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First-principles study of hydrogen permeation in palladium-gold alloys

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Density functional theory and lattice model calculations are combined to study the permeability of hydrogen in Pd lightly alloyed with Au. This study shows that small amounts of Au substitutions in Pd leads to, respectively, an increase and decrease of the diffusivity and solubility of hydrogen in the alloy. The competition between these two phenomena depends on temperature and can yield dilute PdAu membranes with a hydrogen permeability higher than pure Pd. © *2011 American Institute of Physics*. [doi:10.1063/1.3656739]

Palladium-based membranes are used industrially to separate H_2 from a hydrocarbon feedstock.[1,2] To prevent embrittlement of the membrane and increase its resistance to poisoning by gas contaminants, Pd is alloyed with metals such as Au, Ag, and Cu.[3,4] Alloying inevitably influences other key parameters such as the permeability of H. Unexpectedly, however, at low alloying levels Pd membranes show values of the H permeability higher than in pure Pd.[5–9] The origin of this behavior is still elusive to date. This first-principles study addresses this issue in the case of PdAu alloys.

Experimental reports on the enhanced permeability of H in PdAu alloys date back to 1869.[5] Today, this issue is still matter of both experimental[7–9] and theoretical[10–13] scrutiny. Experiments show that at very low Au contents the permeability of the alloy is larger than that of Pd.[6,9] A maximum permeability, about 1.3 times larger than in pure Pd, has been reported to be attained between 4 and 6 wt. % Au.[6–9] At higher Au contents, the permeability of H drops rapidly, due to both a reduced solubility and diffusivity.[6–9] The origin of these behaviors has been attributed to microstructure and defects of the alloy[6] and to anomalous trends of either the diffusivity or solubility of H.[6,9] In the dilute regime, where the role of microstructure and defects can be disregarded, very recent experiments have shown that the higher value of permeability stems mainly from the larger diffusivity of H in the PdAu alloy.[9] This result, however, is in contrast with both earlier experiments, showing an almost constant diffusivity of H in dilute PdAu alloys,[6,14] and recent computational studies,[12,13] supporting the hypothesis that the permeability, follows the trend of the solubility.[6] This work addresses this issue. In particular, our results support the recent experimental findings of a H permeability dominated at low Au contents by a higher diffusivity.[9]

Spin polarized density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP).[15,16] An energy cutoff of 400 eV was used for the planewaves, the exchange and correlation energy was computed as in Ref. 17, and ionic cores were treated by using the projector augmented wave method.[18] Γ-point calculations were carried out by using cubic supercells including 108 metal atoms on a face-centered cubic (fcc) lattice. We considered the following metallic systems: perfect Pd and Au, and selected diluted PdAu alloys. The energy of H in a metal, ΔE_H, was calculated by referring the total energy of the defected metal to those of the perfect metal and half H_2. In our calculations, H was kept fixed in a selected interstitial position of the fcc lattice (Fig. 1), and the positions of the metal ions were optimized subjected to the constraint that their center of mass did not move. To assess the accuracy of our computational approach, a selected set of calculations were repeated by employing either a more recent exchange-correlation functional[19] or a $2 \times 2 \times 2$ Monkhorst-Pack sampling grid of the Brillouin zone. These calculations showed that ΔE_H are converged and that different approximations of the exchange-correlation energy introduce systematic errors of about 0.1-0.2 eV in ΔE_H, while leaving almost unchanged ($\leq$0.05 eV) the relative energy values of H in different fcc interstitial positions.

H is soluble in Pd (Table I). ΔE_H is negative within the interstices of the fcc lattice and, as expected, the lowest energy configuration of H in Pd is in correspondence of the octahedral (O_h) site (Fig. 1). In a tetrahedral (T_d) interstice, the energy of H raises by 0.04 eV. The so-called middle (M) and bridge (TS) interstitial sites (Fig. 1) correspond to metastable positions. Our calculations show that the lowest energy diffusion pathways of H in Pd consist of a sequence of O_h-T_d steps, passing by M points. These diffusion steps involve energy barriers of 0.17 eV and 0.13 eV from the O_h to M site and from the M to T_d site, respectively (Fig. 1, top panel). TS sites are higher in energy than M points by about 0.4 eV. The transfer of H between two adjacent O_h or T_d sites via a TS point can thus be considered statistically irrelevant.

H is not soluble in Au. The computed values of ΔE_H are found to be positive, both within the octahedral and tetrahedral interstices and along the high-symmetry segments joining the O_h and T_d sites (Fig. 1(b)). At variance with Pd, O_h sites in Au correspond to both high energy and metastable states of H. Stable configurations are found in correspondence of the T_d sites. These results show that Au substitutions in Pd modify non-trivially the energy landscape of H in PdAu alloys. Here, we focus on the low Au-content regime.

