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Articles

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Synthetic Study of Some Rare-Earth-Metal Monohalide Hydrides MXH_x and Their Alkali-Metal Intercalates

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The quantitative syntheses of MXH_x phases (M = Sc, La, Gd, Er, Lu; X = Cl (and Br for Gd, Er); $x \simeq 0.6$–0.7) together with their intercalates A_zMXH_x (A = Li, some Na, K; M = Sc, Y, Gd (but not Er, Lu)) have been accomplished by stoichiometric reactions of MX_3, MH_2 (or H_2), M, and AX in sealed Ta or Nb containers at 750–900 °C. All MXH_x phases have the ZrCl- or ZrBr-type (3*R*) heavy-atom structures. The phases $ScClH_x$, nonstoichiometric for $0.3 < x \lesssim 0.75$, and LaClH are indistinguishable from the previously reported monochlorides. The X-ray structure of ScClH has been refined. The lithium intercalates, Li_zMClH_x, for M = Sc, Y, and Gd are also nonstoichiometric in hydrogen, and all intercalates have the ZrBr heavy-atom structure. The $Li_{0.2}YCl$ and $Li_{0.5}GdCl$ phases previously reported from X-ray studies are obtained only in the presence of hydrogen. High values of *x* result in explusion of much of the lithium from the yttrium and gadolinium chloride derivatives. Hydrogen pressure, phase, and volume relationships are also considered.

Introduction

The so-called monohalides of the rare-earth elements, MX, have been reported for M = Sc,[2] Y,[3] La,[4] Ce, Pr, Nd, Gd, Tb, and Ho[5,6] and X = Cl and Br in the ZrCl[7] and ZrBr[8] structures. However, it now appears that all of these compounds are unstable in the absence of interstitial atoms, hydrogen in particular. This is in striking contrast with the stability of the binary parent phases ZrCl and ZrBr with their alternating pairs of close-packed zirconium and halogen layers. A recent reexamination of the gadolinium system has shown that its monohalides are correctly represented by the compositions $GdXH_x$ (X = Cl, Br, I; $0.7 < x < 0.9$) with the heavy atoms in a ZrX or related structure.[9] In the case of $TbClD_{0.8}$, neutron diffraction studies have shown that the hydrogen is located in the tetrahedral interstices between the double metal layers.[10] Similar synthetic and characterizational studies have been made on the YXH_x systems.[11,12] In the cases of ScCl, YCl, and LaCl, the hydrogen presumably originated with the powdered metal reductant, which had been prepared by thermal decomposition of the dihydride.

Although intercalation of the ZrX phases with alkali metal to date has not been accomplished, recent synthetic and single-crystal studies of the phases $Li_{0.2}YCl$ and $Li_{0.5}GdCl$ show that it is apparently possible to reduce the "monochloride" substrate and to insert lithium in trigonal-antiprismatic positions between the double chlorine layers.[13] The relatively low yields achieved in this work were not really understood at that time, but kinetic problems were considered important. However, the use of powdered metal reductant was again found to give improved yields, and so the question has likewise arisen as to whether these apparent ternary intercalates were indeed Li_zMClH_x quaternary phases.

The present article reports the clarification of the Sc/Cl/H system vis-a-vis "ScCl", some similar experiments regarding "LaCl" and "ErBr", and a study of the intercalation reactions of lithium, sodium, and potassium with the gadolinium, scandium, and yttrium monochloride and monobromide hydrides together with some exploratory results regarding analogous products for M = La, Er, and Lu.

Experimental Section

Materials. Lithium was used as purchased from Merck. The rare-earth metals (Sc, Y, Gd, Er, Lu) were obtained either as cold-rolled strips from the Ames Laboratory or as distilled chunks (Lu) or powders (Gd, Er, Lu) from Johnson Matthey, Köln, FRG. Dihydrides, MH_2, were prepared from the metal strips by hydrogenation either in a molybdenum boat at 650 °C or in sealed niobium or tantalum tubes at 800 °C. Powdered Sc and Y were prepared by thermal decomposition of the dihydride at $\simeq$750 °C (just below sintering) in high vacuum until the pressure fell below discharge. The trichlorides and bromides of Gd, Er, and Lu and YBr_3 were synthesized by following the ammonium halide route[14-16] (wet variant), while $ScCl_3$, YCl_3, and $LaCl_3$ were obtained from the metal by using high-purity HCl gas as the chlorinating agent.[17] Ternary halides like $LiGdCl_4$ or $Cs_3Gd_2Br_9$ that were occasionally used were prepared by following known literature procedures.[18-20] Alkali-metal halides (reagent grade or Suprapur) were either sublimed under high vacuum or heated in an HCl or HBr gas stream for 1–2 days at 200 °C prior to use.

Syntheses. A variety of synthetic approaches to the indicated halide hydrides and their intercalated derivatives were tested. In many cases parallel reactions were run in which only the hydrogen source had been omitted. Appropriate reaction mixtures on a millimolar scale were loaded in a nitrogen- or argon-filled drybox into carefully cleaned niobium or tantalum tubes, which were then arc-welded under He.[17] These were sealed under high vacuum in baked, fused-silica jackets, then heated to temperatures of 700–980 °C for several days to a few weeks, and finally air-quenched. Hydrogen was either introduced in the original charge as the $MH_{2.00}$ phase (and possibly via any powdered metal used) or introduced manometrically after the other components had been sealed in the Nb or Ta container and this heated in a quartz container attached to a calibrated vacuum line. The success of the latter method depends on the

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Table I. Reaction Conditions and Structural Data on the Products of $M/MCl_3/H_2$ Reactions[a]

			lattice const, pm		
compn[b]	temp, °C	reactants[c]	*a*	*c*	structure type; remarks
$ScClH_{0.38}$	860	ScH_2, P	347.60 (3)	2671.0 (4)	ZrBr
$ScClH_{0.54}$	860	ScH_2, P	347.60 (5)	2662.2 (7)	ZrBr
$ScClH_{0.70}$	860	ScH_2, P	347.66 (1)	2656.5 (7)	ZrBr, ZrCl (30.70)
$ScClH_{0.78}$	860	ScH_2, P	347.72 (3)	2656.6 (7)	ZrCl
$ScClH_{0.92}$	860	ScH_2, P	347.67 (6)	2653 (1)	ZrCl
$ScClH_{1.02}$	860	ScH_2, P	347.61 (6)	2659.2 (9)	ZrCl
$ScClH_{1.06}$	860	H_2, P	347.85 (2)	2653.1 (8)	ZrCl
"ScCl"	960	P	347.3 (2)	2671 (4)	ZrCl; ref 2
$LaClH_{0.98}$	800	LaH_2, S	409.83 (4)	2756.8 (8)	ZrBr; $LaCl_3$ (≃5%)
$LaClH_{0.82}$	800	LaH_2, 10% KCl[d]	409.91 (3)	2758.5 (5)	ZrBr
"LaCl"	818	P	410.1 (7)	2759.2 (7)	ZrBr; ref 4
$GdClH_{0.68}$	750	GdH_2, P	382.32 (4)	2749.4 (4)	ZrBr
$GdClH_{0.89}$[e]	900	GdH_2	382.40 (5)	2749.4 (6)	ZrBr; ref 9
$GdBrH_{0.68}$	750	GdH_2, P	387.43 (4)	2905.1 (6)	ZrCl
$GdBrH_{0.93}$[e]	900	GdH_2	387.43 (3)	2904.1 (3)	ZrCl; ref 9
$GdBrH_{0.69}$[e]	900	GdH_2, P	386.94 (4)	2915.0 (3)	ZrCl; ref 9
$BrClH_{0.60}$	850	BrH_2, P	370.42 (4)	2720.7 (3)	ZrCl
$ErBrH_{0.70}$	980	ErH_2, P	376.85 (2)	2872.9 (3)	ZrCl
"ErBr"	700	S	377.0 (1)	2882.6 (5)	ZrCl; ref 6
$LuClH_{0.70}$	850	LuH_2, P	363.37 (3)	2713.8 (3)	ZrCl; LuOCl

