First-Principles Study of Superabundant Vacancy Formation in Metal Hydrides

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Abstract: Recent experiments have established the generality of superabundant vacancies (SAV) formation in metal hydrides. Aiming to elucidate this intriguing phenomenon and to clarify previous interpretations, we employ density-functional theory to investigate atomic mechanisms of SAV formation in fcc hydrides of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. We have found that upon H insertion, vacancy formation energies reduce substantially. This is consistent with experimental suggestions. We demonstrate that the entropy effect, which has been proposed to explain SAV formation, is not the main cause. Instead, it is the drastic change of electronic structure induced by the H in the SAV hydrides, which is to a large extent responsible. Interesting trends in systems investigated are also found: ideal hydrides of 5d metals and noble metals are unstable compared to the corresponding pure metals, but the SAV hydrides are more stable than the corresponding ideal hydrides, whereas opposite results exist in the cases of Ni, Rh, and Pd. These trends of stabilities of the SAV hydrides are discussed in detail and a general understanding for SAV formation is provided. Finally, we propose an alternative reaction pathway to generate a SAV hydride from a metal alloy.

Despite receiving considerable attention, detailed mechanisms of SAV formation remain elusive. It had been known from early studies of plasmas-wall interaction in fusion reactors that implanted H isotopes can be trapped by implantation-induced vacancies.11,12 This interesting finding has been investigated with effective-medium theory (EMT), and rather large binding energies of H to vacancies have been reported.13,14 It was on the basis of this knowledge that Fukai et al. suggested the origin of SAV formation to be the lowering of the formation energy of a vacancy by trapping H atoms on its neighboring interstitial sites.15 However, the accuracy and validity of the conclusions from EMT calculations have been questioned by recent first-principles density functional theory (DFT) studies on some H-vacancy complexes.16 Another mechanism based on entropy effects has also been proposed to explain the SAV formation: an increase of the configurational entropy due to creation of metal vacancies should favor the SAV formation.17 A recent calculation with cluster models evaluated the configurational entropy change to be \(-2.6 \text{ eV} \) at \(1000 \text{ K} \) from \( \text{Pd}_{4} \text{H}_{4} \) to \( \text{Pd}_{3} \text{VacH}_{4} \), and thus attributed the effect as the origin of the SAV formation. Considering that the vacancy formation energy in

1. Introduction

Superabundant vacancies (SAV) are vacancies of metal atoms formed in metal hydrides, at concentrations as large as nearly 30 at. %. This novel discovery was reported first by Fukai et al. in 1994 in a X-ray diffraction study of the Pd–H system at high temperatures and high hydrogen pressures, where a vacancy-ordered phase of Cu$_2$Au structure (Pd$_3$VacH$_2$) was observed.1 Since then, similar observations were made on many fcc hydrides of Ni, Rh, Pt, and Au and others,2–7 and the H-induced SAV formation has now become a quite general phenomenon in metal hydrides. SAV formation has many important technological as well as scientific implications. For example, metal hydrides are regarded as a source of hydrogen for portable fuel cells,8,9 and solubility of hydrogen can certainly be benefited from SAV formation; SAV structures are often observed. 1 Since then, similar observations were made on many fcc hydrides of Ni, Rh, Pt, and Au and others,2–7 and the H-induced SAV formation has now become a quite general phenomenon in metal hydrides. SAV formation has many important technological as well as scientific implications. For example, metal hydrides are regarded as a source of hydrogen for portable fuel cells,8,9 and solubility of hydrogen can certainly be benefited from SAV formation; SAV structures are often observed.

pure Pd is \(~1.6\ \text{eV},^{19}\) the reported entropy effect seems to be surprisingly large. In fact, by repeating the calculations used to evaluate the entropy change, we find that the actual value is about 10 times smaller than that reported. Therefore, their conclusion may be inappropriate.

In the present study, we employ first-principles DFT techniques using the supercell method with periodic boundary conditions. The reliability of such approaches to describe metal hydride systems has been verified in recent studies.\(^{20-22}\) Our central objective is to clarify the SAV formation mechanisms, and to elucidate the generality of this intriguing phenomenon. To this end, we study a number of hydrides of fcc metals including Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. Since the vacancy-ordered phase was reported experimentally to be the CuAu type,\(^1\) we chose all the SAV structures to be the same type. The structures of ideal and SAV hydrides are schematically shown in Figure 1. We have also examined the validity of this model in a larger unit cell (i.e., 32-metal atom cell), which will be discussed later. To illustrate the stability of the SAV structures, we compare in detail the energetics between the SAV hydrides and the ideal hydrides and the pure metals. Several effects, including zero-point energies, entropy effects and chemical potential of hydrogen are also taken into account. Aiming to shed light on the origin and the trend of SAV formation in the systems studied, detailed electronic structures of pure metals (M\(_4\)), defective metals (M\(_3\)Vac), ideal hydrides (M\(_4\)H\(_4\)), and SAV hydrides (M\(_3\)VacH\(_4\)) are presented and analyzed. As a side product, we also propose an alternative pathway to generate SAV in hydrides by alloying metals with the understanding accumulated from First-principles studies. The rest of the paper is organized as follows. In section 2, calculation details are outlined. Following this, the validity of our models is discussed by examining the configurations and energetics in large unit cells. In subsection 3.1, the calculated vacancy formation energies, cohesive energies, heats of formation of hydrides, etc are presented, and effects from zero-point energy, entropy and hydrogen chemical potential are discussed in subsection 3.2. In subsection 3.3, we carry out detailed electronic structure analyses. An attempt to generate a SAV hydride from an alloy is considered in subsection 3.4. Finally, our conclusions are summarized in the last section.

