106. Magnetic Susceptibilities of Praseodymium and Terbium Oxides.

By R. C. Vickery and Ardys Ruben.

Magnetic susceptibility–temperature measurements below 300° of three oxides of praseodymium and three of terbium over a range of temperature yield magnetic moments for Pr_2O_3, Pr_6O_{11}, and PrO_2 of 3·55, 2·77, and 2·51 Bohr magnetons respectively and for Tb_2O_3, Tb_4O_7, and Tb_6O_{11} of 9·62, 8·70, and 8·49. The Curie–Weiss law is obeyed. The values agree well with theoretical ones for the proposed formula.

We have determined the magnetic susceptibility, over a range of temperature, of praseodymium and terbium oxides. X-Ray diffraction patterns have been prepared for each oxide studied, and lattice constants determined.

Magnetic Susceptibility.—The few data on the magnetic behaviour of these oxides deal predominantly with praseodymium oxides. Terbium oxides are less well characterised, probably owing in part to lack of pure materials.

The first studies on praseodymium oxides by Cabrera and Duperier[1] and Velayos[2] indicated that Pr_2O_3 and Pr_6O_{11} followed a modification of the Curie–Weiss law, $(\chi + k) = C/(T - \theta)$, where k represents a small positive susceptibility which is independent of temperature. Subsequently Rabideau[3] and LaBlanchetais[4] showed that Pr_2O_3 followed

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[1] Cabrera and Duperier, *Compt. rend.*, 1929, **188**, 1640.
[2] Velayos, *Anales españ. Fís. Quím.*, 1935, **33**, 5.
[3] Rabideau, *J. Chem. Phys.*, 1951, **19**, 874.
[4] LaBlanchetais, *J. Rech. Centr. Nat. Rech. Sci.*, **6**, No. 29, 103—133.

the Curie–Weiss law, $\chi = C/(T - \theta)$, over a wide range of temperature and that Pr_6O_{11} did so only between 200° and 300° K. Rabideau's work is the only systematic study of the magnetic behaviour of all three praseodymium oxides and, in general, our work confirms his temperature-susceptibility data.

Whilst values for the magnetic moment of the Tb^{3+} ion in the sulphate and nitrate are given in the literature, the oxides Tb_2O_3 and Tb_4O_7 have been studied only by LaBlanchetais,[4] and, to our knowledge, no susceptibility data have been reported on Tb_6O_{11}. LaBlanchetais's work covers the temperature range from the b. p. of liquid nitrogen to room temperature; we have carried measurements up to 600° K.

The results obtained at 296° K are in Table 1. $10^6\chi_g$ values listed are for gram-susceptibilities of the oxides and $10^3\chi_M$ susceptibilities per g.-atom of rare-earth metal in c.g.s. units, the latter having been corrected for diamagnetic effects by use of values of -13×10^{-6} per gram-atom of oxygen and -38×10^{-6} for the diamagnetic contribution of the rare-earth ions.[3] This leads to corrections (in units of 10^{-6} per gram-atom of rare earth) of 58, 62, and 64 for the praseodymium oxides and 58, 61, and 62 for the terbium oxides.

TABLE 1. *Susceptibilities of oxides.*

Formula	Specific susceptibility, obs. ($10^6\chi_g$)	Susceptibility per g.-atom ($10^3\chi_M$)	Comparative susceptibilities ($10^6\chi_g$)	Ref.
Pr_2O_3	26·4	4·41	26·8	3
Pr_6O_{11}	14·6	2·54	14·3	3
PrO_2	10·7	1·91	10·75	3
Tb_2O_3	195·5	35·8	213·8	4 *
Tb_4O_7	160·7	30·1	188·7	4 *
Tb_6O_{11} ...	145·0	27·4	—	

* At 288·1° K.

The variation of susceptibility with temperature for the praseodymium system is given in Fig. 1. From 200° to 300° K the graphs can be represented by the equation, $1/\chi_M = C(T - \theta)$, where θ and C have the values in Table 2. From these constants the magnetic moments μ_B were calculated from the formula, $\mu_B = 2{\cdot}839\ [\chi_M(T - \theta)]^{\frac{1}{2}}$, and found to be in good agreement with those of other workers as well as close to the theoretical values predicted by Van Vleck and Frank.[5]

TABLE 2. *Magnetic moment data.*

	Observed values							
	Authors'			Other workers'				Theory
Formula	C	θ	μ_B	C	θ	μ_B	Ref.	μ_B
Pr_2O_3	1·55	−57	3·55	1·662	−64	3·61	4	3·62
				1·575	−55	3·55	3	
Pr_6O_{11}	0·957	−85	2·77	—	—	2·8	3	2·96
PrO_2	0·78	−127	2·51	0·769	−104	2·48	3	2·56
Tb_2O_3	11·49	−24	9·62	11·73	−12·7	9·72	4	9·70
Tb_4O_7	9·38	−19	8·70	10·38	−9·5	9·14	4	8·86
Tb_6O_{11} ...	8·94	−32	8·49	—	—	—		8·57