[a] All products were pure MXH_x to Guinier diffraction unless noted otherwise. [b] Compositions as loaded unless otherwise noted. [c] All reactions included MCl_3; P = powdered metal; S = metal strips. [d] H_2 pumped out at 900 °C to give indicated composition. [e] Hydrogen analysis.

permeability of the container metals to hydrogen above ≃600 °C. Equilibrium hydrogen pressures above several halide hydride systems were also measured in this way, the method having been extensively tested in earlier studies of the $YClH_x$ system.[11]

Compositions were generally taken to be as loaded. In the case of hydrogen this requires consideration of two factors. First, the dissociation pressure of the system studied at temperature puts some gaseous H_2 into both the metal container and, necessarily, the fused silica jacket as well. The volumes of the systems were purposely kept small, generally no more than 20 mL, to limit the amount lost in this way. The dissociation pressures of the MXH_x systems (M = Y, La) are known to be close to those of the corresponding two-phase α-M(H)–MH_{2-y} systems[21,22] at the same temperature (below). The MXH_x compounds with low x values are of course now known to form from only and to be in equilibrium with the α-phase metal hydride plus trihalide, while at the other limit most of the MXH_x phases are in equilibrium with MH_{2-y} and MCl_3 in the presence of a small excess of hydrogen. The only variations in this pattern appear to be with scandium where some additional reduced scandium chlorides are present for $x < x(\min)$ and ScH_{2-y} is absent at the upper limit for x. An H_2 dissociation pressure of about 1 Torr above the $MClH_x$ systems with M = Y and La, $x = 0.8$, and $T = 750$ °C gives an error in x of <0.1%. Pressures above the quaternary $A^I_zYClH_x$ systems appear to be slightly higher than for systems without intercalation.

Small Henry's law solubilities of hydrogen in Nb and Ta are also known[23,24] and allow a correction of the composition when pressures are known, especially at lower temperatures or higher pressures. The correction is small for <3 Torr at 750 °C in tantalum and is somewhat more consequential with niobium, so the former was usually the container of choice when pressures were appreciable.

The above handling techniques and conclusions have been confirmed in several cases in the $YClH_x$[11] and Li_zMClH_x systems (M = Sc, Y, Gd) by direct analysis of the products for hydrogen, which results nearly always agreed with those loaded to within ±0.03 in x. The same applies to pressure measurements with $x \lesssim 0.85$.

Characterization. Characterization was carried out mainly by X-ray powder techniques (Guinier). Because of the pronounced platelike growth of the monohalide hydride crystals, severely falsified powder intensities may be observed owing to preferred orientation. This is especially the case when samples loaded in X-ray capillaries were used (Guinier–Simon technique).[25] Only the set of (00*l*) reflections was clearly visible and strong while (*h*0*l*) reflections and others were strongly reduced. Flat samples have some but much less pronounced problems, giving too high intensities for (*hk*0) reflections.[8] The latter method was therefore used during the main stages of this investigation, and all lattice constants reported were obtained in this way by using silicon or low-quartz as an internal standard.

Hydrogen analyses were performed by a tin-flux method[26] on a number of samples, including some of the powdered metals used as reactants and several intercalates. The former gave $ScH_{0.09}$ and $YH_{0.26}$, and vacuum fusion yielded $GdH_{0.22}O_{0.02}$ for a commercial sample of powdered metal in which GdH_{2-y} was evident to X-rays. X-ray lattice constants were consistent and reproducible for each of the former. The compositions of the dihydrides were established either by synthesis from measured amounts of H_2 or from the close correspondence of their lattice constants with their accepted values.[21,22]

Results

Ternary Systems. The best route to the MXH_x phases for X = Cl and Br and one that has worked in all instances (M = Sc, Y, La, Gd, Er, Lu) is the direct reaction of MX_3, MH_2, and M in the appropriate proportions. These are easily weighed in the drybox and, under the techniques utilized, allow good stoichiometric control and quantitative conversion, although it is important to know the hydrogen content of the metal as well, particularly if a powdered material is used. The hydrogen can also be metered volumetrically and absorbed through the wall of the heated Ta or Nb container. Although this is generally less convenient, it does allow simultaneous, direct measure of the dissociation pressures as a function of x and temperature to define the homogeneity range. The last are presently known only for the scandium and yttrium chlorides. Some stoichiometries, reactants, temperatures, lattice parameters and product descriptions are given in Table I. In all cases, Sc, Y, Gd, Er, and Lu readily yielded the monochloride or monobromide hydride in a quantitative amount, the identities of the products being judged by lattice parameters and comparisons of the powder patterns with those calcualted for a ZrCl- or ZrBr-type (3*R*) structure.

The data listed for the scandium chloride system show (a) that there is a change from a ZrBr-type stacking (ACB) of the four-layer slabs at lower hydrogen content to a ZrCl variety (ABC) for $x \simeq 0.78$, with a 30:70 mixture being obtained for $x = 0.70$,[27] and (b) that there is an easily recognizable decrease of the c lattice constant with increasing x. Both of these features are also seen in the $YClH_x$ system.[11] The lattice constant data for $ScClH_x$ are plotted in Figure 1 to illustrate something of the phase relationships

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(27) Most of the powder pattern lines and therefore the lattice constants of the ZrBr and ZrCl forms of $ScClH_x$ obtained in a mixture for $x \geqslant 0.67$ are not separable, and their proportions are judged from the few distinctive lines that appear in each pattern.[8]

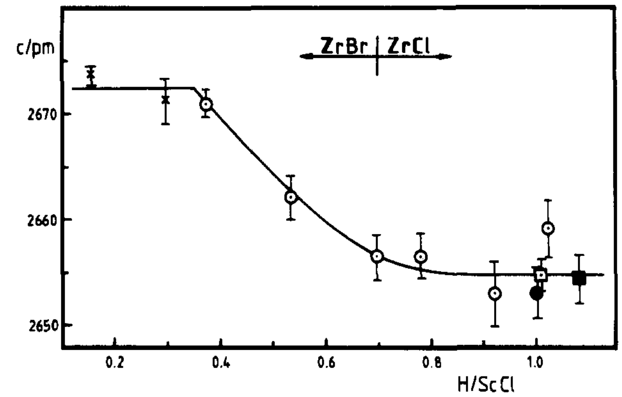

Figure 1. c lattice parameter of $ScClH_x$ as a function of x (3σ limits, 860 °C reaction temperature): (○, ●) single-phase samples (ZrBr- or ZrCl-type structure ($3R$) (solid, single-crystal sample); (×) Sc_2Cl_3 present as a second phase; (□, ■) values obtained with excess H_2 at 500 and 710 °C, respectively (solid, ScH_{2-y} present).

as well. There is no discernible dependence of c on structure type. Experiments run in the same way but with still smaller x values (0.10, 0.25) gave reduced yields of the chloride hydride with c(max) together with α-Sc(H) and 75% and 30% yields (based on total chloride), respectively, of Sc_2Cl_3 ("mouse fur",[28] not related to Y_2Cl_3). A reaction loaded at the same time with only powdered metal ($ScH_{0.09}$) and $ScCl_3$ gave in terms of chloride about 10% $ScClH_x$, 20% Sc_2Cl_3 and 70% Sc_7Cl_{10}.[29] The formation of such binary reduced phases rather than MCl_3 plus α-M below x(min) is not found in the other rare-earth-metal systems studied where lower halides such as Y_2Cl_3 and Gd_2Cl_3 decompose at lower temperatures. (They still are apt to form on cooling.)

