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Concentration dependence of hydrogen diffusion in clamped vanadium (001) films

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Abstract

The chemical diffusion coefficient of hydrogen in a 50 nm thin film of vanadium (001) is measured as a function of concentration and temperature, well above the known phase boundaries. Arrhenius analysis of the tracer diffusion constants reveal large changes in the activation energy with concentration: from 0.10 at 0.05 in H V^{-1} to 0.5 eV at 0.2 in H V^{-1} . The results are consistent with a change from tetrahedral to octahedral site occupancy, in that concentration range. The change in site occupancy is argued to be caused by the uniaxial expansion of the film originating from the combined hydrogen induced expansion and the clamping of the film to the substrate.

Keywords: diffusion, hydrogen, single crystal

(Some figures may appear in colour only in the online journal)

1. Introduction

Hydrogen in vanadium exhibits the fastest diffusion rates of all classical hydrides. This fast diffusion is in part due to the short distances between nearest neighbour interstitial sites where hydrogen resides and its low mass. The short distance between interstitial sites promotes tunnelling, and quantum effects are therefore assumed to be important for the understanding of diffusion at low and intermediate temperatures [1–3]. Investigations of diffusion of hydrogen therefore offer an insight on the boundaries and the crossover between the classical and the quantum regime. However, the interest in the diffusion of hydrogen is not restricted to academic efforts, the knowledge of hydrogen diffusion is also highly relevant for the utilisation of hydrogen as an energy carrier.

Kleiner *et al* investigated the concentration dependence of the tracer diffusion (or self diffusion) of hydrogen in vanadium in the α' phase with NMR. In these experiments they observed an increase in the activation energy with concentration, from

87 meV at $c = 0.17 \text{ H V}^{-1}$ to 132 meV at $c = 0.65 \text{ H V}^{-1}$, while the pre factor D_0 remained largely unaffected [4]. They argued that hydrogen mobility at low concentrations is mediated by tunnelling between sites and adding hydrogen added local strain fields that distorts the co-incidence of the energy levels of the adjacent sites and thereby reducing the tunnelling probability. This would imply that quantum effects are important even at elevated temperatures (435–620 K), at which the measurements were performed.

Quantum effects are often assumed to be less important at and above room temperature, as compared to low temperatures, and classical rate theory and classical *ab initio* molecular dynamics simulations [5] have therefore been used to describe the mobility of hydrogen in this temperature range. The influence of self trapping on diffusion is still important at these temperatures, as demonstrated by Blomqvist and co-workers using molecular dynamics [6]. Partial unbinding of the proton and its associated strain field was observed in these calculations, causing changes in both activation and absorption energies [6]. The activation barriers must therefore be treated as dynamic, which is often ignored. Molecular dynamics could therefore be considered to be more accurate in this sense, albeit with apparent shortcomings as traditional molecular dynamics do not include any tunnelling effects.

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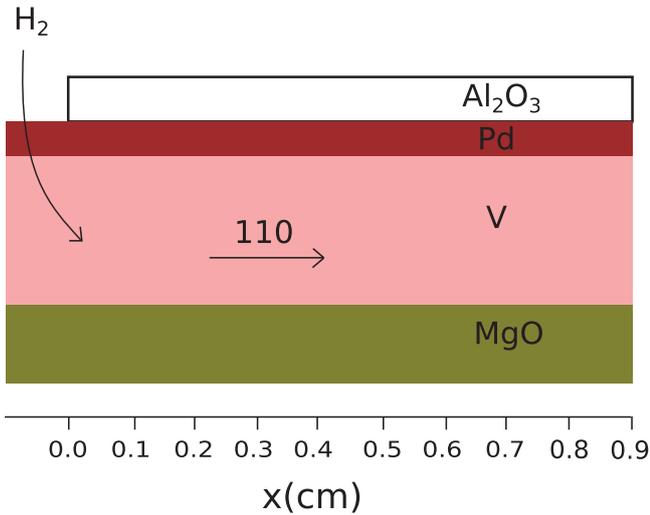


Figure 1. The sample is a 50 nm film of vanadium (001) deposited on MgO (001) followed by 7 nm of palladium and 10 nm of Al_2O_3 . Part of the film surface is left uncovered of Al_2O_3 enabling dissociation and uptake of hydrogen. The edge of the Al_2O_3 layer defines the starting point of the diffusion and the uncovered region can be viewed as a reservoir for the hydrogen.

