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Model-independent measurements of hydrogen diffusivity in the yttrium dihydrides

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Abstract

The hydrogen diffusivities D in yttrium dihydrides YH_x have been measured by means of pulsed-field-gradient nuclear magnetic resonance (PFG-NMR) up to 920 K for $x=1.91$ and up to 620 K for $x=1.95$ and 2.03. The observed D values are generally significantly greater than those in the dihydrides of titanium and zirconium. The activation enthalpy H_a, obtained by fitting an Arrhenius expression to the diffusivities, decreases substantially with increasing x from $H_a = 0.53$ eV ($x = 1.91$) to $H_a = 0.38$ eV ($x = 2.03$). Measurements of the proton spin-lattice relaxation Γ_1 have been performed on the same samples. The temperature and concentration dependences of the dipolar relaxation Γ_{1d} are consistent with the PFG results. Besides Γ_{1d} and the electronic relaxation Γ_{1e}, the Γ_1 data reveal contributions due to very small concentrations of paramagnetic impurities Γ_{1p}, which dominate the measured rates below about 500 K, even at impurity levels as low as 20 ppm or less. © 2002 Published by Elsevier Science B.V.

Keywords: Hydrogen diffusivity; Yttrium dihydrides; Pulsed-field-gradient nuclear magnetic resonance

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1. Introduction

Yttrium, which has a hexagonal close-packed (hcp) structure at room temperature, absorbs hydrogen at elevated temperatures to form homogeneous dihydrides YH_x with an approximate range of compositions from $x = 1.80$ to 2.05 [1]. These dihydrides have a fluorite-type structure with a face-centered cubic (fcc) lattice of the yttrium atoms. At room temperature and below hydrogen atoms occupy only the T-sites when very pure yttrium is loaded to the stoichiometric dihydride composition $x = 2.0$ [1–5]. For $x > 2$, the excess hydrogen atoms are accommodated in O-sites. It is believed that impurities in the yttrium metal block some of the available T-sites, resulting in a substantial occupancy of O-sites even for $x \leq 2.0$ and at low temperatures [1]. In addition to that one expects hydrogen atoms to be thermally promoted to the higher-energy O-sites, as reported in earlier publications [6–10].

Nuclear magnetic resonance (NMR) has been used for many years to investigate hydrogen motion [2,6,11–14], hydrogen locations [2] and the electronic structure [3–6,12] in the yttrium dihydride/trihydride system. The present paper reports on model-independent diffusion measurements on three YH_x samples in the pure dihydride phase by pulsed-field-gradient (PFG) spin-echo NMR. The results will be compared with the diffusivities measured previously in the dihydrides of zirconium [15,16], titanium [17] and lanthanum [18]. The proton spin-lattice relaxation Γ_1 has been measured as well and will be analysed together with information available from the PFG results.

2. Experimental details

The samples were prepared in the Materials Science Division of the Ames Laboratory from high-purity yttrium [12]. The hydrogen concentrations of the three YH_x samples were determined by hot-vacuum-extraction analysis to an accuracy of about 1% of the quoted values $x=1.91$, 1.95 and 2.03. For the NMR measurements the powdered samples were sealed in quartz tubes under a pressure of about 0.1 bar of He. The samples $YH_{1.91}$ and $YH_{2.03}$, which have a very small total magnetic rare-earth impurity content of 20 ppm (mainly Gd^{3+}), are those used in previous NMR studies [12]. The $YH_{1.95}$ sample was prepared from highest-purity yttrium available, with an

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extremely low level of paramagnetic rare-earth impurities, determined by spark-source mass spectroscopy, on the order of 5–10 ppm total.

The PFG measurements were performed using the two-pulse spin-echo sequence [19] and, for $YH_{1.91}$ below 620 K, the stimulated spin-echo sequence [20] with field-gradient pulses up to $25\,T\,m^{-1}$. To avoid thermal desorption of the samples [21], a temperature of about 620 K was not exceeded in the case of $YH_{1.95}$ and $YH_{2.03}$.

