Heats of solution and lattice-expansion and trapping energies of hydrogen in transition metals

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The heat of hydrogen solution in a metal at infinite dilution $\Delta \bar{H}_\infty$ is shown to depend on (1) the distance R between a hydrogen atom and its metallic nearest neighbors, (2) the characteristic band-structure energy $\Delta E = E_F - E_s$, where E_F is the Fermi energy and E_s basically the center of the lowest conduction band of the host metal, and (3) the width W_d of the d band of the host metal. The semiempirical relation $\Delta \bar{H}_\infty = \alpha \Delta E\, W_d^{1/2} \sum R_j^{-4} + \beta$ [with $\alpha = 18.6$ (kJ/mol H)($\text{Å}^4 \text{eV}^{-3/2}$) and $\beta = -90$ kJ/mol H if ΔE, W_d, and R are given in units of eV and Å, respectively] reproduces the experimental values of $\Delta \bar{H}_\infty$ remarkably well. It also reproduces the volume expansion accompanying hydrogen absorption and predicts the correct interstitial site occupancy of hydrogen in a transition metal. Furthermore, it makes it possible to estimate the binding energy of hydrogen to a vacancy.

I. INTRODUCTION

Hydrogen is known to react with a large number of metals, alloys, and intermetallic compounds at moderate hydrogen gas pressure.[1-5] The ability of a metal to absorb hydrogen is to a large extent governed by the so-called heat of solution $\Delta \bar{H}$ which represents the heat involved during the absorption of hydrogen. For very stable metal-hydrogen systems such as Y-H and La-H, $\Delta \bar{H}$ is typically ~ -100 kJ/mol H. For metals to the right of V, Nb, and Ta in the Periodic Table $\Delta \bar{H}$ is strongly positive except for the Pd-H system for which $\Delta \bar{H} \simeq -15$ kJ/mol H. Entropy effects play a secondary role because the entropy of hydrogen solution in a metal $\Delta \bar{S}$ arises almost totally from the entropy loss of gaseous hydrogen during hydrogen uptake by the metal.[6]

In contrast to the wealth of data which is available from experiments the enthalpy of solution (or the heat of formation) has been calculated from first principles only for a very limited number of metal hydrides.[7-20] First-principles calculations are at present still time consuming as a high accuracy in the total energies of the host metal and the metal hydrides are required for the determination of the enthalpy of solution. A review of theoretical works on the stability of metal-hydrogen systems may be found in Ref. 7.

The insufficient accuracy and the important computer time requirements of presently available first-principles calculations of the heat of solution or heat of formation of metal hydride make it still necessary to look for empirical correlations or semiempirical models. In a review paper Griessen and Riesterer[5] came to the conclusion that the majority of empirical correlations (between $\Delta \bar{H}$ and measurable physical quantities of the host metals) have been proposed on the basis of too-restricted sets of experimental data. These correlations are thus not very useful, as they describe in fact mainly the systems from which they have been derived.

The first semiempirical model capable of describing a large class of alloys was the cellular model of Miedema and co-workers.[5,21,22] For metal-hydrogen systems Miedema's model suffers however from the fact that it is not accurate and that it requires a relatively large number of fit parameters (basically two parameters for each type of compound in the "law of reversed stability" in addition to the parameters φ_H^* and V_H of "metallic" hydrogen). Furthermore, Miedema's model has the severe shortcoming that it predicts a monotonously increasing heat of solution $\Delta \bar{H}$ with increasing hydrogen concentration.[5] This implies that phase separation[23] is not possible in sharp contrast with the experimentally determined phase diagrams of metal-hydrogen systems.

More recently Griessen and Driessen proposed the semiempirical band-structure model for the heat of solution of hydrogen in a metal.[24-27] This model which involves only four fit parameters was quite successful. It reproduces $\Delta \bar{H}$ and the molar volume $\bar{V}_H$ of hydrogen in metals and compounds more accurately than Miedema's model. The only parameter characterizing the host metal being the band-structure energy $\Delta E = E_F - E_s$ (where E_F is the Fermi energy and E_s the center of the band with s character with respect to the interstitial site occupied by hydrogen) this model is inherently nonlocal. Similar to Miedema's model it cannot predict the heat of solution for hydrogen occupying various interstitial sites in a metal, an alloy, or a compound.

The purpose of this article is to construct a simple *local* semiempirical model for the heat of solution at infinite dilution, $\Delta \bar{H}_\infty$, for hydrogen in a transition metal. It is the first of a series of articles on hydrogen in metals. In subsequent articles we shall show that the model predicts the correct site occupancy and site enthalpies for hydrogen in compounds and that it can be used to calculate the effective H-H interaction in concentrated metal hydrides.

II. THE MODEL

Our aim is to find a useful correlation between the heat of hydrogen solution in a metal at infinite dilution, $\Delta \bar{H}_\infty$,

and characteristic physical quantities of the host metal. These quantities may be experimentally determined quantities such as the atomic volume Ω, the bulk modulus B, the electronic specific heat coefficient, the crystal structure, and interatomic spacings or/and calculated quantities such as the electronic density of states at the Fermi energy $n(E_F)$, the d-band width W_d, the Fermi energy, E_F or the local electron density at the sites occupied by hydrogen atoms $\rho(\mathbf{r})$.

As we are looking for a *simple* model we assume that $\Delta \bar{H}_\infty$ can be related to *one* yet unknown parameter X so that

$$\Delta \bar{H}_\infty = f(X) . \tag{1}$$

As for any choice of the parameter X it is possible to find a function $f(X)$ satisfying Eq. (1), we need additional requirements to identify both X and $f(X)$. An extra requirement is that the model we are looking for should not only describe $\Delta \bar{H}_\infty$ but also the volume expansion accompanying hydrogen absorption in a metal. This volume expansion is usually characterized by the partial molar volume $\bar{V}_H$ of hydrogen in a metal, which is defined as $(\partial V / \partial n_H)_{p,T}$ where n_H is the number of moles of hydrogen dissolved in the host metal of volume V. As shown by Griessen and Feenstra,[26]

$$\bar{V}_H \equiv \frac{\partial V}{\partial n_H}\bigg|_{p,T} \cong \frac{\partial \Delta \bar{H}}{\partial p}\bigg|_T = -\frac{\partial \Delta \bar{H}}{B \partial \ln V}\bigg|_T . \tag{2}$$

At infinite dilution,

$$B\bar{V}_H = -\frac{\partial \Delta \bar{H}_\infty}{\partial \ln V}\bigg|_T . \tag{3}$$