Experimental observations of hydrogen diffusion in metals can be clouded by effects arising from trapping at grain boundaries and defects. Although experiments on large single crystals of for instance vanadium have been performed, e.g. with quasi-elastic neutron scattering [7], these are rare due to experimental challenges associated to sample growth and hydrogen loading. In this paper, we report on measurements of hydrogen diffusion in thin films, using a newly developed optical approach [8]. All the experiments were performed at and above the known ordering temperature of bulk VH_x , thus, all the results resemble the diffusion in the disordered phase (α and α'). We extend the previously described method to allow the determination of the diffusion constants over a large concentration range in a single H-absorption experiment. The investigation of hydrogen diffusion in vanadium is partially motivated by the delicate impact of strain on the site occupancy (of hydrogen in V) [9] and the unclarity with respect to the role of tunnelling on hydrogen mobility at elevated temperatures. We will show that the boundary conditions (clamping) affects the diffusion rate in a profound way, through a change in site occupancy at relatively low concentrations (0.1–0.2 H V^{-1}). Furthermore, the changes in the diffusion rate are found to be captured by a classical description of the mobility in the investigated temperature range.

2. Experimental details

2.1. Sample preparation

A single crystal vanadium (001) thin film was grown using magnetron sputtering at 527 K on a $10 \text{ mm} \times 10 \text{ mm} \times 0.5 \text{ mm}$ MgO (001) substrate. The purity of the target material (V) is 99.95%. Figure 1 shows the design of the sample, defining the boundary conditions of the diffusion experiments. The

thickness of the vanadium film is 50 nm and the film is capped with 7 nm thick polycrystalline (111) textured palladium, which spontaneously dissociates hydrogen. The palladium also protects the underlying V film from oxidation. The affinity for hydrogen of palladium is much lower than vanadium in the temperature and pressure range considered in this article, hence the hydrogen concentration in palladium can be treated as negligible. A 10 nm thick optically transparent amorphous Al_2O_3 thin film is deposited on top and the sides of the sample, leaving a 0.1 cm strip of the sample uncovered at one end, where hydrogen can migrate into the V layer. The epitaxial relationship between the film and the substrate allows investigations of the net diffusion in a given crystallographic direction. In the experiments described here the net diffusion is in the (110) direction of the vanadium layer. After the sample is inserted into the measurement chamber, the sample and the chamber are outgassed at 423 K for two days under ultra high vacuum conditions. At the end of this procedure the base pressure in the chamber is in the low 10^{-9} mbar range, of which the main residual gas is hydrogen. After choosing the temperature, a constant hydrogen pressure is applied, corresponding to an equilibrium concentration of $c = 0.45 \text{ H V}^{-1}$, determined by independent optical transmission measurements [10]. As a result, a constant hydrogen concentration is obtained in the V below the exposed Pd layer. The constant concentration is maintained by the equilibrium between the influx of hydrogen into the sample and the diffusion along the (110) direction in the V(001) layer. The equilibrium concentration is dynamic and determined by the thermodynamic properties of the V layer. The edge of the oxide layer defines the position $x = 0 \text{ cm}$ in the diffusion experiment. To determine the temperature dependence of the diffusion, we adjust the pressure at each temperature, to keep the final concentration constant to about $c = 0.45 \text{ H V}^{-1}$. Here the optical transmission beneath the Pd window serves as an internal calibration. The concentration dependence is extracted by considering different parts of the concentration profiles as described below.

