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MAGNETIC SUSCEPTIBILITIES AND IONIC MOMENTS IN THE PALLADIUM AND PLATINUM GROUPS

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Abstract

Susceptibility measurements have been made on Ru, Rh, Pd, Os, Ir, and Pt and some of their compounds over a range of temperatures by means of an improved Curie balance.

Pd and Pt are found to follow approximately a Curie-Weiss law. Ru, Rh, Os, and Ir are found to have paramagnetic susceptibilities which increase with temperature.

$RuCl_3$ and IrO_2 are found to follow a Curie-Weiss law which gives for the ion Ru^3 a moment of 9.8 Weiss magnetons per mole and for Ir^4 13.8. The spectroscopically predicted value for each ion is 29.4. The paramagnetic susceptibility of Rh_2O_3 is found independent of temperature while that of RuO_2 increases rapidly with temperature. $RhCl_3$ is found to have an unmeasureably small susceptibility over the temperature range investigated. $IrCl_3$ and $PtCl_2$ are diamagnetic with susceptibilities independent of temperature.

THE determination of ionic magnetic moments in the Pd and Pt groups, by susceptibility measurements on compounds of these elements, is of particular interest in connection with the Hund method[1] of predicting these moments from spectroscopic theory. Hund[2] has employed his method for the moments of the trivalent rare earth ions and obtained remarkable agreement with the measured values of several investigators. In the case of the ions of the iron group, the elements Sc to Ni of the periodic table, the method has been unsuccessful. Laporte and Sommerfeld[3] calculated the moments to be expected for the iron group ions in two cases, infinite separation and zero separation of the J-levels of the ground multiplet predicted by the Hund method. Several of the measured values are found to lie outside of these limits. Bose[4] has pointed out that the measured moments of the iron group ions are best explained by assuming that they are due to the spin of the electrons alone, the orbital moments being ineffective. Stoner[5] has called attention to the striking difference in the structures of the rare earth and iron group ions, and the effect that this difference should be expected to have on the ions with the conditions under which their moments are measured. In the iron group ions the incompleted group of electrons which gives the ion its mechanical and magentic moments is that of highest total quantum number. In the rare

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[1] F. Hund, Zeits. f. Physik **33**, 345 (1925).

[2] F. Hund, Zeits. f. Physik **33**, 855 (1925).

[3] O. Laporte and A. Sommerfeld, Zeits. f. Physik **40**, 333 (1926).

[4] D. M. Bose, Zeits. f. Physik **43**, 864 (1927).

[5] E. C. Stoner, Phil. Mag. **8**, 250 (1929).

earth ions this group of electrons is not that of highest total quantum number. The interaction between the paramagnetic ion and surrounding ions and molecules will presumably effect primarily the electrons in the group of highest total quantum number; in the iron group ions the electrons responsible for the magnetic moment, in the rare earth ions electrons that are not responsible for the magnetic moment. In general this interaction is a strong orbital interaction while the spin moments are left relatively free. In a qualitative way this is an explanation of the apparent ineffectiveness of the orbital moments in the iron group ions and their almost complete effectiveness in the rare earth ions.

There exist few data on the susceptibilities of the elements of the Pd and Pt groups from which ionic moments can be calculated. Bose and Bhar[6] have made measurements at room temperature on some chlorides and complex salts of some of these elements and have calculated ionic magnetic moments assuming that the susceptibilities of the compounds follow the Curie law. Cabrera and Duperier[7] made measurements on $RuCl_3$, $RhCl_3$, $PdCl_2$, $OsCl_2$, $IrCl_3$, and $PtCl_2$ over a range of temperatures from about 20°C to 100°C. They found that $RuCl_3$ approximately followed a Weiss law which gave a moment for Ru^3 of 12.9 Weiss magnetons. The susceptibilities of the other chlorides were found to remain constant or increase with temperature.

For this investigation the compounds $RuCl_3$, RuO_2, $RhCl_3$, Rh_2O_3, $IrCl_3$, IrO_2, and $PtCl_2$ were obtained from the American Platinum Works, Newark, N.J. These compounds were prepared with special regard for purity by Dr. S. Streicher of their chemical laboratory.

Through the kindness of the Bureau of Standards samples of the six metals Ru, Rh, Pd, Os, Ir, and Pt of very great purity were made available for a new determination of their susceptibilities. Several investigators have measured the susceptibilities of these metals but the results have been in very poor agreement.