This implies that the function $f(X)$ must also satisfy the following relation:

$$B\bar{V}_H = \frac{df}{d \ln X}\gamma_X \tag{4}$$

with

$$\gamma_X = -\frac{\partial \ln X}{\partial \ln V} . \tag{5}$$

Most of the characteristic physical parameters mentioned at the beginning of this section depend on volume according to a simple power law so that it is not a serious restriction to consider in the following only parameters X with a constant γ_X. It follows then directly from Eqs. (1) and (2):

$$B\bar{V}_H = \varphi(\Delta \bar{H}_\infty) \tag{6}$$

as both $\Delta \bar{H}_\infty$ and $B\bar{V}_H$ are functions of X only. In Fig. 1 we show that indeed a simple (linear) correlation exists between $B\bar{V}_H$ and the heat of solution at infinite dilution $\Delta \bar{H}_\infty$. Combining Eqs. (1), (4), and (6) we obtain the following condition for the function $f(X)$;

$$\frac{df}{d \ln X}\gamma_X = \varphi(f(X)) . \tag{7}$$
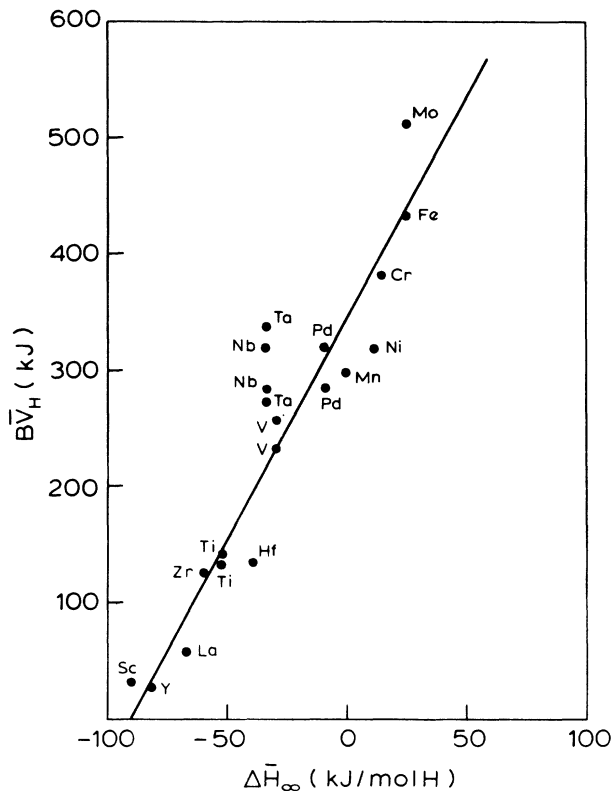
After integration we find that

FIG. 1. Correlation between $B\bar{V}_H$ and the heat of hydrogen solution at infinite dilution $\Delta \bar{H}_\infty$. The experimental data are mainly from Refs. 1–3, 5, 6, and 26.

$$\left[\frac{X}{X_0}\right]^{1/\gamma_X} = \exp[F(f,f_0)] , \tag{8}$$

where

$$F(f,f_0) = \int_{f_0}^{f} \frac{df}{\varphi(f)} \tag{9}$$

and

$$f_0 = f(X_0) . \tag{10}$$

Equations (8)–(10) show that it is possible to calculate $(X/X_0)^{1/\gamma_X}$ once the function $\varphi(f)$ is known. From a weighted least-squares fit to the data shown in Fig. 1 we find that

$$\varphi(f) = 3.83f + 345 \tag{11}$$

if f is expressed in kJ/mol H and after integration [Eq. (9)] we obtain the following relation for the unknown parameter X:

$$\left[\frac{X}{X_0}\right]^{1/\gamma_X} = \left[\frac{3.83f + 345}{3.83f_0 + 345}\right]^{(1/3.83)} . \tag{12}$$

As Eq. (12) must be valid for all values of f which are physically relevant, i.e., for $-90 \leq f \leq 100$ kJ/mol H, it follows that:

$$\gamma_X = 3.83 \qquad (13)$$

and

$$X = k(3.83f + 345) , \qquad (14)$$

where k is a constant which remains to be determined. Dividing Eq. (14) by 3.83 and introducing another constant η for simplification we obtain

$$\eta X = f + 90 . \qquad (15)$$

Equation (15) means that up to a multiplicative constant η the parameter X is linearly related to f, i.e., to the enthalpy of solution at infinite dilution $\Delta \overline{H}_\infty$ as follows from Eq. (1). It is therefore possible to represent ηX as a function of the atomic number of the host metal. The curves obtained in this way for the $3d$, $4d$, and $5d$ transition metals are shown in Fig. 2. The parameter X increases rapidly with increasing atomic number until the electronic d band is approximately half-full. For the late transition metals the variation of X is weaker except at the end of the series where X clearly decreases. A further interesting point is that X for a $5d$ transition metal is clearly larger than for the $3d$ and $4d$ metals of the same column of the periodic system. Such a behavior is also found for other properties of transition metals, e.g., the cohesive energy E_c and the bulk modulus B.[28,29]

At this point one might be tempted to look for correlations between ηX and experimentally determined material constants such as E_c or B. Such correlations are, however, only of marginal interest as they do not take into ac-
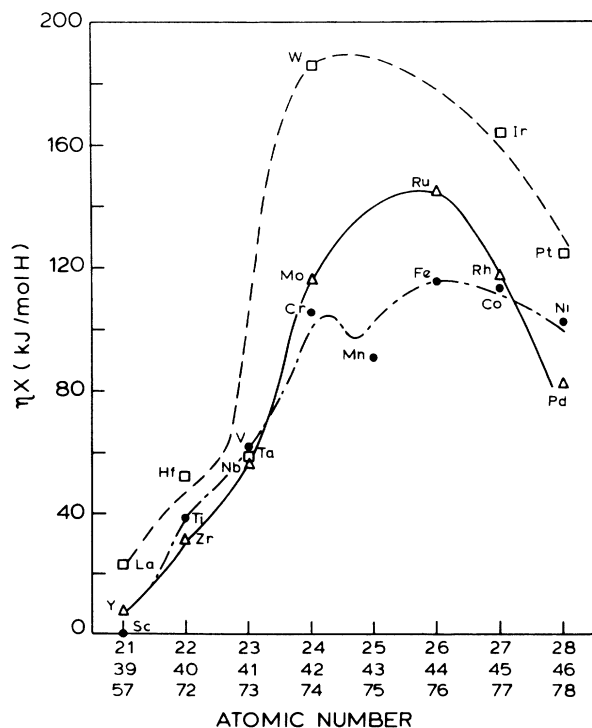
count the dependence of $\Delta \overline{H}_\infty$ on the site occupied by a hydrogen atom in the metallic host lattice. This is the reason why in the following we will primarily search for a parameter X which depends (i) on the local environment of hydrogen and (ii) on characteristic energies of the electronic band structure of the host. If this search is not successful we will consider other parameters such as local electron charge densities and local lattice deformations. This would, however, restrict the applicability of such a semiempirical model to the very limited number of host materials for which first-principles calculations of local physical quantities are at hand.