2.2. Concentration determination

To determine the local hydrogen concentration in the film, we use the optical transmission:

$$I(c) = I_0 e^{-\alpha(\lambda, c)d}, \quad (1)$$

where $\alpha(\lambda, c)$ is the wavelength and concentration dependent absorption coefficient and d is the thickness of the H-absorbing layer. By taking the ratio of the transmission with and without hydrogen, expanding the absorption coefficient into a power series and truncating after the linear term, we obtain [10, 11]

$$c = \beta \ln \left[\frac{I(c)}{I(0)} \right] \quad (2)$$

where β is an effective prefactor. The calibration coefficient has been previously determined to be $\beta = -1.38$ for hydrogen in a 50 nm vanadium film for light of $\lambda = 639 \text{ nm}$. From previous studies we know that this relation still holds for $\lambda = 590 \text{ nm}$ [12], the wavelength used in the present experiment.

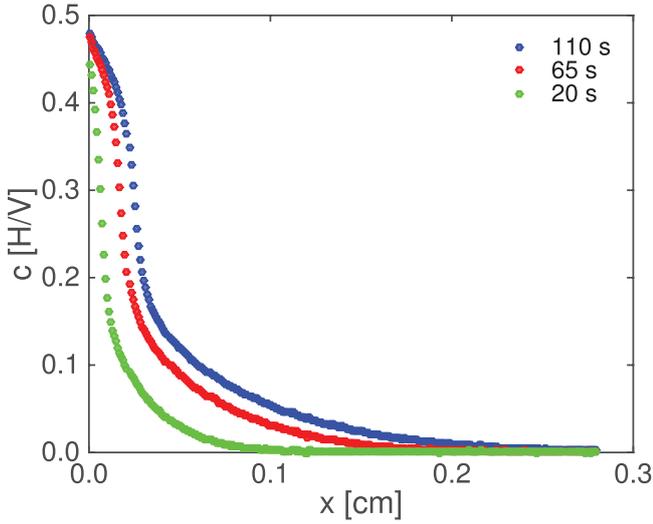


Figure 2. Hydrogen concentration profile at different position and time for 483 K.

The gradual increasing concentration $c(x,t)$ with time for $x > 0$ along the sample can be displayed as concentration profiles $c(x)$ at constant times, such as in figure 2. The full images with the $c(x,t)$ data, saved with 5 s time intervals, were recorded with a charge-coupled device (CCD) camera with a spatial resolution of 0.0010(1) cm.

2.3. Determination of diffusion constants

The present investigation concerns concentration dependent diffusion and in this case, analytic expressions are in general not available. Consequently, the analysis of the data is restricted to times within which the profiles $c(x)$ can be considered as belonging to a semi-infinite sample. Under these conditions we can extract the concentration dependent $D(c)$ from the profiles $c(x)$ at constant times t by an integration method. The idea of integrating ‘Fick’s law’ was introduced by Boltzmann. The above described absorption conditions fulfil the required criterion for applying the Boltzmann method [13], the solution of which is given by:

$$D(c) = -\frac{1}{2t} \left(\frac{dc}{dx} \right)^{-1} \int_{c_0}^c x(c') dc'. \quad (3)$$

A slight variation on Boltzmann’s method can also be formulated as follows [14]. The concentration profiles of hydrogen diffusion can be described by Fick’s second law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D(c) \frac{\partial c}{\partial x} \right) \quad (4)$$

where $D(c)$ is the concentration dependent chemical diffusion constant. One can integrate both sides of the equation for a constant time t from x to ∞ and obtain

$$\int_x^\infty \frac{\partial c(x',t)}{\partial t} dx' = B - D(c) \frac{\partial c(x,t)}{\partial x}, \quad (5)$$

where B is an integration constant. The natural boundary condition is

$$\frac{\partial c(x,t)}{\partial t} = 0, \forall x \geq L, \quad (6)$$

where L is the length of the Al_2O_3 covered part of the sample and

$$\lim_{x \rightarrow L} \frac{\partial c(x,t)}{\partial x} = 0. \quad (7)$$

The diffusion constant can be obtained from equation (5) by dividing by $\frac{\partial c}{\partial x}$, to obtain [14]

$$D(c) = \frac{- \left[\int_x^L \frac{\partial c(x',t)}{\partial t} dx' \right]}{\frac{\partial c(x,t)}{\partial x}}. \quad (8)$$

We have found that these hold for $t \leq 110$ s, under the experimental conditions described here. This approach is highly efficient, since we have all $c(x,t)$ available at constant intervals in x and t , and the derivatives can be found relatively easily. As compared to a Boltzmann integration this method would also be advantageous e.g. if the time $t = 0$ or $x = 0$ were not accurately known (which is not the case here). We use the Boltzmann method however when considering low concentrations due to its smaller sensitivity to the time derivative.

