Diffusion of hydrogen in α' -VH_x

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Measurements of tracer (self-) diffusion coefficients of H in the body-centered-cubic α' phase of VH_x are reported for hydrogen concentrations x = 0.17 to 0.68 and temperatures from 435 to 620 K. Experimental results, obtained from the NMR alternating-pulsed-field-gradient spin-echo technique, fit the relation $D = D_0 \exp(-E_a/k_BT)$. The activation energies E_a depend strongly upon H concentration, but the factors D_0 change relatively little. For x = 0.68, $E_a = 0.132 \pm 0.006$ eV/atom and is more than a factor of 2 greater than E_a for low concentrations with $x \approx 0$. From these data and published chemical diffusion coefficients D_c for H, the empirical dependence of the hydrogen chemical potential μ upon hydrogen density ρ in α' -VH_x, $(\rho/k_BT)(\partial\mu/\partial\rho)$ is calculated. Results are compared to those of other group-V bcc hydrides, α' -NbH_x and α' -TaH_x.

I. INTRODUCTION

In their high-temperature regime, the group-V transition metals can absorb hydrogen continuously, up to about 0.8 hydrogen atom for every host-metal atom with no change in the host-lattice structure (body-centered cubic). These α (low concentration) and α' (high concentration) regions of the same phase provide unusual opportunities to study effects of changing hydrogen concentration on physical properties of the metal. Hydrogen atoms occupy the (distorted) tetrahedral sites in a nearly random way. Occupancy of one site by an H atom is believed to block the occupancy of nearby sites through the secondnearest neighbor. To identify and compare effects of site blocking and H-H interactions on the diffusion of H atoms, it is of interest to determine the concentration dependence of the diffusivity of hydrogen atoms in these systems.

Most of the early experiments on hydrogen transport in α -VH_x measured the H-atom chemical diffusion coefficient D_c at very low concentrations.¹ A proven technique has been the anelastic mechanical relaxation¹ (Gorsky effect) experiments, and in some studies,²⁻⁴ it has been applied to high H-atom concentration α' -phase systems.

The tracer (self-) diffusion coefficient D is the measure of equilibrium diffusivity of hydrogen. In contrast, the coefficient D_c is obtained from hydrogen flux measurements under nonequilibrium conditions. D and D_c are related⁵ by (1) the thermodynamic factor $f_{\text{therm}} = (\rho/k_B T)$ $(\partial \mu / \partial \rho)$, where ρ is the H-atom concentration and μ is the chemical potential, and (2) a correlation factor^{4,6} f_{corr} such that $D_c/D = f_{\text{therm}}/f_{\text{corr}}$. It is possible to calculate f_{therm} from the Gorsky effect relaxation strength and a knowledge of elastic constants for each material. Thus Dcould be calculated from a known D_c in circumstances where f_{corr} is known or is arguably equal to unity. However, as has been noted by Potzel *et al.*,⁴ the accuracy of such calculated values of f_{therm} depends upon the availability of sufficiently accurate hydride elastic constants. At low concentrations,⁵ $D_c = D$.

Nuclear magnetic resonance (NMR) pulsed-fieldgradient spin-echo techniques and quasielastic neutron scattering (QNS) experiments measure D directly.⁷ Analysis of a series of QNS experiments⁸ on the α phases VH_{0.07}, NbH_{0.02}, and TaH_{0.13} has, in addition to determining temperature dependence of D, provided much insight into the jump mechanism of hydrogen at low concentrations. These QNS experiments showed an increasing probability of H-atom jumps beyond the nearestneighbor site as temperature was increased above 300 K, to as high as 581 K. Few QNS measurements of D have been made in higher concentration group-V α' -phase hydrides. The QNS data of deGraaf et al.⁹ can be used to estimate D for x = 0.198, 0.403, and 0.570 in VH_x at 210°C. Recently, Potzel et al.4 compared QNS and Gorsky effect data at 500 K for α' -TaH_{0.28} and TaH_{0.61} and found that $f_{\text{therm}} \approx 1$ for x = 0.28 and $f_{\text{therm}} \approx 20$ for x = 0.61. Their QNS measurements of D were consistent with earlier NMR measurements⁶ of D made for selected values of x ranging from 0.12 to 0.77 in α' -TaH_x.

The NMR pulsed-field-gradient spin-echo technique has been used to measure D of H in NbH_x,⁶ TaH_x,⁶ and NbH_xD_y.¹⁰ NbH_x results⁶ in samples of granular form are consistent with earlier NMR measurements of D in an NbH_{0.6} single crystal¹¹. By varying deuterium content in several samples of NbH_xD_y (with x + y = const), Fukai *et al.*¹⁰ showed that increasing the fractional deuterium content caused D of H to decrease, indicating existence of H-H correlation effects in these α' alloys. Kazama *et al.*¹² repeated the experiment on α' -TaH_xD_y with similar results. NMR measurements of D of H in α' -VH_x have been reported¹³ for just one concentration.

