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Rare Earth–Hydrogen Systems. I. Structural and Thermodynamic Properties[1]

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Received June 15, 1966

Crystallographic studies of hydrogen and deuterium systems with La, Ce, Pr, and Nd were carried out. Using a silica fiber torsion balance, dissociation pressure–composition relationships of the hydrides and deuterides of the rare earth elements were measured, and these were used to compute enthalpy, free energy, and entropy changes. Equations of the type $\log P = A - B/T$ predicted the plateau pressures satisfactorily (two solid phases), and equations of the type $\log P = Dn - E$ (n = hydrogen:metal ratio) roughly predicted dissociation pressures in the hydrogen-rich (one solid phase) regions. An approximately linear contraction of the fcc phase was observed as the dihydride is progressively converted to the trihydride. Statistical mechanical analysis permitted estimation of metal–hydrogen and hydrogen–hydrogen interaction energies within the solid phase and also provided a means of estimating the relative distribution of the hydrogen in tetrahedral and octahedral sites as a function of temperature. The hardness of ytterbium and its dihydride was measured. Evidence is presented that an actinium hydride reported in the literature is the dihydride.

Since the earliest study of the reaction of misch metal with hydrogen by Winkler in 1891, approximately 100 publications dealing with rare earth hydrides have appeared. Most of the literature up to 1960 was reviewed by Mikheeva and Kost,[2] and a more recent review was prepared by Bos and Gayer.[3] Important general publications on hydrides have been prepared by Gibb[4] and by Libowitz.[5] A general picture of the rare earth–hydrogen systems, gleaned from the literature and the present work, is as follows. The rare earth metals, nearly all of which exist at room temperature in cubic or hexagonal modifications, take up hydrogen at ordinary or slightly elevated temperatures to form dihydrides, RH_2. The dihydrides are all face-centered cubic, except for those of europium and ytterbium, which are orthorhombic. These last two compounds do not react with additional hydrogen at 1 atm pressure, but the others do and approach the trihydrides, RH_3, as a limiting composition. The cubic dihydrides are deficient in hydrogen, the composition at room temperature being approximately $RH_{1.85}$. They are formed with the evolution of approximately 50 kcal/mole of hydrogen consumed. The rare earth dihydrides are increasingly thermally stable with increasing atomic number, up to a maximum at Ho or Er. The trihydrides of lanthanum, cerium, praseodymium, and neodymium are fcc, but in the cases of samarium and beyond, and yttrium, a hexagonal close-packed phase appears before RH_3 is reached. These relationships have been thoroughly described by Pebler and Wallace.[6] The fcc dihydrides have the fluorite structure, expanded 20–25% over that of the parent metal, the hydrogen atoms being in tetrahedral interstices; somewhat less than 10% of the sites are vacant in these nonstoichiometric compounds. When the four fcc trihydrides are formed, the hydrogen atoms enter the octahedral sites at the edges and center of each unit cell. The hydrogen positions in the hexagonal trihydrides have been determined by neutron diffraction,[7] which reveals that the true unit cell is three times that found by X-ray diffraction and contains six rare earth and 18 hydrogen atoms.

All of the hydrides are pyrophoric, graphitic-appearing materials and are semiconductors. It is considered that hydrogen is essentially anionic in the dihydride, with the third valence electron of each rare earth atom becoming part of the conduction band. This view of delocalized electrons is supported by the 10^6-fold increase in electrical resistance at 80°K, which takes place when $LaH_{1.98}$ is converted to $LaH_{2.92}$, and the 10^4-fold increase on converting $CeH_{1.98}$ to $CeH_{2.86}$.[8] It has received further confirmation from the magnetic studies of Wallace and his co-workers.[9] The dihydrides are ferromagnetic and antiferromagnetic, the ordering arising *via* the conduction electrons. Further hydrogenation depopulates the conduction band, and the Néel temperature is thus depressed. Moreover, nmr studies of the lanthanum–hydrogen system[10] unambiguously demonstrate that proton self-diffusion takes place at moderate temperatures.

The investigations described in this and the following papers[11] were intended to explore further the dissociation pressures, crystallography, and other features of these systems.

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(1) Based in part on the Ph.D. dissertation of W. L. Korst, University of Southern California, June 1956.

(2) V. I. Mikheeva and M. E. Kost, *Usp. Khim.*, **29**, 55 (1960); *Russ. Chem. Rev.*, **29**, 28 (1960).

(3) W. G. Bos and K. H. Gayer, *J. Nucl. Mater.*, **18**, 1 (1966).

(4) (a) T. R. P. Gibb, Jr., *Progr. Inorg. Chem.*, **3**, 315 (1962); (b) *J. Inorg. Nucl. Chem.*, **24**, 349 (1962); (c) "Nonstoichiometric Compounds," American Chemical Society, Washington, D.C., 1963, pp 99–110.

(5) (a) G. G. Libowitz, *J. Nucl. Mater.*, **2**, 1 (1960); (b) "Nonstoichiometric Compounds," American Chemical Society, Washington, D. C., 1963, pp 74–86; (c) "The Solid-State Chemistry of Binary Metal Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1965.

(6) A. Pebler and W. E. Wallace, *J. Phys. Chem.*, **66**, 148 (1962).

(7) M. Mansmann and W. E. Wallace, *J. Phys.* (Paris), **25**, 454 (1964).

(8) B. Stalinski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **5**, 1001 (1957).

(9) (a) R. L. Zanowick and W. E. Wallace, *Phys. Rev.*, **126**, 536 (1962); (b) Y. Kubota and W. E. Wallace, *J. Appl. Phys.*, **34**, 1348 (1963); (c) D. E. Cox, G. Shirane, W. J. Takei, and W. E. Wallace, *ibid.*, **34**, 1352 (1963); (d) W. E. Wallace, Y. Kubota, and R. L. Zanowick, "Nonstoichiometric Compounds," American Chemical Society, Washington, D. C., 1963, pp 122–130.

(10) D. S. Schreiber and R. M. Cotts, *Phys. Rev.*, **131**, 1118 (1963).

