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Hydrothermal Preparation and Low Temperature Magnetic Properties of TbOOH, DyOOH, HoOOH, ErOOH, and YbOOH

A. NØRLUND CHRISTENSEN*

Laboratoire d'Electrostatique et de Physique du Métal, C.N.R.S., Cedex No 166,
38-Grenoble-Gare, France

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The monoclinic modification of the oxide hydroxides of terbium, dysprosium, holmium, erbium, and ytterbium was prepared using hydrothermal techniques. The magnetic properties of the compounds were investigated between 2.4 and 273 K. TbOOH, DyOOH, and ErOOH are antiferromagnetic with Néel temperatures of 10, 9, and 7.2 K, respectively, and have metamagnetic properties in high magnetic fields. HoOOH and YbOOH were not ordered magnetically at temperatures as low as 2.4 K. In the paramagnetic temperature region all the compounds give molar Curie constants close to the expected values for the free ions.

The magnetic properties of a number of rare earth oxide phases have been investigated, but very little is known about the magnetic properties of the rare earth oxide hydroxides. These compounds can exist in a monoclinic, low-pressure and in a tetragonal, high-pressure modification (*1*, *2*). The magnetic properties of the monoclinic form of thulium oxide hydroxide, TmOOH, was investigated by Katila, Seidel, Wortmann, and Mössbauer (*3*) by using the gamma resonance technique down to 0.04 K, but no ordered state was found. An investigation of the magnetic properties of the monoclinic modification of TbOOH, DyOOH, HoOOH, ErOOH, and YbOOH is reported below.

Experimental

Chemistry. The oxide hydroxides were prepared from the oxides (99.9%) or the trihydroxides by hydrothermal synthesis at the experimental conditions shown in Table I. The trihydroxides were precipitated with a 1 *M* NaOH solution from a dilute solution of the rare earth nitrates, prepared by dissolving the oxides in nitric acid. The precipitated hydroxides were washed with water and were used immediately. The reaction products were washed with water and were dried in air at room temperature.

TABLE I

EXPERIMENTAL CONDITIONS FOR HYDROTHERMAL PREPARATION OF RARE EARTH OXIDE HYDROXIDES

Exp. No.	Liner of bomb	Temp. (°C)	Pressure (atm)	Time (hr)	NaOH (*M*)	Initial conditions	Product
1	Pt	610	320	48	2.0	Tb_4O_7	TbOOH
2	Ag	547	540	24	0.2	$Dy(OH)_3$	DyOOH + $Dy(OH)_3$
3	Au	470	300	264	4.0	Ho_2O_3	HoOOH
4	Au	490	540	360	5.4	Er_2O_3	ErOOH
5	Ag	540	700	24	0.1	$Yb(OH)_3$	YbOOH

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* Present address: Department of Chemistry, University of Aarhus, DK 8000 Aarhus C, Denmark.

TABLE II

CRYSTALLOGRAPHIC AND MAGNETIC DATA FOR SOME RARE EARTH OXIDE HYDROXIDES

	Unit cell parameters (Å and degrees). Space group $P2_1/m$				θ_N	θ_P	Molar Curie constant C_M		Magnetic moment (in μB) (4.2 K, 80 KOe)	
	a	b	c	β	(K)	(K)	Exptl.	Calcd.	Exptl.	Calcd.
TbOOH	6.04	3.69	4.33	109.0	10	0	11.87	11.79	6.03	9
DyOOH	6.02	3.66	4.33	109.0	9	−22.6	13.66	14.17	5.76	10
HoOOH	5.96	3.64	4.31	109.1		−5.4	13.43	14.08		10
ErOOH	5.94	3.62	4.30	109.3	7.2	0	10.79	11.50	7.50	9
YbOOH	5.87	3.58	4.27	109.3		−46.5	2.33	2.58		4

