Site Occupation and Local Vibration of Hydrogen Isotopes in Hexagonal Ti5Si3 H(D)1-x

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Site Occupation and Local Vibration of Hydrogen Isotopes in Hexagonal Ti_5Si_3 $H(D)_{1-x}$

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A structure analysis of $Ti_5Si_3D_{0.9}$ has been carried out to determine the deuterium trap sites by neutron powder diffraction with the Rietveld profile analysis. It is revealed that the deuterium atoms are located at octahedral (2b) sites surrounded by six Ti atoms in the crystal structure of $Ti_5Si_3D_{0.9}$, space group $P6_3/mcm$. Local vibration spectrum of hydrogen in $Ti_5Si_3H_{0.83}$ measured by neutron inelastic scattering supports this result; the energy eigenvalue of the primary vibration mode is found at 7.53 kJ/mol (78 meV). The hole radius and the spring constant of the Ti-H(D) bond are discussed.

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Keywords: *$Ti_5Si_3D_{0.9}$, $Ti_5Si_3H_{0.83}$, neutron diffraction, neutron inelastic scattering, deuterium location, hydrogen vibration*

I. Introduction

Occupation sites and local vibration of hydrogen isotopes (H, D) dissolved in hexagonal metal lattice have not been clarified so well as those in bcc and fcc metals. A recent neutron elastic and inelastic scattering study on hydrogen doped α-$ZrO_{0.4}$ and $TiO_{0.3}$[1] has revealed that hydrogen isotopes are trapped at tetrahedral interstices (t-sites) in $ZrO_{0.4}$, while they occupy octahedral interstices (o-sites) in $TiO_{0.3}$. It is worth noting that hydrogen isotopes can sit at either of the interstices in hexagonal metal lattices, and they tend to sit at o-sites rather than t-sites in the hexagonal lattice with relatively small dimensions; the lattice constants of α-Ti and α-Zr are $a=0.295$, $c=0.468$ nm and $a=0.323$, $c=0.513$ nm, respectively.

The present study is concerned with the determination of occupation site and of local vibration mode of hydrogen isotopes dissolved in a hexagonal compound Ti_5Si_3 with the Mn_5Si_3 type (or $D8_8$-type) structure. The Mn_5Si_3 type structure is found among rather wide varieties of compounds called sometime Nowotny phase[2], in which Mn atoms are replaced by other transition metals and Si atoms by Al, Ga, Ge, Sn, Sb and Pb. For example, Ti_5Ge_3 and Ti_5Sn_3 are isomorphic with Ti_5Si_3[3].

Figure 1 shows schematically the crystal structure of Ti_5Si_3 (space group $P6_3/mcm$). Here a hexagonal symmetry of the atomic arrangement is seen in the (001) projection. In the unit cell, Ti atoms are at $6g(x\ 0\ 1/4)$ $x=0.25$ and $4d(1/3\ 2/3\ 0)$ sites, while Si atoms are at $6g(x'\ 0\ 1/4)$ $x'=0.60$. The lattice parameters of Ti_5Si_3 prepared with high purily Ti and Si are reported as $a=0.7444$ nm and $c=0.5143$ nm, but are influenced by contaminations (O, Mo, Al, Ca and Si)[4]. Nowotny[2] suggested that o-sites of the Mn_5Si_3 type structure can be filled by small metalloid atoms such as boron. Nevertheless, there are three possible hydrogen sites, namely A-sites at $2b(0\ 0\ 0)$, B-sites at $4c(1/3\ 2/3\ 1/4)$ and C-sites at $6f(1/2\ 0\ 0)$, as shown in Fig. 1. The interatomic distances from the A, B and C sites to the nearest Ti or Si atoms are about 0.225 nm (H-Ti), 0.129 nm (H-Ti) and 0.150 nm (H-Si), respectively. The B-site occupation of hydrogen isotopes seems unrealistic because of their narrowness. On the other hand, hydrogen isotopes will be easily trapped at the roomy A-sites or o-sites where metalloid atoms