(11) J. C. Warf, W. L. Korst, and K. I. Hardcastle, *Inorg. Chem.*, **5**, 1726 (1966); K. I. Hardcastle and J. C. Warf, *ibid.*, **5**, 1728 (1966); J. C. Warf and K. I. Hardcastle, *ibid.*, **5**, 1736 (1966).

Experimental Section

A standard vacuum line assembly was employed, equipped with a mercury manometer, cathetometer, McLeod gauge, Toepler pump, gas buret, and gas-storage bulb. In the preparation of samples for X-ray diffraction, a 1-g portion of each hydride was prepared in an apparatus that was joined to the vacuum line through ground-glass joints and a stopcock. This apparatus consisted of a small bulb to which were attached a tubular Vycor reaction vessel and several capillaries as side arms. After hydriding, the apparatus was removed from the vacuum line, and the specimen was pulverized by agitating the apparatus rapidly in a shaker, with a small glass-enclosed iron rod serving as a hammer inside the reaction vessel. A few milligrams of the hydride was shaken into a capillary which was then sealed off. Measured quantities of hydrogen were then removed at 700–800°, and in this way a series of specimens of progressively decreasing hydrogen content was prepared without exposure to any atmosphere other than hydrogen.

The specimens were annealed at 540° for up to 48 hr. This treatment caused some of the capillaries containing hydrogen-rich samples to burst, but X-ray diffraction patterns of such samples were obtained before annealing as well, as a precautionary measure. X-Ray powder photographs were usually prepared using Cu radiation; in a few cases Mo radiation was used. Wavelength values used were those listed by Bragg.[12] A 114.6-mm diameter camera having an asymmetric film mounting was used, and corrections were made for film shrinkage. Lattice constants were usually derived from lines which appeared beyond $\theta = 50$ or 60° on the films, where displacement owing to absorption is small. The average of the last several lines was used in most cases.

The dissociation pressure measurements were made using either a torsion or helix balance to determine the composition. The torsion balance assembly, sketched in Figure 1, was a modification of that described by Kirk, *et al.*[13] The 13-cm silica torsion fiber had a mean diameter of 130 μ and supported a 16.7-cm cantilever beam. One end of the beam held a long silica fiber, suspending a small molybdenum foil bucket at its lower end, and the other end of the beam held a counterweight. Tension was applied by a spring, and torsion through a ground joint holding a pointer. With a 1-g rare earth metal specimen, the sensitivity of the balance was found to be 5–7°/mg, depending on the size of the torsion fiber. Smaller specimens (200 mg) were more conveniently studied using a silica helix balance, the extension from a fiducial pointer being measured with a filar micrometer microscope. The greater sensitivity of the helix balance was to a large extent nullified by poorer reproducibility of the readings, owing to vibration. The balances permitted direct determination of composition at all times, a distinct improvement over the usual means, which involve P–V–T measurements of the hydrogen.

A temperature-controlled furnace similar to that described by Barnes[14] was constructed. The innermost shell of the furnace consisted of a massive Inconel spool, on which was wound a heating element consisting of platinum and nickel–chromium wire in refractory spacers, making up a bridge circuit and constituting the temperature-sensitive element. This spool was placed in an Alundum core which was wound with an independent heating element. This core was in turn contained in a refractory shell, surrounded by insulation, and an outer metal shell. The furnace could be maintained at any desired temperature between 550 and 850° to ±0.5° without difficulty. The silica tube with the suspended specimen was inserted in the hole in the spool. The temperature gradient over the specimen in the small molybdenum bucket was found to be 0.2°. This gradient was generally insufficient to cause detectable slope in the isothermal plateaus; Libowitz[15] has calculated the extent of these effects.

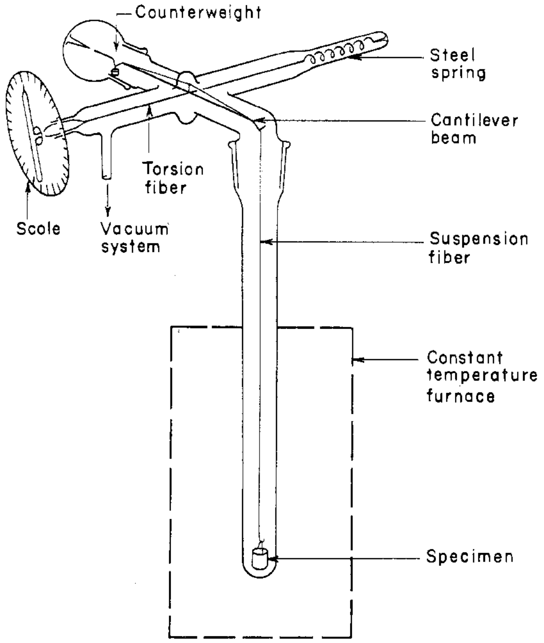

Figure 1.—Torsion balance assembly.

Chromel–alumel thermocouples were calibrated against NBS zinc and aluminum. Equilibria were approached from above and from below, and hysteresis was no problem at the temperatures involved.

The hydrogen and deuterium were generated by the decomposition of uranium hydride or deuteride. The rare earth metals were obtained from Dr. F. H. Spedding of Iowa State University, Ames, Iowa; analyses of these materials have been given by Mulford and Holley.[16]

Results

Structural Studies.—Cell constants of the fcc dihydrides have been reported by several authors. Table I gives cell constants for the annealed dihydrides of La, Ce, Pr, and Nd ($RH_{1.8-1.9}$) and the dideuterides of La and Ce and the results of Holley, *et al.*,[17] and of Pebler and Wallace[6] for comparison.

Table I

Cell Constants for Rare Earth Dihydrides

	This work *a*, A	Holley, *et al.*[17] *a*, A	Pebler and Wallace[6] *a*, A
LaH_2	5.670 ± 0.005	5.667 ± 0.001	. . .
CeH_2	5.580 ± 0.002	5.581 ± 0,001	. . .
PrH_2	5.515 ± 0.002	5.517 ± 0.001	5.518
NdH_2	5.469 ± 0.002	5.470 ± 0.001	5.464
LaD_2	5.662 ± 0.003	. . .	. . .
CeD_2	5.569 ± 0.003	. . .	. . .

