6
25-25

82-1843

UCRL-51244 Rev. 1

A LITERATURE STUDY OF METALLIC TERNARY AND QUATERNARY HYDRIDES

Herbert W. Newkirk

September 19, 1975

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

**LAWRENCE
LIVERMORE
LABORATORY**
University of California/Livermore

MASTER

DISTRIBUTION

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$ *; Microfiche \$2.25

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY
University of California, Livermore, California, 94550

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

UCRL-51244 Rev. 1

A LITERATURE STUDY OF METALLIC TERNARY AND QUATERNARY HYDRIDES

Herbert W. Newkirk

Ms. date: September 19, 1975

Supersedes UCRL-51244, dated June 28, 1972

Contents

Abstract	1
Introduction	1
Storage Systems	2
Metallic Ternary Hydride Systems of the Transition Element Series	2
Group III	2
Group IV	5
Group V	12
Group VIII	12
Metallic Ternary Hydride Systems of the Rare Earth Element Series	15
Metallic Ternary Hydride Systems of the Actinide Element Series	20
Metallic Quaternary Hydride Systems of the Transition Element Series	21
Miscellaneous Complex Metallic Hydride Systems.	24
Absorption and Storage Characteristics of Metallic Systems	24
Stability of Metallic Hydride Phases	27
References	29

A LITERATURE STUDY OF METALLIC TERNARY AND QUATERNARY HYDRIDES

Abstract

Metallic hydrides are being considered as an attractive solution to storage problems involved in using hydrogen as an alternative fuel. In this application, the unclassified literature was surveyed to find metallic ternary hydride systems of the type $MM'H_x$; M is a transition element, a member of the rare earth element series, or a member of the actinide element series,

and M' is a transition element. Reported quaternary hydrides of the same metallic element series were also reviewed. The hydride-forming systems found and some of their most interesting properties are summarized. Recent advances in the understanding of the absorption characteristics and the stability of these hydride materials are reviewed.

Introduction

Hydrogen is currently being considered as an alternative fuel for a wide variety of stationary and mobile energy converters. A major problem involved in this application is the difficulty of storage. One attractive alternative to conventional techniques is storage as a metallic hydride. It is well known that some metallic hydrides are capable of safely, conveniently, and inexpensively containing more hydrogen per unit volume than liquid hydrogen. Often these hydride materials are intermetallic compounds involving elements from the transition, rare earth, and actinide series of the periodic table. Since relevant property data on these compounds are widely scattered in the literature and there has been no single reference source, we summarize such information in this report.

The ternary systems surveyed were those of the type $MM'H_x$, M' being a member of the transition element series and M any of the following: a transition element, a member of the rare earth series, or a member of the actinide series. Also surveyed were quaternary hydride systems involving the same series of elements.

This report lists reported hydride-forming systems and summarizes some of their interesting properties. Recent advances in our understanding of the absorption characteristics and stability of these hydride materials are reviewed. The lists are not exhaustive, and the summaries will be revised and updated periodically. Only confirmed data are included. The structure nomenclature is from the Struckterbericht.

Storage Systems

INTERMETALLIC TERNARY HYDRIDE SYSTEMS OF THE TRANSITION ELEMENT SERIES

Group III

Lanthanum-Cobalt System - Compared with other RCO_5 compounds, LaCo_5 has a large hydrogen absorption capacity.¹ As shown in Fig. 1, a second plateau appears at the hydrogen-rich side of the isothermic diagram, indicating the formation of a new hydride. The existence of two different hydrides is confirmed by x-ray analysis. The first, (β) $\text{LaCo}_5\text{H}_{3.35}$, is orthorhombic and analogous to the hydrides of other

Fig. 1. Desorption isotherms of LaCo_5 at various temperatures (taken from Ref. 1).

RCO_5 compounds. The second, (γ) $\text{LaCo}_5\text{H}_{4.2}$, also is orthorhombic, but the c-axis has regained the value characteristic of the hexagonal LaCo_5 structure (see Table II).

Figure 2 shows the crystallographic structure of the (γ) hydride.² Figure 3 shows the desorption isotherms for the pseudo-binary systems $\text{LaCo}_5\text{-H}$ and $\text{LaCo}_5\text{-P}$.

As shown in Fig. 4, plots of the $\log P$ vs $1000/T$ are straight lines in the rather limited p-T regions where isotherms have been measured. These plots obey the relations $\log P_{\text{atm}} = 6.55 - (2350/T)$ for the $\alpha\beta$ transition and $\log P_{\text{atm}} = 5.90 - (1680/T)$ for the $\beta\gamma$ transition. The heats of reaction of the two hydrides are $\Delta H = -10.8$ kcal/mole H_2 ($\alpha \rightarrow \beta$) and $\Delta H = -7.7$ kcal/mole H_2 ($\beta \rightarrow \gamma$).

Figure 5 shows the considerable influence of absorbed hydrogen on the magnetic properties in this system.

Fig. 2. Unit cell of a (γ) RCO_5 hydride (Ref. 2).

Table 1. Lattice parameters at room temperature for some compounds in the LaCo_5 system (from Ref. 1).

LaCo_5	Two-phase region $\alpha + \beta$		Two-phase region $\beta + \gamma$
	$\alpha: \text{LaCo}_5\text{H}_{0.17}$ hexagonal ^a	$\beta: \text{LaCo}_5\text{H}_{3.35}$ orthorhombic ^c	$\gamma: \text{LaCo}_5\text{H}_{4.2}$ orthorhombic ^c
$a = 5.109 \text{ \AA}$	$a = 5.125 \text{ \AA}$	$a = 8.973 \text{ \AA}$	$a = 9.495 \text{ \AA}$
$c = 3.970 \text{ \AA}$	$c = 3.964 \text{ \AA}$	$b = 5.413 \text{ \AA}$	$b = 5.381 \text{ \AA}$
$c/a = 0.777$	$c/a = 0.774$	$c = 4.088 \text{ \AA}$	$c = 3.966 \text{ \AA}$
$v = 89.74 \text{ \AA}^3$	$v = 90.13 \text{ \AA}^3$	$v = 198.5 \text{ \AA}^3$	$v = 202.6 \text{ \AA}^3$

^aComposition estimated from an absorption isotherm (0.17 ± 0.05).

^bSlight variations in lattice parameters observed, dependent on hydrogen concentration.

^cTwo moles of LaCo_5H_x per unit cell.

Fig. 3. Desorption isotherms for the pseudo-binary systems $\text{LaCo}_5\text{-H}$ and $\text{LaCo}_5\text{-D}$ (Ref. 2).

Fig. 4. $\log p$ vs $1000/T$ for the $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \gamma$ transformations in the system $\text{LaCo}_5\text{-H}$. p is the equilibrium pressure over two-phase mixtures (Ref. 1).

Fig. 5. Magnetization along the c-axis of LaCo_3 and its 3 and 5 hydrides as a function of temperature (Ref. 1).