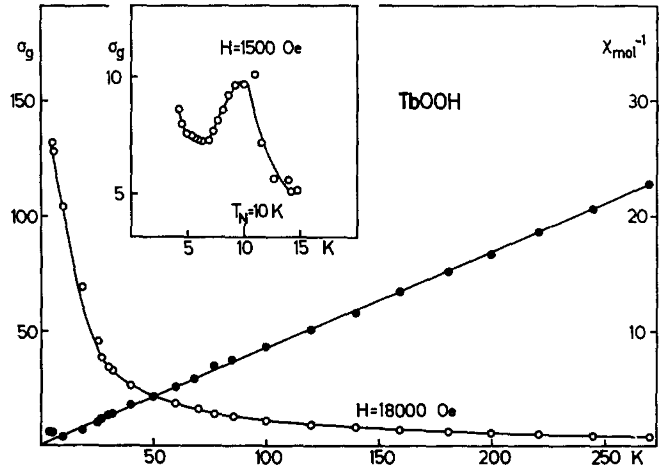

FIG. 1. Magnetization per gram and inverse molar susceptibility vs. temperature for TbOOH. The magnetization is in emu in all the diagrams.

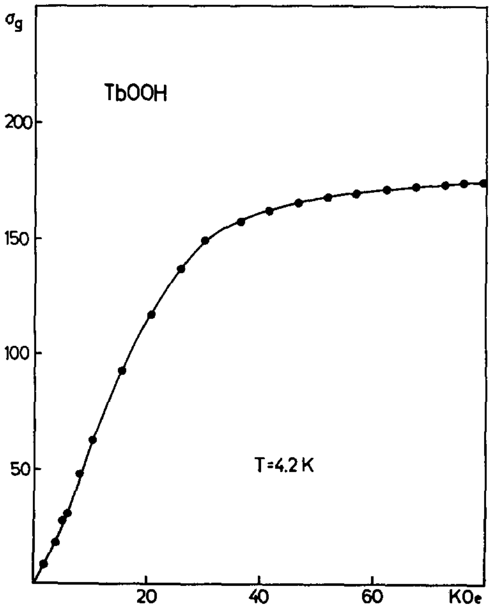

FIG. 2. Magnetization per gram vs. field at 4.2 K.

The pressure bombs used in experiments Nos. 2–5 had a volume of 260 ml and were lined with pure silver or pure gold. The bomb used in No. 1 had a volume of 43 ml. A sample of 0.75 g Tb_4O_7 and 0.5 ml 2 *M* NaOH solution was sealed in a 2 ml platinum ampoule with a wall thickness of 0.1 mm. A mixture of 20 ml of pure water and 0.27 g pure aluminium powder and the sealed ampoule were charged in the pressure bomb. The hydrogen, formed by the reaction of aluminium with water, can penetrate the platinum walls of the sealed ampoule, and a complete reduction of the terbium ions to Tb^{3+} is observed.

Powder patterns of the products from Nos. 1, 2, and 5 were taken with a Guinier camera using Fe*K*α radiation ($\lambda = 1.9359$ Å), and powder patterns of the products from No. 3 and 4 were taken with a Guinier–de Wolff camera using Cu*K*α radiation ($\lambda = 1.5405$ Å). All the products, with the exception of the product from No. 2, were the pure oxide hydroxides. The product from No. 2 was heated to 330 C for 5 hr, and after this treatment the

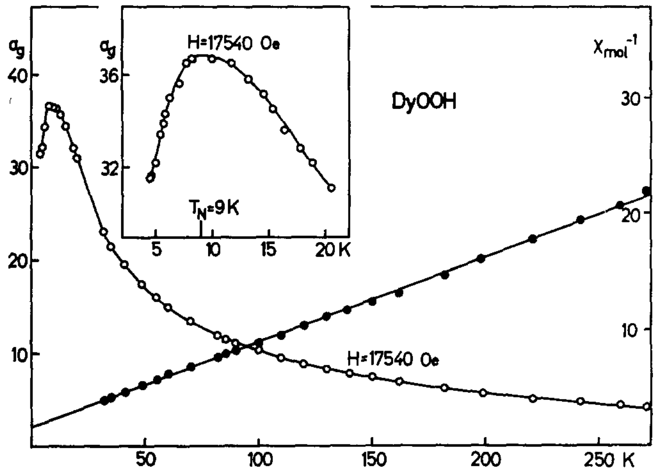

FIG. 3. Magnetization per gram and inverse molar susceptibility vs. temperature for DyOOH.

