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TEMPERATURE VARIATION OF THE MAGNETIC SUSCEPTIBILITY, GYROMAGNETIC RATIO, AND HEAT CAPACITY IN Sm^{+++} AND Eu^{+++}

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Abstract

Calculations of the magnetic susceptibilities in Sm^{+++} and Eu^{+++} inclusive of second order Zeeman terms, previously made at $T=300°K$ only, are extended to include values over a temperature range 0°K–800°K. The value assigned to the screening constant used in computing the multiplet intervals is adjusted to make the theoretical susceptibilities agree as closely as possible with experimental data. This fixes the separation between the lowest two levels with less uncertainty than in existing spectroscopic estimates. The computations show that Sm^{+++} should exhibit an unusual behavior in that, whereas at low temperatures the susceptibility decreases rapidly with increasing temperature, a minimum is reached between 375°K and 450°K. The theoretical values of the temperature coefficients of susceptibility in Sm^{+++} and Eu^{+++} (both of which are much lower than the Curie value $1/T$) are in satisfactory agreement with experiment when the second order Zeeman terms are included. The other elements in the rare earth group do not deviate appreciably from the Curie law. The present computations show an increase in the gyromagnetic ratio in Sm^{+++} with increasing temperature, in contrast with the behavior in Eu^{+++} in which increasing temperature decreases this ratio. The temperature variation of the contribution of the multiplet levels to the heat capacity of Sm^{+++} and Eu^{+++} is also calculated.

Introduction

THE discrepancy between the theoretical and experimental values of the magnetic susceptibilities in the rare earth group was shown in a previous letter to the Editor[1] to be removed by the inclusion of the second order Zeeman terms, the effect of which is important only in Sm^{+++} and Eu^{+++}. A comparison of these theoretical results with those of Hund[2] is given in Fig. 1. In this figure, as well as throughout the rest of the paper, the three plus signs are omitted and every time the chemical symbol for an element is used, it stands for the triply charged ion of that element. Assuming infinite multiplet widths, Hund obtained an expression for the susceptibility

$$\chi = N\beta^2 g^2 J(J+1)/3kT \tag{1}$$

which conforms to the classical Curie law ($\chi \propto 1/T$). In this expression, N is Avogadro's number, g the Landé factor $[3/2+(S^2+S-L^2-L)/2(J^2+J)]$, and β the Bohr magneton ($he/4\pi mc$). Here $\beta^2 g^2 J(J+1)$ is the square of the magnetic moment of the atom and is independent of the temperature. The solid line in Fig. 1 is obtained by plotting the values of $\mu = g[J+1]^{1/2}$ the

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[1] J. H. Van Vleck and A. Frank, Phys. Rev. **34**, 1494, 1625 (1929).

[2] F. Hund, Zeits. f. Physik **33**, 855 (1925).

Bohr magneton number. The vertical lines show the range, obtained by various experimenters, of the effective Bohr magneton numbers at room temperature, defined as

$$\mu_{\mathrm{eff}} = (3kT\chi/N\beta^2)^{1/2} \tag{2}$$

by analogy to Langevin's formula. As Curie's law does not always hold, μ_{eff} is not always independent of temperature and this comparison of theoretical and experimental values of μ_{eff} is merely a convenient way of comparing the susceptibilities at a given temperature. The dotted line shows the theoretical values of μ_{eff} at room temperature when allowance is made for the finite width of the multiplets and the second order Zeeman terms. These differ materially from the values of Hund in Sm and Eu, the values being raised from 0.83 to 1.65 in the former and from 0.00 to 3.51 in the latter, the higher values agreeing with experiment.