Lanthanum-Nickel System - Figure 6 shows that the phase LaNi_5 has a relatively large homogeneity region at elevated temperatures.³ For the compounds LaNi_x within this region, the equilibrium hydrogen pressure, p , of the 40°C isotherms changed from 2.75 atm for $\text{LaNi}_{4.9}$ to about 9.2 atm for $\text{LaNi}_{5.4}$.

Figure 7 shows the smaller equilibrium pressures observed for the compounds with lower x values.³ This suggests that the maximum of the stability of the compounds $\text{LaNi}_{x/y}$ in the ternary La-Ni-H system has shifted to lower x values with respect to the LaNi_x system. The reason for this is still obscure.

The dimensions of the LaNi_5 hexagonal unit cell are $a = 5.0172 \text{ \AA}$, $c = 3.9816 \text{ \AA}$, $c/a = 0.794$, and $v = 86.80 \text{ \AA}^3$. It was converted to a hydride by exposing freshly crushed powder for some hours to a pressure

Fig. 6. Pressure-composition isotherms at 40°C for the homogeneity region of the LaNi_5 phase (Ref. 3).

Fig. 7. Variation of hydrogen equilibrium pressure at 40°C as a function of composition for the concentration at 3.7 at.% per mole of LaNi_x (Ref. 3).

of 50 atm of hydrogen. In this state the unit cell appeared to be still hexagonal but has dimensions $a = 5.440 \text{ \AA}$, $c = 4.310 \text{ \AA}$, $c/a = 0.792$, and $v = 110.5 \text{ \AA}^3$, which means a volumetric expansion of about 25%.

The density of hydrogen at room temperature under 2 atm is 6.7 atoms per LaNi_5 or 7.6×10^{22} atoms/cm³ - twice that of liquid hydrogen. From the isotherms, Fig. 8, we can deduce the heat of reactions as 7.2 kcal/mole H_2 .⁴ The equilibrium pressure at halfway saturation is 2.5 atm.

Figure 9 shows some desorption curves for temperatures from 18°C to 49°C.⁴ The activation energy for the reaction is determined from the initial slopes and is thus roughly estimated to be 12 kcal/mole H_2 (0.25 eV/atom H).

Group IV

Titanium-Vanadium System - Kostiner et al.⁵ have reported the formation of $\text{TiV}_{1.4}\text{H}_{4.6}$ and TiV_4H_8 in this system.

Titanium-Iron System - Wiswall and Peilly⁶ carried out experiments with TiFe alloys. Well-defined plateaus with both deuterium (D) and hydrogen were obtained in the P (atm) range of 0.25-0.40. The respective plateau pressures were 5.8 and 4.8 atm at 30°C; the deuteride was less stable than the hydride.

Fig. 8. Isotherms of hydrogen gas (pressure p atm) in equilibrium with absorbed hydrogen in LaNi_5 (Ref. 4).

Titanium-Nickel System - The compound Ti_2Ni reacts to form the hydride Ti_2NiH_3 (Ref. 7). The structure is primitive cubic similar to the Fe_3 type, with $a_0 = 11.896$ Å. Figure 10 shows the hydrogen uptake by alloys in this system (Ref. 8).

Fig. 9. Desorption rate of hydrogen for LaNi_5 at different temperatures (°C) against 1 atm of hydrogen (Ref. 4).

Fig. 10. Hydrogen uptake by Ti-Ni alloys: pressure vs composition (Ref. 8).

Titanium-Palladium System - The compound Ti_3Pd (Ref. 9) reacts to form the hydride $Ti_2PdH_{1.47}$. The intermetallic compound has the $MoSi_2$ -tetragonal structure.

Titanium-Platinum System - The compound Ti_2Pt reacts to form the phase $Ti_2PtH_{1.05}$ (Ref. 9). The hydride has the $NiTi_2$ -cubic structure.

The compound Ti_3Pt forms the hydride Ti_3PtH_3 in reacting with hydrogen.⁷ The structure is Al₃ with $a_0 = 5.225 \text{ \AA}$.

Zirconium-Titanium Systems - This system has been studied by Libaton et al.¹⁰ and Pessall et al.¹¹ they detect no compound formation. The equilibrium pressure curves studied by these workers are shown in Fig. 11; the provisional phase diagram is shown in Fig. 12. Khodasov et al.¹²

Fig. 11. Equilibrium pressure curves for the Zr-Ti-H system (Refs. 10 and 11).

studied the NMR spectra of hydride phases in this system, namely, $(Ti_{2.1}Zr_{0.7}H_{1.22})$, $(Ti_{28.5}Zr_{71.6}H_{1.75})$, $(Ti_{36}Zr_{36}H_{3.01})$, $(Ti_{45.5}Zr_{54.3}H_{3.21})$, $(Ti_{48}Zr_{52}H_{3.35})$, $(Ti_{53.6}Zr_{46.4}H_{3.52})$, $(Ti_{60}Zr_{40}H_{4.0})$.

Zirconium-Lutetium System - Kotz et al.¹³ have studied this ternary system between 500 and 900°C at pressures of less than 1 atm hydrogen gas from 1-60 at.% hydrogen. Reproducible decomposition-pressure hysteresis occurs mainly at lower hydrogen compositions and at lower temperatures between (a) and (b) and between (b) and (c). Figures 13 through 17 summarize these data.

Confirming experiments have shown two phases in this ternary system:

- Hexagonal with lattice parameters similar to that of the initial ZrHf alloy but slightly enlarged due to dissolved hydrogen;

Fig. 12. Provisional phase diagram for 55 at.% Zr-Ti alloy and hydrogen (Refs. 10 and 11).

Fig. 13. ZrHf_{1.398} (58 at.% Hf) + H system from microgravimetric data. Hysteresis is very prominent (Ref. 13).

Fig. 15. ZrHf_{1.398} (58 at.% Hf) + H system from microgravimetric data. Hysteresis is very prominent (Ref. 13).

Fig. 14. ZrHf_{1.398} (58 at.% Hf) + H system from microgravimetric data. Desorption hysteresis is very prominent (Ref. 13).

Fig. 16. ZrHf_{2.716} (82 at.% Hf) + H system from microgravimetric data. There is no evidence for a eutectoid at the temperatures studied (Ref. 13).

Fig. 17. Isothermal nonisobaric Zr-Hf-H ternary sections (Ref. 13).

- Face-centered cubic (fcc) with properties of a brittle, intermediate hydride compound;
- Face-centered tetragonal with $c/a \approx 1.07$, appearing as a needle-like precipitate;
- Hexagonal, designated θ , with a c/a ratio of 2.37;
- Orthorhombic, designated λ , with $a = 4.67 \text{ \AA}$, and $c = 5.09 \text{ \AA}$, whose microstructural appearance depends on heat treatment.

The tetragonal phase has never appeared without the cubic hydride. Appearance of the θ and λ phases also has depended on the hafnium content of the zirconium.

