Hydrothermal Preparation and Magnetic Properties of $Dy_2O_2CO_3$, $Ho_2O_2CO_3$, $Er_2O_2CO_3$, and $Yb_2O_2CO_3$

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Rare earth oxide hydroxides [1] and rare earth oxide carbonates [2] have been prepared hydrothermally and the magnetic properties of some rare earth oxide hydroxides have been investigated.[3] Little is known about the magnetic properties of rare earth oxide carbonates. Hydrothermal preparation of the compounds $Dy_2O_2CO_3$, $Ho_2O_2CO_3$, $Er_2O_2CO_3$, and $Yb_2O_2CO_3$ and in investigation of the magnetic properties over the temperature range 77 to 300 K is reported below.

The rare earth carbonates were precipitated with a 1 M $KHCO_3$ solution from dilute solutions of rare earth nitrate, prepared by dissolving the oxides in nitric acid. The freshly precipitated carbonates were washed with water, placed in pressure vessels lined with pure gold and kept at the experimental conditions listed in Table 1. The products were washed with water and dried in air at room temperature. X-Ray powder patterns were obtained with a Guinier camera using Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) and NaCl was used as internal standard ($a_{NaCl} = 5.6389$ Å). The intensities of the powder lines were measured using a Joyce double beam recording microdensitometer. The powder patterns are listed in Table 2. The powder patterns are similar to that of $Nd_2O_2CO_3$, and they can be indexed using hexagonal unit cells with dimensions close to the dimensions of the unit cell for $Nd_2O_2CO_3$. It is assumed that the structure of the four compounds is of the same type as that of $Nd_2O_2CO_3$.

The magnetization of the rare earth oxide carbonates was investigated at temperatures from 77 K to 294 K using the Faraday method. Temperatures below room temperature were obtained in a cryostate containing liquid nitrogen or

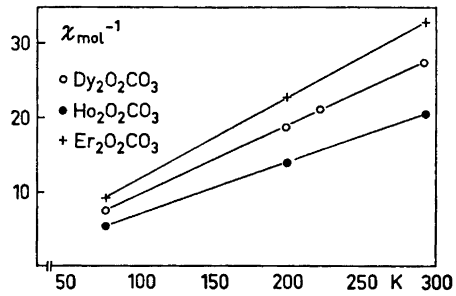

Fig. 1. Inverse molar susceptibility *vs.* temperature for $Dy_2O_2CO_3$, $Ho_2O_2CO_3$, $Er_2O_2CO_3$.

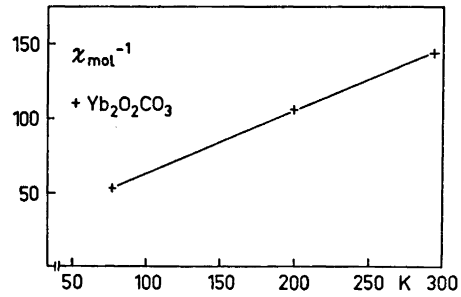

Fig. 2. Inverse molar susceptibility *vs.* temperature for $Yb_2O_2CO_3$.

Table 1. Experimental conditions for hydrothermal preparation of some rare earth oxide carbonates.

Exp. No.	Initial conditions: Freshly precipitated	Temp. (°C)	Pressure (atm)	Time (h)	Product
1	Dysprosium carbonate	575	1400	64	$Dy_2O_2CO_3$
2	Holmium carbonate	490	2000	30	$Ho_2O_2CO_3$
3	Erbium varbonate	570	1700	64	$Er_2O_2CO_3$
4	Ytterbium carbonate	540	3400	64	$Yb_2O_2CO_3$

Table 2. X-Ray powder patterns of some rare earth oxide carbonates.

$Dy_2O_2CO_3$, a = 3.868(3) Å, c = 15.156(9) Å.

h	k	ℓ	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	7.618	7.578	17
0	0	4	3.793	3.789	17
1	0	0	3.364	3.350	33
1	0	1	3.279	3.271	74
1	0	2	3.071	3.064	26
1	0	3	2.800	2.792	100
0	0	6	2.529	2.526	16
1	0	4	2.512	2.510	20
1	0	6	2.018	2.017	15
1	1	0	1.936	1.934	43
1	1	2	1.876	1.874	6
1	0	7	1.819	1.818	15
1	1	4	1.724	1.723	29
2	0	0	1.674	1.675	5
2	0	1	1.667	1.665	5
2	0	2	1.639	1.636	2
2	0	3	1.590	1.590	19
1	1	6	1.536	1.536	21
0	0	10	1.514	1.516	5
1	0	9	1.504	1.505	13
2	0	6	1.395	1.396	8
2	0	7	1.325	1.325	15
2	1	0	1.265	1.266	5
1	2	1	1.261	1.262	10
2	1	3	1.227	1.228	10

$Ho_2O_2CO_3$, a = 3.845(3) Å, c = 15.111(9) Å.

