

## Interaction between hydrogen and the alloying atom in palladium

Y. J. Li,<sup>1,2</sup> S. E. Kulkova,<sup>3</sup> Q. M. Hu,<sup>1,\*</sup> D. I. Bazhanov,<sup>4</sup> D. S. Xu,<sup>5</sup> Y. L. Hao,<sup>1</sup> and R. Yang<sup>1</sup>

<sup>1</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

<sup>2</sup>Shenyang Pharmaceutical University, 103 Wenhua Road, Shenyang 110006, China

<sup>3</sup>Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Science, 2/1 Akademicheskoy, Tomsk 634021, Russia

<sup>4</sup>Faculty of Physics, Moscow State University, 1-2 Lenin Hills, Moscow 119992, Russia

<sup>5</sup>Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

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The interaction energies between interstitial hydrogen and 3*d*- as well as 4*d*-alloying atoms in Pd were calculated by the use of a first-principles plane-wave pseudopotential method. The calculation results show that almost all the considered alloying atoms are repulsive to hydrogen. For the interaction between H and a noble metal alloying atom that binds weakly to the host atom relative to the host atom itself, the traditional elastic model, proposed in the literature to address the interaction between the substitutional and interstitial atoms in metals, works well. However, for the transition metal atom which binds strongly to the host atom, the interaction energy cannot be explained by the traditional chemical/elastic models. We considered that this failure is due to the absence of binding between the alloying and host atoms. We proposed that, for these transition metal alloying atoms, the interaction energy is controlled by a mechanism similar to Miedema's "reverse stability" rule, i.e., the larger the binding energy of the alloys, the stronger the repulsion between the alloying atom and H. The calculated interaction energies were compared to the available experimental information.

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### I. INTRODUCTION

Hydrogen in metals has been the subject of wide and universal importance for about a hundred years, and remains interesting today. Traditionally, the main concern in this area is to improve the solubility of hydrogen in metals since the formation of brittle metal hydrides deteriorates the mechanical properties of metals as structural materials (e.g., Refs. 1 and 2). Although metal hydrides are harmful to the mechanical properties of metals, some of them have drawn much attention as potential hydrogen storage materials to provide clean energy (e.g., Ref. 3) or some other interesting properties (for example, superconductivity<sup>4</sup>). In both cases, alloying effects are particularly important issues: for structural materials, the addition of alloying elements may suppress the formation of metal hydrides so as to improve the mechanical properties, and for the hydrogen storage metal hydrides, alloying elements may be able to improve the kinetics of the hydrogenation and dehydrogenation process.

Although Pd-H system seems to be no longer regarded as a practical hydrogen storage material, there are still some phenomena in this system of scientific interests. Avdyukhina *et al.*<sup>5,6</sup> found that, during the dehydrogenation process, non-monotonic discrete structure evolution takes place in non-equilibrium Pd-based alloys. They suggested that this phenomenon is due to the formation of the alloying atom-H-defect complexes in the alloys.<sup>5,6</sup> To verify this suggestion, knowledge of the interaction between H and alloying atoms is essential.

The interaction between interstitial impurities (e.g., H and O) and substitutional alloying atoms in metals have been investigated both experimentally and theoretically.<sup>7-17</sup> It was believed that this interaction was mainly ascribed to two

effects.<sup>9,16,17</sup> (a) Elastic interaction: undersized alloying atoms are attractive to interstitial impurities since they may release the strain field induced by the insertion of the interstitial impurities into the host, (b) Chemical interaction: substitutional alloying atoms with a higher chemical affinity for the interstitial impurity than the host element are attractive to the interstitial impurity. It was shown in previous investigations that these models explain successfully the trend of the interaction energies between transition metal (TM) alloying atoms and H in the tetrahedral interstice of  $\alpha$ -Ti,<sup>17</sup> as well as the interaction energy between the alloying atoms and O in Nb and V.<sup>9</sup>

The purpose of the current work is to investigate systematically the interaction energy between hydrogen (both in tetrahedral and octahedral interstices) and the alloying atoms, including most of the elements in the fourth and fifth row of the periodic table, in Pd by the use of first-principles methods. We will show in this paper that both models introduced above cannot describe successfully the interaction energy between H and the transition metal alloying atom that binds strongly to the host atom relative to the host atom itself. Instead, we suggest that the trend of the interaction energy with respect to these alloying atoms is controlled by a mechanism similar to Miedema's "reverse stability" rule<sup>18</sup> for the Pd alloys with transition metal alloying elements. For the alloys with noble metal alloying atom that binds weakly to the host atom, the traditional elastic model based on atomic size effect is still responsible.