1. Superabundant Vacancy Formation in Metal Hydrides

2. Calculation Details

All calculations were performed using the plane-wave pseudopotential implementation of density-functional theory.\(^{23}\) Exchange and correlation were treated within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).\(^{24}\) The ionic cores were described by ultrasoft pseudopotentials,\(^{25}\) which improve transferability and reduce the number of plane waves required in the expansion of the Kohn–Sham orbitals. The cutoff energy for the plane-wave expansion was set to be 400 eV, sufficiently high to give well-converged total energies and structures. The maximum k-point spacing used was no greater than 0.02 Å\(^{-1}\), corresponding to a 12 \times 12 \times 12 (or 8 \times 8 \times 8) k-point mesh for a cubic supercell containing four (or 32) metal atoms. All structures including both cell parameters and the ionic positions were fully optimized so as to obtain the minimum total energies. The effect of spin polarization was also included throughout. With this setup, total energies in our calculations are converged to within \(~0.01\ \text{eV}.\) Our calculations reproduce accurately lattice constants\(^{26}\) and bulk moduli\(^{27}\) for all the metal systems studied, as shown in Table 1. The calculated lattice constants of metal hydride also compare well with experiments available, for example, in the cases of Ni and Pd hydrides, the calculated ones are 3.74 and 4.08 Å, very close to the experimental ones 3.72 Å\(^2\) and 4.09 Å,\(^30\) respectively. Also as expected, the insertion of H in metal leads to lattice expansion; and creation of metal vacancies leads to lattice contraction.

3. Results and Discussion

Before presenting our calculation results, it is worth discussing the supercell model chosen in this work. Our choice of the Cu–Au-type structure was motivated by the experimental findings of such a vacancy-ordered phase.\(^{1,5}\) However, in such structures, the H atoms are constrained by symmetry and will remain in the ideal octahedral sites upon relaxation. Therefore, it would be interesting to examine the effects of atomic relaxation around vacancies and also the possibilities of existence of other SAV structures. For these purposes, we have tested structures of the ideal hydride and a number of ordered SAV hydrides in a larger unit cell of Pd (i.e., 32 metal atoms in the ideal cases). More disordered configurations are likely to be energetically unfavorable and thus not considered. The ideal hydride is schematically shown in Figure 2a. For the generation of the SAV structures, we considered first all the possible configurations of two metal vacancies in a 2 \times 1 \times 1 supercell (i.e., vacancies are nearest-

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### Table 1. Equilibrium Lattice Constants \(a\) (Å) and Bulk Moduli \(B_0\) (GPa)

<table>
<thead>
<tr>
<th>Element</th>
<th>(a) (\text{calcd. (M(_4))})</th>
<th>(a) (\text{calcd. (M(_3)Vac)})</th>
<th>(B_0) (\text{calcd. (M(_4)H(_4))})</th>
<th>(B_0) (\text{calcd. (M(_3)VacH(_4))})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>3.53</td>
<td>3.40</td>
<td>202</td>
<td>186</td>
</tr>
<tr>
<td>Cu</td>
<td>3.60</td>
<td>3.46</td>
<td>147</td>
<td>137</td>
</tr>
<tr>
<td>Rh</td>
<td>3.84</td>
<td>3.80</td>
<td>271</td>
<td>270</td>
</tr>
<tr>
<td>Pd</td>
<td>3.90</td>
<td>3.75</td>
<td>209</td>
<td>181</td>
</tr>
<tr>
<td>Ag</td>
<td>4.11</td>
<td>3.96</td>
<td>108</td>
<td>101</td>
</tr>
<tr>
<td>Ir</td>
<td>3.85</td>
<td>3.71</td>
<td>341</td>
<td>355</td>
</tr>
<tr>
<td>Pt</td>
<td>3.96</td>
<td>3.80</td>
<td>269</td>
<td>278</td>
</tr>
<tr>
<td>Au</td>
<td>4.15</td>
<td>3.98</td>
<td>147</td>
<td>173</td>
</tr>
</tbody>
</table>

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neighboring, next-nearest-neighboring and second-nearest-neighboring). We then duplicated these configurations in the $2 \times 2 \times 2$ supercell, and obtained the ordered SAV hydrides (Figure 2b–f). Note that the structure in Figure 2b is essentially the Cu$_3$Au-type SAV hydride, which is the ideal hydride, and the others are less ordered. In the cases which correspond to the ideal hydride and the ordered Cu$_3$Au-type SAV hydride (Figure 2a,b), we have not found the H atoms to relax away from the ideal octahedral sites, although in the large cell the symmetry constraint was lifted and atomic relaxation could take place. Moreover, the energies per Pd calculated in the large unit cell are almost identical to those in the 4-Pd cell. In the cases which correspond to less ordered vacancy structures (Figure 2c–f), we have found significant relaxation of the H atoms away from the ideal octahedral sites. However, the energies of the less ordered vacancy structures are $0.15 - 0.17$ eV (per Pd) higher than that of the more ordered one (Figure 2b), implying very large vacancy formation energies to form those structures. Therefore, the Cu$_3$Au-type structure is indeed the most favorable SAV structure, in agreement with the experiments.

