

Determining drivers of chemical diffusion of hydrogen in the thin transition metallic glass $V_{80}Zr_{20}$

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We demonstrate the feasibility of using optical transmission to determine concentration-dependent hydrogen diffusion coefficients and activation energies of thin metallic glass films over a wide range of temperatures and concentrations. The hydrogen concentration's temporal and spatial profiles are simultaneously extracted without requiring a metal-insulator transition or hydride formation. Different contributions to chemical hydrogen diffusion are quantified and compared. The concentration dependence of the activation energy is in stark contrast to the activation energy found in epitaxial vanadium films of similar thickness. The chemical diffusion is found to increase with hydrogen concentration in the glass, whereas it decreases in the crystalline case driven by differences in the activation energy at concentrations below 0.3 H/M and the thermodynamic factor at concentrations above that. This technique provides detailed insight into the concentration dependence of hydrogen diffusion and constrains theories treating the correlated motion of hydrogen and short-range hydrogen-hydrogen interaction. The method can be applied to other materials that show an optical response to hydrogen uptake.

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I. INTRODUCTION

Hydrogen interactions with metals are intriguing from both a fundamental [1–3] and an applied point of view, such as for hydrogen storage and material durability [4]. Specifically, hydrogen diffusion in disordered metals exhibits experimental anomalies such as non-Arrhenian diffusion [5,6]. Kirchheim, Richards, and others have developed theoretical models for describing the motion of hydrogen in metallic glasses [7–9]; however, many aspects of the mechanisms that drive it are still unknown, such as the influence of the coupling to a thermal bath [10], the dynamics of self-trapping, the appropriateness of the description of hydrogen as a small polaron quasiparticle [11,12], and what drives the non-Arrhenius-like temperature dependence of the diffusion coefficient D . Furthermore, the potential roles of topological disorder, mobility correlation, short-range hydrogen-hydrogen interaction and its effects on blocking and site availability, and the fractal character of the network of diffusive paths remain poorly understood. This is partly due to the difficulty of accurately modeling the influence of the amorphous host structure and partly due to a lack of experimental data required to test the different models. To validate candidate models, it is highly desirable to have consistent data over a wide range of both concentrations and temperatures for both the diffusion coefficient and the activation energy.

The diffusion of the absorbed hydrogen has generally been described with over-barrier hopping between local interstitial sites [12,13]. However, the motion of hydrogen in metals exhibits a plethora of other interesting phenomena, ranging from quantum tunneling and Kondo physics to critical slowing down [13,14]. A strain field emerges during the dynamic self-trapping process, which together with the charge, can be viewed as a small polaron [7,9], a quasiparticle with peculiar properties. *Ab initio* molecular dynamics calculations have even shown that hydrogen can decouple from its strain field, bringing about a new range of diffusive behavior [12].

Thin films offer an interesting playground to investigate metallic glasses due to the high achievable quenching rates during their growth, making it possible to grow films with a high degree of uniformity while avoiding inclusions, voids, and other defects [15]. They allow well-controlled composition, surface termination [16,17], and material interfaces [18]. Furthermore, metallic glasses can be realized with compositions not accessible with bulk methods [19], offering access to unexplored territory. These metastable phases can occur in regions forbidden in the corresponding crystalline phase diagram [19]. However, measuring the diffusion coefficient in thin films is currently not possible using standard techniques such as the Gorsky effect, nuclear magnetic resonance, and quasielastic neutron scattering due to the low sample volume.

In 2012, a method was demonstrated that allows us to determine hydrogen diffusion in crystalline vanadium films optically by relying on the linear dependence between optical transmission and hydrogen concentration [20]. A great advantage is that the temporal and spatial profiles are obtained simultaneously, thereby providing more accurate diffusion coefficients. This enabled a number of studies using the technique to look at diffusion in artificially made structures such as superlattices [20–23]. This method, furthermore, circumvents the need for using indicator layers [24,25], which provide

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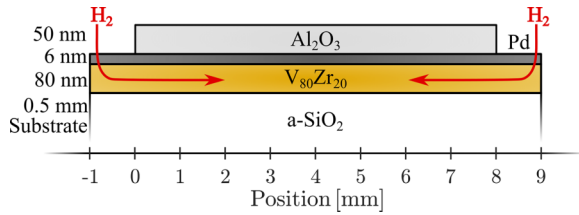


FIG. 1. The film consists of 80 nm of $V_{0.8}Zr_{0.2}$, grown under UHV conditions onto $10 \times 10 \times 0.5 \text{ mm}^3$ $a\text{-SiO}_2$ glass using magnetron sputtering. The sample is covered by 6 nm of palladium and 50 nm of Al_2O_3 , enabling hydrogen uptake only through two opposite stripes of exposed palladium.

indirect measurements of hydrogen concentration. Another advantage of the technique is that the concentration dependence over a wide range can be determined from a single measurement, making it unnecessary to use many different samples with different hydrogen concentrations.