For the lanthanum dihydride phase, Goon[18] obtained a cell constant of 5.663 A, also in close agreement with our result.

The more closely compositions approached RH_3, the less satisfactorily could the diffraction patterns be resolved, owing to their greater diffuseness. This can be attributed partly to less effective annealing. Lattice constants of hydrogen-rich phases of several composi-

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[12] W. L. Bragg, *J. Sci. Instr.*, **24**, 27 (1947).

[13] P. L. Kirk, R. Craig, J. E. Gullberg, and R. Q. Boyer, *Anal. Chem.*, **19**, 427 (1947).

[14] R. S. Barnes, *J. Sci. Instr.*, **28**, 89 (1951).

[15] G. G. Libowitz, *J. Phys. Chem.*, **62**, 296 (1958).

[16] R. N. R. Mulford and C. E. Holley, Jr., *ibid.*, **59**, 1222 (1955).

[17] C. E. Holley, Jr., R. N. R. Mulford, F. H. Ellinger, W. C. Koehler, and W. H. Zachariasen, *ibid.*, **59**, 1226 (1955).

[18] E. J. Goon, *ibid.*, **63**, 2018 (1959).

tions for each of the four metals were determined and are given in Table II for the specimen richest in hydrogen. In agreement with Holley, *et al.*,[17] approximately 1% shrinkage of the lattice on conversion of RH_2 to RH_3 was observed. Plots of *a vs.* composition were linear within experimental error, as also noted by Pebler and Wallace.[6] Equations giving the cell constant as a function of composition are also presented in Table II; these give the lattice constant within ±0.015 A of the observed value for $n = 1.8$–3.0. Extrapolating by these equations, lattice constants (A) of the stoichiometric trihydrides were obtained as follows: LaH_3, 5.602; CeH_3, 5.538; PrH_3, 5.486; and NdH_3, 5.42. The first value, for LaH_3, agrees well with the 5.604 A obtained by Goon.[18] A cell constant of 5.539 ± 0.001 A was found for $CeH_{2.97}$, prepared in the high-pressure bomb,[11] agreeing excellently with the above calculated value. For CeH_3, Stalinski's[19] value (5.53 A) and Streck and Dialer's[20] value (5.52 A) are somewhat lower.

TABLE II

CELL CONSTANTS OF HYDROGEN-RICH PHASES AT ROOM TEMPERATURE

R	n in RH_n	a, A	a as a function of n, A
La	2.78	5.619 ± 0.010	$a = 5.775 - 0.057n$
Ce	2.83	5.545 ± 0.003	$a = 5.654 - 0.040n$
Pr	2.85	5.495 ± 0.003	$a = 5.566 - 0.027n$
Nd	2.40	5.433 ± 0.005	$a = 5.52 - 0.033n$

Dissociation Pressures in the Two-Solid Phase Area.—Isotherms were established at a series of temperatures for lanthanum, cerium, praseodymium, and neodymium systems with hydrogen and in the first two cases with deuterium. The isotherms displayed in general the behavior first described in detail by Sieverts and Müller-Goldegg[21] for misch metal–hydrogen systems at 800°; that is, they consisted of three different branches. These are (1) an initial ascending curve at low hydrogen composition, (2) a constant-pressure plateau indicating the coexistence of two solid phases, and (3) a final ascending curve extending into the region of higher hydrogen composition. The two solid phases represent metal saturated with hydrogen (approximately $RH_{0.4}$) and the hydrogen-deficient dihydride (approximately $RH_{1.85}$), these two phases approaching each other in composition with rising temperatures. Occasionally, even after several sorption–desorption cycles, sudden additional sorption of hydrogen would occur, shifting the composition in the hydrogen-rich direction. This behavior was attributed to breakdown of grain boundaries, exposing hitherto protected areas of metal. This erratic behavior was prevented by saturating the specimens with hydrogen, approaching RH_3, before beginning pressure–temperature–composition measurements.

Equilibrium dissociation pressures in the plateau region were used in a least-squares calculation of the constants in the equation $\log P = A - B/T$ for each of the systems studied. These equations are shown below (P in millimeters, T in degrees Kelvin, valid from 580 to 800°)

La–H $\log P = 10.644 \pm 0.020 - (10{,}847 \pm 19)/T$
Ce–H $\log P = 10.630 \pm 0.014 - (10{,}761 \pm 15)/T$
Pr–H $\log P = 10.526 \pm 0.005 - (10{,}870 \pm 5)/T$
Nd–H $\log P = 10.482 \pm 0.028 - (11{,}031 \pm 28)/T$
La–D $\log P = 10.107 \pm 0.016 - (10{,}173 \pm 14)/T$
Ce–D $\log P = 10.205 \pm 0.006 - (10{,}123 \pm 6)/T$

These equations are based on relatively few plateau pressure measurements (5, 4, 4, 10, 4, and 5 points, respectively, for the systems listed above), and some of the pressures were in the range where the McLeod gauge was least accurate. The limits of error given above are the probable errors calculated as explained by Margenau and Murphy.[22] The equations yield plateau pressures which differ in most cases by less than 8% from those observed. The above data are in general agreement with the results of Mulford and Holley,[16] except for the case of cerium. Jones, *et al.*,[23] for the praseodymium–hydrogen system, reported $\log P_{\mathrm{mm}} = 10.56 \pm 0.16 - (10{,}940 \pm 160)/T$, in close agreement with our result.

From the above data, the thermodynamic quantities shown in Table III were calculated for 298°K. These partial molal quantities pertain to the absorption of 1 mole of hydrogen at a constant pressure of 1 atm by the hydrogen-poor phase (approximately $RH_{0.4}$), to form the hydrogen-rich phase (approximately $RH_{1.85}$). In the calculations, the usual classical assumptions were made, *i.e.*, the validity of the ideal gas law, constant enthalpy with changing temperature, $\Delta C_p = 0$, negligible solid volume compared to gas volume, and negligible variation of the activity of the solids with pressure. These assumptions yielded the following relationships: $\Delta H° = -2.303RB$, $\Delta G° = 2.303RT(A - \log 760 - B/T)$, and $\Delta S° = -2.303R \cdot (A - \log 760)$.

