Hydrogen-impurity binding energy in vanadium and niobium

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HAL Id: jpa-00211057

https://hal.science/jpa-00211057

Submitted on 4 Feb 2008

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Résumé. — L'énergie d'interaction H-défaut, dans les métaux de transition, est estimée par la méthode des opérateurs de Green dans le schéma des liaisons fortes. Cette énergie électronique (ou chimique) est la somme de quatre termes : i) contribution des états liés introduits par l'hydrogène, ii) contribution de la bande, iii) terme d'interaction électron-électron neutre (sans transfert de charge entre le métal et l'hydrogène) et iv) un terme proportionnel au transfert de charge. Nous avons choisi comme matrice le vanadium et le niobium et comme impuretées substitutionnelles les deux éléments à gauche et les deux éléments à droite de la matrice dans le tableau périodique. Une forte répulsion est observée entre deux hydrogènes en premiers voisins dans le vanadium et dans le niobium ; la position la plus stable correspond à une paire H-H en quatrièmes voisins. Nous avons observé une attraction de l'hydrogène par les impuretés substitutionnelles situées à gauche de la matrice et une répulsion par celles situées à droite de la matrice.

Abstract. — H-H and H-substitutional impurity interaction energy are estimated by the Green operator method developed in the tight binding approximation. This electronic (or chemical) energy is split in four terms : i) the bound states (introduced by the hydrogen) contribution, ii) the band structure contribution, iii) the electron-electron interaction without charge transfer and iv) the charge transfer (between matrix and impurity) contribution. The calculations are done for the transition metal matrix vanadium and niobium. The substitutional impurities considered are the two elements located at the left and at the right in the same row as the matrix in the periodic table. Strong H-H repulsion is observed when the hydrogen atoms are at first nearest neighbouring positions ; the stability is obtained for hydrogen interstitials at fourth nearest neighbouring positions. We have observed attraction of the hydrogen by the substitutional impurities located at the left of the matrix in the periodic table and repulsion by those located at the right.

1. Introduction.

Up to now, the *ab initio* determination of the electronic structure of light interstitials in transition metals has attracted only few authors. We can notice the pioneering work of Yussouff and Zeller [1] followed by the one of Klein and Pickett [2]. More recently Akai *et al.* [3] and Oppeneer and Lodder [4] have proposed models for the determination of respectively hyperfine field and de Haas-van-Alphen scattering. This last calculation seems to be most

promising because it takes into account the influence of zero-point motion of hydrogen isotopes.

On the other hand there is a considerable amount of semi-empirical work devoted to this problem (see for exemple Demangeat [5] and Refs. there in). Once the electronic structure calculation of the single interstitial and substitutional has been performed one can try to estimate the binding energy of pair of hydrogen atoms or pair consisting of an hydrogen and a substitutional impurity.

In fact, the hydrogen interstitial put in the lattice has three effects : the first one is the modification of the screening clouds around it, the second is the modification of the stress field exerted on the neighbouring metal atoms of the impurity and the third one is the large vibrations exhibited by the H atom around its equilibrium position. All these effects can be taken into account through the « effective medium » theory [6, 7], which was applied to H-substitutional impurity in vanadium and niobium by Jena *et al.* [8]. The effect of the true inhomogeneous environment on the atom is simulated by that of an effective homogeneous medium. The basic idea is to calculate the binding energy of an atom immersed in an homogenous electron gas which has a density equal to the average value of the host metal density around the impurity site. Interaction with the metal core electrons, hybridization between H s-electrons and transition metal d-electrons and a correction for the inhomogeneity of a real metal are also introduced. One of the advantage of the effective medium theory is the fact that the binding energy is calculated without the separation into the electronic part and the elastic one. Puska and Nieminen [9] included also the hydrogen zero-point motion by considering the quantum-mechanical nature of the hydrogenic impurity. Their model is based on the formulation given by Sugimoto and Fukai [10] : the total energy of the combined light-impurity-metal system is the sum of the lattice energy of the host metal and the impurity energy eigenvalue. All these energies are functions of the displacements of host atoms. The main difference between Puska and Nieminen and Sugimoto and Fukai models is the construction of the potentiel energy field « experienced » by the impurity atom. The first authors use the effective medium to express this potentiel whereas the second adopt the double Born-Mayer form for this potentiel. From this potentiel they deduce the Kanzaki forces [11] and the displacements of the metallic atoms. This procedure is made until self consistency. Other methods cannot take all the effects into account and a splitting is made into an electronic (chemical) part and elastic part.

Along the lines proposed by Einstein and Schrieffer [12] there have been calculations for H-H in Pd [13] in Fe [14] in V, Nb [15] in Ni [16]. In all these calculations the effect of electron-electron term has been neglected. Also calculations relative to H-substitutional binding energy in Pd [13] in V, Nb [15] in Ni [17] have been performed.

In the following the model developed for the electronic structure of a single hydrogen in vanadium and in niobium is outlined in section 2. Only the electronic part of the binding energy between hydrogen and another point defect is reported here. However, we have recently presented [18] the elastic binding energy between a pair of hydrogen in Pd. Unfortunatly, the models reported in references [9] and [18] rely on the lattice Green function of the pure metal and not on the Green function of the alloy as it should be [19] in the case of interstitial alloys. Also, in the same manner, the zero point motion energy must be related to the force constant of the alloy and not only to the force constant of the pure metal as it has been done in [9]. A formalism, for the determination of these force constants, has been proposed recently [20] but no numerical estimation has been performed yet. In a recent study Mokrani *et al.* [21] have derived the field of forces around hydrogen in a bcc transition metal and showed that the leading term is the hydrogen-metal hopping integral. A description of

these non electronic terms remains to be correctly formulated and thus we have restricted ourselves to the derivation of the electronic terms.

The chemical binding energy of a pair of hydrogen atoms in V and Nb is described in section 3. The results are compared to Switendick criterion [22] relative to the minimum distance between the hydrogen atoms. The section 4 is devoted to the determination of defects consisting of an hydrogen atom and substitutional impurity of transition metal type. Conclusion and outlooks are given in the last section.

2. Electronic structure of a single hydrogen atom in bcc transition metals.

The theoretical framework of our model is formed by a tight binding Green function method for hydrogen interstitial [15, 23]. In this section we will focus on two points : 1) the group theoretical analysis of the extended potentiel, 2) the Slater-Koster fit used for the determination of the band structure of pure metal and the hopping integrals between the hydrogen and the metallic atoms.

The band structure of pure transition metal is described by an spd Slater-Koster (S-K) fit to a first principle calculations [24]. The metallic spd orbitals are labelled $[Rm\rangle$, where R is the metallic site, m the orbital symmetry ($m = s, x, y, z, xy, yz, zx, x^2 - y^2, 3 z^2 - r^2$). Let T being the tetrahedral position occupied by the hydrogen atom and $[Ts\rangle$ the corresponding extra s orbital. The perturbed Hamiltonien H_T, for one spin, is given by :

$$H_T = H_0 + h_T \qquad (2.1)$$

where H_0 is the pure metal Hamiltonian, h_T is the perturbation introduced by hydrogen on the interstitial site T :

$$h_T = [Ts\rangle E_T^s \langle Ts] + \left(\sum_{Rm} [Rm\rangle \beta_{RT}^{ms} \langle Ts] + \text{c.c.} \right) + \sum_{Rmm'} [Rm\rangle V_T^{mm'} \langle Rm'] \qquad (2.2)$$

where E_T^s is the energy level introduced by the hydrogen on T, β_{TR}^{sm} is the hopping integral between $\langle Ts]$ and $[Rm\rangle$ and $V_T^{mm'}(R)$ is the matrix element of the hydrogen perturbation V_T concerning the « d » orbitals of the metallic atoms centred on the nearest neighbouring sites R of the hydrogen interstitial T. The difference between (2.1) and the simplified Hamiltonien of reference [23] is in the expression of the matrix element $V_T^{mm'}(R)$. The hydrogen perturbation V_T is expressed in spherical form :

