2. The molal entropies of these compounds at 298.16°K. are found to be 19.75 ± 0.06, 31.77 ± 0.10 and 27.87 ± 0.08 cal./mole/deg., respectively.

3. The free energies of formation of these salts from the elements have been calculated.

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Magnetic Susceptibilities of Some Europium and Gadolinium Compounds

BY P. W. SELWOOD

The objects of this work were: (1) to provide an experimental check on the theoretical magnetic behavior of the trivalent europium ion at low temperatures,[1] (2) to determine to what extent the Sommerfeld–Kossel rule is followed by the ions Eu^{++} and Gd^{+++}, and if possible, to evaluate the spectral term of Eu^{++} from the temperature coefficient of magnetic susceptibility, and (3) by means of magnetic measurements on different gadolinium compounds to examine the influence of the Heisenberg exchange interaction with more precision than was possible in the writer's previous work[2] on neodymium, which, not being in an S state, is subject to the effect of the crystalline field on the orbital component of the magnetic moment.

Magnetic measurements on europium in the oxide and anhydrous sulfate from room temperature to 600° have been made by Cabrera and Duperier,[3] while the oxide has been examined from 183 to 673° by Sucksmith.[4] The values obtained are in fair agreement with the theoretical. However, as measurements on "magnetically dilute" substances are much to be preferred, data are given here on the octahydrated sulfate.

The only measurement made on the recently prepared compound europous sulfate is that of Hughes and Pearce,[5] who find a value some 15% lower than for gadolinium. Their work is open to the criticisms that the temperature is not stated explicitly, it is not stated what diamagnetic corrections, if any, have been made, and, finally, water, which they used for calibration, is very unsatisfactory for the measurement of a susceptibility 140 times as large.

The gadolinium compounds examined were the oxide, anhydrous chloride, and octahydrated sulfate. The first has been studied by Williams[6] over a large temperature range, and also by Cabrera and Duperier,[3] while

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[1] Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1932.

[2] Selwood, THIS JOURNAL, **55**, 3161 (1933).

[3] Cabrera and Duperier, *Compt. rend.*, **188**, 1640 (1929).

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

[5] Hughes and Pearce, THIS JOURNAL, **55**, 3277 (1933).

[6] Williams, *Phys. Rev.*, **14**, 348 (1920).

the last was the subject of the celebrated measurement of Woltjer and Onnes[7] from 1.3 to 294°K. As the author's purpose here was evaluation of the molecular field constant Δ in the familiar Weiss law $\chi = C/(T + \Delta)$, it seemed advisable to remeasure these susceptibilities. As previously pointed out, for any worth-while conclusions to be drawn it seems essential that measurements should be made on the same original rare earth material, where different compounds are being investigated.

Experimental Part

Apparatus.—The apparatus used was the Gouy magnetic balance previously described[2] with a few minor improvements giving a slightly greater field strength and better temperature control. The apparatus was calibrated with a solution of nickel chloride prepared as before, and also with a pure sample of hydrated ferrous ammonium sulfate (Mohr's salt) for which from Jackson's[8] measurements $C = 9500 \times 10^{-6}$, and $\Delta = 1°$ in the relation $\chi = C/T + \Delta$ where χ is the specific susceptibility and T the absolute temperature. The two calibrations agreed well.

Preparation of Materials.—The europium used in this work was of "atomic weight" purity[9] prepared in the Chemical Laboratory of the University of Illinois. The gadolinium[10] had been prepared at the University of Illinois by Dr. L. L. Quill and the writer during the years 1927–1930. Examination by means of the arc spectrum showed that it was free from europium and contained less than 0.2% of terbium, which would at most raise the magnetic susceptibility by 0.3%. This is slightly less than the maximum probable error in the measurements themselves. In view of the fractionation method used, the gadolinium must have been free from all other elements.

Europium oxide was prepared as usual by ignition of the oxalate. The octahydrated sulfate was prepared by a method analogous to that used for the neodymium salt in the writer's previous work.

