[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Magnetochemical Properties of Samarium[1]

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The purpose of this work was to clear up one or two points in connection with the magnetic properties of samarium compounds, and to determine the electronic configuration of the divalent samarium ion.

Experimental Part

Preparation of Materials.—A quantity of samarium of the highest purity was put at the writer's disposal through the kindness of Professor B. S. Hopkins of the University of Illinois. The compounds on which magnetic measurements were made were the oxide, sulfate octahydrate, tribromide and dibromide. With the exception of the dibromide, preparation of these compounds involves no difficulty. Divalent compounds of samarium, however, have been prepared only a few times previously and probably never in a high state of purity.[2,3,4,5,6] The preparation consists of two steps, first, dehydration of the moist tribromide, and second, reduction with hydrogen to the dibromide. Both these steps were carried out conveniently in the same apparatus (Fig. 1). A stream of oxygen-free nitrogen was saturated with hydrobromic acid, dried over phosphorus pentoxide, and passed over the hydrated tribromide at a pressure of a few cm. of mercury. The temperature was held for two hours at 90°, an hour at 130°, and was then slowly raised to 250° when dehydration was complete and the hydrogen bromide was swept out with a stream of pure nitrogen. The resultant product was both anhydrous and free from basic contamination. The statement appears in the literature[7] that nitrogen may effect a surface reduction of samarium salts. This observation was verified at a temperature of 450°. But with the apparatus described, dehydration was complete at 250°, at which temperature no reduction took place.

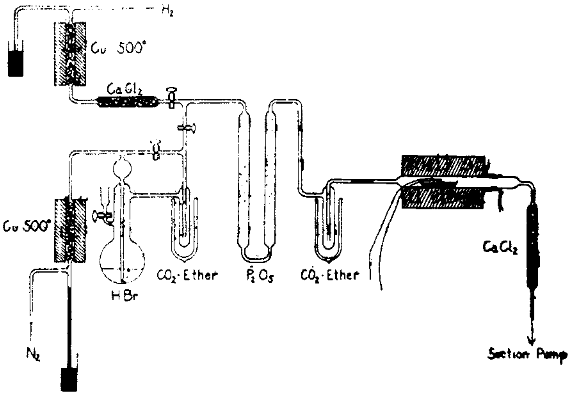

Fig. 1.—Apparatus for the preparation of samarium dibromide.

The anhydrous samarium tribromide having been obtained, pure dry hydrogen at normal pressure was passed over the salt while the temperature was raised slowly to 740° and held there for five hours. Progress of reduction could be followed by development of the intense chocolate-brown color characteristic of divalent samarium. Completion of reaction was indicated by discontinued evolution of hydrogen bromide. The product was analyzed for both samarium and bromine and was found in different batches to run from 50 to 90% pure $SmBr_2$, the remainder being unreduced $SmBr_3$ for which a suitable correction in the magnetic measurements was made. Samarium dibromide proved to be quite stable if kept perfectly dry, preferably in a hydrogen atmosphere. But on exposure to moist air decomposition was almost instantaneous. Measurements taken twelve hours apart, however, on material kept in the magnetic balance gave no indication of decomposition.

Magnetic Measurements.—The magnetic measurements were done on a form of the Gouy balance previously described in detail.[8,9] The same precautions and methods of handling the results were adhered to.

Experimental Results

Table I gives the magnetic susceptibilities of the compounds Sm_2O_3, $Sm_2(SO_4)_3 \cdot 8H_2O$ and $SmBr_3$ at 20°. In this table χ_S is the specific (gram) susceptibility, χ_M the molar susceptibility and $\chi_{Sm^{+++}}$ the susceptibility per gram-ion of the trivalent ion corrected as usual for the diamagnetism of anion, crystal water and cation.

TABLE I

	$\chi_S \times 10^6$	$\chi_M \times 10^6$	$\chi_{Sm^{+++}} \times 10^6$
Sm_2O_3	5.60	1950	1030
$SmBr_3$	2.49	972	1060
$Sm_2(SO_4)_3 \cdot 8H_2O$	2.34	1710	1020

Even in those rare earths having an appreciable orbital component of magnetic moment, the 4f electron shell is so well shielded from external influence that different compounds of the same element may be expected to have approximately the same magnetic susceptibility per gram-ion. Klemm and Rockstroh[5] have, however, reported a wide divergence amounting to 50% between

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[1] Presented at the Cleveland meeting of the American Chemical Society, September 12, 1934.

[2] Matignon and Cazes, *Compt. rend.*, **140**, 1637 (1905); **142**, 83 (1906); *Ann. chim. phys.*, [8] **8**, 418 (1906).

