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# Nuclear magnetic resonance studies of hydrogen diffusion in the layer-structured system $ZrClH_x$

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## Abstract

The proton spin-lattice relaxation rate $\Gamma_1$ in $ZrClH_{0.5}$ shows one maximum and two shoulders, which indicates three distinct modes of hydrogen motion. The frequency dependence of the spin-lattice relaxation rate in the rotating frame, $\Gamma_{1,\rho}$, shows clearly that hydrogen diffusion is confined to two dimensions. Direct measurements of the long-range diffusivity $D_{xy}$ were performed by pulsed field gradient (PFG) spin-echo NMR. These PFG experiments confirmed the two-dimensional character of hydrogen diffusion. The temperature dependence of $D_{xy}$ yields an activation enthalpy, $H_a = 0.49$ eV, which is in good agreement with the value $H_a = 0.47$ eV deduced from the frequency-dependent $\Gamma_{1,\rho}$ data. The different processes of hydrogen motion are discussed on an atomistic scale. The $\Gamma_1$ and $\Gamma_{1,\rho}$ curves measured in $ZrClH_{1.0}$ are consistent with a single mechanism of hydrogen diffusion. Both the relaxation data and the PFG data reveal a strongly reduced hydrogen mobility in $ZrClH_{1.0}$ compared to $ZrClH_{0.5}$. From the analysis of the echo amplitude in the PFG experiments it is concluded that the hydrogen diffusion is restricted to two dimensions as well. The $D_{xy}$ values show Arrhenius behavior with an activation enthalpy of $H_a = 0.58$ eV.

*Keywords:* Transition-metal halide hydride; Two-dimensional diffusion; Spin-lattice relaxation; PFG-NMR

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## 1. Introduction

Zirconium monochloride consists of two-dimensional four-layered sandwiches made up of a double layer of zirconium with a sheet of chloride above and below (see Fig. 1(a)). Three of these sandwiches, which differ only in the stacking, form the overall rhombohedral structure [1]. The pressure composition isotherms of the hydrogenation show that $ZrClH_{0.5}$ and $ZrClH_{1.0}$ are the only two stable hydrides of ZrCl [2]. The structural properties of these hydrides have been investigated by X-ray diffraction [1,3,4]. It can be concluded from NMR studies of the line widths, the spin-lattice relaxation rates [5,6] and the shielding tensors [7] that hydrogen atoms occupy only tetrahedral (T) and octahedral (O) interstitial sites within the Zr metal bilayers. Examples of T-sites and O-sites are indicated in Fig. 1(b). This structure suggests a substantial anisotropy of hydrogen diffusion, with a higher diffusivity in the planes formed by the Zr bilayers than in the direction perpendicular to these planes.

Previous NMR studies found on the basis of the proton second moments that in $ZrClH_{0.5}$ hydrogen atoms predominantly occupy alternate chains of T-sites within the Zr double layer, with a small random occupation of O-sites [5,6]. The occupation of the T-sites distorts the ZrCl lattice by shifting the Cl- and Zr-layers within each sandwich [3]. The resulting zigzag lines, which are alternately filled and empty, are indicated in Fig. 1(c). Neutron scattering experiments on the related system $ZrBrH_{0.5}$ confirmed the formation of these zigzag chains [8]. It is interesting to note that each T-site in the filled chains has an immediate neighboring T-site at a distance of about 2 Å in the adjacent empty chain. These two sites are too close to be occupied at the same time, similar to what has been reported for hydrogen in intermetallic compounds [9].

In $ZrClH_{1.0}$ the shift of the Cl- and Zr-layers is even greater and, in contrast to $ZrClH_{0.5}$, no chain structure is formed. This shift increases the distance between neighboring T-sites and one may expect that in $ZrClH_{1.0}$ all T-sites are occupied, based on the stoichiometry of the compound, the size of the T-site interstices and the analogy to zirconium dihydride. Surprisingly, a neutron powder diffraction study found strong evidence that in $ZrBrD_{1.0}$ deuterium pairs are located on O-site interstices with a distance of 2.2 Å between the two D atoms [10].