3. Results and discussion

The diffusivities of hydrogen in YH_x are shown in Fig. 1. In the concentration range covered by these data ($x=1.91$–2.03) the hydrogen diffusivity at a given temperature increases rather strongly with increasing x. At 600 K, for instance, the diffusivity in $YH_{2.03}$, which contains only about 6% more hydrogen than $YH_{1.91}$, is greater by almost a factor of four than that in $YH_{1.91}$. Quasielastic neutron scattering (QNS) on YH_x ($1.8 \leq x \leq 2.1$) at 450 K also revealed an increase in the hydrogen jump rate with increasing x [22,23]. In lanthanum, which forms non-stoichiometric homogeneous hydrides LaH_x with an fcc lattice of the host metal in the concentration range $x \approx 1.9$–3.0, an increase in the diffusivity with increasing x has been reported for $x \geq 2$ [18]. By contrast, in the dihydrides of zirconium [15,16], titanium [17] and hafnium [24] the hydrogen diffusivity at a given temperature decreases with increasing hydrogen content.

The solid lines in Fig. 1 represent fits of an Arrhenius law

$$D = D_0 \exp(-H_a/k_B T) \tag{1}$$

to the diffusion coefficients with the fitting parameters given in Table 1. The pre-exponential factors D_0 are of the same magnitude as those found in LaH_x [18], for example. Increasing the hydrogen content from $x=1.91$ to $x=1.95$ results in a reduction in D_0, whereas a further increase to $x=2.03$ seems to have no significant effect on D_0. Previous diffusion studies of hydrogen in YH_x by NMR and by QENS yielded an activation enthalpy of $H_a=0.34$ eV for $x=1.98$ [14]. The values $H_a=0.35$ eV [22] and $H_a=0.30$ eV [23] have been deduced from QENS data measured on a YH_x sample with $x=1.97$. Based on relaxation rate and selective inversion NMR measurements on two YD_x samples with $x = 2.04$ and $x = 2.08$, a value of $H_a=0.55$ eV has been reported for the activation enthalpy of deuterium T–O interchanges [2]. These data compare reasonably well with the present results.

Table 1
Diffusion parameters of hydrogen in YH_x obtained by fitting Arrhenius expressions to the diffusivities D measured by PFG-NMR. Estimated uncertainties are ±3% in activation enthalpies H_a and ±20% in pre-exponential factors D_0; D(600 K) has been calculated from the fit parameters; T_{max} denotes the temperature of the dipolar relaxation maximum at $\omega/2\pi=37.7$ MHz

x	D_0 [10^{-8} m^2 s^{-1}]	H_a [eV]	D(600 K) [10^{-12} m^2 s^{-1}]	T_{max} [K]
1.91	4.8	0.53	1.7	665
1.95	0.9	0.40	3.9	610
2.03	1.0	0.38	6.4	570

The diffusivities found for YH_x are generally significantly greater than those in the TiH_x [17] and the ZrH_x [15,16] systems. A comparison of the present results for $YH_{2.03}$ with the diffusivities measured previously in the stoichiometric dihydride of lanthanum and in the nearly stoichiometric dihydrides of titanium and zirconium is given in Fig. 2.

