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The mechanism of hydrogen diffusion in zirconium dihydrides

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Abstract. Hydrogen diffusion in ZrH_x ($1.58 \leq x \leq 1.98$) in the temperature range 600 K to 970 K has been measured by means of pulsed-field-gradient nuclear magnetic resonance. The activation enthalpy for hydrogen diffusion, H_a , obtained by fitting an Arrhenius expression $D = D_0 \exp(-H_a/k_B T)$ to the diffusivities, increases sharply as x approaches the limiting value of two in good agreement with results deduced from the proton spin–lattice relaxation rate, Γ_1 , measured on the same samples. Hydrogen atoms jump predominantly between nearest-neighbour tetrahedral sites in ZrH_x . The observed concentration dependence of both the effective value of H_a and the pre-exponential factor D_0 suggests, however, that at high hydrogen concentrations and high temperatures another interstitial site is occupied in addition. At $x \rightarrow 2$ a small fraction of hydrogen atoms located on an interstitial site other than the tetrahedral site appears to contribute significantly to the diffusivity. The temperature and concentration dependence of the diffusion data can quantitatively be described by such a model. The activation enthalpies for all possible jumps in this system with two different kinds of site are shown to be independent of the hydrogen concentration x . The corresponding attempt frequencies $\nu_a \approx 10^{13} \text{ s}^{-1}$ are compatible with the picture of a classical diffusion mechanism.

1. Introduction

The transition metals Ti and Zr absorb large quantities of hydrogen forming the dihydrides TiH_x and ZrH_x with non-stoichiometric hydrogen concentrations between $x \approx 1.5$ and $x = 2.0$. It is well known that the hydrogen atoms occupy tetrahedral interstitial sites (T-sites), which form a simple cubic (SC) lattice in the face-centred cubic (FCC) dihydrides γ - TiH_x and δ - ZrH_x , and a simple tetragonal (ST) lattice in the face-centred tetragonal (FCT) dihydride ϵ - ZrH_x [1, 2, 3].

Nuclear magnetic resonance (NMR) has proved to be an effective technique for studying metal–hydrogen systems [4, 5, 6]. In particular, measurements of the proton spin–lattice relaxation rate, Γ_1 , have been used frequently to investigate hydrogen diffusion in the dihydrides TiH_x [7, 8, 9, 10, 11, 12] and ZrH_x [13, 14, 15, 16, 17]. The dipolar contribution $\Gamma_{1, \text{dip}}$ to the proton spin–lattice relaxation depends on the mean dwell time of the protons at an interstitial site. The activation enthalpy for hydrogen diffusion in ZrH_x deduced from $\Gamma_{1, \text{dip}}$ increases with the hydrogen concentration x , whereas no variation of H_a with x was found in the case of TiH_x .

The composition dependence of H_a in ZrH_x has been confirmed recently by direct measurements of diffusion coefficients in a series of zirconium dihydrides using the pulsed-field-gradient (PFG) magnetic-resonance technique [18]. Furthermore, a comparison of the

PFG results with Γ_1 data from the same samples [17] yielded the mean jump distance of the diffusing hydrogen atoms and showed that hydrogen atoms jump predominantly between nearest-neighbour tetrahedral sites [18]. Such an analysis was previously applied to titanium dihydrides [19].

The present paper reports on an extension of PFG measurements on ZrH_x to higher temperatures and higher hydrogen concentrations. The main aims are to obtain comprehensive data on hydrogen diffusion in zirconium dihydrides and to develop a diffusion model that is capable of describing the temperature and composition dependence of D with a single set of diffusion parameters.

2. Experimental details

The ZrH_x samples were prepared in the Ames Laboratory from high-purity zirconium. The hydriding was carried out by exposing the metal to hydrogen gas at a pressure appropriate to obtain the desired hydrogen concentration. For high hydrogen concentrations ($x \geq 1.9$) the metal was heated to 1053 K, for lower concentrations ($x \leq 1.9$) to 943 K. In order to assure homogeneous hydriding the system was kept at this temperature for 24 h. Hydrogen concentrations were initially determined from the gain of weight and final hydrogen pressure in the calibrated volume of the system, and the quoted x values were lastly obtained by hot-vacuum-extraction analysis. The brittle metal hydride samples were crushed in a helium-filled glove box with mortar and pestle to a powder of a typical grain size of about 50 μm . Subsequently the samples were sealed under low helium pressure in quartz tubes with an inner diameter of 7 mm and a length of 12 mm. The free volume inside the sample container was so small that the maximum amount of hydrogen gas set free from the samples under equilibrium conditions reduced the hydrogen concentration in the samples by less than 1%. The series of zirconium dihydrides investigated in the present work was previously studied by Γ_1 measurements at Ames [17].

