RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 3 15 JULY 1989-II

H-H interactions in Pd

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(Received 8 May 1989)

A discussion of the H-H interactions in a metal is given. Based on self-consistent total-energy calculations within the local-density approximation for H_2 in a homogeneous electron gas, we show that metallic electrons make the H-H interaction *more* repulsive than in vacuum. Using effective-medium theory to calculate total energies, we show the same tendency for the short-range part of the H-H interaction when two H atoms are squeezed into a single site in Pd or PdH. At longer range (of the order a lattice constant) there is an attractive, lattice-mediated H-H interaction. On the basis of the calculated energetics, the thermodynamical properties of various palladium hydrides are modeled.

The recent claims that nuclear fusion can be observed for deuterium electrochemically loaded into palladium[1,2] raise a number of questions about the nature of the interactions between hydrogen isotopes inside a metal. If the fusion rate is larger for D atoms inside a metal than in gas phase D_2, it could be because the barrier separating two deuterons in Pd is smaller, or that the equilibrium separation between two D atoms in the metal could be made smaller than in the gas phase, so that the tunneling distance is smaller.

In the present paper, we address some of these questions by presenting a calculation of the H-H interactions in Pd. From the point of view of calculating the energetics there is no difference between the various hydrogen isotopes (except for zero-point energies) and we shall use H as a common name for all of them. We show that for distances less than a Pd lattice constant the interactions are repulsive leading to large H-H separations. The short-range part of the H-H interaction is more repulsive in the metallic surroundings than in the free H_2 molecule all the way to zero internuclear separation. We estimate that these effects lead to a D-D fusion rate which is of the order 10^{20} times slower in Pd than for gas-phase D_2 molecules.

The change in the interaction between two H atoms when a H_2 molecule is embedded into a metal can be divided into effects due to the interaction with the metallic electrons and effects imposed by the lattice structure of the metal. The first effect can be singled out by studying two H atoms in a homogeneous electron gas. We start by looking at this point and then return to the question of the effect of the Pd lattice later.

We have performed a set of self-consistent calculations within the local-density approximation for H_2 in a homogeneous electron gas. The calculation is done by placing a system of H_2 molecules on a fcc lattice with a lattice constant large enough that the interactions between the molecules can be neglected. The electronic structure problem is then solved using standard band-structure methods.[3] The result thus obtained for the "free" H_2 molecule shown in Fig. 1 is in close agreement with previous calculations and with experiment.[4] The calculation is then repeated with an extra electron in each unit cell. This corresponds to embedding the molecules in a homogeneous electron gas of a density $n_0 = 1/\Omega$, where Ω is the unit-cell volume. For the lattice constant used ($7.56a_0$) this corresponds to a density of $0.0093a_0^{-3}$ ($r_s = 2.95$). This is well inside the range of interstitial metal electron densities. The H_2 binding energy less the energy of the homogeneous electron gas is included in Fig. 1. The result is in good agreement with previous calculations for H_2 in a homogeneous electron gas using completely different methods.[5]

The results in Fig. 1 clearly show that the H-H interaction is more repulsive in the homogeneous electron gas than in the gas phase for all interatomic distances. Even in the limit of zero internuclear separation the energy of H_2 in a homogeneous electron gas is higher than the ener-

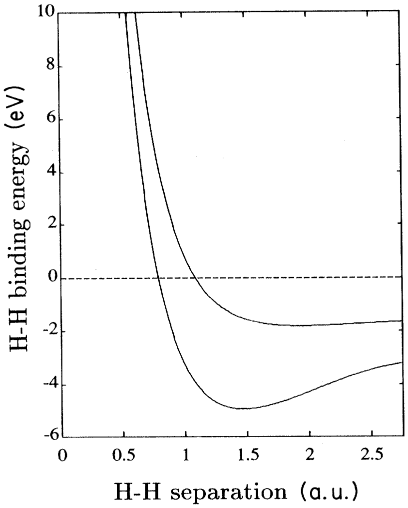

FIG. 1. Binding energy as a function of internuclear separation for two H atoms in vacuum (lower curve) and embedded in a homogeneous electron gas ($r_s = 2.95$ a.u.) (upper curve). The H-H separation is varied from 10^{-3} a.u. to twice the vacuum H_2 bond length. The energy zero is the energy of two isolated H atoms in vacuum. The H-H interaction is seen to be considerably more repulsive in the homogeneous electron gas than in the free molecule.

gy of the free molecule. In this limit the difference is simply the embedding energy of He in the electron gas, which is always positive. In the electron gas there is hardly any minimum (at higher electron gas density it completely disappears[5]) as a function of the H-H separation, and the equilibrium "bond" length is seen to be much larger than in the gas phase.

