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Density functional calculations on hydrogen in palladium–silver alloys

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Abstract

Periodic bulk calculations based on density functional theory within the generalized gradient approximation (GGA) have been used to calculate properties of the palladium–silver metals and alloys $Pd_{4-n}Ag_n$ ($n = 0$–4) with and without absorbed hydrogen. For each of the metals and alloys, we have calculated the equilibrium lattice constant, the preferred hydrogen absorption site, the absorption energy as a function of hydrogen content (indicating the hydrogen solubility), and the equilibrium lattice constant of the resulting metal hydrides. Most of the results are qualitatively in good correspondence with experimental data, showing that periodic electronic structure calculations like this may be useful in understanding qualitative properties of disordered alloy–hydrogen systems. We are not able, however, to obtain satisfactory results for the cohesive energy and the absorption energy of hydrogen in pure silver. The former is a known failure of the GGA functional that we have used, while the latter could most probably be resolved by lattice relaxation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Density functional theory; Hydrogen absorption; Palladium–silver alloys

1. Introduction

Properties of metals in contact with hydrogen are important in a number of phenomena, including heterogeneous catalysis, membrane purification of hydrogen, and storage of hydrogen in metal hydrides [1–4]. It was early understood that pure metals do not have sufficient flexibility to be useful for all such systems, and the study of alloys and hydrogen has long been an important part of surface science and condensed matter physics [5–7].

Of the palladium alloys, palladium–silver is by far the most studied, with research going all the way back to Graham [8,9]. While palladium rapidly absorbs large amounts of hydrogen at room temperature, hydrogen is practically not soluble in silver. Despite this, the solubility of hydrogen is *larger* in some PdAg alloys than in pure palladium at hydrogen storage conditions – at a pressure of 1 atm and temperatures above 400 K, the hydrogen solubility is largest in alloys with a silver content of 20–40% [9,10]. Understanding why this is so may be important to understand how alloys must be mixed to optimize their hydrogen storing qualities. The permeability of hydrogen in such alloys is also improved (the optimal silver content is then about 23% [11]), and the mechanical properties are better than in pure palladium (embrittlement is avoided because of a lower critical temperature at which the α and α' phases can coexist); PdAg alloys are thus well suited as hydrogen selective membranes [12].

Both palladium, silver, and PdAg alloys form face-centered-cubic (fcc) lattices [10,13]. No short range order has been found in the bulk alloys [7] and periodic calculations might thus seem unsuited to describe the alloys. We believe, however, that many bulk properties, like the lattice constant and the bulk modulus, should be nearly independent of short range order or disorder. It is also possible to describe a wide range of hydrogen absorption sites and transition states in a periodic lattice. We have in this study tried to employ an accurate periodic density functional method to investigate the ability of such methods to describe properties of disordered PdAg alloys; both of the hydrogen free alloys, and of their hydrides.

2. Method

We have performed self-consistent density functional calculations on periodic lattices using ADF-BAND [14,15]. The program has been used to calculate densities

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within both the local density approximation (LDA) and the generalized gradient approximation (GGA); the latter by adding gradient corrections to the electron density calculated from the LDA. Results obtained from the LDA differ qualitatively and quantitatively from both experimental and the GGA results, and are not presented here. We have compared two different GGAs; the Becke–Perdew [16,17] (BP) and Perdew–Wang [18] functionals. They show only minor differences, so we only present results from the BP functional in this study. Both numerical atomic orbitals and Slater type orbitals have been used as basis functions for the variational one-electron states, while the inner electrons are described by the frozen core approximation. Scalar relativistic effects have been included by the zeroth order regular approximation [19].

Convergence tests show that the error of the calculated cohesive energy and absorption energy due to numerical approximations and a finite basis set is at most 50 meV, but for most of the cases the error is well below that. The lattice constants are at worst converged to within 0.05 Å. The relative lattice constants that show the deviation from Vegard's law are converged to about 0.005 Å. All in all, our calculations should yield results very close to the true BP approximation for the systems under consideration.

We have used unit cells consisting of four metal atoms, giving the possibility of constructing two metals and three alloys: $Pd_{4-n}Ag_n$, with $n = 0–4$. Since ADF-BAND does not yet have the ability to calculate forces, all geometry optimization has been done manually; that is by calculating the formation energy for a number of geometries, and then minimizing the energy by a third-order fit function.