It is important to note that in a semiempirical approach the choice of parameters used to characterize a metal cannot be justified a priori and that the usefulness of such a model can only be established by comparing predictions based on the model with experimental data. As we are looking here for a local semiempirical model it is, however, clear that in addition to the band-structure energy ΔE used in our previous work,[24–27] the parameter X should depend on local characteristics of the sites which can be occupied in a metal. We consider now possible local and band-structure contributions to X.

(i) Local environment: The simplest characterization of a site occupied by a hydrogen atom is obtained by assuming that $\Delta \overline{H}_\infty$ depends on the distance R_j separating H

FIG. 2. Variation of the parameter ηX [Eq. (15)] along the $3d$, $4d$, and $5d$ series of the periodic system.
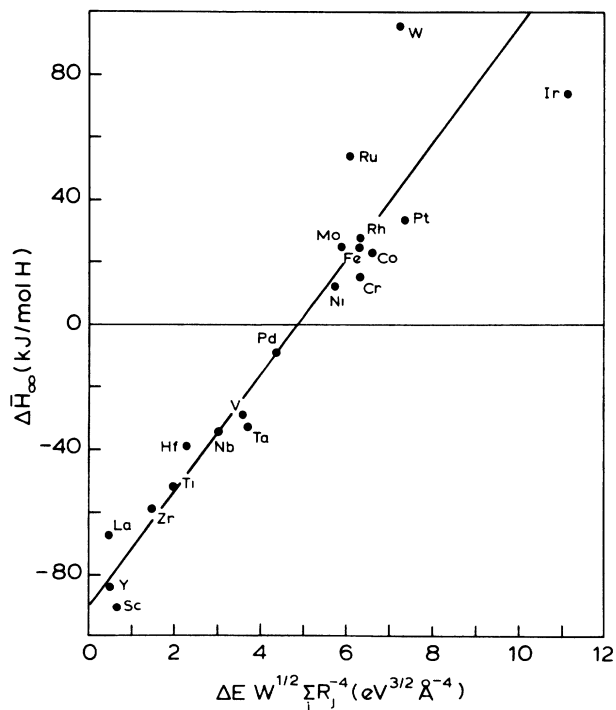

FIG. 3. Correlation between the experimental values of the heat of hydrogen solution $\Delta \overline{H}_\infty$ and the calculated band-structure energies ΔE and W_d. The distance R_j separating a given hydrogen atom from the jth atom in the first nearest-neighbor metal atom shell is derived from standard crystallographic data. These parameters are listed separately in Table I.

from the jth nearest-neighbor metal atom. One expects thus that

$$\Delta\bar{H}_\infty \propto \sum_j R_j^{-n} , \qquad (16)$$

where n is a power which has to be determined and the sum is over all metallic nearest neighbors.

(ii) *Electronic band energies:* In the spirit of a tight-binding approach to the total energy of an alloy (or metal hydride) one might expect that parameters such as the number N_d of d electrons, the d-d and d-s overlap integrals are determining $\Delta\bar{H}_\infty$. The d-d overlap integral is proportional to the d-band width W_d. Further, from a large body of experimental data on metal hydrides (see Ref. 5) we conclude that the d-band filling of the host metal is an important parameter. On the basis of the good correlation which has previously been found[24-27] between ΔE and $\Delta\bar{H}_\infty$, we postulate here that $\Delta\bar{H}_\infty$ is also proportional to $\Delta E = E_F - E_S$. This means very approximately that $\Delta\bar{H}_\infty \propto W_d(N_d/10)$.

Combining (i) and (ii) we expect then that X is a function of R_j, ΔE, and W_d. As from the outset we have restricted the choice of X to the class of parameters with a constant volume dependence γ_X [see Eq. (5)] this implies that X is a product of the form[30]

$$X = \Delta E W_d^m \sum_j R_j^{-n} . \qquad (17)$$

The powers m and n are related to each other through the relation

$$\gamma_X = -\frac{\partial \ln X}{\partial \ln V} = -\frac{\partial \ln \Delta E}{\partial \ln V} - m\frac{\partial \ln W_d}{\partial \ln V} + \frac{\partial \ln\left[\sum_j R_j^{-n}\right]}{\partial \ln V}$$

$$= 3.83 . \qquad (18)$$

which follows directly from Eqs. (5) and (13). Transition metal experiments and band-structure calculations[31,32] show that $W_d \propto V^{-5/3}$. For the energy difference $E_F - E_s$ one expects the same volume dependence as E_s is basically pinned to the lowest d band which has a strong s character at the interstitial sites occupied by the hydrogen.[33] One obtains then from Eq. (18) the following constraint for the unknown powers m and n:

$$5m + n = 6.5 . \qquad (19)$$

As large interstitial sites are more attractive for hydrogen occupation than small sites n must be positive. As shown in Fig. 3 an excellent correlation is found for $m = \frac{1}{2}$ and $n = 4$. The enthalpy of solution at infinite dilution is thus simply related to ΔE, W_d, and R_j through the expression

TABLE I. Characteristic band-structure energy ΔE, d-band width W_d, and geometric factor $\sum_j R_j^{-4}$ for octahedral (oct) or tetrahedral (tetr) site occupancy of hydrogen in transition metals.

