

*25-78*  
*5-22-78*  
SANDIA LABORATORIES

Unlimited Reference

THEORETICAL STUDIES OF HYDROGEN IN METALS:  
CURRENT STATUS AND FURTHER PROSPECTS

A. L. C. Switendick

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115  
and Livermore, California 94550 for the United States Energy Research  
and Development Administration under Contract AT (29-1)-788

Printed April 1978

SAND78-0250  
Unlimited Release  
Printed April 1978

THEORETICAL STUDIES OF HYDROGEN IN METALS:  
CURRENT STATUS AND FURTHER PROSPECTS

A. C. Switendick  
Solid State Theory Division 5151  
Sandia Laboratories  
Albuquerque, New Mexico 87185

-----NOTICE-----  
The report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any of its agencies, nor any of its 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.

**NOTICE** **DX ONLY**  
**PORTIONS OF THIS REPORT ARE ILLEGIBLE. It**  
has been reproduced from the best available  
copy to permit the broadest possible avail-  
ability.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

100-09511-91 539021 OF 8417925 15 M 12/2  
009631 STARS AND PLANETS PROBLEMS

A. C. Switendick

REF ID: A61

Electronic band structure studies of metal-hydrogen systems have demonstrated the existence of large metal-hydrogen and hydrogen-hydrogen interactions. These interactions lead to the formation of stable hydride phases. Factors governing this interaction are investigated for various different structures. Possible new directions for theoretical research are indicated.

\* \* \*

When one looks at the occurrence of transition, rare earth and actinide hydrides, as shown in Fig. 1, one notes certain regularities. The first regularity is the preponderance of dihydrides, greater than 50%, followed by ~35% trihydrides. The second regularity is that with the exception of CrII, NiII and PdII, they all lie to the left of Group VI B. There have been three major approaches to understanding the stability of various hydrides. The first approach, generally classified under "orbital" or screening arguments of a proton in a metallic lattice, ignores structure changes and related hydride properties to the host metal properties such as density of states at the Fermi energy. This approach while somewhat appropriate for the dilute solubility limit and perhaps even less so for those monohydrides where a metal lattice change does not occur (Group V B and VII B) has little to do with systems in which such a structure change occurs. In fact our results show that the density of states at the Fermi energy changes by over a factor of four for chromium in going from the body-centered cubic (bcc) lattice of the metal to the hexagonal close packed (hcp) lattice appropriate to CrII.

The second two approaches are based on the electronic energy band theory of solids and arrive at rather similar physical pictures. Although our results generally preceded those of the Harvard group we shall discuss theirs next pointing out the significant differences between their results and ours.

The major conclusions of the Harvard group as presented in a series of papers<sup>1-3</sup> are now discussed in terms of Fig. 2 taken from Reference 5. The figure shows the gross changes in the density of states as hydrogen is added to a metal lattice. The pure metal as shown schematically on the left has a high density of states region

arising from the d-states of the transition metal overlapped by the relatively low contribution arising from the s-p states. These states are filled (diagonally shaded region) with a number of electrons appropriate to the transition metal (e.g., four for titanium). Upon the addition of small amounts of hydrogen, a new hydrogen state forms below the transition metal state. These states have electronic charge largely associated with the proton and cause scattering and dispersion of states associated with the transition metal. The former phenomena has been observed for dilute solutions of hydrogen in copper (6,7). As the hydrogen concentration increases to approach the stoichiometric composition the states associated with the hydride interact and broaden into a band just as the s-p and d-states of the transition metal ate did. This lower band also reflects metal-hydrogen interaction and consequently some of the states of the metal are modified. The accommodation of the extra electron contributed by the hydrogen is partially in these lower band states and partly in the higher energy states (largely d) at the fermi energy (e.g., states 1 regime). Thus the major contributions to the cohesive energy of the hydride found by these workers are:

- 1) the formation of a metal-hydrogen bonding level derived of states of the pure metal band structure which have symmetry about the site of the added proton
- 2) a slight increase in binding of the metal bands due to the added attractive potential and
- 3) the addition of an extra electron to the metal electron sea.

The fact that a whole electron is added to the metal sea is due to their partitioning of the various energy contributions. The cohesive energy is then made up largely of the large energy lowering associated with the change in the lowest band, counter balanced by the increased energy of an electron around the fermi energy.