The reason that the electron gas makes the interaction more repulsive is that the kinetic energy of the metallic electrons increases because they are excluded from the volume occupied by the molecular electron states. Such a repulsive interaction is commonly observed when a closed-shell atom or molecule interacts with a metal.

Based on the interatomic potentials of Fig. 1, one can calculate the tunneling rate for the two nuclei to get to within a few fm of each other where the nuclear forces take over. We have done that by numerically solving the radial Schrödinger equation to obtain the wave function for the interatomic coordinate. The result is that the tunneling rate for the D_2 in the metal potential of Fig. 1 is a factor of 10^5 smaller than for the free D_2 molecule.

Embedding two H atoms into a real metal like Pd could change the picture of Fig. 1 completely, because of the boundary conditions set by the ion cores of the metallic lattice. The treatment of this problem is considerably more demanding than the H_2 in the homogeneous electron gas problem and calls for more efficient methods for calculating the total energy of the system. This is particularly so, because the systems that one has to consider can be large and many atomic coordinates must be varied to find the equilibrium geometry. We have used the effective-medium theory for that purpose.

The details of the calculational method are given in Refs. 6 and 7. It provides an approximate many-body interaction potential for condensed systems. The functional form of the potential is derived from density-functional theory, and most of the parameters can be calculated directly within the local-density approximation. They can also be determined directly from measured properties of the systems under study.[8] The method has been successfully applied to describe bulk properties of simple and transition metals,[6] surface energies, relaxations and reconstructions,[6,9] chemisorption energies and chemisorption-induced relaxations and reconstructions,[10] adsorption, and dissociation of H_2 outside Ni and Cu surfaces,[7] and in Monte Carlo and molecular-dynamics simulations of thermal properties like thermal expansion and melting.[11] In a simplified version it has been extensively used in describing the interaction of hydrogen impurities in metals and their interaction with lattice defects.[12] Of particular importance for the present discussion, it should be mentioned that by construction the effective-medium treatment reproduces the H-H interactions in a homogeneous electron gas.[7]

Most of the parameters needed for the present calculation are given in Ref. 7. The rest are given in Table I.

Let us first concentrate on the binding energy ΔE of a H atom in a given host:

$$\Delta E = E_{\text{total}}(\text{host}+\text{H}) - E_{\text{total}}(\text{host}) - \tfrac{1}{2} E_{\text{total}}(\text{H}_2)\,. \qquad (1)$$

In calculating the binding energies we neglect contributions from zero-point energies. ΔE will depend on the position of all the atoms in the system. In Table II, we show the result of a total-energy minimization with respect to all the coordinates for a number of different systems. The different systems studied are denoted by their composition. $Pd_{27}H$ thus refers to a lattice built of supercells with 27 Pd atoms (3×3×3 primitive Pd unit cells) and one H

TABLE I. The parameters for Pd and for calculating the Pd-H atomic sphere correction. All other parameters can be found in Ref. 7. All symbols used refer to the nomenclature in Refs. 6 and 7. The parameters are calculated from self-consistent calculations for Pd in a homogeneous electron gas, except for the density parameters, s_0, η, and η_1, which are determined from the experimental lattice constant, bulk modulus, and shear modulus, respectively. The direct *d-d* interactions in Pd are not explicitly included. They are weak in Pd because the *d* band is almost full (Ref. 6) and is included implicitly through the fit of η to the experimental bulk modulus.