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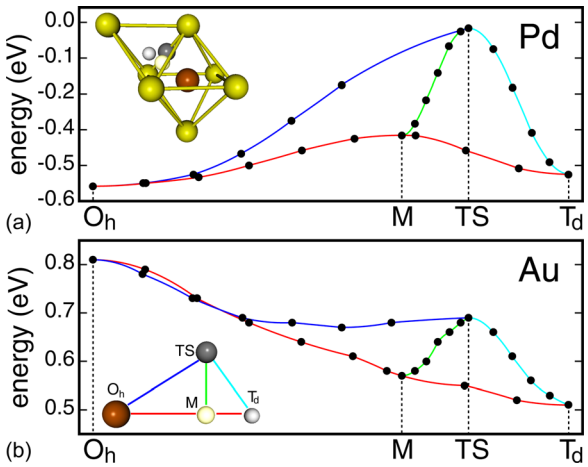

FIG. 1. (Color online) Energy of H in Pd (a) and Au (b) along high-symmetry directions of the fcc lattice (inset, (b)). Discs indicate DFT results while colored lines are guides to the eye. The inset in the top panel shows the location of the O_h (red), T_d (white), M (light yellow), and TS (gray) interstitial sites in a fcc lattice (yellow).

To model dilute PdAu alloys, we considered a 108-atom cubic supercell of fcc Pd with only one Au substitution, corresponding to a molar fraction of $x \approx 0.01$. Our calculations show that an isolated Au substitution in Pd changes the energy landscape of H only locally. The first next nearest neighbor O_h and T_d sites of Au remain stable positions for H, with energies higher than in pure Pd by 0.13 and 0.21 eV, respectively (Table I). The first next nearest neighbor M and TS sites of Au preserve a metastable character and raise in energy by more than 0.2 eV with respect to the same points in pure Pd (Table I). Beyond the first shell of nearest neighbor interstitial sites, the energy of H in the dilute alloy recovers the value as in pure Pd (Table I).

The energy profile of a H atom visiting O_h and T_d sites in contact with an isolated Au substitution in Pd is shown in Fig. 2. As in pure Pd, the O_h sites can be reached by crossing an energy barrier of 0.17 eV through a triangular constriction formed by Pd atoms only. To escape the O_h site, H can either cross an equivalent constriction with an activation energy of only 0.04 eV into a neighboring T_d cage or reach a T_d site in contact with the Au atom by crossing an energy barrier of 0.29 eV (Fig. 2). While the latter migration pathway is unfavorable, the former one occurs as likely as in pure Pd and, due to the nearly flat energy landscape inside the O_h interstice in contact with Au, it proceeds more readily. Overall, these results show that in dilute PdAu alloys the permeability of H varies with Au content because (1) the occupancy of the interstitial sites in direct contact with Au atoms decreases and (2) the migration process across the O_h interstices in contact with the Au substitutions occurs more favorably than in pure Pd.

TABLE I. ΔE_H (in eV) of H at high-symmetry interstitial sites in Pd, Au, and selected model PdAu alloys. Model Pd_{108-n} Au_n alloys are indicated with Au_n, $n=1\ldots6$. Au_1 and Au_1^{Pd} report the energy of H at sites belonging to the first and second shell of next nearest neighbor interstitial sites of the Au substitution, respectively. In Au_n, $n=2\ldots6$, H is positioned in a T_d or O_h site and Au substitutions decorate the corresponding interstitial.

	Pd	Au	Au_1^{Pd}	Au_1	Au_2	Au_3	Au_4	Au_5	Au_6
O_h	−0.55	0.81	−0.56	−0.43	−0.17	−0.09	0.21	0.24	0.64
T_d	−0.51	0.51	−0.53	−0.32	−0.04	0.20	0.42	–	–
M	−0.38	0.58	−0.39	−0.14	–	–	–	–	–
TS	−0.02	0.69	−0.04	0.29	–	–	–	–	–

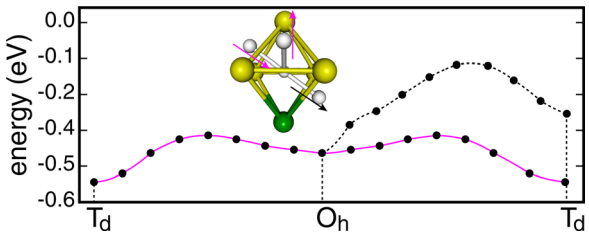

FIG. 2. (Color online) Energy profiles of a H atom diffusing across O_h and T_d cages near an isolated Au substitution in Pd. Symbols (DFT results) connected by the colored line show ΔE_H along a T_d–O_h–T_d diffusion step in which only the O_h site lies within the first shell of next nearest neighbor interstitial sites of Au. Symbols connected by the black line show ΔE_H of a H visiting O_h, T_d, and M sites, all in the first shell of next nearest neighbor interstitial sites of Au. The diffusion steps (white ball and sticks, and arrows) are sketched in the inset (Au and Pd are shown in green and yellow, respectively).