3.1. Vacancy Formation Energy, Cohesive Energy and Heat of Formation. To investigate the vacancy formation in hydrides, it is instructive to examine first the vacancy formation energy (denoted as $E_v$) in pure metals. $E_v$ is defined as

$$E_v = E(M_3\text{Vac}) + E(M,\text{bulk}) - E(M_4)$$  \hspace{1cm} (1)

where the terms on the right-hand side refer to the total energies of defective metal, a single metal atom in the bulk and perfect metal, respectively, where all systems have been lattice-relaxed. Since vacancy formation energy is often understood from the cohesive energy (denoted as $E_c$), we also calculate $E_c$, which is the energy required to break the atoms of metals into isolated atomic species

$$E_c = -\frac{1}{4}E(M_4) - 4E(M,\text{isolated})$$  \hspace{1cm} (2)

As listed in Table 2, given the varied experimental conditions for the measurements, our calculated results are found to be in good agreement with the experiments (in parentheses),

<table>
<thead>
<tr>
<th>$E_v$</th>
<th>$E_c$</th>
<th>$\Delta E$</th>
<th>$\Delta H_{\text{ideal}}$</th>
<th>$E_{\text{hydride}}$</th>
<th>$\Delta H_{\text{SAV}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (1.43 - 1.8)</td>
<td>4.78</td>
<td>1.02</td>
<td>-0.13</td>
<td>0.21</td>
<td>-0.08</td>
</tr>
<tr>
<td>Cu (1.99 - 1.42)</td>
<td>3.65</td>
<td>0.91</td>
<td>0.52</td>
<td>-0.56</td>
<td>0.38</td>
</tr>
<tr>
<td>Rh (1.88)</td>
<td>4.15</td>
<td>0.51</td>
<td>-0.16</td>
<td>0.43</td>
<td>-0.06</td>
</tr>
<tr>
<td>Ir (2.40 - 1.31)</td>
<td>6.32</td>
<td>2.00</td>
<td>0.77</td>
<td>-1.77</td>
<td>0.33</td>
</tr>
<tr>
<td>Pt (0.74)</td>
<td>4.92</td>
<td>3.78</td>
<td>0.40</td>
<td>-1.32</td>
<td>0.07</td>
</tr>
<tr>
<td>Au (0.45 - 0.04)</td>
<td>3.03</td>
<td>1.85</td>
<td>1.17</td>
<td>-1.67</td>
<td>0.75</td>
</tr>
</tbody>
</table>

$^a$ Experimental data are in parentheses. All units are in eV. The effect of including ZPE and finite $T$ and $p$ is reported in Table 3. $^b$ Experimental data in brackets are from refs 19 and 31. $^c$ Experimental data in brackets are from ref 32. $^d$ $\Delta E$ is the relaxation energy, defined as the difference between $E_c$ and $3E_v$. $^e$ Experimental data in brackets are from ref 34.

The cohesive energy $E_c$ is relative to a nonspin-polarized atomic state.\(^{33}\) The empirical understanding of $E_v$ in terms of $E_c$ appears to be true in our results of each series of 3$d$, 4$d$, and 5$d$ metals, however, not in same groups. For example, $E_v$ in some 5$d$ metals (Pt or Au) is much larger than $E_c$ in some 4$d$ metals (Pd or Ag), but $E_v$ in the former is significantly smaller than $E_c$ in the latter. The reason for this is because that the
above relation misses an important term, i.e., relaxation of the metal lattice upon creation of vacancies. If the relaxation is significant, the energy loss due to vacancy formation in metals would be largely compensated, and thus the vacancy formation energy would be much smaller than what the simple relation predicts. To evaluate the relaxation energy ($\Delta E$) of the metal lattice, we calculated the differences between $E_v$ and $3E_v$ and summarize them in Table 2. As can be seen that (i) in each series of the 3d, 4d, and 5d metals, the relaxation energies have similar magnitudes, and thus the dominant factor for the difference of $E_v$ among those metals is the difference of $E_v$; (ii) in each of the three metal groups, the 5d metal has the largest relaxation energy, and thus the relaxation in the 5d metal contributes more to compensate the energy loss due to vacancy formation than in the 3d and the 4d metal. In particular, the relaxation energies of Pt and Au are closer to their $E_v$, leading to the smaller $E_v$ than those in Pd and Ag, respectively. The trend of relaxation energies is in fact consistent with the geometrical trend: the contraction of volume of the 5d metal is larger than that of the 3d and 4d metal in each group (Table 1), when going from M$_4$ to M$_{3\,\text{Vac}}$.

We turn now to the metal hydrides. In the most stable structures of ideal hydrides, the H was found to locate at the ideal octahedral sites (Figure 1a). We calculated the enthalpies of formation of the ideal hydrides ($\Delta H_{\text{ideal}}$) at zero pressure as follows

$$\Delta H_{\text{ideal}} = \frac{1}{4}(E(M_4H_4) - E(M_3) - 2E(H_2)) \quad (4)$$

where all energies have been obtained from lattice-relaxed calculations. As listed in Table 2, Ni, Rh, and Pd hydrides have negative formation energies meaning that they are more stable than the corresponding pure metals, whereas all 5d metal hydrides and all group IB metal hydrides are unstable. Our calculated $\Delta H_{\text{ideal}}$ agree in general with the experimental data. However they do not quite match Miedema’s “law of reverse stability”, which states that the more stable the metal (i.e., the larger the $E_v$), the less stable the hydride. Again, like the relation of $E_v$ and $E_v$ as described above, the $\Delta H_{\text{ideal}}$ also cannot be understood solely from the $E_v$. We argue that the explanation neglects the effect of the H insertion: upon H insertion, the newly formed H-metal bonding would certainly contribute to the energy loss of cohesive energies of metals. We will discuss this later in terms of electronic structures.

