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Reaction of Hydrogen with Metallic and Reduced Halides. The Requirement of Delocalized Electrons for Reaction[1]

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The reactions of hydrogen with a number of metallic halides, cluster compounds, and saltlike halides which are strong reducing agents have been investigated. The following new compounds have been identified from reactions of hydrogen with the binary halide utilizing conditions in the ranges 200–475 °C and 250–1900 Torr: $ThI_2H_{0.7}$, $ThI_2H_{1.8}$, $LaI_2H_{0.75}$, $CeI_2H_{0.82}$, $PrI_2H_{1.2}$, $ScI_{2.17}H_{0.6}$, $TiI_{2.5}H_{0.4}$, $Nb_6I_{11}H_{1.3}$, $Mo_6Cl_{12}H_{0.7}$, $ScCl_{1.5}H_{0.68}$, $GdCl_{1.5}H_{0.90}$, $ZrCl_{1.5}H_{0.7}$, and $CsScCl_3H_{0.35}$. On the other hand, $TiCl_2$, TiI_2, and $ZrCl_3$ do not take up significant H_2 while only $NdCl_2$ of the compounds studied decomposes to known binary phases ($NdCl_3$ and NdH_{2+}). Thermodynamic data from equilibrium pressure measurements in the thorium iodide–hydrogen system are reported. The generalization is developed from these studies that hydrogen is taken up only by those halides which contain delocalized electrons, that is, are metallic or contain clusters with delocalized bonding. Structural and bonding implications of these findings are discussed. The general interpretation of the metallic halide hydrides, of the cluster hydrides, and of the binary hydrides of the same elements is considered in terms of multicenter bonding of hydrogen with metal ions via conduction electrons, the hydrogen thereby acquiring a partial negative charge through overlap with the delocalized electrons. This property is reflected in both the rich variety and the often nonstoichiometric character of the hydrides considered.

Introduction

The reactions of hydrogen with metals and intermetallic phases are relatively well-known, and the character and properties of the products therefrom have been defined to some extent. On the other hand, the general reactions of hydrogen with other inorganic materials and the characteristics which are important for reversible hydrogen uptake have not been delineated. In particular, it has not been previously established whether hydrogen will either react with metallic salts or differentiate between these and strongly reducing but insulating phases. Both of these classes are relatively well populated by newly discovered halides. In an earlier consideration of hydrogen storage candidates,[2] it was predicted that in a comparison of a metal with a metallic halide of the same metal the halogen should compete more effectively than hydrogen for metal electron density and thereby cause an increase in the equilibrium H_2 pressure relative to that from the binary hydride at the same hydrogen content. The metallic halides ZrCl and ZrBr were subsequently shown to reversibly absorb hydrogen to yield hydride phases $ZrXH_{0.5}$ and ZrXH (X = Cl, Br), the equilibrium hydrogen pressures of 1 Torr for the hemihydrides and 40–44 Torr for the monohydrides at 400 °C comparing with 0.06 Torr known for $ZrH_{1.5}$.[2] Recent NMR data suggest that the hydrogen atoms occupy the tetrahedral sites between the zirconium layers present in the X–Zr–Zr–X macro layers,[3] with half the tetrahedral sites being regularly filled at the hemihydride and all these sites occupied at the monohydride composition.[4] The only other metal–metal bonded halide reported to contain hydrogen is Nb_6I_{11},[5] a single hydrogen being located in the center of the octahedron of niobium atoms according to neutron diffraction.

In order to further understand the criteria necessary for reversible hydrogen absorption and the factors influencing the equilibrium hydrogen pressure, the reaction of hydrogen with a number of other metallic halides has been investigated. We have previously synthesized and characterized a variety of metallic iodides, $ThI_2(e^-)_2$,[6] $LaI_2(e^-)$, $CeI_2(e^-)$, $PrI_2(e^-)$,[7,8] and $ScI_{2.17}(e^-)_{0.83}$,[9] in which the added electron is evidently delocalized in a conduction band. Other reduced and conducting halides considered during this study include Gd_2Cl_3,[10] Sc_2Cl_3,[11] $CsScCl_3$,[12] and $TiI_{2.5}$.[13] The reaction of hydrogen with metal cage compounds Nb_6I_{11} and Mo_6Cl_{12} has also been examined. The reversibility of the known hydrogen uptake by Nb_6I_{11} was explored. Likewise, hydrogenation of $MoCl_2$, which contains discrete Mo_6Cl_8 clusters,[14] was also investigated, particularly because elemental molybdenum itself does not absorb hydrogen. The Gd_2Cl_3 studied also contains infinite clusters in the form of chains of metal octahedra which share opposite edges.[10] The hydrogenation characteristics of the foregoing were then compared with this property of a number of insulating but strongly reducing halides (TiI_2, $TiCl_2$, $ZrCl_3$, $NdCl_2$[15]) to provide insight into the importance of delocalized or conduction electrons to reversible hydrogen absorption.