In the α' -NbH_x and α' -TaH_x systems, an increase in H concentration causes a decrease in D and, over most of the range of x, an increase in the activation energy for diffusion. The measurements reported here were made to determine whether, for α' -VH_x, there is a similar dependence of D upon x.

After a description of experimental methods in Sec. II, results are presented in Sec. III and discussed in Sec. IV.

II. EXPERIMENTAL METHODS

Samples were prepared from Materials Research Corporation Marz Grade vanadium which had been zonerefined in the Materials Preparation Facility of the Cornell University Materials Science Center. Hydrogen concentration was determined by reacting the metal with a known volume of H_2 gas and monitoring the pressure. Samples with x > 0.55 and x < 0.3 were hydrided twice; first, to a high concentration of about 0.5 [H]/[V], to make a sample that could be easily ground into a powder. After grinding, particles with sizes nominally in the range from 105–150 μ m were selected, and the hydrogen removed from the particles under vacuum. These particles were then rehydrided to the desired concentration. The first hydriding was done in vanadium foil 100 μ m thick, rolled from vanadium rod. VH_x powder was mixed with quartz powder in a 3:2 ratio, to reduce resistive losses, and sealed in glass sample tubes.

The NMR alternating-pulse-field gradient of Karlicek and Lowe¹⁴, which eliminates effects of background gradients, was used to measure D at an NMR frequency of 15.8 MHz in a magnetic field controlled by an NMR field lock circuit. The bipolar gradient pulser and coil were adapted from the design by Mauger.¹⁵ While a single cycle of four gradient pulses was used in a train of 180° pulses,¹⁴ the signal heights of four echoes at 10τ , 12τ , 14τ , and 16τ were averaged. Signals were fit to the equation¹⁴

$$A(G) = A(0)\exp(-D\eta) , \qquad (1)$$

where

$$\eta = (2/3) [\gamma^2 G^2 \delta^2 \tau (18 - \delta/\tau)], \qquad (2)$$

and γ is the proton gyromagnetic ratio, G is the magnitude of each gradient pulse, δ is the width of each gradient pulse, and 2τ is the spacing between 180° pulses in the pulse train. Typical values of τ and δ are 0.8 msec and 0.5 msec, and were held constant while G was varied.

Tests were made on one sample for evidence of systematic error in measurement of D due to restricted diffusion volume¹⁶ for our small particles. At a nominal value of $D=4\times10^{-5}$ cm²/sec in VH_{0.31}, a 40% increase in the duration time of the pulse sequence (with a constant δ/τ ratio) caused 6% decrease in D, presumably due to restricted diffusion. Similar decreases were found in VH_{0.31} over the entire temperature range. We estimate that the diffusion coefficients reported here are not suppressed by more than 10% by effects of restricted diffusion.

Both in-phase and quadrature echo signals, $v_0(t)$ and $v_{90}(t)$, were detected simultaneously in the NMR receiver.¹⁵ The actual echoes used for data analysis were measured from the computed $v(t) = [v_0(t)^2 + v_{90}(t)^2]^{1/2}$, using Nicolet Digital Oscilloscope model no. 4094 and its associated programs.

III. RESULTS

Hydrogen diffusion coefficients were measured for α' -VH_x for x=0.17, 0.22, 0.31, 0.38, 0.51, and 0.68 for temperatures ranging from abut 435 to 620 K for most sam-

ples. The results are plotted as D versus $10^3/T$ in Fig. 1. Within experimental error, the data for each concentration can be fit to an Arrhenius relation $D = D_0 \exp(-E_a/k_B T)$. From a least-squares fitting program we obtain values of E_a and D_0 shown in Table I. It is clear from Fig. 1 and Table I that the decrease in D associated with an increase in x is caused primarily by an increase in E_a while D_0 does not substantially change. Our results for x = 0.31 agree reasonably well with those of Kruger and Weiss¹³ for x=0.3. Their D values are consistently higher than ours. Although their activation energy is 0.11 eV/atom, their data is compatible, within their experimental uncertainty, to the 0.089 eV/atom value reported here. An uncertainty in hydrogen concentration of $\Delta x = 0.03$ could account for the discrepancy in magnitudes of D measurements.

Most measurements were confined to the α' phase, but the measurements of D in VH_{0.68} were carried to as low as 140°C, to observe the marked decrease in D associated with the transition to the ϵ phase. A temperature hysteresis, having a width about 12 K, existed at the α' - ϵ phase transition.

