

## Magnetic susceptibility of heavy rare-earth sesquioxides

H B LAL, VIRENDRA PRATAP and ASHOK KUMAR\*

Department of Physics, University of Gorakhpur, Gorakhpur 273 001

\*Department of Physics, DAV Degree College, Gorakhpur 273 001

MS received 8 July 1977; revised 12 December 1977

**Abstract.** Measurement of magnetic susceptibility of the powder samples of heavy rare-earth (Tb, Dy, Ho, Er, Tm and Yb) sesquioxides have been reported in the temperature range 300 to 900 K. Curie-Weiss law behaviour has been observed for all samples. The Curie constant, the paramagnetic Curie temperature and the magneton number for magnetic ions in each material have also been evaluated.

**Keywords.** Magnetic susceptibility; heavy rare-earth; sesquioxide; magneton number.

### 1. Introduction

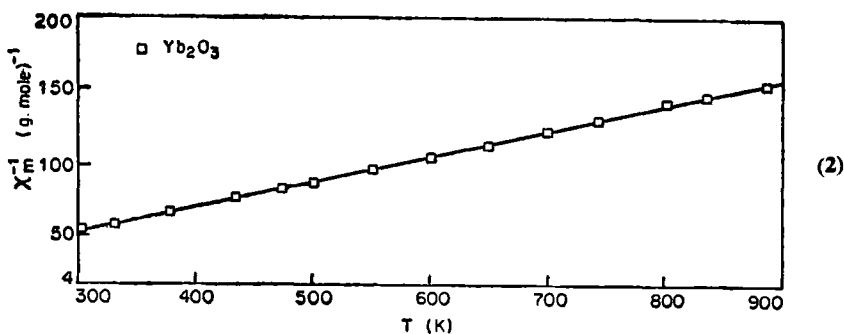
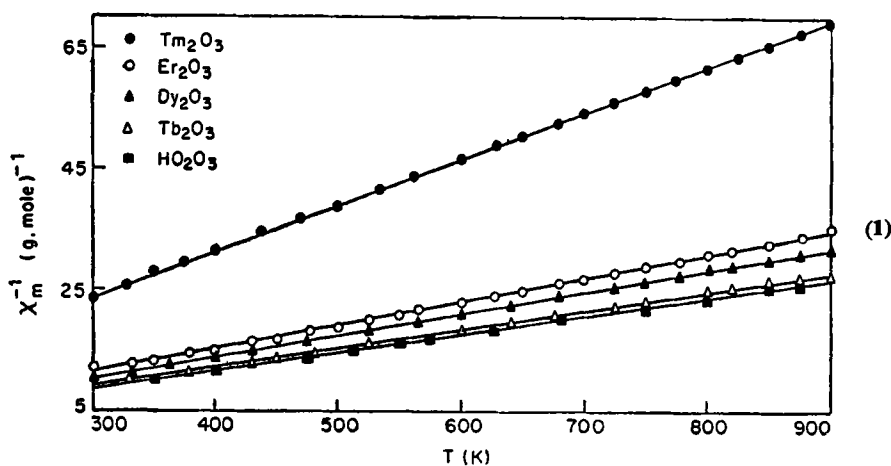
This paper is a part of our study programme of electrical transport and magnetic properties of rare-earth compounds (Lal *et al* 1974, 1975, 1976; Lal and Dar 1975, 1976, 1977) and reports the magnetic susceptibility of heavy rare-earth sesquioxide (HRES) with a general formula of  $R_2O_3$  (where R stands for Tb, Dy, Ho, Er, Tm and Yb) in the temperature range 300-900 K. Such studies were reported only for few HRES (Carbrera 1938, Gerstein *et al* 1962 and Lal and Dar 1976) so far in the literature. All the studied  $R_2O_3$  have cubic lattice structure except  $Tb_2O_3$  which is monoclinic.