Experimental Section

The reduced metal iodide samples used for hydrogenation studies were all prepared by reduction of the normal-valent iodides with the corresponding metal in a sealed tantalum tube. ThI_2 was obtained from the reaction of sublimed ThI_4 with excess thorium at 800 °C.[6] LaI_2, CeI_2, PrI_2, and $ScI_{2.17}$ samples were obtained from rods previously used for resistivity measurements.[7,9] The congruently melting[8] LaI_2 was easily obtained from the reaction of LaI_3 with an excess of lanthanum just above the melting point of LaI_2 (830 °C). Rods of the incongruently melting CeI_2 and PrI_2 were prepared by reacting triiodide and excess metal slightly above the product's melting point (808 and 758 °C, respectively) for 16 h after which the container was slowly lowered through a thermal gradient.[7] The rod of the phase $ScI_{2.17}$ was formed similarly[9,16] by lowering the tantalum container through a thermal gradient which spanned the peritectic temperature (892 °C) for $ScI_{2.17}$. Since conversion to the lower phase limit of incongruently melting phases is generally difficult in these quantities, the compositions of the last three were determined from an iodide analysis ($AgNO_3$–eosin) on a weighed sample to be $CeI_{2.07}$, $PrI_{2.12}$, and $ScI_{2.28}$. Hydride compositions were calculated for the metallic component of each assuming that no hydrogen uptake occurred with the other, less reduced phase present in each ($CeI_{2.4}$, $PrI_{2.5}$, and ScI_3, respectively).

The composition $TiI_{2.06}$ was obtained from heating TiI_4 with excess metal foil in a sealed Ta tube at 925 °C for 21 days. Reaction of stoichiometric amounts of TiI_2 and TiI_3 in tantalum at 800 °C for 10 days afforded the highly conducting composition $TiI_{2.5}$, which is a single phase judging from powder patterns taken as a function of composition.[13] The Nb_6I_{14} was obtained from the reduction of NbI_5 with excess niobium in sealed niobium tubes at 950–1000 °C for 1 week.[17] $Mo_6Cl_{12}\cdot 2H_2O$ was prepared as described[18] from the reduction of $MoCl_5$ with aluminum in a NaCl–$AlCl_3$ melt. The anhydrous Mo_6Cl_{12} material was obtained by heating the hydrate at 300 °C under dynamic vacuum for 1 day.

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Table I. Hydride Compounds Formed by Some Metallic Iodides

Hydride compn[a]	Temp, °C	Final press, Torr	Time, days	Color change
$ThI_2H_{1.77(5)}$[b]	350	1120	6	Gold to violet to yellow-green
$LaI_2H_{0.75(3)}$[c]	400	1583	4	Black to light gray
$CeI_2H_{0.82(1)}$	400	960	7	Black to yellow-orange
$PrI_2H_{1.23(2)}$	400	1115	11	Black to yellow-green
$ScI_{2.17}H_{0.64(5)}$	400	1829	5	Dark violet to gray
$TiI_{2.5}H_{0.37(4)}$[d]	300	1656	18	Black to gray-black

[a] Estimated uncertainty in last significant figure is given in parentheses. [b] The intermediate violet phase is $ThI_2H_{0.7}$. [c] Conversion may be incomplete within the particles—see text. [d] Probable lower limit—see text.

