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Abstract
Hydrogen storage in the Pd_{12} cubo-octahedron cluster is studied theoretically using a self-consistent density-functional scheme with a norm-conserving pseudopotential. A cubo-octahedron Pd_{12} cluster is assumed to be a model for the new PdH structure having superabundant vacancies that was found recently. The cluster calculation predicts that octahedral and tetrahedral sites neighbouring a vacancy in the face-centred cubic lattice are duplicated. The configuration entropy for hydrogen sites is estimated within the cluster model and it is thought to be the cause of the formation of the superabundant vacancies. Since this structure does not lose its configuration entropy when the hydrogen concentration becomes high, it is suitable for use as a hydrogen-storage medium.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metal hydrides are increasing in importance for use as clean energy-conversion media. Although the PdH system is the oldest and the most extensively investigated metal–hydrogen system, new findings are still being reported.

In our previous work [1], we tried to explain the hydrogen-storage mechanism of metal hydrides from the viewpoint of the electronic structure of a cluster model, and the α–β transition of PdH by means of an entropy estimation based on the decomposition of an fcc lattice into Pd_{13} cubo-octahedron clusters. In the fcc bulk, the M_{13} cubo-octahedron cluster is not only a geometrical unit, but also works as a functional unit. The electronic structure of hydrogen in transition metals can be understood as the electronic shell structure of M_{13} and H atoms. In particular, the electronic structure of the cluster model for the inside adsorption is a good approximation of the bulk states, the appropriateness of which is confirmed by a band calculation of the linearized muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA).

In the low-concentration phase (the α-phase), the hydrogen atom occupies only the octahedral site (o-site), which is the most stable site in the Pd fcc crystal. Above $x \approx 0.6$ (the β-phase), the hydrogen atom also occupies the secondary stable tetrahedral site (t-site) to increase the configuration entropy of the hydrogen position. The lattice parameter is simultaneously expanded to 7.608 au (3.5%) by the occupation of the t-site. The driving force for the α–β transition of PdH is thought to be the configuration entropy. Our results are also consistent with the supercell approach, which shows that the o-site and the t-site are the most stable site and the secondary stable one for H occupation, respectively, and that the difference in binding energy between these two sites is slight [2–4]. Furthermore, Elsässer *et al* stated that the main reaction of a Pd lattice to H is an expansion of only the first-neighbour Pd shells, which supports the suggestion that the Pd_{13} cluster is a rather good model for Pd bulk.

Recently, the formation of superabundant vacancies in PdH and other metal hydrides under high hydrogen pressure and high temperature was reported [5, 7]. These hydrogen-induced vacancies have ordered structure of the Cu_3Au type (Pd_3Vac, $L1_2$ structure), and this structure is thought to be a phase of metal hydrides. In this paper, we try to explain this new phase also from the viewpoint of the cluster approach. This time, the structure of superabundant vacancies is modelled by a Pd_{12} cluster lacking the centre atom of the Pd_{13} cubo-octahedron cluster. The cluster calculation predicts that this structure has a large configuration entropy for hydrogen sites that causes the formation of the superabundant vacancies. Since this structure does not lose its configuration entropy when the hydrogen concentration becomes high, it has the possibility of being a good hydrogen-storage medium.

The present numerical calculation scheme is based on the linear combination of pseudo-atomic orbitals (LCPSAO) method using a norm-conserving pseudopotential and described in [8, 9]. The generalized gradient approximation (GGA) exchange–correlation energy due to Perdew, Burke, and Ernzerhof (PBE) [10] is included self-consistently.

In section 2, the fcc lattice decomposition into M_{13} clusters (or Pd_3Vac structure decomposition into Pd_{12} clusters) is described. In section 3, we show the total-energy curves for Pd_{12}/H_n clusters ($n = 6, 8$) and study the electronic structures. In section 4, we estimate the configuration entropy for PdH within the cluster model. In section 5, we discuss the generality of multiply replicated sites for hydrogen adsorption in M_{12} clusters. Section 6 gives our conclusions.