Zirconium-Vanadium System - The intermetallic ZrV_2 reacts with hydrogen to form the hydride ZrV_2H_5 . This compound has the C15 structure with $a_0 = 7.900 \text{ \AA}$. Figure 18 shows the pressure-temperature-composition relationships

Fig. 18. Pressure-temperature-composition relationships for hydrided ZrV_2 (Ref. 7).

Zirconium-Niobium System - Sinha and Singh¹⁴ found that the maximum hydrogen pickup of zirconium at room temperature decreases with increasing niobium content of the alloys (Zr = 5 wt% Nb), Zr + 10 wt% Nb), and (Zr = 20 wt% Nb). The equilibrium plateau pressures and the heats of formation are shown in Fig. 19.

Zirconium-Tantalum System - The compound $ZrTa_2$ reacts with hydrogen to form the hydride $ZrTa_2H_{2.4}$ at the atomic ratio H/M of 0.77.⁷ The structure has not been determined.

Zirconium-Chromium System - The compound $ZrCr_2$ reacts with hydrogen to form $ZrCr_2H_{3.5}$ (Ref. 7). An observed atomic ratio H/M in this system is 1.16. The hydride has the C15 structure with $a_0 = 7.654 \text{ \AA}$.

Zirconium-Manganese System - The compound $ZrMn_2$ reacts with hydrogen to produce $ZrMnH$, which is extremely

pyrophoric.⁷ The structure of the phase with atomic ratio H/M = 0.22 is reported to be C14, and $a_0 = 5.065 \text{ \AA}$, $c_0 = 8.324 \text{ \AA}$, and density = 7.245 g/cm^3 .

Zirconium-Cobalt System - Figure 20 shows the hydrogen uptake by the compound ZrCo at 365°C .⁸

Zirconium-Nickel System - The only definitely confirmed hydride in this system is $ZrNiH_3$. Figure 21 shows hydrogen absorption as a function of the alloy composition in the zirconium-nickel system.¹⁵ This compound has an expanded b_f structure. Tannentaum et al.¹⁶ and Korst^{17,18} have also studied this system, reporting the hydride structure to be of the B_f type, or orthorhombic, with the cell constants $a_0 = 3.53 \text{ \AA}$, $b = 10.48 \text{ \AA}$, and $c = 4.30 \text{ \AA}$. The space group is $CmCm$. The corresponding deuteride has the cell dimensions $a_0 = 3.51 \text{ \AA}$, $b_0 = 10.44 \text{ \AA}$, and

Fig. 19. Plot of $\log_{10} p$ against $1/T$ K for the two-phase region ($\beta + \delta$).

Fig. 20. Hydrogen uptake by Zr-Co at 365°C : pressure vs composition (Ref. 8).

Fig. 21. Pressure-temperature isotherms for the Zr-Ni-H system (Ref. 15).

$c_0 = 4.30 \text{ \AA}$. The compound $\text{Ni}_{10}\text{Zr}_7$ is reported also to form the hydride $\text{Ni}_{10}\text{Zr}_7\text{H}_{1.76}$, but the structure has not been determined.

Zirconium-Uranium System - LaGrange et al.¹⁹ have studied this system at various temperatures from 600 and 800°C. They report no new phases not already known to exist in the related binary systems. Figures 22 through 28 summarize these data.

Hafnium-Vanadium System - The compound HfV_2 forms the hydride HfV_2H_4 (Ref. 7). The structure is C15 (fcc), with $a_0 = 7.610 \text{ \AA}$.

Fig. 22. Hydrogen pressure vs composition for the Zr-U-H system at 795°C (Ref. 19).

Fig. 23. Hydrogen pressure vs composition for the Zr-U-H system at 687°C (Ref. 19).

Figure 29 shows the pressure-temperature-composition relationships.

Hafnium-Cobalt System - The compound HfCo forms the hydride $\text{HfCoH}_{1.6}$ at an observed atomic ratio H/M of 0.79 and also the hydride $\text{HfCoH}_{2.98}$ (Ref. 7). The compound Hf_2Co forms the hydride Hf_2CoH_5 at an observed H/M ratio of 1.54. The structure has not been determined.

Fig. 24. Hydrogen pressure vs composition for the Zr-U-H system at 643 and 617°C. The symbol O indicates $(100 \text{ U/U} + \text{Zr}) = 54.0$ rather than 1.69 as in Fig. 22 (Ref. 19).

Fig. 26. Tentative 687°C section of the Zr-U-H phase diagram (Ref. 19).

Fig. 25. 795°C section of the Zr-U-H phase diagram. The phase boundaries are from dissociation pressure measurements (Ref. 19).

Fig. 27. Tentative 643°C section of the Zr-U-H phase diagram (Ref. 19).

Vandium-Niobium System - Wiswall and Reilly²⁰ carried out experiments with a $V_{0.8}Nb_{0.2}$ alloy. The uptake of hydrogen and deuterium is shown in Fig. 30 and indicates that the ternary hydride formed in this system is less stable than the corresponding deuteride.

Iron-Titanium System - Reilly and Wiswall²¹ report that the intermetallic compound FeTi reacts with hydrogen to form, in succession, FeTiH and FeTiH₂.

The composition limits and diagram are shown in Figs. 31-35. Both hydrides have dissociation pressures over 1 atm at 0°C, unlike the very stable TiH_2 . The lower hydride, FeTiH , has tetragonal symmetry and a density of 5.88 g/cm^3 . The higher hydride has a cubic structure and a density of 5.47 g/cm^3 .

Iron-Vanadium System - Kirschfeld and Sieverts²² have observed the occlusive behavior of three iron-vanadium alloys containing 9.1, 22.0, and 70.9% vanadium. The investigators saturated the alloys at high temperatures and then obtained isobars for 1 atm pressure by cooling the metal in the gas and observing the amounts of gas taken up at 500, 400, 300, and 20°C. From these data, isotherms of solubility were obtained at 100°C intervals from 500 to 1000°C, which resemble the isotherms for the palladium-hydrogen system.

Iron-Chromium System - The solubility of hydrogen in iron-chromium alloys was studied by Luckemeyer-Hasse²³ and Sieverts and Moritz.²⁴ Up to 700°C, they found a regular progression in the positions of the hydrogen solubility isobars at 1 atm from the solubility of chromium to that of iron. However, at temperatures above the α/γ transition, all the iron-rich alloys not exceeding 15% chromium displayed solubilities greater than that in iron itself: in these alloys, the solubility was greater in the fcc γ -lattice than in the bcc α -crystals.

Iron-Manganese System - A cursory study of this system has been reported by Baukloh and Müller.²⁵

Fig. 31. Pressure-composition isotherm for the FeTi-H system. The initial alloy composition was 53.6% Fe and 46.7% Ti. (Ref. 21).

Iron-Nickel System - This system has been studied in detail by Luckemeyer-Hasse and Schenk²³ and by Baronowski.²⁶ Figure 34 shows the regular modification of hydrogen solubility as the composition of the iron-nickel alloy is varied.