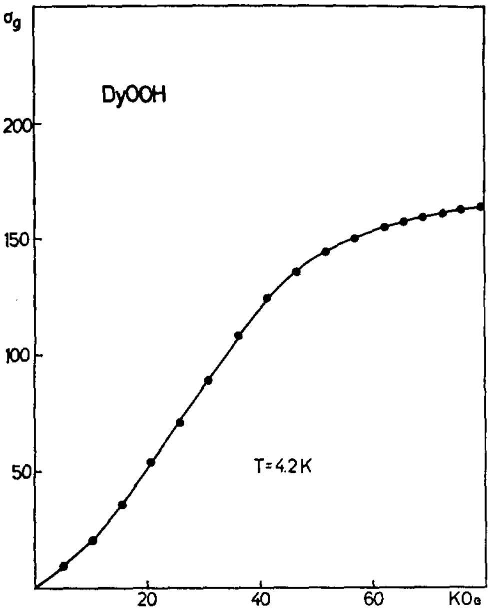

FIG. 4. Magnetization per gram vs. field at 4.2 K.

powder pattern proved the compound to be pure DyOOH. In Nos. 3 and 4 single crystals of the oxide hydroxides, with linear dimensions from 0.5 to 1 mm, were found in the upper part of the pressure bomb.

Magnetic measurements. The magnetization of the oxide hydroxides was measured at temperatures from 2.4 to 273 K in magnetic fields from 200 Oe to 80 KOe using the axial extraction method (*4*). The magnetization of holmium oxide hydroxide was measured at temperatures from 2.4 to 4.2 K by a magnetic field of 400 Oe using a translation balance (*5*). The magnetic parameters of the compounds obtained from the measurements are listed in Table II.

Results

TbOOH. The magnetization and $1/\chi_{\mathrm{mol}}$ vs. temperature are shown in Fig. 1. A peak in the

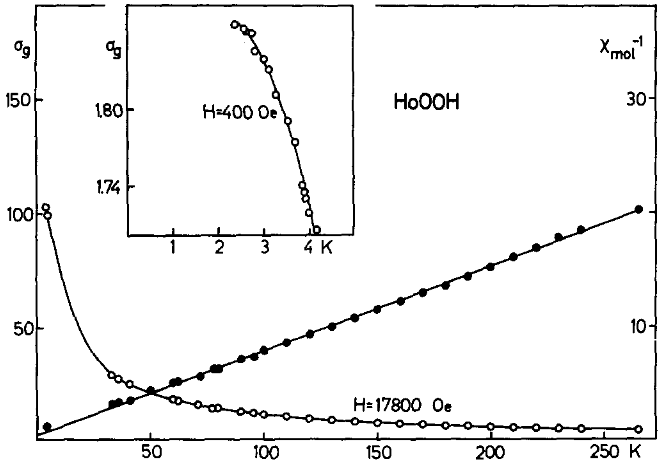

FIG. 5. Magnetization per gram and inverse molar susceptibility vs. temperature for HoOOH.

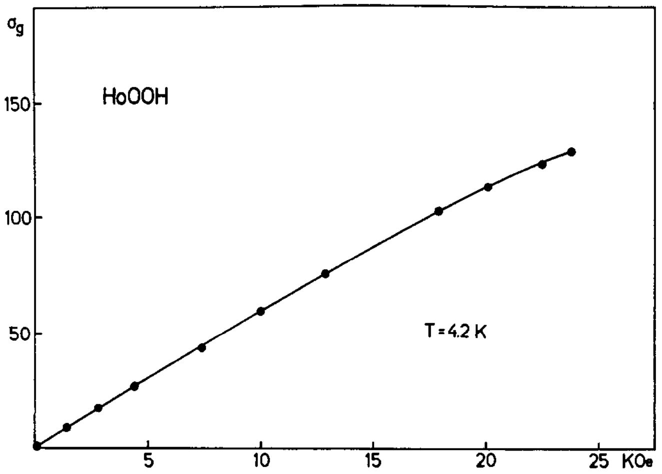

FIG. 6. Magnetization per gram vs. field at 4.2 K.