The samples in the present work were prepared at the Ames Laboratory. A detailed description of the preparation

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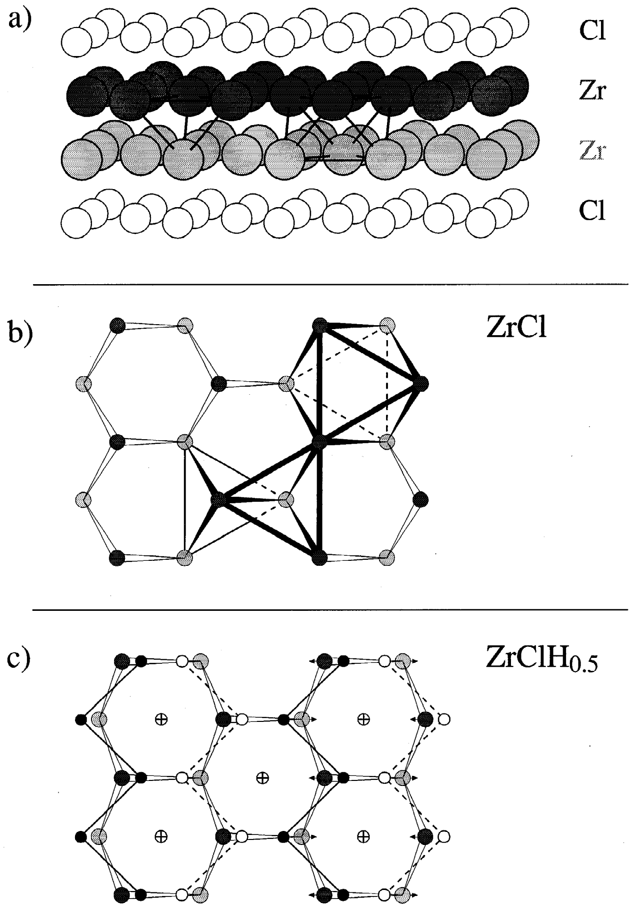

Fig. 1. Structure of $ZrClH_x$: (a) [110] projection of a four-layer sandwiches of ZrCl. One T-site and one O-site within the Zr bilayer are indicated. (b) [001] projection of a Zr bilayer. Dark shaded circles represent Zr atoms in an upper layer, bright shaded circles those in the layer below. Examples of T-sites and O-sites are shown. (c) [001] projection of a Zr bilayer in $ZrClH_{0.5}$. Closed circles are occupied T-sites, open circles empty ones. Open circles with the + indicate empty O-sites. The occupation of T-sites shifts the adjacent Zr layers, which leads to alternating zigzag lines of empty and occupied T-sites (connected by dashed and thick solid lines, respectively) [6].

and characterization of ZrCl is given in [4] and the hydrogenation of the samples is presented in [2].

Previous NMR studies on these samples revealed two stages of motional narrowing in wide-line measurements and two peaks in the temperature dependence of the spin-lattice relaxation rates $\Gamma_1$ and $\Gamma_{1,\rho}$ in the laboratory and rotating frames [5,6]. Both experiments indicate that two distinct processes of hydrogen motion are present. These processes have been ascribed to essentially independent mechanisms of hydrogen motion on the T and O interstitial sublattices. The dimensionality of hydrogen motion was not investigated in [6]. Quasielastic neutron scattering on $YBrH_{0.78}$ (which forms a structure similar to $ZrClH_x$) was interpreted in terms of two-dimensional hydrogen diffusion within the Y bilayers [11]. Indications of an ordered structure on the T-site sublattice in $YBrH_{0.8}$, similar to what has been observed previously in $ZrClH_{0.5}$ [5,6], were found by inelastic neutron scattering [12].

In the present paper we report on diffusion studies of hydrogen in $ZrClH_x$ ($x=0.5$, 1.0) using different NMR techniques. The long-range diffusivity measured by pulsed field gradient (PFG) NMR will be discussed together with information obtained from the spin-lattice relaxation rates $\Gamma_1$ and $\Gamma_{1,\rho}$. The main aims were to further analyze the mechanisms of hydrogen diffusion in $ZrClH_x$ and to determine the dimensional of the hydrogen motion.