Although these calculations were only performed for the monohydride structure which is appropriate for only NiII and PdII they are successful in accounting for the trends of Fig. 1 although quantitative predictions<sup>5</sup> were not possible.

Our results are reviewed in two recent chapters<sup>5,9</sup> with more complete references given therein. In general we have tried to calculate the hydride in the correct structure and to contrast this structure with another which does not form. The fact that the majority of the hydrides choose the CaF<sub>2</sub> dihydride structure involving a metal atom lattice change and do not just involve an incorporation of hydrogen into the host metal lattice implies something unique about this structure and therefore this should be the basic one considered to understand these hydrides. The calculations show that this structure with two hydrogens in the unit cell allows a hydrogen-hydrogen interaction with the formation of new states. As in the second model the energy of these states and the number of electrons which can be accommodated therein contributes

to the hydride cohesive energy and dominates the qualitative trends in hydride formation. Unlike the monohydride structures considered there, where the position of the metal-hydride state is relatively insensitive to the host metal and the change is due to the relative lowering of the lowest band, these dihydride states, characterizing an antibonding hydrogen interaction, depend strongly on the metal involved. This is because these states depend strongly on the hydrogen-hydrogen spacing as in the hydrogen molecule. Calculations which do not include these states cannot get the physics correctly.

In Fig. 3 we show the positive ( $E_c - E_f = +2^*$ ) of the top of these states ( $+2^*$ ) relative to the Fermi energy  $E_F$  for a series of dihydride systems as a function of hydrogen-hydrogen spacing or equivalently the geometrically determined feature, the metal atom size,  $R_p$ . All the stable hydrides have  $\epsilon_c > 0.19$  Ryd, while the unstable ones have  $\epsilon_c < 0.19$  Ryd. Thus, Y, Pr, Tb, Tl, Sc, Cr dihydrides are stable, Ba, Pd, Cr dihydrides are unstable and of the two Nd and Lu with  $\epsilon_c = 0.17$  Ryd, Nd forms and Lu does not. Thus no stable dihydride structure form with a hydrogen-hydrogen spacing of less than 2.14 Å at normal conditions. Similar considerations of the correct trihydride lattice show that a octahedral or hexagonal tetrahedral hydrogen distance of less than 2.3 Å does not lead to stable trihydride lattices. Although we have not calculated the structure associated with the hexagonal trihydride phase characteristic of the heavy rare earths Gd-Lu it appears that the cubic trihydride lattice would have a minimal hydrogen-hydrogen spacing of less than 2.3 Å while in the observed structure this spacing is achieved.

This leaves relatively few hydride structures to be explained NH<sub>3</sub>, NdH<sub>3</sub>, TaH<sub>3</sub>, Th<sub>2</sub>H<sub>5</sub>, PuH<sub>3</sub>, UH<sub>3</sub>, and CrH<sub>3</sub>. The physics leading to the stability of NdH<sub>3</sub>, PuH<sub>3</sub> but not TaH<sub>3</sub> is discussed in detail in reference 3. Calculations have been carried out on NdH<sub>3</sub>, UH<sub>3</sub> and CrH<sub>3</sub> and show the same three factors and physics as stated above to be operative. For example when we consider the bcc lattice appropriate to the first six of the above metal hydrides as shown in Fig. 4 the following systematic are revealed. All seven metals exhibit body centered metal lattices. The tetrahedral interstices are shown in the figure. If one occupied all the tetrahedral interstices the composition MH<sub>3</sub> would be obtained. In fact for this structure the composition MH is the limiting composition. The reason for this is seen when one considers the hydrogen-hydrogen spacing which would be found as given in Table I. The first and second nearest neighbor distances,  $d_1$ , and  $d_2$ , respectively, are too small. The third nearest neighbor distance,  $d_3$ , is too small for V, Cr, Nd, Ta. Thorium easily exceeds both the dihydride (2.14) and trihydride limit (2.3) and compositions exceeding 2-3 are indicated. In fact the largest ratio of hydrogen to metal, 3.75, is achieved in the Th<sub>2</sub>H<sub>5</sub> structure. Protactinium and uranium are close to the 2.14 Å limit and structures with atoms having the  $d_2$  spacings in the faces and  $d_3$  spacings between the faces are found in aNH<sub>3</sub> and aPuH<sub>3</sub>. The fourth nearest neighbor distance,

