



# Effect of substitutional Cr on hydrogen diffusion and thermal stability for the BCT monohydride phase of the V–H system studied by $^1\text{H}$ NMR

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## ABSTRACT

The diffusion of hydrogen in the monohydride phase ( $\beta$  phase) of the  $\text{V}_{1-x}\text{Cr}_x\text{-H}$  ( $x \leq 0.1$ ) system was studied by means of  $^1\text{H}$  nuclear magnetic resonance (NMR). Hydrogen atoms in the hydrides occupied the octahedral ( $O$ ) sites in a body centered tetragonal (BCT) structure. The BCT lattice was contracted by addition of Cr because Cr has a smaller atomic radius than V. The activation energy for hydrogen diffusion,  $E_{\text{H}}$ , and the Korringa constant,  $T_{1e}T$ , were estimated from the temperature and frequency dependence of  $^1\text{H}$  spin–lattice relaxation times,  $T_1$ . The value of  $E_{\text{H}}$  increased with increase in the Cr content. The contraction of the BCT lattice by addition of Cr suppressed the diffusion of hydrogen which occupied the interstitial sites. Addition of Cr also increased the  $T_{1e}T$ , which was accompanied by reducing in the stability of the monohydride phase of the V–H system.

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## 1. Introduction

Solid solution alloys which have a body centered cubic (BCC) structure are one of the most promising hydrogen storage materials for onboard hydrogen storage [1,2]. V based BCC alloys containing Ti, Cr, Mn, Mo and other transition metals [2–10] have been known to suitable for hydrogen storage. V metal with a BCC structure forms the hydrogen solid solution phase with a BCC structure ( $\alpha$  phase), the monohydride phase with a body centered tetragonal (BCT) structure ( $\beta$  phase) and the dihydride phase with a face centered cubic (FCC) structure ( $\gamma$  phase) by hydrogenation at ambient temperatures [11]. The gravimetric hydrogen content of the  $\gamma$  phase of  $\text{VH}_2$  corresponds to 3.8 mass%.

The  $P$  (pressure)– $C$  (composition) isotherm of the V– $\text{H}_2$  system at ambient temperatures shows two clear plateau regions [12,13]; the lower one due to coexistence of the  $\alpha$  and  $\beta$  phases and the upper one due to coexistence of the  $\beta$  and  $\gamma$  phases. In addition, the lower plateau region was divided into two parts because two types of the  $\beta$  phase ( $\beta_1$  and  $\beta_2$  phases) are formed [12,13]. The equilibrium hydrogen pressures for formation and dissociation of the hydride phase at a given temperature depend upon the enthalpy for hydride formation. The enthalpies for formation of the  $\beta$  and  $\gamma$  phases are negative. The increase in the enthalpy for hydride formation corresponds to the increase in the equilibrium pressure of

the plateau region in the  $P$ – $C$  isotherm at a given temperature, and *vice versa*.

Addition of some metal elements to V changes the enthalpies for formation of the  $\beta$  and  $\gamma$  phases. The equilibrium pressures of both the lower and upper plateau regions at a given temperature were decreased by addition of Ti [13,14] and those were increased by addition of Cr, Mn, Fe, Co and Ni [13]. Ti has a larger atomic radius and Cr, Mn, Fe, Co and Ni have smaller atomic radii than V [15], respectively. It seems that the increase in unit cell volume of the BCC lattice makes the enthalpies for formation of the  $\beta$  and  $\gamma$  phases negative. However, addition of Mo, which has a larger atomic radius than V [15], increased the equilibrium pressure of the upper plateau region at 303 K [16]. It was reported that addition of Mo to the BCC alloys reduced the radius of the interstitial site for hydrogen atoms in the lattice, which reduced the stability of the hydride phase [5].

Hydrogen atoms occupy tetrahedral ( $T$ ) sites in the  $\alpha$  and  $\gamma$  phases and octahedral ( $O$ ) sites in the  $\beta$  phase of the V–H system [11]. It is known that a most of hydrogen atoms in the  $\beta$  phase occupies the  $O$  sites between V atoms along the  $c$ -axis of the BCT lattice ( $O_z$  sites) [11]. In our previous work [16], site occupation of hydrogen in the monohydride phase ( $\beta$  phase) of the  $\text{V}_{1-x}\text{Mo}_x\text{-H}$  ( $x \leq 0.1$ ) system was studied by means of  $^1\text{H}$  nuclear magnetic resonance (NMR). Hydrogen atoms occupied both the  $O$  and  $T$  sites at  $x=0.1$ , which was demonstrated by two components observed in the temperature dependence of the  $^1\text{H}$  spin–lattice relaxation times,  $T_1$ . Shift of hydrogen occupation from the  $O$  sites to the  $T$  sites by addition of Mo was possibly attributed to the reduction in the radius of the  $O$  site.

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NMR also provides information about diffusion of hydrogen in metals. Hydrogen diffusion is an important step in kinetics of hydrogenation and dehydrogenation of the hydrogen storage materials. The addition of Mo to V reduced the activation energy for hydrogen diffusion,  $E_H$ , for the *O* sites in the  $\beta$  phase [16]. The value of  $E_H$  for the *T* sites was lower than that for the *O* sites [16]. In consequence hydrogen diffusion in the  $\beta$  phase of the V–H system ( $\beta$ -V–H) was enhanced by addition of Mo. On the other hand, one of the authors has reported that hydrogen atoms occupy the *O* sites in the Ti substituted system of  $\beta$ -V<sub>0.90</sub>Ti<sub>0.10</sub>-H but those occupy the *T* sites in  $\beta$ -V<sub>0.67</sub>Ti<sub>0.33</sub>-H [17–19]. The value of  $E_H$  for the *O* sites in the  $\beta$  phase decreased by addition of Ti [19]. As shown above, we have found that addition of some metal elements to V changes not only the enthalpy for hydride formation but also the hydrogen diffusivity in the hydride phase.