$$V_T = \int d\mathbf{r} |\mathbf{r}\rangle V(|\mathbf{r} - T|) Y_0^0(\mathbf{r} \overset{\wedge}{-} T) \langle \mathbf{r}| \qquad (2.3)$$

where the radial part $V(|\mathbf{r} - T|)$ depends on the distance between the interstitial site T and its nearest neighbouring sites R and $Y_0^0(\mathbf{r} \overset{\wedge}{-} T)$ is the spherical harmonic corresponding to the s orbital of the hydrogen atom. While decomposing the « d » orbital $[Rm\rangle$ as product of radial part $F_2(r)$ and cubic harmonic $d^m(\hat{\mathbf{r}})$ (site R is taken as the origin) the matrix element $V_T^{mm'}(R)$ is given by :

$$V_T^{mm'}(\mathbf{R}) = \int d\mathbf{r} \, |F_2(r)|^2 \, V(r - T) \, d^m(\hat{\mathbf{r}}) \, d^{m'}(\hat{\mathbf{r}}) \, Y_0^0(\mathbf{r} \overset{\wedge}{-} T) \qquad (2.4)$$

these matrix elements are expressed (appendix A) in terms of the direction cosines (l, m, n) of $\mathbf{TR}$ and of the two center integrals $s\tilde{s}\sigma$, $s\tilde{d}\sigma$ and $s\tilde{g}\sigma$ defined by :

$$\int d\mathbf{r} |F_2(r)|^2 \, Y_L^0(\hat{\mathbf{r}}) \, V(r - T) \, Y_0^0(\mathbf{r} \overset{\wedge}{-} T) \qquad (2.5)$$

for $L = 0$, 2, 4 respectively. The difference between these integrals and the usual one [24] is that, in these integrals the radial part is of « d » type. The matrix elements $V_T^{mm'}(R)$ are reported in table I.

Table I. — *Matrix elements of the hydrogen interstitial perturbation on its nearest neighbouring metallic atoms.* (l, m, n) *are the direction cosines of* TR (R *is one of the first neighbour of* T). *The labels* (1, 2, 3, 4, 5) *denote respectively the* « d » *orbital symmetries* $(xy, yz, zx, x^2 - y^2, 3z^2 - r^2)$.

$$V_{11} = 7\,\text{s}\tilde{\text{s}}\sigma + \sqrt{5}\,(1 - 3\,n^2)\,\text{s}\tilde{\text{d}}\sigma + (35\,l^2 m^2 + 5\,n^2 - 4)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{22} = 7\,\text{s}\tilde{\text{s}}\sigma + \sqrt{5}\,(1 - 3\,l^2)\,\text{s}\tilde{\text{d}}\sigma + (35\,m^2 n^2 + 5\,l^2 - 4)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{33} = 7\,\text{s}\tilde{\text{s}}\sigma + \sqrt{5}\,(1 - 3\,m^2)\,\text{s}\tilde{\text{d}}\sigma + (35\,l^2 n^2 + 5\,m^2 - 4)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{44} = 7\,\text{s}\tilde{\text{s}}\sigma + \sqrt{5}\,(1 - 3\,n^2)\,\text{s}\tilde{\text{d}}\sigma + \frac{1}{4}\,(35\,n^4 - 50\,n^2 - 140\,l^2 m^2 + 19)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{55} = 7\,\text{s}\tilde{\text{s}}\sigma - \sqrt{5}\,(1 - 3\,n^2)\,\text{s}\tilde{\text{d}}\sigma + \frac{3}{4}\,(35\,n^4 - 30\,n^2 + 3)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{12} = 3\sqrt{5}\,ln\text{s}\tilde{\text{d}}\sigma + 5\,ln\,(7\,m^2 - 1)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{13} = 3\sqrt{5}\,mn\text{s}\tilde{\text{d}}\sigma + 5\,mn\,(7\,l^2 - 1)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{23} = 3\sqrt{5}\,lm\text{s}\tilde{\text{d}}\sigma + 5\,lm\,(7\,n^2 - 1)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{45} = \sqrt{15}\,(m^2 - l^2)\,\text{s}\tilde{\text{d}}\sigma + \frac{5\sqrt{3}}{4}\,(l^2 - m^2)(7\,n^2 - 1)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{14} = \frac{35}{2}\,lm\,(l^2 - m^2)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{24} = -3\sqrt{5}\,mn\text{s}\tilde{\text{d}}\sigma + \frac{5}{4}\,mn\,(21\,l^2 + 7\,n^2 - 7\,m^2 - 3)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{34} = 3\sqrt{5}\,ln\text{s}\tilde{\text{d}}\sigma - \frac{5}{4}\,ln\,(21\,m^2 + 7\,n^2 - 7\,l^2 - 3)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{15} = -2\sqrt{15}\,lm\text{s}\tilde{\text{d}}\sigma + \frac{5\sqrt{3}}{2}\,lm\,(7\,n^2 - 1)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{25} = \sqrt{15}\,mn\text{s}\tilde{\text{d}}\sigma + \frac{5\sqrt{3}}{2}\,mn\,(7\,m^2 - 3)\,\text{s}\tilde{\text{g}}\sigma$$

$$V_{35} = \sqrt{15}\,ln\text{s}\tilde{\text{d}}\sigma + \frac{5\sqrt{3}}{2}\,ln\,(7\,l^2 - 3)\,\text{s}\tilde{\text{g}}\sigma$$

To determine the phase shifts $Z_T(E)$ introduced by the hydrogen interstitial T, we use the Green operator method. The density of state modification for one spin is given by :

$$\Delta n_T(E) = -\pi^{-1}\,\text{Im}\,(\text{Tr}^{(1)}\,G^T(E) - \text{Tr}\,G^0(E)) \qquad (2.6)$$

Tr and $\text{Tr}^{(1)}$ mean trace in N dimensions (N is the host atomic number) and trace in the $(N + 1)$ dimensions respectively. $G^0(E)$ and $G^T(E)$ are the Green operators associated to the

pure Hamiltonian H_0 and the perturbed Hamiltonian H_T respectively. The well known Dyson relation between the host and the perturbed Green operators used in the substitutional impurity case cannot be applied here because of the difference in the number of sites in the host and the perturbed system. We define a new reference system with $(N + 1)$ dimensions corresponding to the pure metal and an isolated hydrogen interstitial T. The corresponding Hamiltonian is the following :

$$H'_T = H_0 + |Ts\rangle E^s_T \langle Ts| \, . \tag{2.7}$$

Let $G^{T'}$ the Green operator associated to this Hamiltonian. It is related to $G^T(E)$ by the following Dyson equation in $(N + 1)$ dimensions :

$$G^T(E) = G^{T'}(E) + G^{T'}[H_T - H'_T] G^T(E) \, . \tag{2.8}$$

The intrasite matrix element on the interstitial site T of G^T is given by :

$$G^{Tss}_{TT}(E) = [D^s_T(E)]^{-1} \tag{2.9}$$

where :

$$D^s_T(E) = E - E^s_T - \Delta^s_T(E) - \Gamma^s_T(E) \, . \tag{2.10}$$

The $\Delta^s_T(E)$ and $\Gamma^s_T(E)$ quantities are defined as follows :

$$\Delta^s_T(E) = \sum_{Rm} \beta^{sm}_{TR} A^m_T(\mathbf{R}) \tag{2.11}$$

$$\Gamma^s_T(E) = \sum_{Rm} (A^m_T(\mathbf{R}))^2 V^m_T(\mathbf{R}) \tag{2.12}$$

$A^m_T(\mathbf{R})$ is a function of the matrix elements of the host Green operator $G^0(E)$ and of the hopping integrals between the hydrogen interstitial T and its nearest neighbouring metallic atoms.

$$A^m_T(\mathbf{R}) = \sum_{R'm'} \beta^{sm'}_{TR'} G^{0\,m'\,m}_{R'R}(E) \, . \tag{2.13}$$

Through group theoretical arguments, $A^m_T(\mathbf{R})$, for different sites R and different orbital symmetries m, can be expressed in terms of irreducible quantities [25].

