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THE MAGNETIC SUSCEPTIBILITIES OF THE RARE EARTHS

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Introduction

The magnetic properties of the rare earths have at different times been the object of physical research. Only once, however, in the case of Urbain's work, has the investigator who determined the magnetic susceptibilities worked with his own preparations, which enabled him to give the "chemical history" of his substances in detail. The object of the present investigation is to complete Urbain's work, in so far as magnetic numbers are reported for nearly all of the rare earths, together with a detailed description of their chemical history.

Another important property is the temperature coefficient of the magnetic susceptibilities. The only work in this line is that of Onnes and his co-workers on gadolinium and that of E. H. Williams on the oxides of neodymium, samarium, gadolinium, dysprosium and erbium. This last investigator discovered the remarkable fact that the temperature coefficient of samarium oxide is almost zero, while those of the other oxides, though not equal to one another, were all of the same order of magnitude, namely about 1/300.

Unfortunately, we did not possess adequate magnetic equipment for determinations over a wide temperature range. Still we were successful in obtaining a qualitative insight into the temperature coefficients by varying the temperature of the room in which the determinations were carried out. The results obtained by Williams were confirmed and it was found that no other rare earth has such a small temperature coefficient as samarium. Europium and thulium, however, were not investigated.

Method.—A magnetic balance as described by Curie and Cheneveau was used, but with the following improvements. The permanent magnet did not slide, but was turned round a vertical axis. It was operated from a distance of about 1.5 meters by copper wires; the deviation of the suspension carrying the material was read through a telescope by means of a mirror and scale outfit; damping was obtained through a copper segment, protruding from the suspension and turning between the poles of a small permanent magnet. The entire instrument was purchased from a French scientific company, but this description is given because a recent worker in this field still employed the old form without any of these improvements.

Manganese sulfate and cobalt sulfate, both anhydrous, were taken as standard substances, using the values given by Theodorides.[1] The balance was calibrated with these salts at the end of September, 1925, when this investigation was begun and again in July, 1926, when it was completed. The values found at these times differed by about

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[1] Theodorides, *J. phys. radium,* [vi] 3, 1 (1922).

2% and a correction was accordingly made for the values of the rare earths found at different times.

The sulfates crystallizing with eight molecules of water were used throughout; in the case of cerium, however, the salt with five molecules of water was used. Corrections were made for the empty tube and for the anion and water of crystallization, using Pascal's value of 339×10^{-7} for the sulfate group and the usual value of 0.72×10^{-6} for 1 g. of water. The values for the temperature coefficient as directly measured required a correction for possible changes in the strength of the magnet or in the elasticity of the torsion wire. The value for the temperature coefficient of gadolinium sulfate as reported by Onnes, 1/293, was taken as standard. The present authors found 1/261 and their experimental values were accordingly multiplied by $^8/_9$.

Materials Used.—*Cerium* had been purified by the bromate method. Its oxide showed a pale yellow color. thus indicating the absence of praseodymium, or at least its presence in such small amount that the influence on the magnetic property was well within the experimental error.

Praseodymium was concentrated by fractional crystallization of the double ammonium nitrates and then freed from neodymium and lanthanum by similarly treating the bromates. Three fractions were provisionally measured, whence it was found that the least soluble and the intermediate one gave the same results, while the somewhat lower figure of the most soluble indicated the presence of lanthanum. The least soluble showed a very faint trace of the neodymium absorption band, hence the intermediate one was used for the final determinations.

Neodymium was collected from several series of fractionations, purified from samarium by double magnesium nitrate crystallization and from praseodymium by fractionating the bromates. The oxide showed a pure blue color, only slightly altered at the surface, thus indicating the absence of more than 0.1% of praseodymium.

The *samarium* was the material used by Stewart and James in their atomic weight work.[2] They give full details as to its preparation and the reader is therefore referred to their paper.

Gadolinium had been subjected to a long series of bromate crystallizations. Its oxide was of a pure white color, thus indicating the entire absence of terbium. Since terbium is less easily separated from gadolinium than is europium, it may be inferred that this latter element was also absent.

