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# Distribution of hydrogen atoms in $YPd_3H_x$ studied by neutron diffraction and inelastic neutron scattering

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**Abstract**

The $YPd_3H(D)_x$ system was studied by means of neutron powder diffraction as well as incoherent inelastic neutron scattering at various temperatures for $x=0$, 0.19 and 0.30. The $L1_2$ structure of the $YPd_3$ was conserved on hydrogenation. The position and site occupation of H(D) atoms were determined from the neutron diffraction data. The H(D) atoms occupy preferentially the characteristic octahedral interstices composed by 6 Pd atoms. This result is discussed in view of the recently proposed criteria predicting the relative hydrogen occupancy of various interstitial sites in intermetallic hydride.

*Keywords:* Intermetallic compounds; Neutron diffraction; Hydrides; Hydrogen location

## 1. Introduction

A simple model to predict the interstitial sites preferentially occupied by the hydrogen atoms in intermetallic compounds has been suggested by Jacob [1,2] and Griessen [3][1]. According to this model the occupancy of the interstitial sites is determined by the heat of formation of imaginary binary hydrides formed between the hydrogen atom and the host metal atoms forming the interstitial site in consideration. Accordingly, a value $\Delta H$ which is the sum of these heats of formation is assigned to each site. The relative hydrogen occupancy has been calculated in a quantitative manner using Boltzmann's distribution function and the $\Delta H$ values. On the other hand, Westlake [4] and Magee [5] have claimed that interstitial hole size and hydrogen–hydrogen interatomic distance are used to predict the hydrogen occupied sites in hydrides of the intermetallic compounds. They find that an increase in hole size is accompanied by greater stability.

Neutron diffraction and neutron scattering experiments on intermetallic hydrides have provided quantitative information on the distribution of the hydrogen (the relative occupancy) among the various interstitial sites [6–12]. The purpose of the present paper is to examine experimentally the validity of the above mentioned criteria in the case of $YPd_3$ compounds of $L1_2$ structure.

Neutron diffraction and incoherent inelastic neutron scattering measurements have been carried out on the metallic hydride of $YPd_3H(D)_x$ for $x=0$, 0.19 and 0.30 to study the hydrogen (deuterium) sites and their dynamics. The relative hydrogen occupancies among the interstitial sites were examined from the powder neutron diffraction data on $YPd_3D_{0.19}$ at the temperature range between 70 and 518 K. The results were compared with the theoretical predictions concerning the relative occupancy of various interstitial sites in $YPd_3H_x$.

## 2. Experimental

A sample of $YPd_3$ 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 <100 mesh. Before hydrogenation, the powder samples were activated at 773 K for 3.6 ks in a vacuum. Subsequently, they were hydrogenated using high-purity hydrogen (deuterium) at a pressure of 5 MPa for 173 ks between 300 and 773 K. The neutron diffraction experiments were carried out on the Kinken powder diffractome-

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[1] Throughout this work we use the words hydrogen and deuterium indifferently and assume that their chemical behavior is identical.

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ter (KPD) at the JRR-3M reactor of Japan Atomic Energy Research Institute Tokai. The neutron wavelength was 1.767 Å and the diffraction patterns were recorded over the angular range $10° < 2\theta < 104°$ in steps of 0.1°. The inelastic incoherent scattering measurements were performed using a crystal analyzer time-of-flight (CAT) spectrometer which is installed in the neutron scattering facility (KENS) with the pulsed spallation neutron source at the National Laboratory for High Energy Physics (KEK), Japan. The energy resolution of the CAT spectrometer is $\Delta\epsilon/\epsilon \simeq 2\%$.

## 3. Results

Analysis of X-ray and neutron diffraction patterns from the $YPd_3H(D)_x$ for the different H(D) contents have confirmed that the $L1_2$-type structure of $YPd_3$ is preserved on hydrogenation up to $x=0.30$. Neutron diffraction patterns obtained from $YPd_3$, $YPd_3H_{0.30}$ and $YPd_3D_{0.19}$ are shown in Figs. 1–3, respectively. It will be seen from these figures 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 $YPd_3H_{0.30}$, while for $YPd_3D_{0.19}$ 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 occupation of the interstitial sites by H(D) atoms.

In the face-centered cubic $YPd_3$ (space group Pm3m: 1 Y atom in 1a (0, 0, 0) 3 Pd atoms in 3c (0, 1/2, 1/2)), the following interstitial sites have been identified:

1. 1b octahedral site composed of 6 Pd atoms (1/2, 1/2, 1/2).
2. 3d octahedral sites composed of 2 Y and 4 Pd atoms (1/2, 0,0).
3. 8g tetrahedral sites composed of 1 Y and 3 Pd atoms (1/4, 1/4, 1/4).