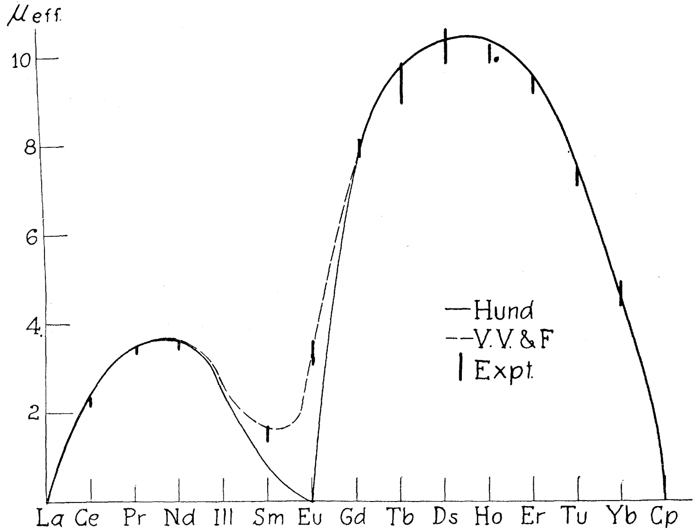

Fig. 1.

In the cases of Sm and Eu, then, it is necessary to use the complete expression for the susceptibility

$$\chi = \frac{N\sum_J \{[\beta^2 g_J{}^2 J(J+1)/3kT] + \alpha(J)\}(2J+1)e^{-W_J^0/kT}}{\sum_J (2J+1)e^{-W_J^0/kT}}, \tag{3}$$

Here $\alpha(J)$ is given[3] by

$$\frac{\beta^2}{6(2J+1)h}\left[\frac{f(J)}{\nu_{J-1;J}} + \frac{f(J+1)}{\nu_{J+1;J}}\right] \tag{4}$$

where

$$f(J) = J^{-1}[(S+L+1)^2 - J^2][J^2 - (S-L)^2].$$

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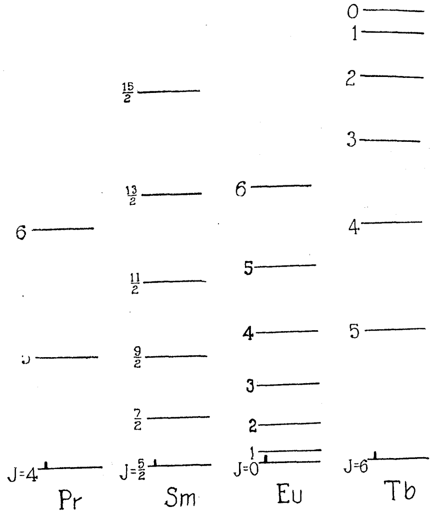
[3] J. H. Van Vleck, Phys. Rev. **31**, 587 (1928).

The first bracket of (3) differs from the expression (1) given by Hund in that multiplet widths are no longer assumed infinite so that it becomes necessary to sum[4] over all values of J. The portion of (3) involving $\alpha(J)$, usually omitted, arises from the fact that the energy expression $W_J{}^0+g\beta MH$ is not always adequate. Instead the energy should be expanded to terms of the second order in the field strength,[5] in cases where the frequency intervals $\nu_{J-1;J}$ and $\nu_{J+1;J}$ occurring in the denominator of (4) are at all comparable with kT/h.

Fig. 2 is given to emphasize again the reason why $\alpha(J)$ is so important in Sm and Eu. These diagrams, giving the relative separation of components with different values of J, show that the interval between two consecutive components may be comparable with kT even though the overall-multiplet width is much larger. For instance with the Landé rule[6] $(W^0_{J+1}-W_J{}^0)\propto(J+1)$ which is assumed in Fig. 2 for the relative multiplet separations, the lowest interval in Sm is 7/55 and in Eu 1/21 of the overall multiplet widths, in contrast with the fractions 5/11 and 6/21 in Pr and Tb respectively. The latter is included to show why the effect of $\alpha(J)$ is negligible in the last half of the rare earth group. Here the interval between the states $J_{\min}$ and $J_{\min}+1$ is small but the multiplets are inverted so that $J_{\min}$ gives the state of highest



(1=kT at 293°C=205 cm^{-1})

Fig. 2.

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[4] Laporte took into account finite multiplet widths in his values for the susceptibilities in the iron group. In this case, however, taking into account finite multiplet widths and second order Zeeman terms improves the agreement with experiment for a few elements but there still remains a considerable difference not yet explained, especially in the last half of the iron group. Cf. O. Laporte, Zeits. f. Physik **47**, 761 (1928).