The band structure of a metallic glass is not a well-defined concept, and interband transitions that drive optical absorption are thus present in a wider energy range [23]. Therefore, whether the method can be applied to disordered materials needs to be shown. In the following, we demonstrate the feasibility of using this contactless, nondestructive, and indicator-free method to determine diffusion coefficients as a function of concentration and temperature to study the diffusion of hydrogen in metallic glasses.

II. METHODS

A. Sample design and growth

The samples were produced using DC and AC magnetron sputtering. The design is shown in Fig. 1. Each sample consisted of 80 nm of $V_{0.8}Zr_{0.2}$ grown onto a $10 \times 10 \times 0.5 \text{ mm}^3$ double-side polished $a\text{-SiO}_2$ substrate. The film was covered with 6 nm of palladium, and the center $8 \times 10 \text{ mm}^2$ were subsequently covered using a mask to allow a 50 nm thick Al_2O_3 layer to be grown. Vanadium, zirconium, and Al_2O_3 were grown in a chamber having a base pressure of 1.5×10^{-10} mbar and argon pressure of 3.33×10^{-3} mbar during sputtering, whereas the palladium layer was grown in an adjacent chamber with a base pressure of 5×10^{-8} mbar and argon pressure of 6.66×10^{-3} mbar. The power-dependent growth rate was calibrated for each target to determine the required sputtering times and power ratios for the combinatorial sputtering process. The sample thicknesses were determined using x-ray reflectometry and extracted by fitting a slab model to the reflectivity data using GENX [26,27]. The substrates were baked for 50 min at 350°C to reduce possible deposits of water and organic contaminants. During growth, the temperature was decreased to 27°C to ensure maximally amorphous sample growth [28,29]. Further details regarding the growth process can be found in the Supplemental Material [30]. Sample composition and thickness for the V-Zr system were verified previously using x-ray reflectometry, x-ray diffraction, and Rutherford backscattering [19,23], verifying the growth procedure to achieve high-quality, x-ray amorphous samples. The palladium layer protects the under-

TABLE I. Applied hydrogen pressure at each temperature.

Temperature (K)	Loading pressure (mbar)
323	2.47
348	7.31
373	20.6
398	58.7
423	169
448	488

lying $V_{0.8}Zr_{0.2}$ from oxidation and catalyzes the hydrogen dissociation without taking up hydrogen in the pressure and temperature ranges applied [31]. Al_2O_3 is inert toward reactions with hydrogen [16] and therefore acts as a barrier, allowing hydrogen uptake into the sample only through the free surface of the catalytic palladium layer. The sample design facilitates diffusion of hydrogen only toward the center of the sample, as shown in Fig. 1, which is important for determining the diffusion coefficients. A total of six identical samples were grown in two separate growth sessions. Each sample was subjected to a hydrogen atmosphere and temperature corresponding to a nominal maximum hydrogen concentration of 0.7 H/M. This was to ensure that the hydrogen diffusion was measured corresponding to a well-defined as-grown configuration of the metal atoms, as the influence of hydrogen cycling is not yet known in $V_{0.8}Zr_{0.2}$ metallic glass thin films. This choice is not necessary to successfully use the method.

B. Measurement technique

The optical technique used to determine the hydrogen diffusion in crystalline samples is explained in detail in [20,22]. Briefly, the samples are placed in a vacuum chamber with two windows: one above and one below the sample. The sample needs to be thin enough to allow for appreciable light transmission but thick enough to show a measurable signal when absorbing hydrogen. A monochromatic, incoherent light-emitting diode is used to minimize interference from the front and back sides of the windows. The sample is exposed to a temperature through external heating of the chamber and a hydrogen atmosphere of pressure p . The atomic and electronic structures of the sample change when hydrogen is absorbed [23], which can cause a change in optical transmission. The changes in transmission are registered through a lens-camera system whose focal point lies in the film plane. In the present experiments, a red diode with wavelength $\lambda = 625 \text{ nm}$ was used. Images were recorded every 30 to 60 s. The hydrogen evolution was tracked over a distance of 2.5 to 3 mm from one edge of the palladium/ Al_2O_3 interface. The applied hydrogen pressure at each temperature is shown in Table I. These pressures were selected to give approximately the same final concentration as that determined from [23,32]. The base pressure of the vacuum chamber was at 1×10^{-8} mbar, with the residual gas dominated by hydrogen. The hydrogen was supplied by a gas bottle of 6N purity that was subsequently passed through a Nupure purifier, bringing the hydrogen purity to the parts per billion level.

Spatial and temporal transmission profiles were obtained from the images by selecting, for each temperature, a rectangular region covering the relevant parts of the sample surface. The transmission values within this region were averaged at each lateral position x , as explained in Sec. II. These transmission profiles were subsequently converted into hydrogen concentration profiles $c(x, t)$ using the calibration curve from Ref. [23].

