

SURFACE SCIENCE LETTERS

**ENHANCEMENT OF HYDROGEN UPTAKE IN METALS AND
SUBSURFACE BONDING ***

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We have calculated the subsurface bonding energy of a hydrogen impurity under the clean Nb(110) and Pd-covered surfaces. At room temperature there exists a deep subsurface bonding well for the Nb(110) surface but not for the Pd(111). This theory explains in a natural way a series of experiments relating to the enhancement of hydrogen uptake by Nb surfaces that are covered by thin overlayers of Pd.

The interaction of metallic surfaces with gases and liquids is an important problem of current interest. In particular, the interaction of hydrogen with the surface of transition metals has received considerable attention. In a series of experiments [1–3] it was shown that the uptake rate of hydrogen by Nb and Ta can be drastically modified by thin overlayers of Pd and Pt. Since an experimental correlation was found between the enhancement of the uptake rate, the transition of the Pd overlayer to its fcc (111) structure (incommensurate with the bcc (110) substrate) [2] and an increase in the Pd 4d density of states close to the Fermi surface, it was assumed that the enhanced rate is due to changes in the electronic structure of the surface, that facilitates the dissociation of molecular into atomic hydrogen [3]. In the present letter we propose a theoretical explanation of these experiments, based on the idea that, due to the surface enhancement of the self-trapping effect, the hydrogen is trapped at subsurface sites [4] (“subsurface bonding”) [5]. The subsurface

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bonding can be even stronger than chemisorption and implies that for some metals (Nb in this case) hydrogen is tightly bonded below the first few layers, preventing the further absorption of hydrogen. The thin overlayer (Pd in our case) decrease the depth of the subsurface well bringing it closer to the bulk interstitial energy. This theory explains in a natural way the high initial rates of absorption and consequent saturation for clean Nb surfaces, the low absorption rates for thin Pd layers, that are commensurate with the Nb substrate and the enhanced uptake rate for Nb covered by a few incommensurate layers of Pd. In addition, the existence of hydrogen subsurface layers, recently observed by photoemission experiments [6,7], follows as an obvious consequence of the present calculations.

The second quantized Hamiltonian for a hydrogen atom in an interstitial site is given by

$$H = H_s + \sum_{\alpha l} \epsilon_{\alpha} c_{\alpha l}^{\dagger} c_{\alpha l} + \sum_{\alpha \beta} \sum_{l=l'} t_{ll'}^{\alpha \beta} c_{\alpha l}^{\dagger} c_{\beta l'} + \sum_l \mathbf{u}_l \cdot \sum_{\alpha \beta} \sum_{l=l'} c_{\alpha l}^{\dagger} c_{\beta l'} \int d^3 \mathbf{r} W_{\alpha l}(\mathbf{r}) \nabla V(\mathbf{r}-\mathbf{l}) W_{\beta l'}(\mathbf{r}). \quad (1)$$

Here H_s is the Hamiltonian of the metal (including the surface), $c_{\alpha l}^{\dagger}$ and $c_{\alpha l}$ create and destroy localized hydrogen (Wannier) states at site l , and α is a band label, $t_{ll'}^{\alpha \beta}$ describes the quantum diffusion of hydrogen from state (αl) to state $(\beta l')$ and the last term describes the interaction of the hydrogen with small amplitude lattice vibrations.

The ionic displacements \mathbf{u}_l have a bulk (b) and surface (s) contribution which are given by

$$\mathbf{u}_l^{(b)} = \sum_{\rho} \sqrt{\frac{\hbar}{2MN\omega_{\rho}}} \hat{e}_{\rho} (a_{\rho} e^{i\mathbf{q}\cdot\mathbf{l}} + a_{\rho}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{l}}),$$

$$\mathbf{u}_l^{(s)} = \sum_{\sigma} \sqrt{\frac{\hbar}{2MN_s\omega_{\sigma}}} A_{\sigma} e^{-\hbar\sigma^1 z} (\hat{e}_{\sigma} a_{\sigma} e^{i\mathbf{Q}\cdot\mathbf{L}} + \hat{e}_{\sigma}^* a_{\sigma}^{\dagger} e^{-i\mathbf{Q}\cdot\mathbf{L}}). \quad (2)$$

