SAND-79-0493C
comp. 790301--9

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BANDSTRUCTURE CALCULATIONS FOR
METAL HYDROGEN SYSTEMS*

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ABSTRACT

The factors contributing to hydride stability are discussed for a variety of metal hydride systems. The formation of a low-lying hydrogen associated state is a common feature. A significant transition metal character is also found in these states.

*This work was supported by the U. S. Department of Energy, DOE, under Contract DE-AC04-76-DP00789.
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EXB

I. INTRODUCTION

Calculations of the bandstructures of metal-hydrogen systems are less than a decade old and it seems appropriate to examine in some detail what light they have been able to shed on the behavior of these systems. Aspects of this subject have been treated in two recent review papers by the author and some replication will occur. In this discussion I will dwell on different aspects and include more recent results. In particular I will discuss the basis of the calculations, including the assumptions and approximations and their influence on the results, by various comparisons of our work and the results of others. I will also emphasize trends both as a function of changing the metal atom and as a result of changing the number of hydrogens associated with each metal atom. In particular we shall look at the electronic charge associated with the hydrogen and the number and location of states added by the hydrogen. Several systems will be examined: Pd-H, the 3d-4d and lanthanide hydrides, as well as some body-centered systems. The physical picture which emerges from the calculations will be presented (somewhat subjectively) in the summary.

II. ENERGY BAND CALCULATIONS

Before I discuss the results of various energy band calculations for metal hydrides, it is appropriate to examine in somewhat more detail the approximations and parameters which enter into the calculations. There are two types of approximations, physical and numerical, and we shall discuss the latter after a brief detailing of the former which leads one to an energy band approach.

The physical approach is the quantum mechanical one of wave functions and operators whose average over the wave function (expectation value) determines the physical observables of the problem.¹ The wave function is a function of the coordinates of the particles and is determined by solving the Schrödinger eigenvalue equation

$$H\psi^n = E_n \psi^n \quad (1)$$

where H is the Hamiltonian for the problem, ψ^n is the wave function corresponding to the n th solution with E_n the energy of this solution. The first approximation is the separation of electronic (e) and nuclear coordinates (R_N) to give

$$H_e \psi_e^n(R_N) = E_n(R_N) \psi_e^n(R_N) \quad (2)$$

This is the Born-Oppenheimer approximation. Eq. 2 is still too complicated to solve for systems involving more than two electrons. The next assumption involves the form of the wave function $\psi_e^n(R_N)$ as a product (determinant) of one electron functions² $\psi_n(\vec{r}_i)$ called orbitals. This assumption, and the fact that a wave function for

the lowest (ground state) energy is variational, (i.e. the true wave function gives the lowest value of the expectation value of the Hamiltonian, the ground state energy eigenvalue, E_0), leads to the one electron Hartree-Fock equations³ for the best approximate one-electron orbitals

$$H(i) \psi(r_i) = \epsilon_n \psi^n(r_i) . \quad (3)$$

The Hamiltonian can be written as

$$H(i) = KE_i + V_C(r_i) + V_{EX}(r_i) + V_N(R_N) \quad (4)$$

The various terms represent the kinetic energy of the electron and its potential energy. $V_C(r_i)$ is the Coulomb potential of the electron in the field of all the other electrons and as such is a function of their charge distribution which is determined by the orbitals, $\psi^n(r_i)$. Similarly V_{EX} is the exchange potential which is a manifestation of the Pauli exclusion principle (or Fermi-Dirac statistics) which prevents any two orbitals from being identical. This leads to the shell structure of atoms $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ etc. $V_N(R_N)$ is the potential energy of the electron in the field of the nuclei and as such contains the nuclear positions as parameters R_N . Knowing the form of the Hamiltonian one can assume a functional form for the orbitals ψ_i , solve equation 3 for the orbitals, select the n orbitals with lowest eigenvalues, ϵ_i , construct the Hamiltonian Eq. 4) from these orbitals and solve iteratively until the equations converge to a numerically stable level (self-consistency). This procedure has been done for atoms and molecules and is responsible for much of our physical picture of atomic structure and chemical bonding.

One is capable of getting results which are accurate to a few percent. One approximation which can be removed is the use of a single product (or small sum of products) for the wave function by using a larger and larger sum. The simple product function gives a certain statistical independence in the positions of the electrons and as such is said to lack correlation. Correlation effects are responsible for the remaining errors and in many cases these effects are large.⁴ One can account for correlation by either 1) ignoring it, 2) adjusting ones results in some fashion⁴ or 3) including it in Eq. 4 in V_{EX} .⁵ Results for solids using Eq. 4 without its inclusion do not agree nearly as well with experiment as result with it. This concludes our discussion of the major physical approximations.