C. Theoretical background

The hydrogen diffusion inside the samples can be seen as a one-dimensional process due to the symmetry of the sample. Hydrogen flows through a unit cross section per unit time in the presence of a one-dimensional spatial gradient in the chemical potential as described by Fick's first law:

$$j(x, t) = -M(c)\Omega c(x, t) \frac{d\mu}{dx}, \quad (1)$$

where j is the flux of hydrogen atoms per $\text{cm}^2 \text{ s}$ ($\frac{\text{H}}{\text{cm}^2 \text{ s}}$), x is the spatial coordinate with origin taken at the palladium edge, μ is the chemical potential, c is the hydrogen concentration in hydrogen per metal atoms (H/M), $M(c)$ is the concentration-dependent mobility, and Ω is the number of metal atoms per unit volume. Fick's law can be rewritten in terms of a spatial concentration gradient in the more commonly used form of Eq. (3):

$$j(x, t) = -M(c)\Omega c(x, t) \frac{d\mu(x, t)}{dc} \frac{dc}{dx} \quad (2)$$

$$= -D_c(c)\Omega \frac{dc}{dx}. \quad (3)$$

In this way, the chemical diffusion coefficient is defined as the proportionality constant between the particle flux $j(x, t)$ and the spatial concentration gradient $\frac{dc}{dx}$:

$$D_c(c) = M(c)c(x, t) \frac{d\mu(x, t)}{dc}. \quad (4)$$

The intrinsic mobility M (in contrast to mobility in the presence of a temperature or strain gradient) is determined through the Nernst-Einstein relation [Eq. (9) in Ref. [9]] as

$$M(c) = f_M \frac{l^2}{6\tau k_B T}, \quad (5)$$

where f_M is the mobility correlation factor, which is discussed in detail below, l is the average jump distance, τ is the mean residence time, k_B is the Boltzmann constant, and T is the absolute temperature. The mobility is the net drift velocity down a chemical potential gradient per unit of potential gradient [9]. By inserting Eq. (5) into Eq. (4), one obtains the following:

$$D_c(c) = f_M \frac{l^2}{6\tau} \left[\frac{c}{k_B T} \frac{d\mu}{dc} \right] \quad (6)$$

$$= f_M \frac{l^2}{6\tau} f_{\text{therm}}, \quad (7)$$

where f_{therm} is the thermodynamic factor, defined through the square brackets in Eq. (6). The thermodynamic factor quantifies the influence of how the chemical potential changes by adding a hydrogen atom to the metal on the diffusion and is an equilibrium property that can be determined from, for

example, solubility isotherms. Finally, the mean residence time of hydrogen on a local site τ is related to the mean time between attempted jumps τ_0 , both of which are activated processes described by an Arrhenius equation. τ_0 specifically is given by

$$\tau_0(c, T)^{-1} = \tau_0^{-1} \exp \left\{ \frac{-E_{\text{act}}}{k_B T} \right\}, \quad (8)$$

$$\tau_0(c, T) = \tau(c, T)V(c), \quad (9)$$

where V is the site-availability factor [9], which is discussed further later. The final expression for the chemical diffusion can thus be written as

$$D_c = f_{\text{therm}} f_M V \frac{l^2}{6} \tau_0^{-1} \quad (10)$$

$$= f_{\text{therm}} f_M V \frac{l^2}{6} \tau_0^{-1} \exp \left\{ \frac{-E_{\text{act}}}{k_B T} \right\}, \quad (11)$$

where $E_{\text{act}}(c)$ is the concentration-dependent activation energy. We can label $\frac{l^2}{6\tau_0}$ as D_{00} and thus obtain

$$D_c = f_{\text{therm}} f_M V(c) D_{00} \exp \left\{ \frac{-E_{\text{act}}}{k_B T} \right\}, \quad (12)$$

and we can define

$$D_0 = D_{00} \exp \left\{ \frac{-E_{\text{act}}}{k_B T} \right\} \quad (13)$$

as the intrinsic diffusion coefficient, which is the microscopic diffusion unencumbered by correlation and site availability. Techniques like NMR and neutron scattering can be used to measure the intrinsic diffusion coefficient to a factor of the tracer correlation factor f_t and the site-availability factor. This is also called the tracer diffusion coefficient:

$$D_t = f_t V D_0.$$

If the thermodynamic factor increases with concentration, it provides a boost to the chemical diffusion, although it does not affect the microscopic jumps in equilibrium. In crystalline vanadium, this quantity decreases at low concentrations, causing the diffusion to slow down before increasing again on the other side of the isotherm plateau. In fact, near a critical point in crystalline materials $\frac{d\mu}{dc}$ is close to zero, and critical slowing down sets in, which is captured by the thermodynamic factor. The site-availability factor $V(c)$, describes the fact that for every attempted jump, there is a chance that the approached site is already occupied by another hydrogen. $V(c)$ is defined as the ratio of available to occupied sites around each hydrogen interstitial. Therefore, the lower the local hydrogen concentration is, the higher the site-availability factor will be. The mobility correlation factor $f_M(c)$ describes the change in the probability of hydrogen making a correlated backward jump in the presence of a chemical potential gradient. With hydrogen moving away from an area of increased concentration, there is a higher likelihood of sites being available in front of the hydrogen while sites behind it are more likely to be occupied.

