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Subsurface bonding of hydrogen in transition metals: dependence on surface orientation

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Abstract

The calculation of the surface-induced enhancement of the binding energy of hydrogen impurities in transition metals, previously reported for close-packed surfaces, are extended to open surfaces in the fcc and bcc structures. The effect is found to be stronger for close-packed surfaces than for open ones. Numerical values for the subsurface bonding energy in Nb and Pd are given, from which changes in the kinetics of hydrogen absorption through specific surfaces are predicted.

The interaction of hydrogen with the surface of transition metals is a subject of continuing interest. Among the several aspects that are now at issue are the condensation of hydrogen in metal solution in the subsurface interstitial layers [1–6], and the effect of this in controlling the up take rate from the gas phase to the metal bulk [4,6,7].

Earlier we called attention to the fact that the contribution of the elastic distortion to the impurity solution energy is notably enhanced when approaching a surface [3,4,7]. When filling an interstitial site, a hydrogen impurity exerts forces on the surrounding crystal ions, which move to new equilibrium positions in order to minimize the total energy, stabilizing this way the impurity state. This energy reduction, of elastic origin, is typically of a few tenths of eV. If the defect is in an interstitial site just below the surface, where the neighboring crystal ions are freer to move than in the bulk, the stabilizing effect is expected to be enhanced. Estimates of the surface induced energy reduction of interstitial hydrogen below close-packed surfaces of fcc and bcc crystals yield values as large as 0.25–0.34 and 0.56–0.8 eV for palladium and niobium, respectively [4].

This effect is particularly interesting in metals like palladium, tantalum or niobium, which spontaneously absorb hydrogen and have thus positive heats of solution. The energy of an interstitial hydrogen state in the subsurface layer, obtained by adding the surface contribution to the bulk solution energy, in these metals is lower, or comparable to that of the chemisorption states [3]. This causes observable phenomena, which have been reported to occur in niobium [1,6,8–10] and palladium [5,11] in good agreement with theoretical estimates [3,4]. Direct experimental evidence of the existence of subsurface hydrogen states with energy close to that of the chemisorbed surface states has been reported for palladium and copper by the diffraction of atomic beams [11,12], LEED [12], the two techniques com-

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bined [12], and flash desorption [13]. Strongly bound surface layers of hydrogen in niobium have been observed by angle-resolved photoemission [1,2,8–10,14] and high resolution EELS [6]. The absorption kinetics of Pd(111), Pd(110), Cu(110) and Nb(100) surfaces exhibit unusual features in agreement with the theoretical ideas described above.

The first experimental indication of the subsurface condensation of hydrogen impurities was discovered by Smith, studying the kinetics of hydrogen absorption in niobium [1,8]. This system was subsequently subjected to extensive experimentation, which yielded new unexpected results [6,14,15]. Some controversy on the interpretation of these results still remains [6,14–18].

The photoemission intensity as a function of hydrogen exposure is found to be strongly dependent on the photon energy [1]. For the case of Nb it is found that at low temperature, the hydrogen uptake is initially fast and then it slows down considerably without much diffusion into the bulk [8]. The uptake is, however, fast and fills up the bulk at high temperatures. This effect has been interpreted earlier as due to the presence of a so-called "surface valve" which opens up as the temperature is raised [4,7]. The unusual kinetics of absorption of the Nb(110) surface is strongly affected by the coverage of a few monolayers Pd(111) [9,10].

Two general categories of explanation have emerged to explain the kinetics: electronic [19] and polaronic [4]. The electronic effect claims that changes in kinetics are due to changes in the electronic density of states at the Fermi surface, which in turn affects the dissociation of molecular hydrogen into atomic hydrogen. In this type of explanation the various surface binding energies arise from sites of different geometrical coordination on the surface of the transition metal. We have been pursuing an alternate explanation which relies on the interaction of the hydrogen atoms with the surface phonons of the transition metal [4,7,17]. The interaction of hydrogen with the surface phonons ("polaronic" effect) produces a surface enhancement of the self-trapping effect and because of this the hydrogen is trapped at subsurface sites ("subsurface bonding"). This subsurface bonding energy is dependent on the atomic coordination of hydrogen, the energy of the surface phonons and the interaction energy between

a transition metal atom and a hydrogen atom. In this latter explanation the various bonding energies for H arise from the various subsurface states and the presence of the temperature dependent surface valve is due to the filling of the subsurface valve.