At the other extreme, values of x greater than about 0.75–0.80 yield single phase $ScClH_x$ (plus H_2 presumably) with a nearly constant value of the c lattice parameter, while ScH_{2-y} does not appear until x is somewhat over 1.0. It might be argued that the x values were in substantial error owing to dissociation and that the system was not at the limit, but the same lower limit for the c parameter has been obtained in two reactions with excess hydrogen, one at 710 °C with ScH_{2-y} present (2654.5 (8) pm) and the other from single crystals of $ScClH_x$ (high x) at 500 °C (2654.8 (5) pm).

The Guinier patterns from the three experiments with x values between 0.75 and 1.0 that exhibited a ZrCl-type structure also contained a weak ZrBr-type component, perhaps 5% in total. The limiting x value, 0.75–0.80, is only slightly beyond $x = 0.67$ where a mixture was obtained, so the 95:5 result may reflect a small driving force and incomplete conversion of the ZrCl-type crystals formed initially. Complete conversion does occur at lower temperatures with excess H_2 (below).

The indicated structural change for $ScClH_x$ with increasing x was also accomplished by starting with 65 mg of single crystals of $ScClH_x$ in equilibrium with α-Sc(H) that was formed at 950 °C in ≃10% yield from powdered metal.[2] These crystals initially had the ZrCl structure and a c lattice constant of 2669 (2) pm. Their reaction at 500 °C with 1 atm of H_2 overnight converted them to the pure ZrBr form, which gave a sharp powder pattern and $c = 2654.8$ (6) pm, very consistent with Figure 1. Although the crystals retained their smooth faces, they were very fragile and showed bad streaking in Weissenberg photographs, reflecting disorder in the stacking introduced during the transformation.

Finally, the identity of the chloride–hydride and the previous "ScCl" was established by a comparative single-crystal structural study of the former. Apparently single crystals as large as 2.0 × 1.5 × 0.2 mm can be grown by vapor-phase transport under natural furnace gradients at 860 °C when a somewhat longer (8 cm) container is used. Low-angle reflections were observed to be slightly streaked, so a 2θ–θ scan mode was employed. Crystallographic data together with the resulting atom parameters and interatomic distances and a comparison with published data for "ScCl" are given in Table II. All nearest-neighbor distances for the two structure determinations are within 3σ of one another, and the tetrahedral cavities are indistinguishable in size. Within this uncertainty, the smaller c lattice constant for the hydrogen-richer ZrCl-type structure appears to come mainly from decreased Sc–Cl and Cl–Cl interlayer separations appropriate to an increased oxidation state for the metal.

Table II. Structural Parameters and Selected Distances for $ScClH_x$ (ZrCl Type) and "ScCl" (ZrBr)[a]

Structural Parameters

	$ScClH_x$[b]	"ScCl"
a, pm	347.85 (8)	347.3 (2)
c, pm	2653.1 (8)	2671 (4)

	$ScClH_x$			"ScCl"		
	z	B_{11}	B_{33}	z	B_{11}	B_{33}
Sc	0.1192 (1)	0.99 (9)	1.8 (1)	0.2137 (1)[c]	0.9 (1)	3.8 (2)
Cl	0.3912 (1)	1.4 (1)	1.7 (1)	0.3914 (1)	1.0 (1)	3.8 (2)

Distances (pm)

	$ScClH_x$	"ScCl"
	Interlayer	
Sc–Sc	322.2 (5)	321.6 (6)
Sc–Cl	258.4 (3)	259.1 (4)
Cl–Cl	367.0 (6)	369.5 (8)
Sc–H[d,e]	206	206
H–H[d]	257	257
H–Cl	289	290
	Intralayer	
Sc–Sc, Cl–Cl, H–H	347.85 (8)	347.3 (2)

[a] ScCl data from ref 2. Both have the $R\bar{3}m$ space group and are here described in the hexagonal setting. [b] Crystallographic parameters: crystal, 0.25 × 0.20 × 0.02 mm, Weissenberg photos confirmed R centering; data collection at room temperature on four-circle diffractometer with Mo Kα (71.073 pm) to $2\theta = 60°$; measured reflections, 596; observed reflections, 464; independent reflections 73; $R_{av} = 0.078$; $\mu = 49$ cm^{-1} (ψ scan at $2\theta = 27.9°$); $0.64 < T < 0.98$; $R = 0.090$, $R_w = 0.107$; difference map flat to <1 e/Å^3. [c] The z parameters of the two structure types are related by $z' = {}^1/_3 - z$. [d] Calculated for H centered in tetrahedra. [e] The value of ScH_2 is 207 pm.

Orientation experiments have also been made in the MXH_x systems for M = La, Gd, Er, and Lu (Table I). Preparations of $LaClH_x$ for $x \simeq 1$ gave single-phase products with lattice constants indistinguishable from those reported[4] for LaCl. A flux of 10% KCl was found useful at 800 °C in overcoming the kinetic problems associated with the low vapor pressure of $LaCl_3(s)$; its use did not lead to an intercalate (below). It will be noted that the preparation of $LaClH_{0.82}$ (Table I) was obtained from LaH_2 and $LaCl_3$ (2:1) by pumping the excess hydrogen through the wall of the niobium container at 900 °C. Otherwise, such a reaction gives only a low yield (≃5%) of $LaClH_{max}$ plus unreacted LaH_{2-y} and $LaCl_3$ when low volume containers are employed. Addition of a hydrogen sink like a metal strip to such a system will give a higher yield of $MClH_x$. With the correct amount of metal, the yield will be quantitative (based on chloride) for the $MClH_x$ composition in equilibrium with α-M(H)–MH_{2-y} at temperature. In additon, the "metal" strip will usually retain its integrity so that it can be readily removed from the product. Hydrogen dissociation pressures were also measured at 750 and 850 °C on a sample of $LaClH_{0.82}$ (corrected) sealed in niobium. The values of 0.98 and 3.1 Torr, respectively, are somewhat below those of the LaH_x plateau, 1.1 and 9.7, respectively.[22] Pressures above plateau values are found for hydrogen-richer samples.

