30.　*The Magnetic Susceptibilities of the Rare-earth Elements. Part II.　Samarium.*

By S. Sugden and S. R. Tailby.

Samarium has been purified by fractional crystallisation of the double magnesium nitrate in the presence of bismuth magnesium nitrate and the process has been followed by magnetic susceptibility measurements.　The value found for $10^6 \chi_{Sm}^{20°}$... is $6\cdot72 \pm 0\cdot03$.

In this series of papers an attempt is made to use accurate measurements of magnetic susceptibility to follow the separation of some of the rare earths.　If fractionation is continued until a series of successive fractions have the same susceptibility, then good evidence is furnished for the purity of these fractions and the value of the magnetic susceptibility of a particular element is then known.　This method has been used by Urbain in some cases (*Compt. rend.,* 1908, **146**, 402, and later papers), but most observations of magnetic susceptibility have been made on specimens supplied by other workers and often on specimens of doubtful purity.

In the present work crude samaria was fractionally crystallised as double magnesium nitrate in the presence of bismuth magnesium nitrate, and eleven fractions ultimately obtained whose properties are recorded below.　Fractions 14—16 showed faint neodymium bands, but fractions 17—24 only samarium bands in the absorption spectra.

Properties of samaria fractions.

Fraction	14	15	16	17	18	19
$10^6 \chi_{Sm}^{20°}$...	6·52	6·67	6·62	6·81	6·70, 6·77	6·77, 7·61

Fraction	20	21	22	23	24
$10^6 \chi_{Sm}^{20°}$...	6·72, 6·68	6·71, 6·63	6·24, 6·72	6·77, 6·86	8·00

Mean of fractions 18—23, $10^6 \chi_{Sm}^{20°}$... $= 6·715 \pm 0·03$; $\mu_{eff.} = 1·545 \pm 0·004$.

It will be seen that traces of neodymium have accumulated in the head and some impurity of higher susceptibility (probably gadolinum) in the tail fraction. Fractions 18—23 inclusive were regarded as pure samarium. The effective magnetic moment in Bohr magnetons is given by $\mu_{eff.} = \sqrt{A\chi . T}$. The atomic weight A was taken as 150·43 and $\mu_{eff.} = 1·545$. Recent determinations of this quantity are listed herewith :

Effective magnetic moment of the samarium ion (Sm···).

Date.	Investigator.	Origin of material.	$\mu_{eff.}$.
1933	Wursman & Schultz, *Physica*, **13**, 171	Urbain	1·54
1934	Rodden, *J. Amer. Chem. Soc.*, **56**, 648	James	1·55
1934	Selwood, *ibid.*, p. 2392	Hobbins	1·57
1938	Frivold & Lunde, *Physikal. Z.*, **39**, 571	von Hevesy	1·55

The theoretical calculations of von Vleck give $\mu_{eff.}$ 1·55 or 1·65 depending upon whether the value of 33 or 34 is chosen for the screening constant (" The Theory of Electric and Magnetic Susceptibilities ", Oxford Univ. Press, 1932, p. 243). The present work confirms recent evidence that the lower value of the screening constant is in better agreement with the experimental data.

EXPERIMENTAL.

The material used was obtained partly from commercial cerium oxalate and partly from a specimen of Norwegian gadolinite. In both cases the crude rare earth had been fractionally crystallised as the double magnesium nitrate. In all, about 100 g. of crude samarium oxide were used.

The oxide was reconverted into the double magnesium nitrate and about an equal weight of bismuth magnesium nitrate added. Fractional crystallisation was then continued, nitric acid (d 1·3) being used as solvent. Throughout this crystallisation care was taken to insure that the double nitrate separated, either by leaving a few small crystals undissolved or by seeding with bismuth magnesium nitrate. The separation of the desired crystals was obvious on inspection, since magnesium nitrate forms long needles, whilst the double salt is rhombohedral. The crystallisation was carried out in 12 fractions with, in all, 1260 crystallisations. The fractions were contained in 150-c.c. flat-bottomed flasks about one-third full, as recommended by Urbain, and losses by bursting of the flasks on heating rarely occurred.

The rare earth was recovered from each fraction by heating to 180—200° in a silica casserole and then pouring into about 600 c.c. of water. This precipitated most of the bismuth as basic nitrate (cf. Marsh, *J.*, 1934, 1972). The filtrate from this was precipitated with hydrogen sulphide until free from bismuth; excess of hydrogen sulphide was then boiled off, and the rare earth precipitated by addition of oxalic acid after adding a few drops of concentrated hydrochloric acid. The oxide was obtained by ignition of the oxalate at about 600°; since it readily absorbs water and carbon dioxide from the air, the oxide was again ignited before being weighed for determinations of equivalent and magnetic susceptibility.

The equivalent of the oxide from fraction 19 was determined by the method described in the preceding paper, and three determinations gave 57·93, 57·94, 58·03. The value calculated from the atomic weight is 58·14. The experimental values are not accurate to more than one part in 500 so the agreement could not be bettered.

The magnetic susceptibility of the samarium ion in solution was determined by the method already described (preceding paper) and the results are recorded above. Fractions 18—23 gave a nearly constant value for the susceptibility of the ion and this gives good evidence for the purity of these fractions. The neighbouring rare earths, neodymium and europium, have notably different susceptibilities and hence cannot be present in appreciable amounts.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.