PHYSICAL REVIEW B VOLUME 58, NUMBER 23 15 DECEMBER 1998-I

Subsurface bonding of hydrogen in niobium: A molecular-dynamics study

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(Received 6 March 1998; revised manuscript received 11 June 1998)

Binding energy of hydrogen in a (100) niobium slab is investigated through molecular-dynamics simulations. We introduce a hydrogen-niobium interaction potential that contains an attractive as well as a repulsive part, which is valid for surface-diffusion calculations. Simulations for high and low temperatures (compared with θ_{Debye}) are presented. For the former case, we found that the hydrogen diffuses in the slab with a diffusion coefficient in agreement with experiment, and in most cases it is trapped inside the slab for $T \leqslant 900$ K. Close to room temperature, there is an enhancement of the hydrogen binding energy, which causes self-trapping close to the surface. [S0163-1829(98)07043-X]

I. INTRODUCTION

The exceptional properties of hydrogen in metals, namely, its large diffusion coefficient and its fast absorption have attracted much attention. A wide range of theoretical and numerical results exist specifically for the case of hydrogen inside transition metals.[1–6] Many have used molecular-dynamics and quantum Monte Carlo techniques to investigate diffusion, local vibrational states, and interstitial site locations.

At high temperatures, interstitial hydrogen in metals diffuses much faster than many other atoms in solids ($\sim 10^{-4}$ cm^2/s for $T \sim 1000$ K).[7] At low temperatures, in some transition metals (Nb, Pt), the initial hydrogen uptake is fast but it slows down considerably without much diffusion into the bulk[8] (for temperatures around T_{room}). Moreover, the hydrogen uptake rate in niobium can be modified drastically by thin overlayers of palladium.[9] This has been assigned either to a change in the electronic structure at the surface that facilitates H dissociation[8,10] or to an enhancement of the self-trapping effect[11–13] close to the surface. The later ''polaronic model''[14] was investigated earlier using a calculation in a second quantized lattice model.[11–13]

Here we present an alternative way for investigating self-trapping using variable temperature simulations of the behavior of hydrogen in a niobium slab in the range of temperatures where experiments are realized and where quantum effects are not very important.[3,2,6] Using classical molecular-dynamic simulations, we are mostly concerned with the dependence of the hydrogen binding energy on the distance from a free surface, caused by the dynamics of the surface and the near-surface atoms.

Section II is dedicated to discuss issues related to potentials. We present the N-body potential used for the Nb, describe different possible hydrogen-niobium potentials and describe the one used here. Section III deals with the simulation setup, time scales, and parameter values used. In Sec. IV, we present and discuss our results, and the conclusions are presented in Sec. V.

II. POTENTIALS

A. Niobium-niobium potential

An important issue in any molecular-dynamics simulation is to account, in the best possible way, for the real intermolecular forces. Much work has been directed along these lines, i.e., to construct empirical sets of two-body potentials for many interesting materials.[15] However, for many metallic systems, a two-body core-core interaction generally fails. The reason for this is that two-body potentials imply Cauchy relation for the elastic constants ($C_{12}=C_{44}$),[16] which is almost never true for transition metals. A model that successfully avoids this problem was proposed by Finnis and Sinclair[17] (FS). The potential energy is constructed from two terms; a two-body core-core repulsive interaction (V_{FS}), and a N-body potential ($U_{N\text{-}body}$), which describes the energy changes due to variation of atomic configurations at constant average ''density'' (ρ). $U_{N\text{-}body}$ incorporates the essential character of metallic cohesion through an ''embedding function'' $f(\rho)$ similar to the one used in the embedded atom method.[18] The parametrization of the potentials used here, has the same form as the one proposed by Finnis and Sinclair.[17]