The hydrogen mobility, describing the motion under the influence of the chemical potential gradient, is determined

based on Eqs. (4), (6), and (12):

$$M(c, T) = \frac{D_c}{c \frac{\partial \mu}{\partial c}} = \frac{D_c(c, T)}{f_{\text{therm}}(c, T) k_B T} \quad (14)$$

$$= f_M V(c) D_{00} \exp\left\{\frac{-E_{\text{act}}}{k_B T}\right\} (k_B T)^{-1}, \quad (15)$$

using $f_{\text{therm}}(c, T)$ from Eq. (6) and $D_c(c, T)$ from Eq. (12). The mobility is therefore determined by an interplay of the underlying correlation factors and site availability $f_M V(c) D_{00}$ and the activation energy term $\exp\{\frac{-E_{\text{act}}}{k_B T}\}$, multiplied by the inverse of the Boltzmann constant and the temperature $k_B T$.

If the concentration profile is known for a given temperature T and time t from experiment, the concentration and temperature-dependent chemical diffusion coefficient $D_c(c, T)$ can be extracted using Fick's second law of diffusion [33,34]:

$$\frac{\partial c(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D_c(c, T) \frac{\partial c(x, t)}{\partial x} \right). \quad (16)$$

Equation (16) can be solved using the Stenlund method [35], which yields

$$D_c(c, T) = \frac{-\int_x^\infty \frac{\partial c(x_1, t)}{\partial t} dx_1}{\frac{\partial c(x, t)}{\partial x}}. \quad (17)$$

It is assumed that the following boundary condition is true:

$$\lim_{x \rightarrow \infty} \frac{\partial c(x, t)}{\partial x} = 0. \quad (18)$$

The derivatives $\frac{\partial c(x, t)}{\partial x}$ and $\frac{\partial c(x, t)}{\partial t}$ as well as the integral $\int_x^\infty \frac{\partial c(x_1, t)}{\partial t} dx_1$ can be determined numerically from the experimental concentration profiles $c(x, t)$. The temperature dependence of the diffusion coefficient $D_c(c, T)$ can be evaluated by repeating the concentration-dependent diffusion measurements at multiple temperatures. Based on the sample geometry, the farthest distance hydrogen can travel in the sample before interfering with the hydrogen gradient coming in from the other side is 4 mm. The boundary condition in Eq. (18) therefore becomes

$$\left(\frac{\partial c(x, t)}{\partial x} \right)_{x=4 \text{ mm}} = 0. \quad (19)$$

This condition places a limit on the maximum time of each measurement.

By combining the experimentally determined chemical diffusion coefficient from Eq. (17) with Eq. (12), one can analyze the individual contributions to the chemical diffusion and identify whether any of the underlying contributions is the dominant driver of changes in the coefficient as well as how their individual behaviors combine to determine the outcome of the measurement.

Error bars for $D_c(c, T)$ are determined at each temperature and concentration as described in [22]. Each diffusion coefficient reported in this paper is the average of 50 to 300 diffusion coefficients determined at that concentration and temperature throughout the measurement time. The error bars provided are the standard deviation of this average. The error bars of the activation energy E_{act} were the error of the least-mean-square fit to the diffusion coefficients, weighted with their respective errors. The spatially dependent transmission

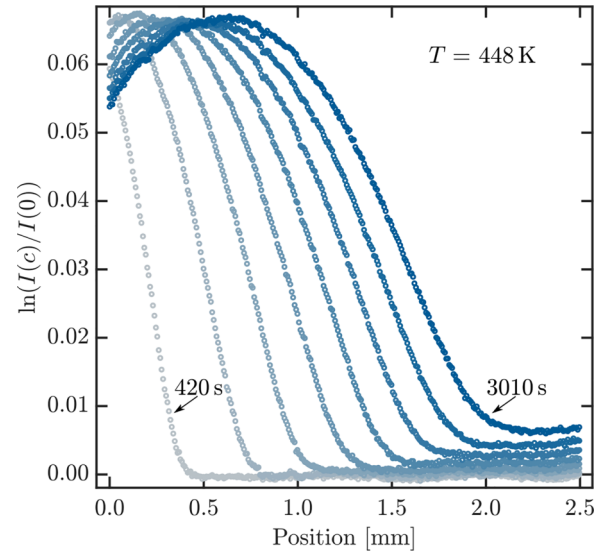


FIG. 2. Transmission profiles of a $V_{0.8}Zr_{0.2}$ metallic glass thin film at 448 K. A position of 0 mm refers to the edge of the Al_2O_3 layer (see Fig. 1). More than 50 individual profiles were evaluated over 3010 s. The profiles depicted here are a selection and show the spatial changes in optical transmission every 370 s. As the sample is constantly exposed to hydrogen gas, the light transmission through the sample changes systematically, tracing the hydrogen absorption into the sample.

data were smoothed using a 15 point, 2nd-order Savitzky-Golay filter before proceeding with the analysis.

III. RESULTS

A representative x-ray reflectivity pattern of the samples, together with a slab fit obtained using GENX, is shown in Fig. S4 in the Supplemental Material [30]. The corresponding fitting parameters are shown in Table S1.