From these measurements of D and published³ measurements of D_c , the thermodynamic factors can be calculated. The assumption $f_{\rm corr} = 1$ will be made⁶, and therefore, $f_{\rm therm} \approx D_c/D$. The highest H concentration that can be considered is about x = 0.45, because published data for D_c does not exist for x > 0.45 in VH_x. Since the values of D_c and D were generally not measured at the same concentrations and temperatures, it was necessary to make interpolations. Resulting values of $f_{\rm therm}$ are shown as the solid line in Fig. 2. A smooth curve has been drawn through our points for $f_{\rm therm}$.

A second independent measure of f_{therm} can be estimat-



FIG. 1. Temperature dependence of the hydrogen tracer diffusion coefficient D for several concentrations in α' -VH_x. The straight lines show fits to the Arrhenius relation $D=D_0\exp(-E_\alpha/kT)$ for E_α and D_0 as shown in Table I. The concentration x for each sample is shown next to the line.

TABLE I. Diffusion parameters of H in α' -VH_x.

x	E_a (meV/atom)	$D_0 \ (10^{-4} \ {\rm cm^2/sec})$
0.17	87±3	4.3±0.3
0.22	89±2	4.0±0.2
0.31	89±8	3.8 ± 0.8
0.38	106±2	4.4±0.1
0.51	121±8	5.2±0.8
0.68	132±6	4.7±0.7

ed from extrapolation of the solubility measurements of Edwards and Veleckis,¹⁷ $f_{\text{therm}} = (\rho/2P)(dP/d\rho)$, where P is the equilibrium hydrogen pressure. Their semiempirical analytic expression was used to calculate f_{therm} for x < 0.16, and their published data were extrapolated to lower temperatures to obtain f_{therm} for x > 0.16. A smooth curve has been drawn through these points. The thermodynamic factor found from solubility data falls consistently below the curve for f_{therm} obtained from the ratio D_c/D .

The concentration dependence of f_{therm} in the TaH_x system has also been determined using both solubility data and D_c/D .⁶ At T=373 K, the concentration dependence of f_{therm} for TaH_x appears remarkably similar to that of



FIG. 2. Concentration dependence of the thermodynamic factor, $f_{\text{therm}} = (\rho/kT) (\partial \mu/\partial \rho)$ for VH_x at $T = 245 \,^{\circ}\text{C}$ (518 K), as determined by two methods. The solid line is the ratio D_c/D , where D_c is the chemical diffusion coefficient obtained from Gorsky effect experiments of Ref. 3 and D is the tracer coefficient measured with NMR pulsed field gradient techniques, as reported here. The dashed line is $f_{\text{therm}} = \frac{1}{2} (\rho/P)(\partial P/\partial \rho)$, as determined from solubility data using the analytic expression of Ref. 17 for 0 < x < 0.16 and their numerical data for x > 0.16. Typical uncertainty in f_{therm} is ± 0.1 . The solid line is in substantial agreement with results for f_{therm} , obtained entirely from the Gorsky effect experiments and shown in Bauberger and Wipf (Ref. 26).

VH_x at T=245 K. In both systems, f_{therm} reaches a minimum at about x=0.2, and in both systems the value of f_{therm} calculated from solubility data is lower than that calculated from D_c/D . Since the concentration dependence of f_{therm} is strongly temperature dependent, it is important to note that the high-temperature boundary for α - α' phase transition occurs at 333 K for TaH_x and 205 K for VH_x. Thus the temperatures compared (373 K for TaH_x and 245 K for VH_x) are both 40 K higher than the α - α' high-temperature phase boundary for their respective systems.

IV. CONCLUSIONS

The concentration dependence of hydrogen tracer diffusion coefficients in the α' -VH_x system is qualitatively similar to that in the other group-V bcc metal-hydrogen systems α' -NbH_x and α' -TaH_x. Concentration dependence of the diffusion activation energy for these systems is shown in Fig. 3.



FIG. 3. Concentration dependence of E_a for D in VH_x, NbH_x, and TaH_x. Data for VH_x (crosses), x > 0, are from NMR results reported here. E_a for NbH_x (solid circles) and TaH_x (open circles) are from NMR data of Ref. 6 with one point (x=0.6) from Ref. 11. The NbH_x and TaH_x results from QNS experiments are shown as a solid square (Ref. 18) and open squares (Ref. 4). Data at x=0 are from Gorsky effect experiments (Ref. 5) for NbH_x and TaH_x, but the x=0 point for VH_x is from Pine and Cotts (Ref. 27), who used a resistiometric technique, selected because its temperature range better overlaps the range of the experiments reported here. The $E_a = 0.059$ eV for x=0 in VH_x exceeds that of Gorsky effect data recorded over a lower temperature range and represents a stronger high temperature dependence for D in α -VH_x, as already noted in Refs. 7 and 8. The dashed lines are a guide for the eye.

