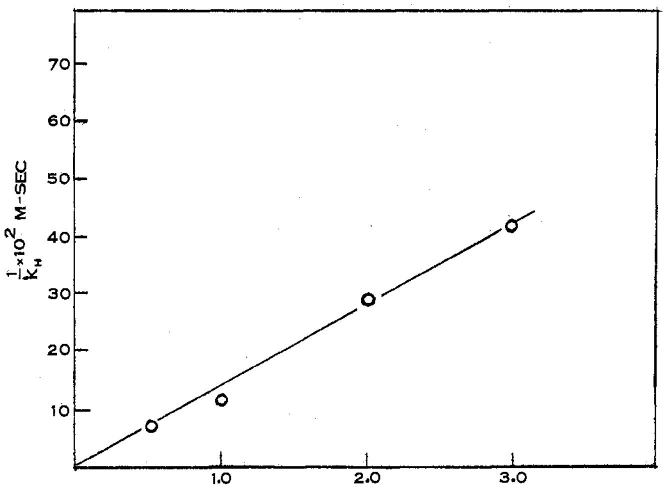

Figure 3.—Plot of $1/k_H$ *vs.* (H^+).

actions produce the $N_2H_3\cdot$ free radical which in acid solution is believed to be protonated[12,13] ($N_2H_4\cdot{}^+$).

Assuming appreciable hydrolysis of Ce^{4+} to $CeOH^{3+}$, a rate law of the form

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = k_H[\mathrm{Ce(IV)}][N_2H_5{}^+] \qquad \text{(III)}$$

is predicted where

$$k_H = \frac{k_2(H^+) + k_3K}{(H^+) + K} \qquad \text{(IV)}$$

and K (= $[(CeOH^{3+})(H^+)]/(Ce^{4+})$) is the first hydrolysis constant of Ce^{4+}. If $k_3K \gg k_2(H^+)$, the reciprocal of eq IV is

$$\frac{1}{k_H} = \frac{(H^+)}{k_3K} + \frac{1}{k_3} \qquad \text{(V)}$$

A plot of eq V is shown in Figure 3. It is linear as predicted with a slope ($=1/k_3K$) of 0.15 sec. Baker, Newton, and Kahn[14] have estimated that in 2 M $HClO_4$ the first hydrolysis of Ce^{4+} is at least 85% complete. This would indicate that the first hydrolysis constant is $K \approx 12$ M. Offner and Skoog[15] also studied this hydrolysis and reported a value of $K \approx 0.2$ M. Because of the significant difference between these reported hydrolysis constants, calculating the value of k_3 from the slope of Figure 3 would be meaningless. It is, however, obvious that k_3 is much greater than k_2.

That $CeOH^+$ is so much more reactive than Ce^{4+} toward protonated hydrazine molecules is similar to Davies and Kustin's[8] observation regarding the relative reactivity of $MnOH^{2+}$ and Mn^{3+} toward $N_2H_5{}^+$. We are therefore also led to the conclusion that the most important oxidation mechanism is H atom transfer. The ultimate fate, however, of the protonated hydrazyl free radical is necessarily different when Ce(IV) rather than Mn(III) is used as the oxidant since N_2 gas is formed in the former case and not in the latter case. In this study, with Ce(IV) as oxidant the hydrazine probably follows the one electron oxidation scheme proposed by Kirk and Browne and discussed by Cahn and Powell[1]

$$N_2H_4 \longrightarrow N_2H_3 \longrightarrow NH_2NHNHNH_2 \longrightarrow 2NH_3 + N_2$$

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High-Pressure Synthesis of Rare Earth Dimanganese Compounds with the $MgZn_2$ (Laves) Structure[1]

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Laves structures of the $MgZn_2$ type were synthesized for $GdMn_2$, $TbMn_2$, $DyMn_2$, $HoMn_2$, YMn_2, and $YbMn_2$ under high-temperature and high-pressure conditions. All but the Yb compound were previously known only in the $MgCu_2$ structure. $YbMn_2$ had not been prepared before this work. Also the synthesis of $ErMn_2$ was verified and $SmMn_2$ was prepared at high pressure.

Introduction

The rare earth dimanganese ($REMn_2$) compounds are known to exhibit some interesting changes in crystal structure as the atomic number of the rare earth varies.[3] Both the light and heavy rare earths (at 1 atm) form $REMn_2$ compounds in the C14 ($MgZn_2$) Laves structure while the intermediate rare earths form $REMn_2$ compounds in the C15 ($MgCu_2$) Laves structure. This information is summarized in Table I as are, also, the high-pressure results of this paper.

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Table I

Crystal Structures of $REMn_2$ Compounds[a]

	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1 atm	H	C	X	X	H	H	X	C,H	X	C	C	C	C	C,H	H	X	H
High pressure		H			X	X		H		H	H	H	H	H	H	H	H

[a] H, C14 ($MgZn_2$) type (hexagonal); C, C15 ($MgCu_2$) type (fcc); and X, no known compound.