### 2. Sample and experimental techniques

All sesquioxide in powder form with a stated purity of 99.99% have been procured from Rare-Earth Product Ltd., England. The impurity contents quoted by them are for other rare-earth sesquioxides. These powders are heated for several hours at 1000°C before use. The magnetic susceptibility is measured using Faraday method (Bates 1951). A 4-inch electromagnet is used which was tapered at an angle of 30° to one inch flattened face providing a vertical zone of constant  $H$  ( $dH/dz$ ) of one cm length, whose position did not vary with increasing field strength. The force exerted on the sample (placed in a small glass tube) when suspended in the magnetic field is measured with a sensitive ( $10^{-5}$  g) magnetic valence (Kerroy type 11, India). Higher temperatures are obtained using a small furnace (having non inductive winding) and measured using Chromel-Alumel thermocouple (Kota, India). Magnetic susceptibility values are obtained using Mohr salt and or  $Gd_2(WO_4)_3$  as standard substance. Correction for container is also taken into account. The overall accuracy of these measurement is about 2.5% round 300 K, this accuracy decreasing with increase of temperature and becomes about 7% round 900 K.

### 3. Results and discussion

The magnetic susceptibility of pure  $R_2O_3$  has mainly two types of contributions (i) a contribution due to  $4f$  electrons of  $R^{3+}$  ions and their cooperative action ( $\chi_m$ ) (ii) a diamagnetic contribution due to all other ions and electrons (except  $4f$  of  $R^{3+}$  ion ( $\chi_d$ ). It has been shown (Kern and Kostecky 1971) that this contribution ( $\chi_d$ ) for all  $R_2O_3$  is equal to the magnetic susceptibility of  $La_2O_3$   $\chi_d$ , is almost temperature independent and is small (being of the order of  $10^{-4}$  gm mole). This is of little interest in the magnetic study of  $R_2O_3$  and, hence it has been subtracted from the total measured value of the susceptibility in order to get the contribution due to  $4f$  electrons. Figures 1 and 2 show the plot of inverse molar magnetic susceptibility ( $\chi_m^{-1}$ ) with temperature. The curves are good straight lines, suggesting Curie-Weiss law ( $\chi_m = C/T - \theta$ , where  $C$  is the Curie constant and  $\theta$  is paramagnetic Curie temperature) behaviour and magnetic ordering at low temperature. The values of  $\theta$  and  $C$  for different HRES evaluated from these straight lines are shown in table 1. It is seen from this table that  $\theta$  values are negative for the sesquioxides of Dy, Er, Tm and Yb indicating antiferromagnetic ordering at lower temperatures. The oxides of Dy, Er and Yb actually show antiferromagnetic ordering (Bonrath *et al* 1966 and Moon



Figures 1 and 2. Inverse of molar susceptibility ( $\chi_m^{-1}$ ) vs  $T$  curve

Table 1. Magnetic parameters of rare-earth sesquioxides

Trivalent ion	Structure	Ground state	Neel/Curie Temperature (K)	Experimental values			Theoretical values of $P$	
				C	K/gm mole	$\theta(K)$	$P$	Hunds
Tb	M	$7F_6$	7.0	32.2	16.1	11.3	9.72	9.70
Dy	C	$6H_{15/2}$	1.20	28.6	-2.9	10.7	10.63	10.60
Ho	C	$5I_8$	—	31.2	3.1	11.1	10.60	10.60
Er	C	$4I_{16/2}$	3.36	23.7	-11.8	9.7	9.59	9.60
Tm	C	$3H_6$	—	13.3	-20.0	7.3	7.57	7.60
Yb	C	$2F_{7/2}$	2.25	5.8	-10.6	4.8	4.54	4.50

C. Cubic

M. Monoclinic

*et al* 1967) with Neel temperatures as given in table 1. However, no magnetic ordering has been observed in  $Tm_2O_3$  up to 4.2 K (Lal and Pratap 1976). Positive values of  $\theta$  have been obtained for  $Tb_2O_3$  (monoclinic) and  $HO_2O_3$  indicating ferromagnetic ordering at low temperatures.  $Tb_2O_3$  (monoclinic) has been shown to be ferromagnetic below 7K (MacChesney *et al* 1965) but no low temperature studies are available for  $HO_2O_3$  in the literature.

