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Heat of formation and band structure of binary and ternary metal hydrides

R. Griessen and A. Driessen
Natuurkundig Laboratorium, Vrije Universiteit te Amsterdam, NT-1007-MC Amsterdam, The Netherlands

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The heat of formation, ΔH, of metal hydrides is empirically found to be linearly related to a characteristic energy ΔE of the electronic band structure of the *host* metal. Independently of the position of the host metal in the Periodic Table (simple metals, noble metals, transition metals, actinides, and rare earths) we found $\Delta H = \alpha\,\Delta E + \beta$, with $\Delta E = E_F - E_s$, $\alpha = 29.62$ kJ/eV mol H, and $\beta = -135$ kJ/mol H (E_F is the Fermi energy and E_s is the center of the lowest band of the *host* metal; ΔH is expressed in kJ/mol H and ΔE in eV). Assuming that this relation also holds for ternary metal hydrides we used the (simple) tight-binding coherent-potential-approximation model of Cyrot and Cyrot-Lackmann to evaluate the characteristic energy ΔE of $A_{y_A}B_{y_B}$ alloys where A and B are both nonsimple metals. The values of ΔH derived from the calculated ΔE are in good agreement with existing experimental data on the heat of formation of ternary metal hydrides.

I. INTRODUCTION

The heat of formation ΔH, i.e., the amount of heat absorbed or liberated during hydrogen uptake by a metal has been measured for many metal-hydrogen systems. The knowledge of ΔH is of great importance for practical applications of metal-hydrogen systems concerning energy storage since the dissociation pressure p_{H_2} for two-phase metal hydrides is related to ΔH via the van t'Hoff relation

$$\ln p_{H_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}\,, \tag{1}$$

where ΔS is the entropy change for H_2 absorption and R is the gas constant. Metal hydrides with negative heat of formation dissolve large quantities of hydrogen while systems with $\Delta H > 0$ dissolve hydrogen only in very small quantities at moderate pressures.

A summary of experimentally determined heat of formation of binary metal hydrides MH_x is given in Fig. 1 as a function of the position of the host metal in the Periodic Table. As pointed out earlier by McLellan and Oates[1] a certain regularity is observed in the long series (${}_{19}$K to ${}_{32}$Ge, ${}_{37}$Rb to ${}_{50}$Sn, and ${}_{55}$Cs to ${}_{82}$Pb) of the Periodic Table. The most negative ΔH are found for the alkaline earths while large positive values are observed for metals on the right of the series. Slightly negative values for ΔH are also observed for ${}_{28}$Ni and ${}_{46}$Pd. Platinum, although belonging to the same group as Ni and Pd, has however a large positive heat of formation and absorbs a negligible amount of hydrogen. Antonov *et al.*[10] have shown that PtH is not formed at hydrogen pressures below ~65 kbar at room temperature. In a recent review article Ponyatovskii *et al.*[6] reported that other late $5d$ metals (${}_{75}$Re,${}_{76}$Os) do not form hydrides below ~70 kbar.

Another marked difference between the thermodynamical properties of two metal hydrides belonging to a same column of the Periodic Table is found for the alkaline earths. From the data of Galaktionowa[4] one estimates that the heat of formation of BeH_x is approximately $+38$ kJ/mol H while for MgH_x (Ref. 3) it is -37 kJ/mol H. Consequently magnesium readily forms a dihydride, while Be does not react directly with hydrogen.

Several attempts have been made to derive ΔH from *a priori* calculations. Using a pseudopotential formalism and nonlinear theories for the screening of the protons, Popovicz *et al.*[11] calculated the heat of solution of hydrogen in Al and Mg. Their theoretical values ($\Delta H = 43$ kJ/mol H for Al and -4.8 kJ/mol H for Mg) are in qualitative agreement with experimental data.

Switendick[12] considered the electronic band structures

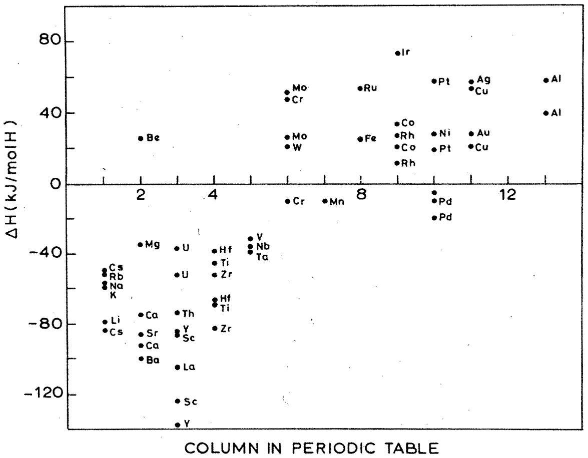

FIG. 1. Heat of formation of binary metal hydrides MH_x. The data are from McLellan and Oates (Ref. 1), Lee (Ref. 2), Mueller, Blackledge, and Libowitz (Ref. 3), Galaktionowa (Ref. 4), and Buschow, Bouten, and Miedema (Ref. 5). Some data were evaluated from high-pressure work (references given by Ponyatovskii *et al.* in Ref. 6) using the equation of state for hydrogen at high pressures (Refs. 7–9). For systems where the heat of solution ($x \rightarrow 0$) differs markedly from that of concentrated alloys, mono-, di-, or trihydrides, several values are indicated for the same metal.

of stoichiometric compounds such as YH, YH_2, and YH_3 and found that for di- and trihydrides a new band is formed below the Fermi energy. The position of this extra band determines the stability of the higher hydrides. Since the position of this new band depends mainly on the hydrogen-hydrogen separation, Switendick[13] proposed that dihydrides are stable when the H—H distance exceeds ~ 2.1 Å. As discussed by Gupta and Burger,[14] Switendick's criterion is, however, not sufficient.

The most comprehensive discussion of the heat of formation of substoichiometric metal-hydrogen systems is probably that of Gelatt *et al.*[15] According to these authors ΔH is determined by four factors: (i) the position of the metal-hydrogen bonding band which contains approximately $2x$ electrons[16,17] in MH_x, (ii) the lowering of the metal d bands by the attractive proton potential, (iii) the filling of empty states at the Fermi energy, and (iv) the Coulomb energy due to the increased charge density in the vicinity of the protons. Using renormalized-atom potentials, Gelatt *et al.* evaluated the four contributions mentioned above and found reasonable agreement with the experimental values for ΔH. The agreement was improved later by carrying out self-consistent calculations[18,19] of the cohesive energies of metal-hydrogen compounds MH.

Since calculations of the heat of formation of more complicated metal-hydrogen systems (for example, ternary metal hydrides such as $LaNi_5H_x$, Mg_2NiH_x, or $FeTiH_x$) would require considerable computing efforts, Nørskov[20] proposed recently to use an effective-medium theory for the calculation of ΔH. Although this method is simpler than a full band-structure calculation, the generalization to alloy systems is not obvious.