3. Cohesive properties of the palladium–silver alloys

The lattice constant has been optimized for the metals and alloys of our study, and the results are shown in the inset of Fig. 1. Also shown in the figure is the experimental lattice constant from Ref. [20]. The lattice constants are found to be overestimated by the GGA, as usual [21,22] for the 4*d* transition metals. The relative errors are less than 2%, and the increase in lattice constant from Pd to Ag is 5.0 and 5.2% for the experimental and calculated data, respectively.

We have further studied the deviation from Vegard's law for the experimental and calculated data. Vegard's law states that the lattice constant of a binary alloy is the linear combination of the lattice constants of the two elements, which would give straight lines in the lattice constant plot. The deviation from this behaviour is shown in the main part of Fig. 1 for both the experimental data [20] and the theoretical results of this study. The fine structure of the experimental curve is of course impossible to reveal with the few theoretical data points of this study, but the qualitative behaviour of the calculated data is still quite good. The quantitative correspondence is comparable to the rigid band model results of Bruno et al. [23]. When they included finite temperature effects in Ref. [24], their results were in even better correspondence with experimental data.

We have also calculated the cohesive energy and the bulk modulus of the metals and alloys, using Murnaghan's equation of state [25,26]. The results are shown in Table 1. They show the same underbinding as above: the bulk

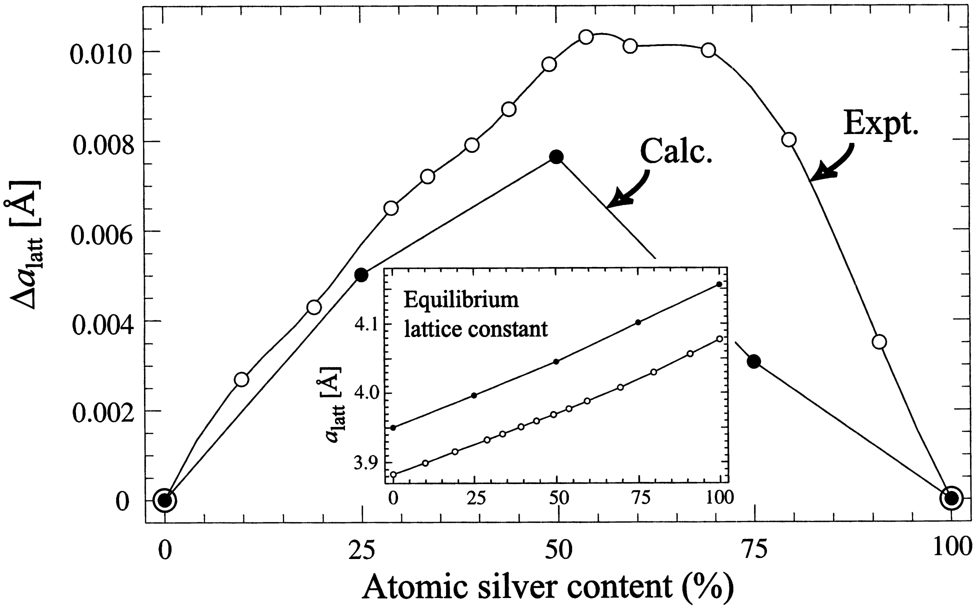

Fig. 1. The deviation Δa_{latt} from linear behaviour of the lattice constant (Vegard's law) of palladium–silver alloys. The inset shows the calculated equilibrium lattice constant a_{latt} of the same alloys. The present calculations (filled circles) are compared to experimental data from Ref. [20] (open circles).

Table 1
The lattice constant a_{latt}, the bulk modulus B_0, and the cohesive energies E_{coh} of the five metals and alloys $Pd_{4-n}Ag_n$ calculated using the BP-GGA, and compared to experimental values

Metal		Pd	Pd_3Ag	Pd_2Ag_2	$PdAg_3$	Ag
a_{lat} [Å]	Calc.	3.950	3.997	4.045	4.101	4.156
	Exp.[a]	3.883	3.926	3.970	4.019	4.077
B_0 [10^{11} Nm^{-2}]	Calc.	1.665	1.394	1.160	1.031	0.943
	Exp.[b]	1.808				1.007
E_{coh} [eV/atom]	Calc.	3.61	3.33	3.04	2.75	2.38
	Exp.[c]	3.89	3.60	3.37	3.16	2.95

[a] Ref. [20] and interpolation from their results.

[b] Ref. [13].

