[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Paramagnetism of Some Rare Earth Ions

BY C. J. RODDEN

From theoretical considerations of multiplet structure, Van Vleck[1] has arrived at values of the effective Bohr magneton number for the rare earths. In the case of samarium and europium he obtains two values for each ion depending upon whether $\sigma = 33$ or $\sigma = 34$, where σ is the screening constant.

The object of the present work was to test out the above theoretical relationships and compare the results found with those of other workers.

Experimental Part

The Gouy method was finally used after trying out the Curie–Cheneveau balance. The method as described by Freed[2] was used except that the tube was filled at the top instead of the bottom. When the tube was filled at the bottom it was found that the salt settled away from the glass partition. The magnet was demagnetized after each excitation. The apparatus and chemicals were kept in an inner room with no ventilation and the temperature of the room could be kept for one to two hours within ±0.1°. No other arrangement to keep the temperature constant was used. The apparatus was calibrated with cobalt sulfate using the value of Theodorides.[3]

$$\chi g = Cg/T - \theta \qquad Cg = 0.02051 \qquad \theta = -29.92$$

This was done before each determination. The data given are believed to be accurate to 0.5%.

Materials Used.—The rare earth salts used were obtained from the collection of the late Prof. C. James, University of New Hampshire. The praseodymium, neodymium and ytterbium were the gift of Prof. James before his death. The samarium was obtained from Mrs. James two years ago and is believed to be the same material used in the atomic weight determination of samarium.[4] The neodymium oxide gave a robin's egg color when freshly ignited, showing the presence of less than 0.1% of praseodymium. The praseodymium in the form of a concentrated nitrate solution gave no neodymium absorption bands through an 8 cm. thickness. The samarium gave no absorption spectrum of neodymium or europium under the same conditions. The oxide was a pale yellow. The ytterbium oxide was pure white. The concentrated solution of the chloride gave no absorption spectrum down to 2100 Å.

In the preparation of the salts recrystallized oxalic and C. P. mineral acids were used. The earths were precipitated three times as the oxalate and ignited to the oxide. The cobalt sulfate was made from Baker analyzed salt, recrystallized from distilled water with a small amount of sulfuric acid added and ignited to constant weight at 450°. The rare earth sulfates were made by the method of Stewart and James. The samarium and neodymium oxides were made by ignition of the oxalate at 1200° for ten hours. The neodymium ferricyanide was made according to James and Grant.[5] The $NdFe(CN)_6 \cdot 4H_2O$ analyzed 39.24% of Nd_2O_3. The hydrated sulfates were analyzed by igniting to the anhydrous sulfates. They checked the theoretical to 1 part in 1000.

Results

The following table contains the results obtained. The anhydrous sulfates, especially $Yb_2(SO_4)_3$, took on water too rapidly while filling the tubes to give consistent results.

TABLE I

Material	T, °C.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{RE} \times 10^6$	$\chi_{RE} \times 10^6$	$\mu_{eff.}$	$\mu'_{eff.}$
$Pr_2(SO_4)_3 \cdot 8H_2O$	23.2	15.08	10775	5525	5495	3.62	3.61
$Nd_2(SO_4)_3 \cdot 8H_2O$	26.7	15.33	11192	5734	5704	3.71	3.70
Nd_2O_3	25.0	31.13	10477	5288	5258	3.55	3.54
$NdFe(CN)_6 \cdot 4H_2O$	22.9	19.01	8138	5237	5207	3.52	3.51
$Sm_2(SO_4)_3 \cdot 8H_2O$	24.2	2.88	2112	1194	1164	1.68	1.66
Sm_2O_3	25.5	5.45	1902	1000	970	1.55	1.52
$Yb_2(SO_4)_3 \cdot 8H_2O$	25.5	21.75	16955	8615	8585	4.54	4.54

χ_s is susceptibility per gram; χ_M is susceptibility per gram molecule; χ_{RE} is susceptibility per gram ion of rare earth; $\mu_{eff.}$ is effective Bohr magneton obtained experimentally; χ_{RE} calculated from χ_M using diamagnetic corrections of Pascal as given in Stoner.[6] Primes mean no diamagnetic correction for R. E. ion. Other value is using -30×10^{-6} for R. E. diamagnetic correction. For the $Fe(CN)_6$ ion correction, the value 2923×10^{-6} was used from Pascal's work on a dilute solution.

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[1] Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932, p. 243, hereafter referred to as Van Vleck.

[2] Freed, THIS JOURNAL, **52**, 2702 (1930).

[3] Theodorides *J. Phys.*, [VI] **3**, 1 (1922).

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

[5] James and Grant, *ibid.*, **39**, 936 (1917).

[6] Stoner, "Magnetism and Atomic Structure," E. P. Dutton Co., New York, 1926, p. 122.