The other reduced chlorides studied were prepared in sealed tantalum tubes according to the reactions

$$GdCl_3(g) + Gd(\text{excess foil}) \xrightarrow[\text{9 days}]{610\ °C} Gd_2Cl_3{}^{10}$$

$$ScCl_3 + Sc(\text{excess foil}) \xrightarrow[\text{10 days}]{650\text{–}750\ °C} Sc_2Cl_3{}^{11}$$

$$2ScCl_3 + Sc + 3CsCl \xrightarrow[\text{2 days}]{700\ °C} 3CsScCl_3{}^{12}$$

$$TiCl_3 + Ti(\text{excess strips}) \xrightarrow[\text{3 days}]{700\ °C} TiCl_2$$

$$ZrCl + 2ZrCl_4 \xrightarrow[\text{4 days}]{500\ °C} 3ZrCl_3{}^{19}$$

$$5ZrCl + ZrCl_4 \xrightarrow[\text{28 days}]{600\ °C} \xrightarrow[\text{17 days}]{500\ °C} 3Zr_2Cl_3{}^{19}$$

The amount of hydrogen absorbed by weighed, powdered halide samples was determined using the previously described[2] hydrogenation apparatus. The halide held at a known temperature in a molybdenum boat within a Vycor jacket was equilibriated with H_2 and the gas uptake calculated from the pressure decrease measured in a calibrated volume with a Heise Bourdon or McLeod gauge. Maximum hydrogen content was established by a two- or three-step hydrogen absorption up to final pressures between 960 and 1830 Torr. For measurements at the lowest pressures, hydrogen leakage into the remainder of the system was limited (to $\leq 6 \times 10^{-4}$ Torr/h) by closing off the sample with a Hoke metal valve during the longer term absorption steps. Since the initial rate of hydrogen absorption was sometimes less than 5 Torr/min, some samples were equilibriated for 4–18 days to ensure complete reaction. Afterward, the hydrogen remaining in the reaction tube was expanded into the calibrated manifold volume to determine the pressure change and hydride composition. At the relatively low pressures studied, absorption was generally faster than desorption.

The error in the $H:MX_n$ composition ratio was calculated as the square root of the sum of the squares of the errors for each absorption step, each contribution being weighed by the square of the $H:MX_n$ ratio for that step. The error in pressure measurement with the Bourdon gauge was listed as ±0.1% for the range 0–2000 Torr, while that for the McLeod gauge was assumed to be equal to ±1 in the least significant figure measured. Standard deviations in calibrated volumes were empirically determined. The temperature variation was considered to be ±1 °C while sample weights were estimated to be correct to ±0.2 mg. All sample transfers naturally took place in the drybox. The latter, a Blickman model with an evacuable entry port, was filled with prepurified nitrogen which continually circulated through a Molecular Sieve mixture. The moisture level during use was generally in the range 5–10 ppm as determined with a Shaw hygrometer. No evidence of sample contamination was ever observed through microscopic or x-ray powder examination or from kinetic effects of apparent surface blockage.

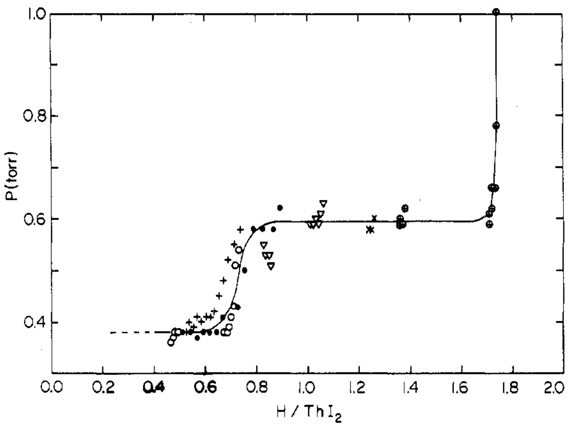

Figure 1. Dissociation pressure isotherm for the ThI_2–H_2 system at 450 °C. The data represented by solid circles are believed to be the most precise.

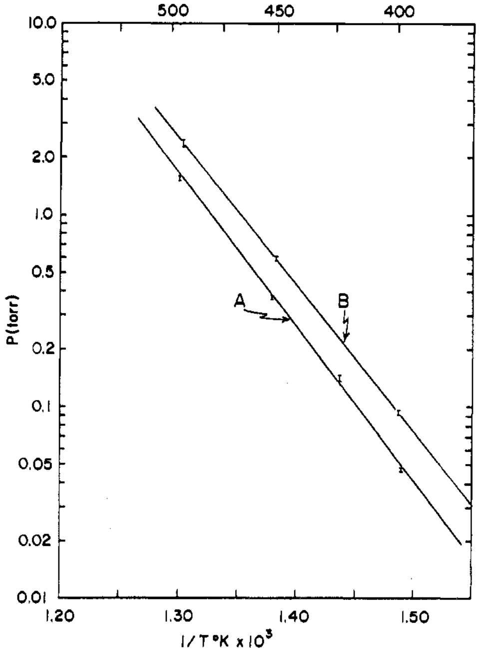

Figure 2. Hydrogen dissociation pressures as a function of $1/T$ for (A) the ThI_2–$ThI_2H_{0.7}$ and (B) the $ThI_2H_{0.8}$–$ThI_2H_{1.7}$ systems.