2. Another cluster decomposition of the fcc lattice

Recently, Fukai and Okuma reported finding a new phase of PdH under 5 GPa of hydrogen pressure at 700–800 °C, that has superabundant vacancies in the ordered Cu_3Au-type ($L1_2$) structure, Pd_3Vac [5,7], where Vac means a vacancy of the fcc lattice. This is a general structure of metal hydrides such as NiH or VH. We can regard this structure as another assemblage of Pd_{12} clusters which lack the centre atom of the Pd_{13} cubo-octahedron cluster, which is different from the crystal of cubo-octahedron clusters that we proposed in our previous work [1]. The Pd_{12} clusters are arranged in fcc packing owning the square faces jointly with neighbouring Pd_{12} clusters, which are shown in figure 1(a). The unit cell of this cluster lattice is rhombohedral, of space group $R\bar{3}m$, with the fundamental lattice vectors (2, 0, 0), (0, 2, 0), and (0, 0, 2), where (1, 1, 0), (0, 1, 1), and (1, 0, 1) are those for the fcc lattice. Since each peripheral atom of the Pd_{12} cluster is shared by four clusters, the number of atoms which belong to one Pd_{12} cluster is three ($12/4 = 3$), and there is one vacancy at the centre of the cluster that is not shared by the clusters. Therefore, the stoichiometry of Pd_3Vac is kept. The cluster stacking is shown by a ball–stick model in figure 1(b).
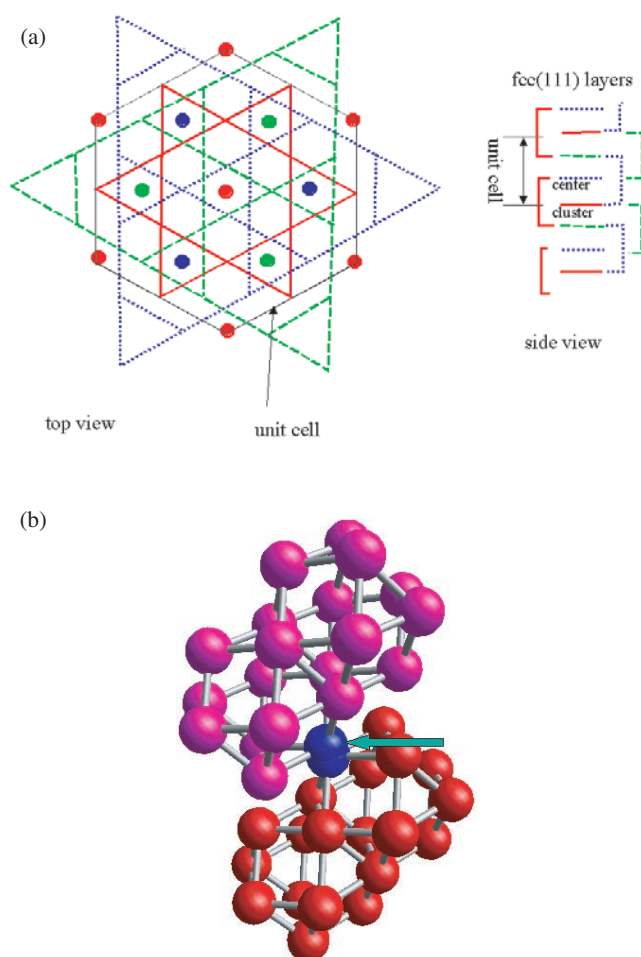
(a)

(b)

Figure 1. (a) An fcc bulk as a crystal of cubo-octahedron clusters. The rhombohedral cell is shown in hexagonal view. The left-hand panel shows the decomposition in the xy-plane (fcc(111)) and the right-hand panel shows that in the z-direction. The centres of clusters are indicated by solid circles, which are vacancies in the model for Pd_3Vac structure. (b) The cluster stacking in this cluster decomposition. The spheres pointed to by an arrow are duplicated as an expedient to show the stacking; they are in fact one atom.

3. Total energy and electronic structure of $Pd_{12}H_n$ clusters

3.1. Cluster model and total energy

Figures 2(a) and (b) show the cluster models of $Pd_{12}H_6$ and $Pd_{12}H_8$ for the superabundant vacancies in PdH. The H atoms are placed on a line connecting the cluster centre and the square-face centre of $Pd_{12}H_6$ and the triangular-face centre of $Pd_{12}H_8$. In this paper 'hydrogen adsorption to the triangular or square face' means adsorption somewhere on the line connecting the cluster centre and the triangular or square face, respectively. The number of H atoms is fixed to keep O_h symmetry. A hydrogen site inside the square face corresponds to the o-site and one inside the triangular face corresponds to the t-site; therefore, $Pd_{12}H_6$ is a model for o-site adsorption and $Pd_{12}H_8$ is a model for t-site adsorption.
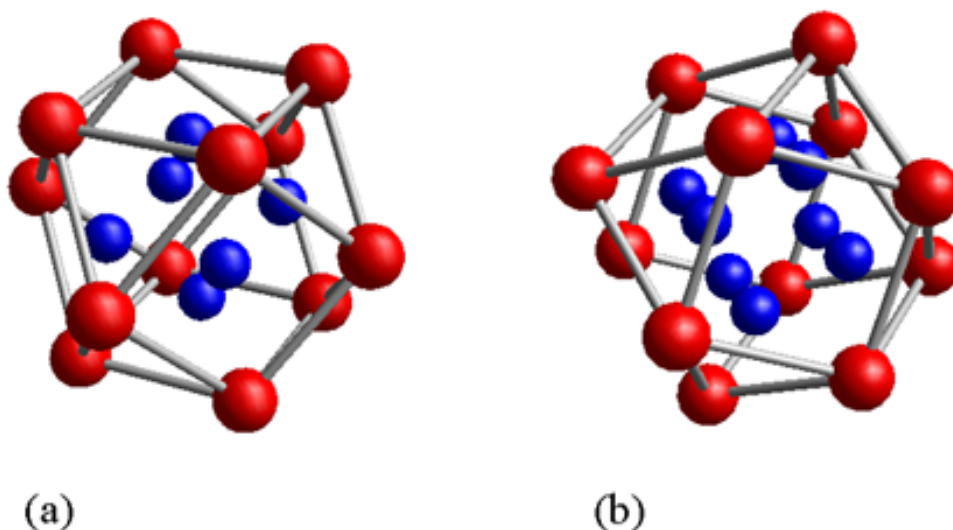
Figure 2. (a) The $Pd_{12}H_6$ cluster. (b) The $Pd_{12}H_8$ cluster. Large spheres indicate Pd atoms and small spheres indicate H atoms.