E_0 (eV)	-4.67
E_2 (eV)	2.20
E_3 (eV)	-0.59
α (eV a_0^{-3})	2400
η (a_0^{-1})	1.97
η_1 (a_0^{-1})	0.16
n_0 (a_0^{-3})	0.0123
s_0 (a_0)	2.87
M_d ($\sqrt{\text{eV}\,a_0^5}$)	6.7
C_d-ε_F (eV)	2.1
V_{pre} (eV a_0^{-3})	26800
ϕ_r (a_0^{-1})	-1.93
ϕ_m (a_0^{-1})	-1.24
ϕ_a (a_0^{-1})	-1.83

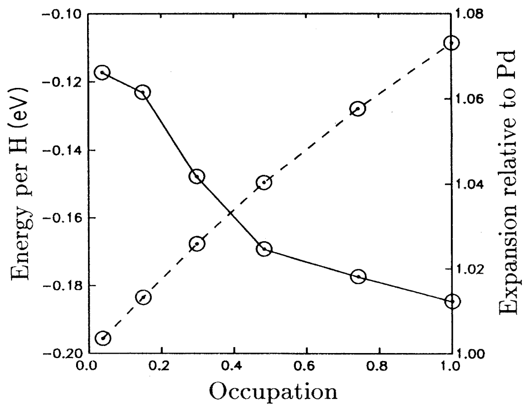

FIG. 2. Binding energy per H atom (solid line) and equilibrium lattice constant relative to that of Pd (dashed line) in PdH_x as a function of x. All atoms are relaxed to find their equilibrium positions in each calculation. All H atoms are in the octahedral sites in the primitive Pd unit cells. The octahedral sites are randomly occupied. The binding energy is seen to decrease (the H−Pd bonds increase in strength) with increasing H/Pd ratio, indicating an attractive interaction between the interstitial H atoms.

atom. Apart from the binding energies we also show the calculated lattice constant and equilibrium site(s) for the H atom(s).

One should first notice that the calculated properties of PdH agree very well with experimentally determined properties. The binding energy of −0.18 eV of H in PdH can be compared[13] to the experimentally determined heat of formation for the hydride of −0.20 eV,[14] and the expansion found for a $Pd_{27}H_{20}$ lattice (with a H/Pd ratio of 0.74) relative to Pd of 5.7% should be compared to the experimentally determined one of 5.5% for $PdH_{0.8}$.[14] Also, the present results compare favorably with previous "first-principles" calculations for PdH.[15] The binding energy of −0.12 eV for the diluted case $Pd_{27}H$ should be compared to the experimentally determined heat of solution which is −0.10 eV.[14]

The binding energy per H atom for a PdH_x lattice decreases (the bond strength increases) continuously with x for x smaller than 1. This is shown in Fig. 2. Here, one can also observe that the calculated equilibrium lattice constant increases monotonically in the same region.

The increase in the bond strength energy with increasing H/Pd ratio is a manifestation of an attractive, lattice-mediated interaction between H atoms at the octahedral sites. The reason is as follows. A single H atom in a Pd lattice lowers its energy by locally expanding the lattice. If two H atoms in adjacent cells can share the cost in elastic energy associated with the expansion of the lattice there is a net gain in energy.

The short-range H-H interaction is repulsive in analogy with the case of H_2 in an electron gas. This is illustrated in Fig. 3, which shows the total energy of $Pd_{27}H_{28}$ as a function of the distance between the H atoms in the Pd unit cell with two H's. In the calculations the H's of the PdH lattice are all kept in the octahedral positions and only the position of the extra H atom is varied. At small distances the curves are similar to those shown in Fig. 1, and the new feature introduced by including the lattice structure of the metal is the preference towards the tetrahedral site for the extra H atom.