Terbium.—The material for this element had been collected by James and Bissel.[3] Unfortunately only a fraction of unknown position in the series of fractionation was available to the present authors.

Holmium could only be obtained in the form of a fraction of unknown origin. The solution of the chloride did not show any dysprosium or erbium band; the color of the oxide was dark yellow, thus indicating perhaps 0.5% of terbium. Recourse was had to an equivalent-weight method (sulfate octahydrate to anhydrous sulfate ratio) in order to determine the amount of yttrium; 154.8 was found, corresponding to 88.3% of holmium.

The *yttrium* was the material used by Fogg and James[4] in their atomic weight work. Reference may be made to their paper for details concerning the preparation.

Erbium.—In a long crystallization series of the bromates of the yttrium earths, the least soluble fractions, which showed absorption bands of holmium and dysprosium, were collected on one side, the most soluble, showing the presence of thulium, on the other. The intermediate fractions, giving only the erbium lines were united and the

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[2] Stewart and James, THIS JOURNAL, **39**, 2605 (1917).

[3] James and Bissel, *ibid.*, **36**, 2060 (1914).

[4] Fogg and James, *ibid.*, **44**, 307 (1922).

erbium was accumulated by the fused-nitrate method. In this way an 85% erbium material was obtained, the rest being yttrium. It was found that from this point on, the method worked very slowly indeed. Hence, recourse was again had to the equivalent-weight method. The mean atomic weight was found to be 155.9, corresponding to 85.0% of erbium.

Ytterbium.—From a bromate crystallization, two samples about ten fractions apart were taken. The least soluble failed to show any absorption band, though from its position in the series it was inferred that it should contain thulium. The most soluble fraction gave, in a preliminary run, a magnetic value about 2% less than the other. Hence, the least soluble was taken for the final determinations.

Discussion of Results.—The values found are compiled in Table I, together with those obtained by other investigators at different times. Generally speaking, the agreement is very good, yet the following discrepancies may be pointed out. In so doing, it should be borne in mind, however, that despite the great number of investigators, the materials they worked on were derived from only four different sources: (1) Urbain's preparations were used by himself, by Onnes and partly by Cabrera; (2) Auer von Welsbach's materials were worked on by Stephan Meyer and by Decker, and partly by Cabrera; unfortunately, this last author does not state exactly which measurements were carried out with materials from the first source and which with preparations from the second; (3) E. H. Williams and Hopkins worked on materials prepared by the latter at the University of Illinois; (4) the materials of the present authors.

Decker's very low value for cerium may indicate that this element, unlike the other rare earths, shows different values in the solid and dissolved state. The numbers for samarium may clearly be divided into two groups: the values of about 1000 c. g. s. units of Urbain, Williams, Meyer and the present authors on the one side, and the value more than 10% higher of Cabrera and Decker, on the other. The value found for gadolinium was so much lower than the three most recent determinations that it was thought that the amount of crystal water in the preparation might be at fault. Experiments on the anhydrous sulfate, however, confirmed the low value, which is also corroborated by the work of Urbain and Onnes. For reasons already given, not too much importance should be attached to the value for terbium which, therefore, may be passed over without discussion. Nor is the value for holmium obtained from material of well established purity. The value here reported is lower than the three concordant numbers of Meyer, Cabrera and Decker, but not too much should be thought of this agreement, since it is probable that these three authors worked on the same material. On the other hand, Hopkins gives a still lower value, but he was more concerned with relative values for his different fractions than precise physical measurements. We must conclude, therefore, that the magnetic susceptibility of holmium is as yet uncertain, and even the interesting question as to the strongest magnetic element (holmium or dysprosium), cannot definitely be answered. On