We define the total energy for an adsorbed H atom as the total energy of $Pd_{12}H_n$ minus those of a Pd_{12} cluster and hydrogen molecules divided by the number of hydrogen atoms. Here, the Pd_{12} has a total energy of -347.5526 Hartree for the equilibrium Pd–Pd distance $R_{Pd} = 5.0$ au, which is the equilibrium value for a naked Pd_{12} cluster, and the hydrogen molecule has a total energy of $-1.053\,58$ Hartree for the H–H distance 1.346 au. We calculated the total energies of the Pd_{12} cluster and hydrogen atoms by changing both the distance R_H between the cluster centre and the hydrogen atoms and R_{Pd}, the distance between Pd atoms. The optimized R_{Pd} are 5.2 and 5.3 au for $Pd_{12}H_6$ and $Pd_{12}H_8$, respectively. The experimentally measured R_{Pd} in a Pd_3Vac structure is 5.119 au [5] which is slightly shorter than that of a $Pd_{12}H_6$ cluster. The peripheral-Pd–H distances at the inner sites are similar for the two clusters, 2.90 au for $Pd_{12}H_6$ ($R_H = 2.4$ au) and 3.04 au for $Pd_{12}H_8$ ($R_H = 2.6$ au). In figure 3(a) the total energies for an H atom in $Pd_{12}H_6$ and $Pd_{12}H_8$ are plotted as functions of R_H, and in figure 3(b) the total energies for an H atom in $Pd_{13}H_6$ and $Pd_{13}H_8$ of $R_{Pd} = 5.1$ au, which are the results from our previous work, are shown for comparison purposes.

In this study, we focus our discussion on the inner sites of Pd_{12} clusters, which correspond to minima in the ranges $R_H < 3.68$ au and $R_H < 4.33$ au for $Pd_{13}H_6$ and $Pd_{13}H_8$, respectively, since the inside of Pd_{12} is effective as a model of the superabundant vacancies in PdH caused by the cluster decomposition described in the previous section. The value of the binding energy for o-sites is smaller in the Pd_{12} cluster than that in the Pd_{13} cluster. However, the notable difference between the total energies of $Pd_{12}H_n$ and those of $Pd_{13}H_n$ is the duplication of the minima inside the Pd_{12} cluster: the minima of $R_H = 3.4$ au for $Pd_{13}H_{6,8}$ are duplicated to the minima of $R_H = 2.4$ and 3.6 au for the $Pd_{12}H_6$ and $R_H = 2.6$ and 3.4 au for the $Pd_{12}H_8$, respectively. The additional minima at $R_H = 2.4$ for $Pd_{12}H_6$ and $R_H = 2.6$ au for $Pd_{12}H_8$ in figure 3(a) exist as points of inflection at $R_H = 2.6$ and 2.8 au for $Pd_{13}H_6$ and $Pd_{13}H_8$, respectively, as shown in figure 3(b). The total energies of H atoms at $R_H = 2.6$ au in the Pd_{12} cluster are lowered by the vanishing of the repulsion energy between the H atoms and the cluster-centre Pd atom. Naked H_6 and H_8 clusters do not bind, but they have minima in the total energy at $R_H = 2.2$ au, which is very close to the values $R_H = 2.4$ and 2.6 au for the additional minima in the $Pd_{12}H_{6,8}$ clusters (figure 3(c)).
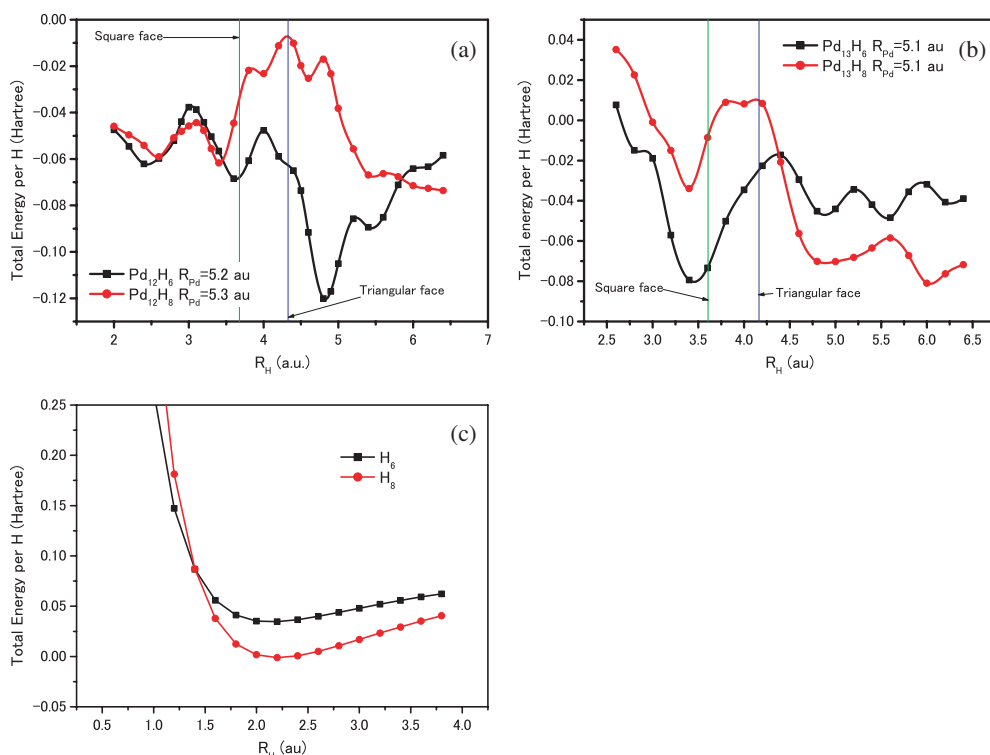
Figure 3. (a) Total energy per hydrogen atom for the Pd_{12} cubo-octahedron/H_6 (■) and Pd_{12} cubo-octahedron/H_8 (●). The distance between Pd atoms R_{Pd} is 5.2 au for $Pd_{12}H_6$ and 5.3 au for $Pd_{12}H_8$. (b) The same for the Pd_{13} cubo-octahedron/H_6 (■) and Pd_{13} cubo-octahedron/H_8 (●). The distance between Pd atoms R_{Pd} is fixed at 5.1 au. (c) Total energy per hydrogen atom for H_6 (■) and H_8 (●) clusters.