The hydrogen diffusion coefficients as a function of position and time can be obtained from equation (8) using numerical methods. This inevitably involves smoothing of the profiles in order to reduce noise in the data (here an 11 point 2nd order Savitzky–Golay filter was used for the $c(x)$ profiles). The final diffusion coefficients D_c were obtained as the average value of the diffusion coefficients from the different profiles in the time window 0–110 s, at the corresponding concentration c . Here the concentration range is divided into intervals of width of $\Delta c = 0.01 \text{ H V}^{-1}$.

3. Results and discussion

3.1. Concentration dependence of the diffusion

The diffusion coefficients were measured in the disordered part of the phase diagram in the concentration range from $c = 0 \text{ H V}^{-1}$ to $c \approx 0.45 \text{ H V}^{-1}$ and at temperatures of $T = 473 \text{ K}$, 483 K , 493 K , 503 K , 513 K and 523 K . Figure 2 shows representative hydrogen concentration profiles extracted from the optical transmission measurement at 483 K for $t = 20$ s, $t = 65$ s, $t = 110$ s. The whole concentration dependence can be determined from a single profile, but to increase the statistical accuracy, the resulting diffusion constants are determined at different times in the interval $t = 0$ –110 s and subsequently averaged. Note that the diffusion constant at the lowest concentration is obtained from the region where the concentration gradient is shallow, resulting in larger uncertainties.

Figure 3 shows the obtained chemical diffusion coefficient as a function of concentration at 523 K. As an important consistency check, we inserted the concentration dependent diffusion, illustrated in figure 3, into a finite element calculation using Fick’s equation. This calculation in turn yielded concentration profiles that agrees with the ones seen in figure 2,

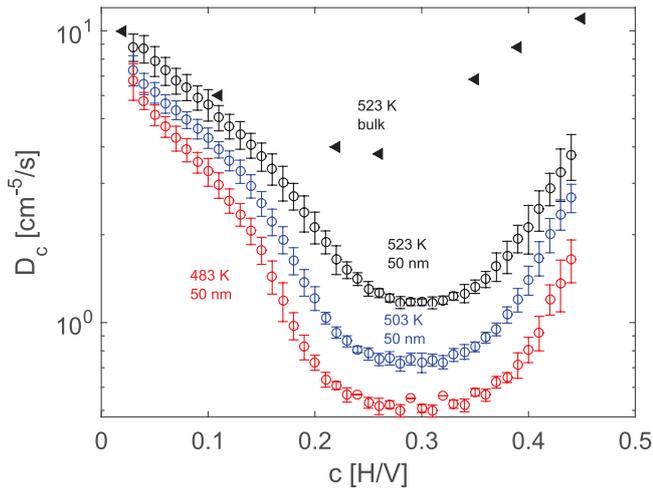


Figure 3. Concentration dependence of chemical diffusion coefficient. The circles are from analysis of the current results, the error is the standard deviation of the averaging. The black triangles represent the concentration dependence of the chemical diffusion of hydrogen in bulk vanadium determined by Gorsky measurement [15].

supporting the robustness of the determination of the relation between D_c and the observed concentration profiles.

As can be seen in figure 3, the chemical diffusion coefficient decreases with concentration at low concentrations, levels out at around 0.3 H V^{-1} and then increases as concentration increases in the 50 nm thin film. A similar trend is also found in bulk vanadium hydride obtained with the Gorsky method [15], however we already note here that there are significant differences in the absolute values for the film as compared to the bulk data.