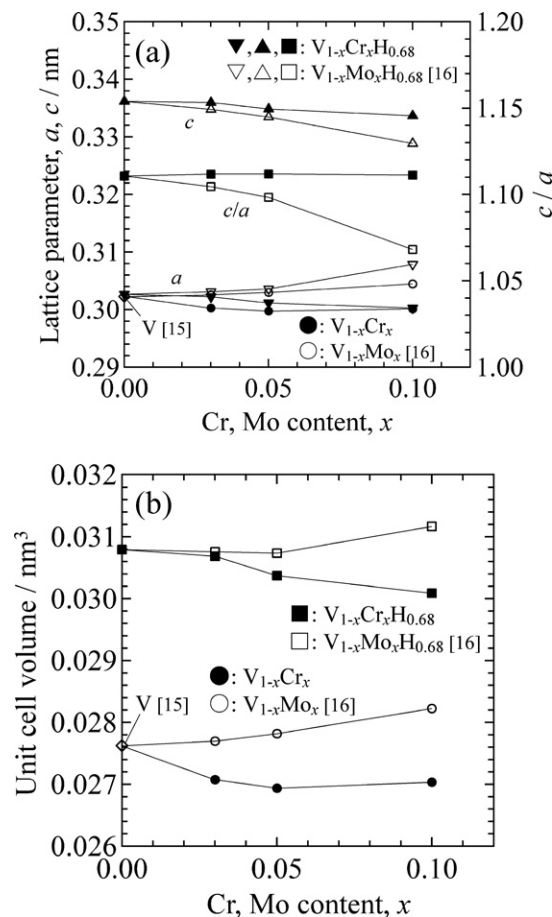
Analyzing the temperature dependence of  $T_1$  gives the Korringa constant,  $T_{1e}T$ . The  $T_{1e}T$  has a relation with the density of states at the Fermi energy,  $N(E_F)$ , because  $T_{1e}^{-1}$  is the relaxation rate due to the conduction electrons. It is considered that the reduction in  $N(E_F)$  decreases  $T_{1e}^{-1}$  and results in the increase in  $T_{1e}T$ . On the other hand, the reduction in  $N(E_F)$  positively shifts the heat of hydrogen solution in metals [20]. The heat of hydrogen solution in group 5 metals, V, Nb and Ta, is negative and that in group 6 metals, Cr, Mo and W, is positive [20]. Variation of the heat of hydrogen solution across the periodic table is very similar to that of the enthalpy for hydride formation [21]. This suggests that the increase in  $T_{1e}T$  by reducing in  $N(E_F)$  causes positive shift in the heat of hydrogen solution and the enthalpy for hydride formation, which corresponds to reducing in the stabilities of the hydrogen solid solution phase and the hydride phase. The effect of additional metal elements on the value of  $N(E_F)$  for  $\beta$ -V–H has not been reported but the  $T_{1e}T$ , obtained from analysis of NMR data, most likely has a relation with the enthalpy for hydride formation, *i.e.*, the equilibrium pressure of the plateau region in the *P*–*C* isotherm at a given temperature.

The V–Cr binary alloy is the BCC isomorphous [22]; each metal randomly dissolves in another. Lynch et al. [23] have synthesized V<sub>1-x</sub>Cr<sub>x</sub> alloys in the region of  $x \leq 0.196$ . With increase in the Cr content the lattice parameter decreased and the equilibrium pressure of the plateau region between the  $\beta$  and  $\gamma$  phases increased in the *P*–*C* isotherm at 313 K [23]. Cr is one of the metal elements often used for V based hydrogen storage alloys, as typified by V–Ti–Cr solid solution alloys with a BCC structure [2,4,5,7–10,24]. To our knowledge, the effect of addition of Cr to V on the site occupation of hydrogen in the lattice has not been reported. The diffusion of hydrogen has been investigated only in the  $\alpha$  phase of V–Cr–H with bulk specimens by means of electric resistivity [25] and gas absorption [26] methods. Addition of Cr to V reduced the hydrogen diffusivity in the  $\alpha$  phase [25,26]. These methods cannot be applied to the  $\beta$  and  $\gamma$  phases because it is difficult to prepare bulk specimens due to pulverization by hydrogenation. NMR can measure the signal from hydrogen in metal powders and therefore the diffusion and site occupation of hydrogen in  $\beta$ -V–H have been investigated using NMR [16,27–30].

In the present work,  $^1\text{H}$  NMR spectra were measured and  $^1\text{H}$   $T_1$  was determined for  $\beta$ -V<sub>1-x</sub>Cr<sub>x</sub>-H ( $x \leq 0.1$ ). The effect of Cr addition to V on diffusion and site occupation of hydrogen was investigated on the basis of the temperature and frequency dependence of  $T_1$ . The relation between the  $T_{1e}T$  and the equilibrium pressure of the plateau region in the *P*–*C* isotherm was clarified and the stability of the  $\beta$  phase was evaluated from NMR data.