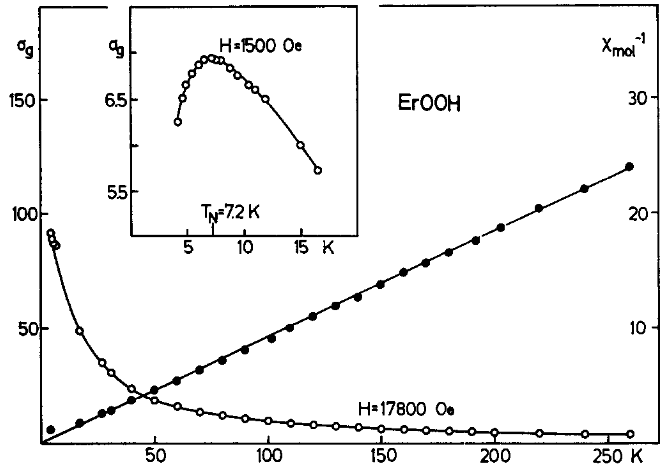

FIG. 7. Magnetization per gram and inverse molar susceptibility vs. temperature for ErOOH.

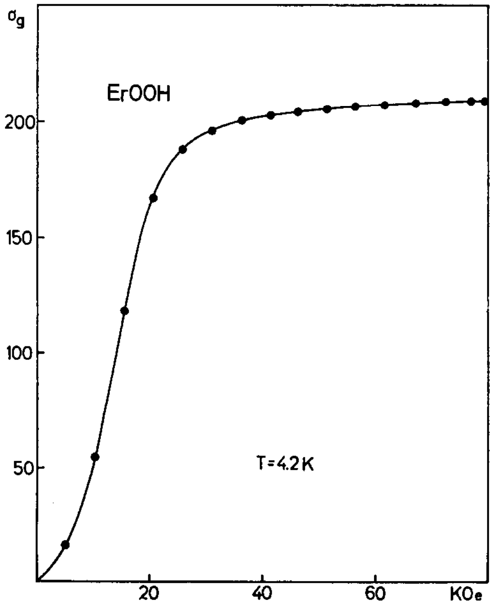

FIG. 8. Magnetization per gram vs. field at 4.2 K.

magnetization is observed at 10 K, the Néel temperature of TbOOH. A paramagnetic temperature $\theta_p = 0$, and a molar Curie constant $C_M = 11.87$ are found. Figure 2 shows the magnetization vs. field at 4.2 K. The compound is metamagnetic. From the magnetization in a field of 80 KOe a moment $\mu = 6.03$ is obtained.

DyOOH. Figure 3 shows the magnetization and $1/\chi_{\mathrm{mol}}$ vs. temperature. The maximum of the magnetization is found at 9 K, the Néel temperature $1/\chi_{\mathrm{mol}}$ vs. temperature follows the Curie–Weiss equation, with a paramagnetic temperature $\theta_p = -22.6$ K. The molar Curie constant $C_M = 13.66$. The magnetization vs. field at 4.2 K is shown in Fig. 4. The compound is metamagnetic. The magnetization at 80 KOe corresponds to a moment $\mu = 5.76$.

HoOOH. In Fig. 5 the magnetization and $1/\chi_{\mathrm{mol}}$ vs. temperature are shown for the compound. The magnetization has no maximum in the temperature range investigated. The inverse molar susceptibility vs. temperature follows the Curie–Weiss

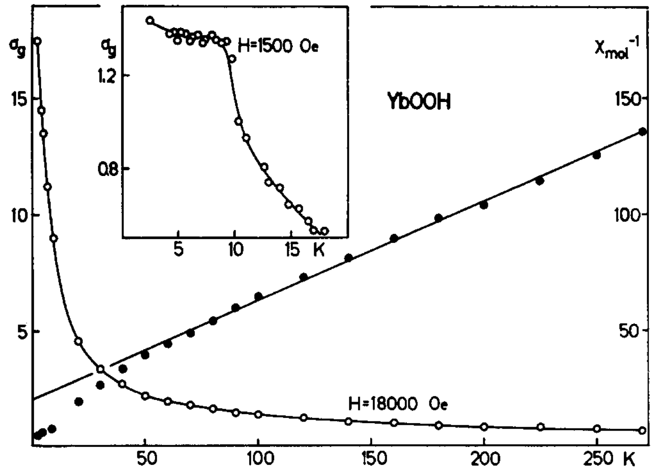

FIG. 9. Magnetization per gram and inverse molar susceptibility vs. temperature for YbOOH.