$LaMn_2$ and $CeMn_2$ have not been prepared. $PrMn_2$ has been reported in the C14 phase[4] but Oesterreicher reports that he could not duplicate this reported result. Rather, he obtained an α Mn type and a Th_6Mn_{23} type.[5,6]

By application of high pressure simultaneously with high temperature, we have synthesized the $MgZn_2$ type structure for the dimanganides of Gd, Tb, Dy, Ho, and Y which were previously known only in the $MgCu_2$ structure and also $YbMn_2$ which was previously unknown. The compound $SmMn_2$, which has reportedly been synthesized at 1 atm in both Laves phases, could not be prepared by us at pressures below 50 kbar. Neither could we prepare the previously reported $NdMn_2$ in the pressure range covered by this work.

Experimental Section

The syntheses were carried out by application of high temperature at high pressure to a stoichiometric mixture of the elements in a tetrahedral anvil apparatus.[7,8] The procedure and sample geometry were the same as has been described previously.[9] Runs were carried out at 1300–1400° for 1 min followed by rapid quenching to room temperature and then release of pressure. Run times up to 2 hr and temperatures up to 2000° at 70 kbar were tried on the Nd–Mn system without success.

The rare earth metals were obtained from Research Chemicals, Inc., Burbank, Calif. Manganese was obtained from Baker Chemical Co. The metals were filed or crushed in air and particles passing a 100-mesh sieve were used for synthesis.

Products from the runs were crushed between two polished WC blocks and loaded in 0.5-mm glass capillaries; X-ray diffraction patterns were obtained with a 143.2 mm diameter Debye–Scherrer camera on a G. E. XRD-5 unit. Chromium (λ 2.29092 Å) radiation and V_2O_5 filters were used. Lattice parameters were obtained by a least-squares fit of 12–24 d values depending upon the pattern. The $MgZn_2$ type structures were identified by comparison of the X-ray diffraction patterns with the pattern for $ErMn_2$ of Wernick and Haszko.[10] All diffraction lines were indexed to the $MgZn_2$ structure except for $GdMn_2$ which showed some weak lines from an unidentified impurity. It was concluded that the products were single phase.

Results

Table II shows the lattice parameters and calculated densities obtained in this study. These parameters give a smooth transition between the previously reported values for the light and heavy $REMn_2$ hexagonal compounds.

The minimum pressure required for synthesis of the $MgZn_2$ structure is shown in Figure 1. Although the synthesis of $MgZn_2$-type dimanganides of Pr, Nd, and Sm has been reported at 1 atm,[3,4] we could not synthesize $SmMn_2$ below 50 kbar and could not obtain $NdMn_2$ or $PrMn_2$ at any pressure between 10 and 70 kbar.

Table II

Lattice Parameters of Hexagonal $REMn_2$ Compounds

	a_0, Å	c_0, Å	Density, g/cm³
$ErMn_2$	5.274 ± 4	8.626 ± 6	8.86
$HoMn_2$	5.316 ± 2	8.672 ± 3	8.60
$DyMn_2$	5.356 ± 3	8.744 ± 5	8.33
$TbMn_2$	5.390 ± 3	8.786 ± 5	8.08
$GdMn_2$	5.447 ± 3	8.893 ± 5	7.76
$SmMn_2$	5.501 ± 2	8.968 ± 4	7.36
$YbMn_2$	5.233 ± 3	8.561 ± 5	9.26
YMn_2	5.404 ± 7	8.848 ± 10	5.90

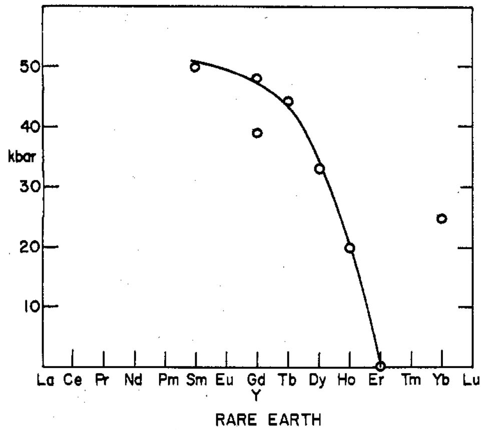

Figure 1.—Minimum pressure required for the synthesis of hexagonal $REMn_2$.

Discussion

Laves phases of AB_2 compounds are known with d_A/d_B ratios from 1.05 to 1.68 and it has been shown that there is no correlation between Laves structure type and the atomic diameter ratio.[11] Since all rare earth dimanganide compounds fall within this range of diameter ratios, the existence of the structure transition from hexagonal to cubic and back to hexagonal as the atomic number of the rare earth increases (1 atm synthesis) shows that other effects must be more important in determining which Laves structure is stable in this series.

The densities of the $MgCu_2$ and the $MgZn_2$ structures calculated from lattice parameters obtained at 1 atm are virtually identical and there is no reason to suspect a significant difference in compressibility of the two structures. Therefore, density differences do not seem to be a determining factor in forming one structure type in preference to another as has been found in other systems.[12]

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