The PFG NMR measurements were performed at the Max-Planck-Institut in Stuttgart. Details of the experimental procedures have been published previously [18]. Data were taken between 600 K and 970 K at a resonance frequency of 35 MHz. All diffusivities were measured by a stimulated-echo sequence [20] with a typical diffusion time of 10 ms and a gradient pulse length of 1 ms. Field gradients up to 25 T m^{-1} over the sample volume were produced by a home-built device [21]. The statistical uncertainties in the diffusivity, shown by error bars in the figures, are of the order of 5%. The presence of background magnetic field gradients, G_i , due to a random variation of the magnetization in powdered metal hydride samples may influence the accuracy of a PFG experiment [19]. For the ZrH_x samples $\sqrt{\langle G_i^2 \rangle} \approx 0.5 \text{ T m}^{-1}$ has been deduced from the attenuation of the spin echo without any applied field gradient. This leads to an upper limit for a systematic error in D well below 5%.

3. Results and discussion

Figure 1 shows the hydrogen diffusivities measured by PFG NMR in five ZrH_x samples over a wide temperature range. The usual procedure to analyse the diffusion data is to fit an Arrhenius law

$$D = D_0 \exp(-H_a/k_B T) \quad (1)$$

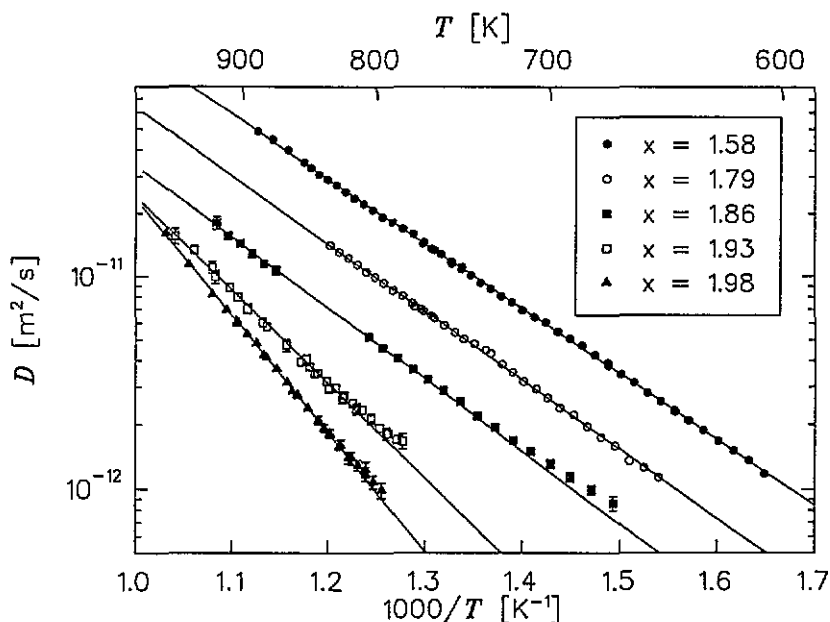


Figure 1. The temperature dependence of the hydrogen diffusivity in ZrH_x measured by PFG NMR. The solid lines are obtained by fitting an Arrhenius expression $D = D_0 \exp(-H_a/k_B T)$ to the diffusion coefficients. The corresponding diffusion parameters are summarized in table 1.

