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^{2}H NMR study of sites and dynamics of deuterium and their isotope effects in $Ti_{0.1}V_{0.9}H_xD_y$ ($x+y\approx0.7$)

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Abstract

$Ti_{0.1}V_{0.9}H_xD_y$ ($x+y\approx0.7$) alloys have been studied by ^{2}H NMR. ^{2}H spectra revealed the sites of deuterium. In the H-rich samples, D atoms occupy both the octahedral (O) and tetrahedral (T) sites. In the deuteride, the D-rich sample and the sample of [H]/[D]=1, D atoms occupy the T sites. The activation energies of D diffusion were estimated from the temperature and frequency dependence of ^{2}H spin-lattice relaxation times (T_1). The activation energy is higher in the O sites than in the T sites, as is the case for H diffusion. The activation energy in the O sites is higher for D diffusion than for H diffusion, and this isotope effect is negligible in the T sites.

Keywords: Hydrogen storage materials; Gas–solid reactions; Order–disorder effects; Nuclear resonances

1. Introduction

Titanium (Ti) and vanadium (V) metals form a random alloy with a body-centered-cubic (b.c.c.) structure over wide ranges of composition and temperature [1]. The Ti–V alloys form stable hydrides as well as Ti and V metals do [2,3]. The crystal structure of monohydride $Ti_{1-z}V_zH_x$ ($x\approx1$) depends on the [V]/[Ti] ratio [3–5]. It is b.c.c. in the range $0.2\leq z\leq0.8$, while it is body-centered-tetragonal (b.c.t.) for $0.9\leq z\leq1.0$. On the other hand, the monodeuteride $Ti_{1-z}V_zD_x$ ($x\approx1$) always has the b.c.c. structure [6,7].

In pure vanadium, the crystal structures are different between monohydride and monodeuteride. If H and D atoms are contained simultaneously, the crystal structure is expected to depend on the [H]/[D] ratio. We studied V–H–D systems with a ([H]+[D])/[V] ratio of 0.8 by means of NMR, and found that the site occupancy, the diffusions of H and D, and furthermore the crystal structure depend on the [H]/[D] ratio [7].

In a previous work [8], we studied $Ti_{0.1}V_{0.9}$–H–D systems by X-ray powder diffraction, differential scanning calorimetry (DSC) and ^{1}H NMR. The $Ti_{0.1}V_{0.9}$–H–D systems have features similar to those of the V–H–D systems, although Ti addition shows some effects on the site occupancies and H diffusion. Similar alloy systems containing vanadium have also been studied by NMR [9–12].

In the present work, we have studied sites and dynamics of deuterium in $Ti_{0.1}V_{0.9}H_xD_y$ ($x+y\approx0.7$) alloys by ^{2}H NMR, and have discussed the isotope effects by comparing with ^{1}H NMR results.

2. Experimental

The samples studied were $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$, $Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$, $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$, $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$ and $Ti_{0.1}V_{0.9}D_{0.69}$, which were the same as those used in the previous work [8].

^{2}H NMR has been measured by Bruker ASX200, MSL400 and ASX400 spectrometers. Larmor frequencies were 30.7 MHz for ASX200 and 61.4 MHz for MSL400 and ASX400. The pulse sequences used and the parameter settings were almost the same as those in the previous work [7].

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3. Results and discussion

3.1. ^2H NMR spectra

^{2}H NMR spectra have been recorded at 30.7 and 61.4 MHz in the temperature range between 140 and 420 K. Fig. 1 shows ^{2}H spectra at 30.7 MHz in $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$, which are similar to those in $VH_{0.6}D_{0.2}$ [7]. The spectra consist of at least two components. The spectra at 140 K have been simulated by the procedures used previously [7], and the simulated results are similar to those in the previous work [7]. Component 1 has QCC (quadrupole coupling constant, e^2Qq/h)=40 kHz, η_Q (asymmetry factor)=0.1, K_{iso} (isotropic Knight shift)=−41 ppm from D_2O and ΔK (magnitude of Knight shift anisotropy)=−130 ppm, whereas QCC=74 kHz, η_Q=0.1, K_{iso}=−24 ppm and ΔK=260 ppm for component 2. Components 1 and 2 are ascribed to D atoms in the T and O sites, respectively. The obtained parameters agree with those in the V–H–D alloys [7], though the little bit lower resolution of the fine structures might suggest a small distribution of those parameters.