## 2. Measuring techniques

The NMR measurements were performed with a home-built Fourier transform spectrometer using phase-alternating pulse schemes and quadrature detection. The sample temperature was maintained by means of a digital PID controller combined with ohmic heating and was determined by two calibrated platinum resistors to about ±0.1 K. (In the PFG probe the sample temperature was monitored with two Pt–PtRh thermocouples). Temperatures below room temperature were achieved by cooling with cold helium gas in a separate cryostat in the room-temperature bore of the superconducting magnet. $\Gamma_1$ was measured with the inversion recovery pulse sequence at the resonance frequencies of 27.7 and 67.7 MHz between 45 and 700 K. In the $\Gamma_{1,\rho}$ experiments, a rotating r.f. field of adjustable amplitude $B_1$ and with a phase shift of $\pi/2$ was applied after the initial 90° r.f. pulse. $B_1$ was limited by heating of the sample and by sparking to a maximum value of $B_1=25.0$ G. The sample heating also limited the length of the rotating field pulses, especially at high $B_1$ amplitudes. Therefore, relaxation rates below $\Gamma_{1,\rho}\approx 5\ \mathrm{s}^{-1}$ could not be measured. The lower limit of the rotating field, $B_1=2.5$ G, was determined by the internal magnetic fields in the $ZrClH_x$ samples.

For the PFG diffusion measurements the two-pulse spin-echo sequence introduced by Stejskal and Tanner [13] was applied with a typical time between the two r.f. pulses of $\Delta=3.0$ ms and a typical gradient pulse length of $\delta=1.0$ ms. Details of the PFG-NMR experiments have been published previously [14]. The echo amplitude of the nuclear magnetization,

$$M(G) = M_0 \exp\left( -D_{\mathrm{eff}} \gamma^2 \delta^2 \left( \Delta - \frac{\delta}{3} \right) G^2 \right) \tag{1}$$

was measured as a function of the applied field gradient $G$ at constant $\Delta$ and $\delta$. $D_{\mathrm{eff}}$ denotes an effective diffusivity along the gradient direction and $\gamma=2.6752\cdot 10^8$ rad $\mathrm{s}^{-1}\ \mathrm{T}^{-1}$ is the gyromagnetic ratio of the protons.

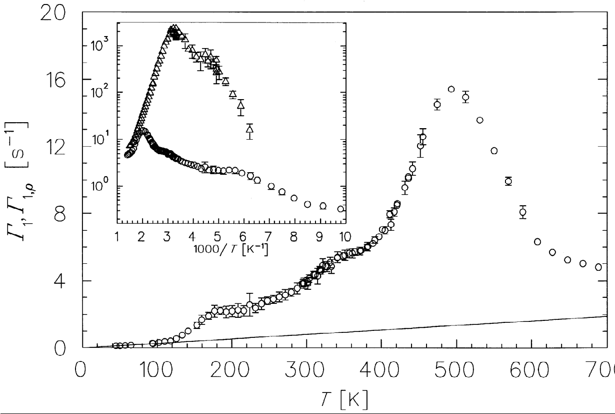

Fig. 2. Temperature dependence of the proton $\Gamma_1$ in ZrClH$_{0.5}$ measured at 27.7 MHz. The solid line indicates the Korringa behavior $\Gamma_{1,e} = T/370$ Ks. The insert shows an Arrhenius plot of both $\Gamma_1$ (open circle) and $\Gamma_{1,\rho}$ (open triangles) of hydrogen in ZrClH$_{0.5}$. The $\Gamma_{1,\rho}$ data were taken at a rotating field of $B_1 = 7.0$ G corresponding to $\omega_1/2\pi = 30$ kHz.

## 3. Results and discussion

Fig. 2 shows the temperature dependence of $\Gamma_1$ at 27.7 MHz and $\Gamma_{1,\rho}$ at 30 kHz in ZrClH$_{0.5}$. In metallic systems the relaxation rate may be decomposed according to

$$\Gamma_1 = \Gamma_{1,e} + \Gamma_{1,\mathrm{dip}}. \tag{2}$$

The electronic contribution $\Gamma_{1,e}$ is due to the interaction with the conduction electrons and is characterized by the Korringa relation $T/\Gamma_{1,e} = c_K$ [15]. Below temperatures of about 100 K the $\Gamma_1$ data clearly show Korringa behavior with $c_K = 370$ Ks (see Fig. 2), confirming the assignment of hydrogen to locations within the Zr metal bilayers.