A hydrogen-free LaCl is not stable in a sealed container at 750 °C, as demonstrated by the result of pumping on an $LaClH_{\simeq 7}$ sample at that temperature for 1 h, which dropped the equilibrium H_2 pressure effectively to zero. Similar results have been obtained

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for $YClH_x$. The hydrogen is easier to remove from $LaClH_x$ than from $YClH_x$, paralleling the lesser stability of the binary hydrides with the larger elements (below).[21]

Exploratory measurements on MXH_x systems for M = Gd, Er, and Lu showed that these phases were also readily formed. This is evident both from a visual inspection, the new phases being characteristically blue-black as opposed to the silvery color of the metals and their hydrides, and, more importantly, from Guinier photographs, which show that single-phase samples are obtained. The $GdClH_{0.68}$ and $GdBrH_{0.68}$ products were obtained in evidently quantitative yields at 750 °C where errors from dissociation should be small, and these gave lattice constants that are virtually identical with those recently reported for analyzed samples of $GdClH_{0.89}$ and $GdBrH_{0.93}$[9] (Table I). The lattice constant data for $ErBrH_{0.7}$ (Table I) are quite different from those reported for "ErBr",[6] suggesting that the latter contained appreciably less hydrogen, as might be expected since the monobromide was obtained in low yield (5%) in presumed equilibrium with α-Er(H). The $ErClH_{0.6}$ and $LuClH_{0.6}$ phases are new. Negligible yields of these phases were obtained in the absence of hydrogen as long as the traditional pitfall, powdered metal made from hydride, was avoided. Earlier unsuccessful attempts to produce MCl (or other highly reduced) phases for M = Ce, Pr, and Nd by reaction of MCl_3 with high-purity metal strips over a wide range of temperatures[30] are consistent with the general view that the binary monohalide phases of the rare-earth elements do not exist.

Early accounts of the formation of ErCl and LuCl[5] were later[6] concluded to have originated with ErOCl and LuOCl impurities, respectively. This is an easy mistake to make since the positions of the heavy atoms in these particular MOCl phases are virtually the same as the $MClH_x$ compounds with the ZrCl arrangement. The SmSI structure type for MOCl can be viewed as ZrCl-type arrangement of M and Cl atoms with oxygen in all tetrahedral holes,[31] and so it is very close in scattering to that of $MClH_x$ with hydrogen[10] in those same tetrahedra. The use of $LuCl_3$ contaminated with LuOCl (which may easily happen during its preparation[32]) in the preparation of $LuClH_x$ gave an overlay of two very similar patterns with *a* and *c* lattice constants for the oxychloride about 0.3 and 61 pm (2.2%) larger, respectively.

Intercalation of Monohalide Hydrides. The foregoing experiences with the $MClH_x$ phases as adventitious derivatives of the supposed binary monohalides strongly suggest that the reported Li_zMCl phases for M = Y and Gd[13] were likewise hydrides. Similar reactions including alkali-metal reactants have therefore been carried out both with and without hydrogen sources and in particular depth for gadolinium. The routes explored are as follows for the example of lithium and gadolinium; for each case route a excludes hydrogen, and only fully stoichiometric GdH_2 is considered in others:

$$z\mathrm{Li} + {}^{1}/_{3}\mathrm{GdCl_3} + {}^{2}/_{3}\mathrm{Gd} = \mathrm{Li}_z\mathrm{GdCl} \qquad (1a)$$

$$z\mathrm{Li} + {}^{1}/_{3}\mathrm{GdCl_3} + {}^{2}/_{3}\mathrm{GdH_2} = \mathrm{Li}_z\mathrm{GdClH}_{4/3} \qquad (1b)$$

$$\mathrm{LiGdCl_4} + 3\mathrm{Gd} = 4\mathrm{Li}_{1/4}\mathrm{GdCl} \qquad (2a)$$

$$\mathrm{LiGdCl_4} + 3\mathrm{GdH_2} = 4\mathrm{Li}_{1/4}\mathrm{GdClH}_{3/2} \qquad (2b)$$

$$z\mathrm{LiCl} + ((1-z)/3)\mathrm{GdCl_3} + ((2+z)/3)\mathrm{Gd} = \mathrm{Li}_z\mathrm{GdCl} \qquad (3a)$$

$$z\mathrm{LiCl} + ((1-z)/3)\mathrm{GdCl_3} + ((2+z)/3)\mathrm{GdH_2} = \mathrm{Li}_z\mathrm{GdClH}_{2(2+z)/3} \qquad (3b)$$

$$z\mathrm{LiCl} + ((1-z)/3)\mathrm{GdCl_3} + ((2+z)/3)\mathrm{Gd} + (x/2)\mathrm{H_2} = \mathrm{Li}_z\mathrm{GdClH}_x \qquad (3c)$$

$$z\mathrm{LiCl} + ((1-z)/3)\mathrm{GdCl_3} + ((4+2z-3x)/6)\mathrm{Gd} + (x/2)\mathrm{GdH_2} = \mathrm{Li}_z\mathrm{GdClH}_x \qquad (3d)$$

A. Gadolinium. As with the results for "GdCl", routes 1a, 2a, and 3a were unsuccessful in producing any other phases (except for unreduced phases in the $LiCl/GdCl_3$ etc. systems) as long as the metal was low in hydrogen. Commercial gadolinium metal powder was found to have the composition $GdH_{0.22}$ by analysis, and its use therefore gave a Li_zGdClH_x product in high yields when a supposed reaction 1a was run.

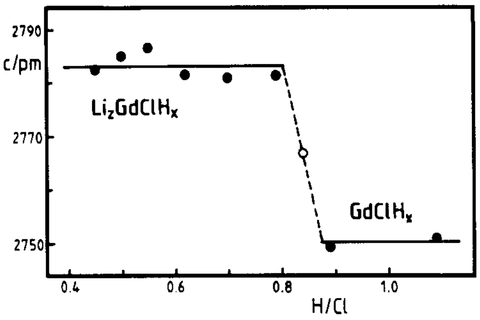

Figure 2. Dependence of the *c* lattice parameter of Li_zGdClH_x ($z \simeq 0.1$) on *x*: (●) 750 °C reactions (single-phase samples); (○) 900 °C reaction.

Inclusion of a hydrogen source gives positive results by all routes although some are more suitable than others. Since the upper limit for *x* in $A^{I}_{z}MXH_x$ phases is not likely to be greater than 1.0 at these temperatures, corresponding to filling all tetrahedra in the monohalide substrate, routes 1b, 2b, and 3b are not suitable for single-phase products as they all provide $x > 1$ and therefore MH_{2-y} as well. Addition of metal strips to soak up the excess hydrogen would work, but one has little control over the stoichiometry as the product would be in equilibrium with either one or both of the metal–hydrogen phases. Likewise, a sufficient container volume to remove the excess hydrogen through dissociation is judged to be unsuitable for predetermined compositions.

In general, the intercalation of MXH_x phases by alkali metal is best accomplished by addition of the appropriate quantity of AX to the above reactions. Excess AX will generally lead to other phases as well; if the system is made up to M:X = 1:1 but less A is incorporated than loaded, then this ratio will be off and a metal or metal hydride phase will also be present.

Although temperatures near 900 °C were first used, 700–750 °C was found to be sufficient, no doubt at least in part because of the low melting point of $GdCl_3$ (≃610 °C). Metal strips react rapidly as well, perhaps aided by their known solution in the melt.[33]

In order to obtain some idea of the stoichiometry of the product Li_zGdClH_x, reactions were loaded by following route 3d, with *x* values between 0.45 and 1.09 for a fixed *z* value of 0.1 and with $z = 0.1$, 0.2, and 0.5 for $x = 0.7$. The $x = 1.09$ sample contained substantial amounts of GdH_2 and the $x = 0.89$ sample a trace, but not those with smaller *x* values, so the *x*(max) limit should be $0.89 \geqslant x \geqslant 0.79$ for a nominal $z = 0.1$. The lower limit, *x*(min), is certainly below 0.45. These results and those for the other rare-earth elements so studied are summarized in Table III.

