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Deuterium Exchange Dynamics in Zr$_2$NiD$_{4.8}$ Studied by $^2$H MAS NMR Spectroscopy

Chul Kim$^{1,2}$, Son-Jong Hwang$^{1,*}$, Robert C. Bowman, Jr.$^3$, Magnus H. Sørby$^4$, and Bjørn Hauback$^4$

$^1$Div of Chem. and Chem Eng, California Institute of Technology, California 91125, USA.
$^2$Department of Chemistry, Hannam University, Daejeon, Korea, 305-811
$^3$RCB Hydrides, LLC, Franklin OH 45005, USA
$^4$Physics Department, Institute for Energy Technology, P.O. Box 40, NO-2027, Kjeller, Norway,
E-mail of the corresponding author: sonjong@cheme.caltech.edu

ABSTRACT

Variable temperature (VT) $^2$H magic angle spinning (MAS) spectroscopy was employed to measure deuterium diffusion behavior in the Zr$_2$NiD$_{4.8}$ phase. $^2$H MAS NMR spectrum at ~190 K provides with well-resolved 4 different site occupancies which can be assigned based on the crystal structure (16k (Zr$_2$Ni$_2$), 32m (Zr$_3$Ni), Zr$_4$ (16l and 4b)). As the temperature rises, the $^2$H peaks sensitively reflect the exchange behavior among the sites with evident change at around 230 K and reaching a uniform distribution of site occupancies, indistinguishable in NMR timescale, above 245 K. This behavior is reflected by the collapse of the $^2$H MAS spectrum into a single peak. From analyses of VT MAS NMR spectra, we were able to extract multiple hopping rates and activation energies among face sharing interstices: for example, 32m ↔ 16l hopping shows $\tau_c = 2.8 \times 10^{-4}$ s at 245 K and $E_a = 62.2$ kJ/mol.

INTRODUCTION

Metal hydrides are suitable for a plethora of applications including hydrogen fuel storage for stationary systems and vehicles, heat pumps and refrigerators, compressors, batteries, getters and purifiers, and others [1-3]. The choice of a hydride for any specific use involves various factors in addition to its net hydrogen content and thermodynamic properties [3]. The kinetics of the hydrogen absorption and desorption processes will often determine the conditions for successful and efficient operation of proposed devices. Knowledge of the hydrogen diffusion parameters can provide valuable insights during selection and development of appropriate candidates in addition to gaining better understanding of the role of crystal structures and compositions on the fundamental transport mechanisms in the hydride phases [4, 5].

Nuclear magnetic resonance (NMR) provides information on both local (e.g., hops among a few closely separated sites or rotations of covalently bonded ions) and long-range (e.g., translations) motions from behavior of spectra and several kinds of relaxation times as described in various reviews [6, 7]. The most common approach to obtain diffusion parameters using NMR is to measure the spectra or relaxation times over a temperature range appropriate for a given hydride, which are generally analyzed by well-developed microscopic models based upon an Arrhenius
relations [6] with an attempt frequency and activation energy ($E_a$). Over the years, NMR studies have been performed on nearly all binary metal hydrides and many intermetallic and alloy hydrides [4, 5, 6, 7]. Unfortunately, these measurements are often insufficient to give more detailed assessments of the specific roles from multiple H-site occupancies on the diffusion processes in the more complicated host structures.