In parallel to these theoretical activities, several semiempirical models have been proposed to explain the observed trends in stability and stoichiometry of metal-hydrogen systems. A review of these models has recently been given by Westlake.[21] One of the most successful models is that of Bouten and Miedema[22] based on Miedema's[23] original approach of the heat of formation of two transition metals. This model can be generalized to ternary metal hydrides $A_{y_A}B_{y_B}H_x$ by using the *rule of reversed stability*[24] according to which the heat of formation of an intermetallic compound $A_{y_A}B_{y_B}H_x$ is approximately given by

$$\Delta H(A_{y_A}B_{y_B}H_x) \cong \Delta H(A_{y_A}H_{x/2}) + \Delta H(B_{y_B}H_{x/2}) - \Delta H(A_{y_A}B_{y_B}) \; . \tag{2}$$

The last term on the right of Eq. (2) is the heat of formation of the metallic alloy. From a comparison of experimental ΔH's with predictions of Miedema's model, one finds that this model tends on the average to overestimate the heat of formation of metal hydrides. This leads to substantial errors in the equilibrium plateau pressures since the hydrogen equilibrium pressure varies exponentially with ΔH [see Eq. (1)]. Furthermore, the validity of the physical basis of the model has been criticized by Williams, Gelatt, and Moruzzi.[25,26]

The objective of the present work is to incorporate electronic band-structure information in a semiempirical model for the heat of formation of metal hydrides. In a first step we show that the heat of formation of *binary* metal hydrides MH_x is simply related to the difference $\Delta E = E_F - E_s$, where E_F is the Fermi energy and E_s the center of the lowest conduction band of the *host* metal (Sec. II). In a second step this model is generalized to the case of ternary transition-metal hydrides by using a theorem of Cyrot and Cyot-Lackmann[27] on the density of electronic states of transition-metal alloys (Sec. III B).

II. MODEL

To introduce our model let us consider the calculated energy levels of the Pd_6H octahedral cluster shown in Fig. 2. Compared to the levels of a Pd_6 cluster one see that the major effect of adding a hydrogen atom at the center of the cluster is to lower the lowest level with a_{1g} symmetry by approximately 4 eV. The other levels are only weakly perturbed because the amplitude of the corresponding eigenstates is very small at the interstitial site occupied by the hydrogen atom. Both in Pd_6 and Pd_6H the lowest level is occupied by 2 electrons. If one assumes that around each hydrogen dissolved randomly in a host metal M the electronic states are perturbed in a way similar to that shown in Fig. 2, then the hydride MH_x should have $2x$ electrons per metal atom in the low-lying states around -13.6 eV.

This has been shown explicitly by Bansil *et al.*[17] for the case of substoichiometric PdH_x alloys. However, since exchange and correlation as well as charge-transfer effects are important the total energy and consequently the heat of formation of a metal hydride MH_x cannot be calculat-

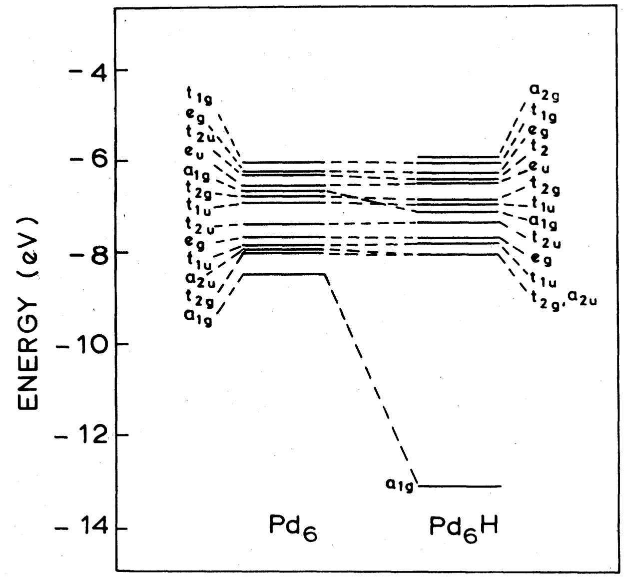

FIG. 2. Energy levels of an octahedral Pd_6 cluster (a) without and (b) with a hydrogen at the center of the octahedron. The method of calculation is the SCF-$X\alpha$-SW method, where the Schrödinger equation is solved self-consistently by means of the scattered-wave technique. The $X\alpha$ approximation is used for exchange and correlation effects. The potentials are of the muffin-tin type.

ed directly from these one-electron energies. For the early transition-metal hydrides the correction due to these effects may represent as much as ~80% of ΔH calculated from one-electron energies only (see Fig. 9 in Ref. 15). This means that the large energy gained by lowering $2x$ electrons from the lowest host-metal band to the low-lying band in the hydride MH_x is to a large extent compensated by the increase in Coulomb energy due to the increased charge density around the protons.[15] Despite these complications, the overall effect of the lowering of $2x$ electrons is to favor hydride formation.

From the results shown in Fig. 2 one sees also that the extra (hydrogen) electron in Pd_6H is accommodated in a level just above the Fermi energy of Pd_6. This increases the total energy of the cluster and is therefore a factor opposing hydride formation. A similar conclusion was reached by Wicke and Brodowsky[28] from an extensive analysis of the pressure-composition isotherms of palladium-based hydrides.

In an attempt to find a correlation between ΔH and the smallest possible number of band-structure parameters of the host metal we found that the experimental values for the heat of formation of binary hydrides MH_x could be reproduced reasonably well by the following simple relation:

$$\Delta H = \frac{n_s}{2}(\alpha \Delta E + \beta) \tag{3}$$

with

$$\Delta E = E_F - E_s \ ,$$
$$\alpha = 29.62 \text{ kJ/eV mol H} \ , \tag{4}$$
$$\beta = -135.0 \text{ kJ/mol H} \ .$$

In Eq. (3) n_s represents the number of electrons per atom in the lowest s-like conduction band of the *host* metal. E_s is the energy for which the integrated density of states of the *host* metal is equal to $\frac{1}{2}n_s$ electron per atom. Except for the alkali metals (for which $n_s = 1$) we have $n_s = 2$, and E_s is then the center of the lowest conduction band since even for transition metals this band has a predominantly s character with respect to the interstitial sites occupied by the hydrogen atoms.[15,29] [In the tight-binding approach this band results from the hybridization of the $(3z^2 - r^2)$ d orbital with the free-electron dispersion curve $\hbar^2 k^2/2m$.]

In Fig. 3 we indicate schematically the electron density of states and integrated density of states for the transition metals Y, Ru, Pd, and Ag (according to Ref. 30). For these metals E_s is the energy corresponding to an integrated density of states of 1 electron per atom. The Fermi energy is taken as the zero of energy.