The starting point of electronic structure of solids is Eq. 4, the one electron Schrodinger equation. One can go back to Eq. 2 and introduce a combined exchange and correlation term into the Hamiltonian⁶ but the net result is still a set of one-electron equations as Eq. 4. This latter approach is the popular $X\alpha$ (Ref. 6) or local density⁷ approximation which has been employed in the majority of hydride energy band calculations. The form of the one-electron Hamiltonian is

$$-\nabla_i^2 + \int \frac{2}{r_i - r_j} \rho(r_j) dr_j - \alpha 3(3/8\pi \rho)^{(1/3)} - \sum_p \frac{2Z_p}{r_i - R_p} \quad (5)$$

where the terms have the same meaning as before and α is called the exchange (correlation) factor. Four common choices have been used: 1) $\alpha = 1$, Slater exchange,⁶ 2) $\alpha = 2/3$, Kohn Sham exchange,⁸ 3) $\alpha = \alpha(Z_p)$, to satisfy some atomic relation⁹ and 4) $\alpha = \alpha(\rho)$, such as Hedin-Lundquist¹⁰

prescriptions. The charge density is given by

$$\rho = \sum_i^N \psi_i^* (x) \psi_i (x) \quad (6)$$

One can summarize the problem as

$$(-\nabla^2 + V_X) \psi_i = \epsilon_i \psi_i \quad (7)$$

One first has to decide on the form of the solid potential V_X and the form to be used for ψ_i . The mathematics of the problem simplifies considerably for the case of a perfect crystal.¹¹ In that case the one electron potential has translational symmetry which means Bloch's (or Flouquet's) theorem holds and we can label the solutions by their translational properties namely

$$\psi(\vec{r} + \vec{T}_n) = e^{-i\vec{k} \cdot \vec{T}_n} \psi(\vec{r}) \quad (8)$$

where $\vec{T}_n$ is a repeat translation vector of the crystal lattice and $\vec{k}$ is a vector giving the phase change the wave function undergoes upon translation. The $\vec{k}$ vectors can be chosen within a certain fundamental domain called the Brillouin zone which bears a certain reciprocal relation to the fundamental cell of the crystal lattice which displays the repeat properties, T_n . The basis is now pretty well determined to begin the band calculation, with the ingredients and steps are outlined below:

A. Select System MH_n

1) Crystal Structure

a) Atom Locations

b) Lattice Constants

B. Calculate Crystal Potential

- 1) Prepare Atoms
- 2) Select Exchange-Correlation Approximation
- C. Solve Eq. 7 for $\epsilon_i(\vec{k})$, $\psi_i^{\vec{k}}$
- C'. Repeat steps B and C to self-consistency.
- D. Utilize Results
 - 1) Plot $\epsilon_i(\vec{k})$
 - 2) Determine Fermi Energy E_F
 - 3) Density of State $N(E)$, $N(E_F)$
 - 4) Charge Distribution Eq. 6.
 - 5) Compare with Experiment
 - a) Electronic Specific Heat γ
 - b) Magnetic Susceptibility χ
 - c) Superconducting Transition Temperature
 - d) Excitation Spectra
 - e) NMR results
 - f) etc.

E. Vary Parameters of A and Assess Influence on D.

Some elaboration of the above outline will be made in the context of metal hydrides and in conjunction with our subsequent discussion. The selection of the system and crystal structure (A.1) is determined by which physical facts and regularities one wishes to understand. Our selection has been determinedly the interrelation between the electronic structure and the crystal structure, e.g. why is the dihydride structure favored even though it usually involves a metal lattice change. The calculation of the crystal potential and its form is generally determined by the method used to solve Eq. 7, e.g. if one is going to use a plane wave expansion for the wave function,

then a Fourier expansion of the potential is appropriate. Since the metal hydrides of interest involve a transition metal (3d, 4d, 5d, 4f, 5f) which have both tightly bound and fairly free electrons, one of the angular momentum based procedures is more appropriate. The majority of calculations have employed the APW¹² method although the KKR method¹³ and others¹⁴ have also been used. The potential prescription is a compromise between physical realism and computational convenience. The initial crystal potential is usually derived from atomic calculations.¹⁵ The atoms should be as representative as possible of the situation in the solid. This may mean some change in the atom to prepare it for the solid. Some such common changes are to choose a configuration more consistent with the solid e.g. a configuration of 3d²4s for scandium, rather than the atomic one of 3d4s². Some attempt should be made to fit the atom into the solid. Two such procedures involve either renormalizing the atom¹⁶ or making a superposition¹⁷ of neighboring atomic charge densities within a unit cell of the crystal. It is also advisable to use the same exchange-correlation potential for the atom as for the solid if one is not going to self-consistency (C'). The options for the exchange-correlation approximation have been discussed above, with some form of a local potential derived from $\rho^{(1/3)}$ usually being used. It has been an empirical observation that a choice of $\alpha = 1$ gives results for non-self-consistent calculations which compare favorably with more physically motivated choices of α for self-consistent calculations.¹⁸ For computational simplicity a "muffin tin" approximation to the potential is usually made.¹⁹ In this approximation the potential is spherically averaged inside a sphere of radius R_m centered on the atomic positions.