With increase in temperature, first the inner doublet corresponding to the T sites disappears at ~200 K, and in place of it the narrow central component grows up. The outer doublet corresponding to the O sites remains the line shape up to ~240 K. Above 240 K, the doublet peak disappears, though the asymmetric line shape is observed up to ~380 K. The diffusion of D atoms in the O sites becomes isotropic above 380 K, much higher than that in the T sites (~200 K). These results demonstrate that the D atoms in the T site have higher mobility than D in the O sites.

The ^{2}H spectra of $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$ obtained at 30.7 MHz are shown in Fig. 2. $Ti_{0.1}V_{0.9}D_{0.69}$ and $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$ show similar line shapes. The spectra of the three samples at 140 K can be simulated only by component 1. D atoms occupy the ordered T sites at low temperatures, and the ordering remains up to ~200 K. The ordered D sublattice collapses by the phase transition from the δ_D phase to the α_D phase, accompanied by the growth

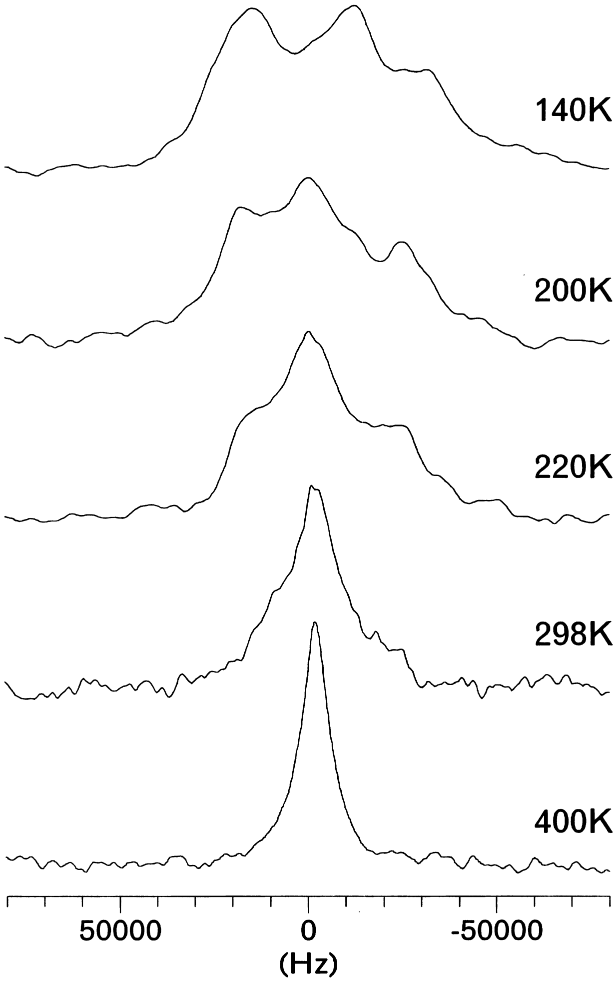

Fig. 1. Temperature dependence of ^{2}H NMR spectra in $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$, measured at 30.7 MHz.

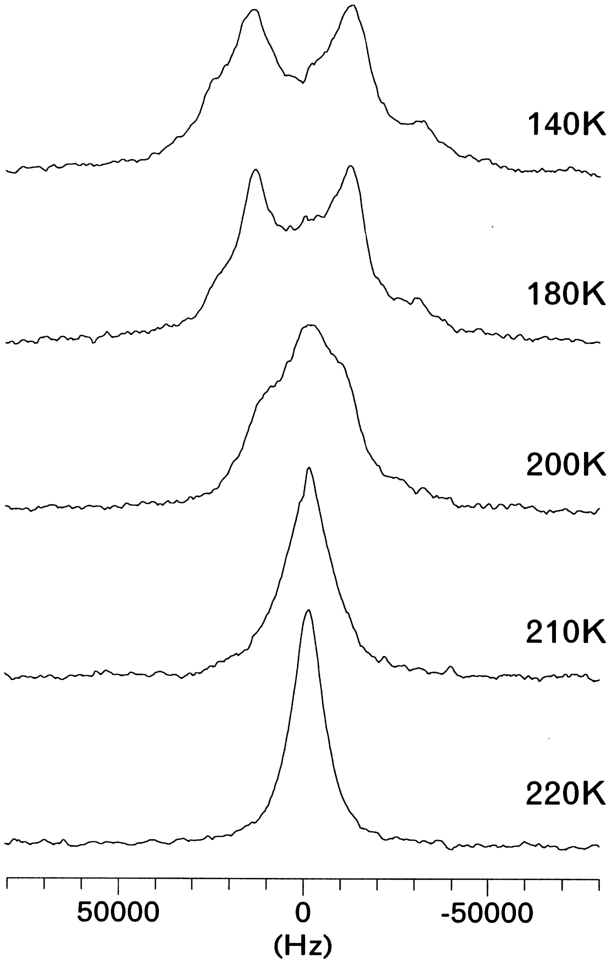

Fig. 2. Temperature dependence of ^{2}H NMR spectra in $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$, measured at 30.7 MHz.