The paper is arranged as follows. The method we used and calculation details are described in Sec. II. In Sec. III, we will present the interaction energies and the mechanism underlying the interaction will be discussed. Finally, we summarize our main results in Sec. IV.

## II. METHODS AND CALCULATION DETAILS

In this paper, we use the same expression as that in Ref. 17 to evaluate the interaction energy between the alloying atom and H, i.e.,

$$\Delta E_{M-H} = [E_{M-H}(N) + E(N)] - [E_M(N) + E_H(N)] \quad (1)$$

with  $N$  denoting the number of the lattice sites in the supercell.  $E_{M-H}(N)$  is the total energy of the supercell with both a substitutional alloying atom  $M$  and an interstitial hydrogen atom.  $E(N)$  is the total energy of the perfect supercell.  $E_M(N)$  and  $E_H(N)$  are the total energies of the supercells with one alloying atom and one interstitial hydrogen atom, respectively. Here, we adopt a quite large supercell with 32 lattice sites ( $N=32$ ). Therefore, the effect of the volume optimization on the interaction energy may not be very significant, and the optimization of the atomic positions in the supercell is enough to yield reliable results. So, if not specified explicitly, all of our calculations are performed with only the optimization of the atomic positions. The lattice constants of all the supercells are set as the theoretical equilibrium value of the pure Pd except for the full relaxation calculations (i.e., with both volume and atomic position optimizations). The alloying atoms involved in this study include most of the 3d- and 4d-transition and noble metal elements in the periodic table.

The total energies of the supercells are calculated by the use of a first principles plane-wave pseudopotential method based on density functional theory (DFT), implemented as CASTEP.<sup>19,20</sup> The ultrasoft pseudopotentials<sup>21</sup> represented in reciprocal space are used for all elements involved in this work. All of the calculations are non-spin-polarized so that the magnetic effect is not taken into account. The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof<sup>22</sup> is adopted for the electronic exchange-correlation potential. The plane-wave cutoff energy and the Monkhorst-Pack  $k$  point sampling have been carefully tested, and finally we chose the optimized cutoff energy of 400 eV and  $7 \times 7 \times 7$  grids for the  $k$  point mesh in order to achieve a compromise between the accuracy of the calculation and the computational effort. The atomic positions are optimized by the use of BFGS minimization scheme<sup>23</sup> with tolerances of  $1 \times 10^{-5}$  eV/atom for the total energy, 0.05 eV/Å for the atomic force, and 0.001 Å for the interatomic distance.

## III. RESULTS AND DISCUSSION

### A. Interaction between alloying atoms and H

Figures 1 and 2 show the interaction energies between 3d as well as 4d atoms and H in the interstice nearest to the alloying atom, respectively. The trends of the interaction energy for both 3d- and 4d-alloying atoms are similar. Most of the alloying atoms (except for Ni with H in the tetrahedral site) are repulsive to H, regardless of the site occupation of the H. The repulsion between most of the alloying atoms (with exceptions of Fe, Co, Ni, and Cu) and tetrahedral-H is stronger than that for octahedral-H. Here, we relax only the positions of the atoms in the supercells while the lattice parameters are fixed. To check if this geometry optimization

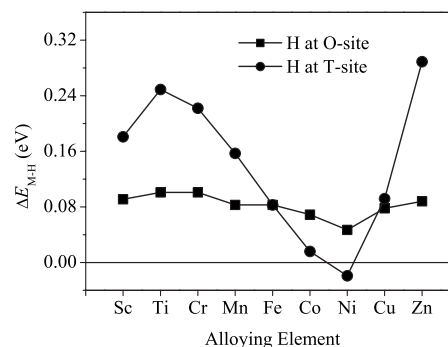


FIG. 1. Interaction energy between 3d-alloying atom and H at octahedral (square symbol) and tetrahedral (circle) interstices.

scheme yields reliable interaction energy or not, we have also calculated the interaction energy between H and Zr, Nb, Ru, as well as Ag with full relaxation of the supercells, denoted by the open square in Fig. 2. As can be seen in the figure, this scheme does not change the interaction energy significantly.

