



STABILITY OF ATOMIC AND DIATOMIC HYDROGEN IN fcc PALLADIUM

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First-principles self-consistent total energy calculations for various

system is controlled by the relative position of the hydrogen-induced antibonding level with respect to the Fermi energy. Diatomic H₂ in crystalline palladium is shown to have but metastable local minima whose internuclear separation are yet larger than that of the isolated H₂ molecule.

Recent claims of observation of room-tem-

In an attempt to further clarify some of

Born-Oppenheimer energy surface $E(R)$ of two deuterium atoms at a distance R , since both the vibrational wavefunction $\psi(R)$ of diatomic deuterium [determines the fusion rate[3]. A

predict the stability of various periodic arrangements of atomic and diatomic hydrogen in fcc palladium. This approach, implemented by the all-electron full-potential relativistic

rium distance R_{eq} for the isolated H₂ molecule

molecule in any other orientation will spontaneously dissociate along [111]. However we

mechanism were sought. It was hoped, for example, that the existence of a metal lattice (e.g. fcc Pd) in which deuterium is embedded

further lower its energy by dissociating into two H atoms each at a tetrahedral interstitial site, leading thereby to a yet longer H-H separation. Subsequent penetration of the dif-

distance and enhance the fusion rate[5].

Some recent theoretical studies have addressed this question. Sun and Tomanek[6]

Bringing two such octahedrally positioned H atoms to the equilibrium internuclear separation of an isolated H₂ molecule requires investment

using a first-principles pseudopotential

special k-points for Brillouin zone integrations

H/D ratio, the octahedrally centered H dimers

unless rather short internuclear distances

that the cohesive energy has a local minimum at a value which is about 0.2 eV lower than

Reducing the convergence error to below 0.1 eV hence required large basis sets (170 basis

1.34 eV/2H was positive. Using an empirical

kinetic energy cut-off of 21 Ry) and correspond-

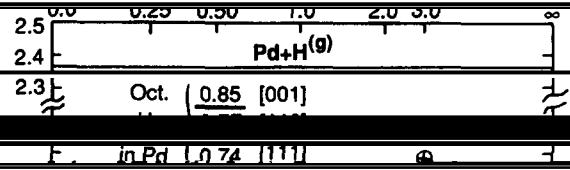
short range part of the H-H interaction is more

per H atom of a Pd-H structure with a hydrogen-

$$\mu_{Pd} = \frac{1}{2} \mu_{Pd_2} = \frac{1}{2} \mu_{Pd_2}(\alpha) = \frac{1}{2} \mu_{Pd_2}(\beta)$$

H/Pd ratio α

where g indicates gas and s indicates solid. In the absence of competing reactions, negative (positive) ΔH_f denotes thermodynamic stability (instability) towards disproportionation into metallic Pd and H_2 .



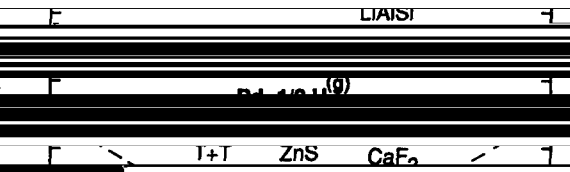
treated non-relativistically). The binding energy for the free H_2 molecule is

lattice parameter $a = 3.59 \text{ \AA}$ where H is centered

This gives a molecular dissociation energy of

total energy is $E_{tot} = 0.54 \text{ eV}$, all in reasonable

energy of free H_2 to within 0.1 eV. However, since a large part of this convergence error is cancelled in calculating the energy difference corresponding to the formation enthalpy of H_2



Our results for the relative energies of

shown for convenience.

DILUTE H IN Pd: We model the small- α (dilute) limit by placing one H atom at an octahedral (O) center of a cubic fcc Pd unit cell ($\alpha = 0.25$, Pd₄H, denoted as SC in Fig. 1). The calculated octahedral formation enthalpy $\Delta H = -0.28 \text{ eV/H}$ is exothermic; it is in fair agreement with the observed formation enthalpy of [12] ~ -0.14 to -0.16 eV/H . Examination of the electronic structure in this dilute limit reveals a simple physical picture consistent with the potential of H^+ pulls to lower energy those Pd

Pd Concentration H/(Pd+H) $1/2 H_2^{(g)}$

Fig. 1. Calculated formation enthalpies $\Delta H_f(\text{eV})$ with respect to Pd(s) and $1/2 H_2(g)$ or Pd(s) + H(g). Solid circles: stable phases; open circles: unstable phases. The notation Pd_nH_n at the bottom refers to compound name (stoichiometry), whereas the symbols SC, γ etc. refer to their structures (see text). The results for $\alpha = 0.5$ (except the NaCl phase) are calculated at their respective equilibrium concentrations (at 700 K), whereas the results for $\alpha = 0.25$ are calculated at their respective equilibrium

rule" [16]), forming bonding H-Pd states near the bottom of the valence band centered at $E_F \sim 1.7 \text{ eV}$. This lowering of the energy of the states of pure Pd stabilizes the system. On the other hand, the antibonding states are calculated to be $E_F \sim 1.7$ to 2.2 eV above E_F for