Element	Structure	a (Å)	Site[a]	$\sum_i R_j^{-4}$[b] (Å^{-4})	ΔE[c] (eV)	W_d^c (eV)
Sc	hcp	3.31	oct	0.200	1.65	4.2
Ti	hcp	2.95	oct	0.317	2.45	6.6
V	bcc	3.03	tetr	0.486	2.90	6.6
Cr	bcc	2.88	tetr	0.595	4.05	6.8
Mn	cubic	8.89				
Fe	bcc	2.86	tetr	0.612	4.60	5.0
Co	hcp	2.51	oct	0.605	4.82	5.1
Ni	fcc	3.52	oct	0.625	4.30	4.6
Y	hcp	3.65	oct	0.135	1.50	~6
Zr	hcp	3.23	oct	0.220	2.50	7.4
Nb	bcc	3.29	tetr	0.350	2.90	9.0
Mo	bcc	3.14	tetr	0.421	4.50	9.8
Tc	hcp	2.74	oct	0.426	~4.6	~9.2
Ru	hcp	2.70	oct	0.452	5.28	6.5
Rh	fcc	3.80	oct	0.460	5.20	7.0
Pd	fcc	3.88	oct	0.424	4.38	5.5
La	hcp	3.77	oct	0.119	1.40	8.4
Hf	hcp	3.19	oct	0.232	3.20	~9.7
Ta	bcc	3.29	tetr	0.350	3.40	9.7
W	bcc	3.16	tetr	0.411	5.30	11.0
Re	hcp	2.76	oct	0.414	5.44	~10.5
Os	hcp	2.74	oct	0.426	6.8	~11.0
Ir	fcc	3.83	oct	0.446	7.35	11.6
Pt	fcc	3.92	oct	0.407	6.45	7.9

[a]Site for which $\sum_j R_j^{-4}$ in the fifth column is calculated.

[b]For tetrahedral sites the sum is over the four nearest-neighbor metal atoms; for octahedral sites it is over the six nearest neighbors.

[c]For references, see Ref. 24.

$$\Delta \bar{H}_\infty = 18.6 \Delta E \ W_d^{1/2} \sum_j R_j^{-4} - 90 \tag{20}$$

when ΔE and W_d are expressed in eV, R_j in Å, and $\Delta \bar{H}_\infty$ in kJ/mol H. The parameters entering Eq. (20) are given in Table I. From Eqs. (3) and (20) it follows immediately that:

$$\bar{V}_H = \frac{1}{B} \left[71.2 \Delta E \ W_d^{1/2} \sum_j R_j^{-4} \right] . \tag{21}$$

The values $\Delta \bar{H}_\infty$, $B\bar{V}_H$, and $\bar{V}_H$ predicted by the present model are compared to existing experimental values in Figs. 4–6. The quality of the agreement is rather remarkable as the model involves in fact only two fit parameters.

Compared to existing semiempirical models for the heat of solution (or formation) of metal-hydrogen systems the present model has the advantage that it is more accurate although it involves a smaller number of fit parameters and, what is even more important, it is site dependent through $\sum R_j^{-4}$. In the following section we consider some direct implications of the local semiempirical model.

III. INCOMPRESSIBILITY OF H IN METALS

As clearly exhibited by Fig. 6 the molar volume of hydrogen in a metal assumes a value of ~ 1.7 cm^3/mol H or 2.8 Å^3/at. which is almost independent of the host metal. This behavior has often been interpreted as a clear evidence for the "rigidity" or "incompressibility" of a hydrogen atom. This view is also strengthened by the high-pressure measurements of Fukai et al.[34] and Syono et al.[35] which show that

$$\frac{\bar{V}_H(p = 130 \ \text{GPa})}{\bar{V}_H(p = 0)} = 0.74 \tag{22}$$

FIG. 5. Comparison of experimental $B\bar{V}_H$ [or equivalently, $\partial \ln \Delta \bar{H} / \partial \ln V$, see Eq. (3)] with values predicted by the local semiempirical band-structure model.

is almost equal to the pressure dependence of the atomic volume of pure vanadium $\bar{V}_V$ for which

$$\frac{\bar{V}_V(p = 130 \ \text{GPa})}{\bar{V}_V(p = 0)} = 0.69 . \tag{23}$$

In his paper on the site preference of interstitial hydrogen in metals, Fukai[36] concludes thus that hydrogen is at least as incompressible as the host lattice. Similar behavior has also been found for hydrogen in niobium.[37]
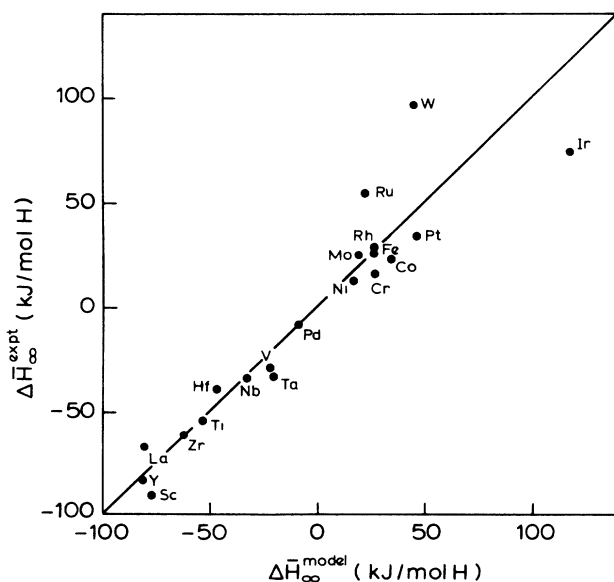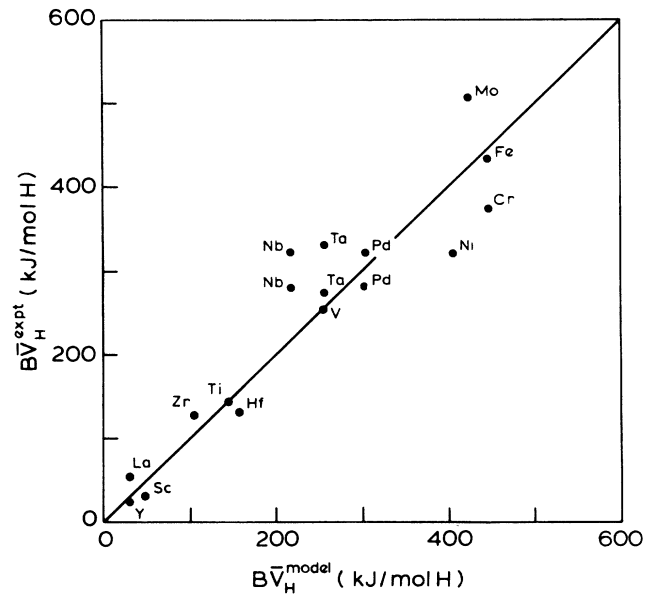

FIG. 4. Comparison of experimental heats of hydrogen solution with values predicted by the local semiempirical band-structure model.
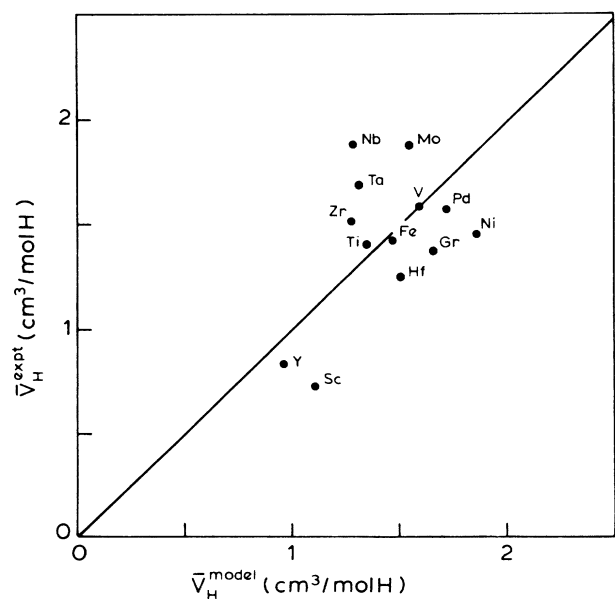

FIG. 6. Comparison of experimental partial molar volumes with predictions of the local semiempirical band-structure model.

