', which spectroscopically should have the same moment as Ru''', the value 12.7 Weiss magnetons.

It is interesting to note that of all the compounds of these elements whose laws of variation of susceptibility with temperature have been determined ($RuCl_3$, $RhCl_3$, $PdCl_2$, $OsCl_2$, $IrCl_3$, $PtCl_2$, IrO_2, RuO_2, and Rh_2O_3), only those containing the ion for which the Hund rule predicts an S normal state ($RuCl_3$ and IrO_2) are found to follow the Weiss law. This is as predicted but the deviation in most of these cases is opposite to that to be expected since the moments of ions with inverted multiplets for ground terms should decrease with increasing temperature.

In the ions of the iron, palladium, and platinum groups the electron configuration is quite different from that in the rare earths where such good agreement between spectroscopic predictions and experimental values is found.[7] The incompleted group of equivalent electrons, which gives the trivalent rare earth ion its mechanical and magnetic moments, is inside two completed groups. In the iron, palladium, and platinum ions the incompleted group of equivalent electrons is the outermost group.

---

[5] Hund, Zeits. f. Phys. 33:345 (1925).
Laporte and Sommerfeld, Zeits. f. Phys. 40:333 (1926).
Van Vleck, Phys. Rev. 29:727 (1927); 31:587 (1928).

[6] Cabrera and Duperier, C. R. 185:414 (1927).

[7] Hund, Zeits. f. Phys. 33:855 (1925).
Van Vleck, Phys. Rev. 34:1494 (1929).