$\mu_{\text{eff.}}$ was calculated from $\mu_{\text{eff.}} = \sqrt{3\chi kT/N}$ or $2.83\sqrt{C}$ (C = Curie constant). No correction has been made for the variation of C with temperature. If this had been considered, then T would be replaced by $(T - \Delta)$, Δ being the Weiss constant. This would have an effect if Δ is really due to interatomic forces rather than to natural multiplet structure as in samarium and europium (Van Vleck, p. 245). Selwood[7] has shown that with the present knowledge it cannot be shown what Δ is really due to though there is some indication that it can be ascribed to crystalline fields.

Table II compares the results with those found by different workers. Only values for the hydrated sulfate are given.

TABLE II

μ_{eff} AT ROOM TEMPERATURE

Author[8]	Material	Pr^{---}	Nd^{---}	Sm^{---}		Yb^{---}
V. V. and F.	Theoretical	3.62	3.68	1.55	$\sigma = 33$	4.5
				1.65	$\sigma = 34$	
Cabrera	Hyd. sulf.	3.60	3.62	1.54		4.4
Meyer	Hyd. sulf	3.47	3.51	1.32		4.6
Z. and J.	Hyd. sulf	3.47	3.52	1.53		4.4
Freed	Hyd. sulf.	..	..	1.54		..
G. and deH.	Hyd. sulf.	..	3.36	..		..
Selwood	Hyd. sulf.	..	3.56	..		..
H. and P.	Hyd. sulf.	..	..	..		4.23
Rodden	Hyd. sulf.	3.62	3.71	1.68		4.54
		3.61	3.70	1.66		4.53

Discussion of Results

From the above results it may be seen that the values obtained for the hydrated sulfates agree with those of Van Vleck. The agreement is very good especially where the diamagnetism of the rare earth ion is not considered. The values obtained for the oxides are lower than the hydrated sulfates with all workers. Sucksmith[9] with Sm_2O_3 obtains a very high value of 1.70 for $\mu_{\text{eff.}}$ Cabrera's measurements in 1925 on the hydrated sulfates are higher than his 1929 measurements[10] of the anhydrous salts except in the case of samarium. It is the writer's belief that if new measurements were made on the hydrated sulfates of samarium using the material worked on in 1929, they would approach the value of Van Vleck with the screening constant 34. The results are more in accord with the value $\sigma = 34$, though since no correction has been made for crystalline fields, the actual value of σ cannot be given from the experimental measurements.

In the case of $NdFe(CN)_6{\cdot}4H_2O$ the value used for the correction due to the $Fe(CN)_6$ ion was obtained from measurements on a dilute solution of $K_3Fe(CN)_6$. Stoner, p. 163, points out that in solution there may be chemical and magnetic changes, especially with iron, which does not have the protective coating of electrons as do the rare earths, and therefore the above correction may be in doubt. If the value of the $Fe(CN)_6$ ion is calculated from the observations of Welo[11] on $Na_2(Fe(CN)_5NH_3){\cdot}H_2O$ in the solid state then the correction for the $Fe(CN)_6$ ion is 2583×10^{-6} and the value for the Bohr effective magneton of the neodymium ion is 3.65 and 3.66, the first value with no diamagnetic correction for the neodymium and the second using the diamagnetic correction as given previously.

The present work would therefore seem to bear out Van Vleck's theoretical work.

The writer wishes to thank the Physics Department of Washington Square College for the use of the magnet.

Summary

Measurements of magnetic susceptibility, at room temperature, have been made for the compounds, $Pr_2(SO_4)_3{\cdot}8H_2O$, $Nd_2(SO_4)_3{\cdot}8H_2O$, Nd_2O_3, $NdFe(CN)_6{\cdot}4H_2O$, $Sm_2(SO_4)_3{\cdot}8H_2O$, Sm_2O_3 and $Yb_2(SO_4)_3{\cdot}8H_2O$. The results obtained are discussed with reference to Van Vleck's theory of paramagnetism and are compared with other work.

NEW YORK CITY RECEIVED DECEMBER 13, 1933

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(7) Selwood, THIS JOURNAL, **55**, 3161 (1933).

(8) Cabrera, *Compt. rend.*, **180**, 668 (1925); St. Meyer, *Phys. Z.*, **26**, 51, 478 (1925); Zernike and James, THIS JOURNAL, **48**, 2827 (1926); Freed, *ibid.*, **52**, 2702 (1930); Gorter and deHaas, *Akad. Wetenschappen Amsterdam*, **34**, 1243 (1931); Hughes and Pearce, THIS JOURNAL, **55**, 3277 (1933)

(9) Sucksmith, *Phil. Mag.*, [VII] **14**, 1115 (1932).

(10) Cabrera and Duperier, *Compt. rend.*, **188**, 1640 (1929).

(11) Welo, *Nature*, **116**, 359 (1925).