[c] The elements: Ref. [13]. The alloys: calculated from Ref. [13], Ref. [28], and interpolation from the latter.

modulus is 6–8% too low, but follows the experimental values qualitatively. The cohesive energy is also too low, by 8% for Pd and almost 20% for Ag. This is in correspondence with previous calculations on the elements [22,27], and the large discrepancy of silver has been addressed by Philipsen and Baerends [22] as a failure of the BP functional. This also results in faulty qualitative behaviour of the cohesive energy as a function of silver content; the mixing enthalpy (the difference between the cohesive energy of the alloy and of the average of the constituent elements) of the Pd_2Ag_2 alloy is calculated to be positive (45 meV), while the corresponding experimental value is negative (−52 meV) [28].

4. Palladium–silver alloys with hydrogen

The randomness of the palladium–silver alloys might be of larger importance when hydrogen is introduced in the lattice. The occupation of the 4*d* band of palladium is known to increase upon alloying with silver [29–32] and Lu et al. [33] have demonstrated that the local environment is important for the electronic structure of the various lattice sites in a random PdAg alloy. If we restrict ourself to only regard the nearest neighbours of the hydrogen atom, however, we are able to describe most of the possible absorption sites that are present in a randomized alloy by using our five periodic lattices. The fcc lattice contains octahedral sites with six nearest neighbours and tetrahedral sites with four nearest neighbours. We are able to calculate the absorption energy of hydrogen in an octahedral interstitial site with 0, 2, 4, or 6 silver atoms as nearest neighbour, while in the tetrahedral site we can describe all four possibilities; 0, 1, 2, or 3 Ag atoms as nearest neighbour.

We have plotted the absorption energy of a single hydrogen atom in the unit cell as a function of the ratio of silver atoms among the nearest neighbour atoms in Fig. 2. The absorption energy is defined as

$$E_{\mathrm{abs}} = E_{\mathrm{f}}(\mathrm{MH}_x) - E_{\mathrm{f}}(\mathrm{M}) - xE_{\mathrm{f}}(\mathrm{H}) - \frac{x}{2}E_{\mathrm{f}}(\mathrm{H}_2), \qquad (1)$$

where E_{f} is the formation energy as calculated by ADF-BAND. All energies are calculated at zero temperature. Our calculations suggest that the octahedral site is pre-

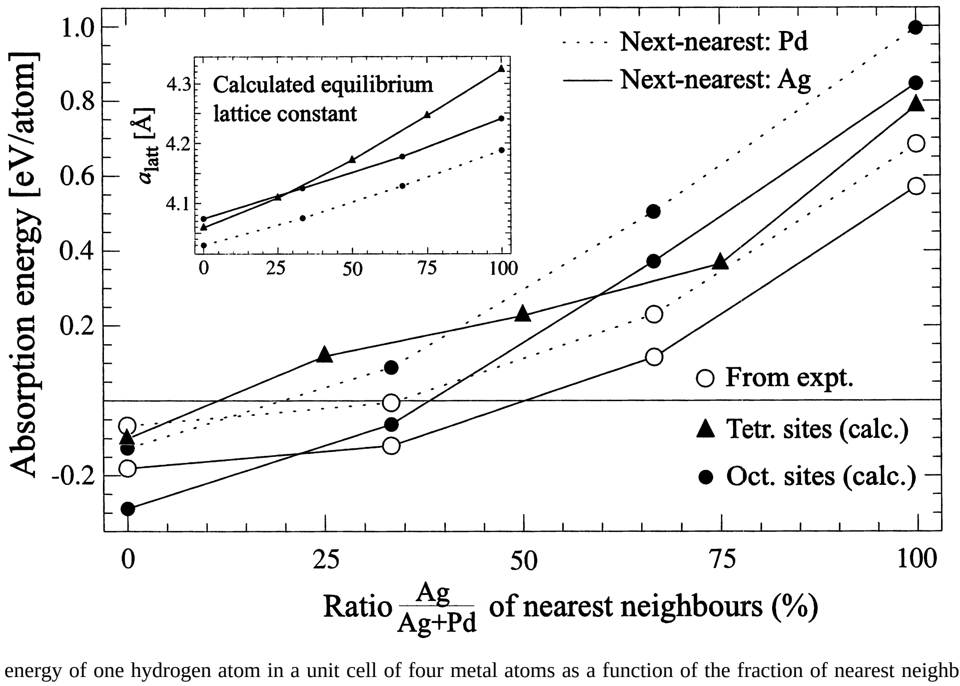

Fig. 2. The absorption energy of one hydrogen atom in a unit cell of four metal atoms as a function of the fraction of nearest neighbour silver atoms. The two curves for the octahedral sites are with palladium and silver as next-nearest neighbours, respectively, and are plotted with filled circles. The open circles show corresponding energies obtained from fitting by Hemmes et al. [35] to experimental data. Calculated energies for tetrahedral sites are shown as triangles. The inset shows the calculated equilibrium lattice constant of the resulting hydrides.