## 2. Experimental

Buttons of V<sub>1-x</sub>Cr<sub>x</sub> ( $x = 0.03, 0.05, 0.10$ ) alloys were prepared by arc melting pellets of V and Cr with the purity of 99.9 mass% under an argon atmosphere. The buttons were treated at 1673 K for 70 h under an argon atmosphere for homogenization. Each of hydride specimens of V<sub>1-x</sub>Cr<sub>x</sub>H<sub>0.68</sub> ( $x = 0.03, 0.05, 0.10$ ) was obtained



**Fig. 1.** (a) Lattice parameters and (b) unit cell volume of V [15], V<sub>1-x</sub>Cr<sub>x</sub> and V<sub>1-x</sub>Cr<sub>x</sub>H<sub>0.68</sub> ( $x = 0.03, 0.05, 0.10$ ), V<sub>1-x</sub>Mo<sub>x</sub> and V<sub>1-x</sub>Mo<sub>x</sub>H<sub>0.68</sub> ( $x = 0, 0.03, 0.05, 0.10$ ) [16].

by hydrogenating the alloy specimen along the *P*–*C* isotherm. Rigaku 2500 V diffractometer with Cu K $\alpha$  radiation was used for measurement of powder X-ray diffraction (XRD).  $^1\text{H}$  NMR measurements were performed using Bruker mq20 and ASX200 spectrometers. The detailed procedures for the NMR measurements are described in the previous report [16].

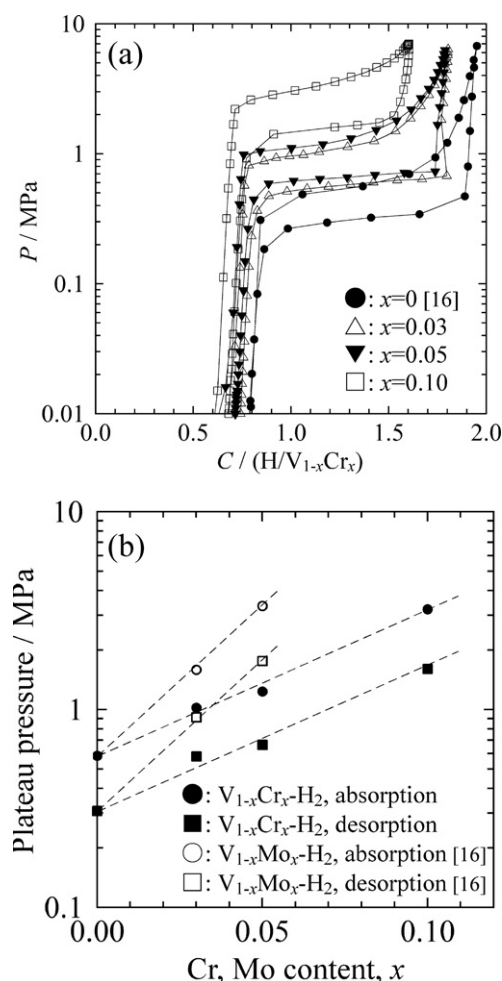
The  $^1\text{H}$  spin–lattice relaxation time,  $T_1$ , determined from the NMR measurements was analyzed by the Bloembergen, Purcell and Pound (BPP) equation [31] modified [16,18,19]. The  $T_1$  is expressed by Eq. (1):

$$(T_1)^{-1} = (T_{1d})^{-1} + (T_{1e})^{-1} \quad (1)$$

where  $T_{1d}$  is contribution from modulation of nuclear dipolar interaction and  $T_{1e}$  arises from fluctuation of hyperfine interaction between the nuclear spin and conduction electrons. Stable NMR active nuclei of V and Cr are  $^{51}\text{V}$  and  $^{53}\text{Cr}$ , respectively. The natural abundance of  $^{51}\text{V}$  is 99.8%. Contribution of Cr to  $^1\text{H}$   $T_1$  in V<sub>1-x</sub>Cr<sub>x</sub>H<sub>0.68</sub> ( $x = 0.03, 0.05, 0.10$ ) was considered to be negligible because the natural abundance of  $^{53}\text{Cr}$  is 9.6% and the nuclear dipole moment is 21.5% of  $^{51}\text{V}$ . The temperature dependence of  $T_{1d}$  was simulated using the second moments between  $^1\text{H}$  spins,  $M_{\text{HH}}$ , and between  $^1\text{H}$  and  $^{51}\text{V}$  spins,  $M_{\text{HV}}$ . The mean residence time at the infinite temperature or the inverse of a frequency factor,  $\tau_{\text{OH}}$ , was assumed to be  $9 \times 10^{-14}$  s for the *O* sites and  $3 \times 10^{-14}$  s for the *T* sites [16,18,19]. The symbols of  $\beta_0$  and  $\beta_Q$  are parameters defining the magnitude of the distributions of  $\tau_{\text{OH}}$  and the activation energy for hydrogen diffusion,  $E_H$ , respectively. The symbol of  $f_1$  is a correction factor which reduces only the effective  $M_{\text{HV}}$ . The temperature dependence of  $T_{1e}$  is given by Korringa relation, *i.e.*,  $T_{1e}T = \text{constant}$ . The values of the parameters were estimated by the fitting of  $T_1$ .