to the experimental results. At first sight, such a straightforward approach seems capable of describing the temperature dependence of D at a fixed concentration x . The corresponding activation enthalpies H_a and pre-exponential factors D_0 are summarized in table 1. Closer inspection, however, reveals a small but distinct deviation from Arrhenius behaviour for intermediate hydrogen concentrations ($x = 1.86, 1.93$). This explains why for $x = 1.86$ and $x = 1.93$ lower H_a values were reported in an earlier publication [18], which covered only the low-temperature range of the present work. It is interesting to note that Korn and Goren [15, 16] previously observed deviations from Arrhenius behaviour of the hydrogen jump frequencies deduced from Γ_1 measurements in ZrH_x . They attributed the curving upwards of the hydrogen jump rate at higher temperatures to a new, very fast channel for hydrogen motion. The H_a values given in table 1 agree satisfactorily with results derived from Γ_1 data taken at similar temperatures [13, 16, 17]. $\Gamma_{1,\rho}$ measurements performed between 300 K and 570 K yielded H_a values that are substantially smaller [14], which is another indication for a temperature-dependent diffusion mechanism. The effective value of H_a apparently depends on the temperature range that is considered in an Arrhenius plot. Furthermore, the sharp increase in the effective H_a as x approaches two can hardly be explained with a unique diffusion mechanism.

As long as only jumps between one kind of interstitial site with a unique jump distance L have to be taken into account, the diffusion coefficient may be written as

$$D = f_T L^2 / 6\tau. \quad (2)$$

L is given by $a_0/2$ for jumps between nearest-neighbour tetrahedral sites in an FCC dihydride with lattice parameter a_0 . In FCT $\epsilon\text{-ZrH}_x$ with the slightly different lattice parameters a_0 and b_0 the relation $3L^2 = 2(a_0/2)^2 + (b_0/2)^2$ holds. Inserting a_0 and b_0 gives $L \approx 2.4 \times 10^{-10}$ m for both types of hydride observed in the present work, i.e., in FCC $\delta\text{-ZrH}_x$ ($x = 1.58$) and in FCT $\delta\text{-ZrH}_x$ ($x \geq 1.79$). The x -dependent tracer correlation factor f_T for hopping on an

Table 1. Diffusion parameters obtained by fitting an Arrhenius expression $D = D_0 \exp(-H_a/k_B T)$ to the experimental data. The concentration-dependent tracer correlation factors f_T are taken from [22]. The attempt frequencies ν_a have been calculated from D_0 for jumps between nearest-neighbour tetrahedral interstices in ZrH_x with a jump distance $L \approx 2.4$ Å. Blocking of occupied sites has been taken into account.

ZrH _x x	H _a (eV)	D ₀ (10 ⁻⁷ m ² s ⁻¹)	f _T	ν _a (10 ¹³ s ⁻¹)
1.58	0.61	1.53	0.740	1.7
1.79	0.64	1.06	0.697	2.5
1.86	0.67	0.80	0.682	2.9
1.93	0.88	6.54	0.666	48.7
1.98	1.10	82.0	0.655	2173

SC lattice, the lattice formed by the T-sites in FCC dihydrides, has been calculated by Fedders and Sankey [22]. The mean time of residence τ may be derived from the relationship

$$1/\tau = 6 \left(1 - \frac{x}{2}\right) \nu_a \exp(-H_a/k_B T) \quad (3)$$

where H_a denotes the barrier height between two T-sites, ν_a the attempt frequency for jumps to one of the six neighbouring sites in the SC lattice and $(1-x/2)$ the probability that a given site is vacant. The ν_a values in table 1 have been calculated from D_0 according to the relation

$$D_0 = f_T L^2 \nu_a \left(1 - \frac{x}{2}\right) \quad (4)$$

which follows from (1)–(3). For $x \leq 1.86$, ν_a depends only weakly on x , as expected, and is in good agreement with the hydrogen vibration frequency $\nu_N = 3.4 \times 10^{13} \text{ s}^{-1}$ observed by neutron scattering [23]. It is evident, however, from table 1 that for higher hydrogen concentrations the picture of a simple diffusion process fails. A model that considers only jumps between one kind of interstitial site with mere blocking of occupied sites cannot explain either the increase in H_a or that in ν_a as $x \rightarrow 2$. Furthermore, the absolute values of ν_a indicate conclusively a more complex situation in the stoichiometric limit. For $x = 1.98$, the calculation outlined above yields $\nu_a \approx 2 \times 10^{16} \text{ s}^{-1}$. This value deviates from the hydrogen vibration frequency by a factor of about 600 and is substantially higher than any ‘attempt frequency’ expected for a hydrogen diffusion mechanism. Since all investigated ZrH_x hydrides with $x \geq 1.79$ exist in the tetragonal ϵ -phase, structural differences cannot account for the strong change of the diffusion parameters as $x \rightarrow 2$. Furthermore, the diffusion behaviour of hydrogen in FCC δ - $ZrH_{1.58}$ and in FCT ϵ - $ZrH_{1.79}$ appears to be quite similar.