TABLE III

THERMODYNAMIC FUNCTIONS FOR THE RARE EARTH DIHYDRIDES AT 298°K

System	$\Delta H°$, kcal/mole of H_2	$\Delta G°$, kcal/mole of H_2	$\Delta S°$, eu/mole of H_2
La–H	−49.6 ± 1.0	−39.0 ± 1.0	−35.5 ± 1.0
Ce–H	−49.2 ± 1.0	−38.7 ± 1.0	−35.4 ± 1.0
Pr–H	−49.7 ± 1.0	−39.3 ± 1.0	−35.0 ± 1.0
Nd–H	−50.5 ± 1.0	−40.1 ± 1.0	−34.8 ± 1.0
La–D	−46.5 ± 1.0	−36.7 ± 1.0	−33.1 ± 1.0
Ce–D	−46.3 ± 1.0	−36.3 ± 1.0	−33.5 ± 1.0

In that the probable errors in the $\log P = A - B/T$ data are very sensitive to the number of experimental points, rather large errors are given in Table III, computed by arbitrarily disregarding one observed point in each $\log P$ *vs.* $1/T$ plot. The value of −33.9

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(19) B. Stalinski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **7**, 269 (1959).

(20) R. Streck and K. Dialer, *Z. Anorg. Allgem. Chem.*, **306**, 141 (1960).

(21) A. Sieverts and G. Müller-Goldegg, *ibid.*, **131**, 65 (1923).

(22) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p 494.

(23) P. M. S. Jones, J. Southall, and K. Goodhead, *U. K. At. Energy Authority, At. Weapons Res. Estab. Rept.*, AWRE 0-22/64 (1964); *Chem. Abstr.*, **61**, 7728g (1964).

kcal/mole of H_2, reported by Mulford and Holley[16] for the enthalpy in the cerium case, is undoubtedly in error. Streck and Dialer[20] computed -55 kcal from their data. Jones, *et al.*,[23] found -50.0 kcal/mole of H_2 for the Pr–H case. The enthalpy terms in Table III become somewhat more positive with rising temperature, being approximately proportional to the difference between the compositions at each end of the plateaus; the plateaus become shorter at high temperature.

The entropy changes shown in Table III are probably 3 or 4 units too negative. For the formation of CaH_2,[24] $\Delta S°_{298}$ is -30.4 eu/mole of H_2; for MgH_2,[25] it is about -31 eu; and for UH_3[26] it is -29.2 eu. Using $S° = 1.3$ eu for H^- in $RH_{0.4}$ and 0.6 eu in $RH_{1.85}$ (values estimated by Gibb, *et al.*,[26] for mono- and dihydrides, respectively) and the NBS value for H_2 (31.21 eu), the expected value of $\Delta S°_{298}$ is approximately -30.4 eu/mole of H_2, assuming the same $S°$ for the metal in both phases.

The difference $\Delta G°$(hydride) $-$ $\Delta G°$(deuteride) for the lanthanum systems at 298°K is -2.3 ± 1.0 kcal/mole, from the data in Table III; the corresponding difference for the cerium system is -2.4 ± 1.0 kcal/mole. These values are almost certainly too negative. The true values are probably closer to the -0.14 ± 0.08 kcal/mole found by Flotow, *et al.*,[27] for yttrium hydride from accurate heat capacity measurements.

Except for the irregularity in the case of cerium, the plateau dissociation pressures at a given temperature decreased in the order of increasing atomic number. Cerium hydride exhibited the highest dissociation pressure, as shown by Mulford and Holley.[16] The deuterides always had dissociation pressures in the plateau region 1.2–1.8 times that of the hydride under comparable conditions.

Dissociation Pressures in the Hydrogen-Rich, One-Solid Phase Area.—At the end of the plateau, the dissociation pressures rose steeply, the composition of the solid phase approaching RH_3. The pressures and compositions could be established readily at various temperatures using the torsion balance and are presented graphically in Figures 2–5 (La–H, Ce–H, Pr–H, Nd–H, La–D, Ce–D, Sm–D). The isotherms shown in these figures agree quite closely with those of Mulford and Holley,[16] for comparable temperatures, except that their curves are shifted slightly to the left of ours. There might have been pockets of unreacted metal in Mulford and Holley's specimens, which would account for the over-all composition differences; this would have no effect on plateau pressures. All of these dissociation pressures are below 1 atm; pressures in the range 10–40 atm, where the solid phase is much richer in hydrogen, have also been measured.[11]

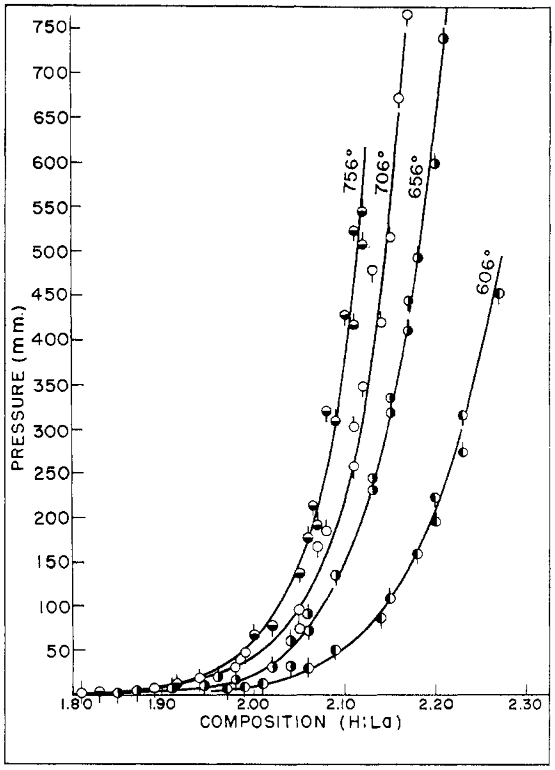

Figure 2.—Dissociation pressure isotherms for the La–H system in the hydrogen-rich region. The short, vertical lines pointing upward indicate that the sample was absorbing hydrogen as equilibrium was approached; those pointing downward indicate desorption.