This potential, however, fails to account for some high pressure properties conditions such as the compressibility.[19] A solution for this problem was proposed by Ref. 19 redefining the two-body potential without modifying the parameters in the initial FS potential. A new term with stronger short-range repulsion (V_{AT}) is added to the core-core repulsion potential. In this way, the potential energy becomes

$$U = U_{pair} + U_{N\text{-}body},$$

TABLE I. Parameters of the FS potential with the correction of Ackland *et al.*

Parameters	Values[a]
A	3.013789 eV
C_0	-1.5664014 eV/Å^2
C_1	2.0055779 eV/Å^3
C_2	-0.4663764 eV/Å^4
B	48.0 eV/Å^3
d	3.915054 Å
C	4.20 Å
b_0	2.8586 Å
n	3
α	0.8 Å^{-1}

[a]From Ref. 2.

$$U_{N\text{-}body} = -\sum_i f(\rho_i),$$

$$U_{pair} = \frac{1}{2}\sum_{i,j,i\neq j}[V_{FS}(r_{ij}) + V_{AT}(r_{ij})],$$

where i,j are indices identifying all particles in the simulation,

$$f(\rho_i) = \left[\sum_{i\neq j}\Phi_{FS}(r_{ij})\right]^{1/2},$$

$$\Phi_{FS}(r) = \begin{cases} A^2(r-d)^2, & r\leq d \\ 0, & r>d. \end{cases} \tag{1}$$

The explicit form for the pair potentials is given by

$$V_{FS} = \begin{cases} (r-C)^2(C_0 + C_1 r + C_2 r^2), & r<C \\ 0, & r>C \end{cases}$$

$$V_{AT}(r) = \begin{cases} 0, & r<0.4b_0 \\ B(b_0-r)^n e^{-\alpha r}, & 0.4b_0<r<b_0 \\ 0, & r>b_0. \end{cases}$$

This potential was shown to be very useful in bulk simulations[2,3,6,17] and in surface calculations,[4] where physical quantities such as phonon spectrum, average thermal vibration, and change in the internal crystal pressure as a function of volume were obtained in agreement with experimental values.

The potential parameters used here, are shown in Table I. They were adjusted[2] to reproduce cohesion energy, lattice parameter, elastic constants, and vacancy formation energy. Moreover, they reproduce qualitatively the experimental Nb phonon spectrum.[20]

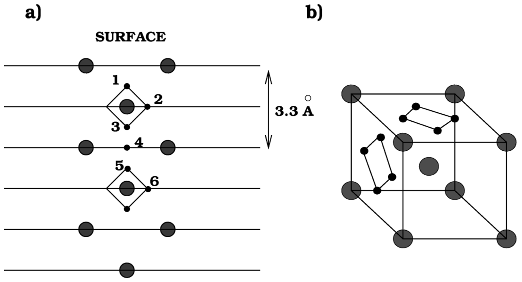

FIG. 1. (a) Cross section and (b) three-dimensional sketch of Nb (●) lattice with tetrahedral sites (•), the possible equilibrium location of the hydrogen atoms.

B. Niobium-hydrogen potential

Several phenomenological models have been proposed to mimic the potential interaction between H and Nb. All of them have been used to study bulk properties, mostly, hydrogen diffusion. Gillan,[6] for example, proposed an exponential repulsive pair potential with two parameters obtained by fitting the local-mode frequencies. This potential reproduces the diffusion behavior at high and low temperatures (dominated by quantum tunneling). However, it is unable to reproduce experimental values of the components of the elastic-dipole tensor, which is a measure of the hydrogen ability to produce lattice distortion.[1,21] This elastic-dipole tensor components can be estimated from x-ray diffraction measurements.[1,22] Another frequently used potential in Nb-H simulations has a two-term repulsive Born-Mayer form as proposed by Sugimoto and Fukai.[3] This reproduces the vibrational energy and the elastic-dipole tensor,[21] but it gives a very low activation energy compared with the experimental value.

