Chemical binding energies of point defects in palladium doped with hydrogen and d impurities
C. Demangeat, M. A. Khan, G. Moraitis, J.-C. Parlebas

To cite this version:

HAL Id: jpa-00208913
https://hal.archives-ouvertes.fr/jpa-00208913
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Chemical binding energies of point defects in palladium doped with hydrogen and d impurities

C. Demangeat, M. A. Khan, G. Moraitis (*) and J.-C. Parlebas

Laboratoire de Magnétisme et de Structure Electronique des Solides,
Université Louis-Pasteur (*), 4, rue Blaise-Pascal, 67070 Strasbourg Cedex, France

(Reçu le 5 décembre 1979, révisé le 18 février, accepté le 22 mai 1980)

Abstract. — Using an extra-orbital model within a generalized « spd » tight-binding approximation, we calculate the chemical binding energy of a pair of hydrogen atoms in palladium within the infinite dilution limit; we find that clusters of hydrogen cannot form in accordance with inelastic neutron scattering data in α-palladium hydride. The strong repulsive interaction between a pair of hydrogen impurities at distance a, where a is the host lattice parameter, seems to be related to the presence of an intermediate metallic site between the two impurities. Also we determine the chemical binding energies between a hydrogen atom and d substitutional impurities and we discuss our results in relation with recent Mössbauer experiments. Finally we calculate the chemical binding energy between two d impurities in palladium which we compare with experimental data on the enthalpy of formation.

1. Introduction. — Since the work of Alefeld [1] it is often assumed that the dominant contribution to the interaction energy between hydrogen atoms in a transition metal is of an elastic nature, especially in a coherent metal — hydrogen system [2]. However Masuda and Mori [3] showed that chemical binding energies, i.e. electronic contributions, might be as large as elastic energies and that the sign depended drastically on the filling of the host d bands under consideration. Similar calculations have been performed in the case of binding energies of ad-atoms [4, and references therein]. This type of result suggests to us that the origin of the hydrogen-hydrogen interaction, in palladium for example, is the sum of a long-ranged elastic part [1, 2] and a short-ranged chemical part [3]. However, as shown by Dietrich and Wagner [5] this type of separation may not be valid in coherent palladium systems (see for example table 1 of [5]). Considering now dilute ternary alloys, the problem of binding energies between hydrogen atoms and foreign d elements in transition metals is of considerable interest for the thermodynamic and kinetic properties in the infinite dilution limit [6]. We will precisely restrict our attention to that limit in palladium alloys doped with hydrogen and d impurities; we will not discuss problems like the change of...
The purpose of the present paper is to extend the extra-orbital model previously considered by Masuda and Mori [3] in a crude case, i.e. a simple cubic structure (with s orbitals) to a realistic host band structure. The electronic structure model of hydrogen in palladium is built from a Slater-Koster fit to first principles band structure for the host, combined with one s extra-orbital for each isolated impurity atom [8].

Table 1. — Matrix elements of the Green functions between the nearest neighbours in the case of s and d orbitals in a f.c.c. crystal. Part of this table has been given by Hayakawa H. (Prog. Theor. Phys. 37 (1967) 213), however with different notations.

<table>
<thead>
<tr>
<th></th>
<th>± a(± 1, 1, 0)/2</th>
<th>± a(0, ± 1, 1)</th>
<th>± a(± 1, 0, 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>G^(0)(1)</td>
<td>G^(0)(2)</td>
</tr>
<tr>
<td>xy</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>± G^(0)(3)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>± 2 G^(0)(6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>± G^(0)(3)</td>
</tr>
<tr>
<td>yz</td>
<td>2</td>
<td>G^(0)(2)</td>
<td>G^(0)(1)</td>
</tr>
<tr>
<td>3</td>
<td>± G^(0)(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>± 3 G^(0)(6)</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>± G^(0)(6)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>± G^(0)(3)</td>
<td>0</td>
</tr>
<tr>
<td>zx</td>
<td>2</td>
<td>G^(0)(2)</td>
<td>G^(0)(2)</td>
</tr>
<tr>
<td>3</td>
<td>± G^(0)(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>± 3 G^(0)(6)</td>
<td>G^(0)(6)</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>x^2 - y^2</td>
<td>2</td>
<td>± 3 G^(0)(6)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>- [G^(0)(4) - 4 G^(0)(5)]/3</td>
<td>2[G^(0)(4) + G^(0)(5)]/3</td>
<td>2[G^(0)(4) - G^(0)(5)]/3</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>s</td>
<td>± G^(0)(3)</td>
<td>± G^(0)(3)</td>
<td>± G^(0)(3)</td>
</tr>
<tr>
<td>s</td>
<td>xy</td>
<td>G^(0)(7)</td>
<td>G^(0)(7)</td>
</tr>
<tr>
<td>yz</td>
<td>± G^(0)(8)</td>
<td>± G^(0)(8)</td>
<td>± G^(0)(8)</td>
</tr>
<tr>
<td>zx</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>x^2 - y^2</td>
<td>2</td>
<td>- 3 G^(0)(9)</td>
<td>G^(0)(9)</td>
</tr>
<tr>
<td>3 z^2 - r^2</td>
<td>- 2 G^(0)(9)</td>
<td>G^(0)(9)</td>
<td>G^(0)(9)</td>
</tr>
</tbody>
</table>