Iron-Molybdenum System - This system has been investigated by Sieverts and Brüning.²⁷ Figure 35 shows their solubility isobars. The iron-like solid solutions of the α -phase and the compound Fe_3Mo_2 (the ϵ phase) possess at like temperatures equal solvent capacities for hydrogen. With increasing content of the molybdenum-rich solution, this capacity is lowered to that of pure molybdenum.

Fig. 32. Equilibrium dissociation pressure vs reciprocal temperature for FeTiH (Ref. 21).

Fig. 33. Pressure-composition isotherms for alloys of various Fe/Ti ratios at 40°C (Ref. 21).

Fig. 34. Fe-H, Ni-H, Fe-Ni-H, and Cr-H solubility isobars at 1 atm (Ref. 23).

Fig. 35. Fe-Mo-H solubility isobars at 1 atm (Ref. 27).

Iron-Palladium System - Flanagan et al.²⁸ showed that the occupancy of a certain interstitial position depends largely on the neighboring atoms. They measured the small hydrogen solubility in ordered and disordered Pd_3Fe . In the disordered state (metal atoms on an fcc lattice), the hydrogen solubility at 25°C in the pressure range 200-10,000 atm was 5 to 10 times smaller than in the ordered state (cubic Cu_3Au -type of structure). In the ordered alloy, one unique interstitial position exists, which has only Pd atoms as nearest neighbors. It is assumed that this site is preferentially occupied.

Iron-Tungsten System - Preliminary studies of this system have been performed by Baublo and Gehlen.²⁹

Nickel-Tungsten System - Lange³⁰ studied the thermodynamic properties and the solubility of hydrogen in this system.

Rhodium-Palladium System - Tammann and Rocha³¹ have investigated the cathodic occlusion of hydrogen in this system.

Witherspoon et al.³² studied hydrogen absorption in palladium with rhodium alloys. The absorption pressure-composition relationships are shown in Fig. 36.

Palladium-Iron System - Flanagan et al.³³ found that the alloy, Pd_3Fe , did not absorb hydrogen at ≤ 1 atm (25°C). Pressures to 10,000 atm were necessary to obtain appreciable hydrogenation.

Palladium-Nickel System - In 1869, Graham³⁴ reported the cathodic absorption of 70 volumes of hydrogen by a 50% palladium-nickel alloy.

Fig. 36. Absorption pC relationships at 25°C (Ref. 32).

Palladium-Manganese System - Burger and McLachlan³⁵ measured the magnetic properties of some $\text{Pd}_{1-x}\text{Mn}_x$ and $\text{Pd}_{1-x}\text{Mn}_x^{\text{IV}}$ alloys.

Palladium-Platinum System - This system has been extensively investigated by Graham,³⁶ Hessehus,³⁷ Tnoma,³⁸ Sieverts et al.,³⁹ Tammann et al.,⁴⁰ Botter et al.,⁴¹ Stetsenko et al.,⁴² and Carson et al.⁴³ Botter's data, shown here in Fig. 37, shows that considerable occlusion and diffusion of hydrogen in alloys with moderate proportions of platinum occurring.

Theland⁴⁴ determined the absorption of deuterium by several platinum-palladium alloys. Pressure-concentration isotherms at 25°C are shown in Fig. 38 and the equilibrium solubilities of deuterium and hydrogen in the alloys in Fig. 39.

METALLIC TERNARY HYDRIDE SYSTEMS OF THE RARE EARTH ELEMENT SERIES

Cerium-Lanthanum System - This system has been investigated by Sieverts et al.³⁹

Fig. 37. Hydrogen absorption isotherms for different alloys of palladium and platinum (Me represents Pd + Pt combined).

Cerium-Cobalt System - At room temperature CeCo_5 absorbs considerable quantities of hydrogen.¹ See Table 2 for the lattice parameters at different compositions. Figure 40 shows the desorption isotherms for this pseudobinary system. The hydrogen-rich phase is reported to be c-centered orthorhombic, analogous to the β phases in the $\text{PrCo}_5\text{-H}$ and $\text{SmCo}_5\text{-H}$ systems. In a neutron-diffraction pattern of a sample of CeCo_5 ,^{2,56} only the lines of the β were visible. Figure 41 shows the influence of adsorbed hydrogen on the magnetic properties of this compound.

Fig. 38. Pressure-concentration isotherms at 25°C for several platinum-palladium alloys (Ref. 44).

Fig. 39. Equilibrium solubilities of deuterium and hydrogen in Pt-Pd alloys at 25°C, 1 atm of D_2 (H_2) (Ref. 44).

Table 2. Lattice parameters at room temperature of some compounds in the $\text{CeCo}_5\text{-H}$ system (from Ref. 1).

CeCo_5	$\text{CeCo}_5\text{H}_{0.4}$	Two-phase region $\alpha + \beta$	
Hexagonal	Hexagonal	α : $\text{CeCo}_5\text{H}_{0.6}$ ^a hexagonal	β : $\text{CeCo}_5\text{H}_{2.05}$ ^b orthorhombic ^c
$a = 4.922 \text{ \AA}$	$a = 4.942 \text{ \AA}$	$a = 4.953 \text{ \AA}$	$a = 8.716 \text{ \AA}$
$c = 4.016 \text{ \AA}$	$c = 4.013 \text{ \AA}$	$c = 4.013 \text{ \AA}$	$b = 5.103 \text{ \AA}$
$c/a = 0.816$	$c/a = 0.812$	$c/a = 0.810$	$c = 4.062 \text{ \AA}$
$v = 84.26 \text{ \AA}^3$	$v = 84.88 \text{ \AA}^3$	$v = 85.22 \text{ \AA}^3$	$v = 180.67 \text{ \AA}^3$

^aH content based on shape of isotherms (0.6 ± 0.05).

^bH content estimated from x-ray diagrams (2.05 ± 0.1).

^cTwo moles of CeCo_5H_x per unit cell.

Fig. 40. Desorption isotherms for the pseudo-binary system $\text{CeCo}_5\text{-H}$ (Ref. 1).

Fig. 41. Magnetization along the c axis of several Ce-Co alloys (Ref. 1).

The α -S transformation in this system occurs at a relatively high pressure. For different RCo_5 -H systems, the α -S transformation pressure at room temperature increases monotonically with increasing R atom number from 0.6 atm (PrCo_5 -H) to 40 atm (GdCo_5 -H). The decreasing stability has been attributed to geometrical factors.

Ytterbium-Cerium System - Shepilan et al.⁴⁵ and Khodosov⁴⁶ prepared the following hydride phases and studied their magnetic properties:

Fig. 42. Desorption isotherms for some pseudo-binary RCo_5 -P systems (Ref. 2).

Praseodymium-Cobalt, Neodymium-Cobalt, Samarium-Cobalt, and Gadolinium-Cobalt Systems - Figure 43 shows the desorption isotherms for these pseudo-binary systems. These data have been essentially confirmed in a more detailed study by Raichlen et al.⁴⁷

Figure 43 shows the isotherms of hydrogen gas in equilibrium with adsorbed hydrogen in SmCo_5 .⁴⁸ The sorption capacity of SmCo_5 is less than half that of LaNi_5 .