Europous sulfate ($EuSO_4$) was prepared by electrolytic reduction in the presence of sulfuric acid according to Yntema's[11] method. Reduction at an amalgamated lead cathode in place of mercury proved unsatisfactory. The compound was washed with alcohol and ether and was dried at 65°. It showed no sign of oxidation after standing in a vacuum desiccator for several days. It was analyzed by oxidation with a little concentrated nitric acid followed by precipitation as oxalate and ignition to oxide. The mean of two closely agreeing analyses gave a weight of Eu_2O_3 less than 0.5% less than the theoretical.

Anhydrous gadolinium chloride was prepared by slow dehydration of the hydrated salt in a stream of dry hydrogen chloride gas.[12] The oxide and sulfate octahydrate were prepared in the usual manner.

In general the writer adhered to the precautions previously described in detail.

Results

In the tables χ_s is the specific (gram) susceptibility, χ_M the molar susceptibility, and χ_{Eu} or χ_{Gd} the susceptibility per gram ion of the tri-

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(7) Woltjer and Onnes, *Proc. Acad. Sci. Amsterdam*, **26**, 626 (1923).

(8) Jackson, *Trans. Roy. Soc.* (London), **A224**, 1 (1923).

(9) Preparation and criteria of purity will be described in a forthcoming paper in THIS JOURNAL by Quill and Selwood.

(10) The writer is indebted to Professor B. Smith Hopkins of the University of Illinois for the loan of both europium and gadolinium used in this work.

(11) Yntema, THIS JOURNAL, **52**, 2782 (1930).

(12) See for instance Little, "Text-Book of Inorganic Chemistry," Vol. IV (Friend), Griffin, London 1917.

valent ions corrected for the diamagnetism of anion, crystal water, and cation, the last being estimated[2] as -30×10^{-6}. Δ is given in °C.

TABLE I

$Eu_2(SO_4)_3 8H_2O$, mol. wt. 728.2, molar diamagnetic correction -335×10^{-6}

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$
343	12.3	8920	4630
293	13.1	9540	4940
223	14.6	10630	5480
153	16.2	11780	6060
83	17.0	12400	6370

Eu_2O_3, mol. wt. 352, molar diamagnetic correction -99×10^{-6}

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$
373	27.8	9800	4950
293	31.3	11020	5560
223	35.7	12560	6330
153	42.2	14860	7480
83	47.8	16830	8470

The experimental and theoretical effective Bohr magneton numbers are given in Table V.

TABLE II

$EuSO_4$, mol. wt. 248.1, molar diamagnetic correction -67×10^{-6}, $\Delta = 4°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Eu} \times 10^6$	$1/\chi_{Eu} \times 10^{-4}$	$\chi_{Eu}(T + \Delta)$
343	88.5	21950	22020	0.4540	7.64
293	103.8	25730	25800	.3880	7.66
223	135.4	33580	33650	.2970	7.64
153	195.3	48430	48500	.2060	7.62
83	353.3	87630	87700	.1140	7.63

TABLE III

Gd_2O_3, mol. wt. 362.5, molar diamagnetic correction -99×10^{-6}, $\Delta = 18°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Gd} 10^6$	$1/\chi_{Gd} \times 10^{-4}$	$\chi_{Gd}(T + \Delta)$
373	107.4	38900	19500	0.514	7.64
293	135.0	48900	24500	.408	7.62
223	173.5	62900	31500	.317	7.62
153	244.7	88700	44400	.225	7.63
83	414.5	150300	75200	.133	7.60

$GdCl_3$, mol. wt. 263.6, molar diamagnetic correction -90×10^{-6}, $\Delta = 14°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Gd} 10^6$	$1/\chi_{Gd} \times 10^{-4}$	$\chi_{Gd}(T + \Delta)$
373	74.7	19700	19800	0.505	7.66
293	94.8	25000	25100	.399	7.70
223	123.0	32400	32500	.308	7.70
153	174.5	46000	46100	.217	7.70
83	300.5	79200	79300	.126	7.69

$Gd_2(SO_4)_3 \cdot 8H_2O$, mol. wt. 746.8, molar diamagnetic correction -335×10^{-6}, $\Delta = 2°$