In the SAV hydrides, the most stable occupation for H was found to be on the interstitial octahedral sites. The SAV formation energy is defined as

$$E_{v,\text{hydride}} = E(M_3\text{Vac}H_4) + E(M_{\text{bulk}}) - E(M_4H_4) \quad (5)$$

where the terms on the right refer to the total energies of the SAV hydride, single metal atom in the ideal bulk and ideal metal hydrides, respectively. The obtained results are also summarized in Table 2. Compared to pure metals, the vacancy formation energies are substantially reduced; in particular, in the cases of all 5d and group IB metals $E_{v,\text{hydride}}$ become negative. Since the vacancy formation energy reflects essentially the relative stabilities of ideal and SAV hydrides (i.e., a negative $E_{v,\text{hydride}}$ means that a SAV hydride is more stable than the corresponding ideal hydride), our calculated results reveal following interesting features. The SAV hydrides of Ni, Rh, and Pd are less stable than their ideal hydrides, whereas the SAV hydrides of all 5d metals and the noble metals are more stable than the ideal ones. Note that the $\Delta H_{\text{ideal}}$ of the ideal hydrides of Ni, Rh, and Pd are negative and those of the 5d and the noble metals are positive. Thus, it appears that if an ideal hydride is unstable compared to its corresponding pure metal, its SAV hydride would be more stable than the ideal hydride, and vice versa. It should be mentioned that similar results also occur in bcc metals, as our preliminary results suggest that the SAV hydrides of group VB metals (V, Nb, Ta) are less stable than the ideal hydrides, and the SAV hydrides of group VB metals (Cr, Mo, W) are more stable than the ideal ones. Bear in mind that the heats of formation of the ideal hydrides in the former are significantly negative whereas those in the latter are significantly positive.

We also consider the relative stabilities of SAV hydrides over pure metals by calculating heats of formation of the SAV hydrides, which are defined as

$$\Delta H_{\text{SAV}} = \frac{1}{4}(E(M_4\text{Vac}H_4) + E(M_{\text{bulk}}) - E(M_4) - 2E(H_2)) \quad (6)$$

It can be seen from Table 2 that the $\Delta H_{\text{SAV}}$ has similar trends as $\Delta H_{\text{ideal}}$: SAV hydrides of Ni, Rh, and Pd are also more stable than pure Ni, Rh, and Pd metals, respectively. Interestingly, the magnitudes of $\Delta H_{\text{SAV}}$ of SAV hydrides of Ni, Rh, and Pd are less negative than those of $\Delta H_{\text{ideal}}$, whereas the magnitudes of $\Delta H_{\text{SAV}}$ of other SAV hydrides are less positive than those of the ideal counterparts, in particular, the SAV hydride of Pt becomes almost as stable as the pure Pt metal. However, although SAV hydrides of Cu, Ag, Au, and Ir are more stable than their ideal counterparts, they are unstable compared to pure metals.

### 3.2. Zero-Point Energy, Entropy Effects and H$_2$ Chemical Potentials

In this section, we discuss several factors affecting the stabilities of SAV hydrides, including zero-point energy (ZPE), entropy, and H$_2$ chemical potentials.

The high temperature ($T$) and pressure ($p$) applied in experiments can affect significantly the H$_2$ chemical potential, and consequently the stabilities of hydrides with respect to the pure systems. Therefore, we first discuss the effect of the H$_2$ chemical potential. In doing so, we replace the total energy of the pure hydride system by the ideal-gas entropy at 1 atm (here we use experimental values from thermodynamic tables). We took $T$ and $p$ as 1000 K and 5 GPa respectively, (which roughly correspond to the experimental conditions), and calculated the heats of formation of ideal and SAV hydrides by using the above equation. As shown in Table 3, both the ideal and the SAV hydrides are destabilized by $\sim$0.29 eV compared to the zero $T$ and $p$ results. This is because, although the high pressure raises the chemical potential of H$_2$, the high temperature lowers it considerably (via

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the $\mu(T,p)$ term) and consequently the overall effect does not favor hydride formation (either the ideal or the SAV hydride).

Note that the chemical potential of H$_2$ is significantly temperature dependent: a use of a lower temperature of 700 K would only destabilize the hydrides by ~0.15 eV, in which case the stabilities of hydrides of some metals (say, Pd) would be significantly different from those at 1000 K. Note too that the vacancy formation energies remain the same as the zero $T$ and $p$ results, because the H$_2$ chemical potential at high $T$ and $p$ exerts same effects on the ideal and SAV hydrides. In other words, the stability of the SAV hydride relative to the ideal hydride is unaffected by the chemical potential of H$_2$.

ZPE is also significant in hydrides due to the light mass of the H atoms. In some cases, ZPE is the dominant factor for determining the most stable interstitial site. Here we calculated ZPE for all the hydride systems within the harmonic approximation. The harmonic modes of H motions were calculated from a finite difference approach. Briefly, the dynamical matrix $D_{ij}$ is obtained by replacing each Cartesian component $x_{cal}$ of each atom $i$ by a finite amount $\pm \delta x_{cal}$, and computing the resulting forces by performing a self-consistent minimization of the total energy functional

$$D_{ij} = \frac{1}{(m_j m_i)^{1/2}} \sum_{\alpha} F_{ij}^{(\alpha)} - F_{ij}^{(\alpha)} \delta x_{cal} \tag{8}$$

where $m_i$ is the mass of atom $i$. Including the ZPE obtained for the ideal hydrides, the SAV hydrides, and the H$_2$, we list the ZPE in the calculation of the heats of formation of ideal and SAV hydrides, and vacancy formation energies in Table 3. As can be seen the ZPE reveals different effects on the ideal and SAV hydrides: ZPE is generally larger in the SAV hydrides than in the ideal hydrides. As a result, the vacancy formation energies including ZPE is more positive than that excluding ZPE. In other words, the ZPE favors the formation of the ideal hydrides.

We approximate the entropy effects as arising mainly from configurational and vibrational contributions. The configurational entropy should favor the SAV formation. This is because that due to formation of metal vacancies, the number of ways to arrange metal atoms to obtain degenerate configurations in SAV hydrides increases, compared to that in ideal hydrides. To evaluate the configurational entropy change from ideal hydrides to SAV structures (denoted as $\Delta S_{\text{config}}$), we first consider the number of ways to arrange $n$ metal atoms in $m$ possible lattice sites, i.e., $C_m^n$, then suppose the vacancy concentration $C_v = (m - n/m)$, and deduce the (ideal, upper-bound) configurational entropy per site as

$$\Delta S_{\text{config}} = -k_B \ln C_v + (1 - C_v) \ln(1 - C_v) \tag{9}$$

At 1000 K the total configurational entropy change is calculated to be 0.19 eV. Note that this value is the same in all the present cases. It should be mentioned that the entropy evaluated here is based on the Cu$_3$Au-type hydrides. In larger unit cell there exists other possible SAV configurations, which need to be taken into account. However, as we showed in the beginning of the discussion, the total energies of those configurations are far too large compared to the Cu$_3$Au-type one and thus it is justified to neglect their contribution to the configurational entropy.