The phase shift $Z_T(E)$, given by the integration of (2.6) from $-\infty$ to E, takes the following form :

$$Z_T(E) = -\sum_{Rm} V^m_T(\mathbf{R}) n^{0\,m}(\mathbf{R}, E) - \pi^{-1}\{\arg D^s_T(E) - \pi\} \tag{2.14}$$

where $n^{0\,m}(\mathbf{R}, \mathbf{E})$ is the local density of states of the pure metal for the symmetry m. The energy level E_ℓ of the bound state introduced by the hydrogen interstitial is determined by the following equation :

$$D^s_T(E_\ell) = 0 \ (n^{0\,m}(\mathbf{R}, E) \equiv 0) \, . \tag{2.15}$$

The pure metal hopping integrals are deduced by Papaconstantopoulos [26] through an adjustable set of parameters determined by the fitting to APW band structure calculations. There are substantial differences depending on how many bands above the Fermi level you want to fit. In the present calculation we want to emphasize on the bands below the Fermi

level because the binding energy between point defects is related only to occupied states. The hopping integrals β_{RT}^{ms} between the hydrogen and the metal are taken from Slater-Koster fit (using an orthonormalized basis) to APW band structure of the dihydrides VH_2 and NbH_2 in CaF_2 structure [27]. In fact, the hydrogen-metal distance for hydrogen at tetrahedral site T in bcc V and Nb metals is little different from that in the dihydrides VH_2 and NbH_2. The correction of the distance has been made through a power law described by Harrisson [28].

$$\beta_{TR}^{ms} \propto d_{TR}^{-(\ell+1)} \tag{2.16}$$

where d_{TR} is the hydrogen-metal distance and l is the orbital momentum corresponding to the orbital of symmetry m. We can also use the exponentiel decreasing law [29], but we have to introduce one parameter.

To perform the numerical calculation we have to determine the unknown quantities E_T^s and the matrix elements $V_T^{mm'}(R)$. The energy level E_T^s introduced by the hydrogen is related to the number of electrons N_T^s in the « s » orbital by :

$$E_T^s = E_H^{at} + U_T^s N_T^s \tag{2.17}$$

where $E_H^{at} = -0.5$ a.u. is the atomic level of an isolated hydrogen and U_T^s is the Coulomb effective integral of the hydrogen which may be taken from [30]. Concerning the $V_T^{mm'}(R)$ term on nearest neighbour R of the hydrogen atom we restrict ourselves to the most important component $(s\tilde{s}\sigma)$. The number of electrons in the s orbital of the hydrogen is given by :

$$N_T^s = N_T^s(E_\ell) - \pi^{-1} \, \mathrm{Im} \int_{E_{bottom}}^{E_F} G_{TT}^{Tss}(E) \, dE \, . \tag{2.18}$$

The first term is the filling of the « s » bound state on the site T, at the energy E_ℓ and the second term is the contribution of the band. The band position of the pure metal was fixed such as to give the experimental value for the work function of Vanadium and Niobium [31]. We have to solve, in terms of $(s\tilde{s}\sigma)$, equation (2.10) and Friedel's screening rule :

$$2 \, Z_T(E_F) = 1 \, . \tag{2.19}$$

In both vanadium and niobium host, we find that the hydrogen interstitial introduces a bound state below the metal conduction bands. The local density of state on the hydrogen interstitial site is illustrated by the figure 1.

3. H-H interaction energy.

The purpose of this paragraph is to calculate the electronic (chemical) interaction energy between an hydrogen atom located at tetrahedral site T and another at tetrahedral site $T_i (i = 1 - 5)$ (Fig. 2). This energy is given by :

$$\Delta E(T, T_i) = \widetilde{\Delta E}_{HF}(T, T_i) - \widetilde{\Delta E}_{el\text{-}el}(T, T_i) + \Delta E_{ion\text{-}ion}(T, T_i) \, . \tag{3.1}$$

The first term is the monoelectronic energy in Hartree-Fock approximation, the second term is the electron-electron energy contribution and the third term is the ion-ion contribution. The monoelectronic interaction is expressed as a function of the density of states modification in the two configurations, with one hydrogen $\widetilde{\Delta n}_\rho(E)(\rho = T, T_i)$ and with two
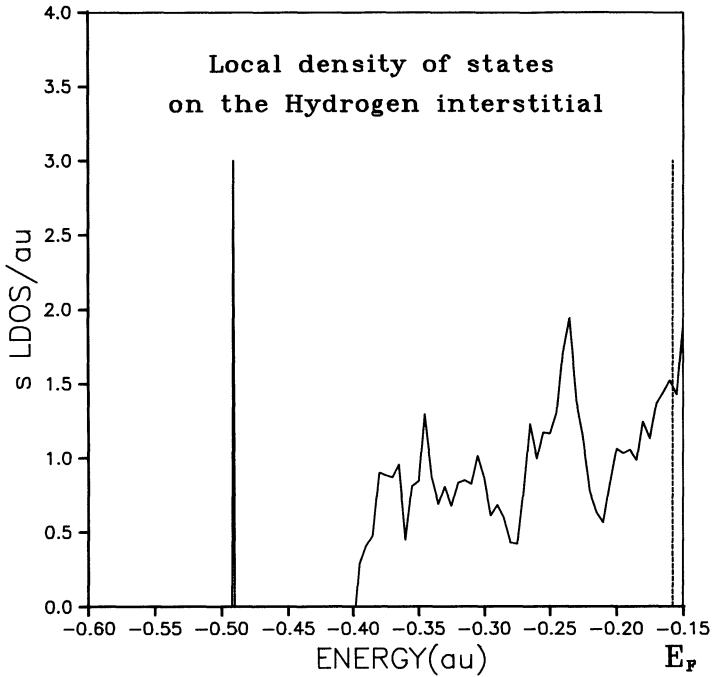
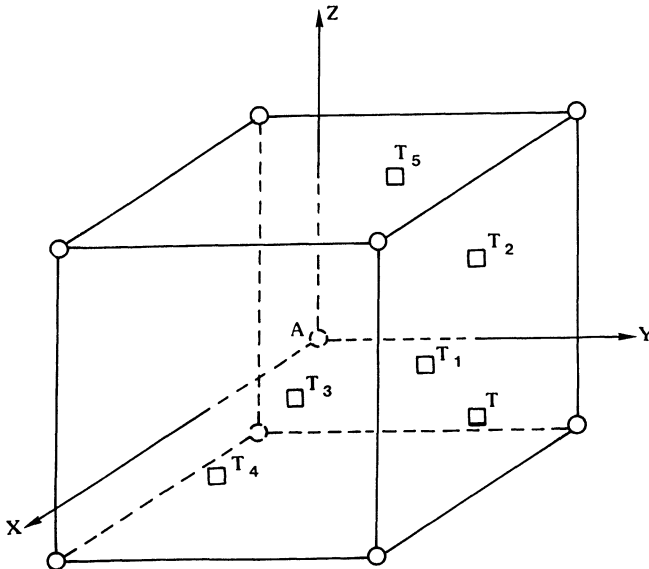Fig. 1. — Local density of states on the hydrogen interstitial in vanadium.

Fig. 2. — Different tetrahedral positions occupied by the two hydrogen interstitials. $T_i (i = 1, 5)$ is the i-th neighbouring of the interstitial T. The distance between the two hydrogen atoms is given by $d_{TT_i} = \sqrt{2\,i}\left(\dfrac{a}{4}\right)$ where a is the lattice constant of the matrix.

hydrogens $\widetilde{\Delta n}_{T T_i}(E)$:

$$\widetilde{\Delta E}_{HF}(T, T_i) = 2 \int_{-\infty}^{E_F} E \left(\widetilde{\Delta n}_{T, T_i}(E) - \sum_{\rho = T, T_i} \Delta n_\rho(E) \right) dE . \qquad (3.2)$$

Due to the Friedel sum rule, the integration of (3.2) by parts gives the following expression for the monoelectronic energy :

$$\widetilde{\Delta E}_{HF}(T, T_i) = -2 \int_{-\infty}^{E_F} (\tilde{Z}_{T, T_i}(E) - \sum_{\rho = T, T_i} Z_\rho(E)) \, dE \qquad (3.3)$$

where the Z's are the phase shifts for the pair of hydrogen atoms at T and $T_i (\tilde{Z}_{TT_i}(E))$ and for isolated single hydrogen at $\rho = T$, $T_i (Z_\rho(E))$.