h	k	ℓ	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	7.575	7.555	16
0	0	4	3.775	3.778	18
1	0	0	3.338	3.330	52
1	0	1	3.258	3.252	96
1	0	2	3.051	3.047	55
1	0	3	2.781	2.778	100
0	0	6	2.513	2.518	23
1	0	4	2.500	2.498	22
1	0	6	2.009	2.009	31
1	1	0	1.924	1.923	92
1	1	2	1.865	1.863	22
1	0	7	1.810	1.811	31
1	1	4	1.714	1.713	26
2	0	0	1.667	1.665	9
2	0	1	1.657	1.655	16
2	0	2	1.627	1.625	6
2	0	3	1.581	1.581	26
1	1	6	1.529	1.528	19
1	0	9	1.496	1.499	5
2	0	6	1.389	1.389	5
2	0	7	1.318	1.318	12
2	1	0	1.258	1.259	5
1	2	1	1.254	1.254	10
2	1	2	1.240	1.241	5
2	1	3	1.219	1.221	15
1	1	10	1.190	1.188	5
2	0	9	1.183	1.182	5

$Er_2O_2CO_3$, a = 3.827(3) Å, c = 15.034(9) Å.

h	k	ℓ	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	7.521	7.517	28
0	0	4	3.764	3.759	30
1	0	0	3.321	3.314	43
1	0	1	3.241	3.236	82
1	0	2	3.039	3.032	39
1	0	3	2.771	2.764	100
0	0	6	2.509	2.506	33
1	0	4	2.489	2.486	24
1	0	6	2.001	1.999	35
1	1	0	1.915	1.913	67
1	1	2	1.856	1.854	16
1	0	7	1.803	1.802	44
1	1	4	1.707	1.705	35
2	0	0	1.659	1.657	10
2	0	1	1.649	1.647	10
2	0	2	1.619	1.618	6
2	0	3	1.574	1.573	35
1	1	6	1.522	1.521	34
1	0	9	1.491	1.492	14
2	0	6	1.381	1.382	11
1	0	10	1.368	1.369	6
2	0	7	1.312	1.312	13
2	1	0	1.251	1.253	10
1	2	1	1.248	1.248	10
2	1	3	1.213	1.215	5

$Yb_2O_2CO_3$, a = 3.723(5) Å, c = 15.39(2) Å

h	k	ℓ	d_{obs}(Å)	d_{calc}(Å)	I
0	0	2	7.700	7.695	45
0	0	4	3.852	3.848	29
1	0	0	3.241	3.224	38
1	0	1	3.168	3.156	63
1	0	2	2.985	2.974	31
1	0	3	2.736	2.730	100
0	0	6	2.562	2.565	30
1	0	4	2.475	2.471	20
1	0	6	2.007	2.007	26
1	1	0	1.865	1.861	47
1	0	7	1.817	1.817	32
1	1	4	1.678	1.676	16
2	0	0	1.616	1.612	6
2	0	1	1.605	1.603	7
0	0	10		1.539	
			1.540		17
2	0	3		1.538	
1	1	6	1.508	1.507	37
1	0	10	1.387	1.389	6
2	0	6	1.365	1.365	7
2	0	7	1.300	1.300	10
2	1	0	1.218	1.219	5
1	2	1	1.214	1.215	5
2	1	3	1.181	1.186	10

Table 3. Magnetic data for some rare earth oxide carbonates.

Compound	$\theta_{P(K)}$	Molar Curie constant C_M		Magnetic moments (in μB)	
		Exptl.	Calc.	Exptl.	Calc.
$Dy_2O_2CO_3$	− 3	10.74	14.17	9.3	10.6
$Ho_2O_2CO_3$	0	14.28	14.08	10.7	10.6
$Er_2O_2CO_3$	− 6	9.08	11.50	8.5	9.6
$Yb_2O_2CO_3$	−47	2.36	2.58	4.3	4.5

mixtures of solid carbon dioxide and methyl alcohol. The magnetic parameters obtained from the measurements on the four components are listed in Table 3. The inverse molar susceptibilities of $Dy_2O_2CO_3$, $Ho_2O_2CO_3$, and $Er_2O_2CO_3$ are shown in Fig. 1, and that of $Yb_2O_2CO_3$ in Fig. 2. The compounds have no magnetically ordered state at 77 K and $1/\chi_{mol}$ *vs.* temperature follows the Curie-Weiss law from 77 K to room temperature. In this paramagnetic temperature range all four oxide carbonates have molar Curie constants close to the values expected for the free ions. Further investigation of the magnetic properties of the compounds over the temperature range 4.2 K to 77 K is planned.

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Crystallographic Computer Programs for CYBER-74

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The series of crystallographic CDC-3300 programs at the University of Oslo [1] has been modified for CYBER-74.

Among the few changes made in the file structures may be mentioned the addition of the raw intensity of each reflection, and an extra record containing estimated standard deviations of atomic parameters.

The file concept of the 6000-computers is somewhat different from that of the 3000-series, and a number of file handling routines have been added to the program system.

Data reduction programs were not adapted to the CYBER-computer since these calculations more conveniently are carried out at CDC-3300.

A new feature in the structure determination programs based upon direct methods is the possibility of changing sign or phase for all reflections of one specified parity group. Peaks from scanned Fourier synthesis may be plotted on line printer.

The program for translation of all (or a part of) the atoms through desired areas of the cell, calculating the R-value for each step, has been rewritten. In the new version, which is more than 10 times faster than the old one, trigonometric calculations are carried out only for the first step.

The maximum number of parameters that can be refined simultaneously by the modified full-matrix least squares refinement program is 300.

The system contains some new routines preparing tables suitable for publication of atomic parameters, observed and calculated structure factors, bond distances and angles *etc.*

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