The pressure–composition isotherm for the ThI_2–$ThI_2H_{0.7}$–$ThI_2H_{1.8}$ system at 450 °C was established using several ThI_2 samples to cover the composition range since the change in composition per desorption step was small. This condition pertained since a small apparatus volume was used to minimize equilibrium time, and sample weights could not be reduced below 0.1 g because of increased weighing error and subsequent composition uncertainty. The number of desorption steps per sample was restricted to 15 so as to limit accumulated error and any possible sample contamination.

Powder diffraction data were obtained using a 114.6-mm diameter camera with Ni-filtered Cu Kα radiation and samples were loaded into 0.2–0.3-mm i.d. Lindemann glass capillaries in the drybox. Data were corrected for film shrinkage. All phase changes reported were confirmed by the x-ray data.

Results

Iodides. Table I summarizes the maximum hydrogen content of the metallic iodides studied at the indicated pressures and temperatures as well as the color changes observed. Distinct color and powder pattern changes were observed in all cases.

Thorium. The thorium diiodide hydride phase compositions were established to be $ThI_2H_{0.7}$ and $ThI_2H_{1.8}$ at 450 °C by the pressure–composition data presented in Figure 1.

Table II. Thermodynamic Values for Thorium Diiodide Hydrides[a]

Reaction	$P_{450\,°C}$, Torr	$\Delta H_f°$, kcal	$\Delta S_f°$, eu
$2.9ThI_2(s) + H_2 \rightleftarrows 2.9ThI_2H_{0.7}(s)$	0.35 (1)	−36.8 (3)	−35.6 (4)
$2.2ThI_2H_{0.8}(s) + H_2 \rightleftarrows 2.2ThI_2H_{1.7}(s)$	0.59 (2)	−35.8 (3)	−35.4 (4)
$Th(s) + H_2 \rightleftarrows ThH_2(s)$[b]	0.073	−35.0	−30.0
$1.1ThH_2(s) + H_2 \rightleftarrows 0.28Th_4H_{15}(s)$[b]	4600	−17.0	−26.6

[a] Per mole of H_2, as written. The uncertainty in the least significant figure is given in parentheses. [b] Data from ref 20.

Table III. Hydrogenation of Other Metal Halides

Product compn	Temp, °C	Final press., Torr	Time, days	Color change
$Nb_6I_{11}H_{1.33(16)}$[a]	305	246	1.5	None
$Mo_6Cl_{12}H_{0.66(11)}$[a]	300	1898	6	None
$ScCl_{1.5}H_{0.68(1)}$	475	6	7	Gray to green
$GdCl_{1.5}H_{0.90(2)}$[b]	300	1019	0.1	Black to gray
$ZrCl_{1.5}H_{0.69(4)}$	200	533	2	None
$CsScCl_3H_{0.35(1)}$[a]	395	1854	12	None
$NdH_{2.58} + 2NdCl_3$[c]	399	1752	22	Black to green
$NdH_{2.19} + 2NdCl_3$[c]	340	346	0.004	Black to green
$TiCl_2$[a,d]	300	1968	8	None
TiI_2[a,d]	300	1800	7	None
$ZrCl_3$[a,d]	200	1132	7	None

[a] No new phase formed. [b] Composition was determined by complete desorption at 800 °C. [c] Products of $NdCl_2$ disproportionation in the presence of H_2. [d] $H:M \leqslant 0.1$.

Nonequilibrium disproportionation to ThI_4 and ThH_2, caused by tetraiodide sublimation to the cooler portions of the reaction tube, becomes appreciable above 450 °C. Three segments of the isotherm between compositions $ThI_2H_{0.4}$ and $ThI_2H_{0.9}$ were used to determine that the first hydride composition in equilibrium with ThI_2 is $ThI_2H_{0.68}$ with additional hydrogen solubility extending to composition $ThI_2H_{0.78}$. Two of the isotherm segments agreed quite closely, while a third indicated a somewhat lower composition. The second hydride equilibrium composition is $ThI_2H_{1.75}$ up to 1120 Torr.