As Figure 2 shows, intercalation of $GdClH_x$ leads to a *c* lattice constant expansion of up to 37.2 pm; lithium intercalated ($z = 0.1$) samples all have $c \geqslant 2781$ pm whereas nonintercalated samples all have $c \simeq 2749$ pm. The *c* parameter seems to pass through a maximum for $x \simeq 0.55$ but this needs further investigation. More importantly, a sharp decrease in *c* occurs at $0.79 \leqslant x \leqslant 0.89$, the latter having the typical *c* of the ternary $GdClH_x$, meaning that no intercalation occurs beyond $x \simeq 0.85$ for $z = 0.1$. This change, although much smaller in effect, is also clearly visible from the *a* lattice constant, which is always a little larger (beyond 382 pm) for nonintercalated products. A limited gain in stability with intercalation seems evident.

One sample synthesized at 900 °C with metal strips at $x = 0.70$ gave $c = 2766.8$ pm, which would mark with a corrected $x \simeq 0.85$ the turning point of the *c* vs. *x* curve (Figure 2).

Attempts to intercalate lithium beyond $z = 0.1$ were not successful, and earlier accounts of $z = 0.5$ ("$Li_{0.5}GdCl$"[13]) were apparently calculational artifacts in the least-squares refinement.

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Table III. Reaction Conditions and Structural Data on the Products of the Intercalation of $MClH_x$ (M = Gd, Sc, Y, Br, Lu)[a]

compn[b]	temp, °C; conditions[c]	lattice const, pm		structure type; remarks
		a	*c*	
Gadolinium				
$Li_{0.1}GdClH_{0.45}$[d]	750	381.15 (4)	2782.4 (8)	ZrBr
$Li_{0.1}GdClH_{0.50}$	750	381.26 (3)	2785.1 (4)	ZrBr
$Li_{0.1}GdClH_{0.55}$	750	381.05 (3)	2786.6 (4)	ZrBr
$Li_{0.1}GdClH_{0.62}$	750	381.52 (4)	2781.5 (7)	ZrBr
$Li_{0.1}GdClH_{0.70}$[d]	750	381.47 (3)	2781.0 (5)	ZrBr
$Li_{0.1}GdClH_{0.70}$[d]	750	381.47 (3)	2781.0 (5)	ZrBr
$Li_{0.1}GdClH_{0.70}$	900; S	381.93 (3)	2766.8 (5)	ZrBr
$Li_{0.1}GdClH_{0.79}$	750	381.45 (2)	2781.2 (4)	ZrBr
"$Li_{0.5}GdCl$"	500	381.5 (1)	2783.2 (7)	ZrBr; ref 13
$Li_{0.1}GdClH_{0.89}$	750	382.43 (6)	2749.3 (7)	ZrBr; GdH_2 (trace)
$Li_{0.1}GdClH_{1.09}$[d]	750	382.29 (3)	2751.0 (3)	ZrBr; GdH_2
$Li_{0.2}GdClH_{0.70}$	750	381.71 (2)	2775.7 (6)	ZrBr
$Li_{0.5}GdClH_{0.70}$	750	382.3 (1)	2752.9 (20)	ZrBr; GdH_2
$Na_{0.1}GdClH_{0.70}$	750	382.30 (6)	2755.0 (10)	ZrBr; two-phase mixture
		381.8 (2)	2960.0 (32)	
$Li_{0.1}GdBrH_{0.70}$	850	387.16 (4)	2938.7 (11)	ZrBr
$Na_{0.1}GdBrH_{0.70}$	850	387.29 (4)	3017.9 (20)	ZrBr
Scandium				
$Li_{0.5}ScClH_{0.39}$	860	347.4 (8)	2690 (2)	ZrBr, LiCl, α-Sc(H)
$Li_{0.1}ScClH_{0.40}$[d]	860	347.09 (6)	2694 (2)	ZrBr
$Li_{0.1}ScClH_{0.58}$[d]	860	347.26 (4)	2693.4 (7)	ZrBr
$Li_{0.1}ScClH_{0.92}$	860	347.45 (5)	2688.0 (9)	ZrBr
$Na_{0.1}ScClH_{0.31}$[d]	860	347.40 (4)	2901 (2)	ZrBr
$K_{0.1}ScClH_{0.64}$	860	348.0 (3)	3280 (50)	ZrBr
Yttrium[e]				
$Li_{0.044}YClH_{0.47}$[f]	900; X	374.58 (3)	2770.3 (8)	ZrBr
$Li_{0.078}YClH_{0.52}$[d,f]	900; X	374.29 (3)	2789 (1)	ZrBr
$Li_{0.3}YClH_{0.47}$	750; X	374.20 (3)	2787.6 (9)	ZrBr
$Li_{0.3}YClH_{0.47}$	750	374.37 (4)	2780.9 (9)	ZrBr; α-Y(H)
"$Li_{0.2}YCl$"	≥875; X	374.81 (3)	2779.6 (7)	ZrBr; α-Y(H), ref 13
$Li_{0.3}YClH_{0.75}$	750; X	375.14 (3)	2754.5 (9)	ZrBr; YH_{2-y}
$Li_{0.1}YClH_{1.05}$	750	375.42 (3)	2740.3 (8)	ZrBr, ZrCl; YH_{2-y}
$Na_{0.1}YClH_{0.5}$	750	374.55 (2)	2851.1 (8)	ZrBr; α-Y(H)
Other[g]				
"$Li_{0.1}ErClH_{0.6}$"	850	370.27 (3)	2723.1 (3)	ZrCl; LiCl, ErH_2
"$Li_{0.1}ErBrH_{0.6}$"	980	376.99 (2)	2873.8 (2)	ZrCl; LiBr
"$Li_{0.1}LuClH_{0.6}$"	850	363.34 (3)	2712.6 (4)	ZrCl; LiCl, LuOCl

[a] All products were pure $A^I_zMXH_x$ and rhombohedral according to Guinier diffraction unless noted otherwise. [b] Compositions as loaded unless otherwise noted. [c] All reactions included MCl_3, MH_2, and powdered M(H) except S = metal strip and X = excess YCl_3. [d] Hydrogen analysis. [e] A^ICl/YCl_3 left in all reactions; see text. [f] Alkali-metal analysis. [g] Negligible intercalation indicated by lattice constants (cf. Table I).

Additional LiCl in the reaction mixture actually leads to decomposition to GdH_2 and the ternary $LiGdCl_4$ and, at high *x* values, more or less $GdClH_x$.

Sodium intercalation for the composition $Na_{0.1}GdClH_{0.70}$ gave a two-phase mixture of the ternary $GdClH_x$ plus some of the quaternary phase, suggesting some minimum *z* value >0.1 is necessary. The Na^+ intercalation results in about a 205-pm expansion of *c* whereas virtually no change is found in *a*. Potassium intercalation was also attempted but yields were low and the Guinier patterns poor. However, the clearly visible (003) reflection yielded an estimated *c* of 3244 pm, a little smaller change than seen in the analogous data for the scandium systems.

It is noteworthy that both lithium and sodium intercalations into $GdBrH_x$ at 100 °C higher temperatures (to allow for the higher melting point of $GdBr_3$) result in the transformation of the ZrCl-type ternary $GdBrH_x$ to a ZrBr-type structure for the quaternary. Both lithium and sodium intercalations cause the usual small contraction in *a* and 33.6-pm (Li^+) and 112.8-pm (Na^+) expansions in *c*.