The heat of formation ΔH determined from solubility measurements and/or from the plateau dissociation pressure in the pressure-composition isotherms of metal hydrogen systems are shown in Fig. 4 as a function of ΔE. For the metals from $_3$Li to $_{49}$In, ΔE is determined from the density-of-states curves of Moruzzi *et al.*[30] For the transition metals $_{49}$Ru, $_{76}$Os, $_{72}$Hf, and $_{40}$Zr, we used the band-structure calculations of Jepsen *et al.*,[31] for $_{75}$Re those of Mattheiss,[32] for $_{45}$Rh and $_{78}$Pt those of Ander-

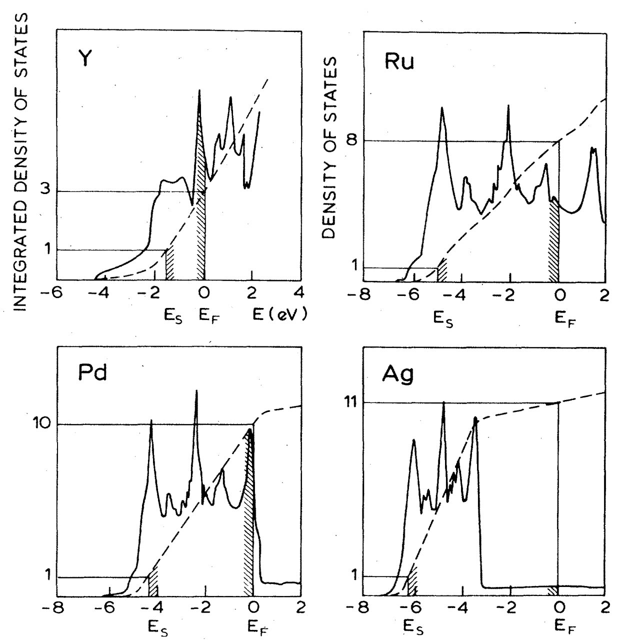

FIG. 3. Electronic density of states (——) and integrated density states (— — —) for four $4d$ metals. Shadowed lines give the position of E_s (right-hand shadowing) and E_F (left-hand shadowing).

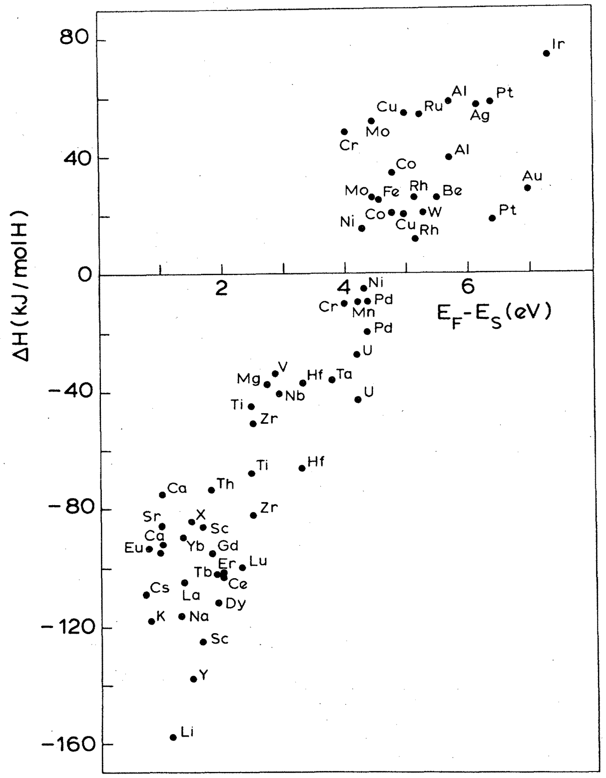

FIG. 4. Correlation between measured values of the heat of formation of binary hydrides MH_x and the band-structure energy $\Delta E = E_F - E_s$. For the alkali metals the plotted values are twice as large as the measured values because $n_s = 1$ (see text). For all other metals n_s, the number of electrons per metal atom in the lowest band with s symmetry at the interstitial site occupied by hydrogen is equal to 2 [see Eq. (3)].

sen,[33] for $_{90}$Th and $_{76}$Os the results of Iyakutti *et al.*,[34] for Ir both the results of Arbman and Hörnfeldt[35] and van der Veen *et al.*,[36] for $_{74}$W the calculations of Christensen and Feuerbacher,[37] for $_{41}$Nb and $_{73}$Ta those of Mattheiss,[38] for α- and ω-$_{22}$Ti and $_{40}$Zr those of Vohra *et al.*,[39] and for $_{39}$Y the results of Loucks.[40]

For the lanthanides we use the results of Glötzel and Fritsche[41] for $_{57}$La and γ-$_{58}$Ce, those of Pickett *et al.*[42] for α- and γ-$_{58}$Ce and those of Fleming *et al.*[43] for $_{57}$La. For $_{63}$Eu we averaged the results of Matsumoto *et al.*,[44] Andersen and Loucks,[45] and Kobayasi *et al.*[46] For $_{64}$Gd, ΔE was determined from the calculations of Harmon and Freeman.[47] For $_{64}$Gd, $_{68}$Er, $_{66}$Dy, and $_{71}$Lu we also used the early calculated density of states of Keeton and Loucks.[48] An estimate of ΔE for $_{65}$Tb was obtained from the results of Mackintosh[49] and Møller *et al.*[50] while the results of Johansen and Mackintosh[51] and Koelling[52] were used for $_{70}$Yb. For $_{71}$Lu we used the relativistic energy bands of Keeton and Loucks.[53] For the actinides ΔE was obtained from Koelling and Freeman[54] for γ-$_{92}$U, from Keeton and Loucks[53] for $_{90}$Th and $_{89}$Ac, from Iyakutti *et al.*[55] for $_{89}$Ac, and Skriver and Jan[56] for $_{90}$Th.

For $_{79}$Au we averaged the two density-of-states curves calculated by Christensen and Seraphin.[57] For $_{56}$Ba, we estimated ΔE from the band structure of Johansen[58] and for $_{32}$Ge we used both the results of Herman *et al.*[59] and of Joannopoulos and Cohen.[60]

For all metals, $n_s = 2$ except for the alkali metals where $n_s = 1$. For these metals the experimental ΔH have been multiplied by 2 to correlate them with the heat of formation of all other metals in Fig. 4. The most remarkable feature of the correlation shown in Fig. 4 is that irrespective of the "type" of the host metal (noble, simple, or transition metals, rare earths or actinides) the heats of formation of hydrides are reasonably well described by the same relation [Eqs. (3) and (4)]. Even the large positive value for the heat of formation[3] of GeH$_x$ is fairly well reproduced. (For GeH$_x$, $\Delta E \cong 10$ eV.)

Regarding the large differences mentioned earlier in the heat of formation of hydrides of metals belonging to certain columns of the Periodic Table, one can make the following comments.

(i) $_4$*Be*,$_{12}$*Mg*. As a result of the small atomic volume the value of ΔE for Be is larger than ~ 4.5 eV and this metal dissolves hydrogen endothermically. The atomic volume of Mg on the other hand is almost 3 times larger than that of Be and consequently ΔE is rather small. The difference between Mg and Be is furthermore slightly amplified by the non-free-electron character of the density-of-states curve of Be.[30]

(ii) $_{46}$*Pd*,$_{78}$*Pt*. The large difference in the heat of formation of these two metals is due to a significant difference in the width of the 4*d* and 5*d* bands. The same is true for Rh and Ir. Very recently Welch and Pick[61] proposed that the dependence of the heat of formation of binary transition-metal hydrides is mainly determined by the ratio μ/Ω of the shear modulus μ to atomic volume Ω of the metal host. For Pd we find $\mu/\Omega \cong 0.35$ and for Pt $\mu/\Omega = 0.41$. This small difference is unlikely to lead to a significant difference for the hydrides formation of Pd and Pt.

(iii) $_{77}$*Ir*,$_{45}$*Rh*,$_{78}$*Pt*,$_{25}$*Mn*. This series of materials has been measured by McLellan and Oates[1] using the same experimental technique for all metals. The large variation in ΔH is therefore very unlikely due to systematic errors. Here again one finds good agreement between measured values and the predictions of our simple model.

III. APPLICATIONS

In this section we shall discuss several applications of the model presented in Sec. II.