$d_{\text{c}}$ , barely makes it for V, fails for Cr and succeeds for Rb and Ta. Thus compositions utilizing this spacing are attainable. However instead of atoms in the planes parallel to  $x$  and  $y$  separated by  $d_{\text{c}}$  translations, we find a combination of  $d_{\text{c}}$  and  $d_{\text{s}}$ . This structure is observed in  $\text{VH}_3$ ,  $\text{NbH}_3$  and  $\text{TaH}_3$ . Structures found for  $\text{V}_2\text{H}$ ,  $\text{Nb}_2\text{H}$ ,  $\text{Ta}_2\text{H}$ ,  $\text{Ta}_2\text{H}_3$ , etc., have fewer neighbors and greater separations. Thorium finally ( $2.29 \text{ \AA}$ ) makes it by the fifth neighbor, but instead forms the hexagonal nickel arsenide structure. The last two columns give the observed distances and the number of neighbors at that distance for the stable structure given in column eight. Vanadium, niobium and tantalum exceed the  $d_{\text{c}}$  value by expanding and distorting. Chromium, thorium, protactinium and uranium as stated above choose another structure. The minimum observed distance is  $2.02 \text{ \AA}$  for  $\text{Th}_2\text{H}_{17}$ . This value was determined from x-ray diffraction<sup>11</sup> (which cannot locate the hydrogens) and was determined on the basis of chemical and symmetry arguments. It was speculated that H-H interactions could displace these atoms from the ideal sites giving better coordination and a H-H spacing of  $2.29 \text{ \AA}$ . This leaves the minimum observed distance of  $1.97 \text{ \AA}$  for protactinium and uranium for one neighbor. Preliminary calculations for these systems indicate the possibility of metal-f-electron-hydrogen interaction. This may account for the unique structure found for these systems and the price of going directly to the trihydrides without an intervening dihydride phase as usually occurs. The main cohesive energy in  $\text{Th}_2\text{H}_{17}$  has been attributed<sup>12</sup> to thorium-hydrogen bonds because of the large ( $3.97 \text{ \AA}$ ) thorium-thorium separation found in this structure.

#### SUMMARY

Calculations for di- and tri-hydride structures have shown that hydrogen-hydrogen interactions lead to the introduction of new states below the metal bandfill which can be occupied with the added electrons. The position of these added states depends on the closest hydrogen-hydrogen distance. Extension of these ideas to other hydride systems appears valid although the correct structure should be considered to get the details right. Further calculations are in various stages to complete this picture. CeII is completed,  $\text{UH}_3$  has been started and  $\text{NbH}_3$ ,  $\text{Rb}_2\text{H}$  are soon to be started. Further work in the area of self-consistency and total energy is needed to put the theory on a true quantitative basis. Work is proceeding along these directions. Possible further directions include the dilute limit and the incorporation of hydrogen, helium and vacancies in metal lattices.

### References

1. Y. Itoizaki and R. O'Handley, *Progress in Solid State Chemistry*, Vol. 4, Ch. 5, H. Riedel, ed., *Fortschritte Physik*, Göttingen (1971).
2. R. Burch, *Trans. Faraday Soc.*, **66**, 735 (1970), *ibid.* 739.
3. C. D. Gelatt, Jr., J. A. Weiss, and H. Ehrenreich, *Solid State Comm.*, **17**, 663 (1973).
4. C. D. Gelatt, Jr., H. Ehrenreich, and J. A. Weiss, *Phys. Rev.* (to be published).
5. C. D. Gelatt, "Proceedings Hydride for Energy Storage Conference," Geilo, Norway, August 15-18, 1977.
6. W. P. Slichter and L. Tengeler, *Phys. Rev. B*, **15**, 4614 (1977).
7. L. Hultman and J. A. Weiss, *Solid State Comm.*, **16**, 993 (1975).
8. A. C. Guillet, "The Change in Electronic Properties on Sparsely Alloying and Hydride Formation in Ni", in *Adv. in Comp. Mat.*, ed. by G. Kieffel and J. Neher (Springer Berlin, Heidelberg) 1978.
9. A. C. Guillet, "Electronic Structure of Transition Metal Hydrides" in *Advances in Ceramics - Iron-Rich Metal Hydrides, Volume 1, Part 2*, May 29 through June 2, 1977, American Ceramic Society, Washington 1977.
10. W. H. Zachariasen, *Acta Cryst.*, **C**, 303 (1953).