To address the role of Au coordination, we considered a 108-Pd atom supercell and we inserted H in a O_h and T_d interstitial enclosed by an increasing number of Au substitutions, up to 6 and 4, respectively. Our DFT calculations show that ΔE_H raises rapidly with the Au coordination (Table I). In particular, in an interstice fully surrounded by Au atoms, but otherwise embedded in pure Pd, H attains an energy very close to that as in pure Au. This result shows that first nearest-neighbor effects account for ~90% of the differences of the energy of H in Pd and Au.

To study the permeability of H in dilute PdAu alloys, we used a simplified computational scheme. To represent the energy landscape of H in the alloy, we employed a periodic 3-D lattice model consisting of the O_h, T_d, and M sites of a fcc lattice. TS sites were not included in the model, due to the high energy H attains at these positions. For a selected composition of the alloy, Au atoms were distributed at random in the fcc lattice, and, on the basis of the Au coordination, our results in Table I were used to assign energy values to the O_h and T_d sites. M points were assigned energy values of either −0.39 eV or −0.14 eV, depending whether or not a Au atom was in first shell of nearest neighbor metal ions. In the limit of low Au content, this lattice model is expected to represent well the geometrical and energetical features of the interstitial network visited by H during its diffusion.[20,21]

To estimate relative values of the H solubility, we used

$$\exp\left(-\frac{\mu_H^{\text{alloy}}-\mu_H^{\text{Pd}}}{k_BT}\right)=\frac{\mathcal{Z}_{\text{alloy}}}{\mathcal{Z}_{\text{Pd}}}\cong\frac{\sum_i e^{-\epsilon_i^{\text{alloy}}/k_BT}}{\sum_i e^{-\epsilon_i^{\text{Pd}}/k_BT}}, \quad (1)$$

where μ_H and $\mathcal{Z}$ are the chemical potential and partition function of H in the metallic systems and ϵ_i are the site energies of the lattice model representation of the interstitial network in the metals. In the right side of Eq. (1), entropy and volume changes of μ_H^{alloy} induced by Au substitutions are considered negligible.[22]

We used Eq. (1) to calculate the change relative to pure Pd of the solubility of H in Au_x Pd_{1-x} alloys with $x \leq 0.12$

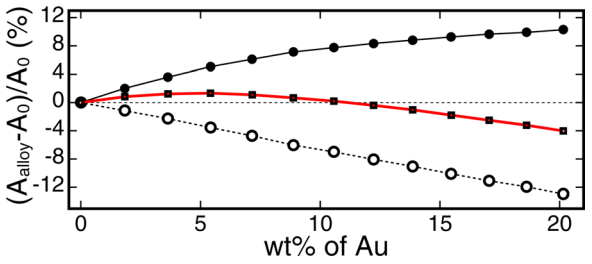

FIG. 3. (Color online) Relative percent values of the diffusion (discs), solubility (circles), and permeability (squares) coefficients of H in PdAu alloys vs. Au content, as obtained from lattice model and Monte-Carlo calculations. The coefficients for the alloy, A_{alloy}, are referred to those obtained for a pure and perfect Pd crystal, A_0. Diffusion and solubility values are calculated independently; their product gives the permeability coefficient. Lines are guides to the eye.

(20 wt% Au). In parallel, we used Monte Carlo simulations to calculate the change relative to pure Pd of the diffusion coefficient of H in the same alloys. Monte-Carlo steps consisted of either O_h–T_d or T_d–O_h elementary moves, and statistical occurrence was calculated according to transition state theory by accounting for the overall energy cost of the migration step, that is, crossing the M point and reaching a new solubility site. The diffusion coefficient was calculated via the Einstein relation. Values of permeability were obtained as product of the solubility and diffusion coefficients (Fig. 3).

Lattice model calculations at 300 K show that the diffusivity of H in dilute PdAu alloys is larger than in pure Pd (Fig. 3). The O_h solubility sites in close proximity of isolated Au substitutions raise in energy, creating spatial regions of nearly constant energy that can be accessed and rapidly crossed as frequently as in Pd (Fig. 2). According to our calculations, the competition between the decreasing solubility and increasing diffusivity leads to a maximum in the permeability at about 5 wt% Au ($x = 0.03$), where it attains a value 1.33 times larger than that in pure Pd. At higher Au content, changes in the solubility dominate, causing the permeability to drop. This behavior of the permeability of H in PdAu alloys depends on temperature. At 400 K, for instance, Monte-Carlo calculations show that solubility dominates over diffusivity at all compositions, leading to a monotonically decreasing permeability. These results are in agreement with recent experiments on the diffusivity and permeability of H in dilute PdAu alloys.[9]

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