A. Transmission and concentration profiles

Figure 2 shows a representative selection of hydrogen-induced changes in the transmission profiles measured at 448 K. Similar results are obtained at other temperatures, as discussed in Sec. IV. The color intensity of the data points indicates the passage of time. The transmitted intensity initially increases before it decreases again as the profiles evolve. This behavior stems from the parabolic dependence of the ratio of the transmitted intensities with and without hydrogen [23] and the evolution of hydrogen concentration inside the sample. The parabolic dependence was found and evaluated before and can therefore be used to determine the underlying concentration profiles. The procedure is susceptible to the accuracy and precision of the concentration-dependent calibration and measurement of the optical transmission through the sample but is conceptually straightforward.

Figure 3 shows the concentration profiles obtained from the optical transmission. The smooth, monotonic nature of the profiles indicates a successful conversion to concentration. The profiles are similar to textbook concentration profiles derived from a linearly increasing diffusion coefficient as seen in [36].

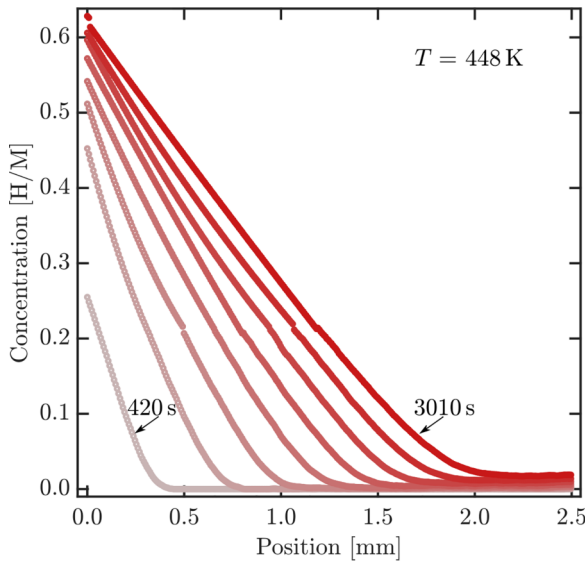


FIG. 3. Concentration profiles $c(x, t)$ in a $V_{0.8}Zr_{0.2}$ metallic glass thin film. The spatial distribution of hydrogen is depicted every 370 s, shown from left to right in the plot. The concentration profiles were obtained from the optical transmission profiles.

B. Diffusion coefficients and activation energy

The concentration and temperature-dependent diffusion coefficient $D_c(c, T)$, obtained from numerical integration of the concentration profiles using Eq. (17), is shown in Fig. 4. The chemical diffusion coefficient generally increases with concentration at all measured temperatures.

Figure 5 shows the Arrhenius plots of the diffusion coefficients of $V_{0.8}Zr_{0.2}H_x$ at concentrations of $\{0.10, 0.15, 0.25, 0.50\}$ H/M. The thermodynamic factor has a temperature dependence that needs to be accounted for prior

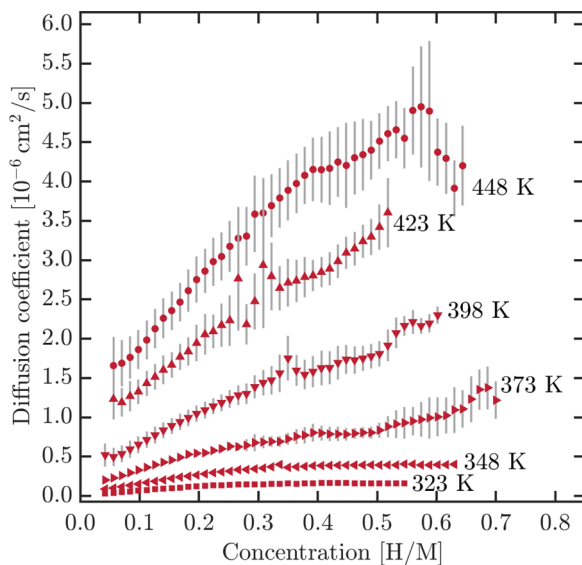


FIG. 4. Concentration-dependent diffusion coefficients at different temperatures. The diffusion coefficients were derived from the time-dependent concentration profiles $c(x, t)$ at each individual temperature using Eq. (17).

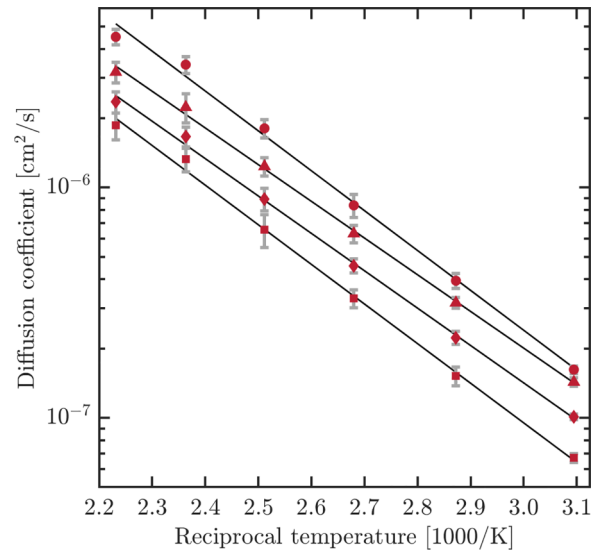


FIG. 5. Arrhenius plots of $V_{0.8}Zr_{0.2}$ for concentrations of $\{0.10, 0.15, 0.25, 0.50\}$ H/M, from bottom to top. Good agreement is found between the linear fits of the Arrhenius model (solid black lines) and the extracted diffusion coefficients (red symbols).