TABLE 3. *Formulæ of oxides.*

Classical formula	Active oxygen (%)	Ratio, oxygen : metal	Actual formula	Classical formula	Active oxygen (%)	Ratio, oxygen : metal	Actual formula
Pr_2O_3 ...	0·019	1·502	$Pr_2O_{3\cdot004}$	Tb_2O_3 ...	0·028	1·53	$Tb_2O_{3\cdot06}$
Pr_6O_{11} ...	3·16	1·836	$Pr_6O_{11\cdot02}$	Tb_4O_7 ...	2·19	1·756	$Tb_4O_{7\cdot02}$
PrO_2 ...	4·52	1·99	$PrO_{1\cdot99}$	Tb_6O_{11}...	2·75	1·82	$Tb_6O_{10\cdot92}$

Above 300° K the Curie–Weiss relationship no longer holds, and variations of $1/\chi_M$ with T, while linear, no longer give the same values of θ and C. Rabideau reports a definite curvature even below 300° K for Pr_6O_{11} but does not report data above this temperature.

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[5] Van Vleck and Frank, *Phys. Rev.*, 1929, **34**, 1494, 1625.

LaBlanchetais measured Pr_2O_3 up to 900° K and found a linear representation up to 680° K. The discontinuities in slope observed are real, and not attributable to instrumental error, as they are not shown in similar studies on similar materials with the same equipment.

Although it might be assumed that for Pr_2O_3 a structural transformation takes place in the neighbourhood of room temperature, yet there is no *X*-ray evidence to support this theory, and we have, therefore, no satisfactory explanation for these discontinuities.

Fig. 2 gives the temperature-susceptibility curves for the terbium oxides, and Table 2 the values for C, θ, and μ_B, calculated from the plot between 100° and 300° K. Again, discontinuities are observed around room temperature. Measurements have been made both with rising and with falling temperature, but the same plot was obtained either way.

FIG. 1. *Reciprocal susceptibility as a function of temperature.*

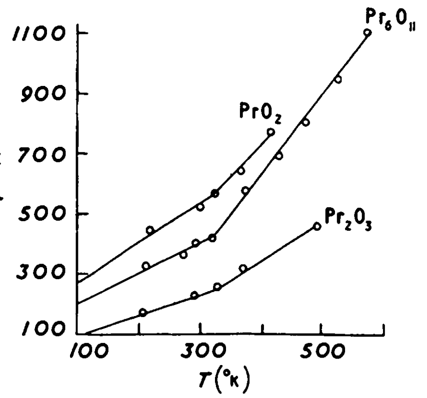
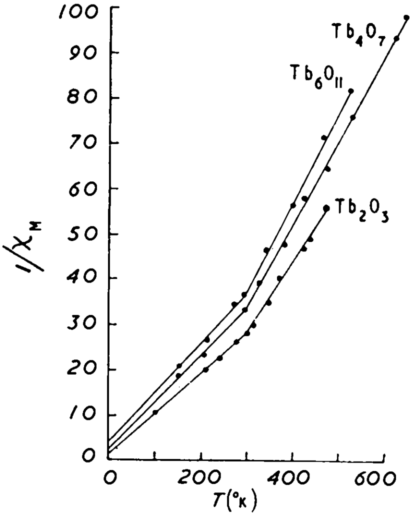


FIG. 2. *Reciprocal susceptibility as a function of temperature.*



The calculated magnetic moments are again in good agreement with theoretical values. Whilst our results are 1—2% lower than theory, LaBlanchetais's are up to 4% higher. In both cases, this is probably due to minor impurities in the starting materials. Our Tb_4O_7 was 99% pure and, although not indicated by spectroscopic analysis, might contain small amounts of gadolinium and/or yttrium which would lower the susceptibilities.

LaBlanchetais's material contained 92—94% of terbium oxide, and her results should therefore deviate more widely from theory. Also, as mentioned by Cabrera and Duperier,[1] absorption of water by terbium salts can appreciably reduce the C value.

The observed moments for Pr^{3+} and Pr^{4+} agree well with those of other workers as well as with theoretical values. The magnetic behaviour is consistent with the Curie-Weiss law for all three praseodymium oxides below 300° K, but not above it.

A moment of 2·77 Bohr magnetons for Pr_6O_{11} agrees well with a theoretical value of 2·96 calculated for $Pr_2O_3,4PrO_2$, and with Rabideau's calculated moment of 2·86 Bohr magnetons.