In section 2 we derive a general formulation of the binding energies between two hydrogen atoms or between a hydrogen interstitial and a substitutional d impurity. In our final expressions we recover the well known formal result previously obtained in the case of two d substitutional impurities [9, and references therein]. In section 3 we summarize detailed numerical calculations for binding energy of a pair of i) hydrogen atoms which is found to be repulsive; ii) a hydrogen-d substitutional impurity which is found to be attractive for a small impurity charge difference and repulsive elsewhere; iii) d substitutional impurities which is found to be repulsive.

2. General formulation for the chemical binding energy between different point defects in a transition metal. — The host band structure is supposed to be given by an extended (spd) Slater-Koster fit to a first principles calculation. The metallic spd orbitals are labelled \( | Rm \rangle \) where \( R \) is a metallic site and \( m \) designates the orbital symmetry (\( m = s, x, y, z, xy, yz, zx, x^2 - y^2, 3 z^2 - r^2 \)). Subsection 2.1 presents the chemical binding energy of a pair of hydrogen atoms whereas paragraph 2.2 formulates the chemical binding energy between an hydrogen atom and a d impurity in a cubic transition metal.
2.1 HYDROGEN-HYDROGEN CHEMICAL BINDING ENERGY. — Let \( \{ \lambda, \mu \} \) be hydrogen interstitial sites and \( | \lambda \rangle, | \mu \rangle \) the corresponding s extra-orbitals. The Hamiltonian \( H \) of the system with \( N + 2 \) sites, i.e. \( N \) metallic sites plus two interstitial sites, can be written:

\[
H = H^0 + V_{\lambda} + V_{\mu} + V_{\lambda \mu}
\]

(2.1)

where \( H^0 \) is the Hamiltonian of the pure metal, \( E_s \) is the hydrogen s level which is assumed to be unchangeable through impurity-impurity interactions (see reference [9] and references therein for a complete discussion on this point in the case of substitutional impurities). \( V_{\lambda}, V_{\mu} \) are given in terms of the hopping integrals between interstitial orbitals and surrounding metallic orbitals whereas \( V_{\lambda \mu} \) is expressed in terms of a direct hopping integral between s orbitals located on \( \lambda \) and \( \mu \) sites:

\[
V_{\lambda \mu} = \sum_{R,m} \langle \rho | \beta_{\lambda\mu}^{m} | Rm \rangle + \text{c.c.} \quad (\rho = \lambda, \mu)
\]

(2.2a)

By taking into account Friedel's sum rule (which states that the number of external electrons brought by the interstitials has to be equal to the total number of the displaced states up to the Fermi energy \( E_F \)) the binding energy can be cast into the following form which is well known for substitutional impurities:

\[
\Delta E(\lambda, \mu) = - \int_{E_F}^{E_F} \left( Z_{\lambda}(E) - Z_{\mu}(E) - Z_{\lambda}(E) \right) dE
\]

(2.3)

where \( Z_{\nu}(E) \) with \( \nu = \lambda, \mu, \lambda \mu \) is respectively the phase shift for isolated interstitial atoms when \( \nu = \lambda, \mu \) and a pair of interacting interstitial atoms when \( \nu = \lambda \mu \).