°K.	$\chi_s \times 10^6$	$\chi_M \times 10^6$	$\chi_{Gd} 10^6$	$1/\chi_{Gd} \times 10^{-4}$	$\chi_{Gd}(T + \Delta)$
343	62.7	46800	23500	0.425	8.11
293	73.4	54800	27500	.364	8.11
223	95.9	71600	35900	.278	8.09
153	139.3	104000	52100	.192	8.08
83	254.8	190200	95200	.105	8.10

It is of interest to compare the above results with earlier work. Values available up to 1926 are summarized by Zernike and James.[13] Work since that time has been published by Cabrera and Duperier,[3] by Sucksmith,[4]

(13) Zernike and James, THIS JOURNAL, **48**, 2827 (1926).

and by Hughes and Pearce.[5] For purposes of comparison all data are converted (interpolated where necessary) to specific susceptibility at 20° with no corrections.

TABLE IV

COMPARISON OF EXPERIMENTAL RESULTS AT 20°

	$\chi_s \times 10^6$					
	Eu_2O_3	$Eu_2(SO_4)_3 \cdot 8H_2O$	$EuSO_4$	Gd_2O_3	$GdCl_3$	$Gd_2(SO_4)_3 \cdot 8H_2O$
Urbain	28.9	..	..	135.6	..	..
S. Meyer	..	15.4	..	...	..	75.1
Cabrera	..	15.4	..	...	..	74.3
Woltjer and Onnes	..	..	..	...	..	68.6 72.2
Zernike and James	..	..	..	...	..	68.8
Williams	..	..	..	129.8	..	..
Cabrera and Duperier	26.6	..	..	139.3	..	70.8
Sucksmith	26.1	..	..	...	..	..
Hughes and Pearce	..	15.0	83.5	...	..	68.9
Selwood	31.3	13.1	103.8	135.0	94.8	73.4

Some comment on these data seems to be called for. The general agreement is far from good, although some discrepancies may be due to misunderstandings on the writer's part as to the diamagnetic corrections and temperatures applying to some of the published data. The most startling discrepancy is in the case of europous sulfate. It is difficult to see how the writer's value could be noticeably too high, and this value is, as predicted by the Sommerfeld–Kossel rule, close to that for gadolinium, while the value of Hughes and Pearce is about 20% lower. In connection with Sucksmith's low value for europium oxide, it may be pointed out that his results for neodymium and ytterbium are also considerably lower than those of other investigators, that for the ytterbium even being about 13% lower than the surprisingly low value reported by Hughes and Pearce.

With regard to the values of Δ for the gadolinium salts, Woltjer and Onnes found for the sulfate octahydrate $\Delta = 0$. This is within the writer's probable error in his value $\Delta = 2$. Williams found for the oxide $\Delta = 9$, while Cabrera and Duperier found $\Delta = 13.3$.

Discussion of Results

The early calculations by Hund[14] led to values for the magnetic moments of the rare earths in good agreement with observed values except for samarium and europium. Various speculations were made as to why the disagreement should occur, until it was shown by Van Vleck and Miss Frank[15] that in the cases of these two elements (and illinium) the multiplet intervals are not infinitely large compared to *kT*, so that the approximations in Hund's calculation are not sufficient. The predictions for samarium have already been reasonably well verified.[16] Van Vleck also

(14) Hund, *Z. Physik*, **33**, 855 (1925).

(15) Van Vleck and Frank, *Phys. Rev.*, **34**, 1494, 1625 (1929).

(16) Freed, THIS JOURNAL, **52**, 2702 (1930).

showed that a fairly large part of the paramagnetism of europium should be independent of temperature. It is the writer's purpose merely to set down Van Vleck's theoretical values and to compare them with the observed data. Only the sulfate octahydrate data are used for reasons mentioned above.