3.2. Analysis and corrections

Chemical diffusion is driven by a gradient in the chemical potential with concentration (a *nonlocal* equilibrium property). Therefore, the chemical potential is routinely used to extract the underlying tracer diffusion constant, D_t , from the chemical diffusion constant (D_c) obtained in the present experiments. Another effect that influences the diffusion coefficient is the correlation between the hydrogen motions, usually captured by Haven's ratio $H_R(c)$, see figure 4, which is the ratio of the tracer correlation coefficient and the mobility correlation coefficient [16]. The tracer diffusion constant may be obtained through:

$$D_t(c, T) = \frac{H_R(c)}{f_{\text{therm}}(c, T)} D_c(c, T) \quad (9)$$

wherein the thermodynamic factor is given by:

$$f_{\text{therm}} = \frac{c}{kT} \frac{\partial \mu}{\partial c}. \quad (10)$$

As can be seen from these expressions, the thermodynamic factor is temperature dependent and might, if not properly accounted for, influence the Arrhenius analysis, e.g. by changing the pre-factor.

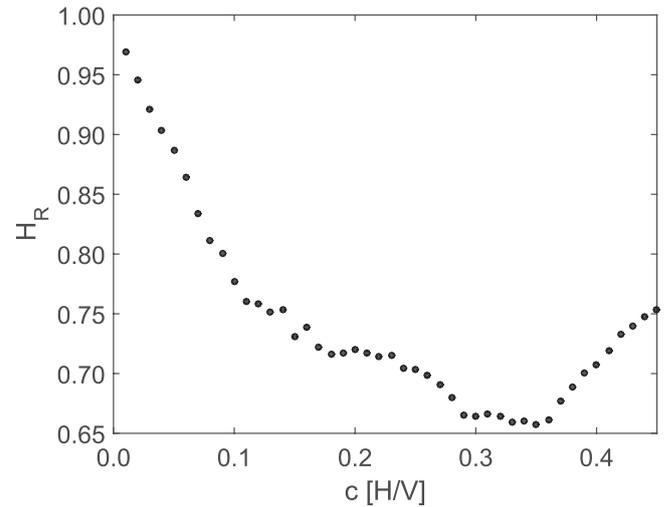


Figure 4. The Haven's ratio extracted from diffusion and mobility coefficients measured by Kleiner *et al* [4].

The dependence of the thermodynamic factor on the derivative of the chemical potential implies that it goes to zero at a second order phase transition with the result of a critical slowing down of the chemical diffusion. Spectacular manifestations of this have been seen in the case of NbH_c where the critical slowing down is even known to be sample shape dependent [17]. This is due to the presence of macroscopic density modes that depend sensitively on the shape of the sample, each with its own distinct critical temperature and cause the thermodynamic factor to go to zero.

The incoherent spinodal in bulk vanadium hydride has its maximum at $\sim 300 \text{ K}$ at $c = 0.25 \text{ H V}^{-1}$, which gives an indication for the critical temperature where critical slowing down would occur in the present thin film vanadium hydride. As this is 170 K below the lowest temperature used in the experiments, eventual effects of any macroscopic density modes are therefore ignored in the analysis. Therefore we use the thermodynamic factor in equation (10) as measured separately with the same optical technique in a solubility experiment on a companion sample without the dissociation barrier (Al_2O_3). At the very least we use a thermodynamic factor that corresponds to the same sample shape as used in the diffusion measurements. Selected solubility isotherms are shown in figure 5 and the corresponding thermodynamic factor is plotted in the inset.

The tracer diffusion coefficient obtained for $T = 483 \text{ K}$, using the approach described above, is illustrated in figure 6. Good agreement is obtained at low concentrations between the literature value of the bulk diffusion constant and the results obtained from the thin film. Furthermore, a strong reduction is obtained in the self-diffusion with increasing concentrations, reflecting the changes already seen in the obtained chemical diffusion coefficient of figure 3.

