31. *The Magnetic Susceptibilities of the Rare-earth Elements. Part III. Gadolinium.*

By S. Sugden and S. R. Tailby.

Gadolinium 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 $10^6\chi^{20°}_{Gd^{...}}$ is 168·4 ± 0·2.

Crude gadolinia from a Norwegian gadolinite was fractionally crystallised as bromate, and as dimethylphosphate, but these methods failed to raise the magnetic susceptibility of the ion to

the value expected theoretically, and some impurity of lower susceptibility was retained tenaciously. Finally success was realised by fractionally crystallising the double magnesium nitrate in the presence of excess of bismuth magnesium nitrate which was continuously added to the tail fractions. This removed a constituent of low susceptibility (probably samarium) at the head of the series and expelled traces of terbium (which coloured the oxides yellow to brown) at the tail. These were rejected and the fractionation continued until about 2700 crystallisations had been carried out. The properties of the oxides obtained from the remaining fractions are listed below.

Magnetic susceptibility of gadolinium.

Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...	Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...
33	White	159·5	36	White	169·2, 169·1
34	,,	168·4	37	Faint yellow	169·5
35	,,	168·4, 167·9	38	Brown	169·0

Fraction 36 was taken as representing the purest gadolinium and was twice precipitated as oxalate, and careful determinations of the equivalent and magnetic susceptibility made by the methods already described. The results were: Equivalent, found 60·56, 60·63; theory, 60·30; $10^6\chi^{20°}_{Gd}$... 168·07, 168·79, 168·45; mean 168·44 $\pm$ 0·24. The atomic weight being taken as 156·9, this gives $\mu_{eff.} = 7·902$. The value calculated theoretically by van Vleck ("The Theory of Electric and Magnetic Susceptibilities", Oxford Univ. Press, 1932, p. 243) is 7·94. Other recent determinations of $\mu_{eff.}$ are collected below:

Effective magnetic moment of gadolinium.

Date.	Observer.	Origin of material.	$\mu_{eff.}$
1933	Selwood, *J. Amer. Chem. Soc.*, **55**, 4869	Hopkins	8·05
1933	Sherwood & Hopkins, *ibid.*, p. 3117	Hopkins	7·80
1935	Velayors, *Anal. Soc. espan. Fis. Quim.*, **31**, 597	A. von Welsbach, Prandtl	7·81

Experimental.

The isolation of gadolinium was first attempted by fractional crystallisation of the bromates from water. After 3350 crystallisations the rare-earth oxides were recovered from each fraction, and the magnetic susceptibility of the ion determined by the method already described (*loc. cit.*). The results are collected below; fraction 2 showed faint bands due to europium in the absorption spectrum, but the other spectra did not show any bands.

Bromate fractionation.

Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...	Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...	Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...
2	Pure white	153·1	10	Pure white	158·3	18	Yellow	160·9
4	,,	155·1	12	,,	159·4	20	Brown	160·2
6	,,	157·7	14	Yellow	160·3	23	Dark brown	160·2
8	,,	157·2	16	,,	160·1			

The value anticipated for $\chi^{20°}_{Gd}$... is about 170. It is clear, therefore, that some impurity of lower susceptibility is contaminating the whole series and is not separating at an appreciable rate.

Fractionation as the dimethylphosphates was next tried, using essentially the technique described by Marsh (*J.*, 1939, 554). After about 400 crystallisations in seven fractions the oxides were recovered and examined with the results shown herewith:

Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...	Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...	Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Gd}$...
12(Head)	Light brown	160·9	15	Yellow	162·5	17	Pale yellow	160·0
13	,,	165·4	16	,,	160·6	18	White	153·5
14	Yellow	164·6						

This method did not seem to be much more effective than the bromate method, and was abandoned.

Finally, fractional crystallisation as double magnesium nitrate was used in the presence of bismuth magnesium nitrate which was continually added to the tail fractions (cf. Sherwood and Hopkins, *J. Amer. Chem. Soc.*, 1933, **55**, 3117: Marsh, *J.*, 1934, 1972; Naeser and Hopkins, *J. Amer. Chem. Soc.*, 1935, **57**, 2183). After 2700 crystallisations in about 20 fractions the rare-earth oxide was recovered and its magnetic susceptibility measured by the method already described (*loc. cit.*). The results are given above for the fractions that are mainly gadolinium. The head fractions were mostly bismuth magnesium nitrate but contained a small amount of rare earth (probably samarium) of low susceptibility, whilst the tail fractions were coloured yellow with terbium.

The Sir William Ramsay and Ralph Forster Laboratories,
University College, London.

[*Received, April 12th*, 1948.]