Let \( G^0(E) \) be the host Green function and \( G_{\nu}(E) \) the Green function relative to isolated interstitials \( (\nu = \lambda, \mu) \) and to an interacting pair \( (\nu = \lambda \mu) \).

The different phase shifts \( Z_{\nu}(E) \) are defined as usually by:

\[
Z_{\nu}(E) = \int_{E_F}^{E_F} \text{Tr} \left[ G_{\nu}(E') - G^0(E') \right] dE'; \quad (2.4)
\]

\( \nu = \lambda, \mu, \lambda \mu \).

After a bit of manipulation we obtain quite a general expression for the chemical binding energy of two \( \times s \) interstitial impurities:

\[
\Delta E(\lambda, \mu) = \frac{2}{\pi} \text{Im} \int_{E_F}^{E_F} dE \times \log \left[ 1 - \frac{\Delta^{\mu}(E) \Delta^{\lambda}(E) + 2 \Delta^{\mu}(E) \beta^{\mu} + \beta^{\mu} \beta^{\mu \lambda}}{\{ E - E_s - \Delta^{\lambda}(E) \} \{ E - E_s - \Delta^{\mu}(E) \}} \right]
\]

(2.5)

where

\[
\Delta^{\nu}(E) = \sum_{R,m} \beta^{m}_{\nu R} G_{Rm}(E) \beta^{m*}_{\nu R}.
\]

(2.6)

The factor 2 in equation (2.5) is due to spin degeneracy.

In the following we shall neglect the direct \( \beta^{\nu} \) terms so that equation (2.5) simplifies to:

\[
\Delta E(\lambda, \mu) = \frac{2}{\pi} \int_{E_F}^{E_F} dE \times \text{Arg} \left[ 1 - \frac{\Delta^{\mu}(E) \Delta^{\lambda}(E)}{\{ E - E_s - \Delta^{\lambda}(E) \} \{ E - E_s - \Delta^{\mu}(E) \}} \right]
\]

(2.7)

This approximation should be reasonable in f.c.c. metal like palladium where the distance between the nearest neighbouring hydrogen impurities is larger than the distance between \( \nu \) and \( R \) which appears in equation (2.6). The chemical binding energy (2.7) can then be expressed in terms of the \( t_{\nu} \) matrices \( (\rho = \lambda, \mu) \) for isolated interstitial impurities which are defined as:

\[
t_{\nu}(E) = V_{\rho} + V_{\mu} G^0(E) t_{\nu}(E).
\]

(2.8)

Expression (2.7) can finally be written in the following compact form:

\[
\Delta E(\lambda, \mu) = \frac{2}{\pi} \int_{E_F}^{E_F} dE \times \text{Arg} \left[ 1 - \text{Tr} \left[ t_{\nu}(E) G^0(E) t_{\nu}(E) G^0(E) \right] \right]
\]

(2.9)

where \( \text{Tr} \) means the trace over the \( N \) metallic sites. Let us point out that it is sometimes (but not always) convenient to use the asymptotic limit of equation (2.9) i.e. to keep only the leading term in the argument appearing in equation (2.9):

\[
\Delta E^{\infty}(\lambda, \mu) = - \frac{2}{\pi} \int_{E_F}^{E_F} dE \times \text{Im} \text{Tr} \left( t_{\nu}(E) G^0(E) t_{\nu}(E) G^0(E) \right).
\]

(2.10)

Before discussing our numerical results on hydrogen-hydrogen chemical binding energies, let us establish a similar formalism in the case of hydrogen-d impurity interactions.

2.2 HYDROGEN-d IMPURITY BINDING ENERGY. — To calculate the binding energy between a hydrogen atom located at the interstitial site \( \lambda \) and a d impurity substituted at site \( R_d \) we proceed as in the above section. The Hamiltonian is now relative to \( (N + 1) \) sites by including the hydrogen atom and it can be decomposed as follows:

\[
H = H^1 + \delta V_{\lambda} + V_{\lambda}
\]

(2.11)
where \( H^1 = H^0 + |\lambda > E_\mu <\lambda | \)

and \( \delta V_\mu = \sum_m |R_\mu m > \delta \nu_d <R_\mu m | \).