Here l denotes an ionic lattice site, M is the mass of a lattice ion, N (N_s) is the number of atoms in the bulk (surface), ρ characterizes bulk modes having frequency ω_{ρ} , polarization \hat{e}_{ρ} , wave vector \mathbf{q} and are associated with the phonon operators a_{ρ} and a_{ρ}^{\dagger} . The index σ denotes surface modes whose attenuation is assumed exponential (Rayleigh), A_{σ} is the normalization factor of surface waves and \hat{e}_{σ} is the complex polarization unit vector for surface waves. Capital letters are used to distinguish two-dimensional vectors, parallel to the surface (e.g., $\mathbf{l} = (\mathbf{L}, l_z)$).

Since the barrier height between interstices is roughly 0.3 eV, ~ 4000 K, only terms with $\alpha = 0$ are retained for calculations up to room temperature.

After neglecting off-diagonal terms ($I \neq I'$) which describe the diffusion and inserting expression (2) into eq. (1), one obtains

$$H = \sum_{\lambda} \hbar \omega_{\lambda} a_{\lambda}^{\dagger} a_{\lambda} + \sum_I \epsilon_0 c_I^{\dagger} c_I + \sum_{I\lambda} g_{\lambda I} c_I^{\dagger} c_I (a_{\lambda} - a_{-\lambda}^{\dagger}), \tag{3}$$

where λ runs over surface (σ) and bulk (ρ) modes. The explicit form of $g_{\lambda I}$ is

$$g_{\rho I} = \sqrt{\frac{\hbar}{2MN\omega_{\rho}}} e^{i\mathbf{q} \cdot \mathbf{l}} \hat{e}_{\rho} \sum_1 e^{i\mathbf{q} \cdot \mathbf{l}} \langle \nabla V(\mathbf{r} - \mathbf{l}) \rangle, \tag{4}$$

$$g_{\sigma I} = \sqrt{\frac{\hbar}{2MN_s \omega_{\sigma}}} A_{\sigma} e^{i\mathbf{Q} \cdot \mathbf{L}} e^{-h_{\sigma} \cdot \mathbf{l}_z} \hat{e}_{\sigma} \sum_1 e^{i\mathbf{Q} \cdot \mathbf{L}} e^{-h_{\sigma} \cdot \mathbf{l}_z} \langle \nabla V(\mathbf{r} - \mathbf{l}) \rangle, \tag{5}$$

where $\mathbf{l} = (\mathbf{L}, l_z)$ is a vector going from the interstitial site I to an ionic lattice site.

Assuming that the lattice-mediated interaction between hydrogen is small (for instance assuming low concentrations) the eigenvalues and eigenvectors of the Hamiltonian (3) are [8]

$$E_{\{\mu_{\lambda}\}I_1 \dots I_m} = \sum_{\lambda} \hbar \omega_{\lambda} \mu_{\lambda} + m \epsilon_0 - m \frac{|g_{\lambda}|^2}{\hbar \omega_{\lambda}}, \tag{6}$$

$$\begin{aligned} |\{\mu_{\lambda}\}I_1 \dots I_m\rangle &= \exp\left(\frac{1}{2} \sum_{\lambda} \left| \sum_{i=1}^m \frac{g_{\lambda I_i}}{\hbar \omega_{\lambda}} \right|^2\right) \\ &\times \frac{(b_{\lambda}^{\dagger})^{\mu_{\lambda}}}{\lambda \sqrt{\mu_{\lambda}!}} \exp\left(-\sum_{i=1}^m \frac{g_{\lambda I_i}}{\hbar \omega_{\lambda}} b_{\lambda}^{\dagger}\right) c_{I_1}^{\dagger} \dots c_{I_m}^{\dagger} |00\rangle, \end{aligned} \tag{7}$$

where $|g_{\lambda}| \equiv |g_{\lambda I}|$ and

$$b_{\lambda}^{\dagger} \equiv a_{\lambda}^{\dagger} + \sum_I \frac{g_{\lambda I}}{\hbar \omega_{\lambda}} c_I^{\dagger} c_I,$$

m is total number of hydrogen impurities in the crystal and $\mu_{\lambda} = 0, 1, 2, \dots$ is the excitation number of the vibrational mode λ .

