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Polarons and Subsurface Bonding

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Abstract

We have calculated the bonding energy of a hydrogen atom below the surface of Nb(110) and Pd(111) due to the interaction with the surface phonons. Our results show that at room temperature, there is a deep potential well just below the surface of Nb(110) with a much shallower well for Pd(111). Due to this, the kinetics of hydrogen absorption by Nb(110) surface and Pd covered Nb is drastically affected. The kinetic equations, modified to include this subsurface potential well, show that the subsurface-trapped hydrogen acts as a valve for the admission of hydrogen into the bulk. A large variety of experimental facts clearly follow from these considerations.

The work presented in this paper was done during a series of visits one of us (IKS) spent at the Catholic University in Santiago, Chile. This fact is related to Ted Holstein not only because it is about polarons but also because when our Chilean friends celebrate their day of independence (September 18) they also celebrate Ted's birthday. In fact, some years ago, we helped Ted celebrate with a bottle of good Chilean wine ("Marques de Casa Concha" 1975).

The behavior of hydrogen in metals is a field of active experimental and theoretical interests. In particular, the absorption of hydrogen by metallic surfaces has drawn much attention not only because of the possible applications, but also because a variety of interesting physical phenomena. In a series of fascinating experiments [1-3], it was shown that the absorption of hydrogen by the surface of niobium and tantalum is drastically modified by the coverage of three or more monolayers of palladium or platinum. This has been conventionally interpreted as due to a change in the electronic density of states at the Fermi surface,

which presumably affects the dissociations of molecular hydrogen into atomic hydrogen [3]. We have proposed an alternate explanation which relies on the idea that in certain metals (for instance Nb) due to the interaction with the surface phonons, the hydrogen is bonded stronger below the surface than in the bulk ("subsurface bonding") [4]. In this fashion, the absorption of hydrogen is initially high, until the subsurface is saturated and then the surface further blocks the absorption into the bulk. The coverage of Nb with a few Pd monolayers reduce this subsurface binding and consequently the bulk absorption is enhanced. The subsurface bonding modifies the absorption kinetics in such a way that the subsurface coverage decrease abruptly at a critical temperature which depends on the bulk concentration [5].

The energy of a hydrogen atom in an interstitial site can be calculated using the standard second quantized Hamiltonian formalism [6]. Since the calculation relates to surface properties both the bulk and surface phonon contributions ought to be taken into account. Neglecting the terms that describe diffusion (i.e., low temperatures) and assuming that the lattice-mediated interactions between the hydrogens is small (low concentrations) the hydrogen energy was shown to be given by [4]

$$E = \sum_{\lambda} m\epsilon_o - m \frac{|g_\lambda|^2}{\hbar\omega_\lambda} \qquad (1)$$

where m is the mass of hydrogen atom, $m\epsilon_o$ is the energy of the impurities in a rigid lattice, ω_λ is the frequency of vibrational mode λ and g_λ is the normalized λ-th Fourier component of the "force" between the hydrogen atom and the host ion and therefore the second term describes the self trapping energy.

In ref. [4] we have calculated explicitly g_λ and performed numerical calculations to evaluate the value of the self trapping energy under some simplifying assumptions.

The surface contributions to the self trapping energy for layer n (= 0,1,2,...) was found

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

where a is the lattice parameter, (N_s/S) is the number of metal atoms per unit surface area, M is the mass of the metal ion, the vibrational modes are assumed to be Debye like i.e., $\omega_\sigma = UQ$ for $Q<Q_D$ and $\omega_\rho = vq$ for $q<q_D$, $\ell_z \equiv na_z$, $h \equiv [1-(U/v)^2]^{1/2}$, $Q_D = (4\pi N_s/S)^{1/2}$, $A_x^2 = 1 - \exp(-2ha_z x/a)$ and

$$F(x,\phi) = \sum_{\vec{\ell}} \exp(i\vec{Q}\cdot\vec{L} - hQ\ell_z)\, F(\vec{\ell})\, \hat{e}_\sigma \cdot \hat{\ell} \qquad (3)$$

with $\vec{\ell} = (\vec{L},\ell_z)$ a vector going from the interstitial site $\vec{\ell}$ to an ionic lattice site. The parameter $F(\vec{\ell}) \equiv |\langle\nabla V(\vec{r}-\vec{\ell})\rangle|$ is the force the hydrogen impurity exerts on the ℓth lattice ion and depends on lattice symmetry and surface orientation.

In spirit the present calculation is similar to the now famous Holstein polaron [7] with the difference that ours is a "hydrogenic" as opposed to "electronic", polaron and that we explicitly calculate the contribution of the surface terms to the energy.

We have calculated the total solution energy at site n by adding the experimentally measured bulk solution energy E_{sol} to the self trapping energy, $\Delta_s(n)$. The parameters used in the calculation are shown in Table I.