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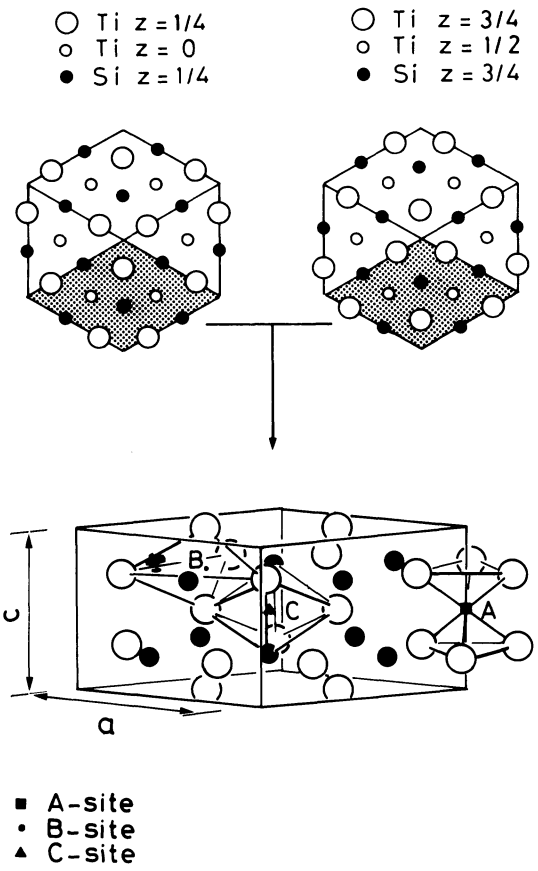


Fig. 1 Crystal structure of Ti_5Si_3, showing a hexagonal unit cell. Three interstitial sites are indicated. A, B and C-sites are 2b(0 0 0, 0 0 1/2), 4c(1/3 2/3 1/4, 2/3 1/3 1/4, 1/3 2/3 3/4, 2/3 1/3 1/4) and 6*f*(1/2 0 0, 0 1/2 0, 1/2 1/2 0, 1/2 0 1/2, 0 1/2 1/2, 1/2 1/2 1/2) sites, respectively.

can also be trapped. The occupation of C-sites may not be ruled out because of the small atomic radius of Si (~0.12 nm) and the natural Si-H distance (0.148 nm) in inorganic compounds[5], even though the hole radius at the C-sites (r=0.036 nm) is slightly shorter than the critical hole radius (r_c=0.037−0.039 nm) for stable hydrides postulated by Westlake[6]. In the present case, the shortest H-H distance, that is the distance between A and C sites 0.373 nm, is adequately longer than the critical H-H distance, 0.21 nm, estimated by Switendick[7].

Recently, McColm *et al.*[8] have found that Y_5Si_3 with the $D8_8$ type structure absorbs hydrogen up to the composition $Y_5Si_3H_{6.3}$, forming three kinds of hydride, i.e. α-$Y_5Si_3H_{1.0}$, β-$Y_5Si_3H_{2.0}$ and γ-$Y_5Si_3H_x$ (x>4.0). However, the hydrogen trap site has not been determined in these phases.

In the following, first we present experimental results of neutron inelastic scattering on $Ti_5Si_3H_{0.83}$ to determine the energy eigenvalue of the local vibration mode of hydrogen atoms. Since the energy eigenvalue is quite sensitive to the local environment of hydrogen atoms, it provides valuable insight into the hydrogen trap site. Then we describe profile analyses of neutron and X-ray powder diffraction on $Ti_5Si_3D_{0.9}$ in comparison with Ti_5Si_3 to determine the site of hydrogen isotopes.

II. Experimental Procedures

A Ti_5Si_3 sample was prepared from sponge Ti(99.5%) and pure Si(99.999%) in an arc-melting furnace under argon atmosphere. The ingots were repeatedly arc-melted on a water-cooled Cu hearth and powdered by crushing. Powder samples of $Ti_5Si_3H_{0.83}$ and $Ti_5Si_3D_{0.9}$ were produced by a gas charging method; i.e. Ti_5Si_3 powders of 100 mesh were heated up to 770 K in a vacuum furnace of 10^{-6} Pa for the surface activation, and then contacted with purified H_2 or D_2 gas introduced into the furnace.

Neutron inelastic scattering experiments of $Ti_5Si_3H_{0.83}$ were carried out using a time of flight (TOF) type spectrometer with a crystal analyzer[9]. A powder sample was sealed in a flat aluminum cassette (85×110×3 mm^3). The experimental energy resolution at about 9.65 kJ/mol (100 meV) is 0.39 kJ/mol (4 meV). The density of states $g(\omega)$ of local vibration mode and the average thermal vibration amplitude $\langle u^2 \rangle$ of hydrogen atoms are obtained from the experimental spectra by an iterative method in a similar way to the previous paper[1].

