Solid State Communications, Vol. 73, No. 5, pp. 327-330, 1990.
Printed in Great Britain.

0038-1098/90$3.00+.00
Pergamon Press plc

STABILITY OF ATOMIC AND DIATOMIC HYDROGEN IN fcc PALLADIUM

[redacted]

Solar Energy Research Institute, Golden, CO 80401, USA

(Received 26 September 1989 by A. A. Maradudin)

First-principles self-consistent total energy calculations for various

[redacted]

system is controlled by the relative position of the hydrogen-induced antibonding level with respect to the Fermi energy. Diatomic H_2 in crystalline palladium is shown to have but metastable local minima whose internuclear separation are yet larger than that of the isolated H_2 molecule.

Recent claims of observation of room-tem-

[redacted]

deuterium atoms at a distance R, since both the vibrational wavefunction ϕ(R) of diatomic deu-

[redacted]

rium distance R_{eq} for the isolated H_2 molecule

[redacted]

distance and enhance the fusion rate[5].

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

[redacted]

that the cohesive energy has a local minimum at

[redacted]

1.34 eV/2H was positive. Using an emperical

[redacted]

short range part of the H-H interaction is more

[redacted]

In an attempt to further clarify some of

[redacted]

arrangements of atomic and diatomic hydrogen in fcc palladium. This approach, implemented by

[redacted]

molecule in any other orientation will

[redacted]

further lower its energy by dissociating into

[redacted]

Bringing two such octahedrally positioned H atoms to the equilibrium internuclear separation of an isolated H_2 molecule requires investment

[redacted]

Reducing the convergence error to below 0.1 eV

[redacted]

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

[redacted]

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

[redacted]

[redacted]

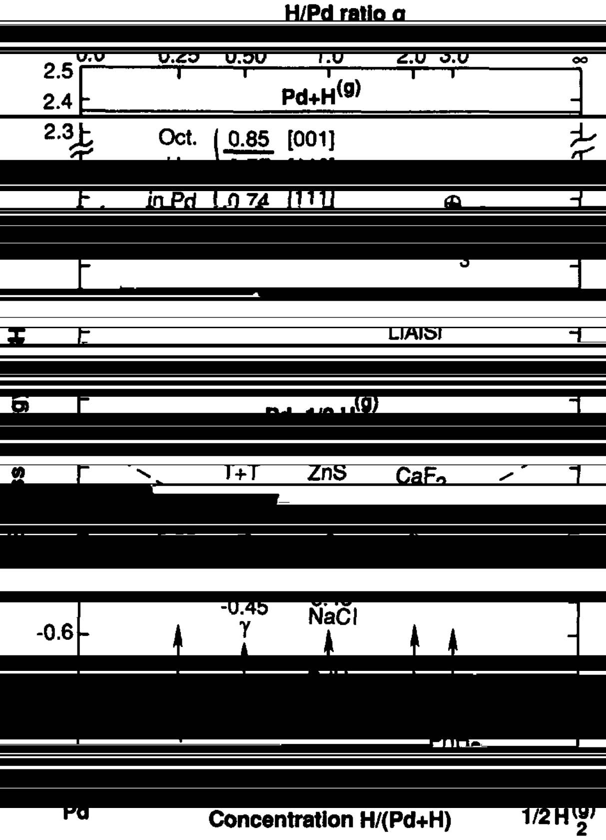
where g indicates gas and s indicates solid. In the absence of competing reactions, negative [redacted] (instability) towards disproportionation into [redacted]

treated non-relativistically). The binding [redacted]

since a large part of this convergence error is [redacted]

shown for convenience.

DILUTE H IN PD: We model the small-α [redacted] octahedral (O) center of a cubic fcc Pd unit cell (α = 0.25, Pd_4H, denoted as SC in Fig. 1). [redacted] = -0.28 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 [redacted] potential of H^+ pulls to lower energy those Pd [redacted] rule"[16]), forming bonding H-Pd states near the [redacted] attractive for low α because the antibonding [redacted] hydrogen in Pd is found to be over-screened by [redacted] larger than for the covalent free-space mole- [redacted]



[redacted] with respect to Pd(s) and 1/2 $H_2(g)$ or Pd(s) + H(g). Solid circles: stable phases; open [redacted] the bottom refers to compound name (stoichiometry), whereas the symbols SC, γ etc. refer to their structures (see text). The results for [redacted]

[redacted] of the O sites by hydrogen, forming the [redacted] Pd_4H_2 of space group $I4_1/amd$, or D_{4h}^{19}. Alter- [redacted] structure of PdH$_3$ (see Ref. 18 for further description of these crystal structures). We calculated the formation energies of all of

[redacted]

structure α. For example, the CaF$_2$ structure of PdH$_2$ has a higher ΔH than PdH + 1/2 H$_2$(g) (a point denoted in Fig. 1 by an asterisk on the

[redacted]

shorter Pd-H distance of ($\sqrt{3}$ a/4) relative to that for O: (a/2). On the other hand, for

[redacted]

in the latter case, leading to a stronger H-H

[redacted]

considerably higher than the CaF$_2$ arrangement

[redacted]

accompanied by a large lattice relaxation.