The choice of the sphere radii should be such that a reasonable approximation to the true potential is obtained. This usually involves trying to fill space as much as possible since the potential outside the spheres is taken to be of constant value -- usually its average value in this region. Removing the muffin tin approximation involves more accurately representing the true potential by a variety of extensions: 1) allowing the spheres to overlap,²⁰ 2) representing the potential outside the spheres by means of a Fourier expansion,²¹ 3) the use of strategically placed interstitial spheres²² and, 4) representation of the non-spherical parts of the true potential inside the spheres.²³ All these extensions require more computational effort and usually only change the details. Depending on how good the initial assumption (B) the same conclusion may be made concerning self-consistency (C').

The methods of solving Eq. 7 are varied but if done correctly the results are independent of the method. We do not wish to dwell on technique since these procedures have been adequately discussed elsewhere.¹² We shall only say that the usual procedures using scattering type methods (APW, KKR, ASW,¹⁴ ASA,²⁴ etc. using a combined angular momentum/plane wave representation combined with the muffin tin approximation) give a useful picture of the transition from atoms to solids in terms of the atomic-like angular momentum components (l) and a somewhat less well described charge outside the "atomic" spheres in the region of flat potential ρ_0 . This representation is particularly suitable for calculating the superconductivity parameters.²⁵

Step D has been discussed in general elsewhere²⁶ and in

specific will form the rest of this paper. In step E such variations include 1) changing the metal, M, and repeating the procedure -- this has been employed successfully by Gelatt²⁷ and coworkers, the author²⁸ and others;²⁹ 2) changing the crystal structure to see what influence this has, -- one can invoke experimental non-attainable ones to assess trends; and 3) varying the lattice parameter to study pressure dependencies.³⁰ The variation of parameters is only limited by the patience of the investigator.

III. THE PALLADIUM AND NICKEL HYDROGEN SYSTEMS

The palladium-hydrogen system is probably the most extensively studied system³¹⁻³³ and this conference hardly reflects a diminution of this interest.

The bandstructures of palladium and nickel hydrides were first calculated in 1972 in conjunction with the First Hydrogen in Metals Meeting in Julich.³² Also at that meeting the occurrence of superconductivity in PdH_x ($x > 0.80$) was reported by Skoskiewicz.³⁴ Since that time there have been over a dozen bandstructure-related publications^{14,35-43} for these systems stimulated largely by this discovery. A summary of these calculations is given in Table I. There are basically six calculations with various extensions and applications. The most extensive investigations are those of Papaconstantopoulos and co-workers,^{38-40,43-4} who have investigated the effects of different exchange potentials, self-consistency, and charge transfer. Their results are probably the "best" existent. Their bandstructure results for Pd and PdH are given in Figures 1 and 2, respectively. As has been pointed out before,²⁸ the major effect of the introduction of hydrogen into the lattice is the formation of a bonding and antibonding combinations of the hydrogen s-functions with the metal 4s function along with hybridization with the palladium d and p electrons. The unhybridized d-states remain unaffected. The bonding combination is significantly lowered below the d states as is seen along the band $\Gamma 1-A1-X1-Z1-W2'-Q2-L2'-A1-Z1-\Gamma 1-K1$. In fact the states at $L2'$ and along A , which have p-like character about the palladium, are lowered by over 5 eV from above the Fermi energy in Pd to almost below the d-bands in PdH. Effects of this

size are observed in all the calculations and are a true physical manifestation of the effect of the hydrogen. The lower (bonding) band has been seen in photoemission at about 5.5 eV below the Fermi energy.³⁶ The position of this band varies from calculation to calculation, ranging from -5.6 eV to -8.2 eV, which is a reflection of the various approximations and thus sets the level of confidence for this feature. A comparison of the separations of various energies is given in Table II. One sees that to within a difference of ~ 0.1 Ry or ~ 1.5 eV the calculations all agree. The calculations of GEW show greater s and d bandwidths due to the use of the renormalized atom potential. The calculations of ZM and NSC_B as well as SC_B show a greater s-d separation since the hydrogen exchange constant ($\alpha \approx 1.0$) is greater than that of palladium ($\alpha \approx .7$). The effect of a starting configuration of d^{10} vs d^9 s (with the same exchange potential) is somewhat less, as the columns SWIT and GF indicate. The d-band width is remarkably constant. The major differences consist of the position of the bonding combination (peak and upper extreme) relative to the d-bands and the Fermi energy. Overall there seems to be no fundamental disagreement of the bandstructure results.

The major difference between the results for NiH and PdH is in the position of the bonding peak. The densities of states at the Fermi energy agree reasonably well although the statistics are bad and the LCAO fit indicates a much larger value as does experiment. Kulikov⁴⁵ uses non-touching spheres and arrives at a much lower interstitial average than seems reasonable. This point will be discussed later.