Neutron diffraction studies were carried out by the use of a diffractometer (KID) in the JRR-2 reactor of JAERI and a TOF type diffractometer at Laboratory of Nuclear Science (Tohoku University). Figure 2 shows a horizontally cutaway section of the TOF diffractometer constructed by Onodera and

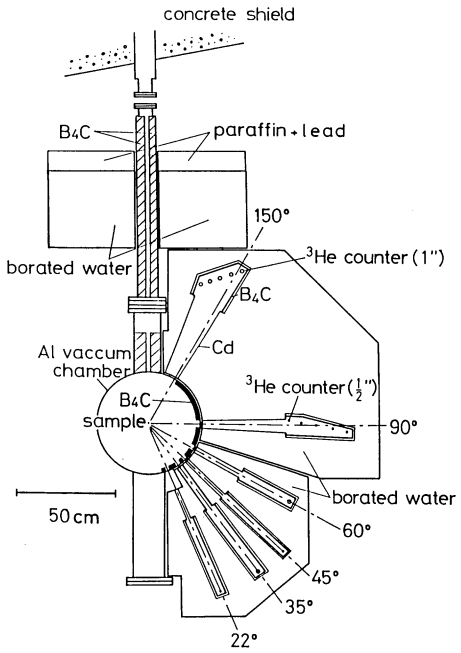


Fig. 2 Horizontally cutaway section of TOF diffractometer[10].

Yamada[10], where pulsed thermal neutrons fly from the top to the bottom. Time-focused counter banks are installed at $2\theta=90°$ and 150° to boost the counting efficiency. An aqua solution of boric acid neutralized by chloric acid was utilized as a sealant against background γ-rays and fast neutrons. The total flight-path length from a neutron moderator to the counters is about 7.2 m. The resolution, $\Delta d/d$, of the TOF diffractometer is within 2% at $2\theta=150°$ and 3% at $2\theta=90°$. Powder samples were set in a cylindrical vanadium sample holder 15 mm in diameter and 80 mm in height.

A sample holder 10 mm in diameter and 40 mm in height was used for the KID diffractometer. The $\theta-2\theta$ neutron diffraction data were obtained by a point-counting mode at a step of 0.1 degree. Using powder sample of 350 mesh, X-ray diffraction spectra were obtained by $\theta-2\theta$ scans at a rate of 0.5 deg/min with a Cu target and an analyzer crystal.

A computer program package (RIETAN) made by Izumi[11] for profile refinements by Rietveld method[12] was used for the analyses of X-ray and neutron diffraction spectra obtained by the conventional $\theta-2\theta$ measurements. A computer program package (TOFLS) made by Von Dreele *et al.*[13] was used for the analysis of TOF neutron diffraction data. The same type of program was utilized by Murata *et al.*[14] for a recent analysis of TOF neutron powder diffraction spectra of Ta_2D.

III. Local Mode in $Ti_5Si_3H_{0.83}$

A well-established peak is observed in the neutron inelastic scattering spectrum of Fig. 3(a) where the abscissa corresponds to the neutron time of flight; the higher the energy,

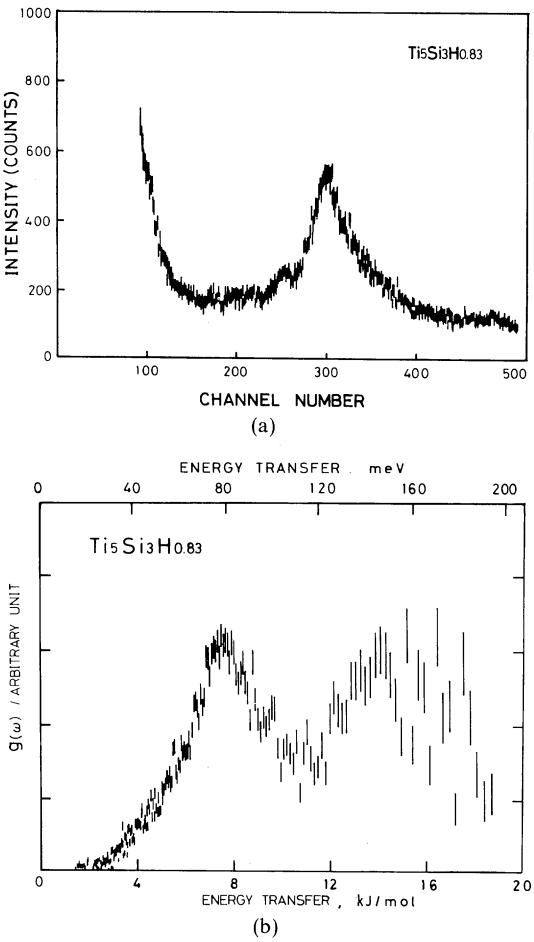


Fig. 3 (a) Inelastically scattered neutron intensity vs time of flight of $Ti_5Si_3H_{0.83}$ at room temperature. Abscissa corresponds to kinetic energy transfered to neutrons. (b) Density of states, $g(\omega)$, of localized thermal vibration of hydrogen atom.

