

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

MAGNETIC SUSCEPTIBILITY OF $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

BY F. H. SPEDDING*

RECEIVED NOVEMBER 30, 1931

PUBLISHED JULY 6, 1932

Hund¹ calculated values for the magnetic susceptibility of the rare earth ions, employing basic levels he had predicted from rules of spectra. His results, except for Sm^{+++} and Eu^{+++} ,² were in excellent agreement with the values which had been obtained experimentally with solids and solutions.

Freed³ has shown very conclusively in his magnetic researches that the discrepancy in the case of Sm^{+++} is due to the presence of electronic isomers. That is, at very low temperatures the electronic configuration of most of the samarium ions is that predicted by Hund ($4f^5$, ${}^6\text{H}_{5/2}$). At higher temperatures, however, Freed showed that many of the atoms due to the Boltzmann distribution are in excited states, the energy values of which are but slightly greater than that of the ${}^6\text{H}_{7/2}$ term.

A confirmation of the existence of these isomers was found by Freed and Spedding⁴ from the absorption spectrum of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ crystals. They found that as the temperature of the crystal was lowered certain lines tended to become more intense while others, usually a few hundred inverse centimeters to the red, faded out and finally disappeared.

At the time these researches were performed Freed was unable to determine the electronic configuration of the excited states as all the usual systems of coupling gave susceptibilities which could not be brought into accord with his data.

Since then from researches on the Gd^{+++} ion it has been shown⁵ that a new type of magnetic coupling is probably effective in the case of the rare earths. In a letter to *Physical Review*,⁶ experimental evidence was presented which showed that when a rare earth ion is excited, a 4f electron jumps through the 5s, 5p completed shells to a 5d, 5f or 5g orbit. Due to its electrical nature this orbit is strongly coupled to the electrical fields of the crystal and cannot orient in the magnetic fields obtainable in the laboratory.

It will, however, have a magnetic moment which will couple with the resultant moment of the remaining 4f electrons and the energy of this

* National Research Fellow.

¹ F. Hund, *Z. Physik*, **33**, 349 (1925).

² J. H. Van Vleck, *Phys. Rev.*, **31**, 587 (1928), has explained the discrepancy in the case of Eu^{+++} .

³ Freed, *THIS JOURNAL*, **52**, 2702 (1930).

⁴ Freed and Spedding, *Nature*, **123**, 525 (1929).

⁵ F. H. Spedding, *Phys. Rev.*, **37**, 771 (1931).

⁶ F. H. Spedding, *ibid.*, **38**, 2080 (1931).

coupling will presumably be so great that ordinary magnetic fields will not disrupt it. Therefore the 4f electrons will not contribute anything as a first approximation to the magnetic susceptibility of the ions. The spin of the external electron, however, will be loosely coupled, as its resonance effect with the other spins will be negligible due to the shielding action of the 5s, 5p shells and it will orient rather freely in ordinary magnetic fields. Thus all the excited levels will have a susceptibility corresponding to the spin of one electron.

While in gaseous Sm^{+++} ions one would expect the $((^5J_4 \cdot d)_6)_{11/2}$ term to be the one of lowest energy, in solids, due to the effect of the surrounding ions in a crystal the $((^5J_4 \cdot g)_8)_{11/2}$ or $((^5J_4 \cdot f)_7)_{11/2}$ might be the lowest due to the greater symmetry of the f and g orbits. In any case the energy difference between them will not be great as they resemble somewhat the single electron in the alkali spectra.

If one assumes the basic level of Sm^{+++} ion in $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ to be a $^6H_{5/2}$ which is free to orient in a magnetic field (Hund's assumption) and that the first excited level is a $((^5J_4 \cdot g)_8)_{11/2}$, in which the g orbit is bound, then the Curie constants per mole using the customary formula

$$C = \frac{N}{3k} j(j+1)g^2\beta^2$$

where N is Avogadro number, k Boltzmann constant, and β the Bohr magneton $eh/4\pi m_0 c$ will be

$$C_0 = \frac{g^2 j(j+1)}{(2.838)^2} = \frac{\left(\frac{2}{7}\right)^2 \frac{5}{2} \times \frac{7}{2}}{(2.838)^2} = 0.08867$$

for the normal state and

$$C_1 = \frac{2^2 \left(\frac{1}{2} \times \frac{3}{2}\right)}{(2.838)^2} = 0.3724$$

for the excited states. The susceptibility at any temperature can be calculated from the relation⁷

$$\frac{C_0 N_0}{T + \Delta_1} + \frac{C_1(1 - N_0)}{T + \Delta_2} = \chi$$

where T is the absolute temperature, N_0 the percentage of ions in the normal state, χ is the susceptibility per mole, and Δ is a blanket correction factor, covering such factors as the effect of restraints on the free orientation of the permanent moment due to the coupling of the spin with the orbit in the excited states, and of the orbits with the crystal fields in the normal term. It would also include any magnetic contributions which might arise from having the orbits warp in the excited state.

