Instability of Diatomic Deuterium in fcc Palladium

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To clarify some of the solid-state aspects of cold fusion in deuterated transition metal electrodes, we have carried out first-principles self-consistent total energy calculations for various configurations of atomic and diatomic deuterium inside fcc palladium. We find that the stability of the Pd + D system is controlled by the relative position of the deuterium-induced *antibonding* level with respect to the Fermi energy. The equilibrium D-D distance in dense PdD_α up to $\alpha = 3$ is found to be much larger than the free space value. The calculated Born-Oppenheimer energy surface of diatomic D_2 in crystalline palladiuim is shown to have but metastable local minima whose internuclear separation is at least 0.2 Å *larger* than that of the isolated D_2 molecule. We conclude that D_2 in *crystalline* Pd will have a substantially lower tunneling probability than hitherto thought and that explanation for fusion mechanisms should be sought elsewhere.

Recent suggestions of room-temperature ("cold") nuclear fusion in deuterated transition metal elecrodes[1,2] have raised interest in the physics of dense deuterium atoms in the field of transition metals. 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 $\psi(R)$ of diatomic deuterium [determining the fusion rate[3] $\Lambda = A|\psi(R=0)|^2$] and the tunneling barrier penetration factor[3] B depend sensitively on $E(R)$. Previous estimates [3] of Λ and B assumed the *free space* form[4] of $E(R)$ of gaseous H_2 [bound at $R_{eq} = 0.74$ Å by $E(R_{eq}) \simeq 4.7$ eV/2H; since $E(R)$ is independent of the isotope mass effects, the discussion below applies equally to H and D]. Because 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 mechanisms 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 Coulmb screening effect and, hence, substantially re-duce the D–D tunneling distance and enhance the fusion rate.

In an attempt to clarify some of the solid-state aspects of cold fusion,[1,2] we have used first-principles self-consistent total energy methods within the local density formalism[5] to predict systematically the stability of various periodic arrangements of atomic and diatomic hydrogen in fcc palladium. This approach, implemented within the all-electron full-potential semirelativistic linearized augmented plane wave (LAPW) method,[6] includes interelectronic Coulomb and exchange-correlation 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 exotermic 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 10 special k-points for Brillouin zone integrations in the fcc structure and their *equivalent*[7] points for the other structures. Large basis sets (~170 basis functions per Pd atom, corresponding to a knetic energy cutoff of 21 Ry) and correspondingly large sets of potential and charge density components ($E_{cutoff} = 204$ Ry) are used. The formation enthalpy per H atom of a Pd–H structure with a hydrogen-to-palladium atom ratio $\alpha = H/Pd$ is defined as

$$\Delta H[\text{PdH}_\alpha] = \frac{1}{\alpha} E[\text{PdH}_\alpha]$$
$$- \frac{1}{\alpha} E[\text{Pd}^{(s)}] - \frac{1}{2} E[\text{H}_2{}^{(g)}] \quad (1)$$

In the absence of competing reactions, negative (positive) ΔH denotes thermodynamic stability (instability) toward disproportionation into metallic Pd and gaseous H_2.

Pure Constituents. We first establish the reference total energies of solid (s) fcc Pd and gaseous (g) H_2. 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 nonrelativistically). 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. 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.[8]

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 an fcc Pd cubit unit cell ($\alpha = 0.25$, Pd_4H, denoted as SC in Fig. 1). The calculated octahedral formation enthalpy $\Delta H_o = -0.28$ eV/H is exothermic; it is in fair agreement with the observed formation enthalpy of[9] ~ -0.14 to -0.16 eV/H. Examination of the elctronic structure in this dilute limit reveals a simple physical picture, consistent with previous studies:[10-12] 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"),[13] 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
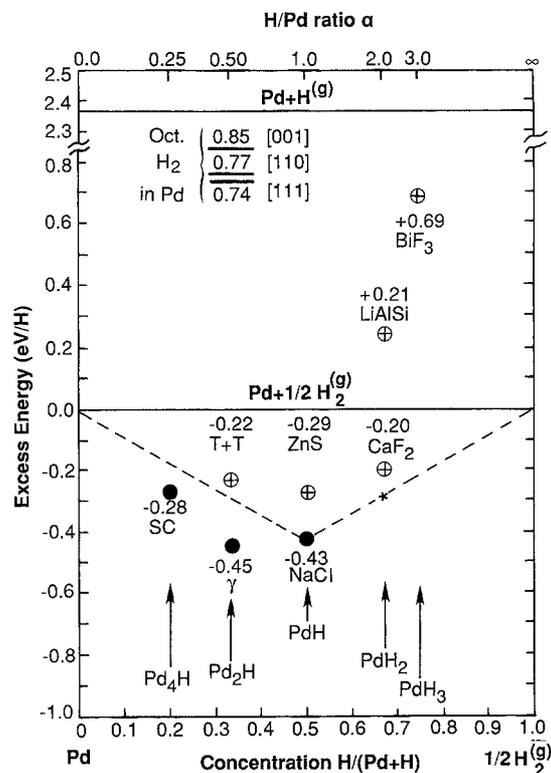

Fig. 1. Calculated formation enthalpies $\Delta H(\text{PdH}_\alpha)$ with respect to $\text{Pd}^{(s)}$ and $1/2\,\text{H}_2{}^{(g)}$ or $\text{Pd}^{(s)} + \text{H}^{(g)}$. Filled circles, stable phases; open circles, unstable phases. See text for notation of crystal structures. The results for $\alpha = 0.5$ (except the γ phase) are calculated at fixed lattice constant ($a = 4.00$ Å); others are calculated at their respective eqilibrium values.

of pure Pd stabilizes the system. On the other hand, the small volume expansion (calculated to be $\Delta V \sim 1.7$ cm^3/g-atom of H for $\alpha < 1$) 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 *overscreened* by the Pd electrons relative to atomic hydrogen, forming a negative ion "$H^{-\delta}$". Despite this, the nearest-neighbor H–H distance (> 2.75 Å) is considerably larger than for the covalent free-space molecule.