the shorter the time necessary for the flight. Figure 3(b) shows the density of states $g(\omega)$ vs the energy transfer $\hbar\omega$ deduced from the experimental spectrum. We note here that the first peak position of $g(\omega)$ is 7.53 ± 0.39 kJ/mol (78 ± 4 meV) with the FWHM of 3.9 kJ/mol (40 meV), and a broad maximum around 15.44 kJ/mol (160 meV) corresponds to the second harmonic peak.

An average thermal vibration amplitude $\langle u^2\rangle$ of hydrogen atoms is obtained as 6.8×10^{-4} nm^2. On the assumption of the harmonic oscillator and the mass law, the Debye parameter $B=8\pi^2\langle u^2\rangle$ of deuterium atoms in $Ti_5Si_3D_{0.9}$ is estimated as 2.68×10^{-2} nm^2. This value is comparable to an experimental value of neutron diffration study given in the following section.

The energy eigenvalue 7.53 kJ/mol (78 meV) obtained above is close to 8.30 kJ/mol (86 meV) of $TiO_{0.3}H_{0.1}$ observed by Mukawa *et al.*[1], but is lower than the value 10.18 kJ/mol (105.5 meV) of $TiH_{0.07}$ at 600 K measured by Hempelmann *et al.*[15]. In $TiO_{0.3}H_{0.1}$ and $TiH_{0.07}$, hydrogen atoms are trapped at o-sites in the hcp metal lattices. Consequently the present result suggests that the hydrogen atoms in $Ti_5Si_3H_{0.83}$ are trapped at o-sites or the A-sites. This result also indicates that the local symmetry at the hydrogen site is almost elastically isotropic, since three local vibration modes are degenerated. This is the case at the A-sites.

IV. X-ray and Neutron Powder Diffraction

Figures 4(a)-(d) show X-ray and neutron diffraction curves, $\theta-2\theta$ scan and TOF spectra at $2\theta=90°$ and 150°, of $Ti_5Si_3D_{0.9}$ at room temperature. For comparison with $Ti_5Si_3D_{0.9}$, Fig. 5 shows a $\theta-2\theta$ neutron diffraction curve of Ti_5Si_3. Solid lines in the figures indicate calculated curves for the profile fitting. The fitting was performed by the Rietveld method to minimize the weighted difference, s, between the experimental data and calculated curve with the formula

$$S=\sum_i w_i\{y_i(\mathrm{obs})-y_i(\mathrm{cal})\}^2, \qquad (1)$$

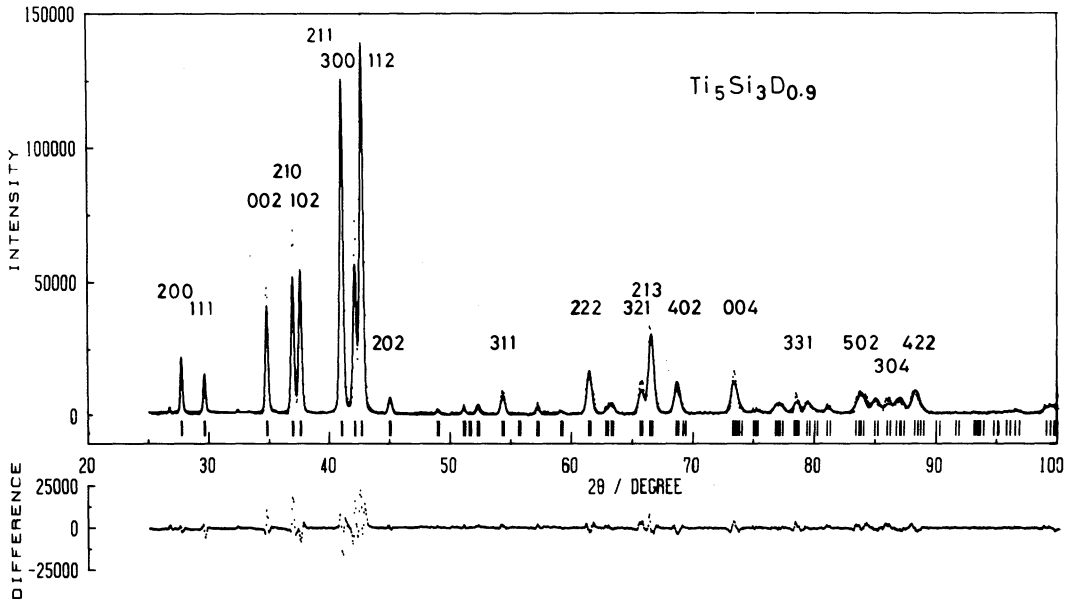
where w_i is statistical weight, y_i(obs) observed intensity, and y_i(cal) calculated intensity. The statistical weight w_i was set reasonably to be related with the observed signal to the background intensity at each point i. Each crystallographic parameter was optimized iteratively using the program packages RIETAN[11] and TOFLS[13] for the X-ray and neutron diffraction data.