3.3. Concentration dependence of the activation energy

To obtain a better understanding of the contribution to the rapid decrease of the diffusion coefficient with concentration, we performed Arrhenius analysis of the results using,

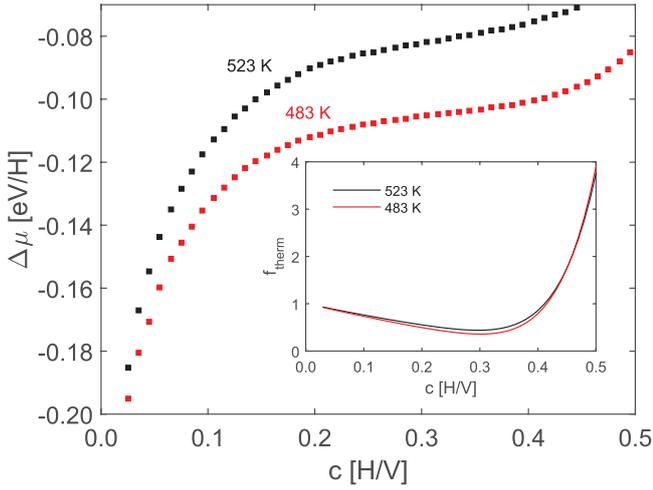


Figure 5. Hydrogen chemical potential obtained from solubility experiments on a companion sample without an oxide capping is shown at 483 K and 523 K. The inset to the figure shows the thermodynamic factor at the two temperatures.

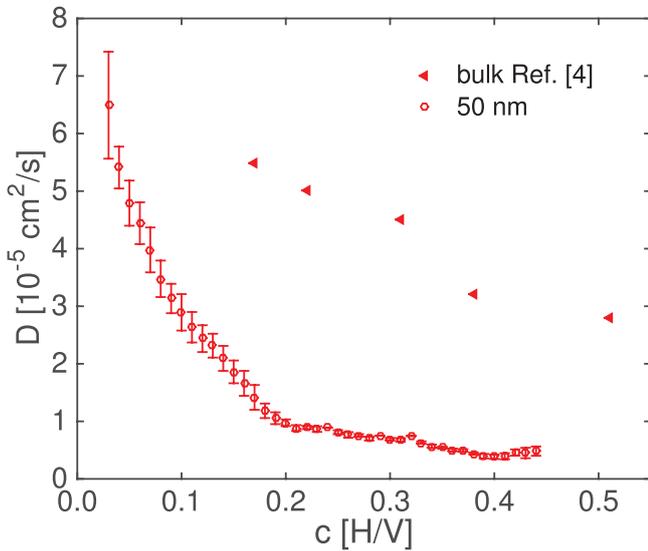


Figure 6. Hydrogen self-diffusion in a thin film (current results) and bulk vanadium [4] at 483 K.

$$D_s = D_0 e^{-\frac{E_a}{k_B T}}, \quad (11)$$

where D_0 is the pre-factor, often viewed as a measure of the attempted jump rate of the interstitial H. There is a concentration dependence to the correlation factor (thermodynamic factor and Haven's ratio) in equation (9). We can get an idea about the contribution from this factor by considering the ratio between the chemical diffusion coefficient and the tracer coefficient in bulk vanadium hydride as described by Kleiner (the influence of coherency stresses were not considered in these analysis). Figure 4 shows the experimentally determined concentration dependence of Haven's ratio for a vanadium hydride (from Kleiner's data). There is no temperature dependence involved in this correlation as long as one remains within a single phase. Representative analysis of the temperature dependence of the diffusion at three concentrations are