Then, the structure factors for the $YPd_3H_x$ are expressed as follows,

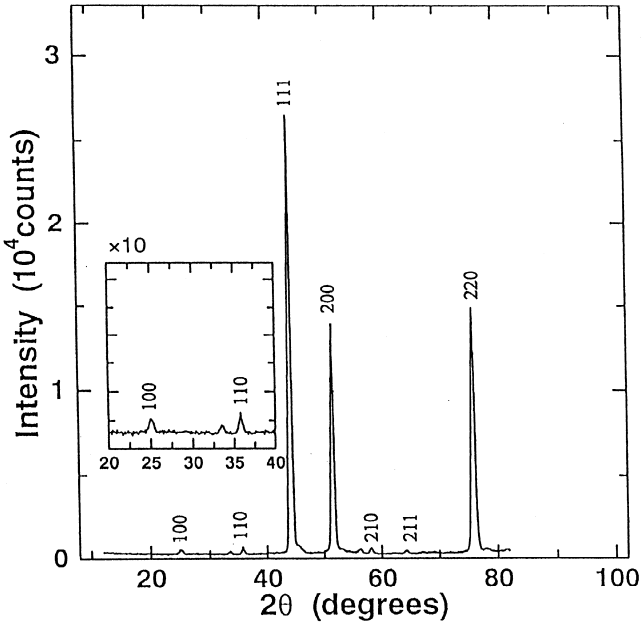

Fig. 1. Neutron diffraction patterns of $YPd_3$ measured at 300 K. The irrational peaks observed at 33.5°, 45.2°, 52.7° and 56.1° presumably originate from $YPd_2$ phase.

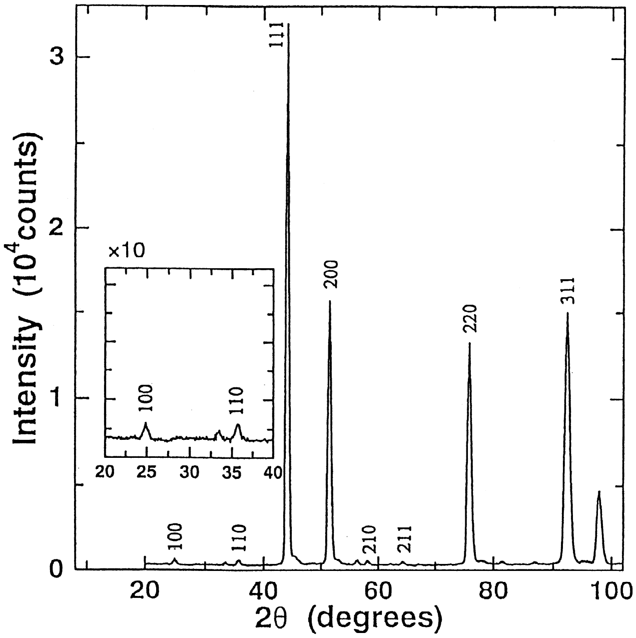

Fig. 2. Neutron diffraction patterns of $YPd_3H_{0.30}$ measured at 300 K.

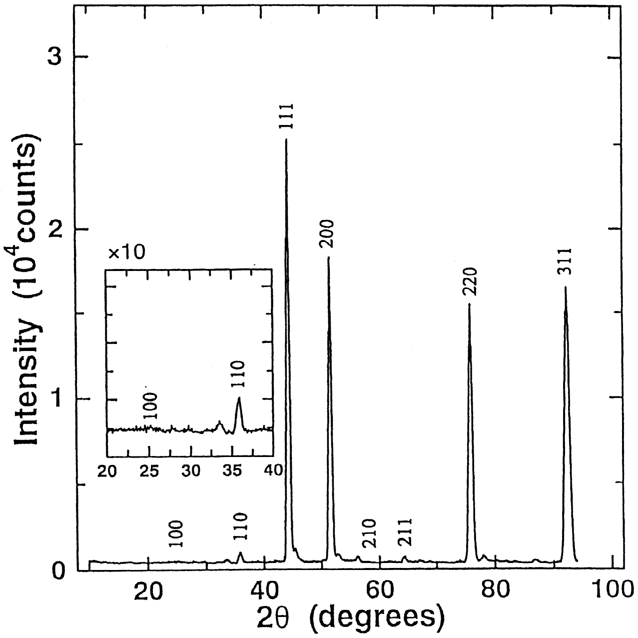

Fig. 3. Neutron diffraction patterns of $YPd_3D_{0.19}$ measured at 70 K.