The electron-electron contribution to the H-H interaction energy is defined as follows :

$$\Delta E_{el\text{-}el}(T, T_i) = (\tilde{E}_{el\text{-}el}(T, T_i) - E_{el\text{-}el}^0) - \sum_{\rho = T, T_i} (E_{el\text{-}el}(\rho) - E_{el\text{-}el}^0) \qquad (3.4)$$

where $\tilde{E}_{el\text{-}el}(T, T_i)$ is the electron-electron interaction energy of the system with two interacting hydrogen interstitials, $E_{el\text{-}el}(\rho)$ is the interaction energy of the single hydrogen system and $E_{el\text{-}el}^0$ is the interaction energy of the host metal taken as reference. We note that all these energies are of the Coulombic form, and can be expressed as an integral over the space of the product of the electronic density $n^{el}(\mathbf{r})$ and the electronic potential $v^{el}(\mathbf{r})$ for each system.

$$E_{el\text{-}el} = \int d\mathbf{r} \, n^{el}(\mathbf{r}) \, v^{el}(\mathbf{r}) \qquad (3.5)$$

where the electronic potential is related to the electronic density as follows :

$$v^{el}(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n^{el}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad (3.6)$$

and the electronic density is related to the Green operator matrix element by :

$$n^{el}(\mathbf{r}) = -\pi^{-1} \, \text{Im} \int_{-\infty}^{E_F} \langle \mathbf{r} | G(E) | \mathbf{r} \rangle \, dE . \qquad (3.7)$$

3.1 ELECTRONIC STRUCTURE OF TWO HYDROGENS SYSTEM. — In order to describe the electronic structure of the system with two interacting hydrogen interstitials, we apply the Green operator method developed in the tight binding approximation. The Hamiltonian of the metal perturbed by the two hydrogen interstitials is expressed as follows :

$$\tilde{H}_{TT_i} = H_0 + \sum_{\rho = T, T_i} h_\rho + \delta V_{TT_i} \qquad (3.8)$$

where δV_{TT_i} is the direct interaction between the two hydrogens. This term is due to the rearrangement which is necessary to satisfy the Friedel sum rule. In our calculation we retain only the terms up to the first order in δV_{TT_i}.

In order to split the H-H interaction energy between direct interaction δV_{TT_i} contribution

and the remainder, we define the following Hamiltonian corresponding to the two hydrogens system without the direct interaction :

$$H_{TT_i} = \tilde{H}_{TT_i} - \delta V_{TT_i} .$$ (3.9)

The associated Green operator is given by :

$$G^{TT_i}(E) = (E + i0 - H_{TT_i})^{-1} .$$ (3.10)

From the Dyson relation :

$$\tilde{G}^{TT_i}(E) = G^{TT_i}(E) + G^{TT_i}(E)\, \delta V_{TT_i}\, \tilde{G}^{TT_i}(E)$$ (3.11)

we show that the phase shift $\tilde{Z}_{TT_i}(E)$, appearing in (3.3), is the sum of the phase shift $Z_{TT_i}(E)$ corresponding to the Hamiltonian H_{TT_i} and a modification $\delta Z_{TT_i}(E)$ due to the direct interaction δV_{TT_i} :

$$\tilde{Z}_{TT_i}(E) = Z_{TT_i}(E) + \delta Z_{TT_i}(E) .$$ (3.12)

The phase shift $Z_{TT_i}(E)$ is obtained by solving the following Dyson equation in $(N + 2)$ dimensions :

$$G^{TT_i}(E) = G^{TT_{i'}}(E) + G^{TT_{i'}}(E)[H_{TT_i} - H'_{TT_i}]\, G^{TT_i}(E)$$ (3.13)

the prime stands for isolated interstitials without interaction with the metal ; the corresponding Hamiltonian is given by :

$$H'_{TT_i} = H_0 + \sum_{\rho = T, T_i} |\rho s\rangle E_\rho^s \langle \rho s|$$ (3.14)

and its associated Green operator :

$$G^{TT_{i'}}(E) = [E + i0 - H'_{TT_i}]^{-1} .$$ (3.15)

The density of state modification due to the indirect interaction between the two hydrogen interstitials is defined by :

$$\Delta n_{TT_i}(E) = - \pi^{-1} \operatorname{Im} [\operatorname{Tr}^{(2)} G^{TT_i}(E) - \operatorname{Tr} G^0(E)]$$ (3.16)

where $\operatorname{Tr}^{(2)}$ means trace in $(N + 2)$ dimensions. We expand these traces in the base of the atomic orbitals centred on the different sites of the respective system, then (3.16) becomes :

$$\Delta n_{TT_i}(E) = - \pi^{-1} \operatorname{Im} \sum_{\rho = T, T_i} G_{\rho\rho}^{TT_i^{ss}}(E) - \pi^{-1} \operatorname{Im} \sum_{Rm} [G_{RR}^{TT_i^{mm}}(E) - G_{RR}^{0\,mm}(E)]$$ (3.17)

where the second summation is over all metallic sites R and orbitals $m = (s, p, d)$. The interasite matrix elements, obtained by solving the Dyson equation (3.13), are expressed as a function of the hydrogen-metal hopping integrals $\beta_{\rho R}^{sm}$, the perturbation $V_\rho^m(R)$ and matrix elements of the Green operator $G^0(E)$. The intrasite matrix element of $G^{TT_i}(E)$ at the T interstitial site of the hydrogen atom is given by :

$$G_{TT}^{TT_i^{ss}}(E) = [D_{TT_i}^s(E)]^{-1}$$ (3.18)

where :

$$D_{\mathrm{TT}_i}^{\mathrm{s}}(E) = D_{\mathrm{T}}^{\mathrm{s}'}(E)\, D_{\mathrm{T}_i}^{\mathrm{s}'}(E) - \Delta_{\mathrm{TT}_i}^{\mathrm{s}}(E)\, \Delta_{\mathrm{T}_i\,\mathrm{T}}^{\mathrm{s}}(E) - 2(\Delta_{\mathrm{TT}_i}^{\mathrm{s}}(E)\, \Gamma_{\mathrm{T}_i\,\mathrm{T}}^{\mathrm{s}}(E) + \Gamma_{\mathrm{TT}_i}^{\mathrm{s}}(E)\, \Delta_{\mathrm{T}_i\,\mathrm{T}}^{\mathrm{s}}(E))\,.$$

(3.19)

The quantity $D_\rho^{\mathrm{s}'}(E)$ is given by (2.9) in which we add the H-H interaction term $\Gamma_\rho^{\mathrm{s}'}(E)$:

$$D_\rho^{\mathrm{s}'}(E) = D_\rho^{\mathrm{s}}(E) - \Gamma_\rho^{\mathrm{s}'}(E)\,.$$

(3.20)

The interaction terms are defined as follows :

$$\Gamma_{\mathrm{T}}^{\mathrm{s}'}(E) = \sum_{\mathbf{R}m} (A_{\mathrm{T}}^m(\mathbf{R}))^2\, V_{\mathrm{T}_i}^m(\mathbf{R})$$

(3.21a)

$$\Delta_{\mathrm{TT}_i}^{\mathrm{s}}(E) = \sum_{\mathbf{R}m} \beta_{\mathrm{TR}}^{sm}\, A_{\mathrm{T}_i}^m(\mathbf{R})$$

