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## Hydrogen site occupation in YPd<sub>3</sub> with L1<sub>2</sub> structure

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Hydrogen site occupation in a binary metal compound of YPd<sub>3</sub> with L1<sub>2</sub> structure is studied experimentally and theoretically. In contradiction to the semiempirical heat of the formation model, which predicts the interstitial site preferably occupied by hydrogen atoms in intermetallic compounds, the present neutron-diffraction study reveals that the hydrogen atoms occupy preferentially the characteristic interstitial site surrounded by six Pd atoms rather than the interstices surrounded by two Y and four Pd atoms. This result is confirmed by the first-principles calculations based on the local-density-functional theory. The difference in the electronic interactions between hydrogen and host atoms is shown to be largely responsible for the occupation of the specified interstitial sites by hydrogen in intermetallic hydride. [S0163-1829(97)03322-5]

Most ternary metal hydrides (throughout this work we use the words hydrogen and deuterium interchangeably and assume that their chemical behavior is identical) derive from binary metal compounds or alloys which absorb hydrogen by filling interstitial sites in their metal atom network. The resulting hydrogen concentrations per unit volume are often higher than that of liquid hydrogen, which makes ternary metal hydrides attractive hydrogen storage materials.<sup>1</sup> The hydrogen storage capacity is limited by the reluctance of hydrogen to occupy all available interstitial sites in the metal atom network. The number of available interstices in the structures generally greatly exceeds the number of hydrogen atoms absorbed. The hydrogen occupancy for various interstices may be rationalized in terms of geometrical factors, lattice distortion created by the hydrogen, and electronic interactions between hydrogen and host atoms.

A simple model to predict the interstitial sites preferably occupied by the H atoms in intermetallic compounds has been suggested by Jacob *et al.*<sup>2</sup> and Giessen and Riesterer.<sup>3</sup> According to this model the occupancy of the interstitial sites is determined by the heat of formation of the imaginary hydride (the embedded hydride cluster) formed from the H atoms and host atoms leading to the interstitial site in consideration. On the other hand, Westlake<sup>4</sup> and Magee, Leu, and Lundin<sup>5</sup> have claimed that interstitial hole size and hydrogen-hydrogen interatomic distance can be used to predict the hydrogen occupied sites in the hydride of intermetallic compounds. They found that an increase in hole size is accompanied by greater stability. In order to make a step towards better understanding the factors which limit hydrogen sorption capacities, we intend to study the hydrogen stability in the ternary metal hydrides, and try to find the hydrogen distributions that minimizes the total energy.

In this paper, we report powder neutron-diffraction experiments and first-principles calculations on the distribution of H atoms in the ternary metal hydride of YPd<sub>3</sub>H(D)<sub>x</sub>. Neutron-diffraction experiments provide quantitative information on the distribution of hydrogen (the relative hydrogen occupancy) among the various interstitial sites.<sup>6</sup> The theoretical calculations were made to determine the preferential site for hydrogen in the YPd<sub>3</sub> compound. A sample of YPd<sub>3</sub> was

prepared by arc melting the appropriate proportions of high-purity (better than 99.9%) metals in an argon atmosphere. The resulting ingot was annealed at 1000 °C for 173 ks in an evacuated quartz tube to ensure homogenization, after which it was pulverized to <250 μm. Before hydrogenation, the powder samples were activated at 733 K for 3.6 ks in a vacuum. Subsequently, they were hydrogenated using high-purity hydrogen (deuterium) at the pressure of 5 MPa for 173 ks between 300 and 773 K. The neutron-diffraction experiments were carried out on the Kinken powder diffractometer at the JRR-3M reactor of the Japan Atomic Energy Research Institute Tokai. The neutron wavelength was 1.767 Å and the diffraction patterns were recorded over the angular range 10° <2θ<104° in a step of 0.1°. The details of the neutron-diffraction studies on the YPdH<sub>x</sub> will be reported elsewhere.<sup>7</sup>