For describing both the temperature dependence of the diffusivity, which deviates slightly from single-exponential behaviour for intermediate x -values, and the observed concentration dependence of the effective values of H_a and ν_a we propose the following model. An interstitial site other than the tetrahedral site becomes occupied as hydrogen concentration and temperature increase. One may think of an additional occupation of octahedral sites similar to those of hydrogen in YH_x [24]. In YH_x , however, an increase in D with x was found at a given temperature [24] whereas in the case of the ZrH_x system the diffusion coefficients decrease with increasing hydrogen concentration. Only at high temperatures does the diffusivity merge as $x \rightarrow 2$ into the D values of samples with lower hydrogen concentration but without exceeding them (cf. figures 1 and 2). This suggests that the energy difference between the tetrahedral site and an additionally occupied site, ΔE , is

rather high, and thus only a very small fraction of the hydrogen atoms occupies sites other than the tetrahedral site.

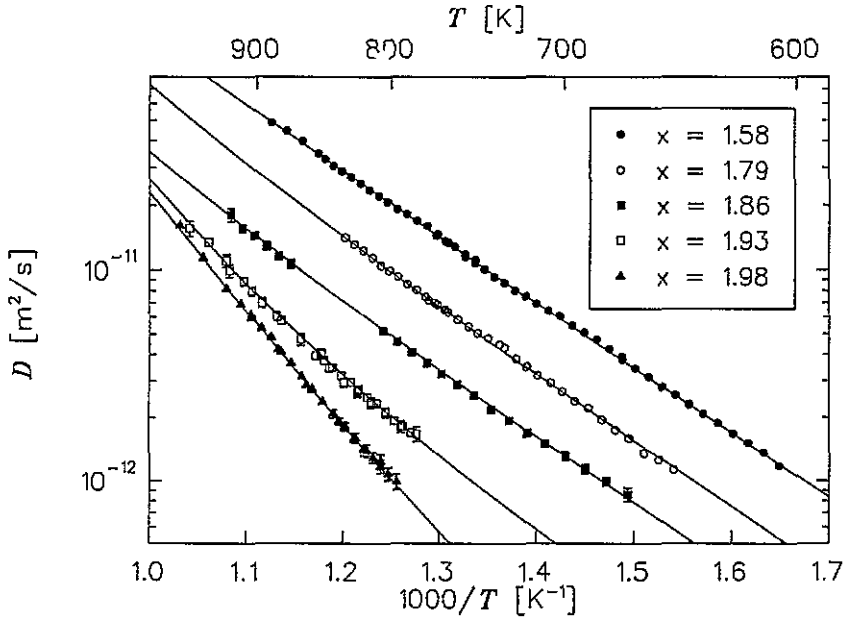


Figure 2. PFG NMR data of hydrogen diffusion in ZrH_x . The solid lines are calculated by taking into account a certain percentage of hydrogen atoms located on a so-called X-site. The corresponding diffusion parameters are $\Delta E = 0.85$ eV, $H_{TT} = 0.62$ eV and 0.61 eV for FCC ZrH_x ($1.79 \leq x \leq 1.98$) and FCC $ZrH_{1.58}$, respectively, $H_{XX} = 0.40$ eV, $H_{TX} = 1.10$ eV, and $\nu_{ij}^0 \approx 10^{13}$ s $^{-1}$, with $i, j = T, X$. For more details, see the text.