### B. Mechanism of the interaction

Since the trend of the interaction energy between 3d-alloying atoms and H is very similar to that between 4d atoms and H, for the sake of conciseness, we discuss only the mechanism underlying the interaction between the 4d atoms and H in this section. However, the mechanism should also be applicable to the interaction between 3d atoms and H.

As mentioned in Sec. I, the interaction between interstitial impurity and substitutional alloying atoms was believed attributable mainly to two effects:<sup>9,16,17</sup> chemical and elastic interactions. As far as the chemical interaction is concerned, it is easy to understand that the substitutional alloying elements with higher affinity for H than the host Pd will be attractive to H. For the elastic interaction, it was suggested that undersized alloying atoms, i.e., those alloying atoms with smaller atomic radius than the host atom, cause contraction of the lattice, whereas a hydrogen atom dissolved interstitially expands the lattice. Both contraction and expansion

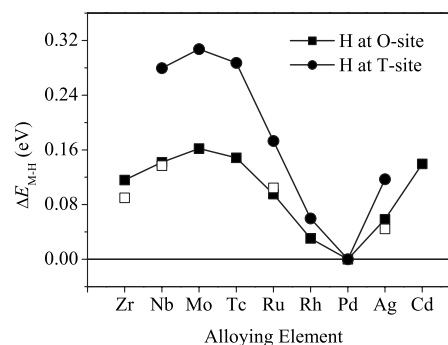


FIG. 2. Interaction energy between 4d-alloying atom and H at octahedral (square symbol) and tetrahedral (circle) interstices. The open squares represent the interaction energies between O-site-H and alloying atoms calculated with full relaxation of the supercells.

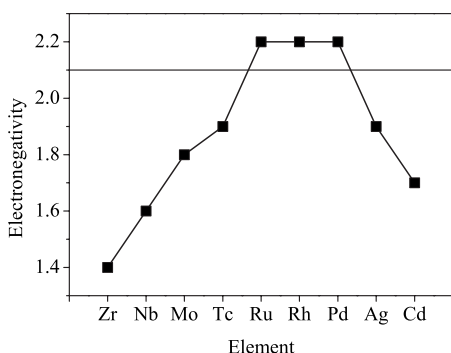


FIG. 3. Electronegativity of the 4d elements, in comparison with that of H (denoted by the line), from Ref. 24.

of the lattice weaken the bonding between the host atoms, and therefore raise the energy of the host. However, the internal strain may be cancelled to a certain extent by the association of the alloying and hydrogen atoms, which rebuild a “favorite” bonding between the host atoms. It was proposed that, because the strain relaxation is more efficient as a hydrogen atom comes closer to an alloying atom, the strain relaxation in effect gives rise to a strong attractive interaction between undersized alloying and hydrogen atoms. However, as we will discuss below, none of the above mechanisms fully explains the trend of the interaction energy between alloying and H atoms obtained in the current work.

Although it is difficult to find a quantitative measure for the H affinity to the alloying element, two quantities, namely, the electronegativity and the heat of formation of the hydride, may provide good approximations. Figure 3 shows the electronegativity of the 4d elements and H. The difference in electronegativity between H and the 4d decreases from Zr to Ru.<sup>24</sup> The electronegativity of Ru, Rh, and Pd are very similar. Therefore, one may expect that the chemical affinity between H and the 4d elements should become weaker gradually from Zr to Ru, whereas the affinity for H of Ru and Rh is similar to Pd. This is also true if we examine the trend of the heat of formation of the 4d-metal hydrides, calculated by Smithson *et al.*,<sup>25</sup> which shows that the heat of formation increases from Zr to Ru and only drops slightly from Ru to Pd.<sup>26</sup> According to the chemical interaction mechanism mentioned in the previous paragraph, the stronger affinity of the 4d-transition elements for H than that of Pd implies that the 4d-alloying atoms should be attractive to H in Pd, and the strength of the attraction decreases from Zr to Ru, which is in disagreement with the repulsive interaction shown in Fig. 2.