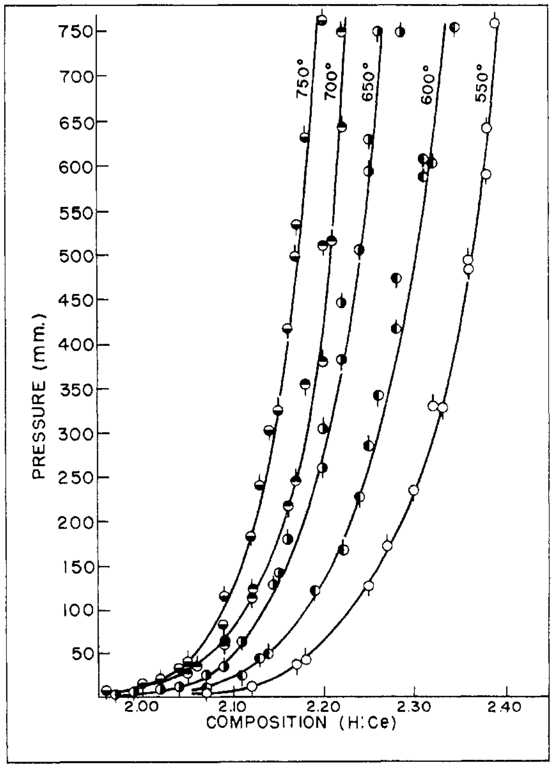

Figure 3.—Dissociation pressure isotherms for the Ce–H system in the hydrogen-rich region.

Ytterbium and Europium Deuterides.—It has already been reported[28] that ytterbium and europium dideu-

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(24) R. W. Curtis and P. Chiotti, *J. Phys. Chem.*, **67**, 1061 (1963).

(25) J. F. Stampfer, Jr., C. E. Holley, Jr., and J. F. Suttle, *J. Am. Chem. Soc.*, **82**, 3504 (1960).

(26) T. R. P. Gibb, Jr., J. J. McSharry, and H. W. Kruschwitz, Jr., *ibid.*, **74**, 6203 (1952).

(27) H. E. Flotow, D. W. Osborne, and K. Otto, *J. Chem. Phys.*, **36**, 866 (1962); H. E. Flotow and D. W. Osborne, "Thermodynamics of Nuclear Materials," International Atomic Energy Agency, Vienna, 1962, p 675.

(28) W. L. Korst and J. C. Warf, *Acta Cryst.*, **9**, 452 (1956).

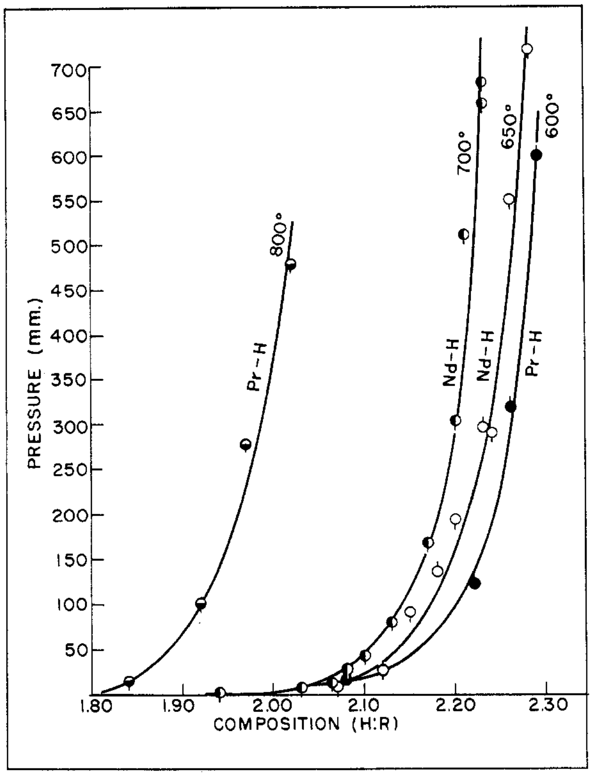

Figure 4.—Dissociation pressure isotherms for the Pr–H and Nd–H systems in the hydrogen-rich regions.

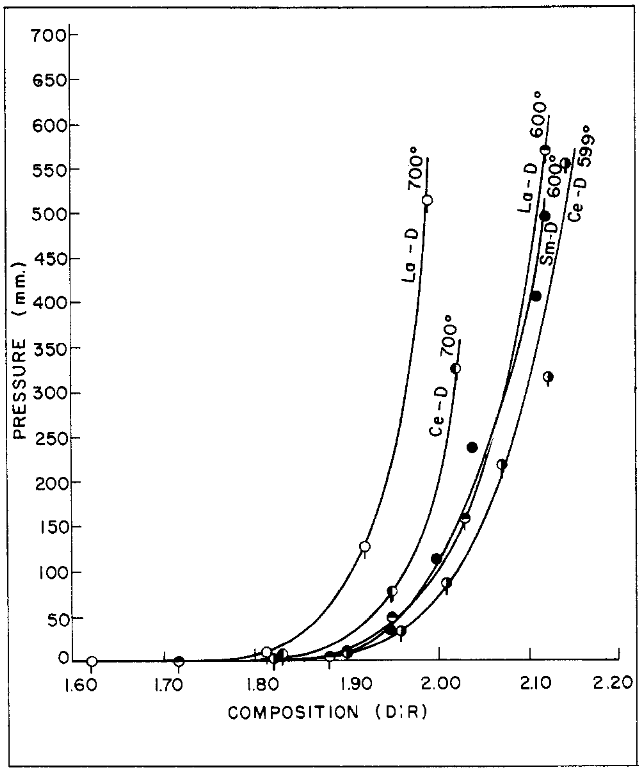

Figure 5.—Dissociation pressure isotherms for some rare earth–deuterium systems in the hydrogen-rich regions.

terides are orthorhombic and thus resemble alkaline earth hydrides rather than the other rare earth dihydrides. Some of the other properties are recorded here. Ytterbium deuteride and hydride are gray-black, graphitic substances, rather stable in air and water, though readily soluble in dilute acids. The hardness of ytterbium increased markedly on hydriding, and lumps of YbD_2 could be easily filed. Hardness measurements of ytterbium and its deuteride were made using a Wilson "Tukon" microhardness tester.[29] A 172.5° included-angle Knoop diamond indenter with a 100-g indenting load was employed, giving the results in Table IV. The hardness of ytterbium deuteride is approximately the same as that of fluorite, which has a Knoop hardness number of 163.