B. Scandium. An expansion of up to 25–30 pm in the *c* axis for the reactions with lithium make clear that intercalation of $ScClH_x$ is possible. Although the fully occupied site would correspond to $Li_{0.5}ScClH_x$, such a stoichiometry with $x = 0.33$ left appreciable LiCl unreacted and α-Sc as well because the resultant Sc:Cl ratio was also wrong. Recalling the refined composition "$Li_{0.15(8)}YCl$",[13] we fixed the lithium thereafter at $Li_{0.1}ScClH_x$. This gave single-phase products with analyzed values of $x = 0.40$ and 0.58 (loaded as 0.33 and 0.60) and only slightly larger *c* lattice constants. The product for $x = 0.9$ was also single phase, indicating a homogeneity range $0.4 \leq x \leq 0.9$. As with gadolinium, the dependence of *c* on *x* at fixed $z = 0.10$ appears to be small. Intercalation of sodium or potassium appears certain, judging from even greater *c* parameters, but the patterns were not of high quality. The compounds with larger cations again appear to be of lesser stability. Only about 50% of the hydrogen loaded with sodium was retained, and the sodium and potassium phases were not seen earlier[13] when higher temperatures, 900–950 °C (and less hydrogen), were employed. Reactions with rubidium and cesium were unsuccessful.

C. Yttrium. The expansion in *c* on intercalation of $YClH_x$ with lithium, 35–40 pm, is larger than with scandium or on formation of Li_zYClO from YClO, 25 pm ($z(\max) = 0.15–0.25$).[34] Intercalation with lithium was not observed at 600 °C even though there is a melt phase present, but 750 °C works well. This reaction and the phase relationships are more complex; the use of stoichiometric amounts of the reactants for a lithium coefficient $z \geq 0.1$ leaves an unreacted $LiCl/YCl_3$ melt and therefore α-Y(H) or YH_{2-y} as well, depending on composition. The latter can be eliminated, and therefore the hydride stoichiometry better defined, through the use of about 10–20% excess YCl_3, the exact excess depending on the lithium content. This still leaves the lithium

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(34) Ford, J. E.; Corbett, J. D. *Inorg. Chem.* **1985**, *24*, 4120.

stoichiometry uncertain, but the excess $LiCl/YCl_3$ can be removed physically with the aid of the small natural temperature gradients present when the reaction is run at 900 °C. Analyses of two such single-phase products that show about 40% of the loaded lithium is retained, and in the one case studied, the hydrogen was close to that expected on that basis (loaded as $Li_{0.20}YClH_{0.46}$, analyzed as $Li_{0.078}YClH_{0.52}$). The excess YCl_3 used above is thus necessary to correct the overall composition because of incomplete lithium uptake ($z < 0.1$)). Samples loaded for correct z values would presumably be single phase as the yield based on hydrogen appears to be quantitative.

The maximum lattice constant c for $YClH_x$, 2752 pm, occurs for x(min).[11] The data for the first three yttrium runs in Table III indicate that the c lattice parameter increases with increasing lithium content and then saturates at a lithium coefficient less than 0.1. One might expect an inverse relationship between the amounts of lithium and of hydrogen that can be incorporated, and this appears to be the case, at least with large amounts of hydrogen. The c lattice constant for x(loaded) = 1.05 and $z = 0.10$ still well exceeds that obtained in the ternary system with YH_{2-y} present (2732 pm). The fourth reaction listed and others not shown, which employed excess strips (plus YH_2), were in effect like those run in the isolation of "$Li_{0.1}YCl$", and these gave products with comparable lattice constants, the c value still being well in excess of anything achieved in the $YClH_x$ system.

The product of a reaction like that which yielded $Li_{0.078}YClH_{0.52}$ but which was run at 750 °C was also subjected to hydrogen dissociation pressure measurements between 800 and 950 °C by using the tantalum container wall as a semipermeable membrane, as with $YClH_x$.[11] The data are very well described by $\log p$ (Torr) $= -15470/T + 13.04$. The corresponding $\Delta H° = 70.8$ kcal/mol of H_2 compares with about 55 kcal/mol for $YH_{1.1}$, the composition with the same fractional interstitial occupancy.[22] The value at 850 °C, 0.18 Torr, compares with 0.89 Torr for the α-Y(H)–YH_{2-y} binary ($\simeq YH_{0.55} - YH_{0.95}$)[22] and 0.017 Torr for $YClH_{0.5}$,[11] indicating that the hydrogen binding decreases with intercalation. The product of the fourth yttrium reaction in Table III was similarly pumped on within a tantalum tube, with the result that only Y, Y_2Cl_3, and a white product were left. Thus lithium intercalation does not stabilize YCl sufficiently by moving E_F off the high density of states calculated for the binary compound.[11,24]

Sodium intercalation of $YClH_x$ at 750 °C was clearly indicated by the lattice constants obtained. The dissociation pressure measured in niobium was very close to that of the lithium compound (above) at 800 °C. The sodium compound is not obtained above 820 °C, but it may be obtained in poorly crystallized form from the action of sodium in NH_3(l) on $YClH_x$. However, this material deintercalates at 200 °C.

D. Others. Intercalation of $ErClH_{0.6}$ and $LuClH_{0.6}$ by 0.1 mol of lithium was also attempted at 850 °C and of that $ErBrH_{0.7}$ at 980 °C. However, comparison of the resulting a and c lattice constants (Table III) with those in Table I make it clear that negligible reaction has occurred.

Discussion

A description of the phase relationships between the halide hydrides MXH_x and the binary hydrides of the same metal is fairly straightforward and also useful in understanding the synthetic reactions. These interrelationships have already been implicitly incorporated in the preceding results presentation. Figure 3 illustrates in the continuous curve the typical pressure–composition behavior of a rare-earth-metal α-M(H)–MH_{2-y} system.[22] Superimposed on this are the idealized relationships with MXH_x that appear applicable when halide is present. It seems clear that "monohalides" of virtually all of these elements may be obtained from MX_3/M systems in small to moderate yields through extraction of hydrogen from impure metal, the phase obtained in the presence of excess trihalide and metal representing the lower limit MXH_x in equilibrium with α-M(H). Increasing amounts of hydrogen first convert the system to the lower limit MXH_x phase, and then this passes through the x range and terminates at some upper limit x(max) in MXH_x. (Of course, $\log p$ vs. x may also exhibit appreciable curvature, especially at the limits.)

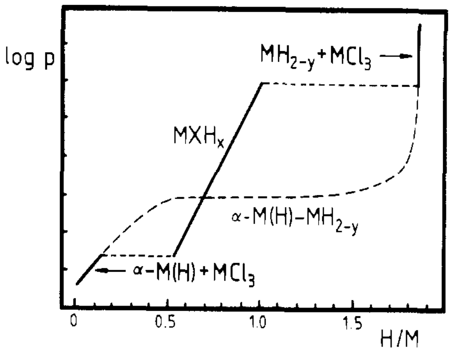

Figure 3. Hydrogen dissociation pressure vs. H/M (x) for a rare-earth-metal system (smooth curve) and, overlaid, the idealized phase relationships for the $M/MCl_3/H_2$ system on formation of $MClH_x$ (total M:Cl fixed at 1:1).

In most cases (M = Y, La, Gd, Er; X = Cl, Br at least), the upper limit phase is in equilibrium with MH_{2-y}. Thus the system with X:M = 1:1 is single phase over the central region ($0.5 < x < 1.0$ shown), while MCl_3 and metal (hydride) are also present beyond either end point. Scandium is different in that (a) α-Sc(H) is capable of reducing $ScCl_3$ to other phases at typical reaction temperatures and (b) ScH_{2-y} does not appear until some excess hydrogen has been added beyond x(max) (Figure 1).