A. Binary hydrides

The analytical expression [Eqs. (3) and (4)] can be used to predict the heat of formation of binary hydrides MH$_x$ of metals which have not been investigated yet. In Table I we indicate the heat of formation for hydrides of $_{75}$Re, $_{76}$Os, $_{30}$Zn, $_{48}$Cd, $_{80}$Hg, $_{31}$Ga, $_{49}$In, $_{81}$Tl, $_{50}$Sn, $_{82}$Pb, $_{33}$As, $_{51}$Sb, $_{83}$Bi, and $_{89}$Ac calculated with ΔE values derived from band structure or density-of-states calculations.

B. Absorption of hydrogen in liquid simple metals

In agreement with the predicted values of ΔH given in Table I all the listed simple metals dissolve negligible amounts of hydrogen. Although some of the experimental data are still doubtful it seems that molten Pb and Sn absorb small amounts of hydrogen. Opie and Grant[68] found a heat of formation of 47 kJ/mol H for molten Pb. The results of Iwasé[69] lead to $\Delta H \cong 14$ kJ/mol H for molten Sn. The enhanced hydrogen solubility in molten Pb

TABLE I. Heat of formation of binary hydrides which have not been synthesized yet. The values for $\Delta E = E_F - E_s$ needed to predict the heat of formation ΔH are evaluated from the band-structure calculations indicated in the fourth column.

Element	ΔE (eV)	ΔH (kJ/mol H)	Reference
$_{14}$Si	~ 10	~ 161	60
$_{30}$Zn[a]	~ 6.7	~ 63	30,62
$_{31}$Ga	~ 6.0	~ 43	61
$_{33}$As	14.7	300	30
$_{48}$Cd[a]	~ 5.1	~ 16	30
$_{49}$In	4.8	-7	30
$_{50}$Sn	6.8	66	63
$_{51}$Sb	12.0	220	64
$_{75}$Re	5.4	25	32
$_{76}$Os	6.8	66	31
$_{80}$Hg[a]	~ 5.5	~ 28	65
$_{81}$Tl	7.4	84	66
$_{82}$Pb	8.7	123	67
$_{83}$Bi	~ 8.8	125	76
$_{89}$Ac	1.9	-79	53

[a] For these metals the *d* bands are relatively narrow and near the bottom of the nearly-free-electron conduction band. In this case E_s is not the center of gravity of the band originating at the lowest Γ_1 level. Contribution of the nearly-free-electron conduction band above the *d*-band complex must also be taken into account.

and Sn can be understood qualitatively by assuming that in the liquid state the electronic structure of a simple metal is well described by the free-electron model. The free-electron values $\Delta E_{\text{free electron}}$ for Pb and Sn are 5.72 and 6.15 eV, respectively. As a result of the absence of large band gaps these values are significantly smaller than the values listed in Table I for the corresponding crystalline metals and therefore lead to smaller ΔH values for the molten metals (34 kJ/mol H for Pb and 47 kJ/mol H for Sn as compared to 123 and 66 kJ/mol H for the solid metals).

In molten Al however, the measurements of Ramsley and Neufeld,[70] Opie and Grant,[71] and Sharov[72] indicate that the heat of formation of AlH_x in the liquid state is higher than in the crystalline state. This is again in qualitative agreement with our interpretation since $\Delta E_{\text{free electron}} = 6.05$ eV in liquid aluminum is *higher* than 5.69 eV derived from the band-structure calculations of Moruzzi *et al.*[30] for solid Al.

For other metals the difference between the heat of formation of a solid hydride and that of a liquid hydride is not large.[3] This is in sharp contrast with the model of Welch and Pick[61] from which it would follow that all liquid metals are excellent hydrogen absorbers (with heat of formation of ~ -80 kJ/mol H) since liquids have a vanishingly small shear modulus.

C. Ternary metal hydrides

The most interesting use of the empirically found linear relation between the heat of formation and the band-structure characteristic energy parameter ΔE is of course to predict ΔH for ternary hydrides $A_{y_A}B_{y_B}\text{H}_x$. Since band-structure calculations are available only for a limited number of alloys we shall use the model of Cyrot and Cyrot-Lackmann[27] to evaluate ΔE for alloys of *transition metals.* The case of alloys with simple metals, rare earths, or actinides shall be discussed elsewhere.

Within the tight-binding approximation Cyrot and Cyrot-Lackmann show that the exact density of states $n(E;y_A,y_B)$ calculated by means of the coherent-potential approximation formalism for an alloy $A_{y_A}B_{y_B}$ has the same moments

$$\mu^\nu = \int E^\nu n(E;y_A,y_B)dE \tag{5}$$

for $\nu = 0,1$, and 2 (and even $\nu = 3$ in the case of two metals with equal bandwidths) as the "simple" density of states $n^*(E)$ given by

$$n^*(E;y_A,y_B) = [y_A n_A'(E) + y_B n_B'(E)]/(y_A + y_B) , \tag{6}$$

where $n_i'(E)$ is a scaled density-of-states function of metal i. The various steps involved in this scaling are schematically indicated in Fig. 5 for the special case of an alloy AB ($y_A = y_B = 1$) when the d-band width W_A of metal A is larger than that of metal B, i.e., $W_A > W_B$.

In the first step the widths of the d bands of both metals are set equal to their weighted average

$$W^* = (y_A W_A + y_B W_B)/(y_A + y_B) . \tag{7}$$

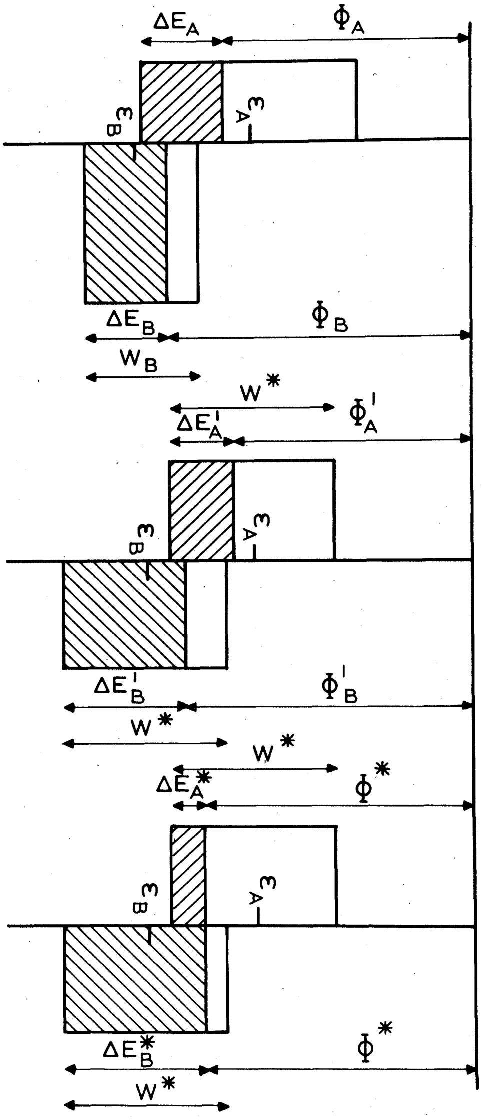

FIG. 5. Illustration of the construction of the density of states function $n^*(E)$ which has the same first three moments as the exact (within the tight-binding coherent-potential approximation) density-of-states function $n(E)$ of an alloy AB. For an alloy $A_{y_A}B_{y_B}$ the partial density-of-states curves are weighted by the corresponding atomic fractions.