[5] This second order term represents an incipient Paschen-Back effect and was calculated in the old quantum theory by A. Landé, Zeits. f. Physik **30**, 329 (1924); and in the new quantum mechanics by E. Hill and J. H. Van Vleck, Phys. Rev. **31**, 715 (1928).

energy and that level is virtually unoccupied. The situation in which there may be a small interval between consecutive components arises when the multiplicity $(2S+1)$ is large but $J_{\min}$ $(=|L-S|)$ is small. This is the case with Sm and Eu, whose multiplet types, according to the Hund theory, are ^6H and ^7F. Then it becomes necessary to include not only the contribution of atoms not in the lowest state, but also the second order Zeeman terms, since the denominators $\nu_{J-1;J}$, $\nu_{J+1;J}$ are sufficiently small to make $\alpha(J)$ appreciable.

In computing the above separations quantitatively, the over-all multiplet width is obtained from Goudsmit's theory for the multiplet separation for equivalent electrons.[6] This gives

$$W^0_{J\max} - W^0_{J\min} = R\left(\frac{2\pi e^2}{hc}\right)^2 (Z-\sigma)^4(2L+1)/n^3l(l+1)(2l+1).$$

Where R is the Rydberg constant, $n=4$ and $l=3$ in the rare earth group, L is the resultant of all the l's, and σ is the screening constant. The screening constant for the rare earths is not obtained directly but is estimated from x-ray data for heavier atoms. In the previous work, Laporte's use of $\sigma=34$ was followed. Wentzel[7] gives $\sigma=34\pm4$ and Coster,[8] 33. In the present paper, the value assigned to σ has been adjusted to make the theoretical susceptibilities agree as closely as possible with experimental data.

Temperature Variation of the Susceptibility of Sm

Table I gives the value of the effective Bohr magneton number for Sm at

Table I. *Effective Bohr magneton numbers for Sm.*

	μ_{eff} (Theory)		μ_{eff} (Experiment)			
T°K	$\sigma=33$	$\sigma=34$	Williams[9] (oxide)	Freed[10] (hyd. sul.)	Cabrera & Duperier[11] (oxide)	(anh. sul.)
0	0.85	0.85				
20	0.91	0.92				
74	1.06	1.09		0.91		
85	1.09	1.12		0.96		
112	1.16	1.20		1.08		
123	1.18	1.23	1.08			
170	1.29	1.35		1.26		
205	1.37	1.43		1.35		
240	1.44	1.52		1.44		
293	1.55	1.65	1.58	1.57	1.50	1.58
375	1.73	1.85	1.77		1.69	
400	1.78	1.91			1.75	
500	2.00	2.15			1.97	
543	2.09	2.25	2.14		2.06	
600	2.20	2.38			2.17	
800	2.58	2.78				
1000	2.91	3.14				

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[6] See e.g. Laporte, Handbuch der Astrophysik **3**, 634 ff. esp. Eqs. (50), (56).

[7] G. Wentzel, Zeits. f. Physik **33**, 849 (1925).

[8] D. Coster, in Müller-Poulliets' Handbuch der Physik, ii, 2057.

[9] E. H. Williams, Phys. Rev. **12**, 158 (1918); **14**, 348 (1919).

[10] S. Freed, J. Amer. Chem. Soc. **52**, 2702 (1930).

[11] These results are as yet unpublished but were kindly communicated to us by Professor Cabrera. Results of previous experiments of Cabrera and Duperier may be found in Comptes Rendus **188**, 1640 (1929).

various temperatures, using for the screening constant both 33 and 34, where μ_{eff} is given by (2) and χ by (3). Assuming the Landé interval rule, this takes the following explicit form in Sm

$$\chi_{\text{mol}} = \frac{0.1241}{xT}\left[\frac{2.14x+3.67+(42.9x+0.82)e^{-7x}+(142x-0.33)e^{-16x}+\cdots}{3+4e^{-7x}+5e^{-16x}+6e^{-27x}+\cdots}\right]$$

where x is 1/55 of the ratio of the overall multiplet width (expressed in ergs) to kT. If we take $\sigma=34$, then $x=191/T$ whereas with $\sigma=33$, $x=220/T$.