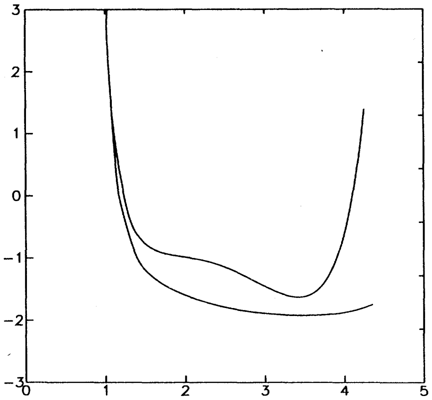

FIG. 3. Binding energy of an extra H atom added to PdH as a function of distance to the nearest H atom. The H atoms of PdH are fixed in the octahedral sites in the Pd fcc unit cell. The calculation is made using a $Pd_{27}H_{28}$ computational unit cell. This corresponds to the limit of a few extra H atoms in the saturated hydride. The minimum seen in the figure is one where the extra H atom is in the tetrahedral site. The upper curve is calculated keeping the atoms at their equilibrium sites in PdH and the lower curve is calculated allowing all the atoms to relax for each internuclear separation. As in Fig. 1, the short-range H-H interaction is very repulsive. This is also the case if one attempts to place two H atoms in a single unit cell in pure Pd. One of the H atoms immediately jumps into one of the adjacent Pd unit cells.

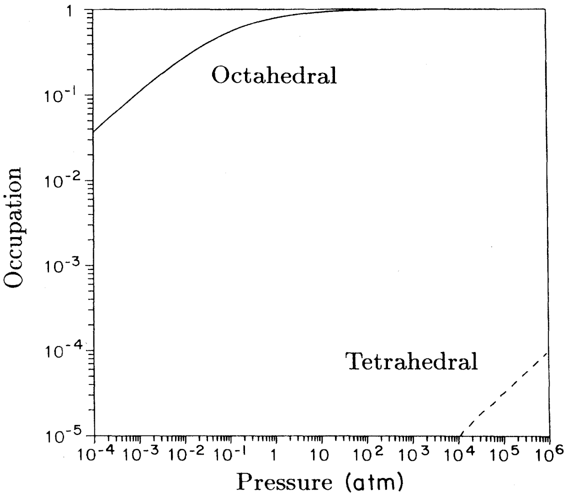

FIG. 4. Calculated occupations for octahedral (solid line) and tetrahedral (dashed line) sites in Pd under H_2 pressure at 300 K. Large pressures are needed to occupy the tetrahedral sites.

The interaction potential shown in Fig. 3 gives an even lower D-D fusion rate than the one in Fig. 1, because of the preference of the second D atom to occupy the tetrahedral site. A direct calculation of the tunneling rate shows it to be of the order 10^{20} times smaller than for the gas phase D_2. The calculation is performed for the atoms in the ground state, and the small tunneling probability is a direct consequence of the large separation between the

TABLE II. Hydrogen binding energies for various Pd-H compounds. The energies given are the binding energies of the last added H atom in the calculational unit cell. The compositions of the unit cells are given and periodic boundary conditions are applied in all three directions. The total energy has been minimized for all coordinates in the system. The resulting equilibrium H sites and the ratio of the lattice constant to that of Pd metal are also given.

	ΔE	H site	a/a_{Pd}
$Pd_{27}H$	−0.12	octahedral	1.003
PdH	−0.18	octahedral	1.073
$Pd_{27}H_{28}$	0.46	27 octahedral +1 tetrahedral	1.077
PdH_2	0.35	1 octahedral +1 tetrahedral	1.165

octahedral and tetrahedral sites.

One may ask if it is possible to load more than one H atom per unit cell into Pd under realistic conditions. Therefore, we have made model calculations of the occupation of tetrahedral and octahedral sites as a function of temperature using a mean-field approximation.[16] The results for H/Pd are shown in Fig. 4. We conclude that with the use of a hydrostatic pressure of H_2 it is extremely difficult to populate the tetrahedral sites at room temperature.

The effects of increasing the partial pressure of H_2 or lowering the temperature may be determined by calculation of the change in thermodynamic activity for hydrogen. A very effective way of achieving high thermodynamic activities of hydrogen is to use the Pd as a cathode in an electrochemical cell. Assuming reversible electrode reactions a hydrostatic pressure of 10^4 atm corresponds to a bias of 0.115 V relative to a reference cathode working under 1 atm H_2 pressure in the same electrolyte. We note that this assumption may be invalidated by transport phenomena, such as bubble formation at ambient pressures or high current densities.

In conclusion, we find that a one-electron description within the local-density approximation gives H-H interactions that keep H atoms away from each other when embedded into Pd. The short-range interaction is repulsive, but there is a long-range, lattice-mediated attraction between two H atoms in Pd.

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