Initially, we performed simulations with the potentials mentioned above in the Nb-H slab geometry. Unfortunately, we found that the hydrogen was always expelled from the slab. This is mainly due to the fact that the form of these potentials is purely repulsive. For this reason, we constructed a phenomenological Lennard-Jones-type potential to represent the H-Nb interaction. This potential has a minimum of depth ϵ, at $r=r_0$,

$$v(r) = \epsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$

with the parameter r_0 chosen as the distance between a niobium atom and a tetrahedral site, the equilibrium hydrogen position in a bcc crystal. The second parameter ϵ was left free, in a range that gives the experimental diffusion coefficient as discussed in Sec. IV.

III. SIMULATION SETUP

The setup of our computer experiment is as follows. We define a Nb slab with periodic boundary conditions in the X-Y plane parallel to the surface and a free surface perpendicular to the Z axis. When only the Nb properties were studied a slab of 576 particles was used, whereas, when hydrogen was included, slabs of 432 Nb particles for studying binding energy and 576 Nb particles to study hydrogen diffusion were used. The hydrogen diffusion at high T was measured using mostly, $6\times6\times8$ unit cells, shown in Fig. 1(b). For the average potential energies and hydrogen dynamical properties several combinations were tried, but most of our results are from $6\times6\times6$ unit cells.

At first, we start with a system without hydrogen. The Nb atoms are located initially in a bcc lattice. The initial velocities are set by a Maxwellian distribution with a temperature

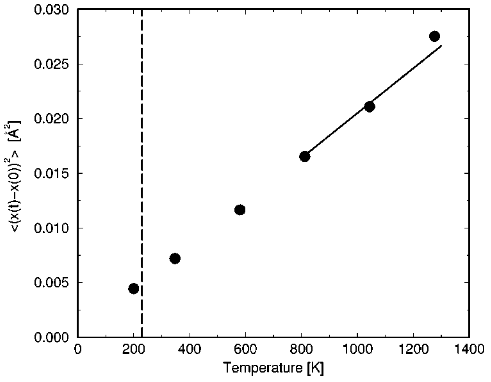

FIG. 2. Mean-square displacement for Nb atoms in Å^2. Dots are the molecular-dynamics (MD) simulations. Solid line corresponds to the quasiharmonic approximation. Classical MD is valid on the right of the dashed line and on the left side quantum effects are more important (Ref. 6).

that matches a predefined temperature. Newton's equations of motion were solved using a modified Verlet algorithm, which gives a constant temperature.[23] We have used the ''linked list'' method[24] to store Nb positions, which is specially suited for N-body potentials. In this simulation there are two typical time scales; when only Nb atoms were present a time step of 1.0×10^{-15} s was used, which was decreased to 1.0×10^{-16} s when hydrogen was included. This small time step is necessary in order to account for the low hydrogen mass and its high mobility at the surface. After the niobium slab relaxed to equilibrium (after more than 10 000 steps), physical quantities were measured using the instantaneous Nb positions and velocities. These results are discussed in the next section.

As a second step, we introduced a hydrogen atom with zero momentum, in one of the tetrahedral sites (T sites). This initial arrangement is illustrated in Fig. 1, with the T sites labeled sequentially from the free surface, as shown in Fig. 1(a). The H-Nb system is relaxed for 1000 steps and from this point measurements are taken every 100 steps for more than 200 000–250 000 steps.

IV. RESULTS AND DISCUSSION

A. Niobium slab

As a first check on our simulation, we studied a niobium slab without hydrogen for 100 000 steps by taking measurements every 100 steps. We calculated the diffusion coefficient and compared these with experimental values or other molecular-dynamics simulations.

The temperature dependence of the mean-square displacement $\langle[r_i(t)-r_i(0)]^2\rangle$ (with $r_i=x,y,z$), averaged over all Nb atoms was monitored as a function of time. Figure 2 illustrates the motion along the X direction, parallel to the surface as a function of temperature. The data is in good agreement with the quasiharmonic approximation valid at high temperatures ($T>\theta_{Debye}$):[2]

$$\langle[x(t)-x(0)]^2\rangle=\frac{3\hbar^2T}{K_B\theta_D^2M_{\mathrm{Nb}}}.$$

This result is also in qualitative agreement with Roux *et al.*,[2] thus justifying the use of these potentials for further simulation.