Since the number of available Bloch states contained in the d band is constant, a change in bandwidth implies a change in height of the density of states curve so that

$$n_i'\left[\frac{E'-\epsilon_i}{W^*}\right] = n_i\left[\frac{E-\epsilon_i}{W_i}\right]\frac{W_i}{W^*} \tag{8}$$

with

$$E' - \epsilon_i = (E - \epsilon_i)\frac{W^*}{W} . \tag{9}$$

In Eqs. (8) and (9), ϵ_i is the center of the density-of-states curve of metal i ($i = A$ or B) measured with respect to the vacuum zero. For the individual metals

$$\epsilon_i = (E_F - E_s)_i - \frac{W_i}{2} + \phi_i , \tag{10}$$

TABLE II. Optimized values of ΔE used for the calculation of the heat of formation of ternary transition-metal hydrides. When inserted into Eq. (3), the optimized ΔE reproduce the experimental values for the heat of formation of binary metal hydrides.

Metal	ΔE (eV)	Metal	ΔE (eV)	Metal	ΔE (eV)
$_{21}$Sc	1.25	$_{39}$Y	0.85	$_{57}$La	1.25
$_{22}$Ti	2.55	$_{40}$Zr	1.90	$_{72}$Hf	2.50
$_{23}$V	3.55	$_{41}$Nb	3.4	$_{73}$Ta	3.30
$_{24}$Cr	4.35	$_{42}$Mo	5.0	$_{74}$W	5.40
$_{25}$Mn	4.30	$_{43}$Tc	4.61	$_{75}$Re	5.44
$_{26}$Fe	5.40	$_{44}$Ru	6.0	$_{76}$Os	6.80
$_{27}$Co	5.10	$_{45}$Rh	5.4	$_{77}$Ir	7.1
$_{28}$Ni	4.40	$_{46}$Pd	3.9	$_{78}$Pt	5.7

where ϕ_i is the work function of metal i. After having brought the densities of states curves $n_i(E)$ to the common width W^* the band energy parameters E_i' and work functions ϕ_i' are given by

$$E_i' = E_i \frac{W^*}{W_i} \tag{11}$$

and

$$\phi_i' = \phi_i + \Delta E_i - \Delta E_i' + \tfrac{1}{2}(W^* - W_i) , \tag{12}$$

since ϵ_A and ϵ_B are assumed to be constant. In both Eqs. (11) and (12), $\Delta E_i \equiv (E_F - E_s)_i$ and $\Delta E_i' \equiv (E_F - E_s)_i'$. On an absolute energy scale the Fermi energy E'_{F_A} and E'_{F_B} are different. This leads to an electron transfer until the Fermi energy is constant throughout the alloy.

In the second step of the construction of $n^*(E;y_A,y_B)$ one equilibrates the Fermi energies by requiring that

$$(\phi - \phi'_A) y_A n'_A(E'_{F_A}) = (\phi'_B - \phi^*) y_B n'_B(E'_{F_B}) , \tag{13}$$

where E'_{F_i} is the "scaled" Fermi energy of metal i obtained by setting $E = E_{F_i}$ in Eq. (9) and ϕ^* is the work function of the alloy $A_{y_A}B_{y_B}$ under consideration. As seen from Eqs. (7)–(13), ϕ^* depends on the bandwidths W_i, the density of states $n_i(E_F)$, and the work functions ϕ_i of the pure metals A and B and, of course, on the concentration y_A and y_B of A and B atoms.

Since according to the results of Cyrot and Cyrot-Lackmann a good approximate density of states $n^*(E;y_A,y_B)$ can be obtained by taking a weighted average of the scaled density of states $n_i(E)$ of the pure constituents, one expects that for the heat of formation of the hydride,

$$\Delta H(A_{y_A}B_{y_B}H_x) = \alpha \left[\frac{y_A \Delta E_A^* + y_B \Delta E_B^*}{y_A + y_B} \right] + \beta \tag{14}$$

with

$$\Delta E_i^* = E_i' + \phi_i' - \phi^* . \tag{15}$$

As indicated in Fig. 5 ΔE_i^* corresponds to the band-structure energy parameter of the scaled density of states of metal i after allowing a transfer of electrons to bring E_{F_i} to a common level.

For the evaluation of $\Delta H(A_{y_A}B_{y_B}H_x)$ by means of Eq. (14) we used the *experimental values* for ϕ given in Ref. 73 and the density-of-states curves given in Ref. 30 for the metals between $_3$Li and $_{49}$In. For the other metals the sources are the same as those used for the ΔE data given in Fig. 4. For metals for which the total width of the d band has not been calculated we estimated W_i by means of the approximation relation

$$W_i = \frac{10\,\Delta E_i}{Z_i - 1} , \tag{16}$$

where Z_i is the number of valence electrons per atom of metal i.

In order to check the predicting power of the present model for the heat of formation of ternary metal hydrides we used the optimized ΔE values given in Table II. These values are such that when inserted in Eq. (1) the experimental values for the heats of formation of the *binary* hydrides are reproduced [using the values for α and β given in Eq. (4)]. In most of the cases the optimized ΔE differ by no more than a few tenths of electron volts from the values derived from band-structure calculations.

The first check of the validity of the present model is shown in Table III. The alloys listed therein have been reported[5] to absorb only negligible amounts of hydrogen at moderate pressures around room temperature. Knowing that an equilibrium plateau pressure of 1 bar at 300 K corresponds to a heat of formation of approximately -19 kJ/mol H [if one assumes that the entropy of formation is -65 J/mol H K for all metals since ΔS is mainly determined by the loss of the entropy of hydrogen in the gaseous phase] we expect for all materials listed in Table III

TABLE III. Heat of formation of ternary hydrides $A_{y_A}B_{y_B}H_x$ which have been reported not to exist at room temperature under moderate hydrogen pressure ($p \lesssim 100$ bars).

Metal	ΔH (kJ/mol H)	Metal	ΔH (kJ/mol H)
ScRu$_2$	-11.1	LaPt$_2$	-1.9
TiMn$_2$	-22.4	LaIr$_2$	-2.5
TiFe$_2$	-1.8	HfFe$_2$	-6.0
TiCo$_2$	-1.8	HfRh	-14.3
TiNi$_3$	$+0.1$	HfPd	-21.6
YNi$_5$	-22.4	HfPt	$+0.3$
ZrPd$_2$	-26.1		

that ΔH is larger than -19 kJ/mol H. This is indeed the case except for $TiMn_2$, YNi_5, and HfPd, but even then the predicted heats of formation are only slightly more negative than -19 kJ/mol H. Quite remarkable in this list of materials are HfPd and $ZrPd_2$ since Hf, Pd, and Zr are known to be good hydrogen absorbers. In the next section we shall show that this is due to the transfer of electrons from Zr (or Hf) to Pd. A similar behavior can be expected for the "nonforming" hydrides of other Pd-based alloys (for example, Pd-La, Pd-Ti, Pd-U, Pd-V).