Although the ZrNiH$_x$ phases are the earliest known intermetallic hydrides and have been used for a number of novel applications [8, 9], their diffusion behavior was not investigated until rather recently [8, 10]. Both the nuclear relaxation times and deuteron magic angle spinning (MAS) spectra were employed on samples of ZrNiH$_x$ and ZrNiD$_x$ with $x$-values of ~1.0 and ~3.0. The orthorhombic ZrNi (space group $C_{mcm}$) forms two distinct hydrides: triclinic $\beta$-ZrNiH(D)$_{~1}$ and orthorhombic $\gamma$-ZrNiH(D)$_{~3}$ where the hydrogen isotopes occupy Zr$_4$ and Zr$_4$Ni$_2$ interstitial sites in the $\beta$-hydride [11] and Zr$_3$Ni and Zr$_2$Ni$_2$ sites in the $\gamma$-phase [12]. With the revised determination [13] of the crystal structure for the triclinic Zr$_2$NiD$_{4.5}$ phase with deuterium located in two types of Zr$_4$ sites and a Zr$_3$Ni site, a more in depth NMR study than the one published 25 years ago on Zr$_2$NiH$_x$ by Aubertin, et al. [14] was felt desirable now with the objective of improving understanding the roles of crystal structure and hydrogen site occupancies on diffusion mechanisms. The approach used in the present work was to follow the behavior of motion from the resolved high-resolution $^2$H MAS spectra over a wide temperature range on the Zr$_2$NiD$_{4.8}$ material previously characterized by powder neutron diffraction [15].

**Experimental Method**

A Zr$_2$NiD$_{4.8}$ crystalline sample that was employed for structural studies [13, 15] was crushed gently using a mortar and a pestle and ground together with fused quartz powder (SiO$_2$, 1:1 weight ratio) since the metal hydride in raw form causes severe probe detuning during MAS NMR experiments [16]. The powder mixture was loaded into a 4 mm ZrO$_2$ rotor. Sample processing was performed in a glove box with a purified argon atmosphere. ZrO$_2$ rotor cap was

![Figure 1](image-url)  
*Figure 1.* Experimental $^2$H variable temperature MAS NMR spectra of Zr$_2$NiD$_{4.8}$, four types of tetrahedral interstices determined from the crystal structure (Zr: yellow spheres, Ni: cyan spheres [see reference [13]]), and a proposed deuterium hopping sequence among interstices.
employed for variable temperature (VT) MAS experiments that underwent sample cooling down to 193 K using dry N\(_2\) gas and a heat exchanger with a liquid nitrogen bath. Solid-state \(^2\)H MAS NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer with an 11.7 T (76.79 MHz for \(^2\)H) magnet and a Bruker 4 mm MAS probe. Signal was collected after a 2 \(\mu\)s rf pulse and sample was spun at 7 kHz. The temperature range was 193 – 310 K. Lab written Matlab code based on the Levenberg-Marquardt [17, 18] fitting algorithm was used to fit \(^2\)H MAS NMR lineshapes at each temperature under an exchange model. NMR shifts were referenced externally to pristine D\(_2\)O (Cambridge Isotope Laboratory) at 0 ppm.

Results and Discussion

\(^2\)H MAS NMR of Zr\(_2\)NiD\(_{4.8}\) Figure 1 shows \(^2\)H MAS NMR spectra recorded at variable temperatures in the 193K-290K range for a Zr\(_2\)NiD\(_{4.8}\) crystalline powder. There is single sharp peak at -18.8 ppm near room temperature (290 K), and narrowed by two times (full width at the half maximum, fwhm ~ 274 Hz to 136 Hz) upon slight temperature increase to 310 K (spectrum not shown in Fig. 1), indicating an active motional narrowing of the deuterium resonance. Cooling of the sample unveiled separate resonances showing two broad peaks at 235 K, four peaks at 220 K, and finally further splitting into 5 different peaks at temperatures below 210 K. The observed variation is in accordance with a typical exchange NMR spectrum with decreasing diffusion of deuterium atoms, or chemical exchange, among inequivalent deuterium occupation sites. Although Fig. 1 focuses on displaying of the centerband of deuterium resonances, there are spinning sidebands appearing at integral multiples of the sample spinning rate (7 kHz) at lower temperatures, which is due to revival of anisotropic interaction of deuterium atoms, reflecting quadrupole interactions. Peak integration estimates the contributions of sidebands to be about 20% of total deuterium signal. The intensity patterns of sidebands look nearly identical to that of the centerband, indicating no distinctive differences in deuterium coordination environments. The spectral broadening was treated as the quadrupole interaction of deuterium atoms (dipolar broadening or shift anisotropy is much weaker), and measured the quadrupole constant \(C_Q = eq^2Q/h\), when the MAS spectra were fitted using DMFIT [19] software. The relative intensity ratio among resonances at 193 K was 0.20:0.48:0.10:0.11:0.11 for -4.0, -13.9, -28.1, -30.6, and -37.1 ppm peaks, respectively, as listed in Table I.