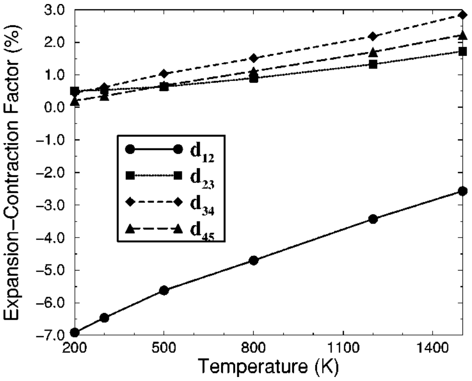

FIG. 3. Normalized change in lattice parameters for different layers of the Nb slab.

The normalized change ($\Delta d/d_0$) in the mean interlayer displacement ($d_{i,i+1}$) measured from the surface as a function of temperature is presented in Fig. 3. The distance between two consecutive planes, normalized by the bulk $T=0$ K equilibrium interlayer distance (d_0), shows an inward relaxation for the surface layer and outward expansions for other layers. These results agree qualitatively with earlier theoretical calculation,[4] which were temperature independent and found a 16% inward relaxation for the surface layer.

The surface thermal expansion ($\alpha_{12}=d_{12}^{-1}\partial d_{12}/\partial T$) at temperatures below 500 K is much higher that the one corresponding to other layers (e.g., for $T=200$ K $\alpha_{12}/\alpha_{23}=16.1$).

Since the interlayer displacement is different at the surface than in bulk due to the smaller number of neighbors, the potential energy of the hydrogen atom is different close to the surface and its dynamics is modified.

B. Hydrogen inside niobium slab

The behavior of H as a function of T was studied after the process described in Sec. III.

1. High temperatures ($T>T_{room}$)

To check the H-Nb potential and ascertain the correctness of our method, we studied the diffusion coefficient $D=\langle[\vec{r}(t)-\vec{r}(0)]^2\rangle/6t$, for several potential depths and temperatures. For $800\leqslant T\leqslant900$ K, the hydrogen atom remains inside, whereas above 900 K it leaves the Nb slab. A summary of these results is shown in Table II.

TABLE II. Diffusion coefficients for different ϵ values.

	Diffusion (10^{-4} cm^2/s)[a]	
ϵ (eV)	$T=900$ K	$T=800$ K
0.2	1.2±0.15	1.0±0.1
0.3	1.2±0.1	0.9±0.1
0.4	0.95±0.15	0.6±0.1
0.6	0.48±0.15	0.4±0.1
Expt.[b]	1.21	1.01

[a] Obtained by fitting a straight line to the mean-square displacement.
[b] From Ref. 1.