Figure 3 shows directly the variation of the susceptibility with temperature.[12] All of the experimental values given have been corrected for the diamagnetism of the cation but not for that of the anion since the latter is not known. The effect would be to raise the experimental points slightly.[13]

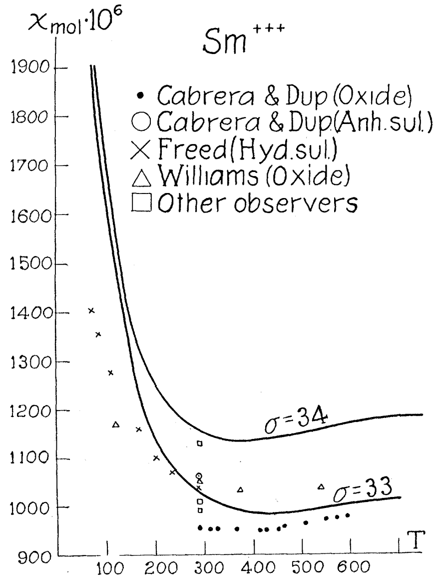

Fig. 3.

Table I and Fig. 3 show that better agreement with experiment is achieved when 33 is taken as the screening constant. Moreover, the agreement is as good as one may expect considering the differences of the experimentally determined susceptibilities among themselves and considering the fact that these determinations were made on solid compounds rather than upon the elements in the ideal gas state to which the theory applies. One may expect the oxide to deviate from theory even more than the sulphate, since

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[12] W. Sucksmith recognized the importance of the second order Zeeman terms and made a qualitative comparison of the theoretical susceptibilities with Cabrera's measurements on Sm and Eu. Proc. Lond. Phys. Soc. **42,** 388 (1930).

[13] This diamagnetic correction has been estimated at about 30×10^{-6} using the method of obtaining screening constants given by L. Pauling, Proc. Roy. Soc. **114A,** 181 (1927) or J. C. Slater, Phys. Rev. **36,** 57 (1930).

the former is a firmer chemical combination. Freed's values at low temperatures show a departure from the theoretical curve, due no doubt to distortion by interatomic forces in the solid. In applying the theoretical expression for the susceptibility in gases to liquids or solids, the results are reliable only if "the work required to turn over an ion against interatomic forces is assumed small compared with kT".[14] This assumption is no longer valid at the low temperatures used by Freed.

Although at low temperatures, the susceptibility of Sm decreases quite rapidly with an increase in temperature, a minimum is soon reached and the susceptibility increases very slowly with further increase in temperature. This minimum is located at about $T_{\min}=0.0628\ (Z-\sigma)^4$ which gives $T=386$°K with $\sigma=34$ and 444°K with $\sigma=33$. If one could determine experimentally a more accurate value for the temperature at which this minimum occurs, the screening constant could be determined more accurately, but this would be difficult since the curve is so very flat in the region of the minimum. Such a minimum has been observed experimentally, however, by Cabrera and Duperier between about 350°K and 425°K in their recent work on Sm_2O_3. Williams also gives a lower value for the susceptibility at 375°K than at 543°K and 293°K although the difference is so small that he has interpreted his data as giving a value of the susceptibility of Sm which is independent of the temperature throughout that range.

This behavior in Sm is a decided departure from the usual Curie law in which the susceptibility continues to decrease with increasing temperature. The Curie value for the temperature coefficient $(\chi^{-1}d\chi/dT)$ at room temperature is 1/293 whereas the theoretical values are 1/2525 for $\sigma=34$ and 1/1517 for $\sigma=33$. The abnormally low value for the temperature coefficient is confirmed experimentally by the measurements of Williams (1/1600), Zernicke and James[15] (1/1700) and Freed (about 1/1600). Here again better agreement is obtained when the smaller value of the screening constant is used.

Comparison of theory and experiment then, indicates that the screening constant for Sm is apparently more nearly equal to 33 than to 34. Certainly values of the susceptibility using σ less than 32 or greater than 34.5 would definitely disagree with experimental results. Thus this comparison of theoretical and experimental magnetic data fixes the screening constant with less uncertainty than do the present spectroscopic estimates. Exception may be taken to this conclusion because Russell-Saunders coupling is used throughout as the basis for the g-factor and the multiplet separations, whereas it is quite probable that there is an appreciable departure from this type of coupling even for the lowest levels in elements of so high an atomic number. This objection may be partially met by considering σ as that screening constant which fixes the interval between the lowest two levels. It then becomes necessary to investigate the effect of the third level on the susceptibility. Reducing this level so that the second interval is only one half the value obtained when

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[14] J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities, p. 193, or p. 254. (In press.)