⁷ The Van Vleck "forgotten term" can be neglected here as the levels are well separated and do not belong to the same multiplet. When N_0 becomes 100% this equation becomes the Curie Weiss Law $\chi = C/(T + \Delta)$.

Not much is known about this Δ ; however, in the case of $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ⁸ where the basic level has a term composed of spin and orbital moments somewhat similar to $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ it is small, amounting to 1.9°K .

In these calculations both Δ_1 and Δ_2 were assumed to be 2°K . N_0 is calculated in the ordinary way⁹.

$$\frac{1 - N_0}{N_0} = \frac{S_1 e^{-\frac{h\Delta\nu}{kT}}}{S_0(1)}$$

where S_1 and S_0 are the statistical weights of the levels and $\Delta\nu$ is the separation in inverse centimeters between them. Using one of Freed's experimentally determined points, $\Delta\nu$ was calculated. It is 195 cm.^{-1} . Then, using this value, other points on the curve were calculated. They are given in Table I and are in good agreement up to 150°K ., after which they deviate. This deviation, however, is to be expected as other terms become effective at higher temperatures; the $({}^5\text{J}_4 \cdot \text{f}_7)_{15/2, 13/2}$ ($({}^5\text{J}_4 \cdot \text{d})_6$)_{13/2, 11/2} are not much higher and also terms of the type $(({}^5\text{J}_4 \cdot \text{g})_7)_{15/2, 13/2}$ ($({}^5\text{J}_4 \cdot \text{g})_6$)_{13/2, 11/2} would occur within a few hundred cm.^{-1} of the $(({}^5\text{J}_4 \cdot \text{g})_8)_{17/2}$ term.¹⁰ From the equations it can be seen that χ is very sensitive to the value of C_1 . The statistical weight of the excited state, since it enters into the calculation of N_0 only and not C , can be varied somewhat if $\Delta\nu$ and the Δ 's are varied also as χ is not very sensitive to them when they are varied as a group. However, for states other than $({}^5\text{J}_4 \cdot \text{g})$ and $({}^5\text{J}_4 \cdot \text{f})$ the Δ 's become so large as to seem improbable. Table II gives the calculated values for a $(({}^5\text{J}_4 \cdot \text{f})_7)_{15/2, 13/2}$ excited level. $\Delta\nu$ comes out 165 cm.^{-1} and Δ has to be 7°K .

⁸ De Haas, Wiersma and Capel, Leiden Communication 201b.

⁹ The statistical weight of the lower level will be equal to $2j + 1$ or 6 as j is equal to $5/2$. The statistical weight of the excited level depends on the fact that the g orbit is bound to the crystal field. This orbit can take $(2j + 1)$ orientations to this field or 9 since j is 4 , and as the spin can be either with or against the orbit the total value is 2×9 or 18 .

The contribution of the frozen $4f$ electrons enters into the weight in giving rise to terms of different energy such as $({}^5\text{J}_4 \cdot \text{g})_8$ and $({}^5\text{J}_4 \cdot \text{g})_7$, where, due to the bound orbit, the multiplicity is again 18 .

$\Delta\nu$ is, of course, the mean distance between the weighted center of the multiplets as both upper and lower levels are non-degenerate due to the electric field of the crystals. (Some of these levels may become degenerate in crystals of high symmetry.) While the splitting in the lower level is negligible, it may be rather large in the excited state, amounting to 70 cm.^{-1} or 80 cm.^{-1} (as in the case of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$). However, the weighted mean (according to the Boltzmann factor) is not very sensitive to temperature in the case calculated here.

¹⁰ In the case of Gd^{+++} where the basic level is known to be single $({}^8\text{S}_{7/2})$ there are over sixty lines occurring in the space of 700 cm.^{-1} . These excited terms are probably of the type

$$({}^7\text{F}_1 \cdot \text{g})_5)_{9/2}, ({}^7\text{F}_1 \cdot \text{g})_4)_{7/2, 9/2}, ({}^7\text{F}_1 \cdot \text{d})_3)_{5/2, 7/2}, \text{etc.}$$

The multiplet of lowest energy is well separated from the rest and they become closer together toward higher frequencies, just as would be expected.

TABLE I

MAGNETIC SUSCEPTIBILITY OF $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

Basic Level $^6\text{H}_{5/2}$, Curie Constant = $C_0 = 0.08867$. First excited level $((^5\text{J}_{4g})_8)^{15/2, 17/2}$,
Curie Constant $C = 0.3724$. $\Delta\nu = 195 \text{ cm.}^{-1}$. $\Delta = 2^\circ \text{ \AA}$.