of the narrow central line. After the phase transition, the doublet disappears, and only the narrow central line is observed, reflecting the isotropic diffusion of D atoms. The doublet begins to collapse at 210, 200 and 220 K in $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$, $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$ and $Ti_{0.1}V_{0.9}D_{0.69}$, respectively, and the narrowing completes at 230, 220 and 240 K, respectively. These temperature ranges agree with the DSC results [8].

$Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$ shows intermediate line shapes between $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$ and $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$. Component 1 (the T site) and component 2 (the O site) are of comparable magnitudes.

In summary, both the O and T sites are occupied in $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$ and $Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$, though the O occupation is larger in the former than in the latter. Only the T site is occupied in $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$, $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$ and $Ti_{0.1}V_{0.9}D_{0.69}$. Generally speaking, the b.c.t. lattice prefers O site occupation, whereas the b.c.c. lattice prefers T site occupation. However, only the T site is occupied in $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$ which is predominantly b.c.t. Consequently, the site occupancy of D atoms agrees with that of H atoms previously reported [8].

3.2. ^{2}H spin-lattice relaxation times

^{2}H T_1 values have been measured at 30.7 and 61.4 MHz in the temperature range between 140 and 420 K. The T_1 values are determined from the recovery of peak amplitudes in the Fourier-transformed (FT) spectra. In all measurements, the time dependence of the peak amplitudes is single exponential within experimental accuracy. The spin-lattice relaxation times after subtracting the contribution of conduction electrons are plotted in Figs. 3–5, which include the contributions from the dipolar interaction and from the quadrupole interaction, being denoted as $T_{1(d+q)}$. ^{2}H Korringa constants ($T_{1e}T$) are estimated from the respective ^{1}H Korringa constant multiplied by 42.44 ($=\gamma_H^2/\gamma_D^2$), which are listed in Table 1. For $Ti_{0.1}V_{0.9}D_{0.69}$, the ^{2}H Korringa constant is assumed to be same as that of $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$.

The dependence of ^{2}H $T_{1(d+q)}$ on the resonance frequency and temperature has been analyzed by the method in the previous work [7], using the following equation:

$$(T_{1d})^{-1} = f_1 \Omega^{\beta-1} M_{DV} \left[\frac{0.5\tau_D^{\beta}}{1+\{(1-\gamma_V/\gamma_D)\omega_D\tau_D\}^{1+\alpha}} + \frac{1.5\tau_D^{\beta}}{1+(\omega_D\tau_D)^{1+\alpha}} + \frac{3\tau_D^{\beta}}{1+\{(1+\gamma_V/\gamma_D)\omega_D\tau_D\}^{1+\alpha}} \right] \quad (1)$$

where ω_D, γ_D and τ_D are the angular resonance frequency, the gyromagnetic ratio and the mean residence time of ^{2}H, respectively. M_{DV} is the second moment caused by the ^{2}H–^{51}V dipolar interaction. β is fixed to 1 in this work, α ($0\leq\alpha\leq1$) reflects the deviation from BPP equation [13],

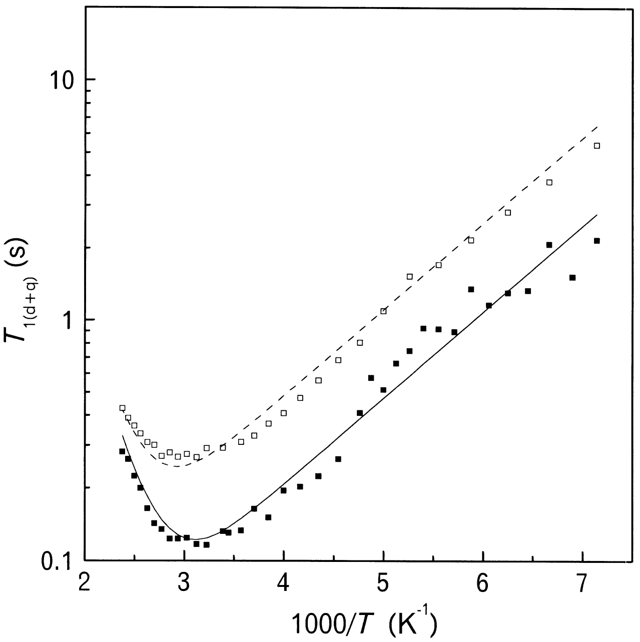

Fig. 3. ^{2}H spin-lattice relaxation times caused by dipole–dipole and/or quadrupole interaction in $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$ (the O site) at 30.7 (■) and 61.4 MHz (□), and their simulated results indicated by solid and chain lines.

