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STABILITY OF ATOMIC AND DIATOMIC HYDROGEN IN fcc PALLADIUM

[redacted]

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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 $\phi(R)$ of diatomic deu-

[redacted]

rium distance R_{eq} for the isolated H_2 molecule

[redacted]

mechanism were sought. It was hoped, for example, that the existence of a metal lattice

[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 two H atoms each at a tetrahedral interstitial site, leading thereby to a yet longer H-H

[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 cancelled in calculating the energy difference

[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

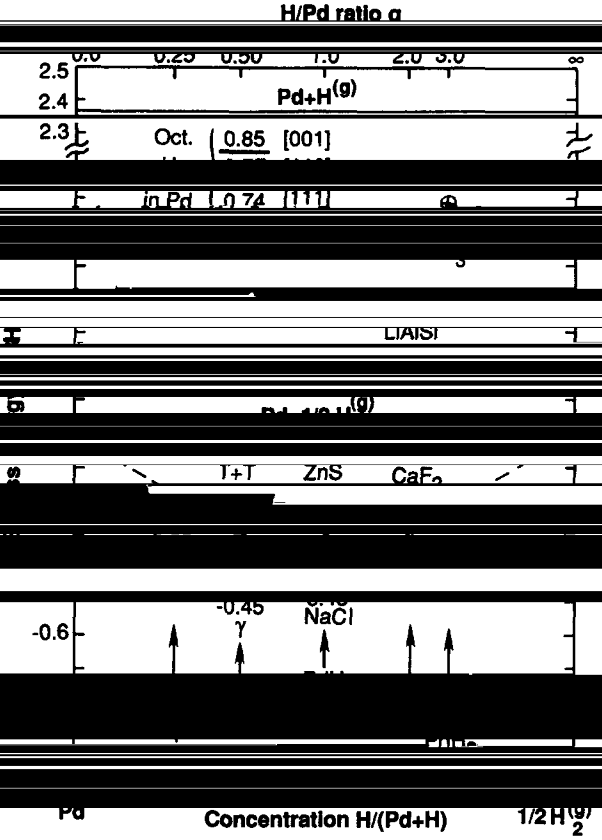
[redacted]

E_F both destabilize the system. The balance is

[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 (stoichimetry), whereas the symbols SC, γ etc. refer to their structures (see text). The results for

[redacted]

of the O sites by hydrogen, forming the

[redacted]

structure of PdH_3 (see Ref. 18 for further description of these crystal structures). We calculated the formation energies of all of [redacted]

sufficient condition to imply local stability of 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]

ponents, releasing the corresponding heat [redacted]

ence for occupation of O over T, since T has a 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]

[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]

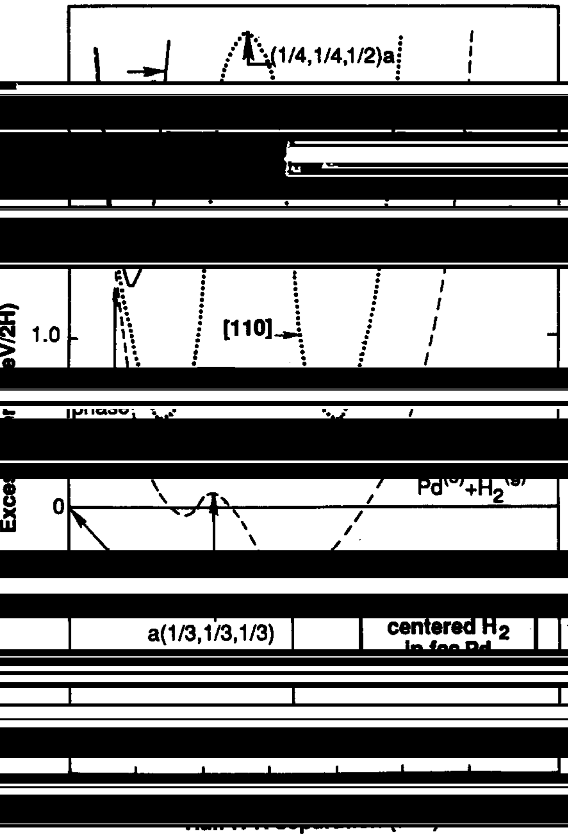
the rapid diffusion[21] of H in Pd.

The pertinent physics here is that as α [redacted]

[redacted]

amount of incorporable hydrogen at equilibrium.

DIATOMIC H_2 IN PD: We next inquire whether there exists a metastable phase of H_7 dimer in [redacted] 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 $\hat{G}$ as function of the [redacted]

[redacted]

2).

(ii) A few local minima exist in the energy [redacted]

[redacted]

concentrations. However, we find here that the H_2 is stablest in the [111] orientation, not in [redacted] molecule in any other orientation would spontaneously reorient to [111]. This indicates that the effective H-H repulsion in Pd [redacted]

[redacted]

[redacted]

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

[redacted]

instability of H_2 in Pd as follows: Dissolving

[redacted]

cule: the molecule seeks to dissociate to avoid

[redacted]

electronic mechanism (not the internuclear

[redacted]

bility 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]

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