A second check of the validity of our model is shown in Fig. 6, where the experimental values for ΔH are compared to the values obtained from Eq. (14). Considering the simplicity of the model, the agreement between experimental and calculated values is remarkably good, the average mean square deviation being significantly better than that of other semiempirical models[22,24] for the heat of formation of hydrides. From a practical point of view this means that the predicting power of the present model is sufficiently high for a meaningful search of potential hydrogen storage alloys. A list of alloys expected to react with hydrogen with a heat of formation between -12 and -25 kJ/mol H is given in Ref. 74.

IV. DISCUSSION

The heat of formation ΔH of a hydride $A_{y_A}B_{y_B}H_x$ depends on the work functions ϕ_i, the bandwidths W_i the density of states $n_i(E_{F_i})$ and on the concentration y_i of metals A and B. To get some insight in the role of these parameters it is useful to consider some special situations for which relation (14) takes a particularly simple form.

The first model we want to discuss is the square density-of-states model for which n_i is independent of energy in the interval $[\epsilon_i - W_i/2, \epsilon_i + W_i/2]$. For this model

$$n_A W_A = n_B W_B \tag{17}$$

and the heat of formation is given by the following relation:

$$\Delta H = (1-c)\Delta H_A + c\Delta H_B + \alpha\left[\frac{\Delta E_A}{W_A} - \frac{\Delta E_B}{W_B}\right](W_B - W_A)c(1-c)\,, \tag{18}$$

where $1-c = y_A$, $c = y_B$, and ΔH_i are the heats of forma-

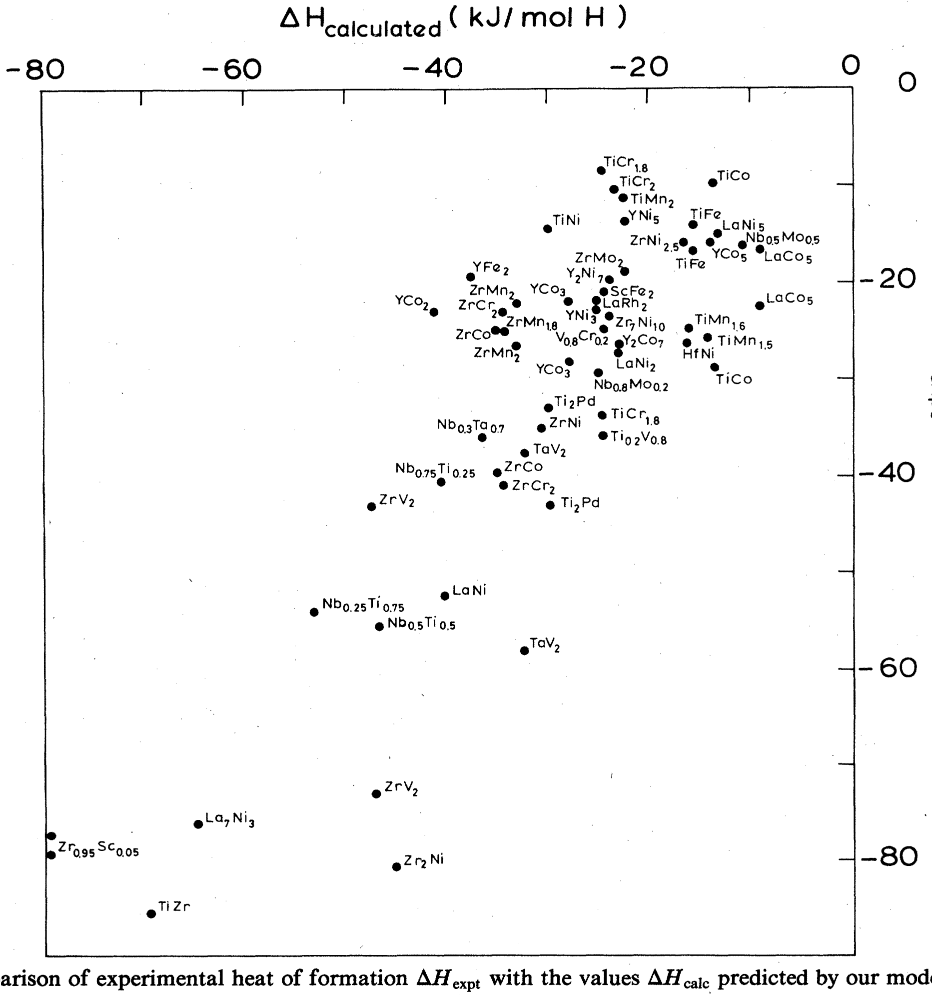

FIG. 6. Comparison of experimental heat of formation ΔH_{expt} with the values ΔH_{calc} predicted by our model (using the optimized ΔE values given in Table II). For alloys for which the heat of formation has not been measured directly we estimated ΔH_{expt} from the equilibrium plateau pressures listed in Ref. 5 by means of Eq. (1) with $\Delta S = -65$ J/K mol H.

tion of the AH_x and BH_x binary hydrides. The third term in Eq. (18) is responsible for a nonlinear variation of ΔH with the concentration of B atoms. The curvature can be positive or negative (depending on the sign of the c^2 term). It vanishes when the two metals A and B have the same bandwidth or when the two metals have the same number of conduction electrons [since in this case $\Delta E_A/W_A=\Delta E_B/W_B$, according to Eq. (16)]. For alloys of an early d metal A with a late d metal B, $Z_A<Z_B$ and $W_A<W_B$. The nonlinear term in Eq. (18) is then positive. It renders hydride formation more difficult. On the other hand a slight increase in the tendency to form hydrides is expected in alloys of an early transition metal (Sc) with a metal in the middle of a series (Nb) because $W_A \lesssim W_B$. A peculiarity of Eq. (18) is that ΔH does not depend on the work functions ϕ_A and ϕ_B. This indicates that, in our model, a transfer of electrons from one metal to the other is not necessarily influencing ΔH, in contradiction with the situation discussed by Cyrot and Cyrot-Lackmann,[27] where electron transfer *always* stabilizes the alloy $A_{1-c}B_c$. A direct consequence of this fact is that the *rule of reversed stability* proposed by Miedema and co-workers[22–24] is not necessarily a general rule.

The independence of ΔH from ϕ_i is, however, a peculiarity of the square density-of-states model. To illustrate this point we consider an alloy $A_{1-c}B_c$ of two metals A and B with a same bandwidth $W_A=W_B$ but with different densities of states, i.e., $n_A(E_{F_A})\neq n_B(E_{F_B})$. In this case $\phi_i'=\phi_i$ and $n_i'=n_i$, and

$$\Delta H=(1-c)\Delta H_A+c\Delta H_B -\alpha c(1-c)(\phi_A-\phi_B)\frac{n_A-n_B}{(1-c)n_A+cn_B}\ . \qquad (19)$$

Since the denominator $(1-c)n_A+cn_B$ is always positive, the nonlinearity in the concentration dependence of ΔH is mainly determined by the numerator of the third term in Eq. (19). The product $(\phi_A-\phi_B)(n_A-n_B)$ determines the magnitude and the sign of the nonlinear contribution to ΔH. As an illustration it is interesting to consider the case of palladium-based alloys since for almost all metals B, $\phi_B<\phi_{\rm Pd}$. Furthermore, for the purpose of this qualitative discussion we shall only consider situations where the d band of Pd has just been filled up so that $n_{\rm Pd}\simeq 0.5$ states/eV atom. This means that $n_{\rm Pd}\lesssim n_B$ and that the third term in Eq. (19) is positive. One expects then that for most of the Pd-based alloys the hydride heat of formation will be larger than that of pure Pd.