The first term in the right hand side of eq. (6) describes the energy due to the lattice vibrations, the second is the energy of the impurities in a rigid lattice and the third is the self-trapping energy of the interstitial hydrogen. The self-trapping term is always negative since it is simply the energy released by the undistorted lattice with one impurity in relaxing to the distorted equilibrium configuration.

Near the surface the self-trapping energy (the last term in eq. (6)) is enhanced by the contribution from the surface terms ($\lambda = \sigma$), which is comparable with the contribution of bulk terms. This observation is the central point of this letter. In spirit the present calculation is similar to the now

famous Holstein polaron [9], with the difference that ours is a "hydrogenic", as opposed to "electronic", polaron and that we explicitly calculate the contribution of surface terms to the energy.

To calculate explicitly the energy for the various interstitial sites, we use the Debye approximation for the vibrational modes, both surface and bulk ones ($\omega_o = UQ$ for $Q < Q_D$, $\omega_p = vq$ for $q < q_D$), and calculate the attenuation, normalization and polarization of the surface waves using the prescriptions given by Rayleigh's theory of surface modes in isotropic media [10].

In this fashion the surface contribution to the self-trapping energy valid for layer n ($= 0, 1, 2, \dots$) is

$$\Delta_s(n) = \frac{1}{8\pi^2 M (N_s/S) U^2} \int_0^{2Q_D} dx \frac{1}{x} e^{-2h(l_z/a)x} A_x^2 \int_0^{2\pi} d\phi |F(x, \phi)|^2, \quad (8)$$

where a is the lattice parameter for cubic symmetry, (N_s/S) is the number of metal atoms per unit surface area, $l_z \equiv na_z$, $h \equiv [1 - (U/v)^2]^{1/2}$, $Q_D = (4\pi N_s/S)^{1/2}$, $A_x^2 = 1 - \exp(-2ha_z x/a)$ and

$$F(x, \phi) = \sum_l \exp(i\mathbf{Q} \cdot \mathbf{L} - hQ l_z) F(l) \hat{e}_o \cdot \hat{\mathbf{l}}. \quad (9)$$

This last factor depends on the lattice symmetry and surface orientation. The parameter $F(\mathbf{l}) \equiv |\langle \nabla V(\mathbf{r} - \mathbf{l}) \rangle|$ is the force the hydrogen impurity exerts on the l th lattice ion. We have obtained F for Nb (bcc, tetrahedral) and Pd (fcc, octahedral) from spectroscopic measurements of the bulk lattice distortion caused by interstitial hydrogen [11,12]. The lattice distortion is related to F by the formula

$$\delta_l = \langle \{ \mu_\lambda \} \mathbf{l} | \mathbf{u}_l | \{ \mu_\lambda \} \mathbf{l} \rangle,$$

where δ_l is the shift of the lattice site l and $|\{ \mu_\lambda \} \mathbf{l} \rangle$ is an eigenvector given by eq. (7).

To calculate the total solution energy at site n we add the experimentally measured *bulk* solution energy E_{sol} to the self-trapping surface energy $\Delta_s(n)$. The parameters used in the calculations are shown in table 1. Since the surface

Table 1
Parameters used in the calculation

	$-E_{sol}$ (eV)	M (10^{-22} g)	N_s/S ($1/a^2$)	a (Å)	v (10^5 cm/s)	$-E_{ads}$ (eV)	F (10^{-4} dyn)
Nb	0.358 [14]	1.543	$\sqrt{2}$	3.30	2.419	0.55 [13]	3.035
Pd*(110)	0.358 [14]	1.765	$\sqrt{2}$	3.30	2.419	0.45? [16]	
Pd(111)	0.20 [15]	1.765	$4/\sqrt{3}$	3.89	2.255	0.45 [16]	1.263