We obtained reliable crystallographic parameters for Ti and Si atoms from the X-ray diffraction data. Regarding deuterium atoms, the TOF neutron diffraction data gave reliable thermal parameters from higher-index reflections, and the $\theta-2\theta$ neutron diffraction data gave occupation probabilities from intense low-index peaks.

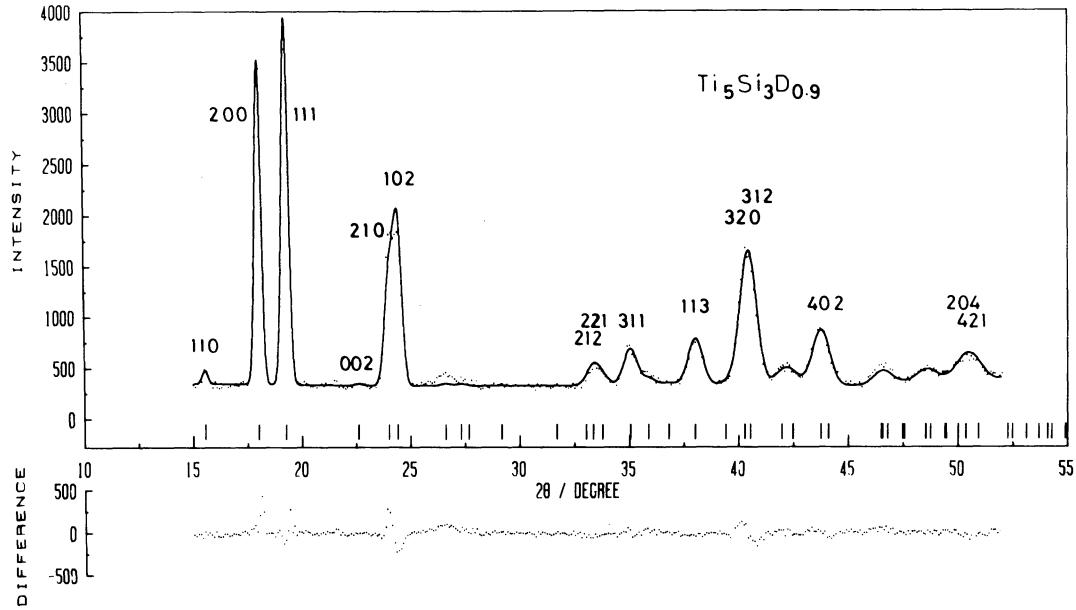
Crystallographic parameters for Ti_5Si_3 and $Ti_5Si_3D_{0.9}$ thus determined are listed in Table 1. Three residuals for structure factors, integrated intensities and profile curves, which are respectively labeled R_f, R_B and R_p, are also listed. The numbers of detected diffraction peaks and consisting Bragg reflections are in the range from 8 to 130. The calculated diffraction curves in Figs. 4(a)-(d) are drawn using the identical crystallographic parameters.

The atomic coordinates of Ti and Si in $Ti_5Si_3D_{0.9}$ are basically identical with those in Ti_5Si_3, $P6_3/mcm$ (No. 193). The deuterium atoms are determined to occupy only the A-sites $2b$(0 0 0) as expected in the previous section. In the least squares calculation, deuterium atoms were assumed in the beginning to occupy A, B and C sites. After several cycles of iteration, the total occupation probabilities at B and C-sites decreased sharply to less than 0.01. The c-axis of $Ti_5Si_3D_{0.9}$ expands about 0.3% but the a-axis shrinks about 0.16% as compared with those of Ti_5Si_3. The volume change is thus about 0.03%, which is within the experimental error. The thermal parameter B of deuterium atoms is 1.96×10^{-2} nm^2 that is slightly below the value (2.68×10^{-2} nm^2) estimated from the hydrogen local mode.