The $\Gamma_1$ curve measured at 27.7 MHz shows a maximum at 500 K and two shoulders at about 330 K and 180 K. As discussed in [6] (in this reference only the maximum and one shoulder was observed due to the restricted temperature range), a superposition of different $\Gamma_{1,\mathrm{dip}}$ peaks has to be ascribed to independent processes of hydrogen diffusion.

Therefore, the present data indicate that three independent processes of hydrogen motion exist in ZrClH$_{0.5}$. Owing to the smaller resonance frequency in the rotating frame ($\omega_1/2\pi = 30$ kHz) the $\Gamma_{1,\rho}$ maximum occurs at about 310 K (compared to 500 K for the $\Gamma_1$ measurements at 27.7 MHz). A shoulder in the $\Gamma_{1,\rho}$ curve has been observed at about 220 K (cf. Fig. 2), which most likely results from the same process that gives rise to the shoulder at about 330 K in the $\Gamma_1$ data. A second shoulder in the $\Gamma_{1,\rho}$ curve, that corresponds to the $\Gamma_1$ shoulder at about 150 K, is expected at even lower temperatures. But in this temperature range $\Gamma_{1,\rho}$ is too small to be measured.

As pointed out by Sholl [16], the dimensionality of motion may be studied via the frequency dependence of $\Gamma_{1,\mathrm{dip}}$ on the high-temperature side of the $\Gamma_{1,\mathrm{dip}}$ maximum. Whereas in the low-temperature limit ($\omega_L \tau_d \gg 1$) the frequency dependence $\Gamma_{1,\mathrm{dip}} \propto \omega_L^{-2}$ is independent of the dimensionality, in the high-temperature limit ($\omega_L \tau_d \ll 1$) it is different for one-, two- and three-dimensional diffusion:

$$1\text{ dim: } \Gamma_{1,\mathrm{dip}} = e\tau_d^{1/2}\omega_L^{-1/2} \tag{3a}$$

$$2\text{ dim: } \Gamma_{1,\mathrm{dip}} = -c\tau_d \ln\omega_L \tag{3b}$$

$$3\text{ dim: } \Gamma_{1,\mathrm{dip}} = a\tau_d - b\tau_d^{3/2}\omega_L^{1/2} \tag{3c}$$

The proportionality constants $e$, $c$, $a$ and $b$ depend on the particular model of hopping motion on a given network of atomic sites. These formulae are also valid for $\Gamma_{1,\rho}$, except for a small additional term due to the relaxation in the static field, which is independent of $\omega_1$. An illustrative explanation of Eqs. (3a)–(3c) can be found in [17], where for the first time indications of two-dimensional diffusion in a metal hydride were obtained from the frequency dependence of $\Gamma_1$.

Since the structure of ZrClH$_{0.5}$ suggests two-dimensional hydrogen diffusion, frequency dependent measurements of $\Gamma_{1,\rho}$ have been performed on the high-temperature side of the main $\Gamma_{1,\rho}$ peak. The amplitude of the rotating field $B_1$ has been varied between 2.5 G and 25 G, which corresponds to resonance frequencies of $\omega_1/2\pi = 10$–$100$ kHz. Fig. 3 shows a plot of the dipolar contribution $\Gamma_{1,\rho} - \Gamma_{1,e}$ vs. frequency for several temperatures between 384 and 455 K. Within the entire range the condition for the high-temperature limit $\omega_1\tau_d \ll 1$ is fulfilled. (At the lowest temperature $T = 384$ K and highest resonance frequency $\omega_1/2\pi = 100$ kHz, $\omega_1\tau_d \approx 0.1$ has been estimated.) The solid lines in Fig. 3 indicate that the observed frequency dependence agrees with that expected for two-dimensional diffusion. According to Eq. (3b) the slopes of these curves