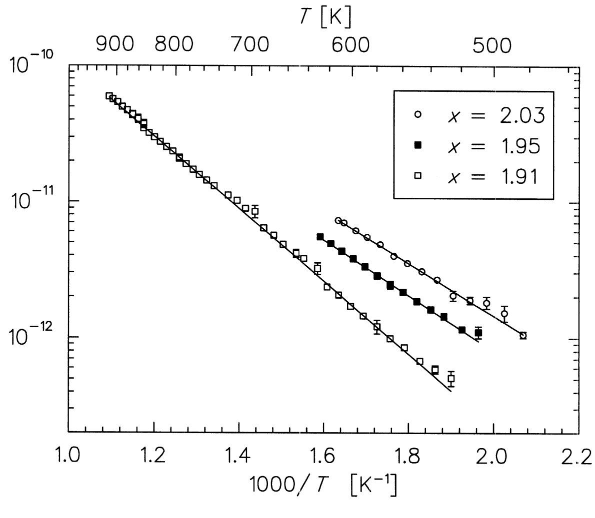

Fig.1. Temperature dependence of the hydrogen diffusivity D in YH_x ($1.91 \leq x \leq 2.03$) measured by PFG-NMR. The solid lines represent Arrhenius laws with the diffusion parameters given in Table 1.

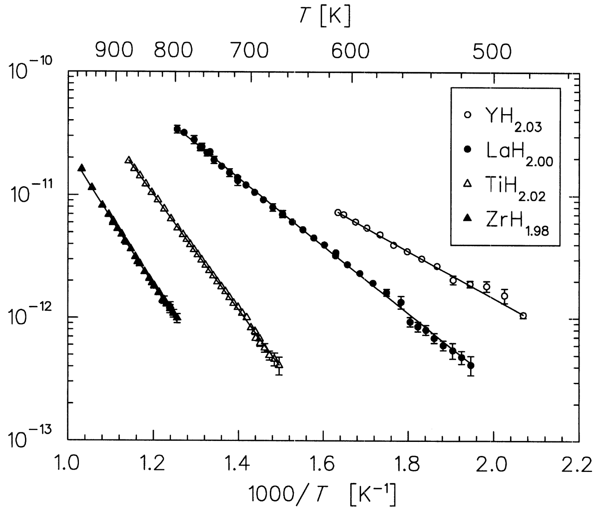

Fig. 2. Comparison of the hydrogen diffusivities measured by PFG-NMR in nearly stoichiometric dihydrides. The solid lines correspond to $H_a=$ 0.38, 0.55, 0.92 and 1.10 eV for $YH_{2.03}$, $LaH_{2.00}$ [18], $TiH_{2.02}$ [17] and $ZrH_{1.98}$ [16], respectively.

The following mechanism of hydrogen diffusion has been found for the dihydrides of the group-IVa transition metals: up to $x \approx 1.9$ hydrogen atoms jump predominantly between nearest-neighbor T-sites. In this concentration range the activation enthalpy, $H_a \approx 0.5$ eV, is nearly concentration independent and the diffusivity decreases with increasing x due to blocking of occupied T-sites. But, as x approaches the limiting value of 2, the effective activation enthalpy increases sharply to $H_a \approx 1$ eV, indicating that in the stoichiometric limit another process plays the dominant role for the hydrogen diffusion [15–17].

This behavior is very different from that in the group-IIIa transition metals lanthanum and yttrium, which form superstoichiometric dihydrides with partial occupation of O-sites. As long as O-sites are not or almost not occupied in those systems, the activation enthalpies for hydrogen diffusion are also of the order of $H_a \approx 0.5$ eV. However, the more hydrogen atoms are added and, thus, the more O-sites are occupied, the smaller is the activation enthalpy. In the lanthanum dihydride/trihydride system, H_a decreases from 0.55 eV at $x = 2.0$ to, for example, 0.44 eV at $x = 2.26$ [17]. The present data indicate that in YH_x, where H_a decreases from 0.53 eV at $x = 1.91$ to 0.38 eV at $x = 2.03$, the change in the activation enthalpy with x is even stronger and occurs already at lower concentrations than in LaH_x.