## 3. Results and discussion

The XRD patterns of V<sub>1-x</sub>Cr<sub>x</sub> ( $x = 0.03, 0.05, 0.10$ ) before hydrogenation indicated that all the alloys had a BCC structure. Their lattice parameters were calculated from the peak positions. Fig. 1(a) and (b) shows lattice parameters and unit cell volume of V<sub>1-x</sub>Cr<sub>x</sub> ( $x = 0.03, 0.05, 0.10$ ) in comparison with V<sub>1-x</sub>Mo<sub>x</sub> ( $x = 0, 0.03, 0.05,$



**Fig. 2.** (a) Pressure–composition isotherms of the  $V_{1-x}Cr_xH_2$  ( $x=0$  [16], 0.03, 0.05, 0.10) systems at 303 K and (b) equilibrium pressure of the plateau region of the  $V_{1-x}Cr_xH_2$  ( $x=0.03, 0.05, 0.10$ ) and  $V_{1-x}Mo_xH_2$  ( $x=0, 0.03, 0.05$ ) [16] systems in the hydrogen absorption and desorption at 303 K.

0.10) [16]. The BCC lattice of V was contracted by addition of Cr but that was expanded by addition of Mo because of the difference in atomic radii of V, Cr and Mo, which are 0.132, 0.125 and 0.136 nm [15], respectively.

Fig. 2(a) shows the  $P$ – $C$  isotherms of the  $V_{1-x}Cr_xH_2$  ( $x=0$  [16], 0.03, 0.05, 0.10) systems at 303 K. The absorption and desorption isotherms of them showed plateau regions which are attributed to coexistence of the  $\beta$  and  $\gamma$  phases. The hydrogen content

under 7 MPa was  $H/V=1.95$  at  $x=0$  [16] and that decreased to  $H/V_{0.9}Cr_{0.1}=1.60$  at  $x=0.10$ . The equilibrium pressure of the plateau region increased with increase in the Cr content from 0 to 0.10. Fig. 2(b) shows the equilibrium pressure of the plateau region of the  $V_{1-x}Cr_xH_2$  ( $x=0.03, 0.05, 0.10$ ) and  $V_{1-x}Mo_xH_2$  ( $x=0, 0.03, 0.05$ ) [16] systems in the hydrogen absorption and desorption at 303 K. The increase in the equilibrium pressure by addition of Cr was smaller than that by addition of Mo, *i.e.*, the increase in the enthalpy for formation of the  $\gamma$  phase by addition of Mo was larger than that by addition of Cr.

The XRD measurements showed that  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) synthesized after the  $P$ – $C$  isotherm measurements were the  $\beta$  phase with a BCT structure. The lattice parameter,  $a$  and  $c$ , decreased with increase in the Cr content and the value of  $c/a$  was around 1.11 in the region of  $0 \leq x \leq 0.10$  shown in Fig. 1(a). The unit cell volume decreased with reduction in the lattice parameters, as shown in Fig. 1(b). It is known that hydrogen atoms on the  $O_z$  sites are most stable at  $c/a \approx 1.1$  in the BCT lattice [21]. The value of  $c/a$  for  $VH_{0.68}$  was 1.11 and that decreased to 1.07 for  $V_{0.90}Mo_{0.10}H_{0.68}$ , which was attributed to shift of hydrogen occupation from the  $O$  sites to the  $T$  sites by addition of Mo [16]. The values of  $c/a \approx 1.1$  for  $V_{1-x}Cr_xH_{0.68}$  suggest that hydrogen atoms on the  $O$  sites are not shifted to the  $T$  sites by addition of Cr.

The  $^1H$  NMR spectra of  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) measured at 19.65 and 200.13 MHz showed a single component which was similar to those of  $VH_{0.68}$  [16]. The temperature dependence of the full-width at half maximum (FWHM) of the signal of  $V_{1-x}Cr_xH_{0.68}$  ( $x=0$  [16], 0.03, 0.05, 0.10) measured at 200.13 MHz is plotted in Fig. 3. The motional narrowing was observed up to 240 K and the FWHM was almost constant above room temperature for all the hydrides. Significant change in hydrogen mobility by addition of Cr was not observed from the temperature dependence of the FWHM.

Fig. 4(a)–(c) shows the temperature dependence of  $^1H$  spin–lattice relaxation time,  $T_1$ , in  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) measured at 19.65 and 200.13 MHz. The temperature dependence of  $T_1$  for the three hydrides showed a single component. This component is assigned to contribution of hydrogen on the  $O$  sites because this temperature dependence is similar to that obtained for  $VH_{0.68}$  [16], in which hydrogen atoms occupy the  $O$  sites. It has been reported that a hydrogen atom occupying one of the  $O_z$  sites migrates to another  $O_z$  site successively passing through three  $T$  sites in  $\beta$ -V–H [27]. The residence time of hydrogen on the  $O$  sites was around two orders magnitude longer than that on the  $T$  sites in  $VH_{0.68}$  at ambient temperatures [16]. The values of  $T_1$  in  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) at 19.65 and 200.13 MHz had a minimum at 300–310 K and at 350–390 K, respectively. With increase in the Cr content the temperature for the minimum of  $T_1$

**Table 1**

$^1H$  Korringa constants and parameters for hydrogen diffusion in  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ),  $V_{1-x}Mo_xH_{0.68}$  ( $x=0, 0.03, 0.05, 0.10$ ) [16],  $VH_{0.82}$  [19],  $VH_{0.60}D_{0.20}$  [19],  $V_{0.90}Ti_{0.10}H_{0.73}$  [17,19] and  $V_{0.67}Ti_{0.33}H_{0.90}$  [18,19].