3.2. Electronic structure

The changes in the energy levels as a function of the hydrogen positions for $Pd_{12}H_6$ ($R_{Pd} = 5.2$ au) $Pd_{12}H_8$ ($R_{Pd} = 5.3$ au) are plotted in figures 4(a) and (b) respectively. The electronic structures are composed of three parts: (1) Pd d states exist in the range -0.2 to 0.3 Hartree, (2) hydrogen induced states lie in the range < -0.3 Hartree below the Pd d states, and (3) hydrogen-induced states lie in the range > -0.2 Hartree. The low-lying states induced by H atoms below the metal d band, which we call the cluster-centre states [1], are illustrated for $Pd_{12}H_n$ ($n = 6, 8$) clusters in figure 5. They are understood as the bonding–antibonding between the electronic shell structures of the Pd_{12} cluster and H_6 or H_8 clusters. The representation of electronic shell states in O_h symmetry is shown in table 1. Hydrogen states compose s, p, and partial d states in the Pd cluster. These electronic structures are similar to those of $Pd_{13}H_n$ ($n = 6, 8$) except for the existence of the $1t_{2g}$ orbital in the $Pd_{13}H_6$ cluster and the $1e_g$ orbital in the $Pd_{13}H_8$ cluster, which originate in the centre Pd atom and have a non-bonding nature.

The minima in the total-energy curves are caused by interactions among the metal d band and the hydrogen-induced states. The total energy at the point where the energy levels cross becomes relatively high. In $Pd_{12}H_6$, $2a_{1g}$ for the bottom of the Pd d band at $R_H = 6.4$ au changes to $1a_{2u}$ near the cluster centre, and $4e_g$ for the LUMO at $R_H = 6.4$ au changes to $4a_{1g}$.
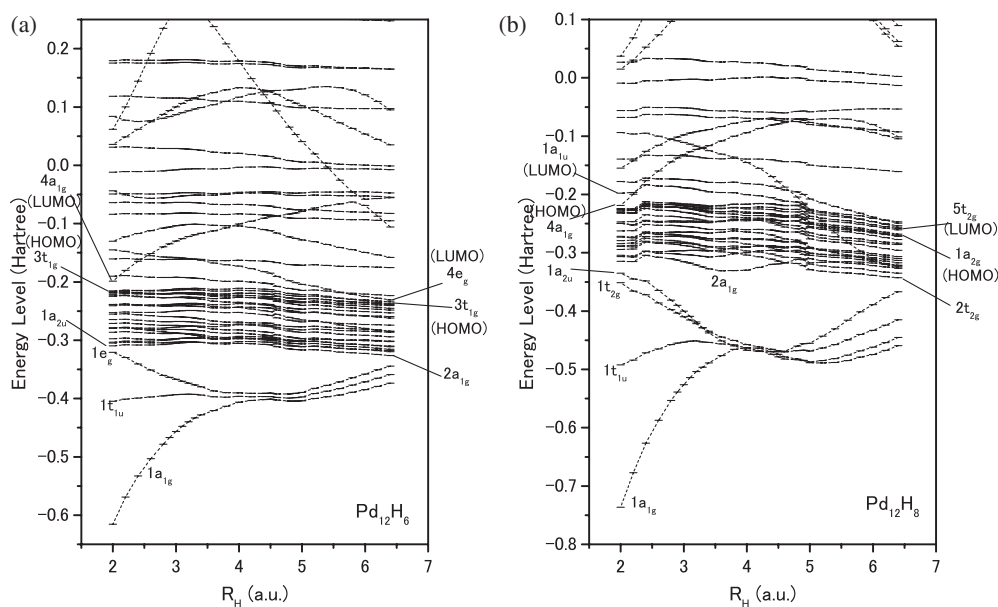
Figure 4. The change in the energy level as a function of the hydrogen positions for (a) the $Pd_{12}H_6$ cluster ($R_{Pd} = 5.2$ au) and (b) the $Pd_{12}H_8$ cluster ($R_{Pd} = 5.3$ au).

Table 1. Electronic shell structure in O_h symmetry.

Shell state	Representation in O_h
s	a_{1g}
p	t_{1u}
d	e_g, t_{2g}
f	a_{2u}, t_{1u}, t_{2u}

In $Pd_{12}H_8$, $2t_{2g}$ for the bottom of the Pd d band at $R_H = 6.4$ au changes to $2a_{1g}$ near the cluster centre, $1a_{2g}$ for the HOMO and $5t_{2g}$ for the LUMO at $R_H = 6.4$ au change to $4a_{1g}$ and $1a_u$ near the cluster centre, respectively.