The temperature dependence of the two equilibria is illustrated in Figure 2, and the enthalpy and entropy changes for these are summarized in Table II where they are compared with those of the two binary thorium hydrides. Quite opposite to the behavior observed for ZrX vs. Zr,[2] the enthalpy changes here for uptake of 1 mol of H_2 are all quite similar, while the entropy changes suggest less rather than greater mobility of the hydrogen in the iodide relative to the metal, thereby producing a higher dissociation pressure.

Lanthanum. The lanthanum diiodide hydride composition in equilibrium with LaI_2 is $LaI_2H_{0.45(5)}$, as established by desorbing hydrogen from maximum composition $LaI_2H_{0.75}$ (Table I) at 600 °C until a pressure plateau was approached. The desorption was very slow, the pressure still increasing ~0.01 Torr h^{-1} after 1 day. Raising the temperature to 700 °C to increase the desorption rate caused the equilibrium pressure of $LaI_3(g)$ to attack the silica tube above the reaction boat at an appreciable rate. Because of the slow desorption rate and low equilibrium hydrogen pressures (<0.001 Torr at 700 °C), further hydrogen pressure measurements were not attempted.

Scandium, Praseodymium, and Cerium. Equilibrium hydrogen pressures and thus thermodynamic data could not be obtained for the hydrides of $ScI_{2.17}$, $PrI_{2.12}$, and CeI_2 because of slow hydrogen desorption rates. After four desorption steps at 400 °C to composition $ScI_{2.17}H_{0.5}$, the pressure still increased 0.0006 Torr h^{-1} to 0.4 Torr in 3 days. Hydrogen pressures above $PrI_2H_{1.0}$ at 600 °C increased initially from 0.06 to 6.3 Torr in 37 h, and this doubled after 4 days. Desorption pressure measurements were not attempted for the cerium system. Glass attack by the equilibrium pressure of PrI_3 became evident at 600 °C, while ScI_3 sublimed from the $ScI_{2.17}H_{0.5}$ phase appreciably above 400 °C. Since LaI_2, CeI_2, and PrI_2 are isostructural,[21] the larger amount of H_2 apparently taken up by PrI_2, Table I, suggests either that $PrI_{2.5}$, which was 25% of the sample used, may have also absorbed H_2 or that conversion of the first two was incomplete. The latter may have pertained to $LaI_2H_{0.75}$ since the gray-white material turned blue-gray on exposure to x rays.

The layered $TiI_{2.5}$ was difficult to grind to a fine powder and appeared only partially hydrogenated since the layer flakes retained the color of $TiI_{2.5}$ in contrast to the gray-black color of the finely divided, hydrogenated powder. However, a powder pattern of these flakes showed lines of only the new hydride. Decomposition of this phase back to $TiI_{2.5}$ did not occur in 24 h at 300 °C under high vacuum (<10^{-5} Torr).

Cage Compounds and Other Halides. Hydrogenation of the octahedral metal cage compounds Nb_6I_{11} and Mo_6Cl_{12} was studied employing conditions listed in Table III. The formation of $Nb_6I_{11}H$ had been previously reported[5] but the reversibility of hydrogen absorption had not been demonstrated. Both clusters were found to take up appreciable amounts of H_2 without formation of a new phase as judged by x-ray diffraction. An attempt to obtain a 300 °C desorption isotherm for the $Nb_6I_{11}H$–Nb_6I_{11} single-phase region was unsuccessful since hydrogen was only desorbed very slowly, the composition $Nb_6I_{11}H_{1.3}$ being reduced only to $Nb_6I_{11}H_{1.25}$ after 6 days by several desorption steps, each one starting under vacuum. The equilibrium pressure was >0.17 Torr at 300 °C, with decomposition being evident at high temperatures. Reabsorption of hydrogen did occur at 300 °C, indicating the process is reversible. Hydrogen uptake by Nb_6Cl_{14} to about $Nb_6Cl_{14}H_{1.2}$ has also been observed though the precision of the composition achieved was not good.