One aim of this paper is to demonstrate that the temperature and concentration dependence of hydrogen diffusion in ZrH_x can be explained quantitatively by taking into account hydrogen atoms located on energetically higher interstices. Further assumptions concerning the type of additional site, however, are not crucial for the diffusion parameters derived from this model. In the following the additionally occupied site will be called the X-site, and, just in order to have concrete figures for the calculations, the same numerical values as for octahedral sites were chosen arbitrarily. If there are twice as many T-sites as X-sites in ZrH_x and a double occupation of an interstice is excluded, the total hydrogen concentration $[H]/[Me]$ is given by

$$x = 2C_T + C_X \quad (5)$$

where C_T and C_X denote the occupation probabilities of a T-site and a X-site, respectively. The chemical potential of the hydrogen lattice gas can be expressed either with respect to C_T or with respect to C_X according to [24, 25]

$$\mu = \Delta E + k_B T \ln(C_X/(1-C_X)) = k_B T \ln(C_T/(1-C_T)). \quad (6)$$

Hence, the occupation probability of an X-site

$$C_X = (1-C_T)^{-1} C_T \exp(-\Delta E/k_B T) \quad (7)$$

is obtained in the limit $C_X \ll 1$. In the following, the symbols ν_{TT} , ν_{TX} , ν_{XT} , and ν_{XX} will be used for the jump frequencies between a given T-site or X-site and a corresponding

vacant nearest-neighbour site. ν_{XT} is related to ν_{TX} due to the detailed-balancing condition (again for $C_X \ll 1$)

$$\nu_{XT}C_X(1-C_T) = \nu_{TX}C_T. \quad (8)$$

Under the assumption of the above jump paths and possibilities, the diffusion coefficients may be written in the form

$$D = [p_T(6\langle r_{TT}^2 \rangle \nu_{TT} + 4\langle r_{TX}^2 \rangle \nu_{TX}) + p_X(12\langle r_{XX}^2 \rangle \nu_{XX} + 8\langle r_{XT}^2 \rangle \nu_{XT})]/6 \quad (9)$$

taking into account that the numbers of individual jump vectors for TT-, TX-, XX-, and XT-jumps are six, four, 12, and eight, respectively. For simplification, the tracer correlation factors were set equal to unity. $p_T = 2C_T/x$ and $p_X = C_X/x$ denote the probability that a given hydrogen atom occupies a T-site and an X-site, respectively. With the squares of the jump vectors according to

$$\langle r_{TT}^2 \rangle = L^2 \quad \langle r_{TX}^2 \rangle = \langle r_{XT}^2 \rangle = 3/4L^2 \quad \langle r_{XX}^2 \rangle = 2L^2 \quad (10)$$

and with (8) and (9) we obtain the diffusion coefficient

$$D = L^2 \left[\frac{2C_T(1-C_T)}{x} \nu_{TT} + \frac{2C_T}{x} \nu_{TX} + \frac{4C_X}{x} \nu_{XX} \right]. \quad (11)$$

The equation above indicates that besides the individual jump frequencies ν_{TT} , ν_{XX} , and ν_{TX} the diffusivity D depends on the occupation probability of an X-site C_X that is determined by ΔE for a given hydrogen concentration x . We want to emphasize here that if one chooses different jump vectors or a different abundance of the X-sites, the general form of this formula remains the same. The jump frequencies may be expressed as

$$\begin{aligned} \nu_{TT} &= \nu_{TT}^0 \exp(-H_{TT}/k_B T) \\ \nu_{XX} &= \nu_{XX}^0 \exp(-H_{XX}/k_B T) \\ \nu_{TX} &= \nu_{TX}^0 \exp(-H_{TX}/k_B T). \end{aligned} \quad (12)$$

It is evident from figure 2 that equation (11) allows us to describe the observed concentration dependence of D consistently with one set of parameters. The solid lines in figure 2 are calculated using the parameters $\Delta E = 0.85$ eV, $H_{TT} = 0.62$ eV (for FCC ZrH_x ; $H_{TT} = 0.61$ eV was taken for the only FCC sample $ZrH_{1.58}$), $H_{XX} = 0.40$ eV, $H_{TX} = 1.10$ eV. All attempt frequencies ν_{TT}^0 , ν_{XX}^0 , and ν_{TX}^0 are between 1×10^{13} s⁻¹ and 2×10^{13} s⁻¹ for the whole concentration range. (Note that taking into account tracer correlation factors smaller than unity would result in slightly greater prefactors.) This set of diffusion parameters appears to be very reasonable. The prefactors are in good agreement with the hydrogen vibration frequency $\nu_N = 3.4 \times 10^{13}$ s⁻¹ observed by neutron scattering [23], as expected for a classical diffusion mechanism. Owing to the high activation energy, $\Delta E = 0.85$ eV, the fraction of hydrogen atoms occupying X-sites is well below 1% even at 1000 K for $x = 1.98$. The temperature dependence of C_X according to (5) and (7) is shown in figure 3 for all five investigated samples. In spite of the small C_X values hydrogen atoms located on X-sites play an important role for hydrogen diffusion in ZrH_x since H_{XX} is substantially smaller than H_{TT} .