(3.21b)

$$\Gamma_{\mathrm{TT}_i}^{\mathrm{s}}(E) = \sum_{\mathbf{R}m} A_{\mathrm{T}}^m(\mathbf{R})\, A_{\mathrm{T}_i}^m(\mathbf{R})\, V_{\mathrm{T}}^m(\mathbf{R})\,.$$

(3.21c)

The phase shift $Z_{\mathrm{TT}_i}(E)$ introduced by the two hydrogens (without direct interaction), up to the energy level E, is given by the integration of (3.17) :

$$Z_{\mathrm{TT}_i}(E) = \sum_{\rho\,=\,\mathrm{T},\,\mathrm{T}_i} \sum_{\mathbf{R}m} V_\rho^m(\mathbf{R})\, n^{0\,m}(\mathbf{R}, E) - \pi^{-1}[\arg D_{\mathrm{TT}_i}^{\mathrm{s}}(E) - \pi]\,.$$

(3.22)

This expression can be written as a sum of the single-hydrogen phase shifts $Z_{\mathrm{T}}(E)$ and $Z_{\mathrm{T}_i}(E)$ and the modification $\Delta Z_{\mathrm{TT}_i}(E)$ due to the indirect interaction between the two hydrogen interstitials :

$$Z_{\mathrm{TT}_i}(E) = \sum_{\rho\,=\,\mathrm{T},\,\mathrm{T}_i} Z_\rho(E) + \Delta Z_{\mathrm{TT}_i}(E)$$

(3.23)

where $Z_\rho(E)(\rho = \mathrm{T}, \mathrm{T}_i)$ is given by (2.14) and the H-H contribution by :

$$\Delta Z_{\mathrm{TT}_i}(E) = \pi^{-1} \arg \left\{ \frac{D_{\mathrm{T}}^{\mathrm{s}}(E)\, D_{\mathrm{T}_i}^{\mathrm{s}}(E)}{D_{\mathrm{TT}_i}^{\mathrm{s}}(E)} \right\}\,.$$

(3.24)

3.2 ELECTRON-ELECTRON INTERACTION ENERGY. — As for the phase shift (3.12), the electronic density of the interacting hydrogen system can be split in two parts :

$$\tilde{n}_{\mathrm{TT}_i}^{\mathrm{el}}(\rho) = n_{\mathrm{TT}_i}^{\mathrm{el}}(\rho) + \delta n_{\mathrm{TT}_i}^{\mathrm{el}}(\rho)\,.$$

(3.25)

The first term is the electronic density corresponding to the $G^{\mathrm{TT}_i}(E)$ (without direct interaction) and the second term is the direct interaction contribution. We note that the matrix element of δV_{TT_i} in the space basis $\{|\mathbf{r}\rangle\}$ is given by :

$$\delta v_{\mathrm{TT}_i}(\mathbf{r}) = \int \frac{\delta n_{\mathrm{TT}_i}^{\mathrm{el}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'\,.$$

(3.26)

After inserting (3.25) into (3.4) we obtain the following splitting of the electron-electron interaction energy :

$$\Delta \tilde{E}_{\text{el-el}}(T, T_i) = \Delta E_{\text{el-el}}(T, T_i) + \delta E_{\text{el-el}}(T, T_i) \qquad (3.27)$$

where

$$\Delta E_{\text{el-el}}(T, T_i) = \frac{1}{2} \int \, dr \, (n_{TT_i}^{\text{el}}(\mathbf{r}) \, \nu_{TT_i}^{\text{el}}(\mathbf{r}) - n^{0\,\text{el}}(\mathbf{r}) \, \nu^{0\,\text{el}}(\mathbf{r}))$$

$$- \frac{1}{2} \sum_{\rho = T, T_i} \int \, dr \, (n_\rho^{\text{el}}(\mathbf{r}) \, \nu_\rho^{\text{el}}(\mathbf{r}) - n^{0\,\text{el}}(\mathbf{r}) \, \nu^{0\,\text{el}}(\mathbf{r})) \quad (3.28)$$

and

$$\delta E_{\text{el-el}}(T, T_i) = \int \, dr \, n_{TT_i}^{\text{el}}(\mathbf{r}) \, \delta \nu_{TT_i}(\mathbf{r}) + \frac{1}{2} \int \, dr \, \delta n_{TT_i}^{\text{el}}(\mathbf{r}) \, \delta \nu_{TT_i}(\mathbf{r}) \qquad (3.29)$$

the second term of the right hand side of (3.29) has been neglected because we restrict ourselves only to terms up to first order in $\delta \nu_{TT_i}(\mathbf{r})$.

The first term is identical to the corresponding one in the monoelectronic energy. Thus, these terms cancel in the final form of the H-H interaction energy [25].

The electron-electron interaction energy (3.28) corresponding to the Hamiltonian H_{TT_i} can be split into two terms (Appendix B) :

$$\Delta E_{\text{el-el}}(T, T_i) = \Delta E_{\text{el-el}}^n(T, T_i) + \Delta E_{\text{el-el}}^{\text{ct}}(T, T_i) \qquad (3.30)$$

the first term is the neutral energy corresponding to the two isolated hydrogens system and the second is the charge transfer contribution. The ion-ion energy is restricted to the Coulombic interaction between the two protons of the two hydrogen atoms at T and T_i. When we add this energy to the neutral term, we obtain the following repulsion energy :

$$\Delta E_{\text{rep}}(T, T_i) = e^{-2\,d_{TT_i}} \left\{ d_{TT_i}^{-1} + \frac{11}{8} + \frac{3}{4}\, d_{TT_i} + \frac{1}{6}\, d_{TT_i}^2 \right\} . \qquad (3.31)$$

The charge transfer interaction energy is given by the relation (B.12) of the appendix B.

3.3 RESULTS AND DISCUSSIONS. — The numerical calculation of the H-H interaction energy has been done in the vanadium and niobium matrix. The energy levels $E_l^{(1)}$ and $E_l^{(2)}$ of the bound states introduced by the two hydrogen interstitials (Fig. 3) are determined by the Green operator poles given by the following equation :

$$D_{TT_i}^s(E) = 0 \qquad (n^0(E) \equiv 0) . \qquad (3.32)$$

The different parts of this energy are represented in figure 4. The bound state contribution given by the splitting of the bound states

$$\Delta E_{\text{bound}}(T, T_i) = E_l^{(1)} + E_l^{(2)} - 2\, E_\ell \qquad (3.33)$$

is found attractive for all positions of the two interstitials, whereas the band contribution given by the integration of (3.24) from the bottom E_{bottom} of the band to the Fermi level E_F :

$$\Delta E_{\text{band}}(T, T_i) = \int_{E_{\text{bottom}}}^{E_F} \, dE \, \Delta Z_{TT_i}(E) \qquad (3.34)$$

Positions of the bound states introduced
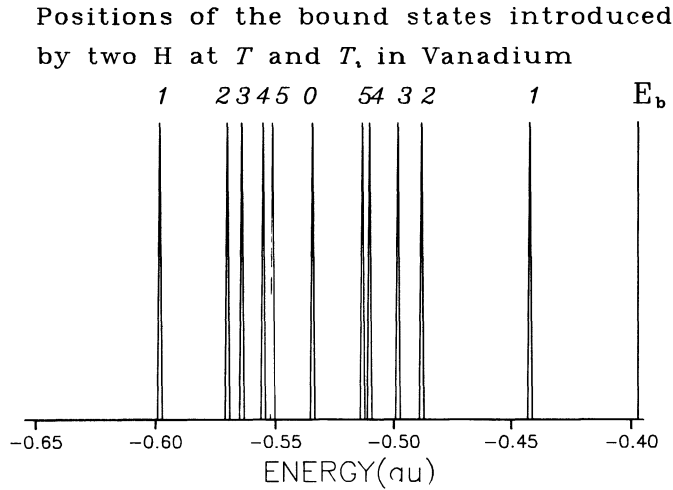by two H at T and T_i in Vanadium

Fig. 3. — Bound states energy levels introduced by the hydrogen atoms at tetrahedral interstitial sites in vanadium. The label 0 correspond to a single hydrogen atom at T whereas the labels i ($i = 1\text{-}5$) correspond to pair of hydrogen atoms at T and T_i (T_i is the i-th neighbouring site of T). E_b is the bottom of the conduction band.

is found repulsive for all positions of the two interstitial atoms. The repulsive energy (3.31) decreases rapidly whith the distance between the two hydrogens. The charge transfer energy oscillates *versus* the H-H distance. When we bring together all these energies we observe a minimum when the two hydrogens are at fourth nearest neighbouring positions. This result is in good agreement with Switendick criterion [22].