The compounds $ScCl_{1.5}$, $GdCl_{1.5}$, and $ZrCl_{1.5}$ all form new phases with H_2 (Table III). The hydride in equilibrium with $ScCl_{1.5}$ has a composition of $ScCl_{1.5}H_{0.5}$ as determined from desorption at both 400 and 475 °C. The equilibrium pressure in the two-phase region is <0.001 Torr, the minimum pressure measured by the McLeod gauge. The hydride retained the fibrous nature of $ScCl_{1.5}$ and changed from gray to dark green.

The small amount of $GdCl_{1.5}$ available (<0.1 g) limited the $GdCl_{1.5}$ study to a three-step absorption to composition $GdCl_{1.5}H_{0.90}$. The hydrogen content was measured by complete hydrogen desorption at 800 °C. The transition to hydride was accompanied by a color change from black to white, and upon exposure to x rays, the latter changed to gray. Incomplete conversion may have been responsible.

The system $ZrCl_{1.5}H_{0.7}$–$ZrCl_{1.5}$ gave equilibrium pressures of about 0.3 Torr at 363 °C. Equilibrium pressures obtained at this composition between 300 and 400 °C are of the same order of magnitude as those found[2] for the $ZrClH_{0.5}$ and $ZrBrH_{0.5}$ phases.

According to x-ray diffraction, no new hydride phases are formed on reaction of hydrogen with $CsScCl_3$, $NdCl_2$, $TiCl_2$, TiI_2, or $ZrCl_3$ under the conditions listed (Table III). Only the first, $CsScCl_3$, takes up a significant amount of hydrogen in the parent structure. Of all the phases studied, only $NdCl_2$ underwent isothermal disproportionation on reaction with H_2 to form known binary halide and hydride phases, although H_2 pressures well in excess of equilibrium values may force such disproportionation in other systems (e.g., ZrX). Since the $NdCl_2$ decomposition takes place rapidly even under the milder conditions of the second experiment, Table III, it seem unlikely that a chlorohydride phase is formed first and subsequently disproportionates.

Discussion

A very useful generalization has developed out of these halide–hydride studies, namely, that hydrogen is taken up in significant amounts either in solid solution or, more frequently, in a way which forms a new halide phase only when the starting halide has *delocalized* electrons associated with its reduced state; that is, the halide is metallic or contains polymetal clusters. In the first category, LaI_2, CeI_2, $ScI_{2.17}$, ZrCl, and ZrBr have all been established as metallic by either conductivity or XPS measurements.[7,9,22] Structural, magnetic, and qualitative resistance data strongly imply this is also true for ThI_2,[6,23] and similar resistance observations together with the structure of $CsScCl_3$ (hexagonal perovskite) indicate that one-dimensional conduction is very likely.[12] $TiI_{2.5}$ shows a qualitatively high conductivity,[13] whereas $ZrCl_{1.5}$, apparently the lower composition limit of the NbS_2-type structure of $ZrCl_2$,[24] is probably also a two-dimensional conductor. Delocalization of electrons in the isolated octahedral clusters in Nb_6I_{11} and Mo_6Cl_{12} clusters is well accepted[5,14] while in $GdCl_{1.5}$ such metal octahedra share edges to form infinite strings.[10] The compound $ScCl_{1.5}$ appears to be very similar to but not isostructural with $GdCl_{1.5}$, though a crystal structure determination has not been possible because of its very fibrous crystal habit.[11,12]

In general, all of these halides react with upward of one hydrogen atom per metal atom, except for ThI_2 which is evidently a two-electron metallic conductor and appropriately takes up more to form $ThI_2H_{1.8}$. Not surprisingly, the quantity of hydrogen absorbed is less in the one-dimensional conductor $CsScCl_3$ and in the niobium and molybdenum clusters, all three of which involve solid-solution processes rather than formation of a new phase according to their x-ray diffraction.