The last term \( V \) has been already defined by equation (2.2a). As usual in the case of d impurities in transition metals we only take into account the diagonal disorder matrix element

\[
\delta \nu_d = \langle R_\mu m | \delta V_\mu | R_\mu m \rangle
\]

of the impurity potential between \( |R_\mu m > \) orbitals localized on the d impurity site. This localized model is less valid for large charge difference \( \delta Z_\mu \) between impurity and host ion cores; however it certainly provides the general semi-quantitative trends along a transition series where \( \delta \nu_d \) is self-consistently determined from Friedel's sum rule:

\[
\delta Z_\mu(E_F) = -\frac{2}{\pi} \sum_{m=1}^{5} \text{Arg}(1 - \delta \nu_d G^{0m}(E_F))
\] (2.12)

The chemical binding energy can be put in the same form as equation (2.3) where \( Z_{dd}(E) \) is now the phase shift relative to an hydrogen-d impurity pair and \( Z_{dd}(E) \) has to be replaced by \( \delta Z_\mu(E) \). After some calculation we get the following expression for the binding energy:

\[
\Delta E(\lambda, R_\mu) = \frac{2}{\pi} \int_{E_F}^{E_F} dE \times
\]

\[
\times \text{Arg} \left[ 1 - \sum_l \frac{A^l(E) \delta \nu_d}{1 - \delta \nu_d G^{0l}(E)} \right]
\] (2.13)

with

\[
A^l(E) = \sum_{R_m} \sum_{T_n} \sum_{n} G_{\mu m}^{\text{dom}} \beta^l_{R_m T_n} G_{\nu d}^{\text{dom}} E - E_n - \Delta_{\lambda l}
\]

where \( l \) labels only the d orbital symmetries whereas \( m \) and \( n \) designate all the different s, p, d, orbital symmetries. Now introducing the \( t \) matrix associated with the isolated d impurity:

\[
\delta t_\mu(E) = (1 - \delta V_\mu G^0(E))^{-1} \delta V_\mu
\]

we recover for the interaction energy between interstitial and substitutional impurities the same formal result as equation (2.9)

\[
\Delta E(\lambda, R_\mu) = \frac{2}{\pi} \int_{E_F}^{E_F} dE \times
\]

\[
\times \text{Arg} \left[ 1 - \text{Tr} \{ t_\mu(E) G^0(E) \delta t_\mu(E) G^0(E) \} \right]
\] (2.14)

and the asymptotic limit is:

\[
\Delta E^{\text{as}}(\lambda, R_\mu) = -\frac{2}{\pi} \int_{E_F}^{E_F} dE \times
\]

\[
\times \text{Im} \left\{ t_\mu(E) G^0(E) \delta t_\mu(E) G^0(E) \right\}
\] (2.15)

The asymptotic results (2.10) and (2.15) have been already obtained for a pair of interacting substitutional impurities (see [9] and references therein). In the present paper we show that this type of result still holds for a pair of interstitial-interstitial or interstitial-substitutional impurities. Although we are doing the calculation in the particular case of a hydrogen interstitial atom, the equations (2.9) and (2.14) are readily extendable to other kinds of interstitial impurities.

3. Numerical investigation of binding energies of point defects in palladium doped with hydrogen and d impurities. — As seen in section 2, the calculation of chemical binding energies requires the knowledge of the host Green function \( G_{RR}^{\text{dom}} \). As the \( p \) contribution to the palladium density of states up to the Fermi energy seems rather unimportant [10], for simplicity, we only keep s and d host orbitals in the binding energy of the point defects. Also, we consider only the intersite Green functions between the first nearest neighbouring sites. These functions, owing to the selection rules of the crystal symmetry, can be expressed in terms of 9 independent terms: \( G^{01} \) \( G^{02} \) which are defined in table I. We call \( G^{01}(T_{1}) \) \( G^{01}(T_{12}) \) and \( G^{01}(T_{2}) \) the host intrasite Green functions for s, eg, and t_{2g} symmetries. All the Green functions are determined by using the Slater-Koster fit of reference [10].