	$T_{1e}/T/s$ K	Site	$\tau_{0H}/s$	$E_H/kJ mol^{-1}$	$\beta_0/kJ mol^{-1}$	$\beta_0$	$f_1$	Ref.
$VH_{0.68}$	185	$O$	$9 \times 10^{-14}$	25.7	2.8	0	0.69	[16]
$V_{0.97}Cr_{0.03}H_{0.68}$	210	$O$	$9 \times 10^{-14}$	26.9	4.2	0	0.67	
$V_{0.95}Cr_{0.05}H_{0.68}$	220	$O$	$9 \times 10^{-14}$	27.2	4.4	0	0.63	
$V_{0.90}Cr_{0.10}H_{0.68}$	220	$O$	$9 \times 10^{-14}$	27.9	4.7	0	0.59	
$V_{0.97}Mo_{0.03}H_{0.68}$	220	$O$	$9 \times 10^{-14}$	26.0	3.6	0	0.66	[16]
$V_{0.95}Mo_{0.05}H_{0.68}$	230	$O$	$9 \times 10^{-14}$	25.4	3.6	0	0.60	[16]
$V_{0.90}Mo_{0.10}H_{0.68}$	250	$O$	$9 \times 10^{-14}$	23.2	3.6	0	0.38	[16]
		$T$	$3 \times 10^{-14}$	17.0	3.0	0	0.13	[16]
$VH_{0.82}$	100	$O$	$9 \times 10^{-14}$	27.0	5.8	0	0.58	[17]
$VH_{0.60}D_{0.20}$	180	$O$	$9 \times 10^{-14}$	25.0	2.7	0	0.50	[17]
		$T$	$3 \times 10^{-14}$	19.0	4.0	0	0.25	[17]
$V_{0.90}Ti_{0.10}H_{0.73}$	145	$O_{21}$	$9 \times 10^{-14}$	25.0	4.0	0	0.58	[17,19]
		$O_{22}$	$9 \times 10^{-14}$	23.0	6.5	0	0.60	[17,19]
$V_{0.67}Ti_{0.33}H_{0.90}$	67	$T$	$3 \times 10^{-14}$	21.3	0	4.3	0.35	[18,19]

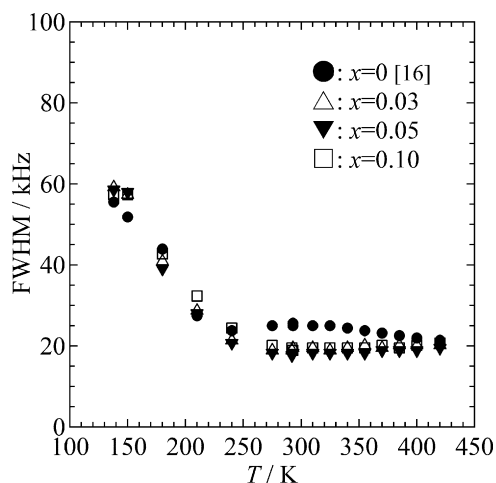


Fig. 3. Full-width at half maximum of  $^1\text{H}$  NMR signal of  $\text{V}_{1-x}\text{Cr}_x\text{H}_{0.68}$  ( $x=0$  [16], 0.03, 0.05, 0.10) measured at 200.13 MHz.

shifted to a higher temperature. This indicates that addition of Cr makes hydrogen mobility in the  $\beta$  phase lower at a given temperature, which leads to the increase in the activation energy for the hydrogen diffusion,  $E_{\text{H}}$ . The temperature dependence of  $T_1$  in each hydride was analyzed by the BPP equation [31] modified [16,18,19]. The solid and dotted lines in Fig. 4(a)–(c) indicated the calculated curves of the temperature dependence of  $T_1$  and  $T_{1e}$ , respectively. Table 1 lists the parameters obtained from the fitting of  $T_1$ . The Korringa constant,  $T_{1e}T$ , and  $E_{\text{H}}$  for the  $O$  sites increased with increase in the Cr content.

The evaluated  $E_{\text{H}}$  in  $\text{V}_{1-x}\text{Cr}_x\text{H}_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) are shown in Fig. 5 in comparison with that in  $\text{VH}_{0.82}$  [19],  $\text{VH}_{0.60}\text{D}_{0.20}$  [19],  $\text{V}_{1-x}\text{Mo}_x\text{H}_{0.68}$  ( $x=0, 0.03, 0.05, 0.10$ ) [16] and  $\text{V}_{0.90}\text{Ti}_{0.10}\text{H}_{0.73}$  [19]. The value of  $E_{\text{H}}$  for the  $O$  sites in  $\text{VH}_{0.68}$  was  $25.7 \text{ kJ mol}^{-1}$  [16] and that increased by addition of Cr. The value for  $\text{V}_{0.90}\text{Cr}_{0.10}\text{H}_{0.68}$  was  $27.9 \text{ kJ mol}^{-1}$ . On the other hand, Mo addition reduced  $E_{\text{H}}$  for the  $O$  sites; the value of  $E_{\text{H}}$  was  $23.2 \text{ kJ mol}^{-1}$  in  $\text{V}_{0.90}\text{Mo}_{0.10}\text{H}_{0.68}$  [16]. For  $\text{V}_{0.90}\text{Ti}_{0.10}\text{H}_{0.73}$  [19] hydrogen on two types of  $O$  sites,  $O_{z1}$  and  $O_{z2}$  sites, was observed in the temperature dependence of  $T_1$  and the values of  $E_{\text{H}}$  for these two sites were  $25.0$  and  $23.0 \text{ kJ mol}^{-1}$ , respectively. This indicates that addition of Cr reduces mobility of hydrogen on the  $O$  sites in the  $\beta$  phase although addition of Mo and Ti enhances the mobility.