In order to distinguish which class of theories describes the experimental situation, it is important to calculate and develop predictions in specific physical situations. Here we have performed an extensive calculation of the predictions of the polaronic theory for closed and open surfaces, for the cases of Nb and Pd. We have calculated the expected energies of the subsurface bonded sites and find that in general close-packed denser surfaces tend to enhance the subsurface bonding, as would be expected.

The second quantized Hamiltonian H for a hydrogen atom in an interstitial site of a transition metal is given by:

$$H = \sum_{\lambda} h\omega_{\lambda}\left(a_{\lambda}^{\dagger}a_{\lambda} + \tfrac{1}{2}\right) + \sum_{l} \epsilon_0 c_l^{\dagger}c_l$$
$$+ \sum_{l\lambda} g_{\lambda}c_l^{\dagger}c_l\left(a_{\lambda} - a_{\lambda}^{\dagger}\right), \tag{1}$$

where the first term in the right-hand side the Eq. (1) describes the energy of the lattice modes λ of the semifinite crystal, the second describes the hydrogen states without including crystal elasticity and the last one accounts for this interaction in the linear approximation. Off-diagonal interaction terms can be neglected for well localized defects. The diagonalization of this Hamiltonian is standard. For a single impurity (low concentration) one obtains the energy eigenvalue:

$$E = \epsilon_0 - \sum_{\lambda} \frac{|g_{\lambda}|^2}{h\omega_{\lambda}}, \tag{2}$$

where ϵ_0 is the energy of the hydrogen atom in a rigid lattice, ω_{λ} is the frequency of vibrational mode λ and g_{λ} is the normalized λth Fourier component of the "force" between the hydrogen and the host ion. The second term in Eq. (2) describes the lattice contribution to the self-trapping energy and it includes a term due to the additional self-trapping by the surface phonons.

The coupling constant g_{λ} can be calculated from the force exerted by the impurity on the neighboring ions and the crystal modes, by writing H in the

coordinate representation. In the linear approximation, the expression for g_λ is obtained from the first-order term in the expansion of the interaction energy in powers of the ionic displacement. Expression (1) simply follows from transforming this equation using the second quantized formalism in the usual way. This calculation is similar to the famous "Holstein" polaron [20] except that this is a "hydrogenic" as opposed to an "electronic" polaron. In addition, we have taken into account the extra terms introduced by the presence of the surface. This latter term enters Eq. (2) because the sum over λ has to be taken over the bulk and surface modes, instead of the bulk ones alone.

To illustrate the effect presented here we have introduced some simplifying assumptions which do not affect significantly the surface induced self-trapping energy.

First, the harmonic approximation is retained in the Hamiltonian (1) thus maintaining the vibrational frequencies. In addition, we retain only the linear term for the ionic displacement surrounding the interstitial position occupied by the impurities. This assumption is quite natural since the ionic displacement induced by interstitial H in bulk is small, of the order of 5% [21]. These displacements give rise to the self-binding energy calculated here and are enhanced in the presence of a surface.

As a second approximation, we assume that the force constants governing the elastic interaction between the crystal ions do not change close to the surface. This hypothesis is justified by accurate measurements of the surface vibration-mode dispersion-relations using inelastic He atom scattering in LiF [22] and Pt [23] and electron scattering from Ni(100) [24] surfaces. In all cases, excellent agreement is obtained with Rayleigh's theory [25] if the surface force constants are assumed to be the same as for the bulk. A slight improvement in the fit, for the short wavelength region, is obtained for the first two layers of Ni(100) if the surface force constants are assumed to be 20% larger than the bulk ones. This does not affect significantly the results presented here and in fact implies a larger self-trapping energy.