The HOMO of the $Pd_{12}H_6$, $3t_{1g}$, is the same as that for the $Pd_{13}H_6$, and the LUMO of the $Pd_{12}H_8$, $1a_{1u}$, is the HOMO in the $Pd_{13}H_8$. The eight Pd d levels that exist just below the Fermi level in the $Pd_{12}H_6$ cluster ($t_{1g} \times 2$, $e_g \times 1$, $a_{2g} \times 1$, $t_{1u} \times 1$, $t_{2u} \times 2$, and $e_u \times 1$) are the same as those in $Pd_{13}H_6$. The energy range of these eight levels becomes narrower when R_H becomes smaller ($0.0188 \rightarrow 0.0094$ Hartree). This tendency is similar in the $Pd_{12,13}H_n$ clusters. Since the equilibrium distance R_H can be smaller in $Pd_{12}H_n$ than in $Pd_{13}H_n$, and the narrower energy range means a higher density of states (DOS), it can be assumed that the Pd_3Vac structure of PdH has a higher DOS at the Fermi level than that of PdH without vacancies.

The largeness of the binding energy, which depends on the number of H atoms, is slightly related to the HOMO–LUMO gap, but it is not the main cause of the gap. In particular, occupation of the p state in the cluster-centre states increases the binding energy; this is shown in table 2 for the values at the inner o-sites. The results for $Pd_{12}H_1$ (C_{4v}) and $Pd_{12}H_2$ (D_{4h}) are also tabulated for comparison. We discuss these results in section 5. For O_h symmetry of the Pd_{12} (or Pd_{13}) potential, the p state is the largest l-state that does not split into representations of lower degeneracies (table 1). The occupation of l-states higher than p is not clear, because of the shell splitting in the O_h symmetry.

Figure 5. The energy level diagram for the low-lying levels of Pd_{12} and $Pd_{12}H_n$ ($n = 6, 8$) clusters.

Table 2. Bonding–antibonding nature of low-lying states from the viewpoint of H–H bonding, HOMO–LUMO gaps, and binding energies per H (E_B) for $Pd_{12}H_{1,2,6,8}$ clusters.

Cluster (symmetry)	R_{Pd} (au)	R_H (au)	Low-lying states induced by H atoms H–H bonding:H–H antibonding	HOMO–LUMO gap (Hartree)	E_B (Hartree)
$Pd_{12}H_1$ (C_{4v})	5.1	1.8	$1a_{1g}(s)$:	0.0018	0.0073
$Pd_{12}H_2$ (D_{4h})	5.1	2.4	$1a_{1g}(s):1a_{2u}(p_z)$	0.0034	0.0553
$Pd_{12}H_6$ (O_h)	5.2	2.4	$1e_g(d)$:	0.0609	0.0621
			:$1t_{1u}(p)$		
			$1a_{1g}(s):1a_{2u}(f)$		
$Pd_{12}H_8$ (O_h)	5.3	2.6	$1t_{2g}(d):1t_{1u}(p)$	0.0120	0.0590
			$1a_{1g}(s):1a_{2u}(f)$		

There is another viewpoint as regards the cluster-centre states. They can also be interpreted as the bonding and antibonding states for the H–H bonding, shown in table 2. The successive occupation of shell states with a small irregularity corresponds to the occupation of alternate bonding and antibonding states for H–H, which prevents the firm formation of hydrogen molecules or hydrogen clusters in the Pd cage. The electronic shell structure of $Pd_{12,13}H_n$ clusters is different from that of alkali metal clusters in the following two points: (1) the number of electrons cannot be specified by the number of hydrogen atoms; (2) the electronic shell structure is formed at the bottom of the energy levels. Since Pd also supplies the shell states with electrons, the number of shell states occupied is higher than the number of H atoms.

4. Configuration entropy estimation based on $Pd_{12}H_n$ clusters

In this section, we estimate the configuration entropy of Pd_3Vac ($L1_2$ structure) using the cluster decomposition of the $Pd_{12}H_n$ cluster, which was explained in section 2. The number of Pd atoms that belong to one cluster element is four for the ordinary Pd bulk and three for the structure with the superabundant vacancies (cf section 2). First, we consider the number of o-sites. The number of ordinary o-sites that belong to one cluster element in both the Pd bulk and the superabundant vacancy structure is four, which is the same as the number of Pd atoms in the cluster element of the Pd bulk. The two sites between triangular faces of the z-direction stacking of $Pd_{12(13)}$ clusters that are shared by two clusters, which correspond to the minimum at $R_H = 6.0$ au in figure 3(b) for $Pd_{13}H_8$ [1], are counted as one ($2/2 = 1$); the six o-sites in the square face of the $Pd_{12(13)}$ cluster are shared by two clusters, so they are counted as three ($6/2 = 3$). For the Pd_{12} cluster, there are six additional o-sites inside the Pd_{12} cluster shown in the previous section, which belong to one cluster. Therefore, the total number of o-sites for one cluster element is four for the Pd_{13} cluster and ten for the Pd_{12} cluster. Next, we consider the number of t-sites in a single cluster element. Both ordinary and additional t-sites are inside the cluster; they are not shared with the neighbouring clusters. The number of ordinary t-sites is eight—that is, the same as the number of triangular faces of the $Pd_{12(13)}$ cluster. This is twice the number of Pd atoms in one cluster element of the Pd bulk, which means that all the t-sites in the fcc lattice are counted. The number of additional t-sites in the Pd_{12} cluster is also eight. Therefore, the total number of t-sites for one cluster element is eight for the Pd_{13} cluster and sixteen for the Pd_{12} cluster. The number of hydrogen sites changes from 12 ($= 4 + 8$) Pd_{13} to 26 ($= 10 + 16$) Pd_{12} by the superabundant vacancy formation. The main cause of this phase transition seems to be the configuration entropy of the hydrogen position, which is the same as for the α–β transition of PdH [1].