We shall now show that the rigidity of hydrogen follows also from the present local semiempirical band-structure model. From Eq. (13) we derive the following relation for the pressure dependence of $\overline{V}_H$:

$$\frac{d(B\overline{V}_H)}{dp} = 3.83 \frac{\partial \Delta \overline{H}_\infty}{\partial p} \qquad (24)$$

which by means of Eqs. (2) and (3) can be cast in the following form:

$$\frac{d \ln B}{dp} + \frac{d \ln \overline{V}_H}{dp} = \frac{3.83}{B} \ . \qquad (25)$$

In general for a transition metal one expects that the bulk modulus B scales with volume approximately as $V^{-8/3}$ since B is proportional to (W_d/V) and the width of the d-band varies as $V^{-5/3}$. In the context of such a simple tight-binding approach we find then that

$$\frac{d \ln \overline{V}_H}{dp} \cong \frac{1.16}{B} \qquad (26)$$

in qualitative agreement with Fukai's conclusion, that $(d \ln \overline{V}_H/dp) \sim (1/B)$, when B is the bulk modulus of the *host* metal. For the specific case of VH_x and NbH_x Eq. (25) can be evaluated more accurately by using the measured values $=5.3\pm0.2$ for $d \ln B/d \ln V$ in vanadium[34,35] and niobium,[37] respectively. We obtain then

$$\frac{d \ln \overline{V}_H}{dp} = -\frac{1.47}{B} \qquad (27)$$

for VH_x and

$$\frac{d \ln \overline{V}_H}{dp} = -\frac{0.41}{B} \qquad (28)$$

for NbH_x. Equations (27) and (28) imply in fact that $\overline{V}_H \propto V^{+1.47}$ for VH_x and $\overline{V}_H \propto V^{+0.41}$ for NbH_x. For VH_x at a pressure of 130 GPa where the volume of pure vanadium is 69% of its zero-pressure volume we expect thus that $\overline{V}_H(130 \ \text{GPa})/\overline{V}_H(0)=0.61$ in reasonable agreement with the measured value indicated in Eq. (22).

For the niobium-hydrogen system the model predicts that $\overline{V}_H \ (p=60 \ \text{GPa})/\overline{V}_H(0)=0.91$ in agreement with the experimental data shown in Fig. 7 of Ref. 37.

IV. INTERSTITIAL SITE OCCUPATION BY HYDROGEN ATOMS

Except for Mn all transition metals crystallize in a hcp, bcc, or fcc structure. The interstitial sites for these structures are either of the tetrahedral type or of the octahedral type. As ΔE and W_d for a given metal are by definition site independent we find that the heats of solution for hydrogen in two different types of sites (I and II) are related to each other by

$$\frac{\Delta \overline{H}_\infty^I - \beta}{\Delta \overline{H}_\infty^{II} - \beta} = \frac{\underset{\text{site I}}{\sum} R_j^{-4}}{\underset{\text{site II}}{\sum} R_j^{-4}} \ . \qquad (29)$$

For hcp, bcc, and fcc host metal crystal structures Eq. (29) leads to

$$\text{hcp}, \Delta \overline{H}_\infty^{\text{tetr}} = 1.185 \Delta \overline{H}_\infty^{\text{oct}} + 16.67 \ ;$$

$$\text{bcc}, \Delta \overline{H}_\infty^{\text{oct}} = 1.172 \Delta \overline{H}_\infty^{\text{tetr}} + 15.47 \ : \qquad (30)$$

$$\text{fcc}, \Delta \overline{H}_\infty^{\text{tetr}} = 1.185 \Delta \overline{H}_\infty^{\text{oct}} + 16.67 \ .$$

The equations for hcp (with ideal c/a ratio) and fcc host metals are identical because the tetrahedral and octahedral sites in these two structures have the same symmetry. In the following we consider some specific examples to check the validity of Eq. (30).

(a) Palladium: Numerous neutron scattering experiments have firmly established that hydrogen occupies octahedral sites.[36] For Pd, $\Delta \overline{H}_\infty^{\text{oct}}$ has been measured to be -10 kJ/mol H. Equation (30) predicts then that $\Delta \overline{H}_\infty^{\text{tetr}} \cong 5$ kJ/mol H. At room temperature this implies that the occupation of tetrahedral sites is much smaller than that of octahedral sites. At low concentrations the ratio of occupation fraction $x_{\text{tetr}}/x_{\text{oct}}$ is approximately given by

$$\frac{x_{\text{tetr}}}{x_{\text{oct}}} = \exp \left[-\frac{\Delta \overline{H}_{\text{tetr}} - \Delta \overline{H}_{\text{oct}}}{RT} \right] \qquad (31)$$

which is of the order of 10^{-3} at room temperature.

(b) Vanadium, niobium, and tantalum: At low concentrations hydrogen occupies tetrahedral sites in the bcc structure of the host metal. For references to the large body of experimental investigations of the V-H(D), Nb-H(D), and Ta-H(D) systems the reader is referred to the review paper of Schober and Wenzl.[38] For all three metals the experimental values for $\Delta \overline{H}_\infty^{\text{tetr}}$ are approximately equal to -35 kJ/mol H. The value for $\Delta \overline{H}_\infty^{\text{oct}}$ predicted by Eq. (30) is then ~ 11 kJ/mol H higher and thus not favorable for hydrogen occupation, in agreement with the experiment. At higher concentrations it is found that hydrogen as well as deuterium occupy octahedral sites. In V_2H and V_2D the monoclinic structure is almost tetragonal with a c/a ratio of 1.10, the interstitials occupying octahedral sites in planes perpendicular to the c-axis. We show in the following that when hydrogen occupies octahedral sites our model predicts a tetragonal distortion which is in excellent agreement with the measured value.