To our best knowledge, there has not been prior \(^2\)H NMR investigation of Zr\(_2\)NiD\(_x\) with this specific composition. In an effort of explaining deuterium resonances of Zr\(_2\)NiD\(_{4.8}\), we mainly rely on deuterium sites determined by previous crystal structure studies. There are four different tetrahedral interstices available within the Zr\(_2\)Ni phase [13, 19, 20]. They have Wyckoff positions 16l, 4b, 32m, and 16k (space group I4/mcm), with the first two coordinated by four Zr atoms, namely Zr\(_4\) sites, while Ni atom positions the corner of tetrahedron to make Zr\(_3\)Ni and Zr\(_2\)Ni\(_2\) sites for 32m and 16k, respectively (see Fig. 1). Note that these Wyckoff positions will be

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
shift (ppm) & C\textsubscript{q} (kHz) & Line width (Hz) & intensity & ratio & T>235 K \\
\hline
-4.0 & 12.6 & 220 & 0.20 & & \\
-13.9 & 12.76 & 300 & 0.49 & 0.67 & \\
-28.1 & 12 & 178 & 0.10 & 0.33 & \\
-30.6 & 15.12 & 172 & 0.11 & & \\
-37.1 & 12.91 & 187 & 0.11 & & \\
\hline
\end{tabular}
\caption{\(^2\)H resonances and site occupation ratios}
\end{table}
used to denote the interstitial sites in the deuteride, even if the space group symmetry is reduced to $P_I$ due to a slight triclinic deformation on deuteration. Total of 68 sites are available in the unit cell for deuterium occupation, and our sample Zr$_2$NiD$_{4.8}$ then has 19.2 deuterium atoms occupied. In the literature, tetrahedral sites such as Zr$_3$Ni show $^2$H resonances at around -11 ppm [12] while addition of Ni tends to move the shift to the downfield (toward positive in the ppm scale). We assign the -13.9 ppm peak in our $^2$H MAS NMR data to deuterium in the Zr$_3$Ni site ($32m$). Addition or subtraction of Ni atom from the Zr$_3$Ni site is expected to move the $^2$H peak position similarly either to downfield or to upfield. Then, it is logical to assign the -4.0 ppm peak to the Zr$_2$Ni$_2$ ($16k$) while the further upfield peaks to the Zr$_4$ sites ($16l$ and $4b$). On the other hand, the site occupancy information of Zr$_2$NiD$_{4.5}$ [13] indicated that 10, 6, and 2 sites are filled or $32m$, $16l$, $4b$ sites, respectively. In another report [15], the deuterium distribution in a more disordered sample Zr$_2$NiD$_{4.8}$, with the excess 0.3 D/formula unit (f.u.), did indicate a slight occupation of the 16k, and the same was also suggested by Chekdene et al [21]. As shown in Table I, the most abundant resonance is the -13.9 ppm peak and its occupancy is 9.3 according to the Zr$_2$NiD$_{4.8}$ formula. The intensity data is in good agreement with 10 site-filling of the Zr$_3$Ni ($32m$) sites. The -37.1 ppm peak explains 2.0 site-filling while two closely positioned peaks at -28.1 and -30.6 ppm contribute 4.1 occupancies, which allow us to assign the Zr$_4$ sites separately into $4b$ and $16l$, respectively. In order to describe the VT behavior of two peaks, we further separate the 16l site into 16l' (-28.1 ppm) and 16l (-30.6 ppm). In this assignment, our NMR data reports 2:4.1 in occupancy ratio (see Table I) for two Zr$_3$ sites ($4b$ and $16ls$), which is noticeably different from the 2:6 of the Zr$_2$NiD$_{4.5}$ [13]. In addition, the Zr$_2$Ni$_2$ ($16k$) sites (-4.0 ppm) show the deuterium site filling of 3.8, which is unexpectedly high in contrast to zero occupancy for the Zr$_2$NiD$_{4.5}$ sample. Therefore, it would be highly interesting to closely monitor such transition. At this point, we can only speculate that the excess 0.3D/f.u. (Zr$_2$NiD$_{4.5}$ $\rightarrow$ Zr$_2$NiD$_{4.8}$) did appear to redistribute the deuterium filling somewhat. Overall, we believe that our $^2$H MAS NMR data represent inequivalent deuterium sites very clearly and measure accurately the occupancies to over four different types of tetrahedral Zr$_{4-y}$Ni$_y$ (0$\leq$y$\leq$2) sites.