[15] Zernicke and James, J. Amer. Chem. Soc. **48**, 2827 (1926).

Russell-Saunders coupling is assumed makes no appreciable change in the susceptibility at room temperature, but the effect increases very rapidly with increasing temperature so that such a large change in this interval changes the shape of the curve. This would give a minimum at too low a temperature and then a rapid increase in χ at higher temperatures, whereas experimental results indicate a very slow increase in χ beyond the minimum. Thus the magnetic data not only fix the interval between the lowest two levels but also indicate that, when the lowest interval is thus fixed, the interval rule for Russell-Saunders coupling gives an approximately good value for the third level.

Comparison of the Above Results in Sm with Corresponding Calculations for Eu

Sm shows an unusual behavior in the variation of susceptibility with temperature because, as the temperature increases, the increasing concentration of ions in states with large J tends to compensate for the T in the denominator of the first bracket of Eq. (3). This is not true in Eu since, for the lowest state ($J=0$), the contribution of the second order terms is so great that increasing the concentration of ions in states of higher J is of less relative importance. For Eu, the temperature coefficient is nearer the Curie value, (1/293), the computed values being 1/525 and 1/542 for $\sigma=34$ and 33 respectively. Cabrera and Duperier give 1/500 for $Eu_2(SO_4)_3$ and 1/522 for Eu_2O_3.

The rest of the rare earths conform very closely to the Curie law in which the temperature coefficient is $1/T$. For example the computed value for Nd at room temperature when $\sigma=34$ is used is 1/304. Neither the second order term nor the change in screening constant to $\sigma=33$ has much effect here on the temperature coefficient. Changing the screening constant changes the temperature coefficient to 1/301 while the omission of the second order term yields 1/294. The departure of the other rare earths from the Curie law is still less.

Table II. *Effective Bohr magneton numbers for Eu.*

	μ_{eff} (Theory)		μ_{eff} (Experiment, Cabrera & Duperier[11])	
T°K	$\sigma=34$	$\sigma=33$	oxide	anh. sul.
0	0.00	0.00		
20	1.07	1.15		
70	2.01	2.14		
100	2.38	2.53		
200	3.09	3.20		
293	3.40	3.51	3.34	3.53
400	3.65	3.75	3.57	3.75
470	3.77	3.89	3.69	3.89
625	4.02	4.14		4.11

Table II and Fig. 4 show the effective Bohr magneton number and susceptibility of Eu as functions of temperature computed from the following expression obtained from (3).

$$\chi=\frac{0.1241}{yT}\left[\frac{24+(13.5y-1.5)e^{-y}+(67.5y-2.5)e^{-3y}+(189y-3.5)e^{-6y}+\cdots}{1+3e^{-y}+5e^{-3y}+7e^{-6y}+\cdots}\right]$$

where $y=365/T$ with $\sigma=34$ and $418/T$ with $\sigma=33$.
Since we may expect the experimental data on sulphates to be more nearly in accord with the theory for gases, it is seen that probably 34 is a better estimate of the screening constant than 33. For Sm, on the other hand, values of the susceptibilities and the temperature coefficients agree better with experiment when 33 is assigned as the screening constant (although Cabrera gives as the temperature at which the minimum occurs in Sm_2O_3 a value more in agreement with that obtained with $\sigma=34$). However, the screening constant increases with atomic number and may well be a little (perhaps 0.3) higher in Eu than in Sm. Whatever doubt there may be as to which of these two values is more nearly correct, it is quite clear that in Eu as well as in Sm, $\sigma=32$ or $\sigma=35$ would not fit the experimental data at all despite the fact that they come within the range 34 ± 4 allowed by the uncertainty in the estimates from x-ray data.