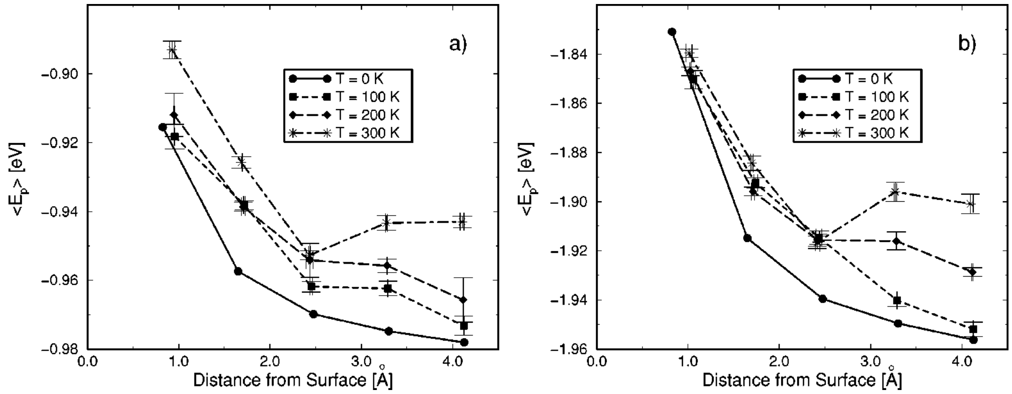

FIG. 4. Average potential energy as a function of the distance from the surface. (a) $\epsilon = 0.2$ eV. (b) $\epsilon = 0.4$ eV.

In the interval $0.2 \leq \epsilon \leq 0.4$ eV the diffusion coefficient is close to the one found in Refs. 1 and 7, but for $\epsilon = 0.6$ eV, it is half the experimental value. This defines a range of parameters where our potential represents the proper hydrogen behavior in Nb.

2. Low temperatures

The low-temperature ($T \leq T_{room}$) simulations mostly concentrated on the two extreme cases $\epsilon = 0.2$ eV, 0.4 eV. At these low temperatures, there is a strong hydrogen localization. In most cases, the hydrogen atom oscillates around a T site without hopping to the next T site. The strong interaction between H and the Nb atoms produce a lattice deformation ($\Delta V/V \approx 3\%$), which then gives rise to a self-trapped state. Energy is lowered by confining the H in the potential well produced by this local relaxation. In a few cases, however, the hydrogen had enough energy to jump over the potential barrier to a nearest neighbor T site. We should point out that our calculation is classical and therefore no quantum effects, like tunneling, are included or observed in these simulations. Figure 4 shows the average potential energy as a function of distance from the surface, for the first five T sites shown in Fig. 1.

There is a monotonic decrease of the potential energy as the hydrogen enters deeper into the Nb slab except at $T = 300$ K, where a minimum appears in the potential energy at a distance of $r \sim 2.5$ Å. These results are qualitatively very similar at $T = 200$ K and $T = 300$ K and for two values of $\epsilon = 0.2$, 0.4 eV indicating that this is a robust result, independent of the exact numerical values of the parameters.

Due to the contraction of the surface, the hydrogen potential energy increases between the first and the second layer, while the expansion of the deeper interlayer distances allows for a local relaxation around the hydrogen atom with the consequent decrease of its potential energy. Note that this is a dynamical effect, which only appears at temperatures close to T_{room}.

The enhancement is of the order of 0.01 eV for $\epsilon = 0.2$ eV and of 0.02 eV for $\epsilon = 0.4$ eV for a T site between the second and third layer. This agrees qualitatively with surface theoretical quantum calculations,[11–13] in which a self-binding energy increase of 0.035 eV between the second and third was predicted.

V. CONCLUSIONS

We have proposed a H-Nb interaction, which contains an attractive as well as a repulsive part. Two parameters define this potential. One is taken from the equilibrium T site in a bcc configuration and the other one is left free within an interval that correctly reproduces the diffusion coefficient.

Two main results are obtained from our simulation. There is contraction of the first-surface layer with a thermal expansion at least five times bigger than the bulk expansion at T_{room}. This is due to the strong asymmetry of the potential near the surface. This creates a different environment for the hydrogen inside the slab. Due to this inward surface contraction, the conditions for H particle diffusion are different close to the surface than in the bulk.

Second, for $T \sim T_{room}$, the relative atom displacement between the first and second layer decreases the distance between the closest niobium atoms and a T site, increasing the potential energy. On the other hand, a lattice distortion develops around the hydrogen when it is located between the second and third layers, creating a minimum in the potential energy tightly binding the hydrogen.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. DOE under Grants Nos. DE-FG03-86ER13606, DE-FG03-87-ER45332, and by Fondecyt (Chile) under Grant No. 1980811. A.R. thanks K. Lindenberg for support and stimulating discussions.

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