TABLE IV

HARDNESS OF YTTERBIUM METAL AND YTTERBIUM DEUTERIDE

Sample	Knoop hardness no. Min	Max	Av
Ytterbium metal	22.8	25.3	23.9
Ytterbium deuteride, specimen I	167	189	175
Ytterbium deuteride, specimen II	145	165	156

Europium deuteride was also a black, hard compound, but much more reactive than ytterbium deuteride. Unlike the metals,[30] the hydrides of europium and ytterbium do not dissolve in liquid ammonia. These compounds decomposed on heating under vacuum, but the metals were volatile at the temperatures required, and the composition of the solid phases became unknown.

Ytterbium hydride was prepared and its diffraction pattern compared with that of the deuteride, all exposures being made with molybdenum radiation. These gave the cell constants in Table V (it will be noted that the cell constants for YbD_2 reported here are slightly smaller than those found using copper radiation,[28] owing to absorption in the front diffraction region). These constants, for an orthorhombic unit cell, were obtained by least squares, using 30 corresponding lines from each film. Calculated X-ray densities were (in g/cc): EuH_2, 6.03 ± 0.03; EuD_2, 6.18 ± 0.03; YbH_2, 8.143 ± 0.011; YbD_2, 8.338 ± 0.011.

TABLE V

CELL CONSTANTS OF YTTERBIUM HYDRIDE AND DEUTERIDE

	YbH_2	YbD_2	Change, A	% change
a, A	5.905	5.861	−0.044	−0.8
b, A	3.561	3.554	−0.007	−0.2
c, A	6.790	6.758	−0.032	−0.5

Discussion

Structural Considerations.—In view of the great difference in electronegativity between hydrogen and the rare earth metals (1.0 unit on the Pauling scale), the hydrides are undoubtedly ionic in nature to a dominant extent. The unit cell dimensions can be rationalized on this basis,[31,32] and also on the basis of delocalized covalent bonding,[17,32] Several previous

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[29] Hardness tests were made by Metal Control Laboratories, Inc., Huntington Park, Calif.

[30] J. C. Warf and W. L. Korst, *J. Phys. Chem.*, **60**, 1590 (1956).

[31] G. G. Libowitz and T. R. P. Gibb, Jr., *ibid.*, **60**, 510 (1956).

[32] T. R. P. Gibb, Jr., and D. P. Schumacher, *ibid.*, **64**, 1407 (1960).

writers have pointed out that the third electron in the rare earth dihydrides, monosulfides, and related compounds of subnormal valency becomes part of the conductance band. These concepts are in harmony with the high heat of formation, high conductivity, hardness, and brittleness of the dihydrides.

As Gibb and Schumacher[32] have pointed out, atomic radii in general are best regarded as useful aids in estimating internuclear distances, with doubtful fundamental significance. They showed that the radius of the tenuous hydride ion can be taken as 1.40 A, with coordination number six, and averages about 1.29 A in many transition metal hydrides, where the coordination number is lower. They also showed that in most dihydrides, the various coordination number corrections and ion repulsion corrections very nearly cancel, so that the sum of the tabular radii ($CN = 6$) agree with the observed interionic distances within ±0.03 A. This was earlier noted by Pauling[33] for several oxides and sulfides. That this simple relationship holds approximately for the dihydrides, monosulfides, and dicarbides is seen in Table VI. In computing the cell constants the radii of the rare earth metals in the sesquioxides were employed,[34] 1.40 A for H^- and 1.84 A for S^{2-}. The dicarbide cell constants were estimated by substituting twice the radius of each rare earth ion for twice the radius of the calcium ion (0.99 A) in the cell constants of tetragonal calcium carbide ($a = 3.87$ A, $c = 6.37$ A).

Table VI

Computed and Observed Cell Constants for Metallic Rare Earth Compounds

	Structure type	Cell constants, A	
		Calcd	Obsd
LaH_2	CaF_2	5.68	5.67[a]
CeH_2		5.61	5.58[a]
PrH_2		5.57	5.51[a]
NdH_2		5.53	5.47[a]
LaS	NaCl	5.80	5.84[b]
CeS		5.75	5.76[b,c]
PrS		5.71	5.73[b]
NdS		5.67	5.68[b]
LaC_2	CaC_2	4.01, 6.51	3.93, 6.57[d]
CeC_2		3.96, 6.46	3.87, 6.48[d]
PrC_2		3.92, 6.42	3.83, 6.42[d]
NdC_2		3.88, 6.38	3.81, 6.38[d]

[a] This work. [b] A. Iandelli, *Gazz. Chim. Ital.*, **85,** 881 (1955). [c] E. D. Eastman, *et al.*, *J. Am. Chem. Soc.*, **72,** 2248 (1950). [d] M. Atoji, *et al.*, *ibid.*, **80,** 1804 (1958); F. H. Spedding, *et al.*, *Trans. AIME*, **215,** 192 (1959); R. C. Vickery *et al.*, *J. Chem. Soc.*, 498 (1959); G. J. Palenik and J. C. Warf, *Inorg. Chem.*, **1,** 345 (1962).

The neutron diffraction studies of cerium deuteride by Holley, *et al.*,[17] led to the conclusion that when cerium reacts with hydrogen, the first two hydrogen atoms enter the tetrahedral sites (CaF_2-type structure, C2) and that the third hydrogen atom enters the octahedral sites ($D0_3$ type). The evidence for the latter point is less substantial than for the former, but nevertheless the $D0_3$ structure is probably correct.

The contraction of the lattice on conversion of the rare earth dihydride to the trihydride phase is believed to be attributable to progressive consumption of the free electrons which give rise to metallic character. As the conduction band is consumed, cohesive forces in the lattice increase. Conduction electrons do not lessen repulsion between cations to the extent electrons do when immobilized as hydride ions.