For this comparison all data are converted to "effective Bohr Magneton" numbers. These are given by $\mu_{\text{eff.}} = \sqrt{3\chi_{\text{Eu}}\, kT/L\,\beta^2}$, where k is the Boltzmann number, L Avogadro's number and β the Bohr magneton 0.9174×10^{-20} e. m. u. In the theoretical computation there exists some uncertainty as to whether the screening constant for europium should be $\sigma = 33$ or 34. Therefore two theoretical values for $\mu_{\text{eff.}}$ are given and it was at first hoped that this work would provide a means of deciding which screening constant is most probable.

There is, however, another consideration in the examination of the experimental data. For ions obeying the Weiss law $\chi = C/T + \Delta)$, Δ frequently remains fairly large (Δ for Nd = 45°) even at the highest magnetic dilution provided the ion is not in an S state. Part at least of Δ in this case is due to the orienting influence of the crystalline field, or field of oriented solvent molecules. Although europium does not obey the Weiss law, there seems to be no reason why the crystalline field should not act in the same manner here as for the other members of the rare earth group. The writer has therefore included in Table V values of $\mu_{\text{eff.}}$ calculated from $\mu_{\text{eff.}} = \sqrt{3\chi_{\text{Eu}}\, k(T + \Delta)/L\,\beta^2}$ where $\Delta = 10$, and 22. In order that the significance of these figures may more readily be grasped they are shown graphically in Fig. 1.

TABLE V

EFFECTIVE BOHR MAGNETON NUMBERS FROM $Eu_2(SO_4)_3 8H_2O$

	$\mu_{\text{eff.}}$ theoretical		$\mu_{\text{eff.}}$ experimental		
Temp., °K.	$\sigma = 33$	$\sigma = 34$	$\Delta = 0$	$\Delta = 10$	$\Delta = 22$
343	3.55	3.64	3.58	3.63	3.68
293	3.40	3.51	3.41	3.47	3.53
223	3.19	3.29	3.14	3.21	3.28
153	2.82	2.94	2.73	2.82	2.92
83	2.18	2.32	2.06	2.18	2.32

There is, of course, little justification for inserting these arbitrary figures 10 and 22, except that they are not unreasonable values compared with those found for praseodymium and neodymium. With $\Delta = 10$ the experimental values are in fair agreement with the theoretical when $\sigma = 33$. With $\Delta = 22$ the agreement is extremely good for $\sigma = 34$. It is to be hoped that a calculation such as that of Penney and Schlapp(17) for the crystalline fields of neodymium and praseodymium sulfate octahydrates may be made for europium to show which Δ, if either, is the more probable. This should settle the screening constant question once and for all.

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(17) Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932).

The susceptibility of the Eu^{++} ion is in very gratifying agreement with that of Gd^{+++}. The compound $EuSO_4$ is scarcely as magnetically dilute as might be desired, but the chemistry of divalent europium is so little known that it scarcely seemed worth while to attempt the preparation of other compounds. With such a compound as $EuSO_4$ it might be expected that the exchange interaction would be appreciable, and the value $\Delta = 4$ is a little lower than might have been anticipated. It indicates, however, that the correspondence $\chi_{Eu^{++}} = \chi_{Gd^{+++}}$ is not accidental, if such a possibility can be considered. No ion other than one in an S state could have such a low value for Δ. The electronic configuration of the europous ion must, therefore, be identical with that of trivalent gadolinium.[18]