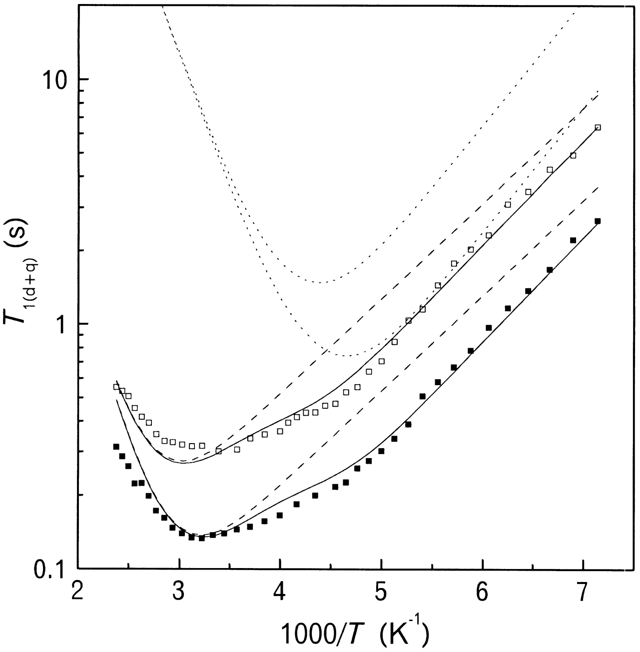

Fig. 4. ^{2}H spin-lattice relaxation times caused by dipole–dipole and/or quadrupole interaction in $Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$ at 30.7 (■) and 61.4 MHz (□), and their simulated results indicated by solid lines. The chain and dotted lines indicate components used for the simulation, corresponding to the contributions of the O and T sites, respectively.

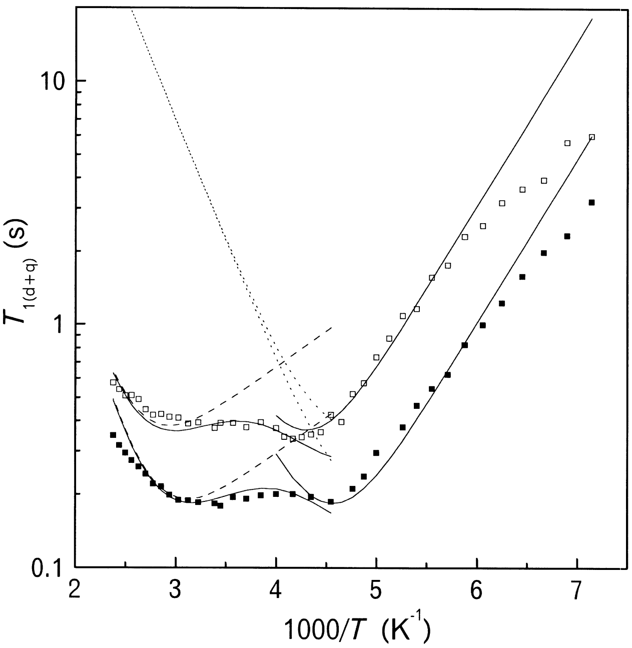

Fig. 5. ^{2}H spin-lattice relaxation times caused by dipole–dipole and/or quadrupole interaction in $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$ at 30.7 (■) and 61.4 MHz (□), and their simulated results indicated by solid lines. The chain and dotted lines indicate components used for the simulation, corresponding to the contributions of the O and T sites, respectively.

and f_1 is a multiplication factor. A distribution of the activation energy is not introduced, since the distribution of the site symmetry is small. The fitted curves are given in the figures by lines, and the parameters obtained are listed in Table 1. E_D is the activation energy for D diffusion.

In $Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$, there is a minimum value of 0.12 s at 300 K when measured at 30.7 MHz, while the minimum at 61.4 MHz is 0.28 s at ~330 K, as shown in Fig. 3. By analogy with ^{1}H T_1, the ^{2}H T_1 values above 250 K predominantly reflect the D motion in the O site. Although ^{2}H spectra confirm the existence of D atoms in two kinds of sites, the O and T sites, parameters of the D diffusion could not be estimated for the T sites.