By selecting the radius of H^- as 1.36 A in the trihydride and using the tabular radii for R^{3+} ions (CN of 6) as before, cell constants for fcc trihydride phases can be empirically computed. These are compared in Table VII with observed or extrapolated values presented in the section on Results.

Table VII

Calculated and Observed Cell Constants for Cubic Rare Earth Trihydrides

	a, A	
	Calcd	Obsd
LaH_3	5.60	5.602
CeH_3	5.53	5.534
PrH_3	5.48	5.486
NdH_3	5.43	5.42

In a similar manner, lattice constants for actinium hydrides may be computed. Farr, *et al.*,[35] observed that the lattice constant for fcc actinium metal is 5.311 A and that of a hydride of unspecified composition is 5.670 A. Since the cell constant for the metal is only 0.004 A larger than that for lanthanum metal, the radius of Ac^{3+} in a hydride phase is estimated to be approximately 0.01 A larger than that of La^{3+}. Thus, AcH_2 is expected to have $a = 5.70$ A, and AcH_3 is expected to have $a = 5.61$ A. The evidence indicates that the hydride prepared by Farr, *et al.*, is AcH_2.

It should be emphasized that the above calculations merely represent empirical estimations of lattice constants, and no suggestion is made that the actual ionic radii are the values given. In the trihydrides, indeed, one finds eight hydrogen atoms inside a unit cell, arranged on the corners of a cube, with a ninth hydrogen atom in the center of the cube. These atoms would interpenetrate if the actual radii were the values stated.

Ytterbium Dihydride and Dideuteride.—Lattice constants of rare earth deuterides were always a little smaller than those of corresponding hydrides, a contraction which has been observed in alkali metal hydrides,[36] hafnium hydride,[37] and others. The radius of the deuteride ion is about 0.01 A smaller than that of the hydride ion. This shortening would be expected from the lower zero-point energy of deuterium, because of the smaller amplitude of vibration of the heavier deuterium atom, among other factors.

In Table V it is shown that each of the three axes of

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(33) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1959, p 533 ff.

(34) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76,** 5237 (1954).

(35) J. D. Farr, A. L. Giorgi, M. G. Bowman, and R. K. Money, *J. Inorg. Nucl. Chem.*, **18,** 42 (1961).

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(37) S. S. Sidhu, *J. Chem. Phys.*, **22,** 1062 (1954).

orthorhombic ytterbium deuteride is shorter than the corresponding axis for the hydride. The smallest contraction is in the *b* direction, in which the hydrogen atoms are situated at only two levels, on the mirror planes at $^1/_4$ and $^3/_4$. The contraction is greater in the *a* and *c* directions, reflecting the fact that hydrogen atoms are situated at six and eight different levels in these directions, respectively.[38]

Statistical Mechanical Model.—Several investigators have applied statistical mechanical computations to metal–hydrgoen systems. The procedure of Takeuchi and Suzuki,[39] applied to the plutonium–hydrogen system, permits evaluation of several component energy terms. If N_{I} and N_{II}, respectively, represent the number of tetrahedral and octahedral sites in the metal, and α and β represent the fractions of these sites occupied by hydrogen atoms, then $\alpha N_{\mathrm{I}}\epsilon$ is the interaction or potential energy between the metal atoms and hydrogen atoms in tetrahedral sites. Similarly, $-\alpha^2 N_{\mathrm{I}}\xi_{\mathrm{HH}}$ is the interaction energy between pairs of hydrogen atoms in tetrahedral sites, $-\beta^2 N_{\mathrm{II}}\eta_{\mathrm{HH}}$ is the potential energy between pairs of hydrogen atoms in octahedral sites, and $-\beta N_{\mathrm{II}}\psi$ is the sum of the interaction energy between metal atoms with hydrogen atoms in octahedral sites and the potential energy between pairs of hydrogen atoms in the two kinds of sites. This last term is important only in the range $2 < n < 3$, where n represents the composition (hydrogen:metal ratio). The sum of the four terms is the total change in crystal energy on absorption of the hydrogen.

Using the graphical methods of Takeuchi and Suzuki, it was found that for the cerium–hydrogen system $\epsilon = -69$ kcal/mole, $\xi_{\mathrm{HH}} = -4.5$ kcal/mole, $\eta_{\mathrm{HH}} = 1.6$ kcal/mole, and $\psi = -72$ kcal/mole; the errors in these quantities are estimated at about ±5%. Using these values, it is possible to estimate the distribution of hydrogen atoms between tetrahedral and octahedral sites at various temperatures. Thus, at absolute zero, $\mathrm{CeH}_{2.00}$ is expected to have the ideal fluorite structure, but with increasing temperature, an increasing proportion of the hydrogen atoms migrate to the octahedral sites. When kT becomes large compared to the energy difference between the two sites, quite a large fraction of the tetrahedral sites are vacated, and the octahedral positions are filled. From the four energy values given above, it was calculated that for $\mathrm{CeH}_{2.00}$ at 300°K, 1% of the tetrahedral sites are vacant, and at 873°K, about 23% are vacant. With increasing hydrogen content, both kinds of sites are filled.

Dissociation Pressures in the Hydrogen-Rich Region.—The statistical mechanical model also affords equations which show the dependency of the dissociation pressures as a function of temperature and composition in the hydrogen-rich region. For a fixed temperature, these equations can be produced in the form