DESCRIPTION OF APPARATUS

The susceptibility measurements were made by means of a Curie balance. In this apparatus the usual mechanically operated torsion head was replaced by an electrically operated one. The ease and speed of making measurements with this arrangement far surpasses that attainable with the usual mechanical types. In Fig. 1 is shown a sketch of the essential parts of the electrically operated torsion head. A coil of small copper wire, A, wound on a flat, hard rubber spool is suspended by a fine wire, B, with its plane parallel to a magnetic field produced by two fixed coils, C, carrying a current. To the coil A is attached the suspension, D, which supports the balance arm and to which is applied the torque to overcome the force on the sample. A plane mirror, E, is attached to the coil A and the twist in the suspension D is read from it by means of a telescope and scale placed about one meter away. In order to fix the axis about which the coil A rotates suspension guides, F, are em-

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[6] D. M. Bose and H. G. Bhar, Zeits. f. Physik **48**, 716 (1928).

[7] B. Cabrera and A. Duperier, C. R. **185**, 414 (1927).

ployed. These guides consist of thin brass strips attached to the box which supports the balance and pierced with small holes through which the suspensions pass. The coil *A* is damped by means of vanes *G* suspended in stanolax. A current, which is controlled so as to give the proper torque to the suspension, is carried through the coil *A* by means of long thin spirals of wire which do not hinder the coils free rotation. The other parts of the balance are of the usual design.[7a]

The apparatus was calibrated by making measurements on distilled water, using as its susceptibility with respect to air at 20°C and 76 cm pressure the value -0.749×10^{-6}.

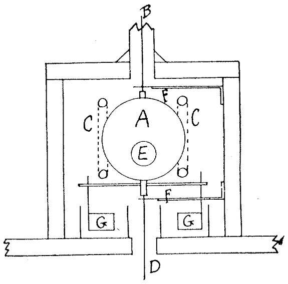

Fig. 1. Sketch of the essential parts of the electrically operated torsion head.

The inhomogeneous magnetic field was furnished by a Dubois electromagnet with its pole pieces set at an angle of about twelve degrees with a line joining their centers. The field strengths obtainable were in the range 1400 to 6400 gausses.

The samples were heated by means of a nichrome resistance furnace. A junction of a Cu-constantan thermocouple was mounted so as to occupy the same relative position in the furnace as the sample on which measurements were being made. The other junction of the thermocouple was kept in a bath of ice and water. Temperatures were read by means of a D'Arsonval galvanometer in the thermocouple circuit. A galvanometer deflection of one mm corresponded to a temperature change of about 2.5°C. The thermocouple was calibrated by means of the boiling points of well-known substances.

EXPERIMENTAL RESULTS

In Tables I, II, III, are given the results of measurements on the various substances indicated.

The susceptibility of Rh was found to decrease with increasing field strengths. At room temperature the change was from 1.60×10^{-6} at 1420 gausses to 1.20×10^{-6} at 6390 gausses. This variation was assumed to be due to ferromagnetic impurities and the method first used by Honda[8] was used to calculate the susceptibility of Rh from these measurements.

[7a] The modification of the Curie balance as used by Foëx was considered but calculation showed that the torsion method could be made more sensitive for our measurements.

[8] K. Honda, Ann. d. Physik (4) **32,** 1027 (1910).

TABLE I.

	$\chi\times10^6$				
T°K	Ru	Rh*	Pd	RuO_2	Rh_2O_3
298	0.427	1.08	5.15	1.21	0.408
333	.431	1.09	4.79	1.24	.409
380	.435	1.11	4.39	1.28	.410
433	.443	1.12	4.03	1.32	.403
480	.452	1.14	3.73	1.36	.403
523	.457	1.15	3.52	1.40	.402
573	.466	1.16	3.27	1.43	.401
623	.475	1.17	3.05	1.46	.398
673	.487	1.18	2.85	1.49	.397
723	.496	1.19	2.66	—	—

* Calculated from the measurements by the method of Honda.

TABLE II.

	$\chi\times10^6$			
T°K	Os	Ir	Pt	IrO_2
298	0.052	0.133	0.982	0.997
348	—	.138	.947	.984
398	.059	.141	.925	.974
473	—	.146	.876	.971
548	.065	.151	.831	.942
623	—	.159	.795	.926
698	.070	.167	.745	.891

TABLE III.

	$\chi\times10^6$			
T°K	$RuCl_3$	$RhCl_3$	$IrCl_3$	$PtCl_2$
298	7.21	0.00	−0.114	−0.151
323	6.64	.00	—	—
348	6.16	.00	−0.114	−0.149
373	5.77	.00	—	—
398	5.44	.00	—	−0.149
423	5.18	.00	—	—
448	4.91	.00	—	—

For comparison the available data on the specific susceptibilities of the metals Pd, Rh, Ru and Pt at 18°C and the investigators who obtained them are given in Table IV.

TABLE IV.