Let us estimate the change in energy by the increase in the number of hydrogen sites at $800\,°C$, which is the temperature at which the formation of superabundant vacancies occurs [5, 7]. The entropy change is written as follows in this cluster approach:

$$\Delta S = \Delta S_{config} + \Delta S_{vib} + \Delta S_{mix}$$

where S_{config} is the configuration entropy for the hydrogen position, S_{vib} is the vibration entropy of the lattice, and S_{mix} is the mixing entropy of the clusters. The contribution of the vibration entropy to the formation of superabundant vacancies is positive (i.e., $-T\,\Delta S$ is negative), which is known experimentally from the lowered frequency number of the lattice [12]:

$$-T\,\Delta S_{vib} \approx -Tk_B = -0.0034 \text{ (Hartree)}$$

where k_B is the Boltzmann constant. Compared against ΔS_{config} calculated below, ΔS_{vib} has the same sign but its magnitude is as little as 4% of ΔS_{config}. The mixing entropy is defined by the following equation:

$$S_{mix} = -k_B T \sum_i y_i \ln y_i$$

where y_i is the concentration of cluster units which have n_i H atoms. The contribution of ΔS_{mix} is negligible, because S_{mix} is thought to be almost the same for the ordinary PdH as for the PdH with superabundant vacancies.

Here m indicates the number of hydrogen sites in one cluster element and n indicates the average number of H atoms in one cluster element ($n = \sum_i y_i n_i$). If the number of configurations of H atoms is roughly approximated by C_n^m and the number of configurations in which both of the duplicated sites are occupied is subtracted, then $-T\,\Delta S_{config}$ arising from
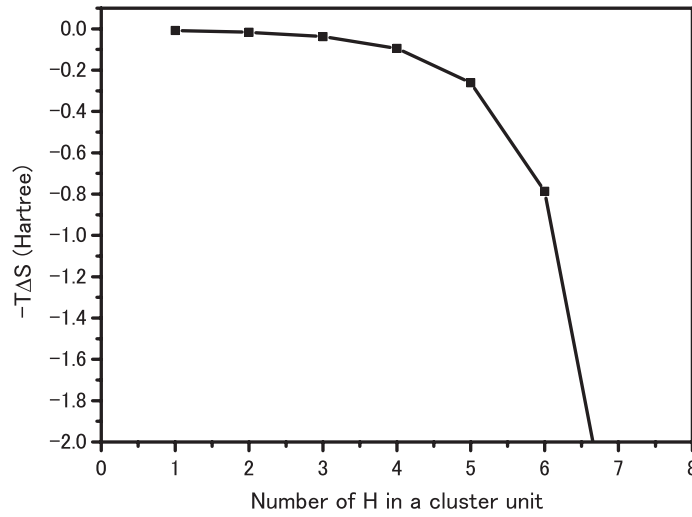
Figure 6. $-T \Delta S_{\text{config}}$ from Pd_4H_n to Pd_3VacH_n as a function of the number of H atoms in the cluster unit.

the formation of superabundant vacancies becomes

$$-T \Delta S_{\text{config}} = -1073 k_{\text{B}} \log \frac{C_n^{26} - \Sigma_{i=1}^{n/2}(C_{n-i}^{14} C_i^{n-i})}{C_n^{12}}.$$

Here 1073 is the temperature in kelvins ($=800\,°\text{C}$). $T \Delta S_{\text{config}}$ rapidly becomes large as n increases, as shown in figure 6. The formation energy of a vacancy in Pd, which is experimentally known, is 1.7 eV ($=0.063$ Hartree) [13]. $T \Delta S_{\text{config}}$ is 0.094 Hartree at $n = 4$ (atomic ratio of H/Pd $= 1.0$), which is large enough to exceed the sum of the difference in binding energies of H for the various adsorption sites ($\leqslant 0.02$ Hartree) and the vacancy-formation energy. The phase transition to the structure with the superabundant vacancies is thought to occur before the atomic ratio becomes $x \approx 1$ for PdH_x.

It is a notable merit of hydrogen-storage media that the configuration entropy of the Pd_3Vac L1_2 structure does not decrease when the hydrogen concentration becomes considerably higher. Experimentally, it is known that one vacancy in a hydrogen-storage metal traps up to six H atoms [6, 11]. This means that the atomic ratio of MH_x in the structure with the superabundant vacancies becomes $x = 2$, which seems to be an excellent value for hydrogen-storage media.