On the other hand, phases without delocalized electrons appear to be unreactive with H_2, even though these may be strong reducing agents ($TiCl_2$, TiI_2, $ZrCl_3$, $NdCl_2$). The contrasting behavior of the metallic $ScI_{2.17}$ which takes up hydrogen with the unreactive behavior of the isostructural insulating TiI_2 is especially striking. Only $NdCl_2$ undergoes disproportionation to known binary phases (NdH_{2+} + $NdCl_3$) on reaction with H_2, while PrI_2, the least stable of the metallic diiodides, takes up H_2 without disproportionation. The classification of $ZrCl_3$ in this group is probably correct; though the ideal crystal structure[25] suggests the presence of metal–metal bonding in one-dimensional chains, the existence of a notable conductivity or a partly filled band has never been demonstrated. A splitting of the σ band with two metal atoms in the cell has been proposed.[26] The experimental situation is also complicated by the fact that the three isostructural zirconium trihalides are significantly nonstoichiometric.[19]

The double-metal sheet structure of the zirconium monohalides, with close-packed layers sequenced X–Zr–Zr–X (X = Cl, Br),[3,22] appears particularly favorable for a metallike reaction with H_2, and the evidence is that the hydrogen atoms are ordered in tetrahedral sites between the double-metal layers in both $ZrXH_{0.5}$ and ZrXH.[4] The conversion to hydride causes only small changes in x-ray scattering, consistent with the ready reversibility of the hydrogenation of these (and a few other) phases. Centers of both the $Nb_6I_8^{3+}$ and $Mo_6Cl_8^{4+}$ clusters as well as of the octahedra linked in chains in $GdCl_{1.5}$ (and possibly in $ScCl_{1.5}$) would also provide an all-metal environment for possible hydrogen incorporation, although only in $Nb_6I_{11}H$ has this location for the proton been established, and substantial changes in the powder patterns suggest larger structural rearrangements take place with the gadolinium and scandium sesquichlorides. Most of the other metallic phases studied here contain interstices which are partly defined by nonmetal atoms, for example, in layered structures involving single-metal sheets, but this seems to be a sufficient condition for reaction as long as delocalized electrons are available. Of course, the degree of structural rearrangement is in most cases not known, but the reversibility in some suggests the change is not kinetically substantial. For example, the layer structure of ThI_2 provides both trigonal-prismatic and trigonal-antiprismatic coordination for the metal atoms in alternate sheets,[23] and formation of the first phase $ThI_2H_{0.7}$ involves only small changes in x-ray scattering. The thorium atoms within the layers are sufficiently well separated (3.97 Å compared with 3.60 Å in the metal) that iodine participation in the conduction band seems necessary in order to account for the metallike conduction and magnetic properties. A similar condition must pertain with LaI_2, CeI_2, and PrI_2[7] as metallike halides are found only with the iodides and not with the lighter halides. The structure of these three is in some respects alloylike ($CuTi_2$ or $MoSi_2$ type[21]) with unusual square sheets of metal atoms separated by pairs of similar sheets of iodine atoms. X-ray powder data indicate that metallic $ScI_{2.17}$ has the CdI_2 structure[16] (presumably with disordered defects), and the hydride formation involves only small changes in x-ray scattering. The one-dimensional conduction in $CsScCl_3$ provides perhaps the severest test of the necessity of delocalized electrons for hydrogen reactions. Here the hexagonal perovskite structure with close-packed layers Cs + 3 Cl contains scandium(II) in infinite strings of octahedral holes normal to the close-packed layers (d(Sc–Sc) = 3.02 Å vs. 3.28 Å in the metal).[12]

In some respects it is convenient to imagine the metallic halides generated from the respective metal by substitution of X^- for e^-, e.g., $La^{3+}(I^-)_2e^-$ from $La^{3+}(e^-)_3$, although this is not meant to imply that the ionic character of the salt is unusual or very different from that in LaI_3. This substitution always increases the hydrogen dissociation pressure for the halide hydride relative to that of the metal hydride, an effect which basically can be understood in terms of a halogen atom competing with the metal core for electrons to form halide much more effectively than does H to form H^-. The present studies of hydride formation by these metallic salts thus provide another dimension to the "chemistry" of metals, particularly, the formation of hydrides and other "interstitials" thereby.

A general bonding picture for hydrides is suggested by the present results, one which is probably also useful in the interpretation of metallic and so-called interstitial compounds as well. Relative to halide, true saline H^- ions have a quite limited stability owing both to the high dissociation energy of the H_2 molecule and to the relatively low electron affinity of the hydrogen atom (<20 kcal/g-atom[27]). Thus as one proceeds from left to right in the periodic table, the last region where something approaching true hydride salts forms may be with the alkaline earth metals and perhaps the rare earth metals. Beyond, the true H^- ion is generally not sufficiently stable, but delocalized electrons in a metal or a metallic halide, sulfide, etc. provide an excellent alternative for binding the hydrogen atom, namely, through multicenter bonding with the neighboring (metal) atoms to allow accumulation of a variable charge density ($H^{\delta-}$, $0 < \delta < 1$) through overlap with the (spin paired) delocalized electrons. Energywise this implies that hydrogen states occur at or below the Fermi level.