3.1 HYDROGEN-HYDROGEN BINDING ENERGY. — In order to compute the expression (2.9) for two hydrogen interstitial sites \( \lambda \) and \( \mu \), we remark that

\[
\Delta E_{\mu \lambda}(E) = \Delta E_{\mu \lambda}^{\text{as}}(E)
\]

and that \( \Delta E_{\mu \lambda}^{\text{as}}(E) \) can be written explicitly in terms of the Green functions defined above. Let \( \mu_1 = \frac{a}{2} (0, 1, 1) \) and \( \mu_2 = \frac{a}{2} (0, 2, 0) \) be the first and the second nearest interstitial sites of a hydrogen atom at \( \lambda \), the origin of the coordinate system (Fig. 1). In a f.c.c. transition metal we have:

\[
\Delta E_{\mu \lambda}^{\text{as}}(E) = 2(\text{ss} s \delta E_0^2 \left[ G^0(T_{1}) + 8 G^0(7) \right] - \left[ G^0(T_{12}) - 6 G^0(5) - 2 G^0(4) \right] - 4 \text{ss} \text{sd} \text{sd} G^0(9)) \]

\[
\Delta E_{\mu \lambda} = (\text{ss} s^2) \left[ G^0(T_{1}) + 8 G^0(7) \right] + (\text{sd} s^2) \left[ 2 G^0(T_{12}) + 9 G^0(4) - 17 G^0(5)/2 + 16 \text{ ss} \text{sd} G^0(9) \right)
\] (3.1)

(3.2)

In equations (3.1), (3.2), ss and sd are the two centre hopping integrals, in Slater-Koster's notation, between hydrogen s orbital and metallic s, d orbitals. These integrals have been estimated (from [8]) to be (in Hartrees): \( \text{ss} = 0.037 \); \( \text{sd} = 0.027 \). A numerical calculation of the chemical binding energy between hydrogen atoms in palladium gives a strong repulsive
contribution for the nearest and the next nearest neighbours (Table II). From our results we observe that the asymptotic expression (2.10) differs sensitively from the exact result (2.9) especially for the next nearest neighbouring hydrogen atoms for which we obtain a very strong repulsive interaction. This result can be related to the presence of a metallic site between the hydrogen atoms when they are in the next nearest neighbouring positions. An analogous situation was found previously in the case of interacting carbon atoms in a b.c.c. α-iron host [11]. Moreover, a strong repulsive elastic binding energy has been also found from lattice statics calculations.

Table II. — Binding energies (in eV) of different pairs of hydrogen atoms consisting of a H atom at octahedral site $\frac{a}{2}(0, 0, 0)$ and another H atom at octahedral site $\frac{a}{2}(x, y, z)$; $n = 1, 2$ labels the nearest and the next nearest neighbours.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$x, y, z$</th>
<th>exact</th>
<th>asymptotic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0, 1, 1</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>0, 2, 0</td>
<td>0.38</td>
<td>0.45</td>
</tr>
</tbody>
</table>

3.2 HYDROGEN-d IMPURITY BINDING ENERGY.

Let us first write explicitly the quantities $A_n^m(E)$ which appear in the binding energy under consideration [Eq. (2.13)]. Let $R_{n1} = \frac{a}{2}(0, 0, 0)$ and $R_{n2} = \frac{a}{2}(1, 1, 1)$ the nearest and the next nearest crystalline sites of an interstitial site $\lambda = \frac{a}{2}(0, 0, 0)$ and the substitutional d impurity is located at the nearest neighbour position $R_{n1} = \frac{a}{2}(0, 0, 1)$ or the next nearest neighbour position $R_{n2} = \frac{a}{2}(1, 1, 1)$.

$$
A_{n1}^{s1} = A_{n2}^{s2} = 0
$$

$$
A_{n1}^{s2} = A_{n2}^{s2} = \left[ s d \sigma G^0(6) \right]^2 \left[ E - E_n - A_{n1}^{s1} \right]^{-1}
$$

$$
A_{n1}^{s2-s1} = (sd\sigma)^2 \left[ G^0(I_{12}) + 2 G^0(4) - 4 G^0(5) \right] + 8 s d \sigma s s \sigma G^0(9) \left[ G^0(I_{12}) + 2 G^0(4) - 4 G^0(5) \right] + 16 [s s \sigma G^0(9)]^2
$$

for the nearest neighbours distance, whereas for next nearest neighbours distance we obtain:

$$
A_{n1}^{s2} = A_{n2}^{s2} = A_{n1}^{s2} = 2 s d \sigma G^0(6) - s s \sigma G^0(8)]^2
$$