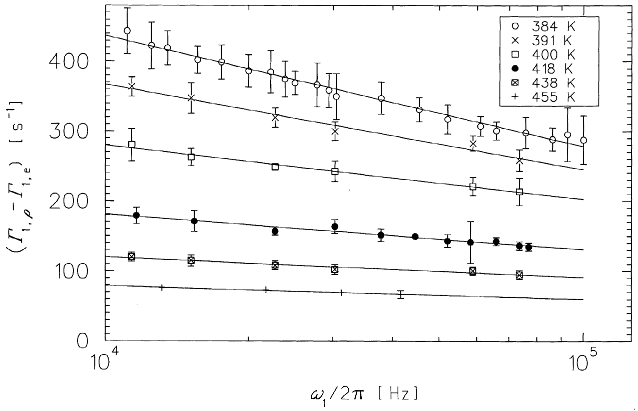

Fig. 3. Frequency dependence of the dipolar contribution to $\Gamma_{1,\rho}$ in ZrClH$_{0.5}$ at several temperatures on the high temperature side of the main $\Gamma_{1,\rho}$ peak. The electronic relaxation $\Gamma_{1,e} = T$ (370 Ks)$^{-1}$ has been subtracted from the measured data. A logarithmic scale of the frequency axis was chosen to prove Eq. (3b) for two-dimensional diffusion. The solid lines are least square fits to this frequency dependence.

are proportional to $\tau_d$. The observed temperature dependence of the slopes is well described by an Arrhenius law, as is expected for a thermally activated diffusion mechanism. This confirms the self-consistency of the analysis of the $\Gamma_{1,\rho}$ data within the framework of a two-dimensional model. Moreover, the corresponding activation enthalpy $H_a = 0.47 \pm 0.02$ eV is in good agreement with the PFG results (see below).

In order to investigate whether, based on the $\Gamma_{1,\rho}$ data, models of one- or three-dimensional diffusion may be excluded, the frequency dependence was also analyzed in terms of Eq. (3a) and (3c). Indeed, the frequency dependence of $\Gamma_{1,\rho}$ can be described by Eq. (3a) for one-dimensional diffusion reasonably well. However, the $\tau_d$ values obtained from such an analysis scatter widely and show no systematic behavior. A satisfactory representation of the $\Gamma_{1,\rho}$ data in terms of a three-dimensional model is not possible.

The long-range diffusion of hydrogen in $ZrClH_x$ ($x = 0.5, 1.0$) has been studied by PFG-NMR in the temperature range between 470 and 700 K. A typical example for the variation of the echo amplitude $M(G)$ with $G^2$ is shown in Fig. 4 (cf., Eq. (1)). The applied field gradient $G$ was varied in 19 steps between 0 and 25 $\mathrm{Tm}^{-1}$. For isotropic diffusion, such a plot yields a straight line whose slope gives the diffusion constant (compare the dash–dotted line in Fig. 4). A pronounced deviation from an exponential dependence of $M(G)$ on $G^2$ is expected in powdered samples in which anisotropic diffusion occurs within each grain particle and this, indeed, has been observed. As discussed below, the observed deviations are consistently described by the picture that in $ZrClH_x$ the hydrogen atoms diffuse more readily in the planes formed by the Zr bilayers than in the direction perpendicular to these planes.

If the z axis is assumed to be normal to the plane formed by the Zr bilayers, $D_z$ denotes the diffusion constant in this direction and $D_{xy}$ the diffusivity within the plane. For a single particle, $\theta$ is the angle between the direction of the applied magnetic field gradient and the z axis. Only motion along the gradient direction contributes to the echo attenuation in a PFG experiment. Therefore, the effective diffusion constant along the gradient direction (see, e.g. [18])

$$D_{\mathrm{eff}} = D_{xy} \sin^2\theta + D_z \cos^2\theta \tag{4}$$

has to be considered. Generalizing Eq. (1) to account for random orientations of the xy planes with respect to the applied field gradient gives

$$M(G) = M_0 \int_0^{\pi/2} \exp\left[ -(D_{xy} \sin^2\theta + D_z \cos^2\theta)\gamma^2\delta^2 \times \left(\Delta - \frac{\delta}{3}\right)G^2 \right] \sin\theta \, d\theta. \tag{5}$$