4. H-substitutional impurity interaction energy.

In this paragraph we report on the H-substitutional impurity interaction. We use the same formalism as for the H-H interaction. The substitutional impurities are chosen from those located in the same row as the host atom in the periodic table. The perturbation potentiel introduced is assumed to be localised on the substitutional site and affecting only the « s » and « d » orbitals.

The hamiltonian of the metal perturbed by the hydrogen atom at interstitial position and substitutional impurity is given by :

$$\tilde{H}_{ST} = H_0 + h_\rho + \sum_{m = s, d} |Sm\rangle V_S^m \langle Sm| + \delta V_{ST} \qquad (4.1)$$

where H_0 is the pure metal Hamiltonian, h_ρ is given in (2.2) ; the third term is the local perturbation at the substitutional impurity and δV_{ST} is the direct interaction between the two defects.

To determine the matrix elements V_S^m of the localised potential we have assumed spherical symmetry so that we have V_S^d for $m = $ d. The matrix element V_S^s is assumed to be proportional to V_S^d : $V_S^s = \alpha V_S^d$, with $\alpha = 1/2$. No bound state is introduced by the substitutional impurity.

As for the H-H interaction the binding energy between the interstitial and the substitutional impurity in the sum of the monoelectronic, electron-electron and ion-ion interaction energies.
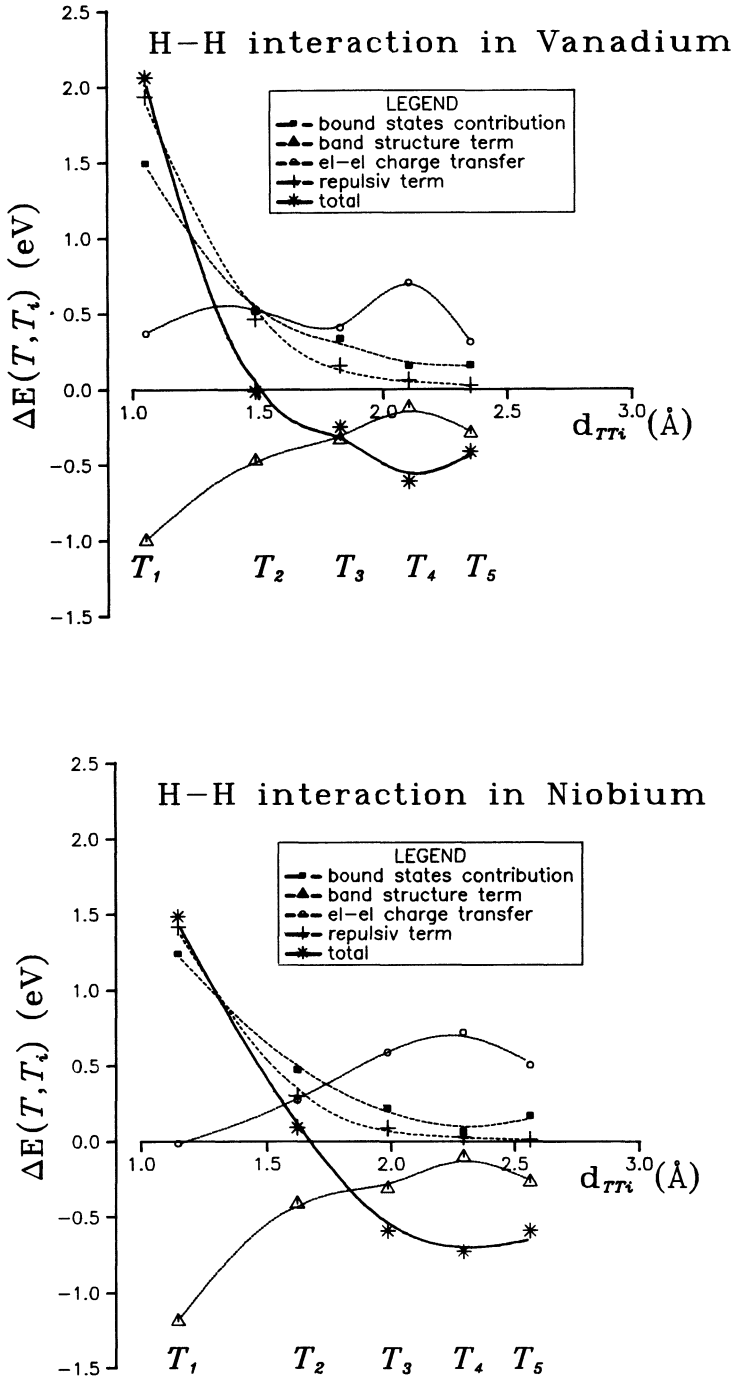
Fig. 4. — H-H interaction energies $\Delta E(T, T_i)$ between two hydrogen interstitials at tetrahedral position T and T_i (T_i is the i-th neighbouring site of T, $i = 1$-5) in vanadium and niobium.

We show that, up to first order in δV_{ST}, the contributions arising from the direct interaction cancel each other. Therefore, the Hamiltonian used to calculate $\Delta E(S, T)$ is the following :

$$H_{ST} = \tilde{H}_{ST} - \delta V_{ST} \, . \tag{4.2}$$

The S-H interaction energy is given by :

$$\Delta E(S, T) = \Delta E_{HF}(S, T) - \Delta E_{el\text{-}el}(S, T) + \Delta E_{ion\text{-}ion}(S, T) \, . \tag{4.3}$$

The first term is the monoelectronic energy and can be splitted into the bound state contribution given by the shift of the energy level of the single hydrogen bound state (E_ℓ) due the substitutional impurity (E'_ℓ) and the band contribution :

$$\Delta E_{HF}(S, T) = (E'_\ell - E_\ell) - \int_{E_b}^{E_F} dE \, \Delta Z_{ST}(E) \, . \tag{4.4}$$

The electron-electron term is determined in the same way as for the H-H interaction and is the sum of a neutral term and of a charge transfer contribution.

$$\Delta E_{el\text{-}el}(S, T) = \Delta E_{el\text{-}el}^{n}(S, T) + \Delta E_{el\text{-}el}^{ct}(S, T) \, . \tag{4.5}$$

A detailed derivation can be found in reference [25].

It can be seen from table II that all the three terms appearing in the binding energy $\Delta E(S, T)$, are of comparable order of magnitude. Therefore they are not in quantitative agreement with our previous calculation [15] where only one electron contributions have been taken into account. The comparison with the semi-empirical effective medium of Jena *et al.* [8] shows a clear discrepancy between the two results. This discrepancy may be related to the rough approximation used in the effective medium theory for the « d » part of the transition metal matrix. On the other hand, Shirley and Hall [35] have used, for the chemical binding energy between H and substitutional impurity, the asymptotic limit of the formulation derived by Demangeat *et al.* [37] for the binding energy between carbon and impurities in α Fe. In fact, this model is only valid when bound states are not extracted from the conduction band. Reasonable agreement is found with the few experimental results [36].

Table II. — H-*substitutional impurity interaction energy in vanadium and niobium* (meV). $\Delta E(S, T) = \Delta E_{bound}(S, T) + \Delta E_{band}(S, T) - \Delta E_{el\text{-}el}(S, T)$.