In order to gain further insight into the mechanism of hydrogen diffusion the proton Γ_1 has also been measured on the same samples. The Γ_1 data shown in Fig. 3 reveal two characteristic features: a maximum due to the dipolar relaxation Γ_{1d} and a shoulder or even a secondary maximum at lower temperatures that results from very low levels of paramagnetic impurities. The temperature of the diffusion-induced Γ_{1d} maximum, T_{max}, decreases with increasing x (cf. Table 1), indicating the increase in the hydrogen diffusivity. The total spin-lattice relaxation rate may be decomposed according to

$$\Gamma_1 = \Gamma_{1d} + \Gamma_{1e} + \Gamma_{1p} \,. \tag{2}$$

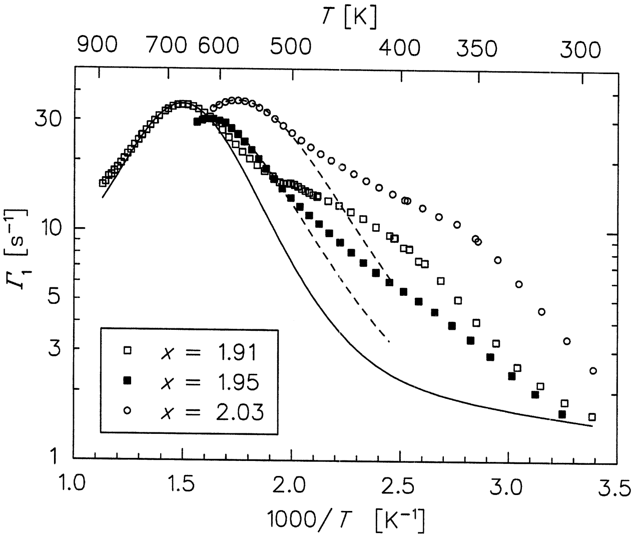

Fig. 3. Spin-lattice relaxation rates Γ_1 of hydrogen in YH_x ($x = 1.91$, 1.95 and 2.03) measured at 37.7 MHz. The solid line represents the sum of Γ_{1e} and Γ_{1d} for $YH_{1.91}$. Γ_{1e} has been calculated using the Korringa relaxation [25] with $\kappa = 269$ Ks, and Γ_{1d} has been obtained from Sholl's calculations [26] for direct T–T jumps with the H_a value of the PFG results. The corresponding curves for $YH_{1.95}$ and $YH_{2.03}$ are plotted as dashed lines above 400 K.

The electronic contribution Γ_{1e} is due to the interaction with the magnetic moments of the conduction electrons, and it is usually expressed by the Korringa relation $\Gamma_{1e} = T/\kappa$ [25]. The dominance of the impurity-related relaxation Γ_{1p} at low temperatures prevents a reliable determination of Γ_{1e}. As an approximation, the temperature dependence of Γ_{1e} has been calculated with $\kappa = 269$ Ks reported for $YH_{1.92}$ [6].

Below about 500 K, Γ_{1p} dominates the measured relaxation rate. As pointed out by Phua and co-workers [12], the appearance of a shoulder or a secondary maximum on the low-temperature side of the Γ_{1d} maximum may be readily misinterpreted in terms of a second motional process with lower activation enthalpy. This complication in the interpretation of Γ_1 data in terms of diffusion parameters underlines the great value of PFG-NMR in measuring the diffusivity directly.

In order to analyse the dipolar relaxation Γ_{1d} in terms of hydrogen diffusion, assumptions on the underlying diffusion mechanisms are required. It is generally accepted that in the dihydrides of the group-IVa transition metals jumps between adjacent T-sites (direct T–T jumps) are, at least up to $x \approx 1.9$, the dominant diffusion mechanism. These T-sites form a simple cubic (sc) sublattice, and the occupation probability of a T-site is given by $c_T = x/2$. For such a diffusion process, lattice-specific Monte Carlo-calculations, that depend slightly on c_T, are available for $c_T = 0.90$ and $c_T = 0.99$ and yield Γ_{1d} values as a function of the mean dwell time of hydrogen τ_d [26]. In the dihydride–trihydride systems of the group-IIIa transition metals, where O-sites are also occupied, the diffusion mechanisms are more complex. Experimental evidence indicates that in both YH_x [2] and LaH_x [18] hydrogen diffusion is dominated by T–O exchanges for $x > 2$. However, it remains an open question at what concentration x (and temperature) T–O exchanges begin to occur more frequently than direct T–T jumps in YH_x. At present it can only be checked whether data are inconsistent with the assumption of direct T–T jumps, since a relaxation model that takes into account T–O exchanges is not yet available.