Fig. 43. Absorption and desorption isotherms for the pseudo-binary system SmCo_5 -H (Ref. 47).

Table 3. Equilibrium pressures at room temperature for some AB₅ compounds at halfway saturation with hydrogen. (From Ref. 3).

Compound	Pressure (atm.)
PrCo ₅	0.6
NdCo ₅	0.8
SmCo ₅	4.0
GdCo ₅	20.0

Table 3 lists the equilibrium pressures at room temperature for the compounds in this system at halfway saturation with hydrogen. Table 4 lists the lattice parameters in the PrCo₅-H system as measured near room temperature. Figures 44 and 45

Fig. 44. Magnetization of PrCo₅ and its hydride along the c-axis as a function of temperature (Ref. 2).

show the influence of hydrogen on the magnetic properties in this system and the SmCo₅-H system.⁴⁹

Table 4. Lattice parameters of some compounds in the PrCo₅-H system at room temperature (from Ref. 2).

PrCo ₅	PrCo ₅ H _{0.3} ^a	PrCo ₅ H _{2.9} ^a	PrCo ₄ H _{3.6}
Hexagonal	Hexagonal	Orthorhombic ^b β II	Orthorhombic ε I
a = 5.022 Å	a = 5.046 Å	a = 8.85 Å	a = 8.868 Å
c = 3.989 Å	c = 3.984 Å	b = 5.27 Å	b = 5.341 Å
v = 87.13 Å ³	v = 87.84 Å ³	v/2 = 189.6 Å ³	v = 193.4 Å ³

^aCompositions of two-phase boundaries estimated from isotherm (±0.05).

^bOrdering of hydrogen on available positions leads to a superstructure (doubling of the c-axis).

Fig. 45. Coercivity (H_c), remanence (B_r), and hydrogen pressure (P) as a function of hydrogen concentration. C is the abscissa; it is the difference in hydrogen concentration between SmCo_5 at the given pressure and 1 atm (Ref. 48).

With reference to the SmCo_5 system, the maximum amount of hydrogen absorbed at room temperature and 10 atm is 3.0 H atoms/ SmCo_5 . In this state, the unit cell of SmCo_5 , which normally has the hexagonal CaCu_5 structure with $a = 4.995 \text{ \AA}$, $c/a = 0.794$, and $v = 85.67 \text{ \AA}^3$, has lost its hexagonal symmetry. The new unit cell can be described as orthorhombic, with $a = 8.818 \text{ \AA}$, $b = 5.272 \text{ \AA}$, $c = 4.050 \text{ \AA}$, and $v = 188.9 \text{ \AA}^3$.

For the isotherms in Fig. 43, the heat of solution in the half-saturated condition has been determined to be 7.4 kcal/mole H_2 , which is about the same as that of LaNi_5 . The absorption capacity seems to be affected by the valence of R in ways not now understood. For example, when R is replaced by a tetravalent element, the absorption capacity decreases.

Praseodymium-Nickel System - The equilibrium pressure for the compound PrNi_5 at room temperature and halfway saturation with hydrogen is 12 atm.³

Neodymium-Nickel System - The equilibrium pressure for the compound NdNi_5 at room temperature and halfway saturation with hydrogen is 20 atm.³

Samarium-Nickel System - The equilibrium pressure for the compound SmNi_5 at room temperature and halfway saturation with hydrogen is more than 60 atm.³

Ytterbium-Nickel System - YbNi_5 is reported to absorb large quantities of hydrogen, but no phase equilibrium data have been published.⁷

Ytterbium-Palladium System - The compound YbPd reacts to form a hydride with an atomic ratio H/M of 1.06. It has a Cl5 (fcc) structure with $a_0 = 7.610 \text{ \AA}$ (Ref. 7).

METALLIC TERNARY HYDRIDES SYSTEMS OF THE ACTINIDE ELEMENT SERIES

Thorium-Titanium System - The compound ThTi_2 absorbs hydrogen to form the phase $\text{ThTi}_{2.6+x}$ (Ref. 9). The intermetallic has the MgZr_2 -hexagonal structure.

Thorium-Zirconium System - The compound ThZr_2 reacts to form the phase $\text{TbZr}_{2.7+x}$ (Ref. 50). The intermetallic compound has the MgCu_2 -cubic structure.

Thorium-Manganese System - The compound ThMn_2 absorbs hydrogen to form the phase $\text{ThMn}_{2.3.57}$ (Ref. 9). The intermetallic compound has the MgZr_2 -hexagonal structure.

$\text{Th}_3\text{Mn}_{23}$ reacts to form a hydride with an atomic ratio H/M of 0.60. The structure is D8, with $a_0 = 12.91 \text{ \AA}$ and the density = 8.23 g/cm³. At an H/M of 0.89, a primitive cubic structure is formed with $a_0 = 12.98 \text{ \AA}$ and the density = 8.13 g/cm³.

Thorium-Iron System - ThFe_5 absorbs hydrogen to form the hydride $\text{ThFe}_5\text{H}_{2.8}$ at an equilibrium pressure of 0.5 atm and room temperature.⁵¹

Thorium-Cobalt System - The compound ThCo is reported to react with hydrogen to form $\text{ThCoH}_{4.2}$ at an atomic ratio H/M of 2.10 (Ref. 7). The structure is of the expanded Bf type. Figure 46 shows the pressure-temperature-composition relationship in this system.

Thorium-Nickel System - The compound ThNi_2 reacts to form ThNi_2H_2 at an atomic ratio H/M of 0.70 (Ref. 7).

Thorium-Palladium System - The compound Th_2Pd absorbs hydrogen to form $\text{Th}_2\text{PdH}_{6-x}$ (Ref. 9). The intermetallic compound has the CuAu_2 -tetragonal structure.

Fig. 46. Pressure-composition isotherms showing the hydriding behavior of several intermetallic phases (Ref. 7).

Thorium-Ytterbium System - The compound ThYb_2H_6 is reported. No additional data are given.

Uranium-Niobium System - Powell et al.⁵² studied the mechanical properties and embrittlement behavior of alloys in these systems.

The maximum composition at 264°C is $\text{UNb}_{0.30/\text{H}_{1.563}}$ in this system. Figures 47 and 48 summarize the results for this system.³

METALLIC QUATERNARY HYDRIDE SYSTEMS OF THE TRANSITION ELEMENT STRIPS

Lanthanum-Zirconium-Nickel System -

Figure 49 shows the hydrogen desorption rate for the hydride $\text{La}_{0.9}\text{Zr}_{0.1}\text{Ni}_5$ compared to LaNi_5 at different temperatures.³

Fig. 47. Reactions of (γ) U-10 wt% Nb-H (Ref. 53).