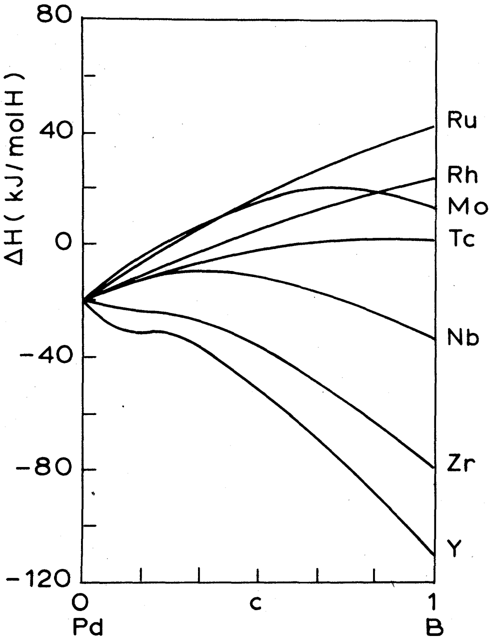

FIG. 7. Calculated heat of formation for the hydrides of alloys of Pd with other $4d$ transition metals. It is important to point out that the heats of formation shown in this figure have been calculated by means of Eq. (14) in which it is implicitly assumed that each hydrogen is surrounded by a fraction $y_A/(y_A+y_B)$ of A atoms and a fraction $y_B/(y_A+y_B)$ of B atoms. The results presented here are thus not applicable to low hydrogen concentrations since then H will occupy sites coordinated by A atoms only (provided AH_x is more stable than BH_x). A treatment of heat of solution of metal-hydrogen systems is given in Ref. 74.

This qualitative conclusion is confirmed by the results shown[75] in Fig. 7. The positive nonlinear term is clearly present for Pd-Y, Pd-Zr, and Pd-Nb alloys. For the other alloys of Pd with $4d$ elements, ΔH varies almost linearly with concentration. A similar behavior is shown in Fig. 8 for alloys of Ni with early $3d$, $4d$, and $5d$ transition elements.

From Eq. (19) one expects that for alloys based on a transition element A in the middle of a long series of the Periodic Table, both $\phi_A-\phi_B$ and n_A-n_B will be small (except of course for $B={}_{78}$Pt, ${}_{46}$Pd, or ${}_{28}$Ni) and that con-

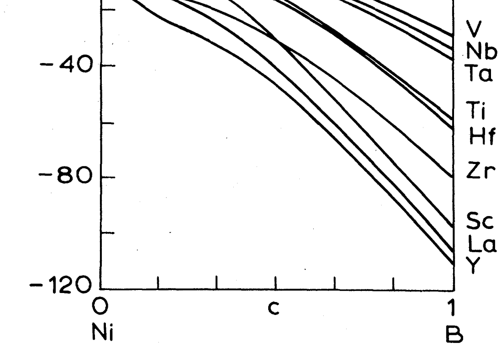

FIG. 8. Calculated heat of formation for the hydrides of alloys of Ni with early $3d$, $4d$, and $5d$ transition metals (see comment in Fig. 6).

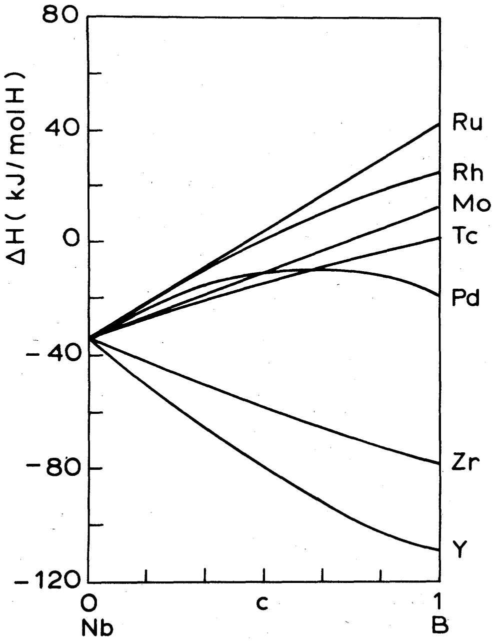

FIG. 9. Calculated heat of formation for the hydrides of alloys of Nb with other 4*d* elements (see comment in Fig. 6).

sequently ΔH will vary almost linearly with concentration. This is illustrated in Fig. 9 by means of Nb-based alloys.

V. CONCLUSIONS

We empirically found that the heat of formation of binary hydrides MH_x is related linearly to the characteristic band energy parameter $\Delta E = E_F - E_s$, where E_F is the Fermi energy and E_s the center of the *host* metal electronic band with a strong *s* character at the interstitial sites occupied by hydrogen. For most metals E_s can be taken as the energy which corresponds to one electron per atom on the integrated density-of-states curve.

Assuming that $E_F - E_s$ is also the parameter determining the heat of formation of ternary hydrides, we derived an expression for ΔH for the hydrides of alloys of arbitrary composition $A_{y_A}B_{y_B}$. For this we used an approximate density-of-states function which has the same first three moments as the exact density-of-states function obtained by means of the coherent-potential approximation within a tight-binding model for electronic states. The predictions of our model are in fair agreement with existing experimental values for ΔH although the crystallographic structure of the alloys is not explicitly taken into account.

For most of the ternary hydrides $A_{y_A}B_{y_B}H_x$, ΔH varies approximately linearly between the heat of formation of AH_x and that of BH_x. For alloys of an early transition metal with a late transition metal, however, large positive nonlinearities occur. This explains, for example, the difficulty of Pd—transition-metal alloys to form hydrides. For such alloys our model leads to a behavior which is qualitatively similar to the rule of reversed stability proposed by Miedema and co-workers.

We are presently refining our model to incorporate (i) structural information about the sites occupied by hydrogen in compounds and dilute alloys and (ii) lattice spacing changes in alloys.

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[1] R. B. McLellan and W. A. Oates, Acta Metall. **21**, 181 (1973).

[2] H. M. Lee, Metall. Trans. **7A**, 431 (1976).

[3] W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, *Metal Hydrides* (Academic, New York, 1968) and references therein.

[4] N. A. Galaktionowa, *Hydrogen-Metal Systems Databook* (Ordentlich, Holon, Israel, 1980).

[5] K. H. J. Buschow, P. C. P. Bouten, and A. R. Miedema, Rep. Prog. Phys. **45**, 927 (1982).

[6] E. G. Ponyatovskii, V. E. Antonov, and I. T. Belash, Usp. Fiz. Nauk **137**, 663 (1982) [Sov. Phys. Usp. **25**, 596 (1983)] and references therein.

[7] R. L. Mills, D. H. Liebenberg, J. C. Bronson, and L. C. Schmidt, J. Chem. Phys. **66**, 3076 (1977).

[8] A. Driessen and I. F. Silvera, J. Low. Temp. Phys. **54**, 361 (1984).

[9] J. van Straaten, R. J. Wijngaarden, and I. F. Silvera, Phys. Rev. Lett. **48**, 97 (1982).

[10] V. E. Antonov, I. T. Belash, E. G. Ponyatovskii, and V. I. Rashchupkin, Fiz. Met. Metalloved. **48**, 75 (1979).