As is well known the octahedral sites in a bcc structure have a tetragonal symmetry. The $\Delta \overline{H}_\infty$ for hydrogen in an undeformed octahedron is therefore mainly determined by the two closest vanadium atoms. A lowering of $\Delta \overline{H}_\infty$ can be achieved by allowing the bcc structure to deform tetragonally. This of course to the detriment of elastic energy. As tetragonal distortions are often volume conserving (this is to a good approximation the case for the V-H system) we consider a tetragonal distortion at constant volume. If the strain along the c axis is denoted by γ then the strains along the x and y axes are $-\gamma/2$. The optimal value of γ is determined by the minimum of the energy $E(\gamma)$ defined as

$$E(\gamma) = \Delta \overline{H}_\infty^{\text{oct}}(\gamma) - \Delta \overline{H}_\infty^{\text{oct}}(\gamma=0) + \tfrac{3}{4}(C_{11} - C_{12})V_m \gamma^2 \ , \qquad (32)$$

where C_{ij} are the elastic constants and V_m the molar volume of the metal-hydrogen system. $\Delta \bar{H}_\infty^{\text{oct}}(\gamma)$ for a deformed octahedral site can be evaluated from a relation similar to Eq. (19). One finds

$$\Delta \bar{H}_\infty^{\text{oct}}(\gamma) - \Delta \bar{H}_\infty^{\text{oct}}(\gamma=0)$$

$$= [\Delta \bar{H}_\infty^{\text{oct}}(\gamma=0) - \beta] \left[\frac{\displaystyle\sum_j R_j^{-4}(\gamma)}{\displaystyle\sum_j R_j^{-4}(0)} - 1 \right]. \quad (33)$$

The sum $\sum_j R_j^{-4}(\gamma)$ over the six nearest-neighbor vanadium atoms of a hydrogen occupying an octahedral site in a bcc lattice with lattice parameters c and a is given by

$$\sum_j R_j^{-4}(\gamma) = \left| \frac{32}{c^4} + \frac{16}{a^4} \right|. \quad (34)$$

From Eqs. (32)–(34) and introducing the quantity $\delta = c/a_0$ where a_0 is the lattice constant of the undeformed bcc vanadium lattice we find that

$$E(\delta) = [\Delta \bar{H}_\infty^{\text{oct}}(\delta=1) - \beta][\tfrac{1}{3}(\delta^{-4} + \delta^2) - 1]$$

$$+ \tfrac{3}{4}(C_{11} - C_{12})V_m(\delta-1)^2 \quad (35)$$

and from $dE(\delta)/d\delta = 0$ that

$$\frac{\delta^6 - \delta^5}{\delta^6 - 4} = \frac{\Delta \bar{H}_\infty^{\text{oct}}(\delta=1) - \beta}{\dfrac{3}{2}(C_{11} - C_{12})V_m} \quad (36)$$

with $\Delta \bar{H}_\infty^{\text{oct}}(\delta=1) = -24$ kJ/mol H, $C_{11} = 229$ kJ/cm^3, $C_{12} = 117$ kJ/cm^3, and $V_m = 8.78$ cm^3 we obtain from Eq. (36) that $\delta = 1.075$ and consequently $c/a = 1.11$ in excellent agreement with the measured value of 1.10.

(c) Yttrium, titanium, and zirconium: From neutron diffraction experiments it is known that hydrogen occupies tetrahedral sites in Ti and Zr. In Y deuterium occupies also tetrahedral sites but hydrogen has been shown by inelastic neutron scattering to occupy both tetrahedral and octahedral sites in Y. For hcp, CrH synthesized under high pressures or by electrolytic techniques neutron diffraction establishes the occupation of octahedral sites (for references, see Ref. 36). For hcp metals Eq. (30) predicts that octahedral sites are always more favorable than tetrahedral sites. The difference $\Delta \bar{H}_{\text{tetr}} - \Delta \bar{H}_{\text{oct}}$ is however relatively small. For Y where $\Delta \bar{H}_{\text{oct}} = -79$ kJ/mol H, we find $\Delta \bar{H}_{\text{tetr}} = -76.9$ kJ/mol H in qualitative agreement with the observed dual occupation of octahedral and tetrahedral sites in this metal. It is important to note that when different interstitial sites have very similar heat of solutions, hydrogen-hydrogen interactions may play an important role in determining which type of sites is actually occupied.[39-41]

The examples discussed here show that our semiempirical model predicts correctly the trends observed for the site preference of hydrogen in transition metals. For the *binary* metal hydrides considered in this work site preference is entirely determined by a geometrical characteristic of a given site, i.e., by the $\sum_j R_j^{-4}$ term [see Eq. (29)]. This suggests a possible relation between the present

model and a purely geometric model such as that proposed by Westlake.[42-44] According to Westlake a site can be occupied by a hydrogen atom when the radius R_i of the inscribed sphere centered at the hydrogen site (which by definition, touches the spheres of radius R_a of the nearest-neighbor metal atoms) is larger than ~ 0.4 Å. This rule has been used with success to predict the site preference of hydrogen in certain intermetallics with $C14$ and $C15$ structure (e.g., ZrMn$_2$ and ZrTi$_2$, ZrV$_2$, TaV$_2$, etc.). A geometric rule, however, cannot predict the stability of hydrides. For example, platinum which has a larger lattice constant ($a = 3.92$ Å) than palladium ($a = 3.88$ Å) does not absorb any hydrogen at room temperature under 1-bar H$_2$ gas, although R_i for both metals is ~ 0.57 Å and thus much larger than the critical value 0.4 Å.