The solid line in Fig. 4 is a fit of Eq. (5) to the experimental data under the assumption that the diffusion is fully restricted to the xy plane (i.e., $D_z = 0$). The fit curve corresponds to $D_{xy} = 7.5 \cdot 10^{-11}\ \mathrm{m^2\,s^{-1}}$, and the quality of the fit indicates that $D_z \approx 0$ is a reasonable assumption. An attempt to analyze the data in terms of a one-dimensional model ($D_{xy} = 0$, $D_z \neq 0$) was not successful. This gives another indication that the hydrogen diffusion is restricted to two dimensions within the Zr metal bilayers. The same behavior was observed in all PFG measurements on both samples; the deduced diffusivities $D_{xy}$ are shown in Fig. 5. For $ZrClH_{0.5}$ an activation enthalpy of $H_a = 0.49 \pm 0.02$ eV was obtained by fitting an

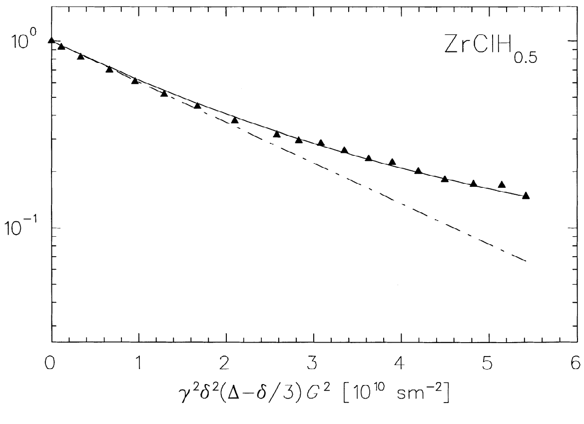

Fig. 4. Amplitude of the nuclear spin-echo as a function of $G^2$ in a typical PFG experiment. The data were taken on $ZrClH_{0.5}$ at $T = 683$ K. The fit curve (solid line) yields $D_{xy} = 7.5 \cdot 10^{-11}\ \mathrm{m^2\,s^{-1}}$ for the two-dimensional diffusion. The dash–dotted line indicates the relation that is expected for three-dimensional diffusion.

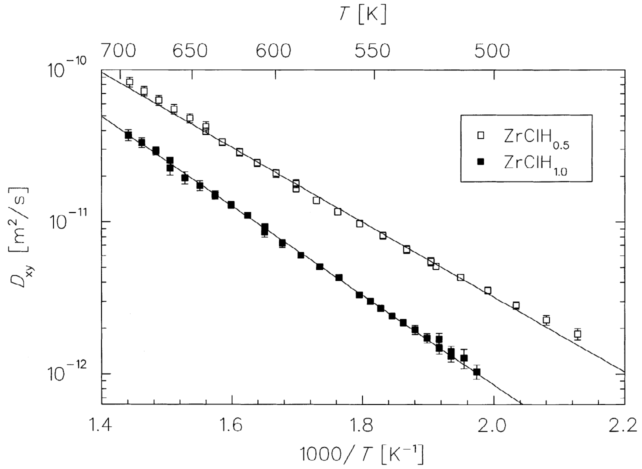

Fig. 5. Temperature dependence of the diffusivities $D_{xy}$ of hydrogen in the planes formed by the Zr bilayers in $ZrClH_{0.5}$ and $ZrClH_{1.0}$. The solid lines represent Arrhenius fits with $H_a = 0.49$ eV and $D_0 = 2.7 \cdot 10^{-7}\ \mathrm{m^2\,s^{-1}}$ for $ZrClH_{0.5}$ and $H_a = 0.58$ eV and $D_0 = 6.4 \cdot 10^{-7}\ \mathrm{m^2\,s^{-1}}$ for $ZrClH_{1.0}$.