**Deuterium hopping mechanism among tetrahedral sites**

$^2$H VT MAS NMR data seen in Fig. 1 don’t reflect simple step wise hopping behavior among separate deuterium sites as manifested due to the lack of new peaks at the mass weighted positions. For example, 16l peak disappeared near 220 K while there was no clear movement of other peaks except the slight upfield shift of the 32m peak. Similarly, 4b and 16k sites disappeared at 225 K and 235 K, respectively, while merging into broadened 32m and 16l sites. After this point, a typical exchange behavior was observed between the two sites as the two peaks coalesced into one peak at 245 K. This allows us to roughly estimate the hopping rate from $\tau_c^{-1} = \Delta\omega/\sqrt{2}$ relation, and calculated value is $\tau_c = 2.06 \times 10^{-4} s$ with $\Delta\omega$=1094 Hz for the frequency splitting between two sites. More detailed exchange information among deuterium sites was sought by establishing a model (see Fig. 1) based on the crystal structure. For example, the 4b sites share a tetrahedral face only with 16l (both 16l and 16l' in NMR peaks) sites [13] and so deuterium in 4b sites can exchange with the 16l sites. In the same way, deuterium occupying 16k sites can hop to 32m sites, vice versa, as they share two faces. The 32m sites contain one face sharing tetrahedron with 16l sites.

Overall, it was possible to simulate the experimental $^2$H MAS NMR lineshapes at variable temperatures reasonably as displayed in Fig. 2. The exchange rate constants showed linear dependence over the temperature range as shown in the Arrhenius plots in Fig. 2. Two examples
of Arrhenius plots, $16k \leftrightarrow 32m$ and $32m \leftrightarrow 16l$, are presented here. The activation energies of various deuterium site exchanges and the correlation times for the deuterium hoping among 5 interstitial sites were compiled in Table II. The correlation times for the deuterium hopping were $10^{-3} \sim 10^{-4}$ s at 245 K. The activation energies in Table II seem to be scattered widely. To our best knowledge, the only prior study of diffusion for Zr$_2$NiD$_x$ systems was the perturbed angular correlation (PAC) experiments performed by Baudry, et al [22] for x~5. They reported an activation energy above room temperature for Zr$_2$NiD$_5$ that was similar to the value from PAC [21] and NMR [14] measurements on Zr$_2$NiH$_{4.8}$ with an additional lower value of $\sim$10 kJ/mol from an unidentified motion in the deuteride. We believe that our attempt in extracting the diffusion parameters from multiple sites via MAS-NMR of $^2$H nuclei is unique in metal hydride studies. Due to limited information, we arbitrarily divide $E_a$ values in Table II into two groups, low and high values. One of low activation energies (i.e. $E_a$=35.2 kJ/mol) measured for $16k \leftrightarrow 32m$ is in good agreement with the observation of highly mobile H atoms [23] due to $16k$ site filling in Zr$_2$NiH$_{4.8}$ system. There was non-site specific activation energy of 30.9 kJ/mol reported for Zr$_2$NiH$_{4.5}$ [14]. We saw no evidence during our study for motions with $E_a$ of $\sim$10 kJ/mol as reported previously by the PAC experiments [21, 22]. On the other hand, $E_a > 60$ kJ/mole were obtained for proton jumping directly between the Zr$_4$ sites in ZrH$_x$ (1.58 kJ/mol $\leq x \leq$1.98 kJ/mol) by NMR measurements on ZrH$_x$ samples [24]. Hence, the $E_a$ values of 60~ 80 kJ/mol determined in our study seem reasonable for direct jumps from Zr$_4$ sites to either other Zr$_4$ or