Fig. 48. Equilibrium pressure curves for U-90 wt% Nb (Ref. 53).

Fig. 49. Hydrogen desorption rate for LaNi_5 at different temperatures vs 1 atm of hydrogen (Ref. 3).

Lanthanum-Nickel-Iron, Palladium, Chromium, and Cobalt Systems - Van Mal et al.⁵¹ studied all four systems by partly replacing nickel in LaNi_5 to form LaNi_4 type compounds with the CaCu_5 type structure. Figure 50 shows the desorption isotherms at 40°C for the various compounds and indicates that in all cases the compounds have reduced absorption capacity relative to LaNi_5 . The palladium compound forms a less stable hydride relative to LaNi_5 .

Lanthanum-Zirconium-Nickel System and Lanthanum-Thorium-Nickel System - Van Mal et al.⁵¹ studied both systems by replacing 20% of the lanthanum atoms in LaNi_5 with zirconium and thorium to form compounds of the type $\text{La}_{0.8}\text{Zr}_{0.2}\text{Ni}_5$ with the AuBe_5 structure. Figure 51 shows the desorption isotherms for these compounds

Fig. 50. Desorption isotherms at 40°C for various compounds of LaNi_4M . (Ref. 51).

Fig. 51. Desorption isotherms at 40°C for various compounds of $R_{0.2}La_{0.8}Ni_5$ (Ref. 51).

at 40°C and indicates that relative to $LaNi_5$ the absorption capacity is reduced and that the hydrides formed are more unstable.

Lanthanum-Cerium-Nickel System - This system has been studied in some detail by van Vucht³ because the two compounds $LaNi_5$ and $CeNi_5$ behave quite differently with respect to hydrogen. $LaNi_5$ absorbs large quantities of hydrogen at room temperature at relatively low pressures (4.5 atm), whereas 150 atm are not sufficient to activate and load $CeNi_5$ (Ref. 3). Figure 52 shows how a gradual substitution of cerium for lanthanum in $LaNi_5$ influences the stability of the hydrided material. The alloy $La_{0.7}Ce_{0.3}Ni_5$ can dissolve seven hydrogen atoms per formula unit.

Fig. 52. Pressure vs H-content curves (indicating the stability of the hydride) as a function of X in the $La_{1-x}Ce_xNi_5$ system at room temperature. Lower plot; lattice parameters of the hexagonal unit cell of $La_{1-x}Ce_xNi_5$ (Ref. 3).

Lanthanum-Neodymium-Nickel System,

Lanthanum-Gadolinium-Nickel System,

Lanthanum-Erbium-Nickel System, and

Lanthanum-Ytterbium-Nickel System - Van Mal

et al.⁵¹ studied all four systems by partly replacing lanthanum in $LaNi_5$ to form $La_{0.8}R_{0.2}Ni_5$ type compounds with the $CaCu_5$ type structure. Figure 53 shows the desorption isotherms at 40°C for the various compounds and indicates that in all cases a less stable hydride is formed relative to $LaNi_5$ while the absorption capacity is unchanged.

Chromium-Manganese-Nickel System -

Laythan et al.⁵⁴ report that the solubility of hydrogen in 21 Cr-6Ni-9Mn stainless steel to be 7.5 cc/cc at 200°C after exposure to 10,000 psi hydrogen for 14 days.

Iron-Chromium-Manganese System -

Laythan et al.⁵⁴ report that 5 cc of

Fig. 53. Desorption isotherms at 40°C for various compounds of $R_{0.2}La_{0.8}Ni_5$ (Ref. 51).

Absorption and Storage Characteristics of Metallic Systems

The concentration of hydrogen, S' , in a metal in equilibrium with hydrogen gas at pressure p is

$$S = S_0 p^{1/2} \exp(-E_s/RT) \text{ cc (NTP)/cc metal. (1)}$$

For most systems S_0 is approximately constant; thus metal-to-metal variations in solubility at any given temperature and pressure are generally dependent on variations in the heat of solution, E_s . Such variations are quite large; for example, measurements of E_s for nickel,

hydrogen dissolve in 304L stainless steel after 30 days (at 10,000 psi and 100°C).

Nickel-Iron-Molybdenum System - Lavthan et al.⁵⁴ report that 3 cc of hydrogen dissolve per cc of Hastelloy N* after 41 days at 10,000 psi and 155°C.

Uranium-Niobium-Zirconium System - Powell et al.⁵² studied the mechanical properties and embrittlement behavior of the phase U-7.5% Nb-2.5% Zr in this system.

Miscellaneous Complex Metallic Hydride Systems⁵⁵ - Wiswall and Reilly⁵⁶ report

that the Misch metal (Mm) nickel system formed the phase $MmNi_5H_{3.6}$. Kuipers⁹ reports the desorption transition pressure of $MmNi_5$ as 20 atm at room temperature.

iron, and copper are 4,600; 6,900; and 9,850 cal/mole ($^{\circ}K$), respectively.

Some investigators^{57,58} have emphasized that hydrogen solubility should be related to atomic and electronic structure. Jones and Pehlke⁵⁸ (see Fig. 54) recently concluded that for Ni-Co and Ni-Cu alloys hydrogen solubility could be correlated with the electron density of states at the Fermi surface $N(E_F)$. If the hydrogen solubility increases linearly with $N(E_F)$, then a graph of F_s and $\ln[N(E_F)]$ should be linear. Using $N(E_F)$ values tabulated by Eastman⁵⁹ and E_s values tabulated by Gallagher and Oates,⁶⁰ and Jones and Pehlke⁵⁸ values, such a correlation was obtained, supporting the conclusions that hydrogen solubility

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

increases with increasing electron density of states at the Fermi surface.

In general, the binary metal alloys A_1-xB_x , whose hydrogen absorption behavior has been extensively studied are solid solutions. Relatively fewer hydrogen absorption studies have been conducted using intermetallic compounds; for example, metal alloys Mm with a high degree of ordering, a definite structure, and a narrowing existence region.⁶¹ Interestingly, all the compounds reported so far contain at least one element that strongly binds hydrogen.

No compounds consisting only of non-hydride formers (e.g., Fe, W) have ever been observed to absorb appreciable

amounts of hydrogen. The absorption of hydrogen is generally accompanied by an increase of volume with the relative positions of the metal atoms remaining unchanged and hydrogen atoms occupying interstitial sites.

The absorption process, governed by structural (geometric) and chemical (electronic) factors, is generally described by a pressure-composition diagram similar to the one shown in Fig. 55. Three areas can be distinguished:⁴

- (1) a region of limited solution of hydrogen in the metallic phase (α phase),
- (2) a region of constant hydrogen pressure where the hydrogen

Fig. 54. Variation of heat of solution for hydrogen with density of states of Fermi structure. High density of available states favors an increased hydrogen solubility (Ref. 58).

Fig. 55. Pressure-composition isotherms for a typical metallic phase-hydrogen (Ref. 4).