Now let us consider the elastic interaction. Figure 4 presents the bond length between Pd atoms nearest to the alloying atoms in Pd-M system relative to that in unalloyed Pd (this parameter roughly represents the strain field induced by the alloying atom) as well as the atomic radius of the alloying atom relative to that of Pd. It can be seen that, the oversized noble metal alloying elements Ag and Cd expand the host lattice, consistent with the repulsive interaction between these alloying atoms and H according to the elastic interaction mechanism described at the beginning of this section. However, for the transition metal elements, the situation is

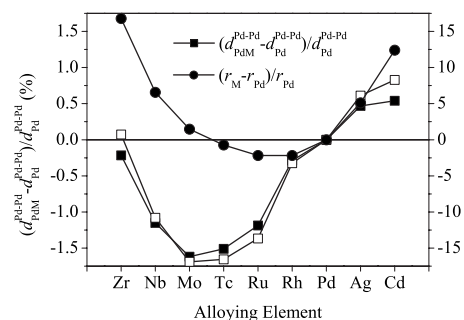


FIG. 4. Bond length between Pd atoms nearest to the alloying atoms in Pd-M system relative to that in unalloyed Pd (square) and the atomic radius of the alloying atom relative to that of Pd (circle). The open squares represent the relative bond length calculated with full relaxation of the supercells.

different. The oversized alloying atoms such as Zr, Nb, and Mo actually decrease the bond length between the nearby Pd atoms. The reduction of the bond length by the oversized alloying atom may be due to the strong binding between the alloying and host atoms. As seen from Fig. 5, the Pd alloys with transition metal elements are of larger binding energies than the unalloyed Pd, in accordance with the experimental binding energy of the alloying atoms in elemental state.<sup>24</sup> In fact the variation of the bond length shown in Fig. 4 provides a more direct description of the strain field induced by the alloying atoms. According to the elastic interaction mechanism described previously, the alloying atoms (Zr, Nb, Mo, Tc, etc.) that reduce the bond length between the Pd atoms should be attractive to H, in disagreement with the interaction energy for these alloying atoms calculated in the current work.

In the above elastic interaction mechanism, the unalloyed host crystal is treated as a reference in considering the alloying and H-dissolving effects, whereas the contribution of the alloying to the energetics of the system is neglected. Namely, one considered only the association effect of alloying and H dissolving on the binding between the host atoms, but did not take into account the effect of H dissolving on the binding between the alloying and host atoms. This simplified model

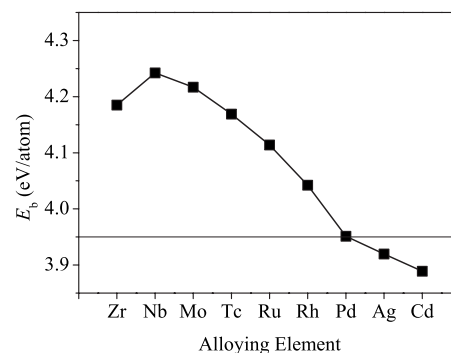


FIG. 5. Binding energy ( $E_b$ ) of the Pd-M alloys. The difference of the binding energies between the calculations with full relaxation (not shown in the figure) and atomic position relaxation only is no more than 10 meV.

works well for the Pd alloys with noble metal alloying elements Ag and Cd since they bind weakly to Pd compared to the binding between Pd atoms (see Fig. 5). However, for the transition-metal alloying elements, the contribution from the strong binding between the alloying and host atoms may not be negligible. To include this contribution, it is more reasonable to take the Pd-*M* alloy as the reference, and then probe the H-dissolving effect. It can be expected that, the lower the binding energy of the Pd-*M* alloy, the larger the energy loss induced by the lattice expansion due to H dissolving. This effect is similar to the Miedema's "reverse stability" rule<sup>18</sup> on the formation of hydride, i.e., the more stable the metallic alloy, the less stable is its hydride. As shown in Fig. 5, the binding energy of the Pd-*M* alloy decreases from Zr to Pd, indicating that Pd alloyed with a transition metal element is more stable than the unalloyed one. Applying the "reverse stability" rule, the energy loss due to the H dissolving for the Pd alloyed with a transition metal element is higher than that for the unalloyed Pd. The closer the H atom is to the alloying atoms, the more significant this effect becomes. This mechanism explains the repulsive interaction between the transition metal alloying atoms and H in Pd, and the stronger repulsion for H in tetrahedral interstice than that for H in octahedral interstice.