Density of states plots for Pd and PdH are shown in Figures 3

and 4a respectively. The bonding states are clearly seen at 0.1 Ry and there appears to be a gap between them and the d-bands although Figure 2 shows overlap at L. The d-bands are significantly narrowed and changed in detail although one sees similar features such as a large peak at the top of the d-bands. The Fermi energy is raised to accommodate the added hydrogen electron, but not as far above the top of the d-band as a rigid band filling of the palladium density of states would predict (indicated by the arrow marked 11 in Fig. 3). This is due to the addition of empty bonding and antibonding states in the valence band region. These antibonding states are associated with the band through the upper Γ_1 - Δ_1 - X_1 - W_2' - Q_2 - L_1 - A_1 - Γ_1 - E_1 - K_1 - Γ_1 . They are seen in Figure 4a at ~ 1.0 - 1.2 Ry. The density of states at the Fermi energy varies from 0.2-0.62. The low values of references 35 and 37 are primarily due to the limited statistical sampling of k space associated with these calculations which also manifests in the crude and noisy densities of states. The high value 0.62 (Ref. 38) was subsequently revised by improved statistical sampling as was the low value. A value of 0.44-0.50 seems to be indicated.

Although the bonding and antibonding bands seem clearly indicated in Figure 4a there is additional hydrogen s-character throughout the region of interest, particularly at the Fermi energy whose value is increasing while the total density of states at the Fermi energy is falling. The s-character on the Pd site is shown in Figure 4c and mirrors the hydrogen s-character. A comparison of Figures 4a, b and c shows a significant fraction of the density of states is un-

accounted for. Some of this unaccounted for charge is due to the partitioning of the real space cell into spheres and intersititial region, but a sizeable portion is of palladium d-character as shown in reference 39. A more detailed analysis of the charge is given in Table III from our calculations. The calculations indicate an increase in the charge in the hydrogen sphere. The differences between SWIT and SC_A is probably due to the relative sphere sizes -- smaller hydrogen, larger palladium in SC_A . Again GEW's use of a different potential form gives quantitatively different results. The d-charge in the palladium sphere actually increases over the atomic sphere as does the p-charge while the s-charge remains the same. The loss from the palladium sphere is more due to a loss of the charge thrown in from the atomic superposition than to a transfer to the hydrogen. In all cases there is more charge associated with the hydrogen sphere than the comparable atomic case. This is in spite of the fact that over 0.60 (0.36 holes + 0.24) of an electron is associated with raising the Fermi energy above its comparable value in palladium.

An illustrative example of the approach of varying the hydrogen concentration is given in Figure 5 and Table IIT. This represents an extension of some of our earlier work. Since a bandstructure calculation requires crystal symmetry only certain concentrations are obtainable. We have chosen cubic unit cells of dimension a_0 and $2a_0$ with various occupancies corresponding to PdH_0 , $Pd_{3/2}H$, Pd_4H , Pd_4H_3 and PdH . (The recently observed order $\sim$ in the $MoNi_4$ structure corresponding to Pd_5H_4 piques ones interest.)⁵³ The same palladium and hydrogen potential was used as in PdH ,

although in the true situation the potential should vary with composition. One sees the development of states below the d-band which fall with increasing hydrogen concentration. For Pd_{32}H the decrease is small and few new states fall below the top of palladium d manifold whose width, as represented by X_5 - X_3 , remains unchanged. One would have to accommodate the added electron near the Fermi level. Even though Table III shows that there is greater than 0.50 electron associated with the hydrogen of that >0.45 is in the low-lying structure. At the composition Pd_4H , however, the state L_2' which is fourfold degenerate splits into R_2' and R_{15} in this structure with the singly degenerate state R_2' falling almost 5 eV compared to PdH . This represents a second nearest-neighbor hydrogen-hydrogen interaction since the hydrogens are now only at the centers of the cubic cells. The 8th like nearest-neighbor interaction of Pd_{32}H , when the hydrogens are $2a_0$ apart, is down about a factor of 5. The changes between Pd_4H and Pd_4H_3 and PdH is just the addition of more second nearest-neighbor interactions (increasing the weight of the top of the structure from 1 to 3 back to 4 again) and a increase in level density in the low-lying structure corresponding to the addition of hydrogens. The bottom of the band falls due to first neighbor hydrogen and metal interactions. Our picture is one of a low-energy structure which splits from the bottom of the band and whose intensity grows with increasing hydrogen concentration. This growth is primarily due to the inclusion of more metal character and not more hydrogen character. This picture differs from that of GEW in which a localized hydrogen state (low in energy) forms for low concentration which broadens into a band.

Table III adds further insight in the development of this structure. For PdH_0 there is only 0.17 electron in the hydrogen sphere with 0.27, 0.20 and 8.27 electrons of s, p, and d character respectively, in the palladium sphere. Since the Pd_{32}H calculation involves 160 d-states/k point we are not in a position to talk about the palladium site but symmetry allows us to find the hydrogen-associated levels. We have found over 0.50 electrons associated with the hydrogen site with over 0.45 electron in the low-lying structure. For Pd_4H things remain fairly constant in the palladium sphere but the charge increases to 0.60 electrons in the hydrogen sphere with 0.52 in the "first band." There is perhaps some increase in d-character in the palladium, over 25% of the low-lying structure is associated with the palladium sphere and the majority is d-like. Nevertheless the biggest change is at the hydrogen site where the perturbation is. For Pd_4H_3 the hydrogen site grows to 0.54 electrons in the low structure. There are dramatic increases in the palladium sphere again (largely d and more in the palladium sphere than in the hydrogen sphere) but considering the relative sizes, 6:1, this is not unreasonable. This admixture is necessary to observe x-ray emission from palladium core levels in this region.⁴⁶ There always is some arbitrariness in partitioning of the charge. For Pd_4H each hydrogen has to share its electron with four palladiums and three interstitial spheres while for PdH there is a compression of the charge within the unit cell. Nevertheless by the time we reach PdH the trends have continued with over half the low-structure charge in the palladium sphere and the hydrogen sphere containing only slightly