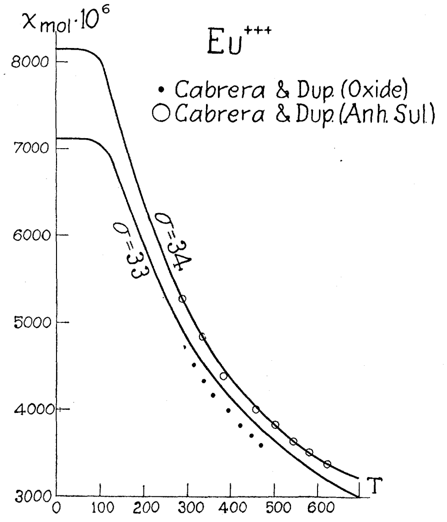

Fig. 4.

Temperature Variation of the Gyromagnetic Ratio in Sm and Eu

In order that a body be magnetized, angular momentum must be given to its atoms. This angular momentum Λ is supplied by the body as a whole, which consequently rotates with the angular momentum $-\Lambda$ if it was at rest before the field was applied (Einstein, Richardson, de Haas effect). The angular momentum supplied by the external field H itself is negligible as it is only a small fraction of the total angular momentum (of the order of magnitude of the diamagnetic correction to the paramagnetic susceptibility).[16] Table III

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[16] J. H. Van Vleck, (reference 14) p. 255 ff.

TABLE III. *Theoretical values of the gyromagnetic ratios in Sm and Eu.*

T°K	Sm $\theta\times 2mc/e$ $\sigma=34$	 $\sigma=33$	T°K	Eu $\theta\times 2mc/e$ $\sigma=34$	 $\sigma=33$
0	0.286	0.286	100	29.54	43.20
20	0.337	0.330	200	9.43	11.02
74	0.476	0.451	293	6.56	7.40
123	0.602	0.560	400	5.10	5.67
170	0.723	0.665	470	4.52	5.00
205	0.780	0.744	625	3.72	4.07
240	0.901	0.822			
293	1.026	0.937			
375	1.184	1.095			
500	1.335	1.268			
600	1.398	1.351			
800	1.448	1.430			

gives the theoretical values of the gyromagnetic ratio θ; i.e., the ratio of the magnetic moment χH to the angular momentum. This ratio can be shown to be the same as the ratio H/Ω in the converse experiment of magnetization by rotation[16] (Barnett effect) where H is the magnetic field which would produce the same magnetization as rotation of the solid with an angular velocity Ω.

The expression for the total angular momentum per cubic centimeter needed by the atoms to produce the magnetic moment is

$$\Lambda = \sum_{JM} \frac{Mh}{2\pi} e^{-W_J/kT} \Big/ \sum_{JM} e^{-W_J/kT}$$

where $Mh/2\pi$ is the free atom's angular momentum in the direction of the field. Here it is unnecessary to include second order terms since the angular momentum is only very slightly perturbed by the field.[17] This expression can be simplified by substituting $W_J = W_J{}^0 + Mg_J\beta H$, expanding the exponentials, and summing over M, which ranges from $-J$ to $+J$. Thus

$$\Lambda = \frac{\sum_{JM} \frac{Mh}{2\pi} e^{-W_J^0/kT}(1 - Mg_J\beta H + \cdots)}{\sum_{JM} e^{-W_J^0/kT}(1 - Mg_J\beta H + \cdots)}. \tag{5}$$

Now

$$\sum_{-J}^{+J} M = 0 \text{ and } \sum_{-J}^{+J} M^2 = \tfrac{1}{3}J(J+1)(2J+1)$$

so that, by using Eqs. (3) and (5), the complete expression for the gyromagnetic ratio becomes

$$\theta = \frac{\chi H}{\Lambda} = \frac{e \sum_J \{g_J{}^2 J(J+1) + 3kT\alpha(J)/\beta^2\}(2J+1)e^{-W_J^0/kT}}{2mc \sum_J g_J J(J+1)(2J+1)e^{-W_J^0/kT}}. \tag{6}$$

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[17] The component of angular momentum in the direction of the field is a constant of the motion unperturbed by the field except for a small diamagnetic correction. See reference 16.