For all three systems, addition of hydrogen increases E_a over most of the concentration range measured. At high concentrations, the slope of E_a versus x levels off or reaches a weak maximum value near $x \approx 0.7$. In addition to E_a from NMR measurements of D, the graph of Fig. 3 also contains three known determinations of E_a from QNS data.^{4,18} There is good agreement between the QNS and NMR data, especially in the data for D where the temperature ranges overlap. Concentration dependences of E_a have been published² for D, calculated entirely from Gorsky effect measurements of D_c and related calculations of f_{therm} for α' -NbH_x and α' -TaH_x. For TaH_x, there is good agreement between the sets of E_a for tracer diffusion, as found from Gorsky effect and from NMR experiments. However, the agreement is not as good for α' -NbH_x. For 0 < x < 0.5 in this system, the slope of E_{α} versus x as found from Gorsky effect data alone is a factor of about 1.75 larger than the slope for the NMR data. The values of E_a for the tracer diffusion coefficients as calculated from Gorsky effect data in NbH_x are subject to large relative uncertainties in f_{therm} for temperatures and concentrations near the critical point of NbH_x where f_{therm} becomes very small. We believe these uncertainties are responsible for the disagreement in E_a versus x for NbH_x. With less uncertainty in TaH_x , the agreement is satisfactory.

 VH_x Gorsky effect data have been analyzed³ for the calculation the diffusion parameter of $D' = D [1 - (\rho/\rho_m)]^{-1}$, where ρ_m is the maximum concentration for H in α' -VH_x. If one makes the assumption that ρ_m is independent of temperature, the E_a for $D' = D'_0 \exp(-E_a/k_b T)$ should be the same for D as it is for D'. From the graph of D' versus 1/T of Ref. 3, values of E_a have been calculated for six concentrations of H, from x = 0.02 to 0.45. These E_a are found to be roughly in agreement with those plotted in Fig. 3, but the concentration dependence of E_a from the Gorsky effect is weaker than it is for values of E_a determined from NMR.

Although E_a increases with increasing x, the largest values of E_a for these bcc metals remain considerably smaller than E_a for hydrides of the fcc host-metal structure. In the group-IV fcc hydrides, for example of Ti, Zr, and Hf, hydrogen atoms occupy tetrahedral sites with considerably higher diffusion activation energies. For these substoichiometric group-IV dihydrides, e.g., for $x \approx 1.7$, E_a is approximately 0.55 ± 0.05 eV.^{19–21} Similarly, large E_a 's are found for Sc and Y fcc hydrides. How-

ever, for PdH_x , with H atoms in octahedral sites, the activation energy is reduced but nevertheless greater than E_a in the bcc metals. For $PdH_{0.7}$, $E_a = 0.23 \text{ eV/atom.}^{22}$ This difference in E_a for fcc and bcc systems was noted in one system by Piper,²³ for $Pd_{0.47}Cu_{0.53}$ with fcc stabilized by quenching and also in bcc, the equilibrium phase. The activation energy for the bcc phase⁵ (0.035 eV) is about one-sixth the E_a for the fcc phase.

For a given temperature in the α' group-V hydrides, addition of H causes a reduction in D. As can be seen from Table I, D_0 is relatively insensitive to x, while E_a is not. Therefore, the marked decrease in D is more due to the increase in E_a than to blocking effects of other H atoms, which would primarily affect D_0 .

Compared to fcc systems such as TiH_x and PdH_x , the activation energies for tracer diffusion coefficients in the group-V bcc hydrides have a strong concentration dependence. The relative change is greatest in α' -VH_x, where (as can be seen from Fig. 3) E_a for x=0.7 is more than twice E_a for $x \approx 0$. One might expect the known lattice expansion, which is directly proportional to x, to cause a decrease in E_a at high x, but the opposite effect holds.

Addition of hydrogen causes an increase in the bulk modulus²⁴ of NbH_x by about 5% from x = 0 to 0.7. If the activation process were limited to the energy needed for a given displacement of host-metal atoms, this change in bulk modulus would be too small to account for the 60% increase in E_a over the same range of x.

In the high-temperature regime of the α' phase, H diffusion has been described^{7,25} in terms of adiabatic transitions from one site to the next. At low concentrations these transitions probably occur by tunneling from one ground-state level to the same state level in an adjacent site. Addition of hydrogen to the α' phase adds local strain that can disturb the coincidence and reduce tunneling rates in low-lying states. In high-concentration samples, excitation to fast-tunneling coincidence events at higher energy levels may compensate for the reduced tunneling rates in the ground states. Thus the E_a would increase with increasing x, as has been demonstrated experimentally.

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