A Numerical Study of Subsurface Trapping of Hydrogen in Niobium.

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Binding energy of Hydrogen in a (100) Niobium slab is investigated through molecular dynamics simulations. We introduce a new Hydrogen-Niobium interaction potential that contains an attractive as well as a repulsive part, which is valid for doing 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 $T \leq 900K$. Close to room temperature, there is an enhancement of the Hydrogen binding energy which causes self-trapping close to the surface.

1 Introduction

The behaviour of hydrogen in metals have attracted much attention. A wide range of theoretical and numerical results exist for the study of 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 $T \sim 1000K$) [1]. 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 [2] (for temperatures around T_{room}). Moreover, the hydrogen uptake rate in niobium can be modified drastically by thin overlayers of palladium [3]. This has been assigned either to a change in the electronic structure at the surface that facilitates H dissociation [2, 4] or to an enhancement of the self-trapping effect [5, 6] close to the surface. The later "polaronic model " was investigated earlier using a calculation in a second quantized lattice model [5, 6].

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 temperature range where experiments are realized and quantum effects are not very important [7].

For the interaction Nb-H we use an N-body potential proposed by by Finnis and Sinclair and modified by Ackland and Finnis [8] This potential was shown to be very useful in bulk simulations [7] and in surface calculations [8], 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. For the H-Nb interaction we use a simple phenomenological Lennard-Jones type potential. This potential has a minimum of depth ϵ, at $r = r_0$. The parameter r_0 was 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 which gives the experimental diffusion coefficient as discussed in section 4.

2 Results and Discussion

At first, we start with a system without hydrogen, with the Nb atoms are located initially in a bcc lattice. Newton's equations of motion were solved using a modified Verlet algorithm which gives a constant temperature [9], in conjunction with the "linked list" method.

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. The data obtained is in good agreement with the quasi-harmonic approximation valid at high temperatures ($T > \theta_{Debye}$) [7]: This result is also in qualitative agreement with Roux et *al.* [7], thus justifying the use of these potentials for further simulation.

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 Figure 1. The distance between two consecutive planes, normalized by the bulk, $T = 0K$, equilibrium interlayer distance (d_0), shows an inward relaxation for the surface layer and an outward expansions for other layers. These results agree qualitatively with earlier theoretical calculation [8], which were temperature independent and found a 16% inward relaxation for the surface layer.

As a second step, we introduced a hydrogen atom with zero momentum, in one of the tetrahedral sites (T-sites).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 $800K \leq T \leq 900K$, the hydrogen atom remains inside, whereas above $900K$ it leaves the Nb slab.In the interval $0.2 \leq \epsilon \leq 0.4$ eV the diffusion coefficient is close to the one found in experiments, 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.

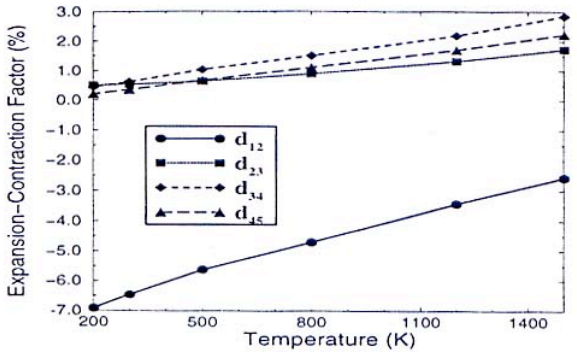

Fig. 1 Normalized change in lattice parameters for different layers of the Nb slab

At low temperature ($T \leq T_{room}$) simulations are mostly concentrated on the two extreme cases $\epsilon = 0.2$ eV, 0.4 eV. Figure 2 shows the average potential energy as a function of distance from the surface, for $\epsilon = 0.2$ eV. A similar result was obtained for $\epsilon = 0.4$ eV

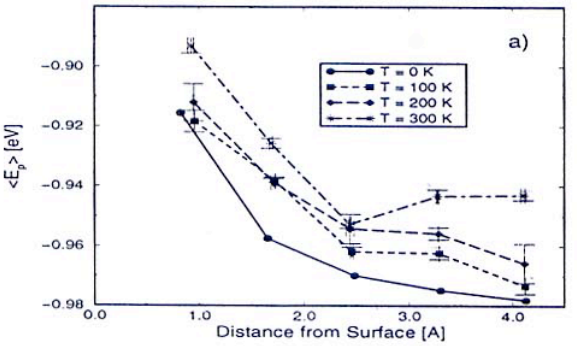

Fig. 2 Average potential energy as a function of the distance from the surface for $\epsilon = 0.2$ eV.

There is a monotonic decrease of the potential energy as the hydrogen enters deeper into the Nb slab except at $T = 300K$, where a minimum appears in the potential energy at a distance of $r \sim 2.5$Å. These results are qualitatively very similar at $T = 200K$ and $T = 300K$ and for two values of $\epsilon = 0.2$, 0.3 eV indicating that this is a robust result, independent of the exact numerical values of the parameters. These results show a local relaxation around the hydrogen atom.

3 Conclusions

We have proposed a new 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 reproduce 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 layer, creating a minimum in the potential energy tightly binding the hydrogen.

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