We show now that the semiempirical model presented in this work also leads to a sort of critical interstitial site size. Starting from Eq. (20) and using the fact that at 1 bar and 300 K only sites with $\Delta \bar{H}_\infty \leq -19$ kJ/moL H are significantly occupied[5,6] we obtain

$$R \geq 0.715 \ (n \Delta E W_d^{1/2})^{1/4}, \quad (37)$$

where R is the distance between H and one of the neighboring metal atoms. For simplicity we consider here only regular octahedral ($n = 6$) and tetrahedral ($n = 4$) sites. As $R = R_i + R_a$ and R_a are simply related to the lattice spacing a, i.e.,

$$R_a(\text{fcc}) = a\sqrt{2}/4, \quad R(\text{fcc}) = a/2,$$

$$R_a(\text{bcc}) = a\sqrt{3}/4, \quad R(\text{bcc}) = a\sqrt{5}/4, \quad (38)$$

$$R_a(\text{hcp}) = a/2, \quad R(\text{hcp}) = a/\sqrt{2},$$

Eq. (37) can be transformed into a condition for the minimum size of the inscribed sphere,

$$R_{\text{min}}(\text{fcc}) = 0.328(\Delta E \ W_d^{1/2})^{1/4},$$

$$R_{\text{min}}(\text{bcc}) = 0.228(\Delta E \ W_d^{1/2})^{1/4}, \quad (39)$$

$$R_{\text{min}}(\text{hcp}) = 0.328(\Delta E \ W_d^{1/2})^{1/4}.$$

We consider now a few representative examples: For Pd, $R_{\text{min}} = 0.587$ Å and $R_i = 0.146a = 0.568$ Å, we have almost $R_i = R_{\text{min}}$ and Pd absorbs H as soon as the pressure is slightly increased; for Pt, $R_{\text{min}} = 0.677$ Å and $R_i = 0.572$ Å and absorption of H is not possible. For V, $R_{\text{min}} = 0.377$ Å and $R_i = 0.382$ Å and for Nb, $R_{\text{min}} = 0.392$ Å and $R_i = 0.415$ Å, so that in both cases H absorption occurs at 1 bar and 300 K. For the hcp metals Sc, $R_{\text{min}} = 0.445$ Å and $R_i = 0.207a = 0.685$ Å, and T_i, $R_{\text{min}} = 0.520$ Å and $R_i = 0.611$ Å so that H absorption occurs readily.

In our model the critical inscribed sphere radius is of the same order of magnitude as in Westlake's purely geometric model but the magnitude of R_{min} depends on the band width W_d and the characteristic band-structure energy ΔE. As shall be discussed elsewhere the dependence on ΔE is important as ΔE depends on electronic band filling.

V. BINDING ENERGY OF HYDROGEN TO VACANCIES

For some transition metals the binding energy of a hydrogen atom to a vacancy has been determined experimentally.[45] One finds that for early transition metals $\Delta E_{binding}$ is relatively small while it is substantial ~ -50 kJ/mol H for the remaining transition metals. This trend is also predicted by the present model. Similarly to Eq. (29) we can write

$$\frac{\Delta \bar{H}_{vac} - \beta}{\Delta \bar{H}_\infty - \beta} = \frac{\sum_j R_{j\,vac}^{-4}}{\sum_j R_j^{-4}} \ . \tag{40}$$

$\Delta E_{binding}$ is defined as the difference between the energy of a hydrogen atom in the most favorable site of the perfect host metal and that of a hydrogen trapped at a vacancy. In a fcc metal a vacancy has 12 nearest neighbors at a distance $a/\sqrt{2}$ so that $\sum_j R_j^{-4} = 48a^{-4}$ which is exactly half of the value corresponding to hydrogen occupying an octahedral site. Consequently,

$$\Delta E_{binding} = \Delta \bar{H}_{vac} - \Delta \bar{H}_\infty^{oct} = -\tfrac{1}{2}\Delta \bar{H}_\infty^{oct} - 45 \ . \tag{41}$$

The same relation holds for hcp metals with an ideal c/a ratio $(c/a = \sqrt{8}/3)$. For a vacancy in a bcc metal the situation is somewhat more complicated as there are eight nearest-neighbor metal atoms at $a\sqrt{3}/2$ and six second nearest neighbors at a, so that $\sum_j R_j^{-4} = 13.11a^{-4}$. Assuming that in the absence of vacancies hydrogen occupies tetrahedral sites we obtain for the binding energy

$$\Delta E_{binding} = \Delta \bar{H}_{vac} - \Delta \bar{H}_\infty^{tetr}$$
$$= -0.6799\Delta \bar{H}_\infty^{tetr} - 61.19 \ . \tag{42}$$

The binding energies to a vacancy calculated by means of Eqs. (41) or (42) using experimental values for the heat of solutions $\Delta \bar{H}_\infty$ are shown in Fig. 7. Our values reproduce the general trend found experimentally across the $3d$, $4d$, and $5d$ series. It is also interesting to point out that the present simple model predicts value for $\Delta E_{binding}$ which are often very close to that calculated by Nordlander et al.[45] using the effective medium theory developed by Nørskov[46,47] and Puska and Nieminnen.[48,49]

VI. CONCLUSIONS

The present local semiempirical model involves only two constant parameters α and β and characterizes a particular site of the host metal by the parameter $\Delta E \ W_d^{1/2}\sum_j R_j^{-4}$. Both ΔE and W_d are band-structure energies and therefore inherently nonlocal in nature. ΔE depends on the number of conduction electrons while W_d is a measure of the d-d overlap in a transition metal. The locality of the model arises from the $\sum_j R_j^{-4}$ term which depends on the distance between a hydrogen atom at a given interstitial site and the neighboring metal atoms. The expression $\Delta \bar{H}_\infty = \alpha \Delta E \ W_d^{1/2}\sum_j R_j^{-4} + \beta$ gives a remarkably good description of the measured heats of solution at infinite dilution.

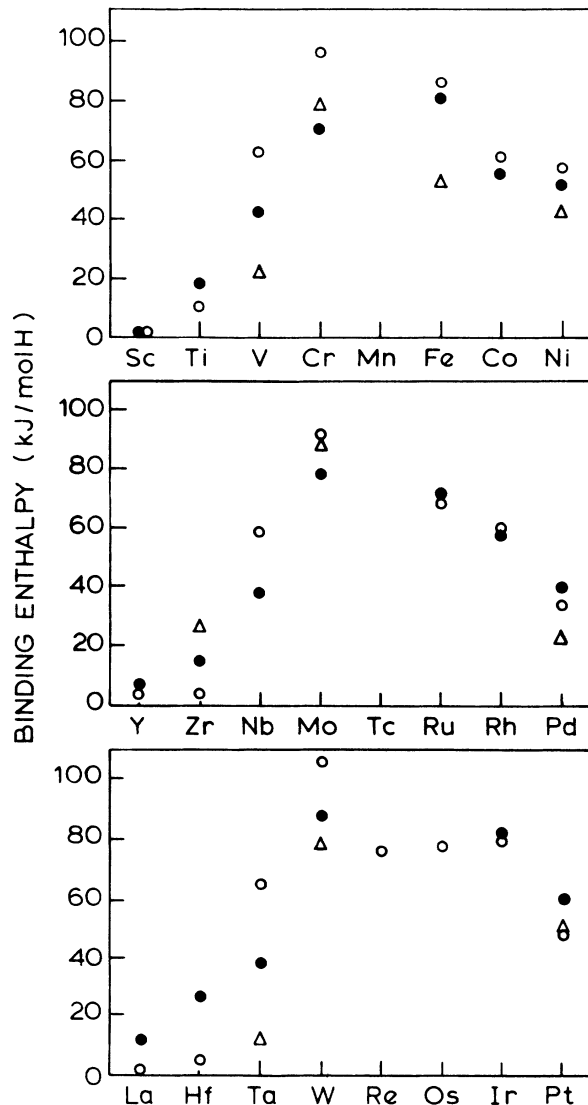All three terms ΔE, W_d, and of course $\sum_j R_j^{-4}$ depend