The effect of the isotopic mass of the defect on the subsurface enhancement of the self-trapping energy is very hard to evaluate and neglected as well. As the particle becomes more localized for the higher

mass, the strength of the mean force F exerted by the impurity on the surrounding ions is expected to decrease, with the consequent decrease of the subsurface effect. Unfortunately, no simple rule can be established for this kind of isotope effect. Moreover the difference between the zero point energies of the different isotopes will not affect significantly the changes in the surface self-trapping energy because it contributes the same way for the bulk and the surface.

Physically the surface self-trapping energy arises from the breaking of the symmetry by the free surface, through the presence of additional surface elastic waves.

Earlier we calculated the surface contribution to the second term and evaluated the self-trapping energy assuming a Debye approximation for the bulk and surface vibrational modes (i.e. $\omega = VQ$ for $Q < Q_D$) and calculated the attenuation, normalization and polarization of the surface wave using Rayleigh's theory of surface modes in isotropic media. The surface contribution to the self-trapping energy calculated in this fashion, is given by [4]:

$$
\Delta_s = \frac{1}{8\pi^2 M(N_s/S)U^2}
$$
$$
\times \int_0^{2\pi} dx \, \frac{1}{x} \exp\left[-2h(l_z/a)x\right]
$$
$$
\times A_x^2 \int_0^{2\pi} d\phi \, |F(x, \phi)|^2, \tag{3}
$$

where a is the lattice parameter, (N_s/S) is the number of surface metal atoms per unit area, M is the mass of the metal ion, $l_z = na_z$, $h = [1 - (U/v)^2]^{1/2}$,

$$
Q_D = (4\pi N_s/S)^{1/2}, \quad A_x^2 = 1 - \exp(-2ha_z x/a)
$$

and

$$
F(x, \phi) = \sum_l \exp(iQ \cdot l - hQl_z)F(l)\hat{e}_\sigma \cdot \hat{l}, \tag{4}
$$

with $l(L, l_z)$ a vector going from the interstitial site l to a metal ion site and U and v the surface and bulk phonon velocities respectively. The quantity $F(l) = |\langle \nabla V(r-1)\rangle|$ is the average force the hydrogen atom exerts on a particular (lth) metal ion site and depends on the symmetry and surface orientation.

Table 1
Parameters used in the calculation of the subsurface bonding energy for Pd and Nb

	a $(10^{-8}$ cm$)$	U $(10^5$ cm/s$)$	v $(10^5$ cm/s$)$	M $(10^{-22}$ gr$)$	F $(10^{-4}$ dynes$)$	$-E_{sol}$ (eV)
Pd	3.89	1.962–2.142	2.255	1.765	1.263	0.20
Nb	3.30	2.105–2.298	2.419	1.543	3.035	0.358

The calculations presented here reduce to the calculations of Eqs. (3) and (4) for particular materials, crystal structures and surfaces. In order to calculate for systems of experimental importance we have calculated and compared the energies of the subsurface bonded states for the fcc(111), fcc(110) and bcc(100). In this fashion, we are able to compare the energy of the subsurface bonding for a dense and a more open surface in the fcc and bcc structures. Moreover, we have calculated numerical values for fcc(Pd) and bcc(Nb) which are systems which have been studied experimentally extensively.

The calculations of Eqs. (3) and (4), for the different surfaces and crystal structures, are included in Appendix A. The parameters used in particular for the calculation of the subsurface bonding energy for Pd and Nb are listed in Table 1. The energies for the close-packed and open surfaces of Pd and Nb are shown in Tables 2–5. A comparison of the energies calculated for the close-packed versus the non-close-packed surfaces is quite revealing. In both cases, the first subsurface bonding energy is lower for the close-packed surface. This may be expected since the contribution to the subsurface bonding from the first monolayer probably is larger for a denser surface. Interestingly, below the second layer the subsurface bonding energy is reversed and larger for the more open surface. This is not as easy to understand in a qualitative fashion.