[3] Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927).

[4] Prandtl and Kögl, *ibid.*, **172**, 265 (1928).

[5] Klemm and Rockstroh, *ibid.*, **176**, 181 (1928).

[6] Jantsch and Skalla, *ibid.*, **193**, 391 (1930).

[7] Owens, Balke and Kremers, THIS JOURNAL, **42**, 515 (1920).

[8] Selwood, *ibid.*, **55**, 3161 (1933).

[9] Selwood, *ibid.*, **55**, 4869 (1933).

samarium oxide and tribromide. It seemed worth while, therefore, to repeat their measurements. Table II gives their values together with the writer's and those of two other recent workers in the field.

TABLE II

SUSCEPTIBILITIES PER GRAM-ION × 10^6 AT 20°

	Sm_2O_3	$SmBr_3$	$Sm_2(SO_4)_3 \cdot 8H_2O$
Klemm and Rockstroh	990	1560	..
Freed[10]	..	..	1060
Williams[11]	1050	..	..
Selwood	1030	1060	1020

As the agreement is satisfactory between values reported by the last three workers named, it seems safe to conclude that the discrepancy with regard to samarium tribromide does not exist.

Table III gives data obtained over a temperature range of about 300° from the compound samarium dibromide, corrected of course for tribromide content. For purposes of comparison the writer's previously published data on trivalent europium are included.

TABLE III

°K.	$\chi_S \times 10^6$	$\chi_M \times 10^6$	$\chi_{Sm^{++}} \times 10^6$	$\chi_{Eu^{+++}} \times 10^6$
373	15.2	4710	4800	4630 (343°)
293	17.2	5330	5420	4940
223	19.6	6080	6170	5480
153	22.9	7100	7190	6060
83	24.6	7630	7720	6370

The only other measurement reported for divalent samarium is that of Klemm and Rockstroh[5] also on the dibromide, at the single temperature 20°. They give $\chi_M = 7100 \times 10^{-6}$, a very considerable divergence from the writer's value.

It may be of interest to add that the reflection spectrum of solid samarium dibromide apparently consists of a diffuse band throughout the visible bearing no resemblance whatever to the discrete bands characteristic of most trivalent rare earth salts.

Discussion of Results

Figure 2 shows "effective" Bohr magneton numbers plotted against temperature. These numbers are given by

$$\mu_{\text{eff.}} = \sqrt{3\chi kT/L\beta^2}$$

where χ is the susceptibility per gram-ion, k the Boltzmann number, L Avogadro's number and β the Bohr magneton 0.9174×10^{-20} e. m. u. No attempt has been made to evaluate the molecular field constant. The solid lines are for the trivalent ions of samarium and europium, the data being taken from the work of Freed[10] and the writer,[9] respectively. The dotted lines indicate theoretical extension of the experimental data to absolute zero.[12] The experimental points shown are for divalent samarium, and, as may be seen, are almost the same as for trivalent europium. This is the result to be anticipated from the Sommerfeld–Kossel rule which states that ions with equal numbers of electrons often have very similar properties. The result is of added interest because both samarium and europium have decidedly anomalous temperature coefficients of magnetic susceptibility.

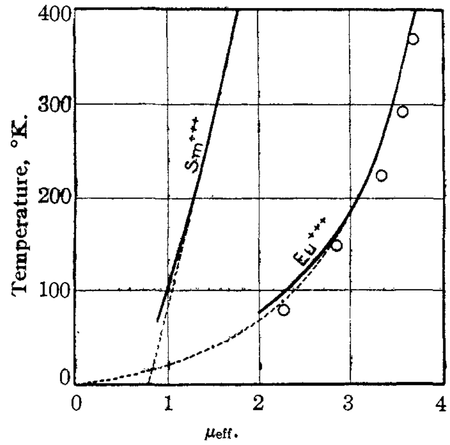

Fig. 2.—Effective Bohr magneton numbers for the ions Sm^{+++}, Eu^{+++} and Sm^{++}: experimental points ○ are for Sm^{++}.

In the previously reported case of divalent europium[9] it was shown that the spectral term must be ^8S and the electronic configuration identical with that of trivalent gadolinium because the low value obtained for Δ, the molecular field constant, in the Weiss law $\chi = C/(T + \Delta)$ excluded any other possibility. For samarium, the anomalous temperature coefficient renders it impossible to determine Δ with any degree of accuracy, and it is doubtful if it would have any significance even if obtained. The evidence in the present case is, therefore, to some extent circumstantial, but in view of the correspondence $\chi_{Sm^{++}} = \chi_{Eu^{+++}}$ at all temperatures investigated, it is probably safe to say that the electronic configurations of these two ions are also identical. This is the conclusion reached by Klemm and Rockstroh on much less complete evidence. The arrangement of electrons in trivalent europium

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

(11) Williams, *Phys. Rev.*, **12**, 158 (1918).