TABLE I

Element	Magnetic Susceptibilities per Gram Atom of Sulfate Octahydrate in C. G. S. Units × 10^{-6} (χ)									(Temperature Coefficient)$^{-1}$ $\frac{1}{\alpha} = \chi \cdot \frac{dT}{d\chi} = \vartheta + 293$		
	Du Bois (in solution)	Urbain^a	Wedekind	Williams^a (20°)	S. Meyer	Cabrera	H. Decker (19°) (in solution)	J. Z. and C. J. (20°)	Error, %	Williams	J. Z. and C. J.	Error, %
Ce	2330	...	2200	...	...	2250	1891	2377	0.3	...	290	8
Pr	3150	...	5100	...	5200	5500	4970	5109	0.23	..	358	9
Nd	5010	4834	5270	4982	5300	5600	5080	5270	0.3	337	348	14
Sm	11170	980	8300?	1050	960^b	1120	1130	997	0.3	1600	1700	100
Eu	...	5090	...	...	5600	5600	6700	...	..	...	..	6
Gd	24600	25300	9850?	23550	28200	27900	26400	25860	0.2	305	305	5
	Onnes: 25750					Anhydrous sulfate: 25750			0.2	..	283	5
Tb	...	37700	...	...	35000	38700	40700	37200	2	..	327	10
Dy	...	47100	...	43570	48800	47500	50400	...	..	308	..	...
Ho	...	...	Hopkins^a: 42060		47500	47200	47200	45470	0.2	..	320	5
Er	35220	...	36700	36190	38200	38400	38900	39250	0.3	306	252	10
Tu	...	...	...	...	24500	22100	...	...	..	..	..	...
Yb	6830	...	...	...	9300	8300	8650	8311	0.3	..	292	8
Y (per g.)^a		<1	dia.	+1.0	R. J. Meyer: −0.14			−0.12	..	..	..	...

[a] Oxides. [b] Corrected by present authors for anion.

REFERENCES. Du Bois, *Ber.*, **33,** 3344 (1899). Urbain, *Compt. rend.*, **147,** 1286 (1908); **149**, 37 (1909); **159,** 323 (1924). Wedekind, *Ber.*, **54,** 253 (1921). Williams, *Phys. Rev.*, **12,** 158 (1918); **14,** 348 (1919). S. Meyer, *Physik Z.*, **26**, 51 (1925). Cabrera, *Compt. rend.*, **180,** 668 (1925). Decker, *Ann. Physik,* [iv] **79,** 324 (1926).

the other hand, it is hopeful to notice the general agreement in the case of erbium. With ytterbium we again find two sets of values: the high reported by Meyer and Decker, and the lower one of 8300 given by Cabrera and the present authors. The negative value for yttrium, agreeing within the experimental error with R. J. Meyer's value, shows that our material is as pure as any yet prepared.

Temperature Coefficient and Numbers of Magnetons.—The qualitative values obtained by the authors check remarkably well with those given by Williams. Our value for erbium is perhaps a little low. These values do not allow any calculation of magnetons, but they clearly indicate that no value can be attached to the numbers calculated by Cabrera on the assumption that $\alpha = (1/293)$ $(\vartheta = 0)$.

In conclusion the junior author wishes to express his indebtedness to the Nederlandsch-Amerikaansche Fundatie and to the International Education Board, who enabled him to carry out this work.

Summary

1. With the exception of europium, dysprosium and thulium, figures for the magnetic susceptibilities of rare earth preparations of known purity are given.

2. Qualitative values for the temperature coefficient of this property are reported.

3. These values are compared with those given by other authors, and discrepancies are briefly discussed.

4. It is pointed out that in the present state of our knowledge it is impossible to calculate magneton numbers, or to draw any conclusion as to the experimental existence of the magneton.

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A METHOD FOR DIFFERENTIAL POTENTIOMETRIC TITRATION

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It has been repeatedly shown[1] that the data obtained from potentiometric titrations can be more readily interpreted if, instead of plotting the electromotive force, E, against the volume of reagent, V, as is the usual practice, the tangent to that curve, $\Delta E/\Delta V$, is plotted against V. The end of the titration appears in the first type of curve as a point of inflection which is not always clearly defined. In the second type of curve, the end of the titration is an unmistakable, sharp maximum. D. C. Cox,[2] in a recent

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[1] See especially Hostetter and Roberts, THIS JOURNAL, **41,** 1341 (1919).

[2] Cox, *ibid.*, **47,** 2138 (1925).