A $Ti_5Si_3H_{0.83}$ powder sample has shown an X-ray diffraction spectrum similar to that of the deuteride. No neutron diffraction measurement has been done because of the tenuous



(a)

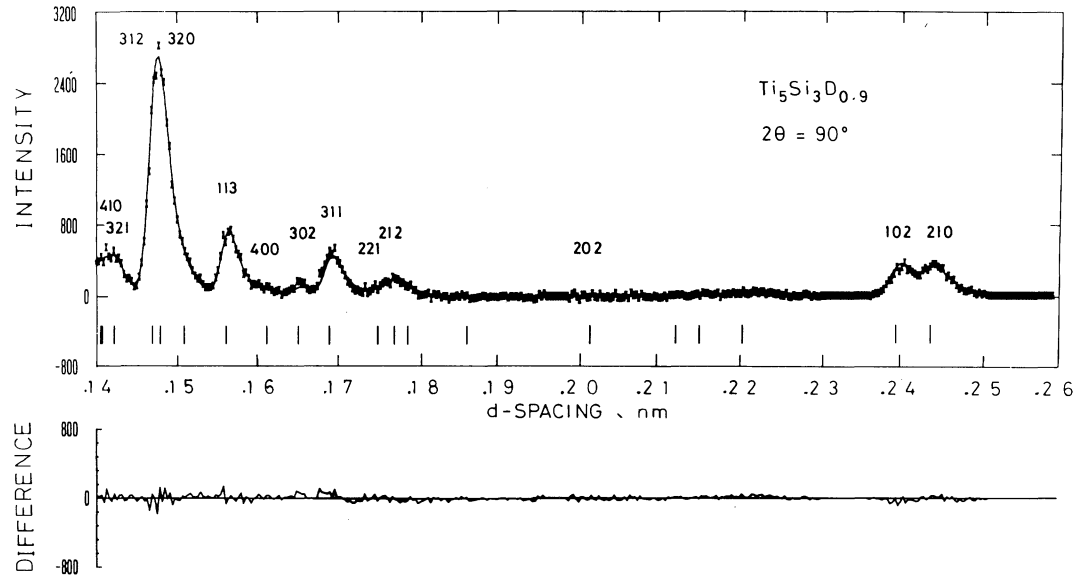


(b)

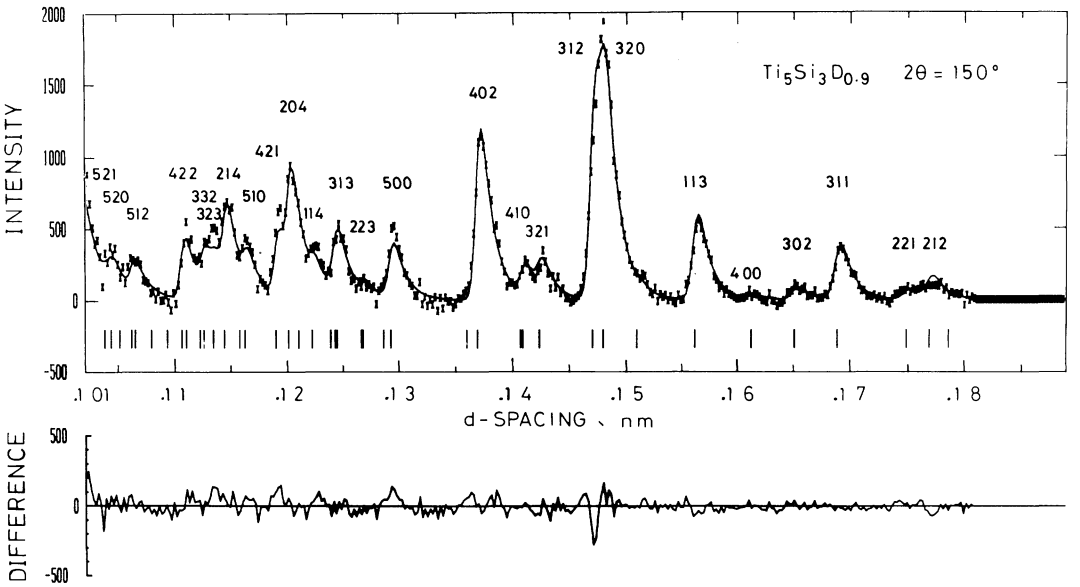
signal to noise ratio S/N due to the strong background intensities arising from hydrogen incoherent scattering.