In a previous study, the vibrational entropy of the lattice was approximated as just the Boltzmann constant. Considering the complexity of the systems, this approximation is too simple. In general, the dominant contribution to the vibrational entropy ($S_{\text{vib}}$) comes from low-energy modes, and these are from the acoustic branches of the phonon dispersion curves. Since these are very difficult to calculate from our first-principles approach, we resort to an approximation, namely the Debye model. In three-dimensions ($d = 3$) the Debye vibrational entropy is

$$S_{\text{vib}}(T)/N_{k_B} = d \int_0^\infty \frac{dx}{e^{x} - 1} + d(d + 1)(T/\Theta_D)^d \int_0^{\Theta_D/T} \frac{x^d dx}{e^x - 1} \tag{10}$$

where $\Theta_D$ is the Debye temperature, which physically represents the highest frequency in the acoustic mode spectrum, and mathematically provides the cutoff for integrals over the modes. The Debye temperature is evaluated as

$$\Theta_D = \frac{3}{4\pi} \frac{1}{\sqrt{2}} \frac{k_B}{h} \sqrt{\frac{r_{WS}^2 B}{M}} \tag{11}$$

where $r_{WS}$ is the equilibrium Wigner-Seitz radius, $M$ is the atomic weight, and $B$ is the bulk modulus. This approach has been proved to be quite accurate in recent studies. With this method, we found that the bulk moduli and subsequently the Debye temperatures in SAV hydrides are generally smaller than those in ideal hydrides, and thus $\Delta S_{\text{vib}}$ from ideal to SAV hydrides is positive. In other words, the vibrational contribution also favors the SAV formation. The magnitudes of the $\Delta S_{\text{vib}}$ obtained between ideal and SAV hydrides are within a range from 0.05 to 0.18 eV.

**Table 3.** Compared to the Zero $T$ and $p$ Results, the Effects of the H$_2$ Chemical Potential ($\mu(T,p)$), the Zero-Point Energy ($\Delta(ZPE)$), the Configurational and Vibrational Entropies ($-\Delta S_{\text{ideal}}, -\Delta S_{\text{vib}}$), and the Vacuum Formation Energies ($\Delta E_{\text{v,hydride}}$) for SAV Hydrides.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\mu(T,p)$</th>
<th>$-\Delta S_{\text{ideal}}$</th>
<th>$\Delta(ZPE)$</th>
<th>$-\Delta S_{\text{vib}}$</th>
<th>$\Delta E_{\text{v,hydride}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.29</td>
<td>-0.05</td>
<td>0.00</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu</td>
<td>0.29</td>
<td>-0.04</td>
<td>0.00</td>
<td>0.77</td>
<td>0.08</td>
</tr>
<tr>
<td>Rh</td>
<td>0.29</td>
<td>-0.01</td>
<td>0.04</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Pd</td>
<td>0.29</td>
<td>-0.10</td>
<td>0.02</td>
<td>-0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Ag</td>
<td>0.29</td>
<td>-0.04</td>
<td>0.00</td>
<td>0.94</td>
<td>0.04</td>
</tr>
<tr>
<td>Ir</td>
<td>0.29</td>
<td>-0.11</td>
<td>0.01</td>
<td>0.95</td>
<td>0.04</td>
</tr>
<tr>
<td>Pt</td>
<td>0.29</td>
<td>-0.12</td>
<td>-0.01</td>
<td>0.57</td>
<td>0.05</td>
</tr>
<tr>
<td>Au</td>
<td>0.29</td>
<td>-0.13</td>
<td>0.05</td>
<td>1.38</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*Taking into account all the above effects, the overall results are also summarized. All units are in eV.*
Taking into account all the above effects, we summarize in Table 3 the overall results of \( \Delta H_{\text{ideal}} \), \( E_{\text{hydride}} \), and \( \Delta H_{\text{SAV}} \). We find that all these effects do not alter the main trend obtained at the zero \( T \) and \( p \) calculations, i.e., the substantial reduction of the vacancy formation energies from metals to hydrides. Moreover, the entropy effect, the only effect to facilitate the SAV formation, is small compared to the change of the vacancy formation energies. Therefore, the substantially reduced vacancy formation energies are the main factor in the understanding of the SAV formation, consistent with experimental suggestions. However, there are two points of note from Table 3. First, in the cases of Ni, Rh, and Pd, there exist some energy barriers (although may not significant, say, in the Ni case) for the SAV formation if the reaction were to occur via the ideal hydrides. Thus, we suggest an alternative pathway for the SAV hydride formation, i.e., via the hydrogenation of metals. Although Table 3 shows that the SAV hydrides of Ni, Rh, and Pd are unstable with respect to pure metals, their \( \Delta H_{\text{SAV}} \) would all become negative if a low temperature (say, 700 K) were used in the calculation of the \( H_2 \) chemical potential as we discussed earlier. Therefore, this SAV formation pathway may become feasible at low temperatures, although the kinetic rate constant of the SAV formation becomes small at low temperature. Second, in the cases of other metals, both ideal and SAV hydrides are clearly unstable with respect to their corresponding metals, and thus it becomes more difficult to form SAV although the SAV hydrides are more stable than the ideal hydrides. These results perhaps are consistent with the experimental fact that the findings of SAV formation in fcc metal hydrides were reported mainly in the Ni and Pd cases.