Higher α's and Ordered Phases. In the fcc structure each 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 $\alpha = 0.5$ we can occupy, in an ordered fashion, half of the O sites by hydrogen, forming the observed[14] low-temperature tetragonal γ-phase Pd_4H_2 of space group $I4_1/amd$, or D_{4h}^{19}. Alternatively, one can

occupy both tetrahedral sites along the [111] direction, forming the "T + T structure" of Pd_4H_2, also with $\alpha = 0.5$. For $\alpha = 1$ we can either occupy 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 $\alpha = 2$ 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 $\alpha = 3$, occupation of all three interstitial holes (2T + O) forms the BiF_3 structure of PdH_3 (see Ref. 15 for further description of these crystal structures). We calculated the formation energies of all of these structures; Fig. 1 shows the results. We find the following.

(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.[16]

(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 $\Delta H_\alpha < 0$, if formed, it, too, will decompose into these components, releasing the corresponding heat[16] (Fig. 1).

(iii) For $\alpha \leq 1$, the system shows preference for occupation of O over T, since T has a shorter Pd–H distance ($\sqrt{3}\ a/4$) relative to that for O: ($a/2$). On the other hand, for larger α (e.g., $\alpha = 2$), 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.[17]

(iv) Hydrogen occupation of the T site is accompanied by a large lattice relaxation. Indeed, the calculated lattice constant 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 the O and T sites 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[18] of H in Pd.

The pertinent physics here is that as α increases from the dilute limit, the coupling between the H and the Pd atoms lowers the hydrogen-induced H–Pd bonding states, thereby stabilizing the system. However, further increase in 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.

Our study indicates that the equilibrium H–H distance in PdH_α up to $\alpha = 3$ (>1.73 Å) is much larger than the free-space value, despite that H is effectively screened in fcc Pd.

Diatomic H_2 in Pd. We next inquire whether there exists a *metastable* phase of H_2 dimer in Pd with a *smaller* R_{eq} than the free-space value. We model this system at $\alpha = 0.5$ by an octahedrally centered H_2 molecule inside an fcc cube with interatomic separation R and orientation $\vec{G}$. Varying R at $a_{eq} = 4.00$ Å (close to the calculated equilibrium lattice constant) for the orientations $\vec{G} = $ [111], [001], and [110], we find the Born–Oppenheimer energy curves $E[a_{eq}, \vec{G}, R]$ shown in Fig. 2. The basic results are as follows.

(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).

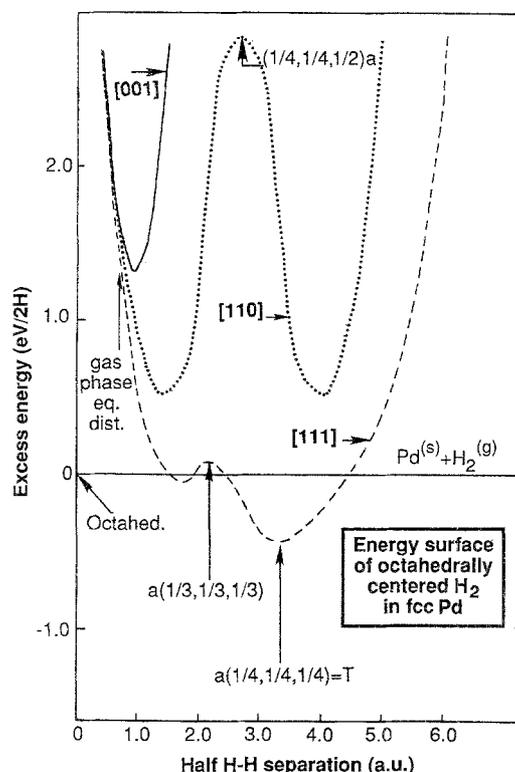**Fig. 2.** Calculated excess energy of the octahedrally centered H_2 molecule in fcc Pd at $a_{eq} = 4.00$ Å for three orinetations G as function of the H–H distance.

(ii) A few local minima exist in the energy surface, corresponding to *metastable* molecules. However, all are characterized by H–H internuclear separations at least 0.2 Å *larger* than the free-space value (denoted as "gas-phase eq. dist" in Fig. 2).

(iii) The H_2 is stablest in the [111] orientation. A molecule in any other orientation would spontaneously reorient to [111].

(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), thereby *lowering* the energy to the value $2\Delta H_T \simeq -0.44$ 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 stable Pd–H bonding state is gradually destroyed and replaced by the weaker H–H interaction, which forms a bonding ("Σ_{1g}") and an antibonding ("Σ_{1u}") state.[19] 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 anitbonding 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). 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) in *crystalline* transition metal which would significantly reduce R_{eq}. Search for such effects should perhaps be sought in noncrystalline environments (e.g., defects, grain boundaries).

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