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STABILITY OF ATOMIC AND DIATOMIC HYDROGEN IN fcc PALLADIUM

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First-principles self-consistent total energy calculations for various configurations of atomic and diatomic hydrogen inside fcc palladium have been carried out to clarify some of the solid state aspects of the physics of dense hydrogen in metals. We find that the stability of the 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-temperature ("cold") nuclear fusion in deuterated transition metal electrodes[1,2] have rekindled interest in the physics of dense deuterium atoms in the field of metallic electrons and transition atoms. Of recent interest here is the Born-Oppenheimer energy surface E(R) of two deuterium atoms at a distance R, since both the vibrational wavefunction $\phi(R)$ of diatomic deuterium [determining the fusion rate[3] $A = A|\phi(R=0)|^2$] and the tunneling barrier penetration factor[3] B depend sensitively on E(R). Previous estimates[3] of A and B assumed the free space form[4] of E(R) of gaseous H_2 [bound at $R_{eq} = 0.74$ Å by $E(R_{eq}) = 4.7$ eV/2H; because the electronic E(R) is independent of the isotope mass effects, the discussion below applies equally to H and D]. Since the equilibrium distance R_{eq} for the isolated H_2 molecule is too large to grant sufficient tunneling events[3], various solid-state R_{eq}- shortening mechanism were sought. It was hoped, for example, that the existence of a metal lattice (e.g. fcc Pd) in which deuterium is embedded could grant a large Coulomb screening effect, hence, substantially reduce the D-D tunneling distance and enhance the fusion rate[5].

Some recent theoretical studies have addressed this question. Sun and Tomanek[6] investigated the binding energy versus the nearest-neighbor H-H distance d_{H-H} in the concentrated limit of an hypothetical PdH_2 crystal using a first-principles pseudopotential approach in a Gaussian basis set. Based on a billiard-ball model, they assumed that for this H/Pd ratio, the octahetrally centered H_2 dimer will be aligned along the [001] fcc direction. For this particular configuration they found that the cohesive energy has a local minimum at a d_{H-H} value which is about 0.2 Å larger than that of gaseous H_2; the formation enthalpy $\Delta H = 1.34$ eV/2H was positive. Using an emperical effective-medium theory, Christensen et al.[7] likewise found that in a metallic matrix the short range part of the H-H interaction is more repulsive than in free space, hence, d_{H-H} is longer.

In an attempt to further clarify some of the solid state aspects of cold fusion[1,2] and to gain a better understanding of metal hydride system in general, we have used first-principles self-consistent total energy methods within the local density formalism[8] to systematically predict the stability of various periodic arrangements of atomic and diatomic hydrogen in fcc palladium. This approach, implemented by the all-electron full-potential semirelativistic linearized augmented plane wave (LAPW) method[9], includes interelectronic Coulomb[8] and exchange-correlation[8b] interactions and provides an accurate solution to the electronic Schrödinger problem for a static periodic atomic configuration {R} of the combined Pd + H system. We study various orientations of H_2 in fcc Pd, finding that [111] is the stablest; a molecule in any other orientation will spontaneously reorient along [111]. However, we find that in this orientation the system can 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 diffusion barries (0.3 eV) leads then to an exothermic hopping into the octahedral sites. Bringing two such octahedrally positioned H atoms to the equilibrium internuclear separation of an isolated H_2 molecule requires investment of 2.4 eV/2H; the same reaction in the gas phase emits 4.7 eV/2H.

In the present study we have used ten special k-points for Brillouin zone integrations in the fcc structure and their equivalent[10] points for the other structures. Since we explore rather short internuclear distances, small (≤ 0.37 Å) muffin-tin radii are needed for describing the potential near hydrogen sites. Reducing the convergence error to below 0.1 eV hence required large basis sets (~170 basis functions per Pd atom, corresponding to a kinetic energy cut-off of 21 Ry) and correspondingly large sets of potential and charge density components (E=204 Ry). The formation enthalpy per H atom of a Pd-H structure with a hydrogen-to-palladium atom ratio α=H/Pd is defined as

$$\Delta H[PdH_\alpha] = \frac{1}{\alpha} E[PdH_\alpha] - \frac{1}{\alpha} E[Pd(s)] - \frac{1}{2}E[H_2(g)], (1)$$