[redacted]

0.11 Å larger than that for PdH in NaCl structure. In a rigid lattice, the T-site formation

[redacted]

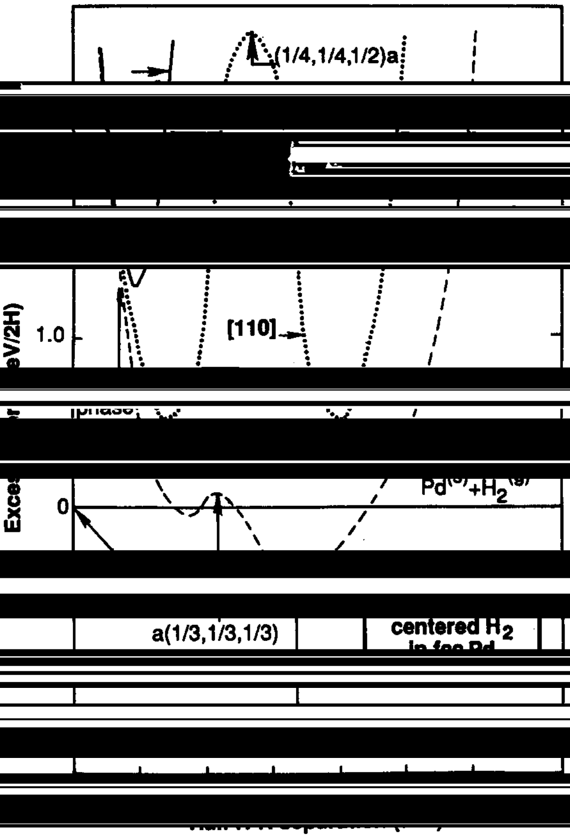
the rapid diffusion[21] of H in Pd.

The pertinent physics here is that as α

[redacted]

DIATOMIC H$_2$ IN PD: We next inquire whether there exists a metastable phase of H$_2$ dimer in Pd with smaller R$_{eq}$ than the free space value. We model this system at α = 0.5 by an octahedrally-centered H$_2$ molecule inside an fcc cube

[redacted]



[redacted]

drally-centered H$_2$ molecule in fcc Pd at a$_t$=4.00 Å for three orientations G as function of the

[redacted]

2).

(ii) A few local minima exist in the energy

[redacted]

concentrations. However, we find here that the H$_2$ is stablest in the [111] orientation, not in

molecule in any other orientation would spontaneously reorient to [111]. This indicates that the effective H-H repulsion in Pd

[redacted]

[redacted]

lattice is relaxed). Subsequently, these atoms

[redacted]

0.36 eV/2H (see Fig. 1). Hence, while bringing two hydrogen atoms together in free space to

[redacted]

hedrally dissolved H's to the same distance in Pd requires investment of ~2.4 eV/2H.

We identify the electronic origins of the instability of H_2 in Pd as follows: Dissolving small amounts of H in Pd stabilizes the system

[redacted]

whelms the energy increase associated with

[redacted]

the Fermi energy, hence even the antibonding H-H

[redacted]

content and for the formation of the H_2 mole-cule: the molecule seeks to dissociate to avoid

[redacted]

electronic mechanism (not the internuclear repulsion which is effectively screened for H_2 inside Pd) which is the origin of the instability of the embedded molecule.

Clearly, none of the equilibrium structures

[redacted]

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

[redacted]

effective masses) which would significantly

[redacted]

References

[redacted]

2. S. E. Jones, E. P. Palmer, J. B. Cair, D. L. Decker, G. L. Jensen, J. M. Thorne, S.

[redacted]

4. W. Kolos and L. Wolniewicz, J. Chem.

[redacted]

Jacobsen, P. Stoltze, O. H. Nielsen, and J. K. Norskov, Phys. Rev. B 40, 1993 (1989).

[redacted]

(1983).

13. A. R. Williams, J. Küler, and C. D.

[redacted]

130, 249 (1987).

[redacted]

Vol. 1 (Interscience, New York 1963).

19. L. Pauling, Nature (London) 339, 105 (1989).

[redacted]