As a straight forward approach to analyse the Γ_{1d} data for $x = 1.91$ we considered only direct T–T jumps and used Sholl's calculations [26] for $c_T = 0.99$. The mean dwell time of hydrogen has been calculated for a single thermally activated motional process according to

$$\tau_d = \tau_0 \cdot \exp(H_a/k_B T) \,, \tag{3}$$

with the activation enthalpy $H_a = 0.53$ eV taken from the PFG results. The τ_0 value of Eq. (3) has been adjusted to match the position of the Γ_{1d} maximum, and the second moment M_2, which determines the relaxation strength, has been calculated for pure T-site occupation. The solid curve in Fig. 3 represents the sum of Γ_{1e} and Γ_{1d} calculated as outlined above and scaled by a numerical factor $f_p = 1.33$ to match the measured relaxation maximum. It is evident that the temperature dependence of the Γ_{1d} data follow quite well the Monte Carlo-calculations [26] for direct T–T jumps with the H_a value obtained by PFG-NMR. This result is not too surprising for a sample with $x = 1.91$, where hydrogen atoms are expected to occupy predominantly the T-sites. The deviation of the relaxation data from the calculated curve above about 900 K indicates the onset of the high-temperature relaxation [27], which does not manifest itself in the diffusion data.

For lack of a more appropriate relaxation model, the Γ_{1d} data of $YH_{1.95}$ and $YH_{2.03}$ have been analysed in the same way as outlined above for $YH_{1.91}$. Again, the corresponding H_a values of the PFG results have been used. The results thus obtained are included as dashed lines in Fig. 3. Within the rather limited temperature ranges where the Γ_1 data of these samples are dominated by the dipolar contributions, these curves represent the data quite well. Thus, the data appear not to be inconsistent with the model of direct T–T jumps. Nevertheless, it can not be excluded that T–O jumps play a prominent role in the mechanism of hydrogen diffusion in $YH_{1.95}$ and/or $YH_{2.03}$. In order to elucidate the diffusion mechanisms, another relaxation model is required that considers also O–T and O–O jumps as well as T–T jumps.

An interesting result are the different numerical factors required to adjust the relaxation maxima. These factors are $f_p = 1.33$ for $YH_{1.91}$ and $f_p = 1.27$ for $YH_{2.03}$. In the case of $YH_{1.95}$, which has been prepared from highest-purity yttrium available, the factor $f_p = 1.13$ is significantly smaller. The differences in f_p reflect mainly different impurity levels of the samples. We note that smaller adjustment factors f_p are obtained, if one takes into account a certain fraction of occupied O-sites in YH_x for $x \leq 2$, which results in greater M_2 values at a given x [6,7].

4. Summary and outlook

The diffusivity D of hydrogen in the yttrium dihydrides YH_x has been measured by means of PFG-NMR over extended ranges in concentration and temperature. The activation enthalpy for hydrogen motion H_a decreases substantially with increasing x, resulting in a strong increase in D. The spin-lattice relaxation rates Γ_1, measured on the same samples, are in good agreement with the PFG results. The Γ_1 data indicate also the increase in D with increasing x, and are well described by the activation enthalpies determined from the model-independent PFG data.

Diffusion measurements of hydrogen in the trihydrides of yttrium are in preparation in our group. These studies should reveal the differences in the diffusion behavior between metal hydrides with fcc and hcp host structures. It is of particular interest to investigate the changes in the hydrogen diffusivity at the temperature of the semiconductor-to-metal transition of the hcp yttrium trihydrides. Moreover, it is still an open question whether hydrogen diffusion in the stoichiometric limit, YH_3, also shows hysteresis, as has been observed in the stoichiometric trihydride of lanthanum [18].

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