Some of the differences between systems with different metals can be understood or predicted on the basis of both expected trends and the contrasting properties of the binary and ternary structures. One expects the relative stabilities of the MXH_x phases (such as measured by $p(H_2)$) to vary in some regular way reflecting strong M–H and moderate M–X interactions in separate filled bands[11,35] together with some M–M bonding. EHMO calculations show that these are likely to be metallic phases, e.g. for YClH,[11] and $LaClH_x$ shows a Knight shift of 0.22% in the ^{139}La NMR spectrum.[36] Hydrogen pressures at fixed x might then be expected to vary somewhat in parallel with the size of the metal M and thence the strength of the bonding. This is known to be true for $LaClH_x$ vs. $YClH_x$ but needs to be investigated for other cases. This trend is known to apply to most α-M(H)–MH_{2-y} systems, where the plateau pressures generally decrease with decreasing size of the metal, e.g., at 750 °C, 7 Torr for La, 2.5 Torr for Gd, 1.3 Torr for Er and a surprisingly small 0.5 Torr for Y.[22] The observed phase relationships (Figure 3) then fix to some degree the pressure (but not the x range) of the corresponding $MClH_x$ systems in a comparable region.

The anomaly occurs with the relatively high scandium hydride plateau pressures, 8 Torr at 750 °C. This must to a considerable degree arise from the close approach of the hydride ions in the fluorite structure of the dihydride, 207 vs. 225 pm in YH_2. Switendick[37] in particular has described theoretically how such close approaches in effect drive the antibonding H–H interactions toward E_F and diminish stability, an extreme arising with the instability of ScH_3. On the other hand, minimum H–H distances in ScClH are estimated to be a comfortable 257 pm, and a relatively lower pressure is to be expected. Thus the contrasting stabilities of the binary vs. the ternary hydride systems for scandium help explain (1) why it is relatively easy to make $ScClH_x$ from α-Sc(H) and (2) the absence of ScH_{2-y} at the upper end of the $ScClH_x$ region of stability since the α-Sc(H)–ScH_{2-y} plateau pressure should lie higher than that for $ScClH_x$ and some overpressure of H_2 ($x > 1$) is necessary to form ScH_{2-y}. The adjustment of Figure 3 necessary to describe such a circumstance is quite consistent with the character of the lattice constant vs. x behavior (Figure 1) and is in contrast to the fairly abrupt termination for $YClH_x$ ($x \simeq 1.0$) and the fairly immediate appearance of YH_{2-y}.

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(37) Switendick, A. C. *Int. J. Quantum Chem.* **1971**, *5*, 459.

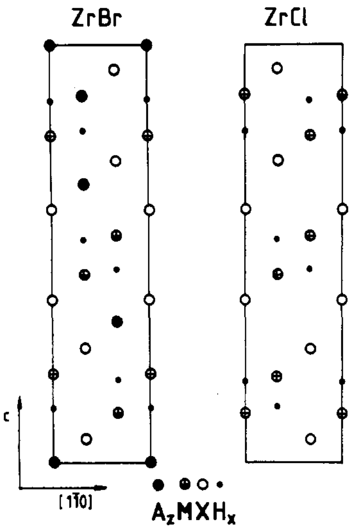

Figure 4. [1$\bar{1}$0] sections of the crystal structures of MXH in the parent ZrBr and ZrCl structure types with hydrogen in tetrahedral and alkali metal (ZrBr type only) in octahedral interstices.

Although Li_zGdClH_x was first obtained from the attempted reduction of KGd_2Cl_7 with metallic lithium,[13] excess ACl solvent in general leads to some disproportionation and metal hydride because of the competitive stability of A^IX/MX_3 phases, e.g. Li_3ScCl_6, $LiGdCl_4$, etc. The use of other alkali-metal halides or ternary phases in an attempt to depress the melting points and thereby enhance crystallinity has led to other phases, e.g. $Cs_2LiGdBr_6$[38] from $Cs_3Gd_2Br_9/LiBr/GdH_2$, $Cs_2LiLuCl_6$ from $CsLu_2Cl_7/Li$, and Cs_2KScCl_6 from $Cs_3Sc_2Cl_9/K$.[39] The last two elpasolites were in fact obtained as single crystals from the molten system at fairly low temperatures.

Intercalation does not lead to substantial increases in stability; in two cases the hydrogen dissociation pressure at about the same x value actually increased somewhat. Lithium is incorporated best, and in a few cases, sodium and potassium are incorporated, while even lithium is not taken up by $ErXH_x$ and $LuClH_x$, judging from lattice constants. The intercalated yttrium chlorides appear to have somewhat borderline stability. The limiting amount of lithium in any case is not large, less than $0.1/MXH_x$ (the structural limit would be 0.5), and there may be a general inverse relationship between z and x in $A^I{}_zMXH_x$ in the reduced limit as such was observed with lithium in the yttrium and gadolinium chloride systems. Many details remain to be ascertained.

The lattice constant expansions that accompany intercalation are easily recognized, but their dependence on z and x in $A^I{}_zMXH_x$ has not been well-characterized although in general an increase in either leads to a decrease in c.

The $ScClH_x$ and $YClH_x$ phases both occur with the ZrBr-type stacking of slabs with lower x and the ZrCl-type with higher values; we infer the same occurs in the gadolinium and terbium chloride systems based on the observation of both structure types from DTA studies of the "monohalides",[6] the ZrBr form being the high-temperature type generated by thermal dissociation of hydrogen. On the other hand, $LaClH_x$ at the presumed upper limit remains ZrBr type. The $ErClH_x$, $LuClH_x$, and $GdBrH_x$ systems have only been seen in the ZrCl form, but in no case has the lower limit of x been established. However, the ZrCl structure was often seen for "monohalide" products where x was presumably near the lower limit.

The difference in stability between the two structure types (Figure 4) is not easily accounted for in terms of just the atom arrangement along c, the expected effect of varying x on the second and third nearest neighbors across the gap, M···X in ZrBr and H···X in ZrCl, being just the opposite to observation. The ZrBr type is favored by anion polarizability,[8] and this presumably becomes less important with increasing M–H covalency. The scandium and yttrium systems show a clear dependence of the c lattice constant on x, and the same may be found for others as well although the ranges of x possible have not been defined.

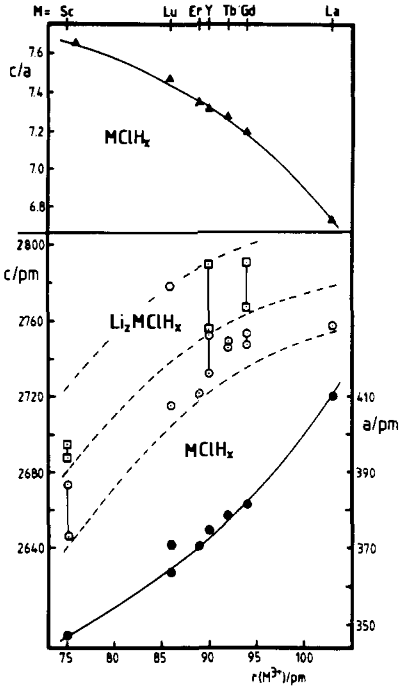

Figure 5. a (●), c (○, □) and c/a (▲) lattice parameters for $MClH_x$ (○) and Li_zMClH_x (□) phases vs. ionic radius of the rare-earth-metal cation M^{3+} (CN 6). For M = Sc, Y, and Gd the ranges of the observed c lattice constants are given. ● and ○ represent a and c, respectively, of LuOCl for comparison with the analogous values of $LuClH_x$.