Within certain limits one could easily find a different set of diffusion parameters that also describes the experimental results. The aim, however, is not to deduce well defined diffusion parameters, but to demonstrate that a consistent explanation of the diffusivities measured in ZrH_x over a wide range in temperature and concentration is possible by introducing the occupation of an interstitial site in addition to the T-site.

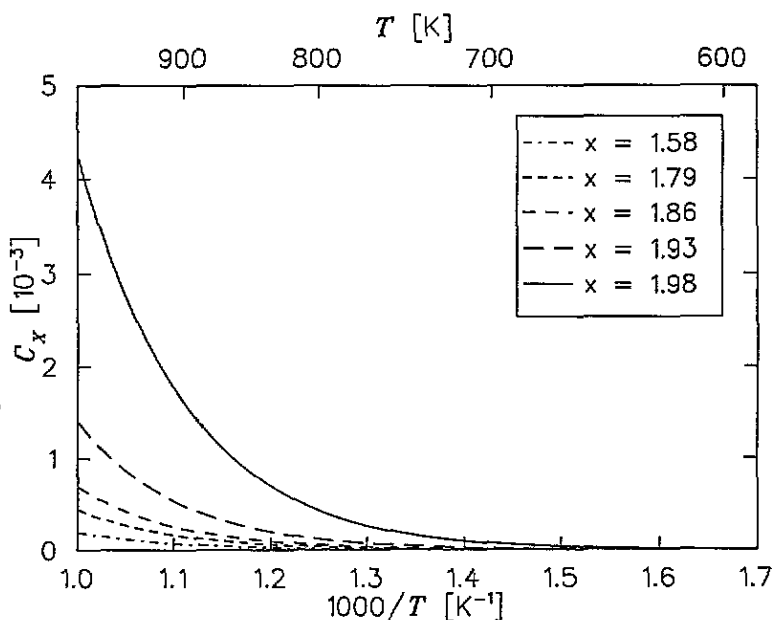


Figure 3. The temperature dependence of the occupation probability C_X of a so-called X-site in ZrH_x ($1.58 \leq x \leq 1.98$) that is energetically higher by $\Delta E = 0.85$ eV than the tetrahedral interstice.

4. Summary and conclusions

We performed PFG NMR studies investigating hydrogen diffusion in zirconium dihydrides ZrH_x . The diffusion coefficients were determined on five samples ($x = 1.58, 1.79, 1.86, 1.93, 1.98$) in the temperature range between 600 K and 970 K. The apparent activation enthalpy, H_a , obtained by fitting an Arrhenius expression $D = D_0 \exp(-H_a/k_B T)$ to the diffusivities, increases strongly as x approaches the stoichiometric limit $x = 2$. A diffusion model that only considers jumps between nearest-neighbour tetrahedral sites with mere blocking of occupied sites yields attempt frequencies for hydrogen diffusion, ν_a , that also increase sharply for $x \rightarrow 2$. This indicates a more complex diffusion process, since neither H_a nor ν_a are expected to vary with the hydrogen concentration x in the framework of a simple diffusion model. Furthermore, the direct measurement of D over a wide temperature range and the high accuracy of the present PFG data allow us to determine a distinct deviation from an Arrhenius law for intermediate x values. All these results could be explained straightforwardly by assuming that a small percentage of the hydrogen atoms is located on an interstitial site that is energetically higher than the T-site. The suggested model is capable of describing the whole set of diffusion data with reasonable diffusion parameters that are independent of the hydrogen concentration.

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