### 3.3. Electronic Structure Analysis

From above results and discussion, the central question in SAV formation mechanism is to understand why the vacancy formation energies reduce substantially from metals to hydrides. On the basis of eqs 1 and 5, the answer must be that the energy of \( E_{\text{M VacH}} - E_{\text{M H}} \) is more negative than that of \( E_{\text{M Vac}} - E_{\text{M}} \), or put it in another way, \( E_{\text{M VacH}} - E_{\text{M Vac}} < E_{\text{M H}} - E_{\text{M}} \). This indicates that the defective metals (M Vac) must be stabilized by the H-metal bonding in M VacH to somewhat greater extents than the ideal metals are stabilized, if at all, by the H-metal bonding in M H. In particular, the differences between \( E_{\text{M VacH}} - E_{\text{M Vac}} \) and \( E_{\text{M H}} - E_{\text{M}} \) should be greater in the cases of 5d and noble metals than those in other cases. To elucidate the origin of these results, we next examine the electronic structures of all the systems involved, i.e., M, M Vac, M H, and M VacH.

In Figure 3 we plot the density of states (DOS) projected onto metal atoms in pure metal systems and ideal hydrides. For the sake of clarity, we only show the DOS projected onto \( d \) orbitals of the metals since contributions of \( d \) orbitals are
dominant in the total DOS. The 1s(H)-s(M), and 1s(H)-p(M) interactions are much smaller than the 1s(H)-d(M) interaction, as illustrated in the top left panel of Figure 3, where the PdH is chosen as an example. In the rest of the Figure, results are arranged in the same order as that of metal positions in the periodic table and in all cases the Fermi levels are zeroed. Let us first consider the DOS in M\textsubscript{4}, which are shown as dashed curves. Our results reproduce the conventional picture of electronic structures of metals (i.e., the Friedel model).\textsuperscript{38} As we move across each series of 3d, 4d, or 5d metals, the Fermi level moves up in the d band and metal is destabilized by the filling of states with antibonding characters. As results, the cohesive energy decreases. Note that the Fermi levels are in fact well above the d-band in the cases of group IB metals, because of fully filled d-bands in those metals. Additionally, the d-bands are narrow compared to group VIII metals. This is because the relatively large nuclear charge in group IB reduces the extent and overlap of the d-bands.

In the DOS of ideal hydrides (solid curves in Figure 3), new features can be seen by comparing with the DOS of pure metals. In the cases of group VIII metal hydrides, significant H-induced $e_g - e_g$ bonding features appear at low energy levels, and the Fermi levels shift downward in hydrides compared to metals. These indicate the H-metal bond formation. Moreover, the second lowest peaks that featured mainly with $t_2g - t_2g$ bonding characters move toward high energy levels compared to metals, reflecting the weakening of the metal–metal bond upon H insertion. Interestingly, the upward movement becomes less significant when moving across the same d series, and more significant when moving down the same group. In other words,

\textbf{Table 4.} Charges of Metals ($e_M$) and $d$ Electron Gains from Metals to Hydrides ($e_d$) in the Cases of Ideal Hydrides and SAV Hydrides

<table>
<thead>
<tr>
<th></th>
<th>Rh</th>
<th>Ir</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Hydrides</td>
<td>$e_M$</td>
<td>+0.24</td>
<td>+0.11</td>
<td>+0.20</td>
<td>+0.12</td>
<td>+0.10</td>
<td>+0.22</td>
<td>+0.25</td>
</tr>
<tr>
<td></td>
<td>$e_d$</td>
<td>-0.13</td>
<td>-0.23</td>
<td>-0.14</td>
<td>-0.12</td>
<td>-0.19</td>
<td>-0.01</td>
<td>0</td>
</tr>
<tr>
<td>SAV hydrides</td>
<td>$e_M$</td>
<td>+0.35</td>
<td>+0.25</td>
<td>+0.30</td>
<td>+0.17</td>
<td>+0.20</td>
<td>+0.32</td>
<td>+0.34</td>
</tr>
<tr>
<td></td>
<td>$e_d$</td>
<td>-0.06</td>
<td>-0.16</td>
<td>-0.11</td>
<td>-0.09</td>
<td>-0.15</td>
<td>+0.05</td>
<td>+0.05</td>
</tr>
</tbody>
</table>

from right to left in the same d series or from the top to bottom in the same group, the metal–metal bond weakening costs more and more energy due to the H insertion. These results coincide well with the trend of formation enthalpies of ideal hydrides. For instance, in the same series, $\Delta H_{\text{ideal}}$(PdH\textsubscript{4}) (or $\Delta H_{\text{ideal}}$(PtH\textsubscript{4})) is more negative than $\Delta H_{\text{ideal}}$(RhH\textsubscript{4}) (or $\Delta H_{\text{ideal}}$(IrH\textsubscript{4})); in the same group, the 5d metal hydrides is the least unstable. In the cases of group IB metals hydrides, there exist somewhat different electronic features from above. First, there are no upward movements of the $t_2g - t_2g$ peaks. This is because that the noble metals have much smaller cohesive energies than others, and thus the relatively less significant weakening of $t_2g - t_2g$ bonding due to H insertion could be easily compensated by the H-metal bonding. Second, there are some H($s$)-metal($e_g$) antibonding states on top of the d bands, for example, between $\sim$ 3 eV to the Fermi level in the case of AuH\textsubscript{4} (Figure 3). Clearly, these antibonding states are responsible for the large positive formation energies of hydrides of noble metals. Note that the similar states also exist in hydrides of group IIIV metals, but they are unoccupied and above the Fermi levels. It is worth mentioning that our results agree well with previously reported electronic structures. For example, in the PdH case, our DOS reproduce the main features reviewed by Gupta and Schlapbach:\textsuperscript{39} the low-lying bonding states have $s$-$e_g$ characters; these states are centered around 7.4 eV; and the metal d-bands are narrowed compared to pure Pd.