Matrix	vanadium				niobium			
impurity	Sc	Ti	Cr	Mn	Y	Zr	Mo	Tc
$\Delta E_{bound}(S, T)$	152	79	-112	-248	125	67	-134	-470
$\Delta E_{band}(S, T)$	-227	-125	189	329	-158	-97	206	532
$\Delta E_{el\text{-}el}(S, T)$	121	75	-140	-174	69	42	-203	-458
$\Delta E(S, T)$	-196	-121	217	255	-102	-72	275	520

Table III. — *This table shows the* H-*substitutional impurities interaction energies* (meV) *in vanadium and niobium.* (a) *corresponds to results of purely electronic origin whereas* (b) *is for calculations for which electronic and elastic terms are taken into account ; comparison is made with a few experimental results* (c).

System	ΔZ	this work	Ref. [8]	Ref. [35]	Ref. [36]
VSc	− 2	− 196			
NbY	− 2	− 102			
VTi	− 1	− 121	+ 3(a) − 45(b)	− 80(a) − 150(b)	− 150(c)
NbZr	− 1	− 72			
VCr	+ 1	+ 217	− 7(a) + 6(b)	+ 80(a) + 130(b)	+ (c)
NbMo	+ 1	+ 275		+ 80(a) + 150(b)	
VMn	− 2	+ 255			
NbTc	− 2	+ 520			

5. Conclusion.

We have derived, within the tight binding approximation of the Green operator method, a general formulation for the electronic part of the binding energy between hydrogen and another point defect in a bcc transition metal. This binding energy takes into account, in a general way, without resorting phenomenological model, the two particles contribution. We have written down a general formulation for this term which is, for the hydrogen perturbation extending up to neighbouring metallic atoms of the hydrogen interstial, numerically untractable. We have therefore restricted ourselves to the most important intrasite Coulomb terms so that the leading contribution has been fully taken into account.

In the case of binding energy between two Hydrogen atoms in a bcc transition matrix we have explicitly shown that the two particle interaction is not negligible in comparison with the one electron contribution. Nevertheless, the result obtained by taking into account the two particle contribution remains in qualitative agreement with our previous result [15] whereas only one electron contribution were present. These results are in accord with Switendick criterion [22] which states that in metal hydride solid solution two Hydrogen atoms cannot come closer than 2.1 Å. However, the values obtained are greater than those expected from the experimental results. These differences may be related to the neglect of the elastic binding energy and the rough approximation used for the calculation of the two particle interaction.

In the case of binding energy between one Hydrogen atom and a substitutional impurity, the two particle term appears also comparable in magnitude to the one electron contribution.

Our results are qualitatively and quantitatively different from those reported by Jena *et al.* [8] in the effective medium approximation.

We have found trapping for the H-substitutional impurity interaction when the defect is located to the left of V, Nb in the periodic table and repulsion when the defect is located to the right. These results are in agreement with the few experimental results.

le A.I. — *Expansion of the product of the spherical harmonics $Y_2^m Y_2^{m'}$ in linear* *hination of the the spherical harmonics Y_0^0, Y_2^m and Y_4^m.*

$$Y_2^2 Y_2^2 = \frac{\sqrt{5}}{\sqrt{14}\,\pi} Y_4^4$$

$$Y_2^{-2} Y_2^{-2} = \frac{\sqrt{5}}{\sqrt{14}\,\pi} Y_4^{-4}$$

$$Y_2^2 Y_2^{-2} = \frac{1}{2\sqrt{\pi}} Y_0^0 + \frac{1}{14\sqrt{\pi}} Y_4^0 - \frac{\sqrt{5}}{7\sqrt{\pi}} Y_2^0$$

$$Y_2^1 Y_2^1 = 5\frac{\sqrt{3}}{7\sqrt{10}\,\pi} Y_2^2 + \frac{10}{7\sqrt{10}\,\pi} Y_4^2$$

$$Y_2^{-1} Y_2^{-1} = 5\frac{\sqrt{3}}{7\sqrt{10}\,\pi} Y_2^{-2} + \frac{10}{7\sqrt{10}\,\pi} Y_4^{-2}$$

$$Y_2^1 Y_2^{-1} = -\frac{1}{2\sqrt{\pi}} Y_0^0 + \frac{2}{7\sqrt{\pi}} Y_4^0 - \frac{\sqrt{5}}{14\sqrt{\pi}} Y_2^0$$

$$Y_2^0 Y_2^2 = -\frac{\sqrt{5}}{7\sqrt{\pi}} Y_2^2 + \frac{\sqrt{15}}{14\sqrt{\pi}} Y_4^2$$

$$Y_2^0 Y_2^{-2} = -\frac{\sqrt{5}}{7\sqrt{\pi}} Y_2^{-2} - \frac{\sqrt{15}}{14\sqrt{\pi}} Y_4^{-2}$$

Appendix A.

The purpose of this appendix is to determine the matrix elements $V_T^{mm'}(\mathbf{R})$ (2.4) of the hydrogen perturbation of the « d » orbitals centred on the first neighbour R of the interstitial impurity. We transform the cubic harmonics $d^m(\hat{\mathbf{r}})$ into spherical harmonics $Y_2^m(\mathbf{r} \doteq T)$ by the following unitary transformation :

$$d^m(\hat{\mathbf{r}}) = \sum_{n=1}^{5} D_{nm}^{(2)} Y_2^n(\hat{\mathbf{r}}) \tag{A.1}$$

where $D^{(2)}$ are the transformation matrix of « d » cubic harmonics into the spherical harmonics. The product of two spherical harmonics can be decomposed as follows :

$$Y_2^m(\hat{\mathbf{r}}) Y_2^{m'}(\hat{\mathbf{r}}) = \sum_{L=0}^{4} \gamma_L^{m+m'} Y_L^{(m+m')} . \tag{A.2}$$

The determination of the coefficients γ are simplified by the following selection rules :

$$\gamma_L^{(m+m')} = 0 \quad \text{if} \quad L < |m+m'| \quad \text{or} \quad L \text{ odd} . \tag{A.3}$$

Expansion of the product of the spherical harmonics « d » (A.2) are given in the table A.I. By insering (A.1), (A.2), (A.3) in (2.4) we obtain the following expression of the matrix elements of the hydrogen perturbation :

$$V_T^{mm'}(\mathbf{R}) = \int dr |F_2(r)|^2 \sum_{n=0}^{5} \sum_{n'=0}^{5} D_{nm}^{(2)} D_{n'm'}^{(2)} \gamma_L^{n+n'} \int d\hat{r} \, Y_L^{(n+n')}(\hat{r}) \, Y_0^0(\mathbf{r} \overset{\wedge}{-} T) \, . \quad (A.4)$$

We define the two centers integral $s\tilde{s}\sigma$, $s\tilde{p}\sigma$, $s\tilde{d}\sigma$ by :

$$\int dr |F_2(r)|^2 \int d\hat{r} \, Y_L^0(\hat{r}) \, Y_0^0(\mathbf{r} \overset{\wedge}{-} T) \quad (A.5)$$

for $L = 0, 2, 4$ respectively. All the matrix elements $V_T^{mm'}(R)$ are given in the table I.

Appendix B.

To determine the electron-electron interaction energy defined in (3.28) we write the electronic densities $n_{TT_i}^{el}(\mathbf{r})$ and $n_\rho^{el}(\mathbf{r})$ ($\rho = T, T_i$) as a function of the intersite matrix elements of the Green operator $G^{TT_i}(E)$ and $G^\rho(E)$

$$n_\rho^{el}(\mathbf{r}) \;\; = - \pi^{-1} \operatorname{Im} \sum_{\lambda n} \sum_{\lambda' n'} \varphi_\lambda^n(\mathbf{r}) \, \varphi_{\lambda'}^{+n'}(\mathbf{r}) \int_{-\infty}^{E_F} dE \; G^\rho(E)_{\lambda\lambda'}^{nn'}, \quad (B.1a)$$

$$n_{TT_i}^{el}(\mathbf{r}) = - \pi^{-1} \operatorname{Im} \sum_{\lambda n} \sum_{\lambda' n'} \varphi_\lambda^n(\mathbf{r}) \, \varphi_{\lambda'}^{+n'}(\mathbf{r}) \int_{-\infty}^{E_F} dE \; G^{TT_i}(E)_{\lambda\lambda'}^{nn'}, \quad (B.1b)$$

where $\varphi_\lambda^n(\mathbf{r})$ is the atomic orbital centred on the site λ :

$$\varphi_\lambda^n(\mathbf{r}) = \langle \mathbf{r} | \lambda n \rangle \, .$$

The summations on λ and λ' are over all the metallic sites R and on the interstitial site ρ in (B.1a) and on the two interstitial sites T and T_i in (B.1b).