TABLE I Tetrahedral distances,  $d$ , appropriate to body centered lattices of lattice constant(s)  $a(c)$  giving metal atom size  $R_m$ . See Fig. 4. Also given is the observed hydrogen spacings and the number,  $n$ , at that distance

IIIB VNB VB VIB VIIIB VIIIIB

| $\text{ScH}_2$ | $\text{TiH}_2$ | $\text{ZrH}_2$ | $\text{HfH}_2$ | $\text{TaH}_2$ | $\text{W}_{1-x}\text{Re}_x\text{H}_2$ | $\text{NbH}_2$ | $\text{RH}_2$ |
|----------------|----------------|----------------|----------------|----------------|---------------------------------------|----------------|---------------|
| $\text{YH}_2$  | $\text{ZrH}_2$ | $\text{NbH}_2$ | $\text{TaH}_2$ | $\text{RH}_2$  | $\text{NbH}_2$                        | $\text{RH}_2$  | $\text{RH}_2$ |
| $\text{YnH}_2$ |                | $\text{NbH}_2$ |                |                |                                       |                |               |

| $\text{ScH}_{2-x}$ | $\text{TiH}_{2-x}$ | $\text{ZrH}_{2-x}$ | $\text{HfH}_{2-x}$ | $\text{TaH}_{2-x}$ | $\text{W}_{1-x}\text{Re}_x\text{H}_2$ | $\text{NbH}_{2-x}$ | $\text{RH}_{2-x}$ | $\text{ScH}_2$ | $\text{TiH}_2$ | $\text{ZrH}_2$ | $\text{HfH}_2$ | $\text{TaH}_2$ | $\text{W}_{1-x}\text{Re}_x\text{H}_2$ | $\text{NbH}_2$ | $\text{RH}_2$  |                |
|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------------------------|--------------------|-------------------|----------------|----------------|----------------|----------------|----------------|---------------------------------------|----------------|----------------|----------------|
| Acty               | $\text{ThH}_2$     | $\text{PaH}_2$     | $\text{UH}_2$      | $\text{NpH}_2$     | $\text{PuH}_2$                        | $\text{AmH}_2$     | $\text{CmH}_2$    | $\text{ThH}_2$ | $\text{PaH}_2$ | $\text{UH}_2$  | $\text{NpH}_2$ | $\text{PuH}_2$ | $\text{AmH}_2$                        | $\text{CmH}_2$ | $\text{ThH}_2$ | $\text{PaH}_2$ |

Figure 1  
Occurrence of stable transition metal,  
rare earth, and actinide hydrides.

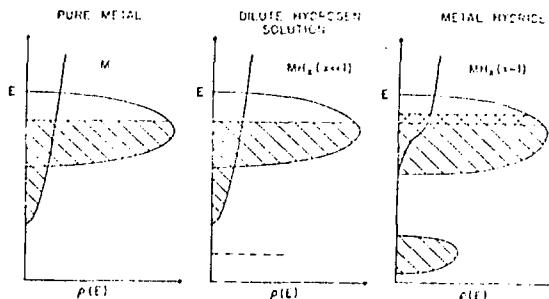
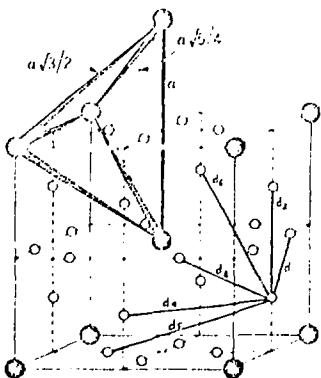


Figure 2  
Schematic picture of change in density of states,  
 $n(E)$ , as hydrogen enters metal lattice.



JOURNAL OF

Early performance of the latter is illustrated by the following table, which shows the greatest intersections with the null hypothesis at the distance  $d_0$  as indicated.

- Metal atoms
  - Tetrahedral interstices