The effective magneton number ( $p$ ) for the rare-earth ions have been obtained using  $C$  values and the relation (Martin 1967).

$$p = \left( \frac{3kC}{N\beta^2} \right)^{1/2} \quad (1)$$

where  $k$  is the Boltzmann constant,  $N$  is the number of rare-earth ions per gram mole and  $\beta$  is the Bohr magneton ( $0.927 \times 10^{-20}$  ergs/Oe). The experimental values of  $p$  together with their theoretical (Hunds as well as Van Vleck and Frank) values (Van Vleck 1932) are also given in table 1.

It is seen from this table that there is fair agreement (within an accuracy of  $\pm 5\%$ ) between experimental and theoretical values of  $p$  for all sesquioxides except for  $Tb_2O_3$ . This indicates that angular momentum  $L$  and  $S$  of  $R^{3+}$  ions are strongly coupled and respond freely to external magnetic field as one expects due to deep embedding of the  $4f$  electrons. The experimental  $p$  value for  $Tb^{3+}$  differs from its theoretical value by about 16%. This may be due to the following reasons. Unlike other sesquioxides, which have cubic lattice structure,  $Tb_2O_3$  is monoclinic. Due to monoclinic lattice  $Tb^{3+}$  ions in  $Tb_2O_3$  faces a nonsymmetrical crystal field, which can affect its  $p$  values to some extent. The electrical conductivity ( $\sigma$ ) of  $Tb_2O_3$  is very high ( $\sigma \sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$  at 300 K and  $\sim 10^{-1} \Omega^{-1} \text{cm}^{-1}$  at 1000 K) (Kumar 1975) compared to  $\sigma$  ( $\sim 10^{-14} \Omega^{-1} \text{cm}^{-1}$  at 300 K and  $\sim 10^{-5} \Omega^{-1} \text{cm}^{-1}$  at 1000 K) of other sesquioxides (Lal *et al* 1977) and is thus expected to have a large number of conduction electrons, which will contribute to magnetic susceptibility. Besides the susceptibility of solids with ions of higher magneton number is field dependent (Thomas and Sienko 1974) which for the field used in our measurement ( $\sim 2k$  Oe) can affect  $\chi_m$  values by about 2% at

300K. The combined effect of all these factors is presumably the reason for getting slightly lower slope in  $\chi_m^{-1}$  vs  $T$  line and higher  $p$  values for  $Tb^{3+}$  ions.

### Acknowledgement

One of the authors (HBL) gratefully acknowledges financial assistance from UGC.

### References

- Bates L F 1951 *Modern Magnetism* (London: Cambridge Univ. Press), p. 51  
Bonrath H, Hellwege K H, Nicolay K and Weber G 1966 *Phys. Kondens. Mater.* **4** 382  
Carbrera B 1938 *J. Phys. Rad.* **9** 249  
Gerstein B C, Jelinek F J and Spedding F H 1962 *Phys. Rev. Lett.* **8** 425  
Kern S and Kostelecky R 1971 *J. Appl. Phys.* **42** 1773  
Kumar A 1975 *Electrical and magnetic properties of some solids* Ph.D. Thesis Gorakhpur University, Gorakhpur  
Lal H B and Dar N 1975 *Z. Naturforsch.* **30 a** 1783  
Lal H B and Dar N 1976 *Indian J. Pure Appl. Phys.* **14** 788  
Lal H B and Dar N 1977 *J. Phys. Chem. Solids* **38** 161  
Lal H B and Pratap V 1976 *Curr. Sci.* **45** 545  
Lal H B, Dar N and Kumar A 1974 *J. Phys.* **C7** 4335  
Lal H B, Dar N and Kumar A 1975 *J. Phys.* **C8** 2745  
Lal H B, Dar N and Lundgren L 1976 *J. Phys. Soc. Jpn.* **42** 1216  
Lal H B, Verma B K and Dar N 1977 *Indian J. Cryogenics* **1** 119  
MacChesney J B, Williams H J, Sherwood R C and Potter J F 1965 *J. Chem. Phys.* **44** 596  
Martin D H 1967 *Magnetism in Solids* (London: Iffe Book) p. 305  
Moon R M, Child H R, Koehler W C and Raubenheimer L J 1967 *J. Appl. Phys.* **38** 1383  
Thomas J F and Sienko M J 1974 *J. Chem. Phys.* **61** 3920  
Vanvleck J H 1932 *The Theory of Electric and Magnetic Susceptibilities* (London: Oxford University Press)