V. Discussion

The energy eigenvalue of the local hydrogen vibration mode was determined as 7.53 kJ/mol (78 meV). As mentioned before, this value is close to that of $TiO_{0.3}H_{0.1}$[1] but is lower than that of $TiH_{0.07}$[15]. In comparison with these values, the difference is interpretable in terms of the hole radius r at the hydrogen sites. The hole radius calculated from the lattice



(c)



(d)

Fig. 4 Diffraction spectra of $Ti_5Si_3D_{0.9}$; X-ray (a), $\theta-2\theta$ neutron (b) and TOF neutron at $2\theta=90°$ (c) and $2\theta=150°$ (d). Each data-point of the TOF spectra (c and d) corresponds to $\Delta t=8\,\mu$sec of time channel. Solid curves are fitted by the Rietveld method.

parameters and the environmental atom positions is 0.078_4 nm for the A-sites in $Ti_5Si_3D_{0.9}$ and 0.059_4 nm for the o-sites in α-Ti at 600 K. Assuming that the atomic force constants between a hydrogen atom and adjacent metal atoms is inversely related with the hole radius, the energy 7.71 kJ/mol (79.9 meV) for $Ti_5Si_3H_{0.83}$ is estimated from 10.18 kJ/mol

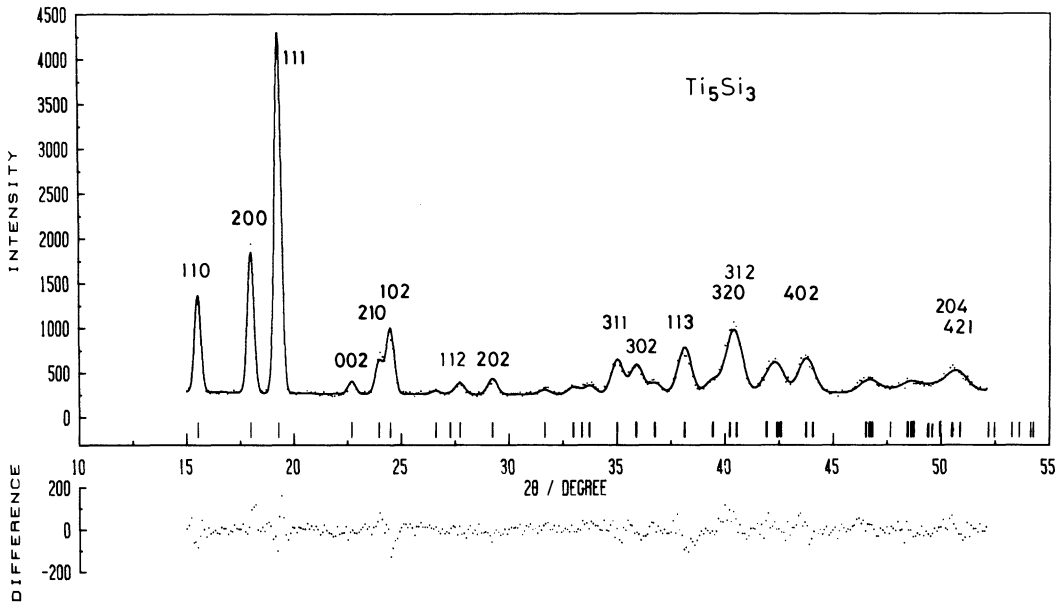


Fig. 5 $\theta-2\theta$ neutron diffraction spectra of Ti_5Si_3; Solid curve is fitted by the Rietveld method.

(105.5 meV) for $TiH_{0.07}$. This value agrees well with the experimental value.

Next we calculate a spring constant, K, of the nearest neighboring Ti-H bond from the energy eigenvalue of a classical Einstein oscillator. From geometry, the doubly degenerated horizontal vibration mode has the energy eigenvalue at $m\omega^2=2.018\,K$ where m is the mass of a hydrogen atom. The vertical singlet which corresponds to the vibration parallel to the c-axis has the energy eigenvalue at $m\omega^2=1.963\,K$. The two values are very close. We may assume that the experimentally obtained eigenvalue 7.53 kJ/mol is a weighted average of both modes. The spring constant becomes $K=1.18\times10^4$ mN/m (dyn/cm). This value is reliably acceptable as the Ti-H spring constant, because the interatomic distance for the second nearest Si-H bonding is more than twice as large as the first nearest Ti-H distance. Although the spring constant in α-$TiH_{0.07}$ has not been evaluated, it is conceivable that the K value is inversely related with the hole radius.