Fig. 6 shows the dependence of  $E_{\text{H}}$  for the  $O$  sites on unit cell volume of the  $\beta$  phase. The  $E_{\text{H}}$  has a linear relation with the unit cell volume; the value of  $E_{\text{H}}$  decreased with the unit cell volume, as shown by a dotted line. The reduction in the unit cell volume suppresses the migration of hydrogen atoms which occupy the interstitial sites of the metal lattice. The increase in  $E_{\text{H}}$  for the  $O$  sites by addition of Cr increases the residence time of hydrogen on the  $O$  sites. In addition, it is suggested that hydrogen is trapped by the nearest  $O$  sites attracted to Cr atoms in  $\text{V}_{1-x}\text{Cr}_x\text{H}_{0.68}$  ( $x \leq 0.1$ ). Yagi et al. have reported that hydrogen in the  $\alpha$  phase of  $\text{Nb}_{1-x}\text{Mo}_x\text{-H}$  ( $x \leq 0.1$ ) is trapped in the  $T$  sites around Mo atoms [32–34]. They observed displacement of hydrogen atoms from the  $T$  sites toward the nearest Mo atom that has a smaller atomic radius than Nb using the channeling method. Meanwhile, Sumin et al. have reported that displacement of hydrogen atoms on the  $T$  sites in the  $\alpha$  phase of  $\text{Nb}_{1-x}\text{Mo}_x\text{-H}$  ( $x=0.05, 0.20$ ) is not observed using the neutron spectroscopy [35]. Yagi et al. considered that the strain field locally introduced by Mo atoms reduced the energy of interstitial sites around them and hydrogen was trapped there [32–34]. The trapping energy was roughly estimated to be an order of  $5 \text{ kJ mol}^{-1}$  [34]. In analogy,  $O$  sites around Cr atoms in  $\beta\text{-V}_{1-x}\text{Cr}_x\text{-H}$  may have lower site energy than  $O$  sites surrounded by only V atoms. On the other

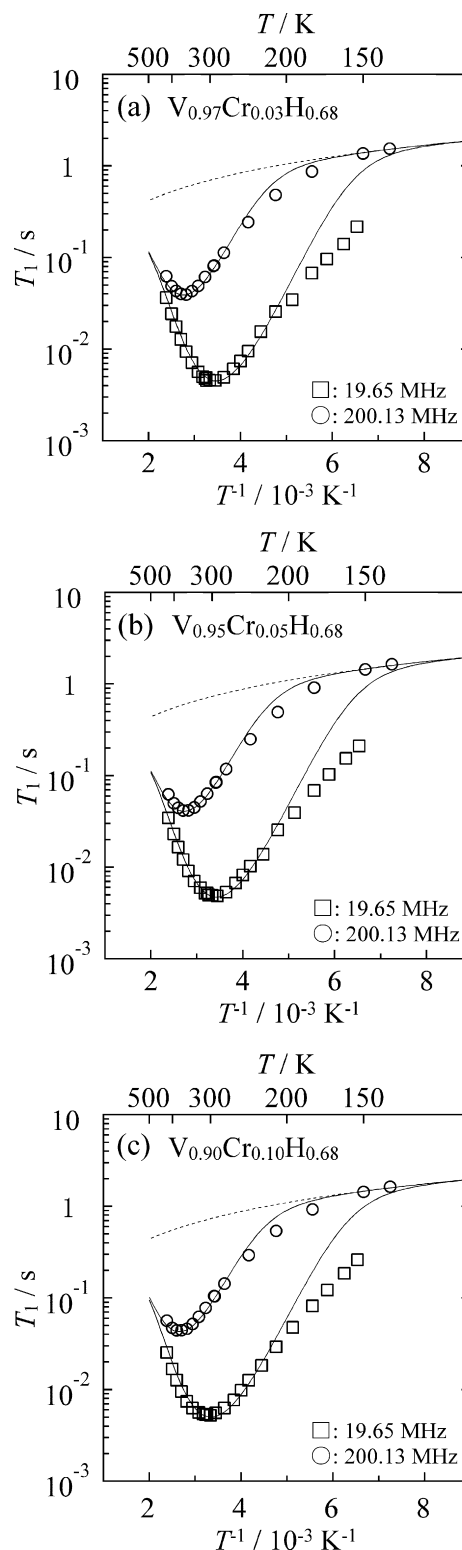
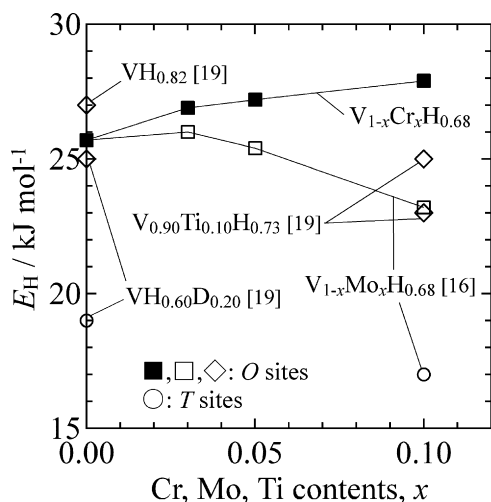


Fig. 4.  $^1\text{H}$  spin–lattice relaxation times in  $\text{V}_{1-x}\text{Cr}_x\text{H}_{0.68}$  ( $x=(\text{a}) 0.03, (\text{b}) 0.05, (\text{c}) 0.10$ ) at 19.65 and 200.13 MHz and their simulated results indicated by the solid lines. The dotted lines indicate the contribution of conduction electrons.