Table 2

Energies of H in Nb(110) in tetrahedral sites (n is the layer index and L and U refer to the lower and upper limits of the subsurface bonding energies)

n	$-E_n^L$ (eV)	$-E_n^U$ (eV)
0	0.808	0.562
1	0.461	0.427
2	0.393	0.385
3	0.374	0.371

speed of sound U , appropriate for this calculation, has not been determined experimentally we have performed calculations using both the lower (E_n^L) and the upper (E_n^U) theoretical limits ($0.87 < U/v < 0.95$).

Table 2 shows the total "subsurface" solution energy for the first few layers of Nb. This calculation indicates that the first subsurface bonded state has a considerably lower energy than the chemisorption well E_{ads} whereas the energy below the second layer is comparable to the chemisorption energy. This shows that subsurface trapping is important in Nb. It is also important to notice that it is energetically favorable to fill the first one to two subsurface layers before chemisorption takes place. In agreement with the theory presented here, the absorption of hydrogen is initially quite high until the first few subsurface layers are saturated; then the chemisorption well is filled and further hydrogen absorption is made difficult because various subsurface layers have to be bypassed before hydrogen can reach a bulk interstitial site.

Table 3 shows the subsurface bonding energy for the Pd(111) surface. For this case the hydrogen chemisorption energy is somewhat larger than the subsurface solution energy. Also the subsurface bonding energy is smaller than that of Nb. Therefore, in this case hydrogen will more readily diffuse into the bulk. Of course, since the subsurface bonding energy critically depends on the existence of surface modes, inspection of tables 2 and 3 shows that after 3 to 4 monolayers below the surface the surface energy of solution becomes comparable to the bulk solution energy.

Table 3

Energies of H in Pd(111) in octahedral sites (n is the layer index and L and U refer to the lower and upper limits of the subsurface bonding energies)

n	$-E_n^L$ (eV)	$-E_n^U$ (eV)
0	0.337	0.253
1	0.234	0.220
2	0.212	0.208

Table 4

Energies of H in Pd*(110) in tetrahedral sites (n is the layer index and L and U refer to the lower and upper limits of the subsurface bonding energies)

n	$-E_n^L$ (eV)	$-E_n^U$ (eV)
0	0.496	0.421
1	0.390	0.379

The calculation for the commensurate Pd*(110) is as easily performed (table 4). However, the choice of parameters is not clear; i.e., the choice for the surface speed of sound or the solution energy is not unique. As an indication we have calculated the subsurface binding energy under one layer of "commensurate" Pd*(110), assuming that the vibrational modes are given by the underlying Nb. This is reasonable if we consider that most of the surface modes penetrate three or more atomic layers into the metal. Assuming that the energy of solution is in the most unfavorable cases, that of pure Pd, we find that in this case subsurface bonding is possible, although this conclusion depends on the choice of the surface speed of sound.

At this point we would like to stress that the existence of the subsurface bonding mechanism is shown by our calculations and that the qualitative conclusions are independent of any reasonable variation of the parameters. Recent experiments on the absorption of H by clean niobium surfaces have shown the existence of a subsurface hydride localized a few layers (~ 2 to 4) below the surface [6,7], giving further experimental support to the ideas presented here. Moreover, we obtain a subsurface binding energy larger than the chemisorption energy in Nb(110).

In conclusion, we have calculated the subsurface binding energies of hydrogen for the Nb(110), Pd(111) and Pd*(110) surfaces. Our results indicate that the uptake of hydrogen in the bulk will be small for Nb(110) and will be enhanced by the addition of more than three monolayers of Pd(111), in agreement with experimental observations. The calculation presented here provides a theoretical basis for the kinetic model [13] and for the unambiguous experimental [1,2,3] fact that the surface plays a rate-limiting role in the hydrogen uptake.

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