The observed magnetic susceptibilities for terbium are close enough to give some information about possible formulæ for Tb_4O_7 and Tb_6O_{11}. Assuming, according to the Sommerfeld-Kossel rule, the moment for Tb^{4+} to be equal to that for Gd^{3+}, we expect the magnetic moment of Tb_4O_7 (based on the formula, $Tb_2O_3,2TbO_2$) to be 8·86 Bohr magnetons, and for Tb_6O_{11} (equivalent to $Tb_2O_3,4TbO_2$), 8·57 μ. Our observed moments are 98·2 and 99·1% of these respectively. Such close agreement does we feel, substantiate the formulæ proposed.

X-Ray Diffraction.—Two forms of Pr_2O_3 have been reported,[6] a yellow low-temperature "*C*" cubic structure and a green high-temperature "*A*" hexagonal structure. Our material was light green, and lines from both the cubic and the hexagonal structure were observed in the *X*-ray pattern. The cubic form predominated, however, and gave a value of 5·61 Å for the lattice constant.

The *X*-ray powder pattern of Pr_6O_{11} showed only the lines of a cubic face-centred compound with a cell edge of 5·45 Å.

The pattern for PrO_2 was very similar to that for Pr_6O_{11}, differing only in yielding a smaller cell size, 5·38 Å. Although no standard is listed for PrO_2 in the A.S.T.M. index, our result compared favourably with the value obtained by McCullough[7] of 5·39 Å and with that of 5·38 Å obtained by Gruen, Koehler, and Katz.[8]

All the *X*-ray diffraction patterns for the terbium oxides can be indexed on the basis of face-centred cubic cells. Tb_2O_3 has a cell edge of 5·33 Å, and Tb_4O_7, 5·28 Å. Although Guth and Eyring[9] believe there to be no evidence for Tb_4O_7 and report instead $TbO_{1\cdot74}$ with a rhombohedral lattice, Gruen *et al.*[8] list Tb_4O_7 as face-centred cubic, with $a_0 = 5{\cdot}29$ Å.

The *X*-ray diffraction pattern for Tb_6O_{11} consists of a single phase which is face-centred cubic with a cell constant of 5·26 Å. Gruen *et al.*[8] report the formation of Tb_6O_{11} with a Tb : O ratio of 1 : 1·83 and a cell constant of 5·265 Å. However, Guth and Eyring[9] consider that the highest state of oxidation obtained is $TbO_{1\cdot81}$, with a cell constant of 5·286 Å.

Experimental.—*Preparation of oxides.* Pr_6O_{11} was purchased from the Lindsay Chemical Company as 99·8% pure, and Tb_4O_7 from the Michigan Chemical Company as 99% pure. All oxide used was first dissolved in acid, precipitated as oxalate, and ignited at 650° c.

The sesquioxides of both praseodymium and terbium were prepared by heating the air-ignited oxide in a stream of dry hydrogen for 2 hr. at 900° c. Even at 900° only a small amount of oxide could be reduced at one time, although both Guth and Eyring[9] and Gruen, Koehler, and Katz[8] report that reduction occurred readily between 600° and 650° c.

McCullough's[7] sodium chlorate–pressure technique was used to prepare the higher oxides, PrO_2 and Tb_6O_{11}. The production of PrO_2 proceeded readily with an oxygen pressure of about 50 atm. However, even at 60—75 atm. it was not possible to oxidise tervalent terbium completely to the 4+ state, the highest oxide obtained appearing, by "active oxygen" analysis, to be Tb_6O_{11}.

"*Active oxygen*" *analysis.* All the oxides prepared were analysed for active oxygen by the method of Barthauer and Pearce;[10] from the active oxygen content the oxygen-to-metal ratio was calculated, and the corresponding formula determined. These results are listed in Table 3.

X-Ray diffraction patterns were obtained with a General Electric XRD powder camera with a radius of 14·32 cm. using Co-K_α radiation at 50 kv and 6 mA with an iron filter. Exposure of 4 hr. was standard.

The apparatus and procedure employed for measurement of magnetic susceptibility has been reported previously[11] and will not be repeated in detail. A Gouy-type assembly was employed using a magnet field strength of 3340 gauss with appropriate standardisation and correction for container paramagnetism. Temperatures higher than 25° c were obtained by a small heating unit between the magnet poles which, for low temperatures, was replaced by a double-jacketed vacuum flask containing solid carbon dioxide, ice, liquid nitrogen, etc. The powder susceptibility data obtained are considered to have an accuracy of ±1·5%.

HORIZONS INCORPORATED, CLEVELAND 4, OHIO.
[Present address (R. C. V.): STANFORD RESEARCH INSTITUTE,
SOUTHERN CALIFORNIA LABORATORIES,
SOUTH PASADENA, CALIFORNIA.]

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[10] Barthauer and Pearce, *Ind. Eng. Chem.*, *Anal. Ed.*, 1946, **18**, 479.
[11] Vickery and Klann, *J. Chem. Phys.*, 1957, **27**, 1161.