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

PURE CONSTITUENTS: For pure fcc Pd we find an equilibrium lattice constant a_{eq}=3.85 Å and a cohesive energy of E_c=5.05 eV (3.95 eV if treated non-relativistically). The binding energy curve for the free H_2 molecule is calculated in a simple cubic supercell geometry with lattice constant a = 4.00 Å where H_2 is centered at the cubic site. At this lattice constant the coupling between H_2 molecules is negligible. This gives a molecular dissociation energy of 4.73 eV/pair at the calculated equilibrium internuclear distance of 0.769 Å; the vibrational energy is $\hbar\omega$ = 0.54 eV, all in reasonable accord with experiment and previous calculations[11]. [We find that an even larger cut-off energy--400 Ry for the charge density and potential--is required to converge the dissociation 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 Eq. (1), a smaller cut-off energy was used in other calculations].

Our results for the relative energies of various PdH_α structures are depicted graphically in Fig. 1, where two reference energies are shown for convenience.

DILUTE H IN PD: We model the small-α (dilute) limit by placing an H atom at the octahedral (O) center of a cubic fcc Pd unit cell (α = 0.25, Pd_4H, denoted as SC in Fig. 1). The calculated octahedral formation enthalpy ΔH = -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 reveals a simple physical picture, consistent with previous studies:[13-15] the attractive potential of H^+ pulls to lower energy those Pd wavefunctions which have an a_1 symmetry about the octahedral site (the "interstitial insertion rule"[16]), forming bonding H-Pd states near the bottom of the valence band, centered at E_F - 7.9 eV. This lowering of the energy of the states of pure Pd stabilizes the system. On the other hand, the small volume expansion (calculated to be ΔV ~ 1.7 ±0.2 cm^3/g-atom of H for α<1) and the lowering of the H-induced antibonding states with respect to the Fermi energy E_F both destabilize the system. The balance is attractive for low α because the antibonding states are essentially unoccupied. Dilute hydrogen in Pd is found to be over-screened by the Pd electrons relative to atomic hydrogen, forming a negative ion "$H^{-\delta}$". The charge transfer from Pd to H is found to be ≤ 0.1 e/H for α<1. However, the presence of a large number of pd valence electrons make the charge surround the H atom in the hydride much larger than in free space. Despite this, the nearest-neighbor H-H distance (>2.75 Å) is considerably larger than for the covallent free-space molecule.

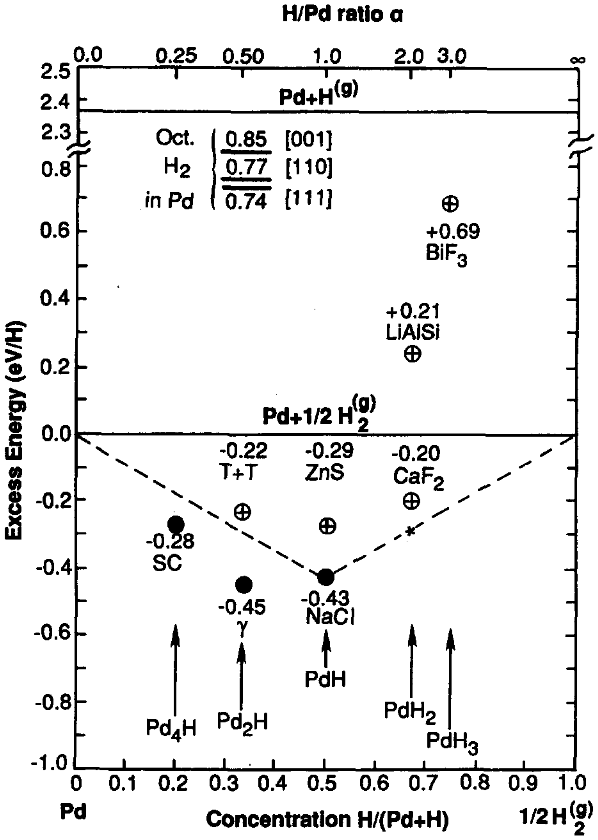

Fig.1: Calculated formation enthalpies $\Delta H(PdH_\alpha)$ with respect to Pd(s) and 1/2 H_2(g) or Pd(s) + H(g). Solid circles: stable phases; open circles: unstable phases. The notation Pd_nH_n at the bottom refers to compound name (stoichimetry), whereas the symbols SC, γ etc. refer to their structures (see text). The results for α=0.5 (except the γ phase) are calculated at fixed lattice constant (a=4.00 Å), others are calculated at their respective equilibrium values.