Table 1
Structure factors of various reflections for $YPd_3H_x$

| Type of reflections | Indices | Structure factor $F$ |
|---|---|---|
| Fundamental reflections | $h, k, l$: all even, $h/2+k/2+l/2=2n$ | $b_Y+3b_{Pd}+b_H(u+3v+8w)$ |
| | $h, k, l$: all even, $h/2+k/2+l/2=2n+1$ | $b_Y+3b_{Pd}-b_H(u+3v-8w)$ |
| | $h, k, l$: all odd | $b_Y+3b_{Pd}-b_H(u+3v)$ |
| Superlattice reflections | $h, k, l$: mixed, $h+k+l=2n$ | $b_Y-b_{Pd}+b_H(u-v)$ |
| | $h, k, l$: mixed, $h+k+l=2n+1$ | $b_Y-b_{Pd}-b_H(u-v)$ |

$b_Y$, $b_{Pd}$ and $b_H$ are the neutron scattering amplitude for yttrium, palladium and hydrogen respectively, and $u$, $v$ and $w$ are the occupation probabilities of hydrogen in the interstitial sites 1b, 3d and 8g respectively.

$$\begin{aligned} F(hkl) = b_Y & \\ & + b_{Pd}(\cos \pi k \cos \pi l + \cos \pi l \cos \pi h \\ & + \cos \pi h \cos \pi k) + u b_H \cos \pi h \cos \pi k \cos \pi l \\ & + v b_H(\cos \pi h + \cos \pi k + \cos \pi l) \\ & + 8 w b_H \cos \pi h/2 \cos \pi k/2 \cos \pi 1/2 \end{aligned}$$

where $b_Y$, $b_{Pd}$ and $b_H$ are the scattering amplitudes of yttrium, palladium and hydrogen, respectively, and three parameters $u$, $v$ and $w$ are occupation probabilities of hydrogen in the sites 1b, 3d and 8g, respectively. The parameters $u$, $v$ and $w$ are related to the hydrogen fraction per formula unit $x$; $x=u+3v+8w$. Table 1 shows the structure factor obtained for the reflections with various indices.

The inelastic incoherent scattering spectrum on the CAT spectrometer for $YPd_3H_{0.30}$ at 6 K is shown in Fig. 4. The inelastic incoherent scattering was employed to determine the relative occupation by hydrogen on the tetrahedral and octahedral sites from the difference of the hydrogen vibrations between the both sites [13]. The large peak observed near 55 meV is identified as the vibrational spectrum of the octahedral site hydrogens. The width of this peak is believed to be result of the dispersion in the optical modes as was observed in the similar system of $PdH_{0.7}$ [14]. The peak at 120 meV which is characteristic of the tetrahedral site hydrogen vibration is not recognized in this spectrum. Consequently most H(D) atoms will occupy the octahedral 1b and 3d sites.

A quantitative comparison of the diffraction intensity with the calculation was made using neutron diffraction data. The observed data are listed in Table 2 in comparison with the calculation. Here the nuclear scattering amplitudes $b$ adopted for yttrium, palladium, deuterium and hydrogen are 0.77, 0.63, 0.65 and $-0.378\times10^{-12}$ cm, respectively. A good agreement is obtained if we assume the values of occupation probabilities $u=0.12$, $v=0.06$ and $w=0$ for $YPd_3H_{0.30}$ at 300 K, and $u=0.175$, $v=0.005$ and $w=0$ for $YPd_3D_{0.19}$ at 70 K. The structure factors calculated using