	$\chi\times10^6$			
Investigator	Pd	Rh	Ru	Pt
Curie	5.2	—	—	—
Honda	5.8	1.14	0.56	1.10
Owen	5.2	1.08	0.43	0.90
Onnes and Oosterhuis	5.3	—	—	—
Foëx	5.27	—	—	1.028
Kopp	5.29	—	—	—
Authors	5.24	1.08	0.426	1.015

In Fig. 2 are plotted the values of $1/\chi$ for Pd, Pt, $RuCl_3$ and IrO_2 as a function of temperature.

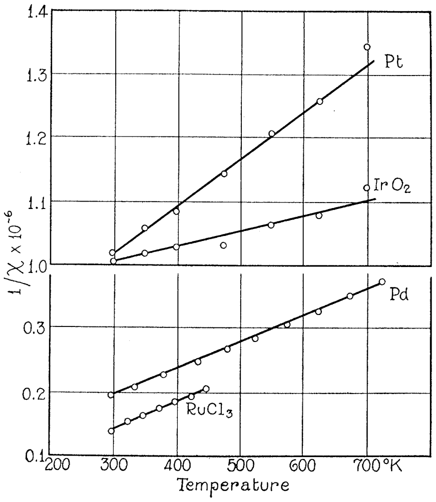

Fig. 2. Values of $1/\chi$ for Pd, Pt, $RuCl_3$ and IrO_2 plotted as a function of temperature.

DISCUSSION OF RESULTS

Pd and Pt are found to follow approximately a Curie-Weiss law, the deviation being accounted for by an underlying diamagnetism independent of temperature. From purely formal theory, it would be expected that the diamagnetic component of the susceptibility would be greater for Pt than for Pd but the experimental results indicate the opposite.

Ru, Rh, Os, and Ir are found to have paramagnetic susceptibilities which increase with temperature. This is, of course, inconsistent with Langevin's theory.

$RuCl_3$ and IrO_2 are found to follow a Curie-Weiss law. For the former the equation is:

$$\chi = \frac{2340}{T + 37} \times 10^{-6} \text{ c.g.s./gram}$$

and for the latter

$$\chi = \frac{4310}{T + 4025} \times 10^{-6} \text{ c.g.s./gram.}$$

These results give for the magnetic moment of the Ru^3 ion 9.8 Weiss magnetons per mole, and for the Ir^4 ion 13.8. The predicted normal state for both ions is ^6S which gives 29.4 Weiss magnetons per mole for the moments. In the iron group, good agreement between measured and predicted moments has been found for all ions with predicted S normal states. In these groups, there is no agreement whatever and the behavior of some of the compounds is such that no moments can be determined from measurements on them. If the susceptibility does not follow a Curie-Weiss law, there is no theory which will give the elementary magnetic moments.

A deviation from the Curie-Weiss law is predicted for compounds containing a paramagnetic ion with other than an *S* normal state due to the increase with temperature of the number of excited ions with moments differing from that of the ions in their normal state. With an *S* normal state there are no excited ions at ordinary temperatures. In these researches only the compounds containing the paramagnetic ion with a predicted *S* normal state are found to follow a Curie-Weiss law but the deviations of the other compounds are opposite to (excepting RuO_2) and much greater than can be accounted for by the theory.

The behavior of those compounds which do not follow a Curie-Weiss law is not due to a permanent chemical or physical change due to heating for at room temperature the susceptibilities are found to be the same after as before heating.

The disagreement between the measured and the spectroscopically predicted ionic moment may be due to error in prediction of the normal state. Hund's rule, combined with present ideas of the electronic arrangement in atoms and ions, predicts for Ru^3 and Ir^4 a ^6S normal state. In the same way the prediction for the normal state of the Pd atom is a ^3F. The atomic spectrum of Pd has been analysed by Beals, Beckert and Catalan, and McLennan and Smith.[9] They all have concluded that the normal state for the Pd atom is a ^1S which means that the Pd atom in its normal state has zero magnetic moment. That the moment of the Pd atom is zero in its normal state has been verified by Copley and Guthrie[10] by the molecular ray method.

The question of the validity of Hund's rule in the wave mechanics has been examined by Slater.[11] He has found that the wave mechanics gives the same normal state as Hund's rule although their predictions differ higher up in the spectrum.

The interpretation of the magnetic moment determined from susceptibility measurements on compounds as the true moment of the paramagnetic ion seems not to be well founded. The ion in chemical combination, surrounded by other ions and molecules, must be a different thing from the ion with which the spectroscopist deals in the Zeeman effect. Therefore, in spite of some past successes it appears hopeless to expect always to find agreement between these two.

The writers wish to express their appreciation to Professors E. H. Williams and Jakob Kunz for their encouragement and advice during the progress of this work.

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[9] See F. Hund, Linienspektren und Periodische System der Elemente (1927).

[10] Not yet published.

[11] J. C. Slater, Phys. Rev. **34**, 1293 (1929).