- saturated metallic phase (α) exists in equilibrium with a separate hydride phase (β), and (3) a single-phase metallic hydride region (δ) where the concentration of hydrogen increases with increasing pressure.

The $\alpha + \beta$ region is a miscibility gap and exists because the solution process becomes more exothermic and because it is energetically more favorable for the hydrogen atoms to be clustered in the lattice than uniformly distributed. As the temperature of the system is elevated, entropy increases counteract this phase separation tendency, and the miscibility gap region decreases, finally disappearing at some critical temperature (T_c) and critical pressure (P_c).

δ -phase materials are considered to be ternary or quaternary metallic compounds in which one of the components is hydrogen. Crystallographically, the hydrogen atoms occupy either well-defined lattice positions or are randomly distributed and/or the sublattice of metal atoms has a different structure than the original compound.

Libowitz^{5,2} has shown that if the ideal gas law is rewritten to express the number of moles of hydrogen, the energy stored (in kcal), E_s , is

$$E_s = (-\Delta H_f) V/RT_C (P_H - P_C), \quad (2)$$

where V is the volume of the hydrogen storage reservoir, R is the gas constant, T_C is the ambient temperature, P_H is the equilibrium dissociation pressure of the hydride, and P_C is the hydrogen pressure in equilibrium with the hydride at T_C .

Thus hydrides with high energy storage capabilities should have large (negative) values of ΔH_f and also large differences between P_H and P_C . These values are not independent of one another. The van't Hoff equation may be written:

$$(\ln P^{-1}/GT) = \Delta H_f/RT^2, \quad (3)$$

where P is the hydrogen pressure. Therefore, the larger the value of ΔH_f , the greater the change in hydrogen dissociation pressure with temperature, and consequently, the greater the difference in P_H and P_C . Since ΔH_f is a measure of the strength of the bond between metal and hydrogen, it appears that in designing new alloy hydrides, alloying elements should be sought which will strengthen the bonding of known hydrides.

To hold the volume of the hydrogen reservoir within reasonable bounds, Libowitz finds that hydrides with fairly high dissociation pressures are necessary. The integrated form of Eq. (3) may be written:

$$\ln P = \{(\Delta H_f/RT) - (\Delta S/R)\}, \quad (4)$$

where ΔS is the entropy change involved in the hydriding reaction. Thus, we see that although a large negative value of ΔH_f is desirable to provide a high heat of reaction, as discussed above, it also is associated with low hydrogen pressures as shown in Eq. (4). In designing new alloy hydrides, therefore, Libowitz suggests that it would be advantageous to maintain as high a negative value of ΔH_f as possible (i.e., strong metal to hydrogen bonding) without significantly reducing the equilibrium value of hydrogen pressure.

According to Eq. (4), it may be possible to accomplish this by having low (large negative) values of ΔS . This means that

the entropy of the alloy hydride should be small, which implies a rigid lattice, but higher than the corresponding metal.

Stability of Metallic Hydride Phases

The equilibrium pressure in the two-phase region, which is a measure of the stability of the β -hydride, can be approximated by

$$\ln P_{H_2} = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (5)$$

where ΔS and ΔH are the entropy and enthalpy changes per mole of hydrogen involved with the reaction $+ xH_2 \rightleftharpoons \beta$. According to Eq. (4), plots of $\ln P$ versus $1/T$ will then yield values for ΔH . In most systems, entropy changes are not large enough to be characteristic and enthalpy changes are relied upon to indicate important differences.

Now, the heat of formation of hydrides from an intermetallic compound of the type

where N and m have the significance indicated above, can be obtained by employing Miedema's nearest-neighbor model⁶³ for binary metal hydrides. This involves a decomposition of the heat of formation of the ternary hydride $NM'_n H_{2x}$ into two binary contributions, namely,

$$\Delta H (NM'_n H_{2x}) = \Delta H (MH_x) + \Delta H (M'_n H_x) - \Delta H (M'_n)_n \quad (7)$$

In the case of a hydrogen-intermetallic compound system, the first term on the righthand side of equation represents the heat of formation of the transition ele-

ment, rare earth, or actinide series hydrides for which experimental values are available. The second term represents only the heat of formation of the transition element hydride which is usually small. The third term, the heat of formation of the intermetallic compound, can be estimated using Miedema's model. For a series of isostructural compounds NM'_n , in which the rare earth or actinide component and the composition n are fixed, the first term is a constant; the enthalpy for hydride formation behaves inversely to the enthalpy effect for compound formation.

This leads to Miedema's rule of reversed stability: "The more stable the original intermetallic compound the less stable the ternary hydride, for example, the larger is the equilibrium pressure."

This rule is illustrated in Fig. 50 for compounds of the type $LaNi_5X$ (or LaX_5), where experimental results indicate that the stability decreases in the sequence $X = Pd, Ni, Co, Fe$, and Cr .

Calculations using Miedema's model are in agreement with these results and show the stability of these compounds decrease in the sequence

Enthalpy values range from -110 kcal/mole for $LaPd_5$ to +12 kcal/mole for $LaCr_5$.

A further confirmation of the validity of the rule of reversed stability is obtained with the series ThNi_5 - ThCo_5 - ThFe_5 and ZrCo_2 - ZrNi_2 . In both sequences, the

stabilities are expected in Miedema's model to decrease while experimentally an increasing tendency to absorb hydrogen has been observed.^{51,64,65}