hand, the  $O$  sites around Mo and Ti atoms may have higher site energy and tend to repel hydrogen. In consequence the diffusion of hydrogen is suppressed by addition of Cr and that is enhanced by addition of Mo and Ti, depending on the difference in atomic radii between V and additional metals. This is consistent with the relation between activation energy of hydrogen diffusion and unit

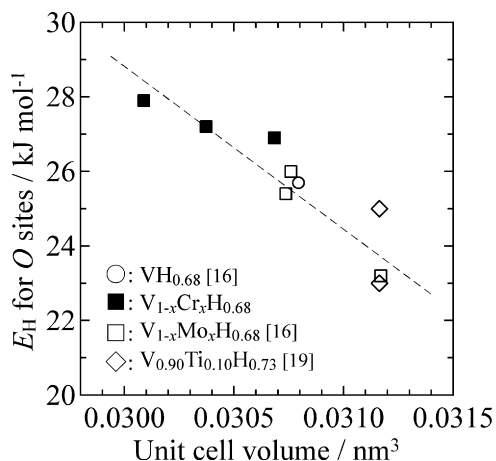


**Fig. 5.** Activation energy for hydrogen diffusion in  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ),  $V_{1-x}Mo_xH_{0.68}$  ( $x=0, 0.03, 0.05, 0.10$ ) [16],  $VH_{0.82}$  [19],  $VH_{0.60}D_{0.20}$  [19] and  $V_{0.90}Ti_{0.10}H_{0.73}$  [19].

cell volume shown in Fig. 6: smaller elements decrease the unit cell volume and reduce the mobility of hydrogen, and larger elements provide the opposite effects.

The  $T_{1e}T$  has a negative correlation with the density of states at the Fermi energy,  $N(E_F)$ , as indicated in the introduction; the reduction in  $N(E_F)$  decreases the relaxation rate,  $T_{1e}^{-1}$ , and increases the  $T_{1e}T$ . The values of  $T_{1e}T$  for  $V_{1-x}Cr_xH_{0.68}$  and  $V_{1-x}Mo_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ) [16] were larger but that for  $V_{0.90}Ti_{0.10}H_{0.73}$  [19] was smaller than that for  $VH_{0.68}$  [16], as listed in Table 1. This suggests that  $N(E_F)$  for  $\beta$ -V-H decreases by addition of Cr and Mo and increases by addition of Ti. The values of  $N(E_F)$  for these hydrides have not been reported so far. Instead, the values for transition metals without hydrogen are referred here.  $N(E_F)$  for group 5 metals, V, Nb and Ta, increases by addition of group 4 metals, Ti, Zr and Hf, but that decreases by addition of group 6 metals, Cr, Mo and W [20]. The variation of  $N(E_F)$  for  $\beta$ -V-H by addition of Cr, Mo and Ti, which is speculated from the  $T_{1e}T$ , agrees well with the variation of  $N(E_F)$  for V metal.

The reduction in  $N(E_F)$  for  $\beta$ -V-H by addition of some metal elements positively changes the heat of hydrogen solution and the enthalpy for hydride formation [20,21]. Therefore, the increase in  $T_{1e}T$  by reducing  $N(E_F)$  corresponds to the increase in the equilibrium hydrogen pressure of the plateau region in the  $P$ - $C$  isotherm



**Fig. 6.** Unit cell volume and activation energy for hydrogen diffusion for the O sites in  $V_{1-x}Cr_xH_{0.68}$  ( $x=0.03, 0.05, 0.10$ ),  $V_{1-x}Mo_xH_{0.68}$  ( $x=0, 0.03, 0.05, 0.10$ ) [16] and  $V_{0.90}Ti_{0.10}H_{0.73}$  [19].

at a given temperature. Referring to the  $P$ - $C$  isotherm of the V-H<sub>2</sub> system, the equilibrium hydrogen pressure of the lower plateau region due to coexistence of the  $\alpha$  and  $\beta$  phases increased by addition of Cr at a given temperature [13]. This indicates that addition of Cr made a positive change in the formation enthalpy of the  $\beta$  phase, which is related to the increase in  $T_{1e}T$ . When the reported values for  $V_{0.90}Ti_{0.10}H_{0.73}$  [19] and  $VH_{0.68}$  [16] are compared, addition of Ti tends to reduce  $T_{1e}T$ , assuming that the difference in the hydrogen contents is negligible. This indicates that the decrease in the equilibrium pressure of the lower plateau region by addition of Ti [13] corresponds to the reduction in  $T_{1e}T$  [19]. To our knowledge, the effect of Mo addition on the equilibrium pressure of the lower plateau region of the V-H<sub>2</sub> system has not been reported. However, the equilibrium pressure likely increase by addition of Mo because the value of  $T_{1e}T$  increased with increase in the Mo content, as listed in Table 1. It is concluded that the thermal stability of the hydride phase can be estimated from the information related to the conduction electrons, which is obtained using NMR.

#### 4. Conclusions

Hydrogen atoms in  $\beta$ - $V_{1-x}Cr_xH_{0.68}$  occupied the O sites in the BCT lattice and the obvious effect of Cr addition on shift of hydrogen occupation was not found in the region of  $x \leq 0.10$ . Addition of Cr reduces the unit cell volume and increases the activation energy for the hydrogen diffusion for the O sites. Additional metal atoms change the site energy of the O sites and the mobility of hydrogen. The O sites around smaller atoms than V trap hydrogen and the O sites around larger atoms repel hydrogen. Since smaller additional atoms reduce the mobility of hydrogen,  $\beta$ -V-H with a smaller unit cell volume tends to have higher activation energy for the hydrogen diffusion.