Analysis of x-ray and neutron-diffraction patterns from the YPd<sub>3</sub>H(D)<sub>x</sub> for the different H (D) contents have confirmed that the L1<sub>2</sub>-type structure of YPd<sub>3</sub> is preserved on hydrogenation up to x=0.30, while the lattice parameter expands slightly from a=4.074 Å for x=0 to a=4.080 Å for x=0.30. A quantitative comparison of the diffraction intensities was made using neutron-diffraction data from YPd<sub>3</sub>, YPd<sub>3</sub>H<sub>0.30</sub>, and YPd<sub>3</sub>D<sub>0.19</sub>. The observed data are listed in Table I in comparison with the calculation. It will be seen from Table I that the relative intensity of the diffraction lines are considerably different from each other; e.g., the 100 diffraction line is stronger than the 110 diffraction line for YPd<sub>3</sub>H<sub>0.30</sub>, while for YPd<sub>3</sub>D<sub>0.19</sub> the 100 diffraction line is weaker than the 110 diffraction line. These characteristic features of the diffraction patterns can be understood quite well assuming the preferential occupation of the specified octahedral interstitial sites by H (D) atoms. In the YPd<sub>3</sub> compound of L1<sub>2</sub> structure [space group *Pm3m*: one Y atom in the (0,0,0) position and three Pd atoms in the (0,1/2,1/2), (1/2,0,1/2), and (1/2,1/2,0) positions], there are only two different octahedral interstitial sites: the 6Pd site surrounded by six Pd atoms and the 2Y4Pd sites surrounded by two Y and four Pd atoms. The coordinates of the 6Pd and 2Y4Pd sites are (1/2,1/2,1/2) and (1/2,0,0), (0,1/2,0), and (0,0,1/2). Then, the structure factors for YPd<sub>3</sub>H<sub>x</sub> are expressed as follows:

TABLE I. A comparison of the diffraction intensity with the calculation.

$h$	$k$	$l$	YPd <sub>3</sub> (300 K)		YPd <sub>3</sub> H <sub>0.30</sub> (300 K)		YPd <sub>3</sub> D <sub>0.19</sub> (70 K)	
			$F_{\text{Obs}}$	$F_{\text{Cal}}$	$F_{\text{Obs}}$	$F_{\text{Cal}}$	$F_{\text{Obs}}$	$F_{\text{Cal}}$
1	0	0	0.15	0.16	0.18	0.18		0.05
1	1	0	0.18	0.16	0.15	0.14	0.28	0.27
1	1	1	0.73	2.68	2.79	2.79	2.56	2.58
27	0	0	2.62	2.68	2.65	2.57	2.86	2.80
2	1	0	0.19	0.16	0.16	0.18		0.05
2	1	1	0.15	0.16	0.11	0.14	0.24	0.27
2	2	0	2.76	2.68	2.50	2.57	2.78	2.80

$$\begin{aligned}
 F(hkl) = & b_Y + b_{\text{Pd}}\{\cos(\pi k)\cos(\pi l) + \cos(\pi l)\cos(\pi h) \\
 & + \cos(\pi h)\cos(\pi k)\} \\
 & + ub_{\text{H}}\cos(\pi h)\cos(\pi k)\cos(\pi l) + vb_{\text{H}}\{\cos(\pi h) \\
 & + \cos(\pi k) + \cos(\pi l)\},
 \end{aligned}$$

where  $b_Y$ ,  $b_{\text{Pd}}$ , and  $b_{\text{H}}$  are the scattering amplitudes of yttrium, palladium, and hydrogen, respectively, and two parameters  $u$  and  $v$  are occupation probabilities of hydrogen in the 6Pd and 2Y4Pd sites, respectively. The parameters  $u$  and  $v$  are related to the hydrogen fraction per formula unit  $x$ ;  $x = u + 3v$ . The nuclear-scattering amplitude  $b$  adopted for yttrium, palladium, deuterium, and hydrogen are 0.77, 0.63, 0.65, and  $-0.378 \times 10^{-12}$  cm, respectively. Good agreement is obtained if we assume the values of the occupation probabilities  $u=0.12$  and  $v=0.06$  for YPd<sub>3</sub>H<sub>0.30</sub> at 300 K, and  $u=0.175$  and  $v=0.005$  for YPd<sub>3</sub>D<sub>0.19</sub> at 70 K. The structure factors calculated using these values are listed in the fourth and sixth columns of Table I, and the reliability factors are less than 0.03. These results indicate that the H (D) atoms prefer the 6Pd site to the 2Y4Pd site.