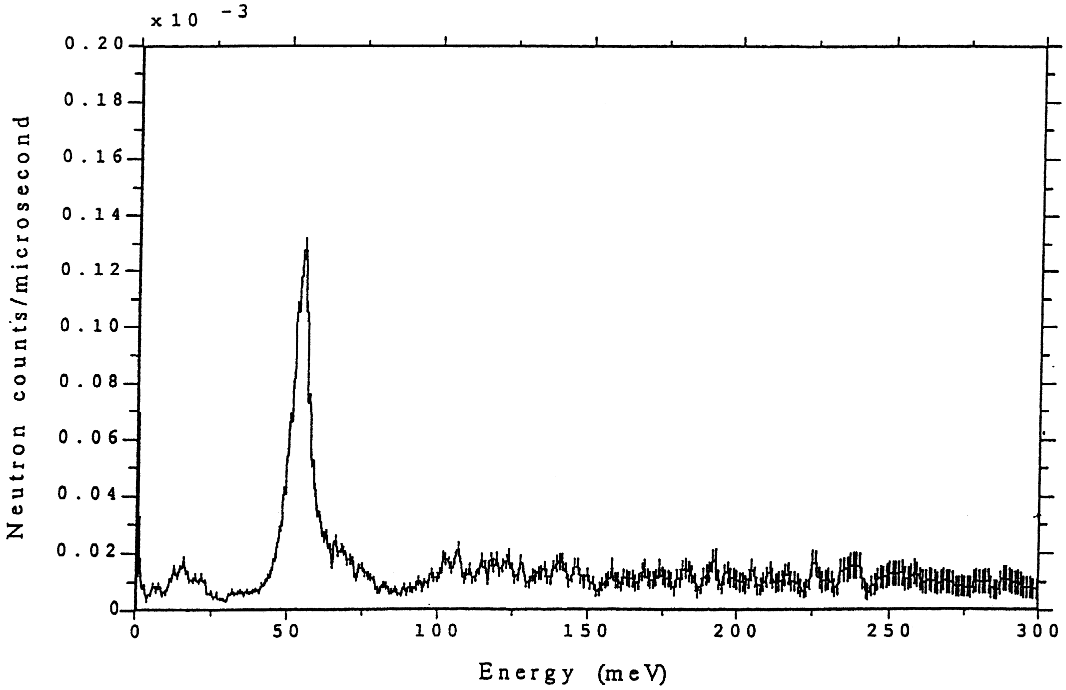

Fig. 4. Incoherent inelastic neutron scattering spectra of $YPd_3H_{0.30}$ measured at 6 K.

Table 2
A comparison of the diffraction intensity with the calculation

| $h$ | $k$ | $l$ | $YPd_3$ (300 K) | | $YPd_3H_{0.30}$ (300 K) | | $YPd_3D_{0.19}$ (70 K) | |
|---|---|---|---|---|---|---|---|---|
| | | | $F_{Obs.}$ | $F_{cal.}$ | $F_{Obs.}$ | $F_{cal.}$ | $F_{Obs.}$ | $F_{cal.}$ |
| 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 | 2.73 | 2.68 | 2.79 | 2.79 | 2.56 | 2.58 |
| 2 | 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 |

these values are listed in the fourth and sixth columns of Table 2, and the reliability factors are less than 0.03. These results indicate that the H(D) atoms occupy preferentially the octahedral 1b site composed of 6 Pd atoms.

The intensities of 100 and 110 reflections of $YPd_3D_{0.19}$ sample were measured as a function of temperature to investigate the temperature dependence of the occupation probabilities for the octahedral 1b and 3d 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 1b and 3d sites, respectively, are obtained from the diffraction data at various temperatures between 70 and 518 K. Since the number of interstitial sites is larger than the number of H(D) atoms, the relative occupation numbers of the 1b and 3d sites is calculated by the Boltzmann distribution function with a good approximation [2]. In Fig. 5, the $v/u$ values are plotted against reciprocal temperature ($1/T$). From this plot, the potential energy difference between 1b and 3d sites $\Delta\epsilon = \epsilon_v - \epsilon_u$, is evaluated to be 2.0+0.1 kJ/mol H.

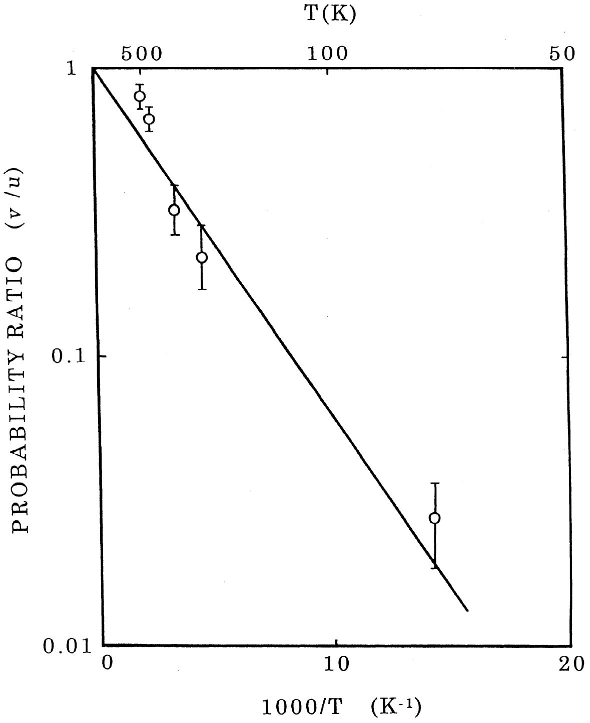

Fig. 5. Ratio of occupation probabilities $v/u$ against reciprocal. $\Delta\epsilon =$ 2.0+0.1 kJ (mol H)$^{-1}$.