References

1. F. A. Kuipers, J. Less Common Metals **27**, 27 (1972); J. Phys. Chem. Solids **35**, 301 (1974).
2. "Hydrogen in Metals: International Conference on Hydrogen Technology, West Germany, March 20, 1972" in Phys. Chem. Berichte **76** [8] 705 (1972).
3. K. H. J. Buschow and H. H. Van Nal, J. Less-Common Metals **29**, 203 (1972).
4. J. H. N. Van Vucht, F. A. Kuipers, and H. C. A. M. Bruning, Philips Res. Reports **25**, 133 (1970).
5. F. Kostiner and T. R. P. Gibb, Jr., Intermetallic Hydride Systems, B. S. Thesis, Tufts University, Medford, Mass., 1960.
6. R. P. Wiswall and J. J. Reilly, Inorg. Chem. **11** (7) 1691 (1972).
7. Investigation of Hydriding Characteristics of Intermetallic Compounds, University of Denver, Denver Research Institute, Denver, Colorado, Rept. IAR-55 (1961), and Rept. DRI-2059 (1962).
8. Annual Report, Brookhaven National Laboratory, Upton, New York, Rept. BNL-50023, p. 36 (1966).
9. F. A. Kuipers, Philips Res. Repts. Suppl. **2** (1973).
10. V. Y. Labaton, F. V. Garner, and F. Whitehead, J. Inorg. Nucl. Chem. **24**, 1197 (1962).
11. N. Pessall and A. D. McQuillan, Trans. AIME **224**, 536 (1962).
12. Y. E. F. Khodasov and A. I. Linnik, Fiz. Metal. Metalloved **31** (4), 339 (1971).
13. O. M. Katz and J. Alfred Berger, Trans AIME **233**, 1005 (1965).
14. V. K. Sinha and K. P. Singh, Met. Trans. **3** (6), 1581 (1972).
15. G. G. Libowitz, H. F. Hayes, and T. R. P. Gibb, Jr., J. Phys. Chem. **62** (1958).
16. I. R. Tannenbaum, W. L. Korst, J. S. Wahl, and G. C. Libowitz, Study of the Nickel-Zirconium-Hydrogen System, Atomics International - North American Rockwell, Los Angeles, Rept. NAA-SR-7132 (1962).
17. W. L. Korst, J. Phys. Chem. **66**, 370 (1962).
18. S. W. Peterson, V. N. Sadana, and W. L. Korst, J. Phys. (Paris) **25**, 451 (1964).
19. L. D. LaGrange, L. J. Dykstra, J. M. Dixon, and U. Merten, J. Phys. Chem. **63**, 2035 (1959).
20. R. H. Wiswall and J. J. Reilly, Inorg. Chem. **11** (7), 1691 (1972).
21. J. J. Reilly and R. H. Wiswall, Jr. Inorg. Chem. **13**, 218 (1974).
22. L. Kirschfeld and A. Sieverts, Z. Elektrochem. **36**, 123 (1930).
23. L. Luckemeyer-Hasse and H. Selenck, Arch. Eisenhüttenw. **6**, 209 (1932); Tech. Mitt. Krupp **1**, 121 (1933).
24. A. Sieverts and H. Moritz, Ber. Deutsch. Chem. Ges **75**, 1726 (1943).
25. W. Baukloh and R. Muller, Arch. Eisenhüttenw. **11**, 509 (1937).

26. B. Baranowski and S. Filpek Rocyniki, Chem. Ann. Soc. Chem. Polonorum 47, 4105 (1973).
27. A. Sieverts and K. Bruning, Z. Physik, Chem. A. 168, 411 (1934).
28. T. B. Flanagan, S. Majchrzak, and B. Baranowski, Phil. Mag. 25, 257 (1972).
29. W. Bauflöh and K. Gehlen, Arch. Eisenhüttenw. 12, 39 (1938).
30. K. Lange, Zeik. Fur Metallkde. 64 (2), 111 (1973).
31. G. T. Tammann and H. J. Rocha, Festschr. Siebertsch. Platinschmelze. 309 (1931).
32. T. C. Witherspoon, W. D. McFall, and F. A. Lewis, Nature Physical Science, 242, 44 (1973).
33. T. B. Flanagan, S. Majchrzak, and B. Baranowski Phil. Mag. 250, 257 (1972).
34. T. Graham, Proc. Roy. Soc. London 17, 212 (1869); Phil. Mag. 37, 122 (1869); Compt. Rend. 68, 101 (1869); Proc. Physik. 136, 317 (1869); Researches 290 (1869).
35. J. P. Burger and D. S. McLachlan, Solid State Comm. 13, 1563 (1973).
36. T. Graham, Proc Roy Soc London 17, 500 (1869); Phil Mag. 37, 452 (1869); Compt Rend 68, 1511 (1869); Ann Physik 138, 49 (1869).
37. N. Hessehus, Soc Phys St. Petersburg 11, 78 (1879).
38. M. Thoma, Centralbl. Elektrotechnik. 11, 131 (1889); Z Physik Chem 3, 69 (1889).
39. A. Sieverts, E. Juresch, and A. Netz, Z. Anorg. Allg. Chem. 92, 329 (1915).
40. G. Tammann and H. Rocha, Festschr. Siebertsch. Platinschmelze. 309 (1931).
41. F. Botter, J. Minis, P. Charpin, and C. Dirian, J. Chinic. Plupique. 63 (10), 1367 (1966).
42. A. I. Stetsenko, J. P. Tverdokskii, Zh. Fiz. Khim. S.S.S.R., (1952).
43. A. W. Carson, T. B. Flanagan, and F. A. Lewis, Trans. Faraday Soc., 56, 1332 (1960).
44. A. Maeland and T. B. Flanagan, J. of Phys Chem 68 (6), 1419 (1964).
45. M. A. Shepilan, E. F. Khodosov, and A. K. Prokopenka, Phys. Stat. Sol. 61, K111 (1974).
46. F. F. Khodosov, V. K. Prokopenka, and A. I. Linnik, Sov. Phys. Solid State 16 (1), 157 (1974).
47. J. S. Raichlen and R. H. Doremus, J. Appl. Phys. 42, 3166 (1971).
48. F. A. Kuipers and H. H. van Mal, J. of the Less Common Metals 23, 395 (1971).
49. H. Zijlstra and F. F. Westendorp, Solid State Common 7, 857 (1969).
50. R. Van Wauten and S. Bartram, Metallurgical Trans. 2, 527 (1971).
51. H. H. Van Mal, K. H. J. Buschow, and A. R. Miedema, J. of the Less Common Metals 35, 65 (1974).
52. G. L. Powell and J. B. Condon, Hydrogen in Uranium Alloys, Oak Ridge Y-12 Plant, Oak Ridge, Tenn., Rept. Y-DA-531: (1973).

51. O. M. Kutz and F. A. Culbransen, J. Nucl. Mater., 5, 269 (1962).
54. M. P. Lavthan, G. R. Coslev, J. A. Donovan, and D. E. Rowe, Mater. Science Eng., 12, 357 (1972).
55. Ronson Metals Corporation, Newark, New Jersey. Circular #14.
56. R. F. Wilsall and J. J. Reilly, Inorg. Chem., 11 (7), 1691 (1972).
57. Y. Fbisuzaki and M. O'Keeffe, Progr. Solid State Chem., 4, 187 (1967).
58. F. G. Jones and R. D. Pehlke, Met. Trans., 2, 2655 (1971).
59. D. F. Eastman, J. Appl. Phys., 40, 1367 (1969).
60. P. T. Gallagher and W. A. Gates, Metallurgical Society AIME Trans., 245, 179 (1969).
61. R. L. Beck, quoted by F. A. Aitken, in Intermetallic Compounds, J. H. Westbrook, ed. (John Wiley and Sons, Inc. New York, 1967), p. 511.
62. G. G. Libowitz, 9th Intersociety Energy Conv. Eng. Conf. Proceedings, San Francisco, California, August 26-30, 1974 (ASME, 1974), p. 322.
63. A. P. Miedema, J. of the Less Common Met., 32, 117 (1973).
64. A. Pehlke and E. A. Culbransen, Electrochem. Techn., 4, 211 (1966); Metallurgical Society AIME Trans., 239, 1593 (1967).
65. K. H. J. Buschow, F. A. Kuipers, A. R. Miedema, and H. H. van Mal, "Hydrogen in Rare Earth Intermetallics" in Proc. of the 11th Rare Earth Research Conf.-741C02-Pl, USA EC, TIC, Oak Ridge, Tenn. (1974), p. 417.