THE MAGNETIC PROPERTIES OF SOME RARE EARTH OXIDES AS A FUNCTION OF THE TEMPERATURE.

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THE existence or non-existence of the magneton, the elementary quantity of magnetism corresponding to the electron of electricity, has attracted the attention of investigators since it was first suggested by Ritz. Much work has been done, especially by Weiss, Kammerling Onnes, du Bois, Honda, Perrier, Piccard and Terry, and while the preponderance of the results obtained by these investigators is against the elementary moment of magnetism as suggested by Weiss, yet the idea is still strongly maintained by some. Within the last three years Piccard[1] maintains that there is a group of bodies (paramagnetic) which obey strictly Curie's law and hence he argues that the foundations of the theory are sound and there is still evidence in favor of the magneton.

Not only was it hoped to get evidence for or against the magneton theory, but the opportunity to obtain from the Chemistry Department of the University of Illinois rare earths in a very pure state from which were being made atomic weight determinations made it desirable to investigate their magnetic constants. My thanks are due to Dr. Hopkins and his associates of the Chemistry Department for their hearty coöperation in supplying me with samples of the rare earth materials.

The method used was that of Curie[2] which consists in measuring the pull exerted on an object placed in a non-uniform magnetic field. According to this method X, the magnetic susceptibility per unit mass, is given by the expression

$$X = \frac{1}{MH_y \frac{\partial H_y}{\partial x}} \cdot \frac{C\phi}{l} \tag{1}$$

providing the force is measured by means of the twist of a suspension. In this expression M is the mass of the sample, H_y the field at right angles to the direction of motion of the sample, $\partial H_y/\partial_x$ the variation of this field along the direction of motion, C the couple necessary to twist the

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[1] Piccard, Arch. des Sci. Phys. et Nat., 40, 278, 1915.

[2] P. Curie, Ann. de Chem. et de Phys., (7), 5, 298, 1895.

suspension through one radian, ϕ the angle of twist in radians and l the lever arm from the line of suspension to the sample.

The torsion balance was contained in a wooden box put together without the use of any magnetic material. The suspension consisted of a phosphor-bronze wire the torsion couple of which was 940 dyne cm. at 25° C. It was found that this varied with the temperature, the variation being about -0.6 dyne cm. for 1° C. Since, in some cases, the box containing the torsion balance warmed up five or six degrees Centigrade, a correction was made for the variation of the torsion couple.

During the first part of the work an aluminum rod was used for the lever arm and pointer of the balance but the zero corrections for this were so large that it was deemed advisable to find another system. The system finally adopted consisted of glass which was slightly diamagnetic counterpoised with a small amount of aluminum which was slightly paramagnetic. By using the right amount of aluminum the zero correction could be made very small.

Several sets of values of H_y and dH_y/dx were plotted and from the mean curve values were taken for the product $H_y(dH_y/dx)$. These products were in turn plotted and the point in the field where the product was a maximum was determined. The apparatus was now set so that the center of the test coil was at the point in the field where the product $H_y(dH_y/dx)$ was a maximum and the values of H_y and dH_y/dx determined for various currents in the electromagnet. The mean of four such sets is given in Table I.

Table I.

I.	H.	$\Delta H/\Delta X$.	$H(\Delta H/\Delta X.)$
1.5 amp.	1020	205.4	209.5×10^3
2.0	1352	273.7	370.1
2.5	1687	338.5	571.1
3.0	2012	407.2	819.2
3.5	2351	473.0	1112.1
4.0	2659	530.7	1411.0
4.5	2968	596.4	1770.0
5.0	3267	648.9	2120.0

The couple C necessary to twist the suspension through unit angle was found by the ordinary vibration method. An accurately turned disc and ring were used for known moments of inertia and C calculated from the formula

$$C = \frac{4\pi^2 I}{(t'^2 - t^2)}, \tag{2}$$

where I is the known moment of inertia added to change the period from t to t'.