ferred when most of the neighbours are palladium atoms, while the tetrahedral site seems to be preferred when silver dominates (the tetrahedral site is 6 meV more stable than the octahedral in $PdAg_3$, and 60 meV more stable in pure Ag). It is well known that hydrogen occupies octahedral sites in palladium [10], but we do not know of any site determination of hydrogen in silver or silver-rich PdAg alloys. The equilibrium lattice constant for the different hydrides is also shown in the inset of Fig. 2, and we see that occupation of the tetrahedral site is followed by a large expansion of the lattice. The expansion seems unphysically high for the silver-rich alloys, most likely caused by the BP functional's underbinding of silver. We should, however, expect that instead of the homogeneous expansion of the lattice that we have performed, a local expansion should occur around the hydrogen atom, and also that the hydrogen–silver distance should be larger than the hydrogen–palladium distance. This would lower the average lattice constant, and also make the absorbed hydrogen more stable. We have also not calculated the zero point energies of the absorption sites, which also might be important for the relative stability of the sites. No clear conclusion can thus be drawn on which site is most stable in the silver-rich alloys.

In Fig. 2 there are two different curves for the calculated absorption energy of hydrogen in octahedral sites. Because of symmetry, three of the four atoms in the unit cell contributes to the six nearest neighbours of the hydrogen atom, and the last one represents the next-nearest neighbours. This means that two different lattices can give the same silver ratio of nearest neighbours: one with silver as the next-nearest neighbours, and one with palladium. We see from Fig. 2 that the most stable sites do all have silver as the next-nearest atoms. These sites also give the highest equilibrium lattice constant, as shown in the inset. As an example, the octahedral site with only palladium atoms as nearest neighbours is more stable in the Pd_3Ag alloy than in Pd_4. This may partially be understood as an effect of the larger lattice constant in the alloys with more silver, and is in agreement with solubility measurements at low pressure and moderate temperature (and low hydrogen content): the solubility of hydrogen in the alloys then increases with increasing silver content, due to the increasing size of the interstitial sites [34].

We have also in Fig. 2 compared our results to data from Hemmes et al. [35], which were obtained by fitting experimental data to a model with linear energy dependence on the silver concentration. The agreement with their data is not particularly good, except for hydrogen in pure palladium, (we have not calculated zero point energies, which means that our values should be slightly lower than the experimental). When the number of nearest silver atoms increases, however, the discrepancy between theory and experiment increases; the calculated and experimental [36] value for E_{abs} in pure silver are 0.79 and 0.59 eV, respectively. But, as stated above, we would expect lower absorption energy if the lattice were allowed to be fully relaxed. Because of the repulsive interaction between silver and hydrogen, this effect should increase when the number of silver neighbours increases. The experimental value for hydrogen in silver is also based on low hydrogen concentrations (10^{-6}–10^{-5}), far from our value of 25%. We believe that lower hydrogen concentration and full lattice relaxation would resolve most of the discrepancy. We have further found that the energy difference between equal sites with, respectively, Pd and Ag as next-nearest neighbours is between 0.13 and 0.16 eV, while the corresponding difference from Ref. [35] is 0.11 eV. This is not too surprising, since this energy difference is primarily because of expansion of the lattice, which we have seen is too easily obtained in the GGA.

The qualitative picture changes when the hydrogen content is increased. We have plotted the absorption energy as a function of the hydrogen content in Fig. 3, showing only the most stable site of each hydride. We see that, while Pd_3Ag has the most stable hydrogen absorption site at low hydrogen content (25%), the most stable sites are all found in Pd_4 above this. This agrees with experimental results at moderate temperature and high pressure (and high hydrogen content); then the solubility of hydrogen in the alloys decreases with increasing silver content [34]. This is explained as an electronic effect: when the Ag content increases, the unfilled part of the 4*d* states are filled, and the H solubility in the 5*s* band region (high pressure region) is reduced [34]. The experiments show that the lowest pressure needed to create a hydride with hydrogen content of 25% is that of $Pd_{0.80}Ag_{0.20}$, followed by Pd and $Pd_{0.70}Ag_{0.30}$. (The silver content was varied in steps of 10%). These data were measured at 323 K and are not directly comparable to our zero K calculations – we still find the accordance satisfying, since the main effect of reducing the temperature is to reduce the separation pressure between increasing and decreasing solubility [34].