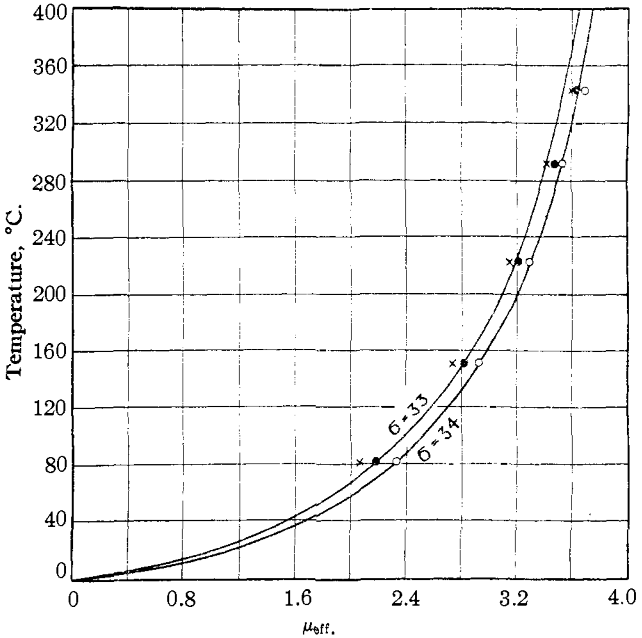

Fig. 1.—Effective Bohr magneton numbers of europium. Solid lines are theoretical for screening constants 33 and 34. Experimental points X are for $\Delta = 0$; ● for $\Delta = 10$, and ○ for $\Delta = 22$ in $\mu_{eff.} = \sqrt{3\chi_{Eu}k(T + \Delta)/L\beta^2}$.

As in the case of neodymium, the value of Δ in the gadolinium compounds is proportional to the magnetic concentration, with the difference that the effect in gadolinium is not complicated by orbital dissymmetry. The values for Δ in Nd_2O_3 = 59°, NdF_3 = 54°, $Nd_2(SO_4)_38H_2O$ = 45°, and Gd_2O_3 = 18, $GdCl_3$ = 14, $Gd_2(SO_4)_3 \cdot 8H_2O$ = 2 (or 0) show that the exchange forces are roughly the same in both cases. As Δ, at least in ferro-

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[18] As suggested by Hughes and Pearce, this, of course implies that the remaining outer electron, probably one of the 5d electrons, slips back into the 4f shell in Eu^{++}. Its ready removal again is attested by the ease of the oxidation $Eu^{++} \longrightarrow Eu^{+++}$.

magnetic substances, is readily related to the Heisenberg exchange integral, it may be possible to evaluate the variation of the integral with interionic distance when crystal structure data on the various gadolinium compounds are available. As in the case of neodymium the fairly large variation in Curie constant from one compound to another remains unexplained.

Summary

The magnetic susceptibilities of Eu_2O_3, $Eu_2(SO_4)_3 \cdot 8H_2O$, $EuSO_4$, Gd_2O_3, $GdCl_3$, and $Gd_2(SO_4)_3 \cdot 8H_2O$ have been measured from −190 to 70 or 100°. The effective Bohr magneton numbers for europium are in good agreement with quantum mechanical predictions. The susceptibility and electronic configurations of Eu^{++} are the same as those of Gd^{+++}. The Heisenberg exchange interaction forces for the gadolinium compounds are shown to be proportional to the magnetic concentration as in the case of neodymium.

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The Heat Capacity and Entropy of Nitrogen. Heat of Vaporization. Vapor Pressures of Solid and Liquid. The Reaction $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$ from Spectroscopic Data

BY W. F. GIAUQUE AND J. O. CLAYTON[1]

Besides being one of the more important elements nitrogen is interesting as a light molecule possessing two non-combining forms comprised of the alternate rotation states. Thus one of the principal reasons for the present investigation is to decide whether the lack of equilibrium between the two forms persists into the solid state in some manner similar to that existing in solid hydrogen. It will be shown later that like iodine[1a] and unlike hydrogen, the type consisting of the odd rotational levels of the normal electronic state loses, in solid nitrogen, the rotational *a priori* weight of three associated with the lowest state in the gas. The three states are replaced by one and that, presumably, is a vibrational rather than a rotational state. This corresponds to the expectation of Pauling.[2]

The present work on nitrogen also includes a calculation of its free energy from band spectra.

Preparation of Nitrogen.—The nitrogen was prepared by passing gaseous ammonia into bromine water: $8NH_3 + 3Br_2 = 6NH_4Br + N_2$. About twenty-five or thirty moles of bromine was used for each preparation. In the first experiment ammonium bromide was used to increase the solubility at the start. However, the ammonium

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(1) Shell Research Fellow, Academic year 1929-1930.

(1a) Giauque, THIS JOURNAL, **53**, 507 (1931).

(2) Pauling, *Phys. Rev.*, **36**, 430 (1930).