The appearance of only the ZrBr type on intercalation is completely in accord with expectation; the alkali-metal cation is in a trigonal-antiprismatic halogen environment[13] and then has hydrogen rather than rare-earth metal as second nearest neighbors in both slabs (Figure 4). This change also occurs for $GdBrH_x$, which is known only in the ZrCl structure type, on intercalation with lithium or sodium. Modeling based on the parameters known for $TbClD_{0.8}$[10] (ZrBr) and like distances within the ZrCl polytype slabs gives not only a 1% smaller Madelung enregy (via MAPLE[40]) for the lithium intercalate of the latter but also, more importantly, Li–M distances that are an impossible 66 pm too short. Retention of the ZrCl structure is thus good evidence for little or no intercalation (Er, Lu; Table III).

The number of rare-earth-metal monohalide hydrides that are now known, intercalated or not, allows us a first view of their crystallographic and volume chemistry behavior. In Figure 5 the a and c lattice constants of $MClH_x$ and Li_zMClH_x phases as well as the c/a ratios are plotted against the ionic radii of the trivalent rare-earth-metal cations.[41] Both the a and c axes increase with increasing ionic radii but with completely different slopes so that the c/a ratio decreases from Sc^{3+} to La^{3+}. The relatively large a and small c constants of $LaClH_x$ are not surprising, judging from these curves. While the a axis remains practically constant during intercalation with lithium and insertion of more or less hydrogen, the c axes clearly show two ranges, one for the ternary and another for the intercalated halide–hydrides.

In Figure 6 the molar volumes, V_m, of a variety of highly reduced chlorides are plotted against the same scale, namely, the ionic radii of M^{3+}. The volume per chloride in the formula unit is used to allow comparison of the monochloride–hydrides with the sesquichlorides M_2Cl_3 ($\equiv M_{0.67}Cl$), which do not contain in-

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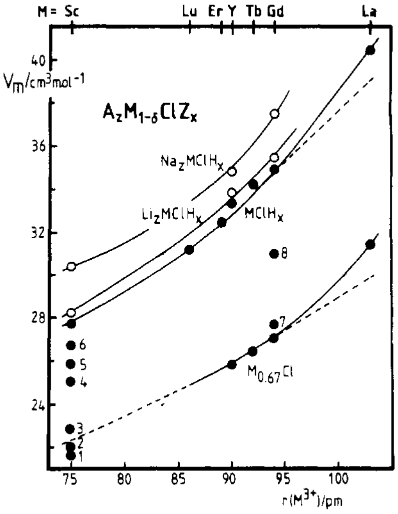

Figure 6. Molar volumes per chloride for $MClH_x$, $A^I_zMClH_x$ (A = Li, Na), and M_2Cl_3 = (=$M_{0.67}Cl$), etc. as a function of the ionic radius of M^{3+}: 1, $Sc_7Cl_{12}X_2$; 2, $Sc_5Cl_8X_2$; 3, $Sc_7Cl_{10}X_2$ (X = B, N, C); 4, Sc_4Cl_6N; 5, Sc_2Cl_2N; 6, Sc_2Cl_2C; 7, $Gd_5Cl_9C_2$; 8, Gd_3Cl_3C.

terstitials. Additionally, various scandium chlorides with carbon, nitrogen, etc. interstitials are included in this plot. The molar volumes of both the mono- and sesquichlorides lie on curves that have comparable appearances. Interestingly, the volumes of both $LaClH_x$ and La_2Cl_3 deviate equally from the broken lines in Figure 6. Generally, the monochloride-hydrides have much higher molar volumes than the sesquichlorides, $GdClH_{0.9}$:$^1/_3Gd_2Cl_3$ = 34.85:26.86 = 1.30:1. This large increase has to be attributed to the double-metal-layer structure of $GdClH_{0.9}$ and the volume necessary for hydrogen (and $^1/_3$Gd). Or, to put it the other way around, only because of the larger monohalide volume *can* hydrogen be inserted into the tetrahedral holes.

It is impressive to note that the sum of the molar volume increments that were derived by Biltz[42] some 50 years ago model the observed molar volumes of even these novel compounds. With his volume increments V_i (cm^3 mol^{-1}) of 20 for Cl^-, 11 for H^-, 2 for Sc^{3+}, 8 for La^{3+}, 6.5 for Gd^{3+}, and 5 for Lu^{3+}, one gets 39 ($\sum V_i$) vs. 40.4 (observed) for LaClH, 37.5 vs. 34.8 for GdClH, 36 vs. 31.2 for LuClH, and 33 vs. 28.0 for ScClH, all in cm^3 mol^{-1}. For Gd_2Cl_3, the sum of volume increments is 24 × 3 cm^3 mol^{-1} vs. 26.8 × 3 cm^3 mol^{-1} observed.

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Supplementary Material Available: A table of the observed and calculated structure factors for ScClH (1 page). Ordering information is given on any current masthead page.

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Siloxy-Zirconium Chemistry. 1. Reaction of Zr-C σ-Bonds with R_3SiOH and the Crystal Structure of (1,2-Dimethoxyethane)bis(triphenylsiloxy)dichlorozirconium(IV), $(DME)ZrCl_2(OSiPh_3)_2$

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Bis(cyclopentadienyl)dimethylzirconium reacts with R_3SiOH compounds to give $Cp_2Zr(OSiR_3)_2$. Tetrakis((trimethylsilyl)methyl)zirconium, $Zr[CH_2Si(CH_3)_3]_4$, reacts similarly, producing $Zr(OSiR_3)_4$. The disubstituted product $Zr(CH_2Si(CH_3)_3)_2(OSiR_3)_2$ could not be produced by this method, however. Synthetic strategies involving crown ether adducts of $ZrCl_4$ were used. Zirconium tetrachloride reacts with 12-c-4 to give the adduct (12-c-4)$ZrCl_4$. The compound is a poorly soluble, moderately air-stable solid. (12-c-4)$ZrCl_4$ reacts with $Na(OSiPh_3)$ in 1,2-dimethoxyethane (DME) to produce $(DME)ZrCl_2(OSiPh_3)_2$ and free 12-c-4. The compound crystallizes from C_6H_6 solution as the bis(benzene) solvate, $(DME)Zr(Cl)_2(OSiPh_3)_2\cdot 2C_6H_6$, in the monoclinic space group *C*2/*c*: a = 22.273 (8) Å, b = 10.233 (9) Å, c = 27.518 (9) Å, and β = 126.92 (4)° with Z = 4. This compound contains the first Zr-$OSiR_3$ bond to be structurally characterized. There is significant d_π-p_π interaction between the Zr and O atoms as evidenced by the short Zr-O bond distance of 1.91 (1) Å and the nearly linear Zr-O-Si bond angle of 171 (1)°.

Introduction

Over the years the Zr-carbon σ-bond has been studied intensely in compounds of the type $(\eta^5\text{-L})_2ZrR_2$, where η^5-L represents an η^5-bonded π-ligand such as $C_5H_5^-$, $C_5(CH_3)_5^-$, $C_9H_7^-$, or $C_{13}H_9^-$.[1] These species, while formally 16e complexes, are 8-coordinate and thus coordinatively saturated. This fact limits their usefulness as potential catalysts since the availability of sites on the metal is a necessary requisite for reaction. This problem can be obviated by removing the η^5 ligands from the metal's coordination sphere. Without these ligands, the number of stable Zr-alkyl complexes decreases dramatically, however.[2] We have undertaken a project

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