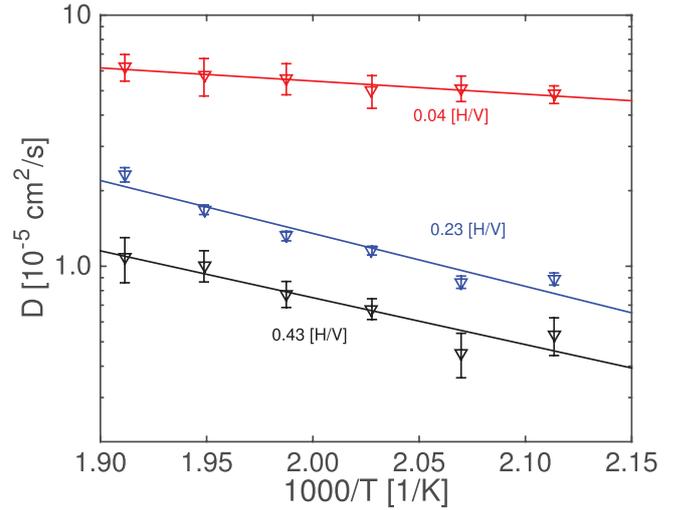


Figure 7. Temperature dependence of hydrogen diffusion coefficient D for three concentrations (α and α' phases). The straight line shows the fits to the experiment result with Arrhenius equation $D = D_0 \exp(-\frac{E_a}{k_B T})$. The lowest temperature is close to the phase boundary in bulk V (473 K).

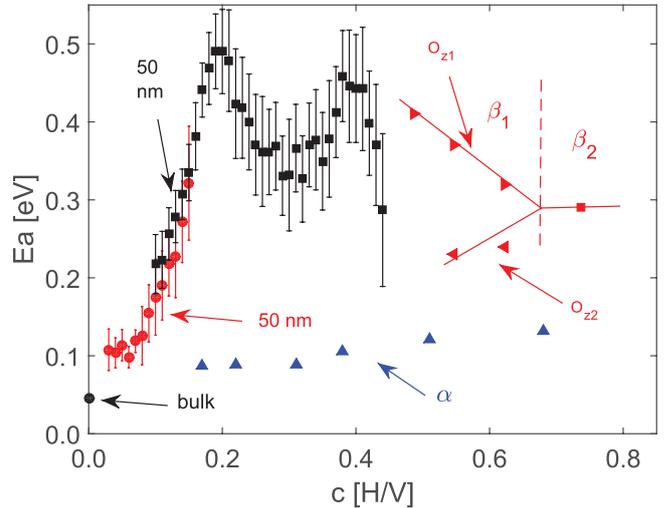


Figure 8. Concentration dependence of hydrogen activation energy E_a in vanadium thin film (current results, red circles for results extracted from the Boltzmann method and black squares for direct integration) and bulk (literature). The activation energies marked by red triangles and square are from O_{z1} and O_{z2} sites in β_1 and β_2 phase [18] and the activation energies marked with blue triangles are obtained in the bulk α phase [4]. The activation energy for bulk at the lowest concentrations is 0.045 eV, as shown with black solid circle [19].

illustrated in figure 7. Arrhenius analyses are found to capture the concentration dependence in an adequate way, as judged from the linearisation of the displayed data. However, the changes in the obtained D_0 is large (almost four orders of magnitude).

The deduced change of the activation energy E_a with hydrogen concentration is illustrated in figure 8. The activation energy is obtained with the two different types of analyses described above (Boltzmann and modified Boltzmann), which are applicable at low and moderate/high hydrogen

concentration regimes, respectively. The results of both methods overlap around $0.1\text{--}0.2\text{ H V}^{-1}$ which confirms the consistency of the methods. At the lowest concentrations we obtain an activation energy that is close to the activation energy found in bulk V. The blue triangles mark the results of the tracer diffusion experiments by Kleiner (using NMR) and show the increase in the activation energy with concentration, up to about 0.12 eV at 0.67 H V^{-1} . We observe much larger changes in the deduced activation energy with concentration than seen by Kleiner, in that the activation energy goes from 0.1 eV to almost 0.5 eV in a relatively narrow concentration range. This difference highlights the profound impact of boundary effects on the obtained diffusion rate, as discussed in next session.