5. Discussion

5.1. Potential cage of the M_{12} cluster

The duplication of o-sites and t-sites for hydrogen adsorption in the M_{12} cluster is a general phenomenon in metals. In figure 7, total energies per hydrogen atom are plotted for Pd_{12}H_6, Ti_{12}H_6, and Al_{12}H_6 clusters; these show that o-sites inside the clusters of these three metals are duplicated. Hydrogen insolubility in Al bulk is well known; this is understood as an influence of hydrogen-induced s and p states of the cluster-centre states upon the binding energy. Al_{13} already has a native p state of the centre Al atom, which prevents hydrogen penetration. Even Al has binding energy for hydrogen adsorption when vacancies exist, which means hydrogen adsorbability in an Al_{12} cluster that has fewer s and p states in the cluster-centre states. This
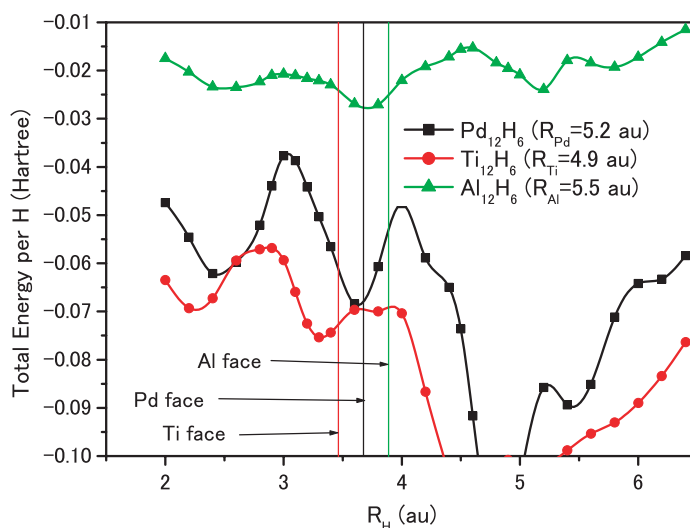
Figure 7. Total energy per hydrogen atom for Pd_{12} cubo-octahedron/H_6 ($R_{Pd} = 5.2$ au) (■), Ti_{12} cubo-octahedron/H_6 ($R_{Ti} = 4.9$ au) (●), and Al_{12} cubo-octahedron/H_6 ($R_{Al} = 5.5$ au) (△). The minima outside the Pd cluster are shown in figure 3(a). The minima outside the Ti cluster are $R_H = 4.6$ au (-0.1162 Hartree) and $R_H = 5.2$ au (-0.1018 Hartree). The energy range of this figure is set to compare minima inside the clusters.

is also observed experimentally [14]. It is said that the adsorption energies of hydrogen in Pd and Ti are too large for hydrogen-storage media, which require high temperature to extract hydrogen. On the other hand, the binding energy for hydrogen adsorption of Al clusters in figure 7 is too small. A metal or an alloy that has an intermediate binding energy, between those of Al and Pd (or Ti), will be suitable as a hydrogen-storage medium.

