

THE MAGNETIC SUSCEPTIBILITIES OF OSMIUM, IRIDIUM, AND PLATINUM*

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Spectroscopic investigation has been the most useful tool for studying the structure of matter. The study of the magnetic properties of matter has given promise of becoming an important supplement by checking spectroscopic results on ionic magnetic moments and predicting new spectroscopic data. Very limited success has attended attempts in these directions, F. Hund's calculation of the magnetic moments of the ions of the rare earth elements is an almost unique example. A general theory of the paramagnetism of metals seems even more remote. Contribution to the mass of data which must underlie such a theory is the object of measurements of the magnetic susceptibilities of metals and their compounds.

The United States Bureau of Standards has furnished pure samples of the platinum metals which have been prepared for the purpose of making precise measurements of their physical properties. The data on the magnetic susceptibilities of these metals as given in the literature are conflicting and it is probable that such pure materials have not been available to investigators in the past. For these reasons it was proposed to repeat the measurements of these susceptibilities.

Susceptibility measurements on the compounds of the platinum metals are necessary to the calculation of their ionic magnetic moments. The American Platinum Works has furnished iridium dioxide, iridium chloride and platinumous chloride which have been used for this purpose.

A modification of the Curie magnetic balance having several advantages has been developed. The torsion head of this balance is electrically controlled in order to eliminate the possibility of disturbing the balance during adjustment. For the purpose in hand the balance must permit an accurate measurement of forces on the magnetic sample varying from one tenth of a dyne to several dynes. This indicates the necessity of

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protecting the balance arm from the influence of air currents. The situation is complicated by the requirement of measurements at high temperatures. By using a shield which reduced the air currents set up by the electric furnace to a minimum, satisfactory operation was obtained over the temperature range 300°K to 700°K.

The force on a paramagnetic substance is proportional to $H(dH/dx)$; where H is the intensity of the magnetic field and dH/dx is the gradient of this field in the direction perpendicular to the line joining the centers of the pole pieces. The point of maximum $H(dH/dx)$ was determined by a search coil. The field was calibrated by means of the magnetic balance deflections due to distilled water. The susceptibility of distilled water has been quite definitely fixed by the concordant determinations of several investigators. The value adopted by the International Critical Tables is -0.720×10^{-6} in vacuo. Taking the volume susceptibility of air as 0.029×10^{-6} the susceptibility of water measured against air is -0.749×10^{-6} , in c.g.s. units. The susceptibility data given below are referred to this value as standard.

The susceptibilities were calculated by the formula from electrodynamics $F = mXH(dH/dx)$. F is the force on the magnetic specimen; m is the mass of the sample; X is the magnetic susceptibility per unit mass.

Each of the susceptibilities given in the following tables is the average of several values taken at different field intensities.

TABLE I
OSMIUM

Temperature	Susceptibility
299°K	0.040×10^{-6}
398	.047
548	.053
698	.058

TABLE II
IRIDIUM

Temperature	Susceptibility		
298°K	0.140	0.125	0.133×10^{-6}
348	.139	.135	.139
398	.138	.140	.146
473	.145	.142	.152
548	.147	.148	.159
623	.156	.157	.165
698	.165	.167	.169

TABLE III
PLATINUM

Temperature	Susceptibility		
298°K	0.981	0.980	0.986×10^{-6}
348	0.944	0.946	0.950
398	0.920	0.922	0.932
473	0.875	0.875	0.877
548	0.831	0.831	
623	0.799	0.791	
698	0.747	0.744	

Within experimental error the susceptibilities of the platinum metals were independent of the magnetic field intensity, indicating that they were substantially free of ferromagnetic impurities.

The susceptibility of iridium dioxide varied with the field as shown by Table IV.