to an Arrhenius analysis. For that purpose, it was extracted from the isotherms at several different temperatures (see Fig. S1 [30]) and was found to be weakly temperature dependent. It therefore did not significantly influence the concentration dependence of the activation energy. The linear behavior of the data in Fig. 5 further supports this argument. We find no evidence of anomalous non-Arrhenius behavior over the studied temperature and concentration range, in contrast to measurements of metallic glasses of $TiCuH_{1.41}$ and Zr_2PdH_x [5,37–39]. Since a change in the diffusion mechanism is expected to correspond to a change in slope in the Arrhenius plot, we conclude that a change in the diffusion mechanism underlying the hydrogen diffusion in $V_{0.8}Zr_{0.2}H_x$ is unlikely in this temperature and concentration range. Studies of Arrhenius behavior in other metals have been done over temperature ranges as large as 500 K, so it is likely that temperature ranges larger than those presented here would be needed to detect such deviations.

The activation energy $E_{act}(c)$ as obtained from the Arrhenius analysis is shown in Fig. 6 as open red circles. Also shown are the concentration dependence of the activation energy of hydrogen in epitaxial vanadium films (open black triangles) [22] and α - and β -phase polycrystalline bulk vanadium hydride determined by nuclear magnetic resonance (solid black shapes) [40,41]. The activation energy in $V_{0.8}Zr_{0.2}H_x$ decreases from (0.44 ± 0.03) eV at $c = 0.06$ H/M to (0.33 ± 0.01) eV at $c = 0.2$ H/M and reaches a shallow minimum at (0.31 ± 0.01) eV near $c = 0.4$ H/M. It is a factor of 3 higher than for hydrogen in the α phase of bulk vanadium and of the same order of magnitude as found in the β phases of vanadium hydride. In epitaxial vanadium, on the other hand, the activation energy increases from 0.1 eV at concentrations below 0.1 H/M to 0.47 eV at 0.2 H/M, likely due to a change in site owing to the one-dimensional nature of the allowed expansion.

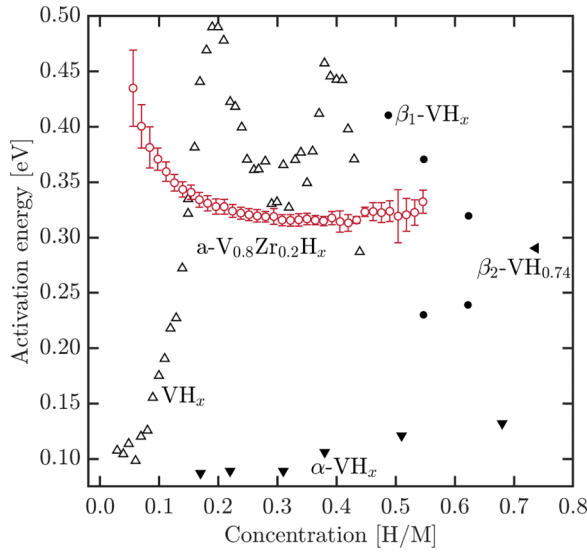


FIG. 6. Activation energy $E_{\text{act}}(c)$ of $V_{0.8}Zr_{0.2}$ (open red circles) at varying concentrations and comparison to activation energies of crystalline vanadium thin films [22] (open black triangles) and bulk vanadium hydride (solid black symbols) [40].

In our experiments, we expose the sample to a chemical potential gradient, which modifies the potential barriers and results in a different quantity obtained than those determined with equilibrium techniques, where the thermodynamic factor and the mobility correlation are absent and the tracer correlation factor is present. Since we have estimated the thermodynamic factor, we can determine the mobility M of hydrogen under the generalized force of the chemical potential gradient using Eq. (14), the results of which are shown in Fig. 7. The mobility exhibits a monotonically decreasing behavior over the concentrations shown. Lower concentrations

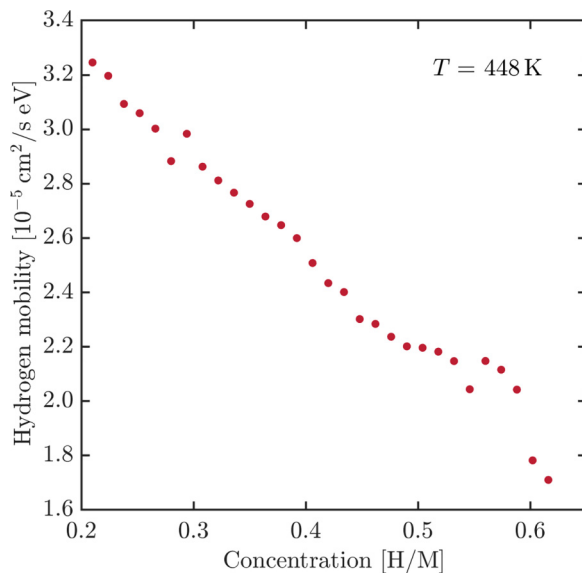


FIG. 7. Hydrogen mobility derived from the chemical diffusion coefficient D_c and the thermodynamic factor f_{therm} as explained in the text.