more charge than the starting superposition (the charge in palladium sphere has increased to only slightly less (1.5%) of the valence charge) so it would appear the results are fairly self-consistent. All calculations indicate a buildup of charge in the hydrogen sphere with some diminution of charge in the metal sphere. One could say that the PdH_0 calculation lost the most charge and is the least self-consistent but such reasoning may be specious since the palladium potential was derived for PdH . The trends are the significant features: buildup of low-energy structure (magnitude not width after Pd_4H_3) about 0.50 electrons associated with the hydrogen in the low structure and 1.0 electron associated with the palladium.

IV. THE TITANIUM HYDROGEN SYSTEM

There have been four calculations summarized in Table IV of the hydrides of titanium.^{45,47,48} The calculations of Gelatt, et al.²⁷ are for a hypothetical monohydride having the sodium chloride structure and cannot be compared with the other three or with experiment. This series of monohydride calculations is useful in examining trends in level positions and binding energies while ignoring structural factors. The other three calculations for the observed cubic dihydride structure are quite similar. A comparison⁴⁷ of the band structure of face-centered cubic titanium to that of TiH_2 in the fluorite structure is given in Figs. 6 and 7, respectively, and shows the lowering of the hydrogen metal bonding band (as represented at the zone center by Γ_1) of over 4.5 eV. More significant is the introduction of the antibonding band formed from the two hydrogens in the unit cell at Γ_2' . Away from the zone center this state hybridizes with d states having the same symmetry, Δ_2' , X_3 , W_3 , K_3 , etc. The calculations vary somewhat in the position of Γ_2' relative to Γ_{25}' , the latter being approximately the Fermi energy in all calculations. Switendick finds Γ_2' about 1.75 eV below, Gupta less than 0.5 eV below and Kulikov almost 1 eV above Γ_{25}' . Gupta's d bands are lower due to her assumption of the $d_{s^2}^2$ atomic configuration. Kulikov's potential prescription differs from ours in several features. His sphere radii are non-touching and only 37% of the cell volume is filled by spheres whereas our choice yields 49%. His value of the constant potential outside the spheres is -1.853 Ry while ours is -1.38 Ry. Although different procedures are used to determine this value, our value using his radii and our prescription is -1.42 Ry. This potential does raise the

value of Γ_2' relative to Γ_{25}' by about 1 eV. Kulikov chooses his sphere radii to give minimum jumps at the sphere surfaces. For our choice of (65:35) $(a\sqrt{3})/4$ and using our averaging procedure we get jumps of 0.22 Ry and 0.38 Ry at the metal and hydrogen spheres respectively. To minimize or equalize the jumps the hydrogen sphere should be made larger not smaller. Using our averaging procedure with Kulikov's spheres we obtain jumps of 0.26 Ry and 0.45 Ry respectively, a change in the direction indicated. Kulikov's spheres are 30% smaller than ours; this may account for the elevation of the Γ_2' state.

Our model for dihydride formation and stability involves the ability to fill these new low-lying antibonding states with some of the added hydrogen electrons and the relative position of these levels relative to the Fermi level. This position is related to the hydrogen-hydrogen spacing which is related to the interstitial site and the metal atom size such that VH_2^+ (with a metal atoms size of 1.34 Å) is more unstable than TiH_2 (with a metal radius of 1.47 Å). Kulikov's antibonding band falls relative to the d-band upon decreasing the lattice constant, contrary to our results. I shall return to these points in the discussion section.

All calculations indicate the Fermi energy intersects the bandstructure in the A direction twice, producing two pockets of holes from the orbitally-degenerate empty A_3 states. These states are split by the tetragonal distortion to lower the net crystal energy. The filling and emptying of these states by vanadium additions or hydrogen removal respectively is consistent with the phase diagram.⁵⁵ All calculations show a peak at or above the Fermi energy. The statistics of

Gupta's density of states are the best and she has a sharp narrow peak at the Fermi energy. Her density of states values are larger than the specific heat derived value, the latter was obtained from a sample composition $\text{TiH}_{1.97}$ which has already undergone the tetragonal distortion which reduces the experimental value. The peak in the density of states due to the bonding-antibonding hydrogen combination, observed 6.0 to 8.0 eV below the Fermi level, may be related to the hydrogen-induced peak observed by Eastman.⁴⁹ The charge distribution from our calculations is given in Table V. We see that there is less than a quarter of an electron in the calculation without the hydrogen potential (TiH_0) which increases by over a factor of four upon the addition of the hydrogen. The growth in charge upon adding the hydrogen potential and the two electrons is a net gain in the palladium sphere of less than 0.30 electron. Again there is as much charge in the palladium sphere associated with the low energy structure as in each hydrogen sphere.