$$
A_{n1}^{s2-s1} = A_{n2}^{s2-s1} = 0
$$

for fourth nearest neighbouring positions in α-FeC alloys (see Table 2 of reference [11]). Actually the chemical binding energy is competing with the elastic binding energy which is known to be important, especially in the case of ordered interstitial systems (12, 13, 1, 2). However, as far as we know, there is no numerical self-consistent calculation of H-H elastic binding energies in the case of dilute PdH alloys. So it is difficult to estimate the total binding energy and to compare with experimental results. Let us just remark that the sign of our results in table II seems in agreement with inelastic neutron scattering experimental data in α-palladium hydrides [14] because these data show the absence of clustering among hydrogen atoms.
On figure 3 we compare the binding energies $\Delta E(\lambda, R_{\mu})$ given by equation (2.14) and $\Delta E^{\text{as}}(\lambda, R_{\mu})$ given by equation (2.15). For small charge differences

$$|\delta Z_{\mu}(E_F)| < 3,$$

the asymptotic limit seems quite valid whereas for large charge differences, it diverges more and more from the exact limit. Also, using equation (2.15) and expanding up to first order with respect to $\delta Z_{\mu}$, we recover the well known perturbing limit i.e. $\Delta E^{\text{as}}(\lambda, R_{\mu})$ is proportional to $\delta Z_{\mu}(E_F)$ [3, 11]; but this limit is not valid in the present case. Let us note that a similar behaviour as figure 3 (i.e. first slightly

Fig. 3. — Chemical binding energy $\Delta E(\lambda, R_{\mu})$ of an interstitial-substitutional pair of hydrogen and « d » impurities at the nearest neighbouring positions (see Fig. 2) versus $\delta Z_{\mu}$, the difference in charge between the substitutional impurity and the matrix ion core. The exact form (△) and the asymptotic limit (×) are plotted.

attractive and then repulsive) has been found previously for chemical binding energies between a carbon interstitial and a nearest neighbouring d impurity atom in a b.c.c. host (see Fig. 3 of reference [15]). Now, in the case of a next nearest neighbouring d impurity at the site $R_{\mu 2}$, the binding energy is found to be attractive and roughly independent of $\delta Z_{\mu}(E_F)$ :

$$\Delta E(\lambda, R_{\mu 2}) \simeq \Delta E^{\text{as}}(\lambda, R_{\mu 2}) \simeq -0.015 \text{ eV}.$$ 

So there is a change of sign of the chemical binding energies from the nearest to the next nearest neighbouring d impurities (except when $\delta Z_{\mu}(E_F) = -1$). This type of interaction has been studied by Mössbauer techniques in hydrogen doped palladium system [16]: the local environment around cobalt and iron impurities was found different; both impurities repel hydrogen but Fe does it more strongly than Co. A direct comparison of our results with these experimental data is however difficult because: i) the experiments are performed in β palladium hydride; ii) and the magnetic contributions should be important in the case of cobalt and iron impurities.

In order to get an overall view about point defects interactions in palladium, it seems interesting to calculate the chemical binding energy between two d impurities which can be related to the formation enthalpies of the corresponding alloys.

3.3 d-d IMPURITIES BINDING ENERGY. — Let us first recall the expressions for the electronic binding energy of a pair of substitutional d impurities at sites $R_1$ and $R_\mu$ in a transition metal (see [9])

$$\Delta E(R_1, R_\mu) = \frac{2}{\pi} \int_{E_F} \text{d}E \times$$

$$\times \text{Arg} \left[ 1 - \text{Tr} \{ \delta t_{\mu}(E) G^0(E) \delta t_{\mu}(E) G^0(E) \} \right] \quad (3.4)$$

and

$$\Delta E^{\text{as}}(R_1, R_\mu) = -\frac{2}{\pi} \int_{E_F} \text{d}E \times$$

$$\times \text{Im} \text{Tr} \{ \delta t_{\mu}(E) G^0(E) \delta t_{\mu}(E) G^0(E) \}. \quad (3.5)$$

In the case of the first nearest neighbouring impurities, the trace is expressed in terms of the host Green functions listed in table I:

$$\text{Tr} \{ \cdots \} = [\delta t^{(25)}]^2 \times$$

$$\times \left\{ [G^{0}(1)]^{2} + 2[G^{0}(2)]^{2} + [G^{0}(3)]^{2} \right\}$$

$$+ [\delta t^{(12)}]^{2} \left\{ [G^{0}(4) - 4G^{0}(5)]^{2} / 2 + [G^{0}(4)]^{2} \right\}. \quad (3.6)$$

with

$$\delta t^{\mu} = \delta t^{\mu} [1 - \delta t^{\mu} G^0(\Gamma_m)]^{-1}; \quad \Gamma_m = \Gamma_{12}, \Gamma_{25}.$$ 