The intensities of 100 and 110 reflections of the YPd<sub>3</sub>D<sub>0.19</sub> sample were measured as a function of temperature to investigate the temperature dependence of the occupation probabilities of the 6Pd and 2Y4Pd sites. It is noted that the intensity of 100 and 110 reflections changes appreciably with temperature; with increasing temperature the 110 peak is lowered while the 100 peak become higher. The parameters  $u$  and  $v$  which represent the occupation probabilities by the D atoms on the 6Pd and 2Y4Pd sites, respectively, are obtained from the diffraction data at various temperatures between 70 and 518 K. Since the numbers of the octahedral sites are larger than the number of H (D) atoms, the relative occupation numbers can be calculated using a Boltzmann distribution function to good approximation. In Fig. 1, the  $v/u$  value is plotted against the reciprocal temperature ( $1/T$ ), where the solid line corresponds to the theoretical values for  $\Delta\epsilon=0.024$  eV. From this plot, the potential energy difference between 6Pd and 2Y4Pd sites is evaluated to be  $0.025 + 0.005$  eV/atom. At temperature above 400 K, however, the observed values increase suddenly, and this phenomenon is presumed to be associated with an order-disorder transition in the hydrogen distribution.

According to the semiempirical heat of formation model by Jacob *et al.*<sup>2</sup> and Giessen and Riesterer,<sup>3</sup> the occupancy of the interstitial site is determined by the heat of formation of imaginary ternary metal hydrides formed between the hydrogen atom and the host metal atoms forming the interstitial site in consideration. In the YPd<sub>3</sub> structure, there are two kinds of octahedral sites coordinated by six nearest-neighbor metal atoms and formation of Y<sub>2</sub>Pd<sub>4</sub>H <sub>$x$</sub>  and Pd<sub>6</sub>H <sub>$x$</sub>  hydrides is expected. The heat of formation of these hydride clusters was calculated by Driessen *et al.*,<sup>8</sup> and the  $\Delta H_{2Y4Pd}$  and

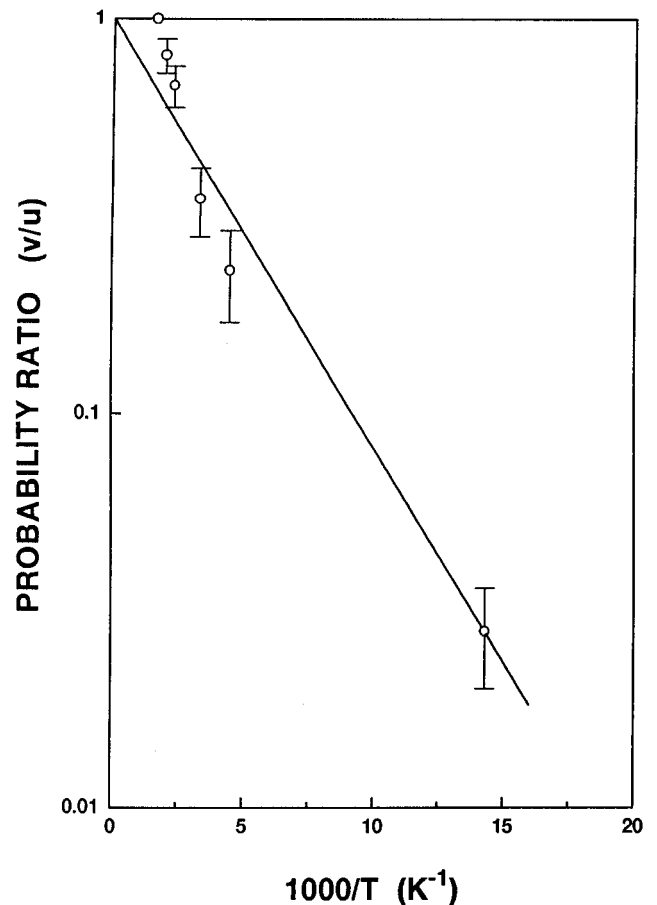


FIG. 1. Ratio of occupation probabilities  $v/u$  versus reciprocal temperature. The solid line corresponds to the theoretical value for  $\Delta\epsilon=-0.024$  eV.

$\Delta H_{6\text{Pd}}$  values were evaluated to be  $-0.38$  and  $-0.20$  eV/atom, respectively. As for the size of holes at interstitial sites, the hole radii for the 6Pd and 2Y4Pd sites are evaluated to be  $0.76$  and  $0.42$  Å, respectively, if we use the covalent radii which are  $1.62$  and  $1.28$  Å for yttrium and palladium atoms, respectively. Therefore, the present neutron-diffraction result which shows the preference of the 6Pd site occupancy by the H atoms is consistent with the hole size criteria, but is in contradiction to the prediction by the imaginary hydride model.