V. LANTHANIDE AND OTHER GROUP III HYDRIDES

The first published energy band calculations for hydrides were for rare di- and trihydrides.²⁸ The results showed, as in the palladium and titanium systems, that for the monohydride system the bonding metal hydrogen band was lowered but the added electron went into the d-band states at the Fermi energy. The antibonding metal-hydrogen band was too high to be occupied by the four valence electrons. In the case of the dihydride the antibonding hydrogen-hydrogen band lay below the d-bands and could hold the two electrons added by the hydrogens. Furthermore, in the case of the cubic trihydride where in addition to the tetrahedral sites the octahedral site is occupied, another band (Γ_1 at zone center) is added below the d-bands and can be filled. This band is characteristic of an antibonding tetrahedral-octahedral hydrogen state. The results are summarized in Figure 8. The results are capable of explaining the semiconducting behavior of the trivalent trihydrides⁴ in terms of a gap between the occupied valence bands and the d-like conduction bands. Figure 8c also shows that a gap would exist for the divalent dihydride. Additional calculations for cubic di- and trihydrides confirm this picture and show the sensitivity of the antibonding levels to hydrogen separation. There recently have been calculations of ErH_2 ⁵⁶ and TbH_2 .⁴⁸ The bandstructures have not been published but agree with the results of Figure 8.

Peterman et al.⁵⁷ have recently calculated the bandstructures of ScH_2 and YH_2 . Their calculations are self-consistent and used the Hedin-Lundquist¹⁰ local density exchange approximation. Their band-

structure is shown in Figure 9. The dashed lines show the results of the first iteration using this exchange approximation and an atomic d^2s configuration. One sees little quantitative difference between Figures 9 and 8c. The major effect of self-consistency is to raise the bonding and antibonding hydrogen-like states 1.0 eV for the former and 2.0 eV for the latter. This is primarily due to the increase of charge associated with the hydrogen sphere as compared with the initial assumptions. This effect is even more dramatic for ScH_2 where Γ_2' rises over 2.5 eV while achieving self-consistency and in fact goes through the Fermi energy and empties. Since we attribute stability of the dihydride structure to the ability to accommodate the added hydrogen electrons in these antibonding states, then the emptying of these hydrogen-associated states and the filling of d-band states account for the relative instability of this dihydride and account for the large region of solubility of hydrogen in scandium before the hydride phase forms, and accounts for the fairly large deviation of the upper phase boundary from a stoichiometric dihydride (1.4 vs 2.0). A comparison of Figures 8 and 9 shows considerable similarity between different workers and approximations, the major difference again being the position of the bonding-antibonding combination relative to the d-bands. This similarity persists for all dihydride band structures and justifies the application of a rigid band approach in the d-manifold as has been done in the $Ti_{1-x}V_xH_2$ system.^{47,58} However the low-lying structure owes its existence to the introduction of the hydrogens and is absent in the parent metal. This structure has been seen in x-ray emission,⁵⁹ photoemission⁴⁹ and optical studies.⁶⁰ The interrelation of these studies and the band-

structures will be discussed further by weaver.⁶⁰

VI. DISCUSSION AND CONCLUSIONS

Based on our non-self-consistent results but using a similar procedure for all the systems treated, we have calculated the band structures and densities of states for a series of dihydrides. The results are summarized in Figures 10 and 11 for the 3d and 4d transition series respectively. In the upper part of the figure, the transition metal size, which determines the hydrogen-hydrogen spacing in the lattice, is plotted. Several effects are seen and their influence on the energetics of the system will be discussed. The levels X1 and X5 are related to the transition metal d-bands and increase slightly as the atomic volume decreases. The width is fairly constant with the top state X5, rising perhaps more rapidly than the bottom, X1. The wider 4d manifold (as compared to the 3d) is well known and appears in Gelatt's²⁷ survey. The top of the antibonding band (Γ_2') is below the d-bands in the rare earths and yttrium, overlaps the d-bands in the middle of the 3d series and is above the d-bands in nickel⁴⁵ and palladium.³⁵ It is the filling of these states that the dihydride structure favors. This level rises as the hydrogens get closer together. This systematic broadening of the bonding-antibonding splitting and its elevation have been observed by Weaver in photoemission and optical studies. Both this rise and the Fermi energy rise increase the average one-electron energy. Finally, at about chromium and tungsten, this level is very close to or above the Fermi level and can barely or no longer be filled. This accounts for the instability or lack of formation of these dihydrides. Recall that the self-consistent calculations of Peterman et al. and those of Gupta gave this level 1-2 eV higher.

In our earlier work we set a criterion of $E_F - \Gamma_2' > .10$ Ryd for the condition of stability of the dihydride. This was arrived at specifically for our calculations and should not be taken as inflexible since the calculations clearly show variations greater than this magnitude.