Figure 2. NMR data and site hopping rate calculations of Zr$_2$NiD$_{4.8}$. (a) Experimental $^2$H VT MAS NMR spectra and $^2$H MAS NMR spectra simulated with an exchange model proposed (see Fig. 1). The exchange rate constants (k) obtained for $16k \leftrightarrow 32m$ and $32m \leftrightarrow 16l$ site hopping, and the Arrhenius fit for activation energy calculation.
Table II. Activation energies and correlation times for deuterium diffusion between two face-sharing tetrahedral sites.

<table>
<thead>
<tr>
<th></th>
<th>16k ↔ 32m</th>
<th>32m ↔ 16l'</th>
<th>32m ↔ 16l</th>
<th>16l' ↔ 4b</th>
<th>16l ↔ 4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>35.2 ± 1.6</td>
<td>80.2 ± 4.1</td>
<td>62.2 ± 3.5</td>
<td>28.7 ± 1.8</td>
<td>75.4 ± 20</td>
</tr>
<tr>
<td>$\tau_c$ (s) at 245 K</td>
<td>5.4 × 10^{-3}</td>
<td>1.3 × 10^{-3}</td>
<td>2.8 × 10^{-4}</td>
<td>6.7 × 10^{-3}</td>
<td>4.6 × 10^{-4}</td>
</tr>
</tbody>
</table>

Zr$_3$Ni sites. Furthermore, comparable activation energies were also found from ZrNiD$_{3.0}$ (59.8 kJ/mol) for jumps involving the Zr$_3$Ni and Zr$_3$Ni$_2$ sites in the $\gamma$-phase [8].

On one hand, we observe that the hopping between 16l' ↔ 4b showed the lowest activation energy of 28.7 kJ/mol in our Zr$_2$NiD$_{4.8}$ sample. On the other hand, the 16l site shows a higher $E_a$ value (75.4 kJ/mol) with the same 4b site. At the moment, we are not certain whether or not the discrepancy is mainly associated with the structural difference between 16l' and 16l sites. According to the crystal structure of Zr$_2$NiD$_5$ [13], there is an indication that 16l sites along the [011] direction show two types of filling patterns in the chain of so called “alternating face- and corner-sharing tetrahedral”. One type experiences about 50% of filling while the other type has more empty (25% filling) nearby sites. We believe it is not unreasonable to speculate that our 16l and 16l' sites might represent the two types to reveal the different behavior. Further investigation is needed to elucidate the exchange phenomena observed in this study.

Conclusions

We have investigated deuterium sites and exchange dynamics in Zr$_2$NiD$_{4.8}$ crystalline phase via $^2$H MAS NMR measurements over a wide range of temperatures (193K-310K). Based on inequivalent deuterium resonances resolved at temperature below 200 K, it was possible to quantify deuterium occupation over four different tetrahedral interstices of Zr$_2$Ni$_2$ (16k), Zr$_3$Ni (32m), and Zr$_4$ (16l, 4b). The ratio was found to be 3.8:9.3:4.1:2, which appeared to be larger redistribution of deuterium occupancy and greater filling of the 16k sites for the slightly more disordered Zr$_2$NiD$_{4.8}$ phase when compared to the ordered Zr$_2$NiD$_{4.5}$ phase. The activation energies and the correlation times for hopping among 5 different sites were measured from the line shape analysis of $^2$H VT MAS spectra. From these experiments, we were able to address the presence of site-specific variations in the diffusion parameters. Our data further confirm that the Zr$_2$NiD$_{4.8}$ phase contains more highly mobile deuterium than observed for the ZrNiD$_x$ phases [10] as indicated by low activation energy for the 16k ↔ 32m hopping.

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$^2$H VT MAS NMR determines the site occupancies and hopping motions of deuterium atoms among Zr$_4$ (4b, 16l), and Zr$_3$Ni (32m), and Zr$_2$Ni$_2$ (16k) interstices in Zr$_2$NiD$_{4.8}$.