Our results for $\Delta E(R_1, R_\mu)$ and $\Delta E^{\text{as}}(R_1, R_\mu)$ diverge more and more as $\delta Z(\mu)$ increases (Fig. 4). We note

Fig. 4. — Chemical binding energy $\Delta E(R_1, R_\mu)$ of a pair of identical d substitutional impurities at the nearest neighbouring positions versus $\delta Z$ ($\delta Z_{\mu} = \delta Z_{\tau} = \delta Z$), the difference in charge between the substitutional impurities and the matrix ion core. The exact form (△) and the asymptotic limit (×) are plotted.
a tendency of segregation among d impurities in palladium along the whole transition series. A detailed comparison with experiment is difficult because of few thermodynamical data in palladium based alloys: let us comment on the order of magnitude we find (in the case of PdRu alloys) as compared with the experimental curve of the enthalpy of formation (for isoelectronic PdFe alloys [17]).

Actually the enthalpy of formation $\Delta H$ is equal to the energy of formation when volume effects due to alloying are negligible as we assume here for d impurities in Pd host, the assumption being more valid for Ru in Pd than for Fe in Pd. So, in a perfectly disordered dilute alloy (no short-range order; concentration c → 0) we have the following relation [9]:

$$\frac{\partial^2 \Delta H}{\partial c^2} (c = 0) = \sum \Delta E(R_n, R_m)$$

(3.7)

where the summation in (3.7) is over all sites $R_n(\neq R_i)$ of the crystal. As shown in reference [9], a good approximation of equation (3.7) is obtained by a summation restricted to the first nearest neighbours of $R_i$. The results of figure 4 (providing a multiplying factor of 12, the number of nearest neighbours) give a semi-quantitative insight on the initial curvature of the formation enthalpies along the transition series. Now, in the particular case of a regular solution we can write:

$$\frac{\partial^2 \Delta H}{\partial c^2} (c = 0) = -8 \Delta H(c = 0.5)$$

(3.8)

which yields an estimation of about 0.8 eV for PdFe alloy from reference [17]. This is to be compared with our result of about 2.7 eV for $\delta Z = -1$ repel hydrogen atoms when located in the first nearest neighbouring position; but attract them when located in the second nearest neighbouring positions.

The recent experimental study concerning the substitutional «d» impurity and a hydrogen atom in Pd is due to Pröbst et al. [16]. They have performed Mössbauer experiments to study the local environment of the substitutional Co and Fe impurities in hydrogen doped palladium. Unfortunately, these experiments are performed on $\beta$PdH and not on $\alpha$PdH (the case under study in the present paper). However, even in $\beta$ phase of PdH both Co and Fe repel hydrogen as a first neighbour and that Fe does so more strongly than Co. Our theoretical results do show this trend.

(iii) Two identical nearest neighbouring d impurities in palladium repel each other along the whole transitions series. The experimental value for the enthalpy of formation for PdFe alloy [17] is in qualitative agreement with our result.

4. Conclusion. — Using an extra-orbital model and a generalized spd tight-binding approximation, we treated the formal derivation of the chemical binding energy of the pairs of hydrogen-hydrogen and hydrogen-d impurity in transition metals. As well known for substitutional impurities, the binding energy has been expressed in terms of $t$ matrices for isolated point defects.

The main results of our numerical calculations can be summarized as follows:

(i) The short-range chemical binding energy between hydrogen atoms (in the nearest and the next nearest neighbouring positions) is repulsive for dilute PdH system. This result is in disagreement with the recent ATA calculations [18] but the inelastic neutron scattering experiments [14] show the absence of the hydrogen clusters in $\alpha$PdH, hence in good agreement with our results.

(ii) d impurities on the left of Pd in the periodic table (except for $\delta Z = -1$) repel hydrogen atoms when located in the first nearest neighbouring positions but attract them when located in the second nearest neighbouring positions.

The main results of our numerical calculations can be summarized as follows:

References