More insight can be obtained by examining charge transfer upon hydride formation. In Figure 4 we plot the total electron density difference by subtracting the total electron density in metals (with exactly same structures as those in hydrides but without H) from that in hydrides. Remarkably clear charge accumulations (the red or gray areas in black/white print) in H can be seen in each case, indicating the negatively charged H in hydrides. Moreover, in ease case of group IIIV metals and hydrides there are significant charge depletions on metals (the blue or dark areas in black/white print), which feature with some metal $e_g$ states, and noticeable charge accumulations on metal $t_2g$ states (the red or gray areas in black/white print). This shows that H not only attracts electrons from metals, but also induces electron redistribution within metals themselves. On one hand, the $e_g$ electron loss on metals and the electron gain on H mean the strengthening of metal-H bonds and lowering the energies of systems. On the other hand, the $d$ electron gain in metals means that the electrons must be promoted to the top of d bands, which feature coincidently with $t_2g - t_2g$ antibonding characters (Figure 3), and thus increase the energies of systems. It should be mentioned that a recent LDA study on hydrides of 3d metals also reveal similar features of $d$ electron loss and gain,\textsuperscript{21} although


\textsuperscript{39} Gupta, M.; Schlapbach, L. Topics in Appl. Phys. 1988, 63, 139.
4d and 5d series were not considered. In the present study it is evident from Figure 4 that in Ni, Rh, and Pd cases, the electron losses in metals are large and the electron gains are small, whereas quite opposite results exist in Ir and Pt cases. To further support this, we list in Table 4 charges of metal atoms in hydrides and $d$ electron gains (from $M_4$ to $M_4H_4$) on metal atoms from Mulliken charge analysis. The Mulliken analysis is performed using a projection of the plane-wave states onto a localized basis using the formalism described by Segall et al.40 As can be seen, in Pt and Ir hydrides the metal charges are less positive and the $d$ electron gains are more significant than those in Ni, Pd, and Rh hydrides. These indicate clearly that the hydrides of the 5d metals are less stable than other hydrides. In the cases of group IB metals and hydrides, the $d$-states are filled so that there are only negligible $d$ electron losses and gains from $M_4$ to $M_4H_4$, as also can be seen from Figure 4. Therefore, the bonding between H and these metals is weak.

Next we discuss the DOS of $M_3$ Vac and $M_3$ VacH$_4$, which are shown in Figure 5. Compared to $M_4$, DOS of $M_3$ Vac (dashed curves in Figure 5) reveal some new features due to the vacancy formation. Again, we discuss first the group VIII metals and hydrides. At the lowest energy a small peak emerges (for example, at $\sim 6.5$ eV in the Ir case) and it has $e_g-e_g$ bonding characters. The second lowest peak (for example, at $\sim -5.0$ eV in the Ir case) has mainly some $t_{2g}$ bonding characters and some $t_{2g}$ nonbonding characters. Furthermore, due to vacancy formation the $e_g-e_g$ and particularly the $t_{2g}-t_{2g}$ bonding states in $M_3$ Vac are more localized and are significantly higher in energy than those in $M_4$. This is because that the $t_{2g}-t_{2g}$ bonding is along the metal–metal axis and thus the vacancy formation affects the $t_{2g}-t_{2g}$ states more than it does on the $e_g-e_g$ states. Near the Fermi level, in addition to $t_{2g}-t_{2g}$ antibonding states, $t_{2g}$ nonbonding characters can also be seen. These features have important implications when hydriding the $M_3$ Vac. First, like ideal hydrides, upon H insertion to $M_3$ Vac there are also H($s$)-metal($d$) bonding features and downward movements of the Fermi levels (solid curves in Figure 5). More importantly, more extensive $s-e_g$ bonding is formed in $M_3$ VacH$_4$ than $M_4$ H$_4$, evidenced by the more pronounced peaks. This is due to the more localized $e_g$ states in $M_3$ Vac than in $M_4$, making them more easily to form bonding with H. Second, unlike ideal hydrides, the second low-energy states featured mainly with $t_{2g}-t_{2g}$ bonding and nonbonding characters in SAV hydrides move downward compared to the corresponding metals. This is mainly because that the $t_{2g}$ nonbonding states can form bonding with H($s$) and thus decrease energies of the systems. We also carried out Mulliken charge analyses on $M_3$ Vac and $M_3$ VacH$_4$. As summarized in Table 4, in $M_4$ VacH$_4$ the charge transfers from metals to H are generally more significant than those in $M_4$ H$_4$ indicating the stronger H-metal interaction than in $M_4$ H$_4$. On the other hand, the $d$ electron gain in metals in $M_3$ VacH$_4$ is less significant than in $M_4$ H$_4$.

Moreover, because states at or just below the Fermi levels in M4 VacH4 feature with some nonbonding states, the electrons added to the top of the occupied states do not increase the energy as much as in M4H4. All these indicate that H insertion indeed stabilizes M4 Vac more than it does on M4. Therefore, this is the reason responsible for the reduction of vacancy formation energies in hydrides compared to those in metals. In addition, because 5d metals have more diffuse d states (i.e., lower \( \epsilon_{g} - \epsilon_{e} \)) bonding states than 3d and 4d metals, the metal-H bonding in 5d SAV hydrides should benefit more from the lower energy (metal)-\( \epsilon_{g}(H) \) bonding states than in 3d and 4d ones. On the other hand, due to the much less d electron gain in SAV hydrides than in ideal hydrides and also the presence of many nonbonding states in vacancy systems, the instability caused in the 5d SAV hydrides is greatly reduced and is much closer to the instability caused in 3d and 4d hydrides than those in the ideal cases. Therefore, the reduction of \( E_{v} \) is more significant in the cases of 5d metals than others, as we showed in section 3.