We have examined whether the minimum of the total energy for an H atom in the Pd_{12} is duplicated or not, and whether a hydrogen molecule is formed in the Pd_{12} cluster, using the $Pd_{12}H_1$ (C_{4v}) and $Pd_{12}H_2$ (D_{4h}) clusters. The total energies per hydrogen atom are plotted in figure 8(a), which shows that duplication of o-sites occurs in the models of an H and two H atoms. In the $Pd_{12}H_2$ cluster, there is a third o-site at $R_H = 1.2$ au. This is interpreted as an elongated and weakened H–H bond caused by an H–H antibonding occupation that is shown as $1a_{2u}$ in figure 8(b). This H–H antibonding is simultaneously a p_z state from the cluster-centre states, which was already mentioned in section 3.2. There is not a firm bond like that for a molecule in the Pd_{12} cluster. The minimum at $R_H = 2.4$ au of $Pd_{12}H_2$ corresponds to the minimum at $R_H = 2.6$ au of $Pd_{12}H_6$ that results from the equilibrium distance of the naked H_6 cluster. In the case of $Pd_{12}H_2$ clusters, the H–H distance is too long (4.8 au) for the H atoms to have influences on each other. There must be another reason for this minimum. In figure 9, the potential of the Pd_{12} ($R(Pd) = 5.1$ au) along an o-site direction is shown calculated up to the $L = 4$ component. We have solved for eigenstates, assuming this potential to be a one-dimensional quantum well, which is shown together with the potential in figure 9. The minimum at $R_H = 2.4$ or 2.6 au corresponds to the first peak of the squared probability distribution of the 3p wavefunction. The hydrogen atom seems to take the position that maximizes the integral of the overlap of its atomic orbital with the eigenstates for the quantum well of the Pd_{12} cage. A similar interpretation holds for the minimum at $R_H = 1.8$ au of the $Pd_{12}H_1$ cluster that corresponds to the first peak of 2s wavefunction of the quantum well. Furthermore, the position of the old o-sites at $R_H = 3.6$ au correspond to the bottom of the potential and the peaks of the 1s and 2p wavefunctions.
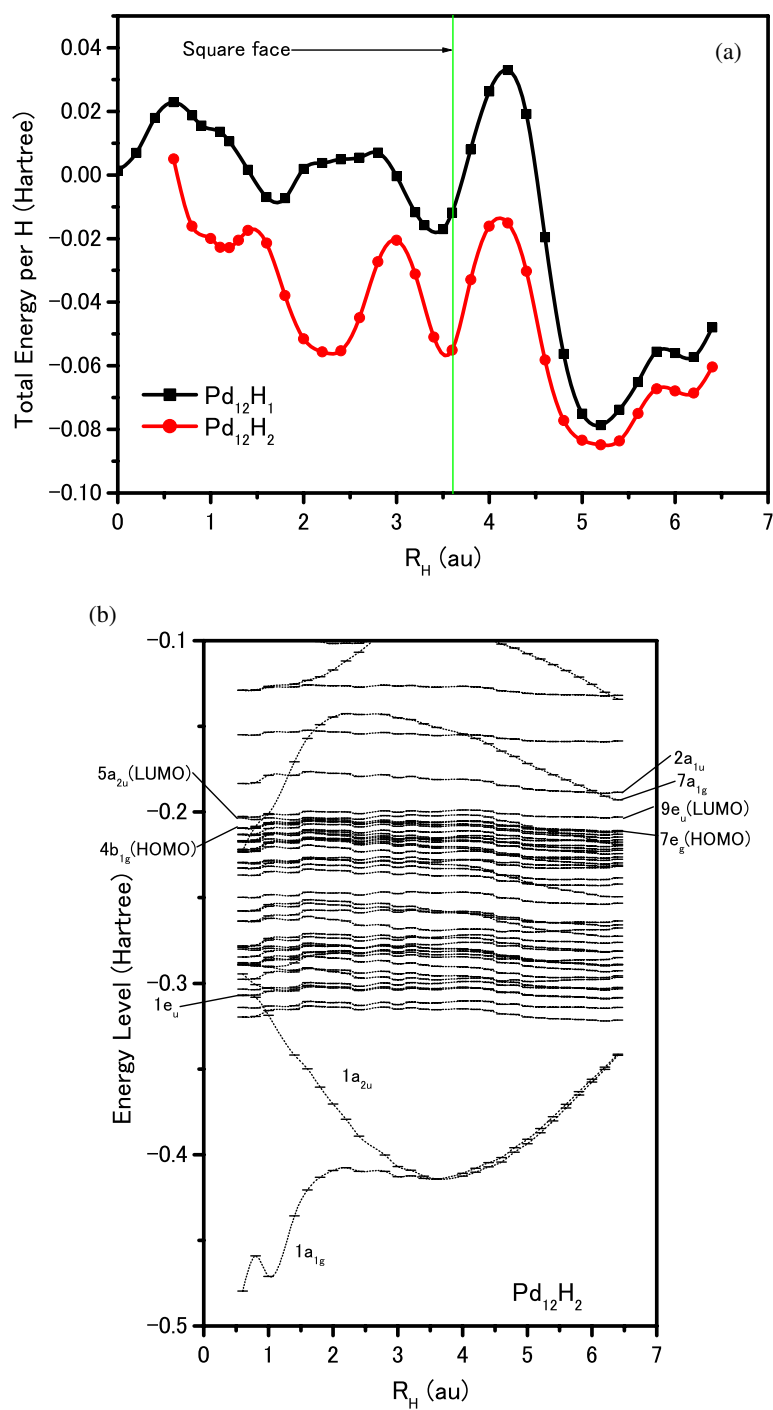
Figure 8. (a) Total energy per hydrogen atom for Pd_{12} cubo-octahedron/H_1 (■), and Pd_{12} cubo-octahedron/H_2 (●). The distance between Pd atoms R_{Pd} is fixed at 5.1 au. (b) The change in the energy level as a function of the hydrogen positions for Pd_{12} cubo-octahedron/H_2.
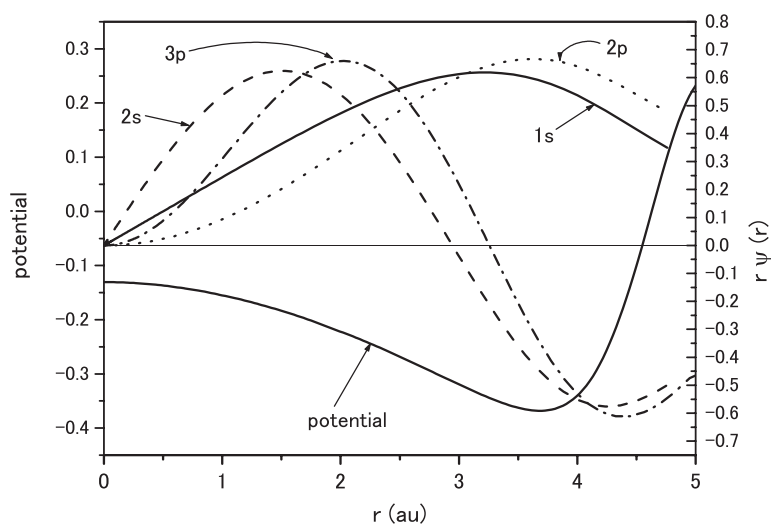
Figure 9. The potential along an o-site direction of the Pd_{12} cluster ($R(Pd) = 5.1$ au) calculated up to the $L = 4$ component, and eigenstates obtained using this potential as a one-dimensional quantum well.

There is a limitation on cluster model study for this system. In this cluster decomposition that shares the peripheral M_{12} atoms among the neighbour clusters, the number of Pd atoms in a cluster (twelve) is inconsistent with the number of Pd atoms in one cluster unit (three). This would affect the Fermi level of the electronic structure of the PdH system modelled. However, the minima of the total energy for R_H inside the cluster will not be substantially affected by H atoms existing outside the cluster, because the H positions are decided by the local potential in the Pd_{12} cage. It is of importance to investigate hydrogen behaviour in Pd bulk [2–4]. We will discuss it in the bulk of Pd_3Vac structure in the near future.

6. Conclusions

We studied $Pd_{12}H_n$ clusters theoretically using the self-consistent density-functional scheme with a pseudopotential. We modelled bulk Pd_3Vac ($L1_2$ structure) by using a $Pd_{12}H_n$ cluster, because the fcc lattice can be regarded as a fcc assemblage of Pd_{13} clusters. The structure in which the Pd_{13} clusters are arranged in fcc packing owning the square faces jointly with neighbouring Pd_{13} clusters reproduces the fcc lattice. This structure agrees with the Pd_3Vac bulk of $L1_2$ structure when the centre Pd atoms of Pd_{13} clusters are lacking. Inside the Pd_{12} cluster, both the o-sites and t-sites, which are the positions where the total energy of hydrogen adsorption becomes minimum, are duplicated. This causes the large increase of the configuration entropy for hydrogen positions in PdH, which is the reason for the formation of the superabundant vacancies.

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