Eq. (6) reduces under the assumption of infinite multiplet widths to the usual expression $\theta = eg_J/2mc$ for the gyromagnetic ratio. In the case of Sm and Eu, however, θ is a function of T because we must add the contribution of atoms not in the lowest state, and because the terms involving $\alpha(J)$ are so important in their contribution to the magnetic moment. For example in Sm at room temperature, $\theta \times 2mc/e$ is 0.323 with $\sigma = 34$ and 0.305 with $\sigma = 33$ when the second order terms are neglected, while the table shows the much higher values, 1.026 and 0.937 at this temperature. These second order terms are particularly important in Eu for without them, the gyromagnetic ratio is independent of temperature, inasmuch as here g_J is independent of J. This situation arises in Eu since $S = L$ so that the g-factor reduces to $3/2$ ($J \neq 0$). Thus from (6) it is clear that $\theta = g_J e/2mc$ or 1.5 $e/2mc$ when the second order terms are omitted. When the second order terms are included, there is a decided change in θ with temperature. Unfortunately there are no precise experimental data available as yet although Sucksmith,[18] in a preliminary report on this very difficult experimental work which he is undertaking, indicates that the results at room temperatures favor the values found in the table, rather than $1.5e/2mc$. The great importance of the second order terms in Eu is particularly evident here since the gyromagnetic ratio decreases with increasing temperature, in striking contrast to the behavior in Sm. The explanation for this difference is again to be found in the fact that in Sm, increasing the temperature increases the concentration of atoms into states of higher J and higher g_J. Thus the numerator of (6) increases more rapidly than the denominator. In Eu, however, the term involving $\alpha(J)$ for the lowest state is so large that increasing the ions in states of higher J has less relative importance in the numerator than in the denominator where there are no $\alpha(J)$ terms.

The gyromagnetic ratio for the rest of the rare earths is very nearly equal to $g_{J\min} \times e/2mc$ and is almost independent of temperature. For instance, $g_{J\min}$ for Nd is 0.73. The gyromagnetic ratio ranges from $0.73e/2mc$ at 0°K to $0.79e/2mc$ at 600°K, with no appreciable difference whether σ is taken as 33 or 34. There is even less dependence on temperature for the rest of the rare earths.

Temperature Variation of the Heat Capacity in Sm and Eu

The contribution of the multiplet levels to the heat capacity of Sm and Eu, assuming the ideal gas state, is given by the expression

$$C = N \frac{d}{dT} \left\{ \frac{\sum_J (W_J^0(2J+1)e^{-W_J^0/kT}}{\sum_J (2J+1)e^{-W_J^0/kT}} \right\}.$$

Table IV shows the variation of C with temperature for Sm and Eu, again assuming the Landé interval rule in obtaining W_J. This calculation illustrates again the difference between Sm and Eu, and the rest of the rare earth group.

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[18] W. Sucksmith, Paper delivered at the British Association (1930).

TABLE IV.

T°K	Sm C (cal./mol.) $\sigma=34$	 $\sigma=33$	T°K	Eu C (cal./mol.) $\sigma=34$	 $\sigma=33$
0	0.00	0.00	0	0.00	0.00
170	0.06	0.03	50	0.21	0.10
205	0.17	0.08	70	0.85	0.54
240	0.31	0.18	100	1.79	1.46
293	0.57	0.38	200	2.10	1.94
400	1.04	0.83	293	2.02	2.05
500	1.34	1.16	400	2.00	2.02
600	1.52	1.38	470	1.99	2.01
800	1.73	1.64	625	1.99	2.00

In the other rare earths, all levels except the lowest are virtually unoccupied since $W_J \gg kT$. Fig. 2 shows that W_J is comparable with kT in Sm and Eu, especially for the lowest interval. Thus a change in temperature gives an appreciable change in the number of ions which occupy states other than that for which J is a minimum and hence a change in total energy. Eu shows a more rapid change in C than Sm for low temperatures, since the first interval is so much smaller that the total energy is even more sensitive to a change in temperature. Thus, whereas the values given for C in Table IV increases somewhat with temperature for Sm, for Eu it shows a much more rapid rate of increase for low temperatures, but reaches a maximum at room temperature or less.

I am very grateful to Professor J. H. Van Vleck, under whose direction these computations were made.