Similar features also exist in the cases of group IB metals, i.e., the appearance of \( \epsilon_{g} - \epsilon_{e} \) bonding states at the lowest energy levels and many nonbonding states. In particular, the \( \epsilon_{g} \) nonbonding states appeared at \(-2.0 \) eV (for example, in the Au case) are available to form bonding with H, as indicated in Figure 5. Note that the similar states also exist in the cases of group IIIV metals, but they are unoccupied and above the Fermi levels. In addition, from Mulliken charge analyses we see that compared to their corresponding metals, the amounts of \( d \) electrons in SAV hydrides of group IB metals actually decrease, meaning more \( d \) electrons are involved in forming bonding with H. Therefore, the vacancy formation energies are significantly reduced in SAV hydrides compared to those in pure metals.

3.4. An Alternative Pathway to form SAV Hydride from Alloy. Among the systems investigated, Palladium metal has long been regarded as an attractive H-storage medium, ever since the discovery in 1886 by Graham.\(^{41}\) Moreover, the first SAV hydride discovery was made on Pd. Thus, it is worth commenting on our results of Pd hydrides. From our calculations, although the Pd SAV hydride could be stable with respect to pure Pd at an appropriate temperature, it is less stable than the ideal hydride implying that an energy barrier must be overcome if the SAV formation were to occur via the ideal hydride. On the other hand, the vacancy formation energies in noble metals and 5d metals are negative, indicating that their SAV hydrides could be easily formed if the ideal hydrides were obtained. Utilizing these results, here we propose a reaction pathway by alloying a noble metal and Pd, leading to an easier route for SAV formation from ideal hydrides. It is worth re-emphasizing that the relative stability between SAV and ideal hydrides (i.e., \( M_{4}H_{4} \rightarrow M_{4}VacH_{4} + M(bulk) \)) is unaffected by the H₂ chemical potential. In other words, a feasible pathway to form SAV hydrides from ideal hydrides is significant because it does not resort to extreme conditions. Here, we chose a Cu and Pd alloy to realize a reaction to generate an SAV hydride. Cu is chosen because it is relatively inexpensive and because ordered Cu-Pd alloys have been reported.\(^{42}\) We have tried different compositions of Cu and Pd, and found that a CuPd₃ alloy may be a good candidate.

As shown schematically in Figure 6, starting from the ideal Pd (the zero energy in the Figure) we have found that the process to generate the ordered CuPd₃ alloy is exothermic with a formation energy of \(-0.30 \) eV. Hydriding the alloy also has an exothermicity of \(0.32 \) eV. There are two alternative pathways to create metal vacancies from the ideal hydride, CuPd₃H₄. As shown in Figure 6, the formation of Pd₃VacH₄ is clearly favored with a formation energy of \(-0.16 \) eV, whereas the reaction to form CuPd₃H₄ is endothermic by \(0.50 \) eV. The more favorable path to form Pd₃ VacH₄ can be understood from the fact that the Cu-\( \rightarrow \)H bond is weaker than Pd-\( \rightarrow \)H bond, as can be seen from Table 2 or 3. In addition, the ideal hydride of CuPd₃ alloy has a heat of formation (per H) of \(-0.08 \) eV, which is significantly more positive than that of Pd₃H₄ (\(-0.35 \) eV). In fact, it is even more positive than the heat of formation of Ni₃H₄ (\(-0.18 \) eV), whose vacancy formation energy is close to zero. From our discussion in above sections: the less stable the ideal hydride, the more stable the SAV hydride, thus, the SAV hydride (Pd₃VacH₄) should be more stable than its corresponding ideal hydride, CuPd₃H₄. For the sake of comparison, the mechanism to form Pd₃VacH₄ directly from pure Pd is also drawn on the left-hand side of the Figure. In all the calculations, the ZPE and entropy effects are included.

4. Conclusions

In this work, we have carried out detailed investigations on the formation of SAV hydrides of a series of fcc transition metals. Some of our key findings and implications are now briefly recapitulated as follows.

1) In agreement with the experimental suggestions, we have found that the vacancy formation energies in metals reduce substantially due to the insertion of H.

2) We have shown that the conventional understanding of vacancy formation energies or the stabilities of hydrides in terms of cohesive energies is incomplete. The lattice relaxation (in the case of pure metals) and H insertion (in the cases of hydrides) need to be taken into account.

3) Although ideal hydrides of 5d metals and noble metals are unstable compared to their corresponding pure metals, the SAV hydrides are found to be more stable than the corresponding ideal hydrides, whereas opposite results exist in the cases of Ni, Rh, and Pd.

4) We have also demonstrated that the previous explanation of the SAV formation mechanism based on the configurational entropy effects is incorrect. The entropy change from ideal

\(^{(41)}\) Graham, T. Proc. R. Soc. 1869, 17, 212.
hydrides to SAV hydrides is not significant enough to alter their relative stabilities, although the entropy effects favor SAV formation.

(5) The electronic structure is shown to be crucial in determining the SAV formation mechanism and the relative stabilities of metal hydrides. We have found that in the two hydriding processes of M₄ and M₃Vac, more electrons are transferred from metals to H and fewer electrons are promoted to the high-energy antibonding states in the latter than in the former. Thus, M₃Vac is stabilized by the H-metal bonding in SAV hydrides to a much greater extent than M₄ is stabilized by the H-metal bonding in ideal hydrides. Consequently, the vacancy formation energy is reduced substantially.

(6) Finally, we have shown that instead of generating a Pd SAV hydride from pure metal, the former may be generated via a more kinetically favorable path from a CuPd₃ alloy.

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