By inserting the Dyson relation (2.8) in (B.1a) and (3.13) in (B.1b), the perturbed electronic densities can be decomposed as a sum of the pure metallic density $n^{0\,el}(\mathbf{r})$, the electronic density introduced by isolated neutral hydrogen atoms $\Delta n_\rho^n(\mathbf{r})$ and the charge transfer contribution $\Delta n_\rho^{ct}(\mathbf{r})$ in case of one hydrogen or $\Delta n_{TT_i}^{ct}(\mathbf{r})$ in case of two hydrogens :

$$n_\rho^{el}(\mathbf{r}) \;\; = n^{0\,el}(\mathbf{r}) + \Delta n_\rho^n(\mathbf{r}) + \Delta n_\rho^{ct}(\mathbf{r}) \quad (B.2a)$$

$$n_{TT_i}^{el}(\mathbf{r}) = n^{0\,el}(\mathbf{r}) + \Delta n_{TT_i}^n(\mathbf{r}) + \Delta n_{TT_i}^{ct}(\mathbf{r}) \, . \quad (B.2b)$$

If $n_\rho^H(\mathbf{r})$ is the electronic density of an isolated hydrogen atom at site ρ, the neutral modification of the electronic densities of the perturbed systems is :

$$\Delta n_\rho^{el}(\mathbf{r}) \;\; = n_\rho^H(\mathbf{r}) \quad (B.3a)$$

$$\Delta n_{TT_i}^{el}(\mathbf{r}) = \sum_{\rho = T, T_i} n_\rho^H(\mathbf{r}) \, . \quad (B.3b)$$

With this decomposition of the electronic densities, the electron-electron interaction energy (3.28) can be splitted into two terms :

$$\Delta E_{el\text{-}el}(T, T_i) = \Delta E_{el\text{-}el}^n(T, T_i) + \Delta E_{el\text{-}el}^{ct}(T, T_i) \quad (B.4)$$

where the first term is the neutral interaction energy and is expressed as the Coulombic interaction between the electrons of the two hydrogen atoms on T and T_i :

$$\Delta E_{\text{el-el}}^{\text{n}}(T, T_i) = \frac{1}{2} \int d\mathbf{r} \, [n_T^H(\mathbf{r}) \, \nu_{T_i}^H(\mathbf{r}) + n_{T_i}^H(\mathbf{r}) \, \nu_T^H(\mathbf{r})] \tag{B.5}$$

where $\nu_\rho^H(\mathbf{r})$ is the Coulombic potential of an isolated hydrogen atom associated to $n_\rho^H(\mathbf{r})$.

The charge transfer term takes the following form :

$$\Delta E_{\text{el-el}}^{\text{ct}}(T, T_i) = \int d\mathbf{r} \, \nu^{0\,\text{el}}(\mathbf{r}) \left[\Delta n_{TT_i}^{\text{ct}}(\mathbf{r}) - \sum_{\rho = T, T_i} \Delta n_\rho^{\text{ct}}(\mathbf{r}) \right]$$

$$+ \frac{1}{2} \int d\mathbf{r} \left[\Delta n_{TT_i}^{\text{ct}}(\mathbf{r}) \, \Delta \nu_{TT_i}^{\text{ct}}(\mathbf{r}) - \sum_{\rho = T, T_i} \Delta n_\rho^{\text{ct}}(\mathbf{r}) \, \Delta \nu_\rho^{\text{ct}}(\mathbf{r}) \right] \tag{B.6}$$

$$+ \frac{1}{2} \int d\mathbf{r} \left[\Delta n_{TT_i}^{\text{ct}}(\mathbf{r}) \, \Delta \nu_{TT_i}^{\text{n}}(\mathbf{r}) - \sum_{\rho = T, T_i} \Delta n_\rho^{\text{ct}}(\mathbf{r}) \, \Delta \nu_\rho^{\text{n}}(\mathbf{r}) \right] . \tag{B.7a}$$

In the following, we introduce the density matrix modification for one hydrogen system :

$$\Delta N_{\rho\lambda\lambda'}^{nn'} = -\pi^{-1} \operatorname{Im} \int_{-\infty}^{E_F} dE \, (G_{\lambda\lambda'}^{\rho nn'}(E) - G_{\lambda\lambda'}^{\rho'nn'}(E))$$

$$\Delta N_{TT_i\,\lambda\lambda'}^{nn'} = -\pi^{-1} \operatorname{Im} \int_{-\infty}^{E_F} dE \, (G_{\lambda\lambda'}^{TT_i\,nn'}(E) - G_{\lambda\lambda'}^{TT_i'nn'}(E)) . \tag{B.7b}$$

Then the first integral in expression (B.6) takes the following form :

$$\sum_{Rm} \sum_{R'm'} N_{RR''}^{0\,mm'} \sum_{\lambda n} \sum_{\lambda'n'} \left(\Delta N_{TT_i\,\lambda\lambda'}^{nn'} - \sum_\rho \Delta N_{\rho\lambda\lambda'}^{nn'} \right) I_{RR'\,\lambda\lambda'}^{mm'\,nn'} \tag{B.8}$$

where $I_{RR'\,\lambda\lambda'}^{mm'\,nn'}$ is the fourth centre Coulombic integral :

$$I_{RR'\,\lambda\lambda'}^{mm'\,nn'} = \int d\mathbf{r} \int d\mathbf{r}' \, \frac{\varphi_R^m(\mathbf{r}) \, \varphi_{R'}^{+m'}(\mathbf{r}) \, \varphi_\lambda^n(\mathbf{r}') \, \varphi_\lambda^{+n'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \tag{B.9}$$

In all our calculation we restrict ourself to the intrasite integrals :

$$I_{RR'\,\lambda\lambda'}^{mm'\,nn'} = I_\lambda^{mm'\,nn'} \tag{B.10}$$

between the « d » orbitals for the metallic sites ($\lambda = R$ noted U_2^d) and between the « s » orbitals ($\lambda = T, T_i$ noted U_λ^s). These Coulombic integrals can be related to those defined in [34] by transforming the cubic harmonics into the spherical harmonics.

In order to give a simple expression for the final result of the charge transfer energy (B.6) we define the following quantities :

$$\Sigma_0^d(R) = \sum_m N^{0\,m}(R) \tag{B.11a}$$

$$\Sigma_\rho^d(R) = \Sigma_0^d(R) + \sum_m \Delta N_\rho^m(R) \tag{B.11b}$$

$$\Sigma_{TT_i}^d(R) = \Sigma_0^d(R) + \sum_m \Delta N_{TT_i}^m(R) . \tag{B.11c}$$

These quantities are the « d » electron number on the metallic site R in the host metal (B.11a), in the single hydrogen system (B.11b) and in the two hydrogen system (B.11c). We determine all the integrals present in (B.6) in the same way as for the first integral (B.8). Finally we obtain the following result :

$$\Delta E^{ct}_{el\text{-}el}(T, T_i) = \frac{1}{2} \sum_{R} \left\{ (\Sigma^d_{TT_i}(R))^2 - (\Sigma^d_0(R))^2 - \sum_{\rho} [(\Sigma^d_\rho(R))^2 - (\Sigma^d_0(R))^2] \right\} U^d_2 +$$

$$+ \frac{1}{2} \sum_{\rho} \left\{ (N^{ss}_{TT_i}(\rho))^2 - (N^s_\rho(\rho))^2 \right\} U^s_\rho . \quad (B.12)$$

In the numerical calculation the summation over R is restricted to the nearest neighbouring shell of the hydrogen atom.

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