TABLE IV
IRIDIUM OXIDE

Current in amperes in electro-magnet coils	Susceptibility	
	298° K	698° K
1.5	1.082×10^{-6}	0.948
2.0	1.032	0.922
2.5	1.027	0.915
3.0	1.008	0.899
3.5	0.997	0.896
4.0	0.985	0.888
4.5		0.889

This variation with the field is probably due to the presence of a slight trace of some ferromagnetic substance in the sample. Averaging the results at each temperature, for the three highest magnet currents gives the variation with temperature shown in Table V.

TABLE V
IRIDIUM OXIDE

Temperature	Susceptibility
298° K	0.997×10^{-6}
348	.984
398	.974
473	.971
548	.942
623	.926
698	.891

Platinous chloride and iridium chloride were found to be diamagnetic with susceptibilities independent of temperature and field within experimental error. The chlorides are unstable at temperatures above 100°C (373°K); hence the temperature range of the measurements was restricted. The measured susceptibilities were: PtCl_2 , -0.150 ; IrCl_3 , -0.114×10^{-6} .

Weiss' law $(X + X_d) (T - \Theta) = C$ is followed by platinum and iridium dioxide. X is the measured paramagnetic susceptibility, X_d is the correction due to diamagnetism, T is the temperature in absolute degrees (Kelvin) and C is a constant. It is possible to calculate the magnetic moment, M , per mole from the Langevin theory of paramagnetism which gives the expression $M^2 = 3mRC$ where m is the atomic weight and R is the gas constant per mole. For platinum $X_d = -0.141$, $\Theta = -1390$, $C = 1890$, and $M = 9600$ c.g.s. units or 8.52 Weiss mag-

netons. One Weiss magneton = 1126 c.g.s. units. This does not agree with the Weiss theory requiring an integral number of Weiss magnetons.

Application of Hund's rules (which he applied to the rare earth ions with success) to the Ir^{4+} ion gives a prediction of 5 Bohr magneton units for the magnetic moment of this ion. J , the total moment of momentum of the ion in the theory of line spectra, is 2.5 Bohr units. The old quantum theory gives the expression $M^2 = 3JmRC/(J+1)$ in place of the Langevin expression. The constants in the Weiss formula which were found for Ir^{4+} (i. e. IrO_2 , neglecting the contribution of the O_2) are $X_d = 0$, $\Theta = -3980$, $C = 4260$, giving $M = 12,100$ c.g.s. units, or 2.16 Bohr magnetons. (One Bohr magneton is equal to 4.97 Weiss magnetons.) This does not agree with the prediction of the Hund rules.

Osmium and iridium do not obey the Weiss law, and hence their magneton numbers could not be calculated. A quantitative theoretical interpretation is also lacking for the diamagnetic substances platinous chloride and iridium chloride.

The Pauli theory of paramagnetism, in which the Fermi statistics is applied to a degenerate "gas" of spinning electrons, does not predict any of the results of this investigation. The following table gives the results of an application of this theory to osmium and iridium on the assumption that each atom has contributed one free-spinning electron to the paramagnetic gas.

	m	n	X per gram Pauli cal- culation	X per gram measured at 298° K
Ir	193.1	3.14×10^{21}	0.0144×10^{-6}	0.047×10^{-6}
Os	190.8	3.18×10^{21}	0.0144×10^{-6}	0.13×10^{-6}

In this table m denotes the atomic weight of the metal and n is the number of atoms per cubic centimeter. The Pauli theory gives $X = 2.209 \times 10^{-14} n^{1/3}$ per cubic centimeter. The assumption that the number of free electrons is equal to the number of atoms, made for the computation of the above data, is less tenable here than in the case of alkali metals because of the greater number of electrons outside of a rare gas shell in the case of osmium and iridium. Laporte and Sommerfeld have modified the Hund theory by assuming that each term of the ground multiplet contributes to the magnetic moment of an ion. They show that this assumption leads to a dependence of the magneton numbers on the temperature with a temperature coefficient positive for regular and negative for inverted terms. This may give a hint for future progress, but is not quantitatively applicable at present to the explanation of the behavior of iridium and osmium.