T , Absolute	N_0	N_1	N_0C_0	N_1C_1	Calcd. χ	Experimental χ
73.8	0.9359	0.0641	830	239	$\times 10^6$	$\times 10^6$
					1410	1402
80	.9159	.0841	813	313	1373	1375
90	.8808	.1192	781	444	1332	1338
100	.8443	.1557	749	580	1303	1308
120	.7716	.2284	684	851	1260	1254
140	.7096	.2904	629	1081	1205	1206
160	.6558	.3442	581	1282	1150	1171
180	.6107	.3893	542	1450	1094	1140
200	.5734	.4266	508	1589	1038	1119
250	.5042	.4958	447	1846	910	1065
300	.4578	.5422	406	2019	803	1035

TABLE II

MAGNETIC SUSCEPTIBILITY OF $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

Excited Level $((^5\text{J}_{4f})_7)^{13/2, 15/2}$. $\Delta = 7^\circ$. $\Delta\nu = 165 \text{ cm.}^{-1}$

T , Absolute	N_0	N_1	N_0C_0	N_1C_1	Calcd. $\chi \times 10^6$	Obs. $\chi \times 10^6$
73.8	0.9130	0.0870	810	324	1403	1402
80	.8912	.1088	790	405	1374	1375
90	.8551	.1449	758	540	1337	1338
100	.8196	.1804	727	672	1307	1308
120	.7519	.2481	667	924	1256	1254
140	.6982	.3018	619	1124	1185	1206
160	.6520	.3480	578	1296	1122	1171

From the above it would appear that the excited electronic isomers of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ consist of $4f^6g$, $4f^65f$, $4f^65d$ configurations where the $4f^6$ electrons combine among themselves and the resultant couples firmly with the orbit of the excited electron, which itself is firmly coupled with the electric field of the crystal lattice. Thus only the spin of the external electron contributes to the magnetic susceptibility and all excited terms have a Curie constant of 0.3724. At present it is impossible to determine whether the excited electron in the first excited state is in a $5g$ or $5f$ orbit but it is hoped an answer will be found shortly from a study of the absorption spectra which is being carried out by Mr. Bear and myself.

Since the above paper was written considerable work has been done in this field.

Spedding and Bear, *Phys. Rev.*, **39**, 948 (1932), have investigated the absorption and reflection spectra of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ and have identified a group of levels occurring about 160 cm.^{-1} above the basic level. Recently they have also identified another group of levels occurring between 250 cm.^{-1} and 300 cm.^{-1} from the basic level, just as predicted above, and will publish their results shortly in *Physical Review*. Preliminary photographs with $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ indicate that the same levels occur in approximately the same positions.

Ahlberg and Freed have measured the specific heats of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, *ibid.*, **39**, 540 (1932), and have concluded that Sm^{+++} in $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

has "electronic isomers" which are separated from the basic level by about 160 cm.^{-1} and which have approximately twice the statistical weight of the basic level. These values are in excellent agreement with those calculated in Table II above.

Amelia Frank, *ibid.*, 39, 119 (1932), in extending the work of J. H. Van Vleck and A. Frank, has attempted an alternative explanation. In view of the experimental facts, her calculations cannot be correct as stated, as her first excited level occurs around 900 cm.^{-1} . However, the ${}^6\text{H}_{7/4}$ term would be expected to occur at a slightly greater value than that and at higher temperatures an effect such as they predict probably exists.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 318, AND FROM THE CHEMICAL LABORATORY AT THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE KINETICS OF THE REACTION BETWEEN POTASSIUM PERMANGANATE AND OXALIC ACID. I

BY HERBERT F. LAUNER

RECEIVED DECEMBER 21, 1931

PUBLISHED JULY 6, 1932

Introduction

The over-all reaction between permanganate and oxalic acid is expressed by the equation



The rate of this reaction has been studied by several investigators¹ all of whom used an iodimetric method for the analysis of the reaction mixtures.

In this paper are presented the results of a new investigation of the reaction between permanganate ion and oxalate ion.

The author wishes to express here his appreciation of the aid and criticisms of Prof. Don M. Yost and Dr. J. B. Ramsey.

A large number of experiments were made on this reaction by an improved method which show that the mechanism previously suggested by Skrabal is not consistent with all of the experimentally found facts. Because of the rather complicated nature of the reaction the outstanding experimental results and theoretical conclusions will, for greater clearness, be stated briefly at this point.

When a solution of permanganate ion is added to one of manganous ion in which acid and oxalate ion are also present, a cherry-red solution of a complex ion formed from manganic ion and oxalate ion results, whereas in the absence of oxalate ion or other anion capable of forming a complex, a precipitate of manganese dioxide is obtained. It will be shown that the formula of the manganic complex ion is $\text{Mn}(\text{C}_2\text{O}_4)_2^-$.

The rate of the reaction when manganous ion was present initially in

¹ Harcourt and Esson, *Phil. Trans.*, 201 (1866); Schilow, *Ber.*, 36, 2735 (1903); Skrabal, *Z. anorg. Chem.*, 42, 1 (1904).