[at $\alpha(1/4, 1/4, 1/4)$ and $\alpha(3/4, 3/4, 3/4)$] and a

E_F both destabilize the system. The balance is attractive for low α because the antibonding

of the O sites by hydrogen, forming the

transition from Pd to H is found to be $\sim 0.1 \text{ eV}$

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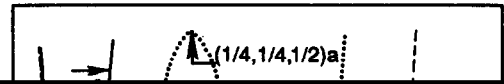
larger than for the covalent free-space mole-

forming the CaF₂ structure or occupy one T and

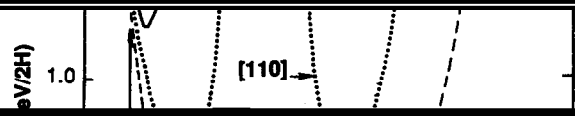
structure of Pd (with Pd at the (0,0,0) position)

these interstitial holes (27 + 0) forms the PdH

structure of PdH₂ (see Ref. 18 for further description of these crystal structures). We calculated the formation energies of all of these structures. Fig. 1 shows the results. He

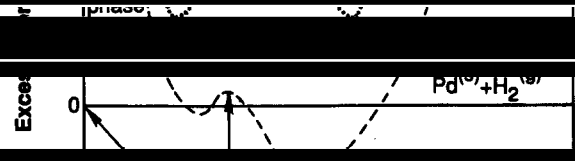


sufficient condition to imply local stability of structure α . For example, the CaF₂ structure of PdH₂ has a higher ΔH than PdH + 1/2 H₂(g) (a point denoted in Fig. 1 by an asterisk on the dashed tie-line), hence despite its $\Delta H < 0$, if



ponents, releasing the corresponding heat.

ence for occupation of 0 over 1, since 1 has a shorter Pd-H distance of ($\sqrt{3} a/4$) relative to that for 0: ($a/2$). On the other hand, for



in the latter case, leading to a stronger H-H repulsion. This is consistent with experimental the results of Ref. 7, where it was found that

a(1/3, 1/3, 1/3) centered H₂ in fcc Pd

the PdH₂ geometry used in Ref. 6 (an [001]-

considerably higher than the CaF₂ arrangement ($\Delta H = 0.40$ eV/2H) at the same composition.

accompanied by a large lattice relaxation. Indeed, the calculated lattice constant for PdH

drally-centered H₂ molecule in fcc Pd at a_t=4.00 Å for three orientations C as function of the

0.11 Å larger than that for PdH in NaCl structure. In a rigid lattice, the T-site formation energy ΔH is 0.26 eV higher than the O-site value. Allowing for lattice relaxation lowers

The basic results are:

(i) Octahedrally centered diatomic H₂ kept

cases through a barrier located near the the rapid diffusion[21] of H in Pd.

2).

(ii) A few local minima exist in the energy surface corresponding to metastable mole-

The pertinent physics here is that as α increases from the dilute limit, the coupling

the system. However, further increase of α lowers the hydrogen-induced antibonding states

space value (denoted as gas phase eq. dist. in Fig. 2)

amount of incorporable hydrogen at equilibrium.

DIATOMIC H₂ IN Pd: We next inquire whether there exists a metastable phase of H₂ dimer in Pd with smaller r_{eq} than the free space value.

We model this system at $\alpha = 0.5$ by an octahedrally-centered H₂ molecule inside an fcc cube with its

concentrations. However, we find here that the H₂ is stable in the [111] orientation, not in the [001] orientation postulated in Ref. 6. A molecule in any other orientation would spontaneously reorient to [111]. This indicates that the effective H-H repulsion in Pd increases[7] with the local charge density

(iv) At this position, the molecule will

see Fig. 2), lowering thereby the energy to the lattice is relaxed). Subsequently, these atoms could penetrate the O-T diffusion barrier and

0.36 eV/2H (see Fig. 1). Hence, while bringing two hydrogen atoms together in free space to $2a_0/2$ (where a_0 is the lattice constant) and then gradually dissolved H's to the same distance in

we identify the electronic origins of the instability of H₂ in Pd as follows: Dissolving

principally because the energy lowering associ-

whelms the energy increase associated with volume expansion and with a slight lowering of

binding (ϵ_{H_2}) state[22]. The H-H bonding energy is screened by the conduction electrons separated from the antibonding state by a "molecular

in Pd host where the odd (ϵ_{H_2}) and even (ϵ_{H_2})

gap E is even smaller. The significant point the Fermi energy, hence even the antibonding H-H state is occupied. This is the principal reason

content and for the formation of the H₂ molecule: the molecule seeks to dissociate to avoid population of its antibonding state. It is this electronic mechanism (not the internuclear repulsion which is effectively screened for H

bility of the embedded molecule.

Clearly, none of the equilibrium structures

fusion since the equilibrium H-H distance in Pd

studies[6,7], equilibrium fusion rates must be

effective masses) which would significantly

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