The K value estimated above is about 1/3 to 1/4 of those for ZrH_2[16] and CeH_2[17], where the hydrogen atoms are located at t-sites in the CaF_2 type structure. The difference in the spring constant reflects the difference in the environment of hydrogen atoms at the t- or o-sites.

Among the residuals R_f, R_B and R_p listed in Table 1, those for X-ray diffraction data are relatively high. A possible reason is that most suitable fitting parameters for very sharp peaks are rather difficult to be optimized throughout the spectra. On the other hand, the wider the peaks, the less the residuals are figured. Low level residuals for the TOF neutron diffraction data at $2\theta=90°$ reflect such a tendency.

The crystallographic data obtained above indicate that Westlake's criterion[6] on the hole radius of stable hydrides $r_c=0.037-0.039$ nm is quite reasonable. In this respect, the C-sites $6f(1/2\ 0\ 0)$ may not be occupied by hydrogen atoms in Ti_5Ge_3($r=0.030$ nm) and Ti_5Sn_3 ($r=0.018$ nm) which have the isomorphic structure of Ti_5Si_3 with a smaller axial ratio c/a.

VI. Conclusion

The occupation sites of hydrogen isotopes dissolved in Ti_5Si_3 hexagonal crystal are determined at the octahedral or $2b(0\ 0\ 0)$ sites by the Rietveld profile analysis of neutron powder

Table 1 Crystallographic data of $Ti_5Si_3D_{0.9}$ and Ti_5Si_3 determined at room temperature. Residuals (R_f, R_B and R_p) and number of diffraction peaks and of contained Bragg reflections are also listed for each experimental method.

			$Ti_5Si_3D_{0.9}$			Ti_5Si_3		
Atomic coordinate	Ti(1)	6*g*	0.2487(3)	0	1/4	0.2473(9)	0	1/4
	Ti(2)	4*d*	1/3	2/3	0	1/3	2/3	0
	Si	6*g*	0.6029(2)	0	1/4	0.6063(9)	0	1/4
	0.9D	2*b*	0	0	0			
Debye parameter, B (10^{-2} nm^2)	Ti		0.11(13)			0.17(8)		
	Ti		0.11(13)			0.17(19)		
	Si		0.29(3)			0.81(12)		
	D		1.96(28)					
Lattice parameters (nm)								
$a=b$			0.74492(2)			0.74610(3)		
c			0.51682(1)			0.51508(1)		
Residuals (%)			R_f	R_B	R_p	R_f	R_B	R_p
X-ray			7.5	10.0	17.2	12.7	16.2	17.2
$\theta-2\theta$ neutron			9.5	8.4	6.1	3.7	5.3	5.2
TOF neutron								
$2\theta=$ 90°			5.9	5.5	5.2	3.9	6.3	5.3
150°			5.4	8.2	3.8	7.6	9.2	4.4
Number of peaks and reflections				peaks	reflections	peaks	reflections	
X-ray				30	130	30	120	
$\theta-2\theta$ neutron				15	49	21	55	
TOF neutron								
$2\theta=$ 90°				8	22	13	22	
150°				20	55	22	58	

diffraction data. Six Ti atoms at 6*g*(x 0 1/4) with $x=0.2487$ and 4*d*(1/3 2/3 0) sites surround the D atom in $Ti_5Si_3D_{0.9}$. The c-axis of Ti_5Si_3 slightly expands by the deuterium charging but the a-axis shows a compensative shrinking.

The energy eigenvalue of the hydrogen local vibration mode in $Ti_5Si_3H_{0.83}$ is found to be 7.53 kJ/mol (78 meV). The spring constant of the Ti–H bond is estimated at 1.18×10^4 mN/m (dyn/cm), and the average thermal vibration amplitude of hydrogen atom is $\langle u^2\rangle = 6.8\times10^{-4}$ nm^2.

The criterion on the hole size of stable hydrides posturated by Westlake is supported. It is indicated that the profile analysis of powder neutron diffraction data is quite effective for the structural studies of metal hydrides (deuterides).

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