In this picture, different sources of delocalized electrons would provide a variable degree of hydrogen binding and charge transfer thereto, as observed. This variability does not appear as obvious or important when halide anions are involved, although participation of iodide in band formation (π^*?[7]) in LaI_2 etc. may be related. The amount of hydrogen bound is a reflection of, in different words, the relative chemical potential of electrons or the electron density in the available interstices and changes induced in this. It is this variability of bonding and population of the hydrogen orbital which gives rise to the rich variety of binary metal–hydrogen stoichiometries plus an evidently analogous behavior in the metallic halide hydrides reported here. There seems to be no fundamental difference between hydrogen reactions with metals and with metallic hydrides except for the low dimensionality often provided by the latter. In both cases sufficient H_2 may be taken up to yield an insulating phase, as suggested by the color changes found at the hydrogenation limit with some metallic halides (Tables I, III). The orbital population of a hydrogen atom can, of course, attain an appreciable negative value without loss of the metallike conduction properties (the ZrXH phases remain good conductors).

Descriptions of metal–hydrogen systems in terms of screening of protons by conduction electrons is no different in substance[27] from the above, though to a chemist the qualitative description utilized here merges naturally into the familiar polycenter description involving many types of electron-deficient bonding.

Interstitial is an inappropriate term to apply to many metal-rich compounds of the lighter nonmetals which are frequently nonstoichiometric and conducting. With the metals involved in this study, the generation of evidently strong interactions with substantial structure changes during hydrogenation is in fact the rule. Nonstoichiometry may represent just the variable hydrogen atom interaction with electrons in a conduction band, while the conduction property attests to a well-delocalized system which is still orbitally rich and electron poor. It is unlikely that the "interstitial" hydrides of the metals considered here are very different from the metallic halides of the same metals at the same nonmetal content, i.e., $La^{3+}(H^-)_2e^-$ vs. $La^{3+}(I^-)_2e^-$, allowing that covalency is probably important in the latter. Hydrogen's widely varying radius presents perhaps a clearer diagnosis; indeed, the abnormally large M–H distances in the highly expanded structures of some metal hydrides, i.e., UH_3 and ThH_2, first suggested that a relatively ionic description was appropriate.[28,29] More recent and complete distance comparisons for metallic hydrides from group 2 through transition group 5 suggest that the radius sum for normal-valent metal ion plus H^- is a surprisingly good approximation for the observed separations with the hydrides of metals considered in this work.[30] Probably similar effects and interpretations are applicable to many other conducting "interstitial" cases as well (carbide, nitride, etc.), though the generally greater number of valence electrons in the nonmetal brings complications to such a simple picture.

Clearly more definitive data are needed regarding the bonding, charge states, and theory characterization of these *relatively* simple hydrogen systems.

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Registry No. ThI_2H_2, 15599-93-6; LaI_2H, 65530-51-0; CeI_2H, 65530-50-9; PrI_2H, 65530-49-6; ScI_2H, 65573-00-4; Ti_2I_5H, 65605-20-1; ThI_2H, 65530-48-5; $Nb_6I_{11}H$, 12339-12-7; $Mo_6C_{12}H$, 65605-21-2; Sc_2Cl_3H, 65605-19-8; $Gd_2Cl_3H_2$, 65605-18-7; Zr_2Cl_3H, 65605-17-6; $CsScCl_3H$, 65545-43-9; NdH_2, 13863-22-4; $NdCl_3$, 10024-93-8; $TiCl_2$, 10049-06-6; TiI_2, 13783-07-8; $ZrCl_3$, 10241-03-9; ThI_2, 13779-95-8; LaI_2, 19214-98-3; CeI_2, 19139-47-0; PrI_2, 65530-47-4; ScI_2, 15513-82-3; Gd_2Cl_3, 12506-69-3; Sc_2Cl_3, 12432-55-2; $CsScCl_3$, 65545-44-0; Nb_6I_{11}, 12196-47-3; Mo_6Cl_{12}, 11062-51-4; $NdCl_2$, 25469-93-6; Ti_2I_5, 65605-16-5.

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