## 4. Discussion

According to the semiempirical imaginary hydride model by Jacob [1], the occupancy of the interstitial site is determined by the heat of formation of imaginary binary metal hydrides formed between the hydrogen atom and the host metal atoms forming the interstitial site in consideration. In $YPd_3$ structure there are two kinds of octahedral sites coordinated by $N=6$ nearest-neighbor metal atoms, and formation of the binary metal hydrides of $Y_2Pd_4H_x$ and $Pd_6H_x$ is expected. The heat of formation of these hydride cluster was calculated by Griessen et al. [15]. From the tables in ref. [15] we find that $\Delta\ H_{2Y4Pd}$ and $\Delta\ H_{6Pd}$ values are −36.4 and −19.5 kJ/mol H, respectively. On the other hand, the present neutron diffraction and scattering experiments show that the H(D) atoms in $YPd_3H(D)_x$ occupy preferentially the octahedral 1b site in contrast to the prediction by the imaginary hydride model.

Next we will compare the size of the holes at 1b and 2d sites to test the criteria proposed by Westlake [4]. Judging from the lattice constant for $YPd_3$ ($a=4.074$ Å), the covalent radii which are 1.62 and 1.28 Å for yttrium and palladium atoms respectively may be used to calculate the hole sizes. The hole radii thus estimated would be 0.76 and 0.42 Å for 1b and 3d sites respectively. It is suggested, therefore, that the H(D) atoms occupy preferentially the larger hole at 1b site in agreement with the experimental result. As pointed out by Sugimoto and Fukai [16], the relative stability of the interstitial sites occupied by the H(D) atoms depends on the lattice distortion surrounding the interstitial H(D) atoms. The discrepancy between the prediction by imaginary hydride model and our experiment may indicate the significance of the local lattice distortion by H atoms in the binary metallic compounds or alloys.

## 5. Conclusion

The neutron diffraction and inelastic neutron scattering experiments show the preferential occupation by the H atoms of the larger octahedral hole composed of 6 Pd atoms. This result is consistent with the hole size criteria, but is in contradiction to the imaginary hydride model prediction of hydrogen occupancy of interstitial sites. The neutron diffraction and inelastic neutron scattering experiments should be performed on the other intermetallic compounds or alloys of $L1_2$-type structure with different hydrogen contents in order to reveal how the relative stability of the H atoms in the interstitial sites will vary with the interaction of H atoms with the surrounding metal lattice.

## References

[1] I. Jacob, J.M. Bloch, D. Shaltiel and D. Davidov, *Solid State Commun., 35* (1980) 155.
[2] I. Jacob and J.M. Bloch, *Solid State Commun., 42* (1982) 541.
[3] R. Giessen and A. Driessen, *J. Less-Common Met., 103* (1984) 245.
[4] D.G. Westlake, *J. Less-Common Met., 75* (1980) 177.
[5] C.B. Magee, J. Leu and C.E. Lundin, *J. Less-Common Met., 78* (1981) 119.
[6] J.J. Didisheim, K. Yvon, P. Fischer and D. Shaltiel, *J. Less-Common Met., 73* (1980) 355.
[7] D. Fauchart, A. Rouault, C.B. Shoemaker and D.P. Shoemaker, *J. Less-Common Met., 73* (1980) 363.
[8] M. Latroche, V.P.-Boncour, J. Prjewoznic, A. Percheron-Guegan and F.B.-Vigneron, *J. Alloys Comp., 231* (1995) 99.
[9] M.I. Bartashevich, A.N. Pirogov, V.I. Voronin, T. Goto, M. Yamaguchi and I. Yamamoto, *J. Alloys Comp., 231* (1995) 104.
[10] M. Yoshida, E. Akiba, Y. Shimojo, Y. Morii and F. Izumi, *J. Alloys Comp., 231* (1995) 755.
[11] J.L. Soubeyroux, M. Bououdina, D. Fruchart and P. de Rango, *J. Alloys Comp., 231* (1995) 760.
[12] J.J. Udovic, J.J. Rush, R. Hempelmann and D. Richter, *J. Alloys Comp., 231* (1995) 144.
[13] J.A. Goldstone, J. Eckert, P.M. Richards and E.L. Venturini, *Solid State Commun., 49* (1984) 475.
[14] Y. Nakai, E. Akiba, H. Asano and S. Ikida, *J. Phys. Soc. Jpn., 61* (1992) 1834.
[15] R. Griessen, A. Driessen and D.G. de Groot, *J. Less-Common Met., 103* (1984) 235.
[16] H. Sugimoto and Y. Fukai, *Phys. Rev. B, 22* (1980) 670.