3.4. Discussion

Clamped epitaxial layers have previously been shown to display profound differences in thermodynamic properties, as compared to bulk [20, 21]. The binding energy of hydrogen is less negative and H–H interaction becomes repulsive at relatively low concentrations, when vanadium is under biaxial compressive strain [22, 23]. When the absorbing layer is clamped by a MgO substrate, the expansion is restricted to the direction perpendicular to the layers. With increasing hydrogen concentration, the expansion of the layers will consequently alter the tetragonality of the structure. This results in changes in the thermodynamic properties [23] as well as changes in the site occupancy of hydrogen [9]. Further insight in the involved processes is provided by DFT studies [24] which confirm a shift from tetrahedral to octahedral site occupancy at around $c = 0.1\text{ H V}^{-1}$ in a bi-axially clamped structure. This appears to agree with a transition, from low to high activation energy which is seen in figure 8. Furthermore, *ab initio* molecular dynamics studies demonstrated a five times larger activation energy when hydrogen is diffusing between octahedral sites as compared to jumps between tetrahedral sites [25]. Thus, the increase in activation energy is consistent with a change of site occupancy, from tetrahedral to octahedral, in the concentration range 0.1 to 0.2 H V^{-1} . The observed increase in activation energy is therefore concluded to be caused by the uniaxial expansion of the vanadium layer with concentration and the resulting change from tetrahedral to octahedral sites.

To further validate this point, we have compared the expansion measurements from Bloch with the current concentration measurements and find that there is a change in slope in the expansion versus concentration around $c = 0.15\text{ H V}^{-1}$ and another change at $c = 0.4\text{ H V}^{-1}$. Thus a correlation between changes in the expansion coefficient and changes in activation energy are observed, supporting the conclusion given above. Still the hydrogen induced static displacement fields makes x-ray diffraction measurements questionable for accurate determination of expansion coefficients [26]. Thus, an independent verification, e.g. using neutron reflectivity is needed to confirm the relation between the changes in expansion coefficient and the observed changes in the activation energy.

For sake of completeness we also mention three alternative, but unlikely, interpretations of the results. The first

alternative is the crossing of a phase boundary. All measurements were performed above 470 K , which is above any phase boundary in this concentration range according to the work of Bloch [20, 21] and Prinz [10]. The second possibility is critical slowing down, due to the presence of a coherent or incoherent spinodal, where the thermodynamic factor approaches zero. We determined the thermodynamic factor and it does not go to zero in the measured concentration and temperature range. In addition we know from Bauer [27] that the incoherent boundary of the bulk has a maximum of about $\sim 300\text{ K}$ at $c = 0.25$. Therefore, any effect due to critical slowing down can be excluded. The third possibility is that macroscopic density modes are excited in the film and influence the diffusion in a nontrivial way due to the imposed clamping and the non-uniform concentration in the sample. The interaction energy eigenvalues and eigenmodes of a bi-axially clamped film are not known at present so it is difficult to estimate its influence on the diffusion. However, the effects are expected to be small in the actual temperature range.

As noted in the analysis above, D_0 exhibits large changes with concentration, as previously noticed in analysis of diffusion of hydrogen [15]. The consequences of these observations casts a shadow on the interpretation of the pre-factor as a well defined physical property such as attempted jump rate of the hydrogen. At the same time, it opens up questions concerning the validity of the analysis, such as performed here, when calculating self diffusion from obtained chemical diffusion of light interstitials. Hence, it is fair to say that our understanding of diffusion of hydrogen in vanadium is not sufficient. Quantum effects might play a role in this context, while it is not clear in which way and how these effects should be implemented to obtain more self-consistent view on the diffusion process.

4. Conclusions

The chemical diffusion of hydrogen is found to be profoundly slower in clamped V(001) single crystal films, as compared to bulk, at concentrations above 0.1 H V^{-1} . The inferred five fold increase in the activation energy of diffusion is concluded to be associated to a change of site occupancy: from tetrahedral to octahedral sites. The results clearly demonstrate the importance of strain on hydrogen mobility in V, in which the site occupancy of hydrogen can be affected by a tetragonal distortion. The observed changes are captured by a classical description of diffusion involving the effect of the local strain field on the mobility. Large changes in the pre-factor describing the diffusion process is noticed (D_0). These changes are not currently understood which calls for both theoretical and experimental efforts and might require the inclusion of quantum effects in the description of diffusion at elevated temperatures. We further conclude that the described approach, which allows a simultaneous determination of the diffusion coefficients for a range of concentrations in a single experiment, is highly promising as a route towards obtaining better understanding of hydrogen in metals.

Acknowledgments

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