Arrhenius expression to the $D_{xy}$ data. This value is in good agreement with $H_a$ deduced from the frequency dependence of $\Gamma_{1,\rho}$. It is interesting to note that the Arrhenius plot shows a very small but systematic curvature, which might indicate the onset of a low-temperature process with smaller activation enthalpy. Such a process would also explain the shoulders in the $\Gamma_1$ and $\Gamma_{1,\rho}$ curves. In the case of $ZrClH_{1.0}$ the diffusivities $D_{xy}$ are well described by an Arrhenius law, with $H_a = 0.58 \pm 0.02$ eV.

The activation enthalpy of hydrogen diffusion can in principle also be deduced from the temperature dependence of the relaxation rates. Unfortunately, in the case of $ZrClH_{0.5}$ the shoulders in the $\Gamma_1$ and $\Gamma_{1,\rho}$ curves on the low-temperature side of the main peaks (cf. Fig. 2) limit the temperature range accessible to such an analysis. Furthermore, the electronic contribution, $\Gamma_{1,e}$, has to be extrapolated from low temperatures, which introduces uncertainties in the determination of $H_a$ from $\Gamma_1$ data. A fit of the Bloembergen–Purcell–Pound (BPP) model [19], that was originally proposed for isotropic diffusion in liquids, to both $\Gamma_1$ (for 410 K$\leq T \leq$600 K) and $\Gamma_{1,\rho}$ (for 280 K$\leq T \leq$550 K) yields $H_a \approx 0.36$ eV. This value is in good agreement with $H_a = 0.35$ eV that has been deduced in [6] from $\Gamma_1$ and $\Gamma_{1,\rho}$ data also using a BPP model. $H_a = 0.40$ eV was obtained from high-temperature line narrowing data [6]. The values obtained from the frequency dependence of $\Gamma_{1,\rho}$, $H_a = 0.47$ eV, and from PFG-NMR, $H_a = 0.49$ eV, are substantially higher. On the other hand, the BPP model is unsatisfactory in both amplitude and functional form for two-dimensional systems [20]. Relaxation models for two-dimensional lattice diffusion have been developed in recent years (see, e.g., [20–25]). Since none of these models consider the crystal structure of $ZrClH_x$, the data were analyzed using the spherically averaged results of mean-field calculations for a single plane of spins on a square lattice [20]. In the framework of this model, the $\Gamma_1$ and $\Gamma_{1,\rho}$ data can be reasonably well described with an activation enthalpy of $H_a \approx 0.47$ eV.

In $ZrClH_{1.0}$ $\Gamma_1$ studies at 27.7 MHz and 67.7 MHz and $\Gamma_{1,\rho}$ studies at 50 kHz were performed between 300 and 550 K. For both frequencies the temperatures of the $\Gamma_1$ maxima are found to be above this temperature range. This indicates a reduced hydrogen diffusivity in $ZrClH_{1.0}$ compared to $ZrClH_{0.5}$, in which the $\Gamma_{1,dip}$ maximum at 27.7 MHz has been observed at 500 K (cf. Fig. 2). A substantially smaller hydrogen diffusivity $D_{xy}$ in $ZrClH_{1.0}$ than in $ZrClH_{0.5}$ follows also from the PFG measurements that are shown in Fig. 5. The decrease in $D_{xy}$ is found to be due to an increase in the activation enthalpy from $H_a =$ 0.47 eV for $ZrClH_{0.5}$ to $H_a = 0.58$ eV for $ZrClH_{1.0}$. This increase in $H_a$ may be ascribed to an almost completely filled sublattice of interstices in $ZrClH_{1.0}$. A similar increase in $H_a$ has been observed for hydrogen on the T-site sublattice in the zirconium dihydrides $ZrH_x$ as $x$ approaches the limiting concentration [14,26,27]. The $\Gamma_1$ and $\Gamma_{1,\rho}$ data of hydrogen in $ZrClH_{1.0}$ show no indications of any additional diffusion mechanisms, in contrast to what has been observed in $ZrClH_{0.5}$. The temperature dependence of the relaxation data can be well described by a BPP model with an activation enthalpy of $H_a = 0.59$ eV. This value is in good agreement with the PFG result, but, as discussed above, the BPP model may not be appropriate to these layer-structured systems. An analysis of the relaxation data is also possible by applying the model of spins on a square lattice [20]. This approach yields a significantly higher activation enthalpy of $H_a \approx 0.8$ eV.