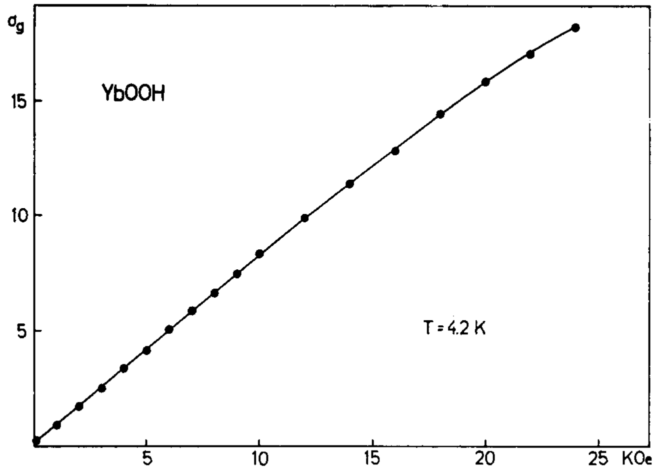

FIG. 10. Magnetization per gram vs. field at 4.2 K.

equation. θ_p is −5.4 K and C_M is 13.43. Figure 6 shows the magnetization vs. field at 4.2 K.

ErOOH. The magnetization and the inverse molar susceptibility vs. temperature are shown in Fig. 7. At 7.2 K a peak in the magnetization is observed. $1/\chi_{\mathrm{mol}}$ vs. temperature follows the Curie equation. θ_p is 0 K and C_M is 10.79. The metamagnetic nature of the compound is shown in Fig. 8, which gives the magnetization vs. field at 4.2 K. The magnetization at 80 KOe corresponds to a moment $\mu = 7.50$.

YbOOH. In Fig. 9 the magnetization and $1/\chi_{\mathrm{mol}}$ vs. temperature are shown. The magnetization has no maximum in the temperature range investigated. However, the magnetization increases rather slowly at temperatures from 9 to 2.4 K. $1/\chi_{\mathrm{mol}}$ vs. temperature follows the Curie–Weiss equation from 70 K to room temperature. $\theta_p = -46.5$ K and $C_M = 2.33$.

Discussion

Of the five rare earth oxide hydroxides investigated, only TbOOH, DyOOH, and ErOOH are magnetically ordered at 4.2 K. HoOOH and YbOOH have no magnetically ordered state at 4.2 K, possibly due to blocking of the spins. All the three antiferromagnetically ordered compounds display metamagnetic nature in strong magnetic fields. In the paramagnetic temperature region, all five compounds have molar Curie constants close to the values expected for the free ions. The moments calculated from the magnetization at 4.2 K in a magnetic field of 80 KOe are smaller than the theoretical values (see Table II). Investigations of the magnetic structures of TbOOH, DyOOH, and ErOOH are in progress.

Acknowledgments

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References

1. A. N. Christensen, *Acta Chem. Scand.* **19**, 1391 (1965).
2. A. N. Christensen, *Acta Chem. Scand.* **24**, 3074 (1970).
3. T. E. Katila, E. R. Seidel, G. Wortmann, and R. L. Mössbauer, *Solid State Comm.* **8**, 1025 (1970).
4. G. Rimet. Une installation de mesure des aimantations entre 2 et 1200 K. thesis, Université de Grenoble, Grenoble, 1960
5. P. Mollard. Contribution à l'étude des substances antiferromagnitiques en grains fins, thesis, Université de Grenoble, Grenoble, 1971.