The oxides of seven of the rare earths, namely, erbium (Er_2O_3), dysprosium (Dy_2O_3), gadolinium (Gd_2O_3), samarium (Sa_2O_3), neodymium (Nd_2O_3), lanthanum (La_2O_3) and yttrium (Yt_2O_3), were investigated. Before using any of the oxides, they were heated to a temperature of about 1000° C. in a platinum crucible in order to decompose any carbonate which may have formed and to drive off all moisture.

The samples under investigation were contained in a silica capsule which was fitted to one arm of the torsion balance. The balance, with thermocouple and empty capsule in place, was first calibrated for fields due to currents of from 1.5 to 5 amperes and for temperatures from 25° C. to 300° C.

Table II. gives a sample set of data for Gd_2O_3 with the thermocouple

TABLE II.

Gd_2O_3 99 + *Per Cent. Pure.*

Mass of sample = .11912 gm. Lever arm of sample = 10.55 cm. Scale distance of torsion balance = 105.7 cm.

Temp.	Current in Magnet.	Deflection of Torsion Balance.	Corrected Deflection.	$X \times 10^6$.
21.8° C.	1.5 amp.	7.81 cm.	7.59 cm.	128.3
"	2.0	13.79	13.47	128.9
"	2.5	21.31	20.93	129.8
"	3.0	30.21	29.86	129.1
			Mean..........	129.0
103.2	1.5	6.12	5.98	101.1
"	2.0	11.11	10.93	104.6
"	2.5	16.80	16.64	103.2
"	3.0	23.74	23.61	102.1
"	3.5	31.82	31.75	101.1
			Mean..........	102.4
178.0	1.5	5.16	5.07	85.5
"	2.0	9.13	9.04	86.3
"	2.5	14.15	14.10	87.2
"	3.0	20.03	20.03	86.4
"	3.5	26.63	26.73	84.9
			Mean..........	86.1
269.5	1.5	4.15	4.07	68.6
"	2.0	7.43	7.37	70.3
"	2.5	11.65	11.63	71.9
"	3.0	16.49	16.59	71.5
"	3.5	21.87	22.10	70.2
			Mean..........	70.5

and torsion balance readings omitted. Four such sets of data were taken with different samples of the same material. One curve representing the four sets of data was drawn in which magnetic susceptibility was plotted against temperature. From this curve values were taken to test Curie's law.

In like manner the other oxides were tested and results plotted. From these curves the results in the first and third columns of Tables III., IV., V. and VI. were obtained. For each temperature the value of the magnetic susceptibility X, is the mean of the values obtained from four or five fields as in Table II.

Table III.

Gadolinium Oxide 99 + Per Cent. Pure.

t.	T.	$X \times 10^6$.	$XT \times 10^6$.	$X(T + 12) \times 10^6$.
20	293	130.1	38119	39680
60	333	115.1	38328	39709
120	393	98.2	38593	39771
180	453	85.5	38731	39757
240	513	75.6	38783	39690
300	573	67.8	38849	39663

Table IV.

Erbium Oxide 99.6 + Per Cent. Pure.

t.	T.	$X \times 10^6$.	$XT \times 10^6$.	$X(T + 13.5) \times 10^6$.
20	293	189.1	55406	57954
60	333	167.2	55678	57935
120	393	142.6	56042	57967
180	453	124.4	56354	58033
240	513	110.1	56462	57969
280	553	102.2	56516	57895

Table V.

Dysprosium Oxide 99.5 + Per Cent. Pure.

t.	T.	$X \times 10^6$.	$XT \times 10^6$.	$X(T + 15) \times 10^6$.
20	293	234.1	68591	72103
60	333	207.4	69064	72175
120	393	176.7	69443	72094
180	453	153.9	69717	72025
240	513	136.6	70076	72125
300	573	122.6	70250	72089

TABLE VI.

Neodymium Oxide 99.5+ Per Cent. Pure.

t.	T.	$X \times 10^6$.	$XT \times 10^6$.	$X(T+44) \times 10^6$.
23	296	29.3	8672.8	9962.0
103.4	376.4	23.7	8920.7	9963.5
179.4	452.4	19.8	8957.5	9828.7
283.0	556	16.6	9229.6	9960.0

TABLE VII.