It is interesting to note that the traditional elastic mechanism works well for the interaction between alloying atoms and H in Ti (Ref. 17) but not for that in Pd. We consider that the reason for the different *M*-H interaction mechanism in Ti than that in Pd is that the Ti-*M* binding is not stronger than the Ti-Ti binding, in contrast to the case of Pd where Pd-*M* binding is stronger than that of the Pd-Pd (see Fig. 5). As implicated previously in this paper, for the alloying atoms that bind weakly to the host atom relative to the host atom itself, the traditional elastic model without considering the binding between the host and alloying atoms is still valid (as shown by the Ag-H and Cd-H interactions in Pd). This is indeed the case for the interaction between alloying atoms and H in Ti. The binding energy of pure Ti (4.86 eV) is larger than that of the other pure 3*d* metals (for example, 3.93 for Sc, 4.10 for Cr, 2.98 for Mn, 4.29 eV for Fe, 4.39 for Co, 4.44 for Ni, 3.50 for Cu, and 1.35 for Zn) except for V (5.30 eV). Approximately, one may expect that the binding between Ti and other 3*d*-alloying atoms is not stronger than that between Ti atoms. Similar to the Ag-H and Cd-H interactions in Pd, the *M*-H interaction in Ti is determined by the association of the H and alloying atom induced strain energies of the host so that the traditional elastic model works fine.

### C. Comparison with experiments

Experimentally, the interaction energy between the alloying atom and H can be roughly estimated by comparing the diffusivity data of H in the pure and alloyed Pd. The electrolytic measurements of Yoshihara and McLellan<sup>11</sup> have shown that the addition of Fe, Co, Mn, Cr, Ni, or Nb decreases the diffusion rate and increases the effective activation energy,

indicating that these alloying atoms should provide traps for H. Therefore, the interaction between these alloying atoms and H should be attractive, in disagreement with the repulsive interaction between the alloying atoms and its nearest neighbor H obtained in the present calculation. To account for this discrepancy, an immediate idea is to check if the second nearest interstice can be a trap for H. We have calculated the interaction energies between Nb as well as Mo and H at their second nearest neighbor interstice. However, the interaction energies are about 0.03 eV for both Nb and Mo, indicating that the interactions are still weakly repulsive. Concerning the discrepancy between the experimental information and our calculations, we would like to emphasize that the experimental interaction energy between the alloying atom and H was obtained by an empirical fit of the diffusivity data that can be easily interfered by many other factors (e.g., dislocations, phase structure, vacancies) apart from the alloying effect. Instead, our theoretical modelling provides a well-defined framework for describing the interaction that excludes the influence of other factors.

In spite of the discrepancy between the theoretical and experimental H-alloying atom interaction energies, the absorption energy of H in pure Pd calculated in the current work is in good agreement with other theoretical and experimental results. Here, the absorption energy is defined as  $E_{\text{ab}} = -[E(\text{Pd}_n\text{H}) - E(n\text{Pd}) - \frac{1}{2}E(\text{H}_2)]$  with  $E(\text{Pd}_n\text{H})$  and  $E(n\text{Pd})$  being the total energies of the *n*-site Pd supercell with and without H atom, respectively, and  $E(\text{H}_2)$  the total energy of a hydrogen molecule. The H absorption energy for diluted Pd-H system (Pd<sub>32</sub>H in our case) calculated in the present work is -0.13 eV, in comparison with the values from self-consistent total energy calculations within effective-medium theory (-0.12 eV for Pd<sub>27</sub>H) (Ref. 27) and from the experiment (-0.10 eV).<sup>28</sup>

## IV. CONCLUSIONS

In conclusion, we have calculated the interaction energy between alloying atoms and interstitial H in Pd using a first-principles method. Almost all of the alloying atoms considered are repulsive to H. The trend of the interaction energy can be roughly explained by a mechanism similar to the Miedema's "reverse stability" rule for Pd alloys with transition metal alloying elements whereas the traditional elastic model works well for the alloys with noble metal alloying elements.

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\*qmhu@imr.ac.cn

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