## 4. Summary and conclusion

The mechanism of hydrogen motion in $ZrClH_x$ ($x = 0.5$, 1.0) has been investigated by different NMR techniques. Previous NMR studies indicated two mechanisms of hydrogen motion in $ZrClH_{0.5}$ [6]. In the present work, $\Gamma_1$ and $\Gamma_{1,\rho}$ measurements were performed over extended ranges in temperature and frequency and revealed three essentially independent processes of hydrogen motion in $ZrClH_{0.5}$.

The frequency dependence of $\Gamma_{1,\rho}$, measured at seven temperatures on the high-temperature side of the main $\Gamma_{1,\rho}$ peak, gives clear evidence that the long-range hydrogen diffusion is confined to two dimensions. The activation enthalpy observed for this process is $H_a = 0.47$ eV.

As outlined in Section 1, the T-sites in $ZrClH_{0.5}$ form chains and every second chain is occupied by hydrogen atoms, while the other chains are empty (see Fig. 1(c)). Hydrogen jumps to vacancies along an otherwise filled chain of T-sites certainly contribute to long-range diffusion. In order to explain the two-dimensionality of long-range diffusion, exchange mechanisms between the filled chains have to be considered. To get to a vacancy in a neighboring chain of occupied T-sites, the hydrogen atoms have to pass two T-sites in the intermediate empty chain. The distance between an occupied T-site and an immediate neighboring one in an empty chain is substantially shorter than that between T-sites within the chains. Thus it can be assumed that the barrier heights for jumps off a chain are smaller then for jumps within a chain and that hydrogen atoms already perform such jumps quite frequently at low temperatures. If a hydrogen atom jumps into an empty chain it may proceed to a neighboring T-site within the same chain on condition that this T-site is adjacent to a vacancy in the next filled chain. Since this jump is essentially equivalent to a jump on a filled chain, a similar value for the activation enthalpy is expected. Finally, the hydrogen atom may jump into the vacancy, which completes the motion from one filled chain to another (see Fig. 1(c)). Such processes also contribute to long-range diffusion and explain the two-dimensional character of hydrogen motion. If, on the other hand, there is no vacancy in the neighboring filled chain of T-sites, the only possible jump from the intermediate site in the empty chain is back to the vacancy from which it came. Such processes of localized motion give rise to additional spin-lattice relaxation and may explain the observed low-temperature shoulders in $\Gamma_1$ and $\Gamma_{1,\rho}$, but they do not manifest themselves in PFG measurements. A similar mechanism with O-sites as intermediate sites can be assumed in order to explain the second shoulder in the $\Gamma_1$ data.

The spin-lattice relaxation rates $\Gamma_1$ and $\Gamma_{1,\rho}$ measured in $ZrClH_{1.0}$ reveal a strongly reduced hydrogen mobility and indicate a single mechanism of hydrogen motion. The observed two-dimensional diffusion mechanisms may easily be interpreted by a vacancy mechanism in an almost filled sublattice. It cannot be decided on the basis of the present data whether the almost filled sublattice results from the occupation of essentially all T-sites or from the occupation of the O-sites by hydrogen pairs, similar to what has been observed in $ZrBrD_{1.0}$ [10]. But the interpretation given above is independent of the actual structure of the two-dimensional sublattice in $ZrClH_{1.0}$.

In addition to the relaxation measurements, the long-range diffusivity $D_{xy}$ of hydrogen in $ZrClH_x$ ($x = 0.5$, 1.0) has been measured directly by PFG-NMR. The relation between the echo amplitude and the applied magnetic field gradient confirms the two-dimensional character of hydrogen diffusion within the Zr bilayers in $ZrClH_x$ ($x = 0.5$, 1.0). The activation enthalpies of $H_a = 0.49$ eV and 0.58 eV have been obtained by fitting an Arrhenius expression to the diffusivities $D_{xy}$ of hydrogen in $ZrClH_{0.5}$ and $ZrClH_{1.0}$, respectively.

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