The physics of the conclusions regarding hydride stability is very similar to those of Gelatt.²⁷ The introduction of hydrogen into the metal lattice is a very large perturbing feature. This results in the lowering of certain states of the host structure which contributes to hydride stability. This lowering decreases as one goes to the right in the transition series and supplements an increase of the d electron energy and rising Fermi energy. The unique feature of the dihydride structure is that many states are lowered from above the Fermi energy to below it and hence can be filled with the added electrons. Because of the antibonding nature of this state, it is very sensitive to hydrogen-hydrogen spacing. It is not the specific position of the Γ_2' level but rather the center of gravity or average energy of these states which matters, and the latter's increase with decreasing hydrogen-hydrogen spacing. Similar conclusions were reached regarding the antibonding band formed from the octahedral-tetrahedral hydrogens in the trihydrides. These are already closer together than the tetrahedral hydrogens by 15% and this state, even more sensitive to hydrogen spacing, accounts for the lack of occurrence of SCH_3 .

Although we have only discussed structures based on face-centered cubic metal lattices, we have done calculations for CrH and MnH where the metal lattice is hexagonal and for prototypic hydrides based on a body-centered cubic lattice such as V_2H and UH_3 . All

these hydrides display common features: a fairly low-lying set of states associated with the hydrogens and the addition of electrons at the Fermi level within the d-states of the metal. Calculations based on filling all the octahedral sites for VH_3 ⁵¹ show that at least two electrons must be accommodated at the Fermi energy raising the Fermi energy in our calculations by 3 eV. The situation is even worse when the tetrahedral sites are filled to give VH_6 , with three electrons going in at the Fermi energy and raising it almost 5 eV. When one considers the neighbor spacings in the body-centered cubic structures as shown in Figure 12, for vanadium the nearest-neighbor octahedral distance is 1.5 Å and the tetrahedral distance is 1.1 Å. If we assume that a minimum hydrogen-hydrogen spacing of 2.10 Å (as was found for the fluorite structure) and that tetrahedral site occupancy is preferred, we obtain the results shown in Table VI. Here we assume a body-centered metal lattice with touching spheres based on an observed bcc metal phase, and then catalog the tetrahedral distances d_t . We see that V, Nb and Ta do not achieve a distance of greater than 2.1 Å until fourth nearest-neighbor hydrogens and chromium hasn't even then. The last three columns give the observed hydride of highest hydrogen concentration and the number at that spacing. Vanadium, niobium and tantalum form monohydrides based on the distorted bcc lattice with a combination of d_4 and d_6 . Chromium forms hexagonal monohydride in the nickel arsenide structure with the minimum distance satisfied. Thorium could achieve a composition of ThH_3 with d_2 pairs in the faces of the cube but instead finds a better accommodation in the Th_4H_{15} structure (the greatest hydrogen to metal ratio attained in a hydride) by getting the second nearest neighbor closer. This structure of pairs in the faces

is found in UH_3 and presumably in the protactinium system. This involves considerable expansion of the metal lattice (20%) and is metastable with regard to the more complicated βUH_3 structure. This large metal lattice expansion is probably indicative of metal hydrogen bonds as had already been inferred for the thorium hydrogen system.⁶²

In conclusion, energy band calculations for metal hydride structures have shown the introduction of new states below the Fermi level of the metal. This introduction is particularly favored by the di- and trihydride structures since they are low and can be largely occupied. 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. The recently observed superlattice in the $\text{PdH}_{0.8}$ system, as well as the various bcc systems, appears particularly of interest.

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TABLE I. SUMMARY OF PALLADIUM HYDRIDE
AND NICKEL HYDRIDE CALCULATIONS

CALC	METHOD	POTENTIAL	α_M/α_H	SC	$N(E)$ (STATES/EV-CELL)	E_{PEAK}	REF.
PALLADIUM HYDRIDE							
SWIT	APW	OAP $D^{9.1}$	1/1	N	0.20		
	LCAO				0.45	-5.6	35
ZM	APW	OAP D^{10}	.707/1	N	0.24	-7.0	37
PAPA	APW		.707/.777	YR			
	QUAD ₂₀				0.62		38
	QUAD ₈₉				0.49	-7.1	39
	LCAO				0.46		40
GF	APW	OAP D^{10}	1/1	N	0.50	-7.6	41
GEN	KKR	RFA	--	N	--	-8.2	27
WKG	ASH	LDA	--	Y	0.52	-6.6	14
	EXPERIMENT				0.33 ^a 0.64 ^b	-5.4 ^c	
NICKEL HYDRIDE							
SWIT	APW	OAP $D^{9.1}$	1/1	N	0.91	-8.0	35
	LCAO				1.82		
K	MH	OAP	1/1	N	1.07	-9.6	
	EXPERIMENT				1.96 ^d		