HIGHER α's AND ORDERED PHASES: The fcc structure of Pd [with Pd at the (0,0,0) position] has two tetrahedral (T) interstitial sites [at a(1/4,1/4,1/4) and a(3/4,3/4,3/4)] and a single octahedral (O) interstitial site [at a(1/2,1/2,1/2)], all empty in pure Pd. Partial or full occupation of these sites by H leads to a number of possible ordered phases. For α = 0.5 we can occupy, in an ordered fashion, half of the O sites by hydrogen, forming the observed[17] low-temperature tetragonal γ phase Pd_4H_2 of space group $I4_1$/amd, or D^{19}_{4h}. Alternatively, one can occupy both tetrahedral sites along the [111] direction, forming the "T+T structure" of Pd_4H_2 also with α = 0.5. For α = 1 we can occupy either the O site to form the NaCl structure of PdH or occupy one of the T sites, to form the ZnS structure of PdH. For α = 2 it is possible to occupy all the T sites, forming the CaF_2 structure, or occupy one T and one O site to form the LiAlSi-like structure of PdH_2. Finally, for α = 3, occupation of all three interstitial holes (2T + O) forms the BiF_3

structure of PdH_3 (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. We find that

(i) ΔH is negative for all but the LiAlSi and BiF_3 structures of PdH_2 and PdH_3 respectively; if formed, these two compounds would disproportionate, releasing their ΔH's thermally, as recently suggested[19].

(ii) $\Delta H_\alpha < 0$ is a necessary but not a 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 dashed tie-line), hence, despite its ΔH_α <0, if formed, it too will decompose into these components, releasing the corresponding heat[19] (Fig. 1).

(iii) For $\alpha \le 1$, the system shows preference 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 larger α (e.g. α=2), we find that the system prefers occupation of two T sites over occupation of O + T, since the H-H distance is shorter in the latter case, leading to a stronger H-H repulsion. This is consistent with experimental observations[20], but is in contradiction with the results of Ref. 7, where it was found that the LiAlSi-like structure is stabler than the CaF_2 structure. Our result also suggests that the PdH_2 geometry used in Ref. 6 (an [001]-oriented H_2 in Pd) does not correspond to a locally stable structure: it has ΔH=1.34 eV/2H, considerably higher than the CaF_2 arrangement (ΔH=-0.40 eV/2H) at the same composition.

(iv) Hydrogen occupation of the T-site is accompanied by a large lattice relaxation. Indeed, the calculated lattice constatnt for PdH in the zincblend structure (4.17 Å) is about 0.11 Å larger than that for PdH in NaCl structure. In a rigid lattice, the T-site formation enthalpy ΔH_T is 0.23 eV higher than the O-site value. Allowing for lattice relaxation lowers this value to 0.13 eV.

(v) The diffusion path between O and T passes through a barrier located near the a(1/3,1/3,1/3) position. The rather small barrier value we find (~0.3 eV) is consistent with the rapid diffusion[21] of H in Pd.

The pertinent physics here is that as α increases from the dilute limit, the coupling between the H and Pd atoms lowers the hydrogen-induced H-Pd bonding states, thereby stabilizing the system. However, further increase of α lowers the hydrogen-induced antibonding states below the Fermi energy, causing destabilization. The H-induced lattice dilation of the host also contribute to destabilization. This self-limiting process controls the maximum amount of incorporable hydrogen at equilibrium.

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 with interatomic separation R and orientation $\underset{\sim}{G}$. Varying R at a_t = 4.00 Å (the calculated equilibrium lattice constant of Pd_4H_2 in T+T structure) for the orientations $\underset{\sim}{G}$ = [111], [001], and [110], we find the Born-Oppenheimer energy curves $E[a_t, \underset{\sim}{G}, R]$ shown in Fig. 2.