Our calculations give a hydrogen solubility in Pd of at least 100% at 0 K (Fig. 3). Duś and Nowicka [37,38] have shown that the atomic concentration of hydrogen in Pd is close to, but not above 100% at 78 K and pressure up to 13 Pa. It is possible, however, to exceed 100% solubility by increasing the pressure: The deuterium content in Pd has been measured to be as high as 134% at temperatures between 4.3 and 400 K and at pressures up to 10.3 MPa by Silvera and Moshary [39]. This indicates that our results give a good description of the hydrogen solubility in palladium at zero temperature.

5. Conclusions

Palladium–silver alloys with and without hydrogen have been studied using a periodic density functional calculation scheme. Short range order has not been found in the real alloys, and one of the motivations of this study is to check

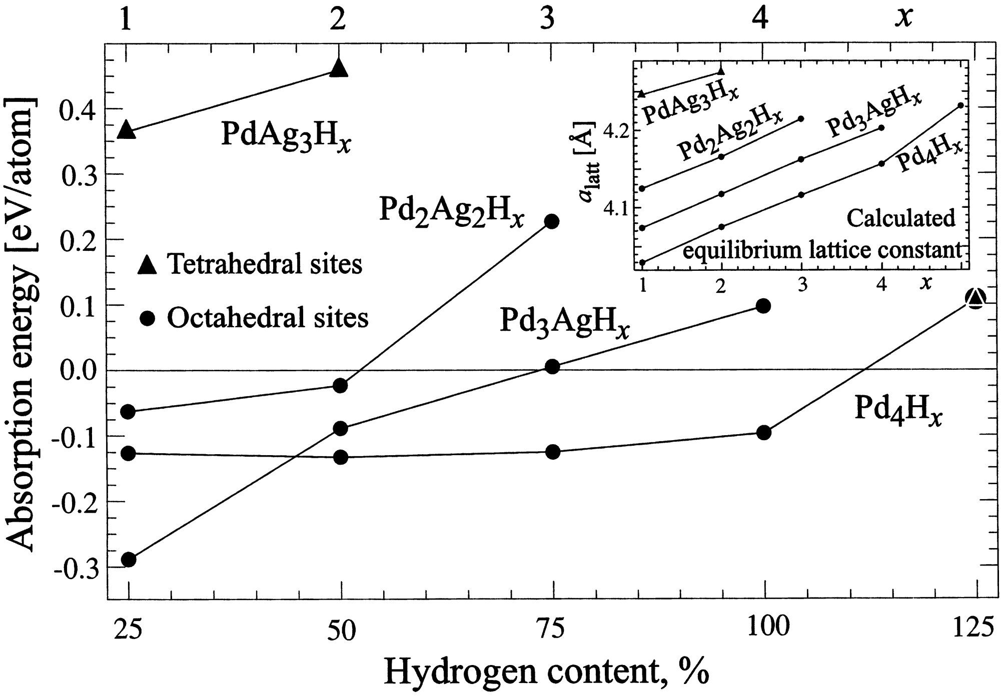

Fig. 3. The absorption energy of hydrogen in a unit cell of four metal atoms as a function of the number of absorbed hydrogen atoms per unit cell, *x*, for different palladium–silver alloys. The inset shows the calculated equilibrium lattice constants for the various hydrides, also as a function of the hydrogen content.

the viability of accurate periodic calculations to study hydrogen in random alloys.

Our calculations perform quite well for the hydrogen free metals and alloys. The familiar poor result of the Becke–Perdew generalized gradient approximation for the cohesive energy of silver was indeed found (Table 1), but the qualitative behaviour of the equilibrium lattice constant as a function of the silver content was good. We were able to reproduce the trends in the deviation from Vegard's law from these results (Fig. 1).

The description of absorption of hydrogen in the metals and alloys by our periodic calculations is also qualitatively satisfactory. The octahedral site is preferred in the Ag-lean alloys, while we have not been able to draw any clear conclusions concerning site preference when the silver content is 75% or more. We have further shown (in Fig. 2) that at low hydrogen concentration (25%), the absorbed hydrogen is most stable when the next-nearest metal atoms are silver, at least partly due to the larger lattice constant. This corresponds with the experimental trend that the solubility of hydrogen increases with increasing silver content of the alloy at low pressure. The opposite trend seen at high pressure (decreasing hydrogen solubility with increasing silver content) is clearly reproduced in Fig. 3 at atomic hydrogen concentrations of 50% and more.

We have not been able to establish satisfactory quantitative correspondence between our results and experimental values for the absorption energy of hydrogen in silver and the alloys. We believe that this would be resolved if the lattice were allowed to relax, and possibly by decreasing the hydrogen concentration. Work in these lines is in progress.

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