^a REFERENCE 50

^b REFERENCE 51

^c REFERENCE 36

^d REFERENCE 52

TABLE II. COMPARISON OF ENERGY SEPARATIONS
OF PDH EXPRESSED IN R_V

	SWIT ^a	ZH ^b	NSC _A ^c	SC _A ^c	NSC _B ^d	SC _B ^d	NSER ^c	GF ^e	GEW ^f	
$X'_4 - \Gamma_1$	0.868	0.997	0.880	0.867	0.953	0.922	0.871	0.90	0.95	S BANDWIDTH
$X_5 - X_3$	0.307	0.353	0.328	0.333	0.323	0.332	0.313	0.29	0.43	
$\Gamma_{12} - \Gamma'_{25}$	0.081	0.103	0.091	0.092	0.083	0.087	0.084	0.08	0.12	D BANDWIDTH
$\Gamma'_{25} - \Gamma_1$	0.423	0.631	0.538	0.546	0.632	0.627	0.541	0.50	0.46	S-D SEPARATION
$\Gamma_1 - \Gamma_1$	1.558	1.462	1.533	1.554	1.493	1.519	1.550	---	---	
$X_1 - X_1$	0.910	~0.98	0.929	0.936	0.944	0.950	0.904	---	---	S-BAND SEPARATION
$L_1 - L_1$	0.824	~0.85	0.746	0.754	0.734	0.744	0.754	---	---	

^a $a_H = a_{PD} = 1.0$; REFERENCE 35.

^b $a_H = 1.0$, $a_{PD} = 0.707$; REFERENCE 37.

^c $a_H = 0.7772$, $a_{PD} = 0.702$; REFERENCE 39

^d $a_H = 0.978$, $a_{PD} = 0.702$; REFERENCE 39

^e REFERENCE 41.

^f REFERENCE 27.

TABLE III. COMPONENT CHARGES FOR VARIOUS
PALLADIUM HYDRIDE CALCULATIONS

CALC	Q_M^A	Q_M^O	Q_H^A	Q_H^O	Q_M^S	Q_M^P	Q_M^D	Q_M^X	ΔQ_M	Q_H^X	ΔQ_H
SWIT											
PdH	44.68	45.29	0.50	0.65	0.26	0.29	8.57	45.15	-0.14	0.69	+0.04
LOW					0.18	0.13	0.67			0.54	
Pd ₄ H ₃					0.26	0.26	8.48			0.60	
LOW					0.15	0.10	0.47			0.54	
Pd ₄ H					0.26	0.22	8.33			0.60	
LOW					0.04	0.04	0.13			0.52	
Pd ₃₂ H										>0.50	
LOW										0.45	
PdH ₀	44.68		0.00	0.15	0.27	0.20	8.27		-0.58	0.17	
PAPA											
SC _A									-0.29		+0.14
GUPTA			0.49							>0.67	
GEW			0.47					44.76	0.01	1.00	0.79

TABLE IV. SUMMARY OF TITANIUM HYDRIDE CALCULATIONS

CALC	METHOD	POTENTIAL	a_M/a_H	SC	$N(E)$ (STATES/ eV/CELL)	E_{PEAK}
SWIT ^a	APW LCAO	OAP d^3s	1/1	N	1.52	-8.0
KUL ^b	MH	OAP d^2s^2	1/1	N	0.95	(-6.0)
GUP ^c	APW	OAP d^2s^2	1/1	N	~3.46	(-6.0)
GEW ^d	KKR	RFA	---	N		
[TiH]						
	EXPERIMENT				1.91	(-5.0)

^a REFERENCE 47^b REFERENCE 45^c REFERENCE 48^d REFERENCE 27^e REFERENCE 54^f REFERENCE 49

TABLE V. COMPONENT CHARGES FOR TITANIUM DIHYDRIDES

CALC	Q_M^A	Q_H^O	Q_H^A	Q_H^O	Q_M^S	Q_M^P	Q_M^D	Q_H^X	ΔQ_M	Q_H^X	ΔQ_H
TiH ₂	20.52	21.10	0.47	0.58	0.16	0.28	1.59	19.96	-0.56	0.83	0.25
LOW					0.15	0.23	0.50			0.76	
TiZ ₂	20.52			0.11	0.22	0.23	1.29			0.20	
TiH									-0.04	1.14	0.92

FIGURE CAPTIONS

1. Energy bandstructure of palladium from reference 39.
2. Energy bandstructure of palladium hydride.
3. Density of states of palladium.
4. Density of states of a) palladium hydride, b) hydrogen s-like density of states, c) palladium s-like density of states.
5. Evolution of low-lying structure as a function of hydrogen composition.
6. The energy bands for cubic titanium using the same titanium potential as for TiH_2 .
7. The energy bands for titanium dihydride, TiH_2 .
8. Energy bandstructures for yttrium hydrogen systems.
9. The energy bands of YH_2 according to Peterman, et al.
10. Energy levels for 3d transition metal dihydrides.
11. Energy levels for 4 transition metal dihydrides.
12. Tetrahedral distances in the body-centered cubic lattice.

a. Energy bands for cubic YH_3 (fcc Y with lattice constant appropriate to YH_3).

c. Energy bands for cubic YH_3 (CaF_2 structure).

d. Energy bands for cubic YH (NaCl structure).

e. Energy bands for cubic YH_3 (BiF_3 structure).

● Metal atoms

○ Tetrahedral interstices