[11] Z. D. Popovic, M. J. Stott, J. P. Carbotte, and G. R. Piercy, Phys. Rev. B **13**, 590 (1976).

[12] A. C. Switendick, Solid State Commun. **8**, 1463 (1970).

[13] A. C. Switendick, Z. Phys. Chem. N.F. **117**, 89 (1979).

[14] M. Gupta and J. P. Burger, Phys. Rev. B **24**, 7099 (1981).

[15] C. D. Gelatt, H. Ehrenreich, and J. A. Weiss, Phys. Rev. B **17** 1940 (1978).

[16] H. L. M. Bakker, R. Feenstra, R. Griessen, L. M. Huisman, and W. J. Venema, Phys. Rev. B **26**, 5321 (1982).

[17] A. Bansil, R. Prasad, S. Bessendorf, L. Schwartz, W. J. Venema, R. Feenstra, F. Blom, and R. Griessen, Solid State Commun. **32**, 1115 (1979).

[18] A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979).

[19] M. Methfessel and J. Kübler, J. Phys. F **12**, 141 (1982).

[20] J. K. Nørskov, Phys. Rev. B **26**, 2875 (1982).

[21] D. G. Westlake, J. Less-Common Met. **91**, 1 (1983).

[22] P. C. P. Bouten and A. R. Miedema, J. Less-Common Met. **71**, 147 (1980).

[23] A. R. Miedema, J. Less-Common Met. **32**, 117 (1973).

[24] H. H. van Mal, K. H. J. Buschow, and A. R. Miedema, J.

Less-Common Met. **35**, 65 (1974).

[25] A. R. Williams, C. D. Gelatt, and V. L. Moruzzi, Phys. Rev. Lett. **44**, 429 (1980).

[26] A. R. Williams, C. D. Gelatt, and V. L. Moruzzi, Phys. Rev. B **25**, 6509 (1982).

[27] M. Cyrot and F. Cyrot-Lackmann, J. Phys. F **6**, 2257 (1976).

[28] E. Wicke and H. Brodowsky, in *Hydrogen in Metals II,* Vol. 29 of *Topics in Applied Physics,* edited by G. Alefeld and J. Völkl (Springer, New York, 1978).

[29] R. Griessen and L. M. Huisman, in *Electronic Structure and Properties of Hydrogen in Metals,* edited by P. Jena and C. B. Satterthwaite (Plenum, New York, 1983), p. 235.

[30] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[31] O. Jepsen, O. K. Andersen, and A. R. Mackintosh, Phys. Rev. B **12**, 3084 (1975).

[32] L. F. Mattheiss, Phys. Rev. **151**, 450 (1966).

[33] O. K. Andersen, Phys. Rev. B **2**, 883 (1970).

[34] K. Iyakutti, R. Asokamani, and V. Devanathan, J. Phys. F **7**, 2307 (1977).

[35] G. O. Arbman and S. Hörnfeldt, J. Phys. F **2**, 1033 (1972).

[36] J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B **22**, 4226 (1980).

[37] N. E. Christensen and B. Feuerbacher, Phys. Rev. B **10**, 2349 (1974).

[38] L. K. Mattheiss, Phys. Rev. B **1**, 373 (1970).

[39] Y. K. Vohra, S. K. Sikka, and R. Chidambaram, J. Phys. F **9**, 1771 (1979).

[40] T. L. Loucks, Phys. Rev. **144**, 504 (1966).

[41] D. Glötzel and L. Fritsche, Phys. Status Solidi B **79**, 85 (1977).

[42] W. E. Pickett, A. J. Freeman, and D. D. Koelling, Physica **102B**, 341 (1980).

[43] G. S. Fleming, S. H. Liu, and T. L. Loucks, Phys. Rev. Lett. **21**, 1524 (1968).

[44] M. Matsumoto, I. Shibata, Y. Sakizi, M. Fukuchi, and S. I. Kobayasi, J. Phys. Soc. Jpn. **49**, 1030 (1980).

[45] O. K. Andersen and T. L. Loucks, Phys. Rev. **167**, 551 (1968).

[46] S. I. Kobayasi, M. Fukuchi, and S. Nagai, Physica (Utrecht) **86-88B**, 26 (1977).

[47] B. N. Harmon and A. J. Freeman, Phys. Rev. B **10**, 1979 (1974).

[48] S. C. Keeton and T. L. Loucks, Phys. Rev. **168**, 672 (1968).

[49] A. R. Mackintosh, Phys. Lett. **28A**, 217 (1968).

[50] H. B. Møller, J. C. G. Houmann, and A. R. Mackintosh, J. Appl. Phys. **39**, 807 (1968).

[51] G. Johansen and A. R. Mackintosh, Solid State Commun. **8**, 121 (1970).

[52] D. D. Koelling (unpublished); see A. J. Freeman, Physica (Utrecht) **102B**, 3 (1980).

[53] S. C. Keeton and T. L. Loucks, Phys. Rev. **146**, 429 (1966).

[54] D. D. Koelling and A. J. Freeman, Phys. Rev. B **7**, 4454 (1973).

[55] K. Iyakutti, M. Dakshinamoorthy, and R. Asokamani, Solid State Commun. **40**, 555 (1981).

[56] H. L. Skriver and J. P. Jan, Phys. Rev. B **21**, 1489 (1980).

[57] N. E. Christensen and B. O. Seraphin, Phys. Rev. B **4**, 3321 (1971).

[58] G. Johansen, Solid State Commun. **7**, 731 (1969).

[59] F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *II-VI Semiconducting Compounds, 1967 International Conference,* edited by D. G. Thomas (Benjamin, New York, 1967).

[60] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B **7**, 2644 (1973).

[61] D. O. Welch and M. A. Pick, Phys. Lett. **99A**, 183 (1983).

[62] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

[63] G. Weisz, Phys. Rev. **149**, 504 (1966).

[64] D. W. Bullett, Solid State Commun. **17**, 965 (1975).

[65] S. C. Keeton and T. L. Loucks, Phys. Rev. **152**, 548 (1966).

[66] P. M. Holtham, J. P. Jan, and H. L. Skriver, J. Phys. F **7**, 635 (1977).

[67] D. A. Papaconstantopoulos, A. D. Zdetsis, and E. N. Economou, Solid State Commun. **27**, 1189 (1978).

[68] W. R. Opie and N. J. Grant, Trans. Metall. Soc. AIME **191**, 244 (1951).

[69] K. Iwasé, Sci. Rep. Tohoku Univ. First Ser. **15**, 531 (1926).

[70] C. E. Ramsley and H. Neufeld, J. Inst. Met. **74**, 599 (1948).

[71] W. R. Opie and N. J. Grant, Trans. Metall. Soc. AIME **188**, 1237 (1950).

[72] M. V. Sharov, Legkie Splavy, Akad. Nauk SSSR Inst. Met. **1955**, 365 (1958).

[73] *CRC Handbook of Chemistry and Physics,* edited by R. C. Weast (Chemical Rubber Company, Boca Raton, Florida, 1978).

[74] R. Griessen, A. Driessen, and D. G. de Groot, J. Less Common Metals (in press).

[75] For Pd-, Ni-, or Pt-based alloys the condition in Eq. (12) is replaced by an integral equation as a consequence of the rapid variation of $n(E)$ above the Fermi energy of the host metal.

[76] S. Golin, Phys. Rev. **166**, 643 (1968).