Table I

Parameters Used in the Calculation

	$-E_{sol}$ (eV)	M (10^{-22}g)	N_s/S ($1/a^2$)	a (Å)	v (10^5cm/s)	$-E_{ads}$ (eV)	F (10^{-4} dyn)
Nb(110)	0.358[8]	1.543	$\sqrt{2}$	3.30	2.419	0.55[10]	3.035
Pd(111)	0.200[9]	1.765	$4/\sqrt{3}$	3.89	2.255	0.45[11]	1.263

F is obtained for (Nb, tetrahedral) and Pd (fcc, octahedral) from spectroscopic measurements [12,13] of the bulk lattice distorsion caused by the interstitial hydrogen and theoretical calculation of ref. [4].

The surface speed of sound U, has not been determined experimental so we performed calculations using both the upper and lower theoretical limits ($0.87 < U/v < 0.95$). The total solution energy are given in Table II.

Table II

Total Solution Energies for Various Depths

	Tetrahedral site in Nb(110)	Octahedral site in Pd(111)
n	$-E_n$(eV)	$-E_n$(eV)
0	0.562 - 0.808	0.253 - 0.337
1	0.427 - 0.461	0.220 - 0.234
2	0.385 - 0.393	0.208 - 0.212
3	0.371 - 0.374	

Recently, experimental evidence [14,15] has been found which is claimed to prove conclusively the existence of subsurface bonding in accordance with our theoretical ideas.

From a comparison of Table I and II it is clear that subsurface bonding is more important for Nb than Pd because E_o (subsurface bonding energy) > E_{ads} (chemisorption energy) for Nb and $E_o < E_{ads}$ for Pd. As a consequence the absorption kinetics of Nb and Pd will be quite different [5]. In the case of Nb, the initial uptake will be large until the subsurface is saturated and then the H saturated surface, blocks the bulk from further absorption. Since the subsurface self trapping is much smaller in Pd the bulk uptake in Pd (or Pd covered Nb) will be much higher.

In order to calculate the temperature dependence of the surface coverage θ_b we have modified [5] the kinetic equations originally written down by CONRAD, ERTL and LATTA [11,16] to include the deep subsurface bonding. In this calculation the site to site transfer rate perpendicular to the surface is taken to be activated. Assuming a quasistationary state the kinetic differential equations can be solved and the dependence of surface coverage can be calculated relatively easily. Figure 1 shows the

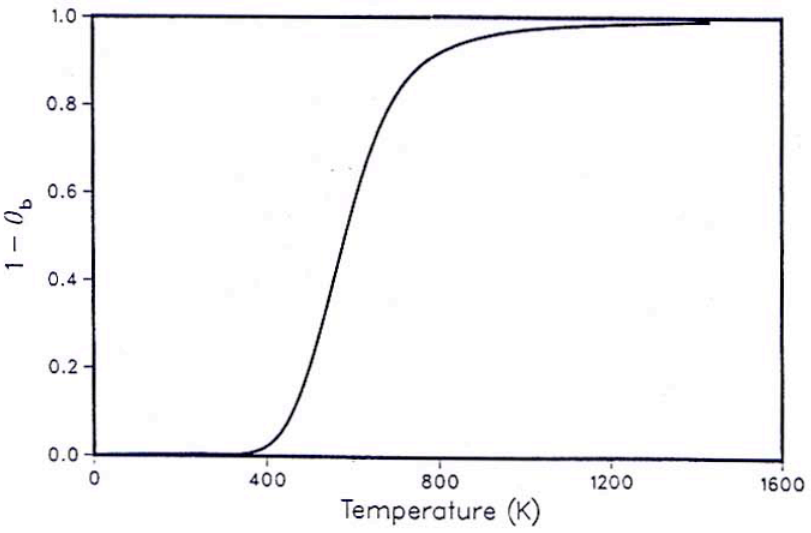

Fig. 1. Temperature dependence of the $1-\theta_b$ for a critical temperature T_c = 600 K, where θ_b is the coverage of the subsurface layer.

dependence of $1-\theta_b$ on temperature with reasonable choices of parameters for the case of Nb.

It is easy to understand the experimental hydrogen absorption by Nb(110). At low temperature, $\theta_b \sim 1$, the subsurface becomes saturated fast initially and then the surface and bulk become decoupled, as observed [10]. A thin (~ 3 monolayers) overlayer of Pd decreases the depth of the subsurface well bringing it closer to the bulk interstitial energy. In this fashion, the surface does not block the passage of hydrogen into the bulk and therefore the uptake increases. At this point, we would like to stress that the existence of the subsurface bonding mechanisms is shown by our calculations and that the qualitative conclusions are independent of any reasonable variation of the parameters. Moreover, it is clear that the existence of a deep subsurface well has to affect the kinetics of hydrogen absorption in a fundamental way [17].

Our theory also predicts several new phenomena which can be tested experimentally. In particular, the strong temperature dependence of the subsurface coverage θ_b has not yet been studied experimentally.

To summarize, a calculation of the interaction of hydrogen with surface phonons shows the existence of a deep potential well under the subsurface of certain transition metals. A variety of experiments have confirmed the existence of the subsurface bonded hydrogen predicted here. As a result of the subsurface bonding the kinetics of absorption is modified so that the bulk and surface become completely decoupled. This calculation is in agreement with a variety of experimental observations related to the absorption of hydrogen by the Nb(110) and Pd covered Nb(110) surfaces.

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