The temperature dependence of T_1 in $Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$ (Fig. 4) shows a change of slope in the low temperature side of the T_1 minimum, probably originating from the motion of D atoms in the T sites. The activation energy is much smaller in the T sites than in the O sites. With increase in temperature diffusion between the T sites takes place. Further increase in temperature leads to diffusion of D atoms in the O sites. The diffusion between the O sites might use the T sites as the diffusion path.

The rest of the samples, viz. $Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$ (Fig. 5), $Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$, and $Ti_{0.1}V_{0.9}D_{0.69}$ exhibit two minima at ~330 and 230 K. The former is related to the motion of deuterium in the O sites, and the latter to the T sites. ^{2}H spectra indicate that the D atoms occupy the ordered T sites in the δ_D phase. Hopping among the ordered T sites neither averages out the structured quadrupolar line shape, nor produces effective quadrupolar spin-lattice relaxation. Above 240 K in the α_D phase, where the deuterium sublattice becomes disordered, there might be considerable quadrupolar relaxation of ^{2}H, since the quadrupolar line shape collapses. The parameters of deuterium diffusion change around the phase transition temperature, and, moreover, it seems that there exist simultaneously more than one type of motion at high temperatures. The O sites might be used as a diffusion pathway, as has been suggested in the V–H–D alloys [7].

In summary, the activation energy of D diffusion is higher in the O sites than in the T sites, as is the case for H diffusion. The activation energy in the O sites is higher for D diffusion than for H diffusion, and this isotope effect is negligible in the T sites. D addition to the hydride decreases the activation energies of D diffusions in the O

Table 1
^{2}H Korringa constants and parameters of deuterium diffusion

Sample	$T_{1e}T$ [a] (s K)	D site	τ_{0D} [b] (s)	E_D (eV/atom)	α	f_1
$Ti_{0.1}V_{0.9}H_{0.63}D_{0.12}$	5560	O	13×10^{-14}	0.325	0.22	1.50
$Ti_{0.1}V_{0.9}H_{0.50}D_{0.20}$	5560	O	13×10^{-14}	0.31	0.25	1.40
		T	4.2×10^{-14}	0.225	0.45	0.30
$Ti_{0.1}V_{0.9}H_{0.35}D_{0.35}$	5860	T[c]	4.2×10^{-14}	0.225	0.60	1.25
		T[d]	4.2×10^{-14}	0.20	0.60[e]	1.25[e]
		O′[d]	13×10^{-14}	0.33	0.18	0.90
$Ti_{0.1}V_{0.9}H_{0.22}D_{0.52}$	8830	T[c]	4.2×10^{-14}	0.225	0.60	1.40
		T[d]	4.2×10^{-14}	0.205	0.60[e]	1.40[e]
		O′[d]	13×10^{-14}	0.31	0.25	0.90
$Ti_{0.1}V_{0.9}D_{0.69}$	8830[e]	T[c]	4.2×10^{-14}	0.24	0.50	1.20
		T[d]	4.2×10^{-14}	0.22	0.50[e]	1.20[e]
		O′[d]	13×10^{-14}	0.345	0.20	0.60

[a] Estimated from ^{1}H Korringa constants [8].

[b] Assumed to be $1.4\tau_{0H}$ [6,7].

[c] Below 220 K.

[d] Above 240 K.

[e] Assumed.

sites. The Ti addition decreases the activation energies of D diffusions in the O sites. The D mobility in the T sites is not affected by the Ti addition or by the [H]/[D] ratio.

4. Conclusions

$Ti_{0.1}V_{0.9}$–H–D alloys with $([H]+[D])/([Ti]+[V])\approx 0.7$ have been studied by means of ^{2}H NMR, and the following conclusions have been obtained.

1. In the H-rich samples, D atoms occupy both the O and T sites, and the D atoms in the T sites diffuse faster than those in the O sites. In the deuteride, the D-rich sample, and the sample of [H]/[D] = 1, D atoms occupy the T sites. Ti addition enhances the occupation of the T sites. In the δ_D phase, D atoms diffuse among the ordered T sites. In the α_D phase, the diffusion takes place between the disordered T sites, and the O sites also contribute to the diffusion.
2. The activation energy of D diffusion is higher in the O sites than in the T sites. The activation energy in the O sites is higher for D diffusion than for H diffusion, and this isotope effect is negligible in the T sites. D addition to the hydride and Ti addition decrease the activation energies of D diffusion in the O sites. The mobility in the T sites is not affected by the Ti addition or by the [H]/[D] ratio.

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