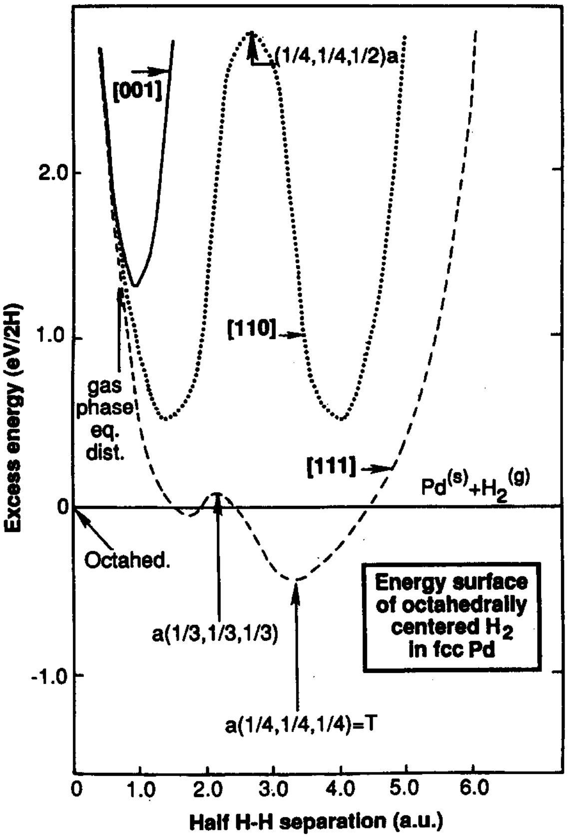

Fig.2: Calculated excess energy of the octahedrally-centered H_2 molecule in fcc Pd at a_t=4.00 Å for three orientations $\underset{\sim}{G}$ as function of the H-H distance.

The basic results are:

(i) Octahedrally centered diatomic H_2, kept at its gas phase internuclear separation $R_{eq}[H_2(g)]$ is unstable by as much as ~1.5 eV with respect to disproportionation into Pd(s) + H_2 for all principal orientations (Figs. 1 and 2).

(ii) A few local minima exist in the energy surface, corresponding to metastable molecules. However, all are characterized by H-H internuclear separations larger than the free-space value (denoted as "gas phase eq. dist" in Fig. 2).

(iii) Our results for the [001] orientation (R_{eq}=0.95Å, ΔH=1.3 eV/2H) are very similar to those of Ref. 6 [R_{eq} = 0.94Å, ΔH=1.34 eV/2H) even though they are calculated at different H concentrations. However, we find here that the H_2 is stablest 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. This mechanism[7] also explains the local maximum at (1/3, 1/3, 1/3)a (Fig. 2).

(iv) At this position, the molecule will spontaneously dissociate into two isolated T sites (separated by a distance $\sqrt{3}a/2$ = 3.5 Å, see Fig. 2), lowering thereby the energy to the value $2\Delta H_T = -0.44$ eV/2H (-0.54 eV if the host lattice is relaxed). Subsequently, these atoms could penetrate the O-T diffusion barrier and relax to the O sites, releasing $2\Delta H_T - 2\Delta H_O =$ 0.36 eV/2H (see Fig. 1). Hence, while bringing two hydrogen atoms together in free space to $R_{eq}[H_2(g)]$ emits ~ 4.7 eV/2H, bringing two octahedrally 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 principally because the energy lowering associated with the formation of deep Pd-H bonding states near the bottom of the valence band overwhelms the energy increase associated with volume expansion and with a slight lowering of the yet empty antibonding states. On bringing closer together two initially isolated and screened H atoms inside Pd, the increased H-H coupling forms a bonding ("$\sum_{1g}$") and an antibonding ("$\sum_{1u}$") states[22]. The H-H bonding state lies at about 13 eV below E_F and is separated from the antibonding state by a "molecular gap" E_g. In the free molecule, E_g is ~10 eV. In the Pd host, where the odd (u) and even (g) state are screened by Pd valence electron, the gap E_g is even smaller. The significant point here is that this molecular gap is smaller than the Fermi energy, hence even the antibonding H-H state is occupied. This is the principal reason for the system's instability at high hydrogen content and for the formation of the H_2 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_2 inside Pd) which is the origin of the instability of the embedded molecule.

Clearly, none of the equilibrium structures shown in Figs. 1 and 2 are conducive to cold fusion, since the equilibrium H-H distance in Pd is considerably larger than that of the free molecule (Fig. 2). Consistent with other studies[6,7], equilibrium fusion rates must be enormously smaller than what was previously[3] thought. Use[3,4] of free H_2 potential to estimate fusion probabilities inside Pd would seem unreasonable. We conclude that there are no spectacular solid state effects (e.g., enhanced effective masses) which would significantly reduce[5] R_{eq}.

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