FIG. 7. Binding energies of hydrogen at vacancies. △, experimental values (see Ref. 42); ●, predictions of the local semiempirical model [Eqs. (41) or (42)]; ○, values calculated by means of the effective-medium theory (Ref. 42).

on the volume V of the host metal. Using the results of simple transition metal band-structure models for which $\Delta E \propto V^{-5/3}$ and $W_d \propto V^{-5/3}$ we showed that without introducing any additional fit parameters the model predicts also correct values for the molar volume $\bar{V}_H$ of hydrogen in a transition metal and reproduces the observed incompressibility of hydrogen.

Furthermore the model is capable of reproducing the measured binding energies of hydrogen to vacancies and explains the trends of interstitial site occupancy of hydrogen in transition metals.

Our model is easily generalized to the case of hydrogen in compounds and alloys. This shall make the object of subsequent papers.

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

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

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

[4]R. Wiswall, *Hydrogen in Metals II*, Vol. 29 of *Topics in Applied Physics,* edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), p. 201.

[5]R. Griessen and T. Riesterer, in Vol. 63 of *Topics in Applied Physics,* edited by L. Schlapbach (Springer, Berlin, 1988), p. 219.

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

[7]A. C. Switendick, *Hydrogen in Metals I,* Vol. 28 of *Topics in Applied Physics,* edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), p. 101 and references therein.

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

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

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

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

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

[13]M. Gupta, J. Less-Common. Met. 88, 221 (1982).

[14]M. Gupta, Phys. Lett. 88A, 469 (1982).

[15]D. A. Papaconstantopoulos and A. C. Switendick, J. Less-Common Met. 88, 273 (1982).

[16]W. M. Temmermann and A. J. Pindor, J. Phys. F 13, 1869 (1983).

[17]M. Gupta, J. Less-Common Met. 103, 315 (1984).

[18]M. Gupta, E. Belin, and L. Schlapbach, J. Less-Common Met. 103, 389 (1984).

[19]A. C. Switendick, J. Less-Common Met. 130, 249 (1987).

[20]S. Cabus, Ph.D. thesis, Universität Darmstadt, 1987.

[21]A. R. Miedema, K. H. J. Buschow, and H. H. van Mal, J. Less-Common Met. 49, 463 (1976), and references therein.

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

[23]R. Griessen, Phys. Rev. B 27, 2069 (1983).

[24]R. Griessen and A. Driessen, Phys. Rev. B 30, 4372 (1984).

[25]R. Griessen, A. Driessen, and D. G. de Groot, J. Less-Common Met. 103, 235 (1984).

[26]R. Griessen and R. Feenstra, J. Phys. F 15, 1013 (1985).

[27]R. Feenstra and R. Griessen, Solid State Commun. 59, 905 (1986).

[28]K. A. Gschneider, Solid State Phys. 16, 275 (1964).

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

[30]In general $X = \Delta E^p W_d^m (\sum_j R_j^{-n})^r$ could be chosen in order to satisfy our assumption that the Grüneisen-like parameter γ_x is a constant. From the work on palladium-based hydrides (see, e.g., Ref. 27 and references therein) we conclude, however, that $p = 1$. Furthermore we found that allowing for $r \neq 1$ did not improve the correlation between $\Delta \bar{H}_\infty$ and X, significantly.

[31]W. Joss, R. Griessen, and E. Fawcett, *Electron States and Fermi Surfaces of Homogeneously Strained Metallic Elements,* Vol. 12 of Landolt-Börnstein New Series, *Metals: Phonon States, Electron States and Fermi Surfaces* (Springer, Heidelberg, 1983), p. 1.

[32]V. Heine, in *The Physics of Electronic Structure of Metals, Metals I, Electrons,* edited by J. M. Ziman (CUP, Cambridge, 1969), p. 1.

[33]R. Griessen, in *Hydrogen in Disordered and Amorphous Solids,* edited by G. Bambakidis and R. C. Bouwman (Plenum, New York, 1986), p. 153.

[34]Y. Fukai, K. Watanabe, and A. Fukizawa, J. Less-Common Met. 88, 27 (1982).

[35]Y. Syono, K. Kusaba, K. Fukuoka, Y. Fukai, and K. Watanabe, Phys. Rev. B 29, 6520 (1984).

[36]Y. Fukai, J. Less-Common Met. 10, 1 (1984).

[37]A. Fukizawa and Y. Fukai, J. Phys. Soc. Jpn. 52, 2102 (1983).

[38]T. Schober and H. Wenzl, *Hydrogen in Metals II,* Vol. 29 of *Topics in Applied Physics* (Springer, Berlin, 1978), p. 11. 11.

[39]P. M. Richards, Bull. Am. Phys. Soc. 32, 453 (1987), and private communications.

[40]M. W. McKergow, D. K. Ross, J. E. Bonnet, I. S. Anderson, and O. Schaerpf, J. Phys. C 20, 1909 (1987).

[41]I. S. Anderson, J. J. Rush, T. Udovic, and J. M. Rowe, Phys. Rev. Lett. 57, 2822 (1986).

[42]D. G. Westlake, J. Less-Common Met. 90, 251 (1983).

[43]D. G. Westlake, J. Less-Common Met. 91, 275 (1983).

[44]D. G. Westlake, J. Less-Common Met. 88, 17 (1982).

[45]P. Nordlander, J. K. Nørskov, and F. Besenbacher, J. Phys. F 16, 1161 (1986).

[46]J. K. Nørskov, Phys. Rev. B 26, 2875 (1982); For a discussion of the relation which exists between the semiempirical band-structure model of Griessen and Driessen and the effective-medium theory of Nørskov et al. the reader is referred to Ref. 5.

[47]J. K. Nørskov, Phys. Rev. B 28, 1138 (1983).

[48]M. J. Puska and R. M. Nieminnen, Phys. Rev. B 29, 5382 (1984).

[49]M. J. Puska and R. M. Nieminnen, Phys. Rev. B 32, 1353 (1985).