A measurement of the energies of the different surface states found for hydrogen near the surface of Pd and Nb provide a direct experimental check of the theory presented here. As predicted here, the subsurface bonding energy is expected to be higher for the close-packed surfaces than for the open ones.

The kinetics of hydrogen absorption by these

Table 2
Subsurface energies of H in the octahedral sites below the Pd(111) surface for the two limiting surface velocities

n	$\Delta_s^L(n)$ (eV)	$\Delta_s^U(n)$ (eV)
0	0.137	0.053
1	0.034	0.020
2	0.012	0.009
3	0.005	0.004

Δ_s^L and Δ_s^U refer to the lower and upper limits of the subsurface bonding contribution to the energy.

Table 4
Subsurface energies of H in the tetrahedral sites below the Nb(100) surface for the two limiting surface velocities

n	$\Delta_s^L(n)$ (eV)	$\Delta_s^U(n)$ (eV)
0	0.450	0.204
1	0.103	0.069
2	0.035	0.028
3	0.015	0.013

Δ_s^L and Δ_s^U refer to the lower and upper limits of the subsurface bonding contribution to the energy.

Table 3
Subsurface energies of H in the octahedral sites below the Pd(110) surface for the two limiting surface velocities

n	$\Delta_s^L(n)$ (eV)	$\Delta_s^U(n)$ (eV)
0	0.131	0.048
1	0.057	0.027
2	0.027	0.016
3	0.015	0.010

Δ_s^L and Δ_s^U refer to the lower and upper limits of the subsurface bonding contribution to the energy.

Table 5
Subsurface energies of H in the tetrahedral sites below the Nb(100) surface for the two limiting surface velocities

n	$\Delta_s^L(n)$ (eV)	$\Delta_s^U(n)$ (eV)
0	0.379	0.149
1	0.136	0.073
2	0.057	0.038
3	0.028	0.021

Δ_s^L and Δ_s^U refer to the lower and upper limits of the subsurface bonding contribution to the energy.

surfaces will also be modified drastically. Since the subsurface bonding energy is considerably smaller for a more open surface in Nb, it is expected that the "subsurface valve" will open at a lower temperature for the Nb(100) surface than for the Nb(110) surface. On the other hand, since the changes in Pd are only slight in changing from an fcc(111) to a fcc(110) surface, no major qualitative changes are expected as a function of crystallographic orientation for Pd.

Acknowledgement

Appendix A. Calculation of the F function

A.1. fcc(111) surface

$$l_z(n) = \frac{a}{2\sqrt{3}}(2n+1),$$

$$N_s/S = 4/\sqrt{3}a^2,$$

$$A^2(x) = 1 - \exp(-2hx/\sqrt{3}),$$

$$aQ_D = 4(\pi/\sqrt{3})^{1/2},$$

$$\begin{aligned}
\text{Re } F(x, \phi) &= \frac{4}{\sqrt{6}} \frac{F}{\sqrt{1+h^2}} \sum_{i=1}^{3} \left[\frac{1}{\sqrt{2}}\cosh\left(\frac{hx}{2\sqrt{3}}\right) \right. \\
&\quad \times \sin\left(\frac{\cos\phi_i}{\sqrt{6}}x\right) - h\sinh\left(\frac{hx}{2\sqrt{3}}\right) \\
&\quad \left. \times \cos\left(\frac{\cos\phi_i}{\sqrt{6}}x\right) \cos\phi_i \right],
\end{aligned}$$

$$\text{Im } F(x, \phi) = \frac{4}{\sqrt{6}} \frac{F}{\sqrt{1+h^2}} \sum_{i=1}^{3} \left[\frac{1}{\sqrt{2}}\sinh\left(\frac{hx}{2\sqrt{3}}\right) \right.$$