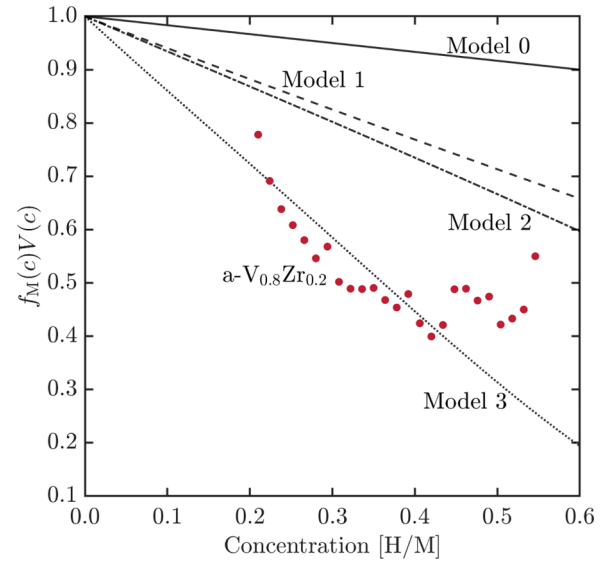


FIG. 8. Product of $f_M(c)V(c)$ for $V_{0.8}Zr_{0.2}$ (red circles, $T = 448 \text{ K}$) and various models derived in [9]. The data were obtained with an estimate of $D_{00} = 7.83 \times 10^{-3} \text{ cm}^2/\text{s}$, as explained in the text. The black lines correspond to polynomial fits for different degrees of interstitial site blocking: On-site blocking (solid line), first- (dashed line), second- (dash-dotted line), and third-nearest-neighbor blocking (dotted line).

are not shown due to the lack of data for the determination of the thermodynamic factor in this range.

To the extent that the experimental uncertainties allow, a first glimpse into the correlated behavior of hydrogen in the metallic glass, under the influence of a chemical potential gradient, can be obtained by dividing the chemical diffusion by the thermodynamic factor and the exponential term. Such a quantity should resemble

$$\frac{D_c}{f_{\text{therm}} \exp \left\{ \frac{-E_{\text{act}}}{k_B T} \right\}} = f_M(c)V(c)D_{00} \quad (20)$$

and is shown in red in Fig. 8. The mobility correlation and site-availability factor were determined using Monte Carlo simulations for hydrogen in bcc metals by Faux and Ross [9] for different models of blocking. It is of interest to compare our results to see whether the short-range repulsive nature of the hydrogen-hydrogen interaction bears any resemblance to the one found in the bcc metals. The comparison with bcc metals is meaningful since the glass is composed of 80% vanadium, which is bcc in its ground state. The estimate for D_{00} was determined ($D_{00} = 7.83 \times 10^{-3} \text{ cm}^2/\text{s}$) by comparing our data to the models [30]. We treat this as the only free parameter in this paper and, with this caveat, can see that the concentration dependence resembles model 3 proposed by Faux and Ross, which corresponds to third-nearest-neighbor blocking. Faux and Ross found that model 2 most resembles the experimental case in the disordered α phase in bcc tantalum. The estimated blocking in amorphous $V_{0.8}Zr_{0.2}$ is therefore stronger than in the crystalline case and seems to stagnate for concentrations between 0.45 and 0.55 H/M. We call for theoretical treatment of the mobility correlation and

site-availability factor for metallic glasses to further assess the veracity of this statement.

IV. DISCUSSION

We evaluated the diffusion of hydrogen in a metallic glass over a very wide range of concentrations compared to many other studies. The increase in the chemical diffusion coefficient with concentration is in stark contrast to the same quantity in bulk vanadium or epitaxial vanadium films. Based on close examination of Eq. (12) and the data provided in Sec. III, however, one can explain the monotonic increase of $D_c(c, T)$ shown in Fig. 4. The product $f_M(c)V(c)$ monotonically decreases over the measured concentration range until it stabilizes around $c = 0.4$ H/M. It therefore cannot drive the monotonic increase in the diffusion coefficient. The activation energy shows a substantial decrease until $c = 0.3$ H/M, which causes an initial increase in chemical diffusion up to that concentration. The monotonic increase at higher concentrations is caused by the remaining quantity. The thermodynamic factor, shown in Fig. S3 [30], increases with hydrogen concentration over the entire measured range. This is in contrast to the thermodynamic factor in crystalline vanadium that goes down monotonically from 0.00 to 0.35 H/M and then increases owing to the large changes in slope of the pressure-composition isotherms, which is generally seen in crystalline materials. The thermodynamic factor therefore increases the diffusion of hydrogen in glasses (in the linear range), whereas it reduces it in crystalline materials. The monotonic increase of the diffusion coefficient in $V_{0.8}Zr_{0.2}H_x$ is therefore driven by an interplay of the activation energy and the thermodynamic factor.