Samarium Oxide 99.5+ Per Cent. Pure.

Temp.	$X \times 10^6$.
22.3	6.02
101.8	5.93
270.2	5.98
Mean...........	5.98

TABLE VIII.

Lanthanum Oxide 99+ Per Cent. Pure.

Temp.	H_y.	Corrected Def.	$X \times 10^6$.
24° C.	2025	−0.09	−0.49
"	2660	−0.13	−0.41
"	3010	−0.14	−0.36
"	3328	−0.16	−0.34
		Mean.............	−0.40

TABLE IX.

Yttrium Oxide 99.5+ Per Cent. Pure.

Temp.	H_y.	Corrected Def.	$X \times 10^6$.
22° C.	2025	.09	.60
"	2351	.11	.52
"	2660	.13	.48
"	3010	.17	.51
"	3328	.21	.52
		Mean	.53

Samarium oxide, Table VII., shows no variation of magnetic susceptibility with temperature. Three sets of data similar to that in Table II. were taken, all of which are summarized in Table VII. In the case of lanthanum oxide and yttrium oxide, Tables VIII. and IX., the magnetic susceptibility was so small that no attempt was made to study the variation of the susceptibility with the temperature. In the case of lanthanum oxide the magnetic susceptibility is negative, thus indicating that this oxide is diamagnetic whereas all the others are paramagnetic.

According to Curie's law the susceptibility of paramagnetic bodies times the absolute temperature is equal to a constant; that is, $XT =$ constant. An examination of Tables III., IV., V. and VI. shows that the law does not hold for any of the materials investigated. However, they are found to follow quite closely a modification of Curie's law, namely, the susceptibility times the absolute temperature plus a constant is equal to a constant, $X(T + \theta) =$ constant, in which each material has its own value of θ.

Table X.

Oxideof	Williams. $X \times 10^6$	Levy. $X \times 10^6$
Yttrium	.53 (22° C.)	−.14
Lanthanum	−.40 (24° C.)	−.18
Neodymium	29.3 (23° C.)	33.5
Samarium	5.98	6.5
Gadolinium	130.1 (20° C.)	161.
Dysprosium	234.1 (20° C.)	290.
Erbium	189.1 (20° C.)	

Table X. gives a summary of the results obtained together with results quoted by Levy in his book on "The Rare Earths," page 153, 1915.

Various explanations have been advanced for the variation from Curie's law. Oosterhuis,[1] from a consideration of zero point energy, deduces an explanation as follows:

Taking the value of the rotational energy of the molecule as deduced by Einstein and Stern[2] to be

$$U = \frac{hn}{e^{hn/kT} - 1} + \tfrac{1}{2}hn,$$

where h is Planck's constant and n the frequency of the rotation, and further assuming that this rotational energy is inversely proportional to the magnetic susceptibility X as developed by Langevin,[3], Oosterhuis deduces the relation

$$X(T + \theta) = C, \quad \text{where} \quad \theta = \frac{1}{6} \cdot \frac{hn_0}{k}.$$

Since

$$n_0 = \frac{h}{4\pi^2 I},$$

where I is the moment of inertia of the molecule, he concludes that molecules with a small moment of inertia will have a large value of θ, a large zero point energy ($\tfrac{1}{2}hn_0$) and deviate markedly from Curie's law.

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[1] Phys. Zeit., 14, 862, 1913.

[2] Ann. d. Phys., 40, 551, 1913.

[3] Ann. Chem. Phys., (8), 5, 70, 1905.

Although the results given above (Tables III., IV., V. and VI.) follow a modified form of Curie's law, θ does not vary inversely as the moment of inertia of the molecule as is shown in Table XI.

TABLE XI.