$$\times \cos\left(\frac{\cos\phi_i}{\sqrt{6}}x\right) + h\cosh\left(\frac{hx}{2\sqrt{3}}\right)$$

$$\left. \times \sin\left(\frac{\cos\phi_i}{\sqrt{6}}x\right) \cos\phi_i \right],$$

$$\phi_1 = \phi, \quad \phi + \frac{2\pi}{3}, \quad \phi + \frac{4\pi}{3}.$$

A.2. fcc(110) surface

$$l_z(n) = \frac{a}{2\sqrt{2}}(n+1),$$

$$N_s/S = \sqrt{2}/a^2,$$

$$A^2(x) = 1 - \exp(-hx/\sqrt{2}),$$

$$aQ_D = 2(\sqrt{2}\pi)^{1/2},$$

$$\begin{aligned}
F(x, \phi) &= \frac{2iF}{\sqrt{1+h^2}} \left[h\sin\left(\frac{x}{2}\cos\phi\right)\cos\phi \right. \\
&\quad + \sqrt{2}h\sin\left(\frac{x}{2\sqrt{2}}\sin\phi\right) \\
&\quad \times \sin\phi\cosh\left(\frac{hx}{2\sqrt{2}}\right) \\
&\quad \left. + \sqrt{2}\cos\left(\frac{x}{2\sqrt{2}}\sin\phi\right)\sinh\left(\frac{hx}{2\sqrt{2}}\right) \right].
\end{aligned}$$

A.3. bcc(110) surface

$$l_z(n) = \frac{a}{2\sqrt{2}}(2n+1),$$

$$N_s/S = \sqrt{2}/a^2,$$

$$A^2(x) = 1 - \exp(-\sqrt{2}hx),$$

$$aQ_D = 2(\sqrt{2}\pi)^{1/2},$$

$$F(x, \phi) = \frac{2i}{\sqrt{5}} \frac{F}{\sqrt{1+h^2}}$$

$$\times \left\{ h(\cos\phi + \sqrt{2}\sin\phi)\sin\left[\frac{x}{4}(\cos\varphi\right.\right.$$

$$+ \sqrt{2} \sin \phi) \Big] \exp\left(\frac{hx}{2\sqrt{2}}\right)$$

$$+ h(\cos \phi - \sqrt{2} \sin \phi) \sin\left[\frac{x}{4}(\cos \phi\right.$$

$$\left. - \sqrt{2} \sin \phi)\right] \exp\left(-\frac{hx}{2\sqrt{2}}\right)$$

$$+ \sqrt{2} \cos\left[\frac{x}{4}(\cos \phi + \sqrt{2} \sin \varphi)\right]$$

$$\times \exp\left(\frac{hx}{2\sqrt{2}}\right)$$

$$- \sqrt{2} \cos\left[\frac{x}{4}(\cos \phi - \sqrt{2} \sin \phi)\right]$$

$$\times \exp\left(-\frac{hx}{2\sqrt{2}}\right)\bigg\}.$$

A.4. bcc(100) surface

$$l_z(n) = \frac{a}{4}(2n + 1),$$

$$N_s/S = \sqrt{2/a^2},$$

$$A^2(x) = 1 - \exp(-hx),$$

$$aQ_D = \sqrt{4\pi},$$

$$F(x, \phi) = \frac{2i}{\sqrt{5}} \frac{F}{\sqrt{1 + h^2}} \left\{ 2h\left[\sin\left(\frac{x}{2}\cos \phi\right)\right.\right.$$

$$\times \cos \phi \exp\left(-\frac{hx}{4}\right)$$

$$+ \sin\left(\frac{x}{2}\sin \phi\right) \sin \phi \exp\left(-\frac{hx}{4}\right)\bigg]$$

$$- \cos\left(\frac{x}{2}\cos \phi\right) \exp\left(-\frac{hx}{4}\right)$$

$$+ \cos\left(\frac{x}{2}\sin \phi\right) \exp\left(\frac{hx}{4}\right)\bigg\}.$$

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