In Refs. [23,42] it was reported that at low concentrations, hydrogen has a greater affinity for zirconium than for vanadium. It is therefore plausible that this affinity might affect the diffusive behavior, especially the initial decrease in activation energy, as strongly bound interstitial sites near the zirconium atoms are increasingly filled up, opening access to more weakly bound states near the vanadium atoms. This could explain why the activation energy decreases rapidly only until the ratio of H/Zr atoms reaches a level near unity, where all sites near the zirconium atoms are filled. In that case, the width of the reduction in activation energy in Fig. 6 should be proportional to the concentration of Zr atoms in the metallic glass alloy. This investigation would be a promising subject for future experiments. The hydrogen mobility decreases monotonically with concentration, despite the initial reduction in activation energy. Following Eq. (15), this can be explained by the decreased availability of sites and/or mobility correlation, indicated by the decrease in $f_M(c)V(c)$, together with a slightly increasing activation energy at higher concentrations.

It has been shown that clamping of thin films (adhesion to the substrate) significantly affects the hydrogen diffusion coefficients in crystalline VH_x [22]. In crystalline vanadium, hydrogen is known to occupy specific interstitial sites within the crystal lattice. Located on either a tetrahedral or an octahedral site, hydrogen expands the atomic lattice around it, leading to local and global lattice deformations and, ultimately, a phase change of the material from a solid solution

to a hydride. In contrast to the bulk case, where the sample can expand freely in all three spatial dimensions, the thin film sample can expand freely only in one dimension: away from the substrate. In crystalline vanadium, this clamping of the sample material effectively limits the number of sites that can freely be occupied by the hydrogen, leading to an overall reduction in diffusion coefficients [22]. In metallic glasses, the sites are distributed more homogeneously throughout the solid. The thin film form is still likely to lead to a reduction in energetically favorable sites as the sample is clamped just like the crystalline one.

From a broader perspective, a low concentration dependence of the activation energy, as exhibited in the range of $c = 0.2$ – 0.52 H/M, could be advantageous for applications regarding the distribution of hydrogen throughout the system. Since hydrogen diffusion is faster as concentration increases, local accumulation of hydrogen within the material is inhibited. These local accumulations result in large local stress fields, which can lead to deformation and, eventually, hydrogen embrittlement. As metallic glasses do not exhibit grain boundaries or hydride phases of different specific volumes, having a uniform diffusion coefficient means consistent delivery of hydrogen in and out of the material. In MgH_2 , for example, the diffusion in the hydride phase is prohibitively slow and is the limiting factor for hydrogen uptake and release. This problem is completely avoided in materials with a flat activation energy profile with hydrogen concentration.

Examined through grazing incidence x-ray diffraction measurements, the samples used in this paper remained x-ray amorphous after the measurements were completed. This is in line with the findings of Bylin *et al.*, who found that samples of the same composition remained x-ray amorphous when loaded with deuterium, even after several loading cycles with concentrations as high as 1 deuterium per metal atom [32]. It is therefore unlikely that the diffusion is influenced by crystallization of the sample. For times beyond those shown in this paper, we can see that there is a slow leakage of hydrogen through the thin lateral edges of the samples perpendicular to the Pd stripes. This could be the origin of the small, gradual rise in the concentration level in Figs. 3 and 2 at 2.1 to 2.5 mm.

V. CONCLUSIONS

The optical transmission method can be used to determine the concentration-dependent diffusion coefficient $D_c(c, T)$ and activation energy $E_{act}(c)$ of metallic glass thin films, as long as they are optically responsive to the absorption of hydrogen. The results shown here are concentration-dependent diffusion measurements of metallic glasses over a range of concentration as large as 0.0 to 0.6 H/M. The diffusion behavior found in thin metallic glass films of $V_{0.8}Zr_{0.2}H_x$ is in stark contrast to that of crystalline VH_x films since in the glass the chemical diffusion coefficient increases monotonically with concentration but initially decreases in the crystalline phase. The difference is attributed to the thermodynamics factor as well as the activation energy behaving radically different in crystalline materials and metallic glasses. The main driver of diffusion in the thin metallic glass film of $V_{0.8}Zr_{0.2}H_x$ is the activation energy at low hydrogen concentrations up to 0.3 H/M and the thermodynamic factor, specifically its

proportionality to the hydrogen concentration at concentrations above. However, more concentration-dependent measurements of diffusion coefficients and activation energies in other metallic glasses are needed to gain further insights into the generality of this trend. The straightforward nature of simple light transmission measurements makes the method an attractive choice for studying hydrogen motion in metallic glasses. By increasing the pressure of the hydrogen atmosphere, the concentration range can be extended up to the maximum concentration possible in the sample. This measurement platform together with the thin film design allows the exploration of the physics of hydrogen in low-dimensional structures, such as changes in elastic boundary conditions, that lead to clamping, uniaxial volume changes, and finite-size effects. This method paves the way for combinatorial screening of H diffusion in metallic glasses, whereby multiple

compositions can be measured simultaneously without the need for moving parts or exchange of samples.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [43].

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