On the other hand, it was indicated that the Korringa constant for hydrogen was related to the thermal stability of the  $\beta$  phase. The increase in the Korringa constant corresponds to the decrease in the density of states at the Fermi energy and the positive shift of the enthalpy for hydride formation.

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#### References

- [1] D. Mori, K. Hirose, Int. J. Hydrogen Energy 34 (2009) 4569–4574.
- [2] T. Matsunaga, M. Kon, K. Washio, T. Shinozawa, M. Ishikiriyama, Int. J. Hydrogen Energy 34 (2009) 1458–1462.
- [3] H. Iba, E. Akiba, J. Alloys Compd. 253–254 (1997) 21–24.
- [4] E. Akiba, H. Iba, Intermetallics 6 (1998) 461–470.
- [5] K. Kubo, H. Itoh, T. Takahashi, T. Ebisawa, T. Kabutomori, Y. Nakamura, E. Akiba, J. Alloys Compd. 356–357 (2003) 452–455.
- [6] M. Shibuya, J. Nakamura, H. Enoki, E. Akiba, J. Alloys Compd. 475 (2009) 543–545.
- [7] Y. Tominaga, S. Nishimura, T. Amemiya, T. Fuda, T. Tamura, T. Kuriwa, A. Kamegawa, M. Okada, Mater. Trans. JIM 40 (1999) 871–874.
- [8] T. Kuriwa, T. Tamura, T. Amemiya, T. Fuda, A. Kamegawa, H. Takamura, M. Okada, J. Alloys Compd. 293–295 (1999) 433–436.
- [9] T. Tamura, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 42 (2001) 1862–1865.
- [10] T. Tamura, T. Kazumi, A. Kamegawa, H. Takamura, M. Okada, Mater. Trans. 42 (2002) 2753–2756.
- [11] T. Schober, H. Wenzl, in: G. Alefeld, J. Völkl (Eds.), Hydrogen in Metals, vol. 2, Springer-Verlag, Berlin, 1978, p. 11.
- [12] T. Schober, in: F.A. Lewis, A. Aladjem (Eds.), Hydrogen Metal Systems. I. Solid State Phenomena, vols. 49–50, Scitec Publications, Zuerich, 1996, p. 357.

- [13] H. Yukawa, D. Yamashita, S. Ito, M. Morinaga, S. Yamaguchi, *Mater. Trans.* 43 (2002) 2757–2762.
- [14] S. Ono, K. Nomura, Y. Ikeda, *J. Less-Common Met.* 72 (1980) 159–165.
- [15] *Metal Databook Ver. 3*, Japan Institute of Metals, 1993, p. 8 (in Japanese).
- [16] K. Asano, S. Hayashi, Y. Nakamura, E. Akiba, *J. Alloys Compd.* 507 (2010) 399–404.
- [17] B. Bandyopadhyay, S. Hayashi, *J. Alloys Compd.* 305 (2000) 136–143.
- [18] S. Hayashi, *J. Solid State Chem.* 170 (2003) 82–93.
- [19] S. Hayashi, *J. Phys. Chem. Solids* 64 (2003) 2227–2234.
- [20] Y. Ebisuzaki, M. O'Keefe, in: H. Reiss (Ed.), *Progress in Solid State Chemistry*, vol. 4, Pergamon Press, London, 1967, p. 187.
- [21] Y. Fukai, *The Metal–Hydrogen System, Basic Bulk Properties*, 2nd ed., Springer-Verlag, Berlin, Heidelberg, 2005.
- [22] B. Predel, in: O. Madelung, W. Martienssen (Eds.), *Landolt–Börnstein New Series, Group IV*, vol. 5d, Springer-Verlag, Berlin, Heidelberg, 1994, p. 102.
- [23] J.F. Lynch, J.J. Reilly, F. Millot, *J. Phys. Chem. Solids* 39 (1978) 883–890.
- [24] G. Mazzolai, *Int. J. Hydrogen Energy* 33 (2008) 7116–7121.
- [25] D.J. Pine, R.M. Cotts, *Phys. Rev. B* 28 (1983) 641–647.
- [26] T. Eguchi, S. Morozumi, *J. Jpn. Inst. Met.* 41 (1977) 795–802 (in Japanese).
- [27] Y. Fukai, S. Kazama, *Acta Metall.* 25 (1977) 59–70.
- [28] R.C. Bowman Jr., A. Attalla, W.E. Tadlock, D.B. Sullenger, R.L. Yauger, *Scripta Metall.* 16 (1982) 933–938.
- [29] R.C. Bowman Jr., A. Attalla, B.D. Craft, *Scripta Metall.* 17 (1983) 937–942.
- [30] B. Bandyopadhyay, S. Hayashi, *Phys. Rev. B* 60 (1999) 10302–10315.
- [31] N. Bloembergen, E.M. Purcell, R.V. Pound, *Phys. Rev.* 73 (1948) 679–712.
- [32] E. Yagi, S. Koike, T. Matsumoto, T. Urai, N. Tajima, K. Ogiwara, *Phys. Rev. B* 66 (2002) 024206.
- [33] E. Yagi, *ISIJ Int.* 43 (2003) 505–513.
- [34] E. Yagi, S. Nakamura, F. Kano, T. Kobayashi, K. Watanabe, Y. Fukai, T. Matsumoto, *Phys. Rev. B* 39 (1989) 57–60.
- [35] V.V. Sumin, H. Wipf, B. Coluzzi, A. Biscarini, R. Campanella, G. Mazzolai, F.M. Mazzolai, *J. Alloys Compd.* 316 (2001) 189–192.