Oxide.	At. Wt.	θ.	Molecular Wt.	Molecular Wt. $\times\theta$.
Erbium	167.7	13.5	383.4	5176
Dysprosium	162.5	15.	373.0	5595
Gadolinium	157.3	12.	362.6	4351
Neodymium	144.3	44.	336.6	14810

Starting from an entirely different viewpoint Kunz[1] has derived the same expression for the variation of the magnetic susceptibility with the temperature. He points out that since it is quite likely that the electrons responsible for the paramagnetism revolve in the outer layer of the atom, the molecular moment will be the resultant of all the atomic moments of the atoms. Furthermore, with increasing temperature, it is quite likely that the atoms share the energy of temperature agitation which also will affect the resultant magnetic moment of the molecule. Therefore, in general, we may express the molecular moment as

$$M = M_0 f(T).$$

In solid or liquid paramagnetic substances the forces which oppose the tendency of the external field to direct the elementary magnets is composed of the temperature agitation RT together with a force due to the mutual effect of the molecules on each other and which would be a certain function of the temperature $f_1(T)$. With these assumptions Kunz obtains for particular values of $f(T)$ and $f_1(T)$,

$$X(T + \theta) = \text{constant}.$$

All of the substances included in this investigation which vary with the temperature obey the modified Curie law instead of the law itself. In the case of samarium oxide the magnetic susceptibility is found to be independent of the temperature. This is also probably true of lanthanum oxide and yttrium oxide.

It may appear from Table II. that the magnetic susceptibility varies with the field strength thus indicating that the substance is ferromagnetic in nature but the remainder of the data does not bear out this conclusion. In some cases the magnetic susceptibility came out very nearly constant for the different field strengths, while in others it varied in the opposite way to which it appears to vary in Table II. A careful study of all the data leads one to conclude that all the oxides are paramagnetic.

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[1] PHYS. REV., VI., 2, 113, 1915.

It was thought worth while to test the accuracy of an analysis of rare earths by the magnetic method. To do this two pure substances were mixed in known proportions and the magnetic susceptibility of the mixture determined. The results, given in Tables XII. and XIII., show very close agreement between the percentage by weight and the percentage by the measurement of the magnetic susceptibility. The magnetic method would not be adaptable if the mixture consisted of more than two substances.

Table XII.

Er_2O_3	.09095 gm.
Yt_2O_3	.06735 gm.
Total	.15830 gm.
Per cent. of Er_2O_3 by weight	57.45 per cent.

Per Cent. by the Magnetic Method.

Substance.	$X \times 10^6$.
Er_2O_3 (99.6 per cent. pure)	187.7 (at 22.3° C.)
Yt_2O_3 (99.6 per cent. pure)	.53
Mixture	108.1 (at 22.3° C.)
Per cent. Er_2O_3 by the magnetic method	57.71 per cent.

Table XIII.

Per Cent. by Weight.

Er_2O_3	.06985 gm.
Sa_2O_3	.06767 gm.
Total	.13752 gm.
Per cent. of Er_2O_3 by weight	50.79 per cent.

Per Cent. by the Magnetic Method.

Substance.	$X \times 10^6$.
Er_2O_3 (99.6 per cent. pure)	187.9 (at 21.7° C.)
Sa_2O_3 (99.5 per cent. pure)	5.98
Mixture	98.9 (at 21.7° C.)
Per cent. of Er_2O_3 by magnetic method	51.08 per cent.

Summary.

The mass susceptibilities for the oxides of erbium, dysprosium, gadolinium, samarium, neodymium, lanthanum and yttrium have been measured for temperatures from 25° C. to 300° C. and all found to be paramagnetic with the exception of lanthanum which was slightly diamagnetic.

In those cases where the susceptibility varies with the temperature Curie's law is not found to hold but the results follow quite closely a modification of this law, namely, $X(T + \theta) =$ constant. It follows that in so far as Curie's law is essential to the existence or determination of the magneton the results obtained are unfavorable.

The magnetic susceptibility does not vary with the field strength.

The results are explainable either by the theory worked out by Kunz or the zero point energy theory of Oosterhuis.

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