In order to determine the preferential site for the H atoms in the  $\text{YPd}_3$  compounds theoretically, first-principles calculations of the total energy of the hydride cluster with different hydrogen positions have been carried out. All theoretical results presented here are obtained within the local-density-functional theory<sup>9</sup> using a pseudopotential approach. The electronic wave functions are presented in terms of plane waves, and we have taken into account plane waves up to a kinetic energy of 500 eV. The atomic configurations  $1s^2 2p^0$  for H,  $4d^1 5s^2 5p^0$  for yttrium, and  $4d^{10} 5s^0 5p^0$  for palladium are used for generating the norm-conserving pseudopotentials in Kleinman-Bylander form.<sup>10</sup> The exchange-correlation potential due to Ceperley and Alder is employed as parametrized by Perdew and Zunger.<sup>11</sup> Brillouin-zone integrations are carried out with four  $k$  points in the irreducible part. To accelerate the energy convergence in our conjugate-gradient optimization of total energy, we introduce a smearing of band structure which is about 0.1 eV. This procedure has been applied very successfully to the relaxation calculations of many systems, especially for metallic systems. Details of the method can be found in Ref. 12. The hydride supercell used for the calculation consists of  $2 \times 2 \times 2$  unit cells, which corresponds to  $\text{Y}_8\text{Pd}_{24}\text{H}$  ( $\text{YPd}_3\text{H}_{0.125}$ ) composition. In order to find the most favorable position of hydrogen, we move the hydrogen atom along the line from the 6Pd site to the 2Y4Pd site and calculate the total energy. All atoms except hydrogen are allowed to relax freely. Figure 2 shows the result of the total energy as a function of distance from the 6Pd site to the hydrogen atom. From this figure we find that the 6Pd site is energetically more favorable than the 2Y4Pd site and the total-energy difference is 0.49 eV. The energy barrier from the 6Pd site to the 2Y4Pd site is 1.185 eV. At the interstitial 6Pd and 2Y4Pd sites, the lattice distortion created by the hydrogen contributes about 0.04 eV to the total energy and the atom displacements of the surrounding Pd atoms are within 0.02 Å. It is concluded, therefore, that the difference in the electronic interactions between hydrogen and host atoms is largely responsible for the hydrogen occupancy of interstitial sites in intermetallic hydrogen. We have also calculated the vibrational frequencies of hydrogen at the 6Pd

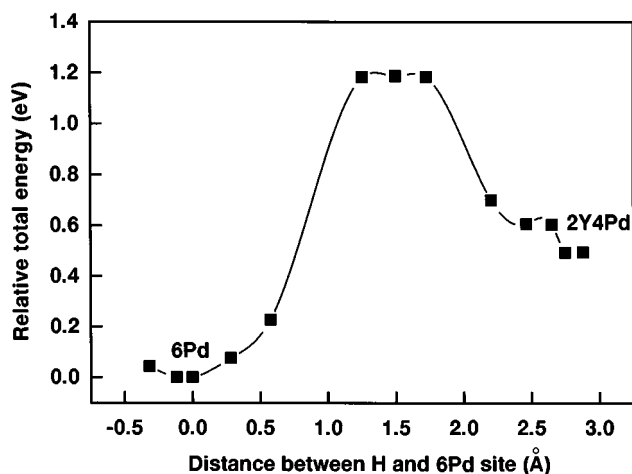


FIG. 2. Total energy as a function of distance from the 6Pd site to the hydrogen atom.

and 2Y4Pd sites, respectively, and the results show that at the 6Pd site the frequencies are threefold degenerate and real, while at the 2Y4Pd site the frequencies are imaginary, which indicates that the 2Y4Pd site is a saddle point, not a stable site for a hydrogen atom to occupy.

The total-energy calculation for the hydride cluster with different hydrogen content reveals that the total-energy difference depends on the hydrogen concentration; the total-energy difference for the hydride cluster of the  $\text{YPd}_3\text{H}_{1.0}$  composition is evaluated to be 0.18 eV/atom. The discrepancy in the total energy between experiment and the first-principles calculation described above may be attributed to the difference in hydrogen concentration or the deviation from stoichiometric composition, as well as the neglect of the thermal effects in the calculation.

In conclusion, the hydrogen site in the binary metal compound of  $\text{YPd}_3\text{H}_x$  has been studied experimentally and theoretically. The neutron diffraction gives clear evidence that the hydrogen atoms preferentially occupy the octahedral site formed by six Pd atoms rather than the site formed by two Y and four Pd atoms. The first-principles calculations based on local-density-functional theory show that the most favorable position for hydrogen corresponds to the 6Pd site, and the difference in the electronic interactions between hydrogen and host atoms is responsible for the occupation of specified interstitial sites by hydrogen in the intermetallic hydride.

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