$$\log P = 2 \log \frac{n-2}{3-n} + Dn - E$$

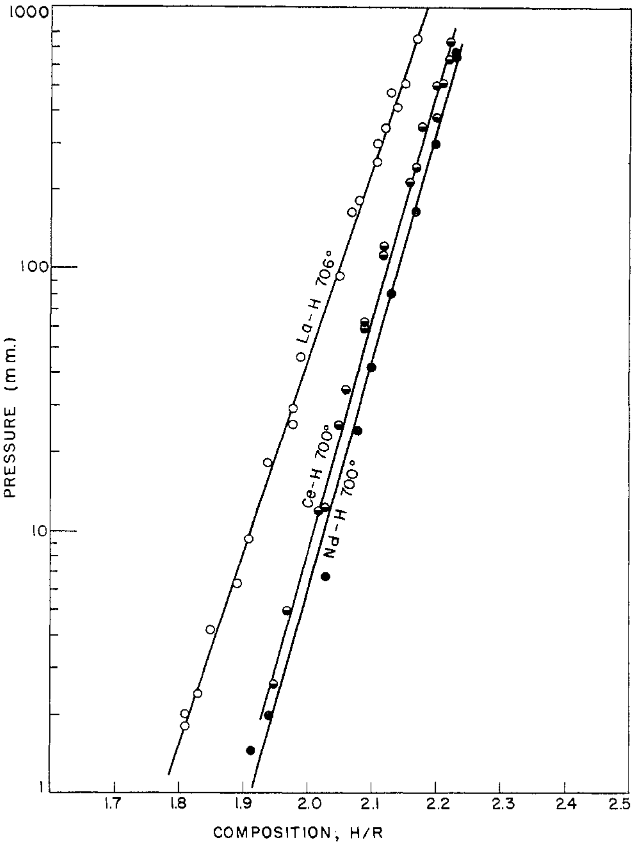

Figure 6.—Test of log $P = Dn - E$ for some rare earth–hydrogen systems.

where n is the composition (H:R atomic ratio), and D and E are constants. Of the three terms to the right of the equality sign, the first is small when compared to the other two, except near the dihydride and trihydride compositions, and we found that dissociation pressures could be approximated simply by $\log P_{\mathrm{mm}} = Dn - E$. Some graphical tests of this equation are shown in Figure 6, and the parameters D and E are given in Table VIII. The equations appear to be valid down to the plateau. It should be emphasized that the equations of type $\log P = Dn - E$ are rough and predict values only within approximately 15% of the

TABLE VIII

CONSTANTS IN LOG $P = Dn - E$ (P IN MM OF Hg)

System	Temp, °C	*D*	*E*
La–H	606	6.2	11.2
	706	7.5	13.3
	756	8.3	14.9
La–D	600	7.8	13.7
	700	9.3	15.8
Ce–H	600	7.1	13.7
	650	8.1	15.5
	700	8.7	16.4
	750	8.9	16.8
Ce–D	599	6.9	15.0
Pr–H	600	7.4	14.2
Nd–H	700	8.1	15.6
Sm–D	600	8.3	14.6

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[39] S. Takeuchi and K. Suzuki, *Trans. Japan Inst. Metals*, **3**, 41 (1962).

observed dissociation pressures, between $n = 1.8$ and 2.3.

Acknowledgment.—This work was supported in part by the Office of Naval Research (Contract Nonr 22815). W. L. K. acknowledges with thanks the grant of a U. S. Atomic Energy Commission predoctoral fellowship, 1951–1953.

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Rare Earth–Hydrogen Systems. II. Dispersions in Mercury[1]

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Received June 15, 1966

Solid hydrides of metals behave differently toward mercury, this behavior depending to some extent on the bonding type. Pulverized lanthanum and cerium hydrides were found to be wet by mercury, forming dispersions with a strong tendency to adhere to glass. Cerium hydride dispersions decomposed into hydrogen and cerium amalgams above approximately 115° and reacted vigorously with water at room temperature. On exposure to air, dilute dispersions oxidized to cerium(IV) oxide, while the more concentrated preparations oxidized, in part, and precipitated the unchanged hydride, in part. Lanthanum and ytterbium hydride dispersions in mercury yielded X-ray diffraction patterns different from those of the pure hydrides, showing surface formation of new compounds. Uranium hydride in mercury gave the normal diffraction pattern of UH_3. Freezing and melting curves of uranium hydride and cerium hydride dispersions showed no depression of the freezing point of the mercury. Filtration of cerium hydride dispersions through sintered glass removed nearly all of the dispersed phase and gave a filtrate 0.008% in cerium hydride.

Introduction

The behavior of hydrides toward mercury is varied and may afford a probe into their constitution. Lithium hydride, an ionic compound, was treated with mercury by Moers,[2] who observed the evolution of hydrogen and the formation of lithium amalgam. The reaction is slow at the boiling point of mercury, and there is no particular interaction at room temperature. In ammonium amalgams[3] and in the more stable tetramethylammonium amalgams,[4] the freezing point of mercury is depressed, showing that they are true solutions. There is also a large decrease in the interfacial tension of mercury upon incorporation of ammonium radicals.[5] Oxley,[6] on the basis of investigations of the magnetic susceptibility of the palladium–hydrogen system, recognized a similarity in electronic structure between a metal containing hydrogen in a 1:1 atomic ratio and the metal of one higher atomic number. This hypothesis was extended by Ubbelohde,[7] who considered that the bonding in a metal hydride MH_n is, with regard to further metallic bonding, approximately like that of the atom whose atomic number is n higher than that of M. Thus NH_4 and OH_3 amalgams are expected to resemble Na amalgams, and PdH is expected to resemble Ag.

Uranium hydride is a compound manifesting metallic character, even though metal–metal bonding is unimportant in its structure.[8] Warf, *et al.*,[9] found that it forms pseudo-amalgams; *i.e.*, the hydride surface is tenaciously wet by mercury, apparently through metallic bonding. The preparations are evidently not true solutions, but dispersions ranging from solids through gels to liquids, depending on concentration. The treatment of uranium hydride with mercury depresses the mercury–glass interfacial tension, as strong adherence to the glass is noted, forming mirrors. There is no heat effect, in contrast to amalgamation of finely divided uranium, which reacts to form intermetallic compounds. Other metals also wet uranium hydride.

Paal and Steyer[10] showed that mercury extracts aqueous colloidal palladium hydride. Ubbelohde[7] found that palladium hydride ($PdH_{0.6}$) is wet rapidly by mercury, evolving considerable heat and some hydrogen. Both palladium amalgam ($PdHg_{5.2}$) and the hydride amalgam ($PdH_{0.15}Hg_4$) are diamagnetic, suggesting that the d orbitals of palladium are saturated. Mercury was found to wet palladium, iron, and platinum after these metals, immersed in aqueous solutions, were connected to a cathode; this was ascribed to the formation of metallic bonds between the mercury atoms and the surface hydride groups, produced by electrolysis.

There is no mention of the interaction of the hydrides of the rare earth metals with mercury in the chemical literature. The metallic character of these hydrides

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