(12) Van Vleck, "Theory of Electric and Magnetic Susceptibilities, Oxford University Press, 1932.

from the 4f shell out is $4f^65s^25p^6$. In divalent samarium it is probably the 6s and one of the 5d electrons which are lost $4f^55s^25p^65d(^26s)$. The remaining 5d electron does not, however, stay in that position, but migrates back to the 4f shell. Its ready removal again is attested by the extremely easy oxidation of the ion.

It has been claimed by Prandtl and Kögl[4] that divalent samarium does not exist, and that its supposed compounds are merely solutions or compounds of the normal salts with the free metal. But the magnetic evidence shows beyond all question that such cannot be the case.

Table IV shows all the known valence states of all the rare earths arranged so that ions having equal numbers of extranuclear electrons are on the same row. The table also indicates the normal spectral term probably associated with each ion, together with the number of 4f electrons present. These spectral terms were originally assigned to the trivalent ions only. It has now been shown that they are equally applicable to the divalent ions of samarium and europium, and most likely to the other non-trivalent ions indicated.

TABLE IV

ISOELECTRONIC ARRANGEMENT OF THE RARE EARTH IONS

No. of electrons	Term	Divalent	Trivalent	Quadrivalent
54	$4f^0\ {}^1S$		La^{+++}	↗ Ce^{++++}
55	$4f^1\ {}^2F_{5/2}$		Ce^{+++} ↗	↗ Pr^{++++}
56	$4f^2\ {}^3H_4$		Pr^{+++} ↗	
57	$4f^3\ {}^4I_{9/2}$		Nd^{+++}	
58	$4f^4\ {}^5I_4\ldots$		Il^{+++}	
59	$4f^5\ {}^6H_{5/2}\ldots$		↙ Sm^{+++}	
60	$4f^6\ {}^7F_0\ldots$	Sm^{++} ↙	↙ Eu^{+++}	
61	$4f^7\ {}^8S$	Eu^{++} ↙	Gd^{+++}	↗ Tb^{++++}
62	$4f^8\ {}^7F_6$		Tb^{+++} ↗	
63	$4f^9\ {}^6H_{15/2}$		Dy^{+++}	
64	$4f^{10}\ {}^5I_3$		Ho^{+++}	
65	$4f^{11}\ {}^4I_{15/2}$		Er^{+++}	
66	$4f^{12}\ {}^3H_6$		↙ Tu^{+++}	
67	$4f^{13}\ {}^2F_{7/2}$	? ↙	↙ Yb^{+++}	
68	$4f^{14}\ {}^1S$	Yb^{++} ↙	Lu^{+++}	

The capacity of certain rare earths to form non-trivalent ions is very readily seen from this table to consist of a striving to reach the normal condition of lanthanum, gadolinium or lutecium. To be sure, in some cases such as praseodymium and samarium, the atom is not able to go all the way, and this condition is characterized by intense color and chemical instability. The question now arises: what is it that is so desirable about the normal states of lanthanum, gadolinium and lutecium? The answer must obviously be that these three elements alone are in S states, they have no multiplet structure, the orbital component of magnetic moment in each is lacking.

On the basis of such consideration, Klemm[13] was able some years ago to predict the existence of divalent ytterbium. Another possibility concerns thulium. It will be noticed that thulium stands in precisely the same relationship to ytterbium as does samarium to europium. It seems probable, therefore, that thulium will form a series of intensely colored, unstable, divalent compounds, analogous to those of samarium. Thulium is, unfortunately, so rare, that it has not as yet been possible to put this prediction to experimental test.

Summary

Magnetic susceptibility measurements have been made on the compounds Sm_2O_3, $Sm_2(SO_4)_3\cdot 8H_2O$, $SmBr_3$ and $SmBr_2$. Divalent samarium is shown to have a definite existence, and confirmation is not obtained for a discrepancy reported by Klemm and Rockstroh in the susceptibilities of Sm_2O_3 and $SmBr_3$. The susceptibilities and hence electronic configurations of divalent samarium and trivalent europium are shown to be identical.

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[13] Klemm, *Z. anorg. allgem. Chem.*, **184**, 345 (1929).