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Deuterium Exchange Dynamics in $Zr_2NiD_{4.8}$ Studied by 2H MAS NMR Spectroscopy

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ABSTRACT

Variable temperature (VT) 2H magic angle spinning (MAS) spectroscopy was employed to measure deuterium diffusion behavior in the $Zr_2NiD_{4.8}$ phase. 2H 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_2Ni_2), $32m$ (Zr_3Ni), Zr_4 ($16l$ and $4b$)). As the temperature rises, the 2H 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 2H 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, $32m \leftrightarrow 16l$ 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 deuterium 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 β - $ZrNiH(D)_{-1}$ and orthorhombic γ - $ZrNiH(D)_{-3}$ where the hydrogen isotopes occupy Zr_4 and Zr_4Ni_2 interstitial sites in the β -hydride [11] and Zr_3Ni and Zr_3Ni_2 sites in the γ -phase [12]. With the revised determination [13] of the crystal structure for the triclinic $Zr_2NiD_{4.5}$ phase with deuterium located in two types of Zr_4 sites and a Zr_3Ni site, a more in depth NMR study than the one published 25 years ago on Zr_2NiH_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 2H MAS spectra over a wide temperature range on the $Zr_2NiD_{4.8}$ material previously characterized by powder neutron diffraction [15].

Experimental Method

A $Zr_2NiD_{4.8}$ 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

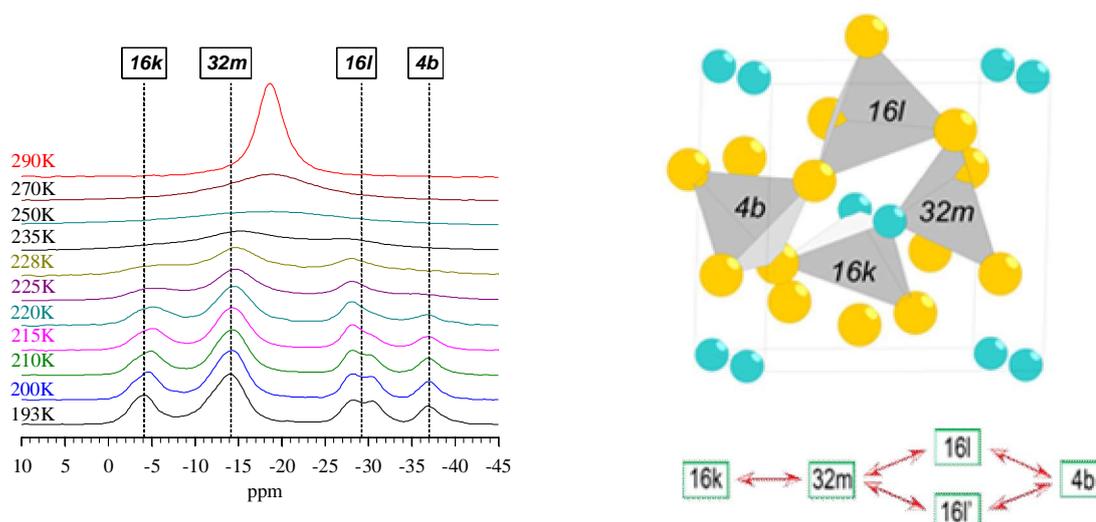


Figure 1. Experimental 2H variable temperature MAS NMR spectra of $Zr_2NiD_{4.8}$, four types of tetrahedral interstices determined from the crystal structure (Zr: yellow spheres, Ni: cyan spheres [see reference [13]]), and a proposed deuterium hopping sequence among interstices.

employed for variable temperature (VT) MAS experiments that underwent sample cooling down to 193 K using dry N₂ gas and a heat exchanger with a liquid nitrogen bath. Solid-state ²H MAS NMR spectra were recorded using a Bruker Avance 500 MHz spectrometer with an 11.7 T (76.79 MHz for ²H) magnet and a Bruker 4 mm MAS probe. Signal was collected after a 2 μs 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 ²H MAS NMR lineshapes at each temperature under an exchange model. NMR shifts were referenced externally to pristine D₂O (Cambridge Isotope Laboratory) at 0 ppm.

Results and Discussion

²H MAS NMR of Zr₂NiD_{4.8} Figure 1 shows ²H MAS NMR spectra recorded at variable temperatures in the 193K-290K range for a Zr₂NiD_{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

Table I. ² H resonances and site occupation ratios					
shift (ppm)	C _q (kHz)	Line width (Hz)	intensity T<220 K	ratio T>235 K	
-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		

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 ²H NMR investigation of Zr₂NiD_x with this specific composition. In an effort of explaining deuterium resonances of Zr₂NiD_{4.8}, we mainly rely on deuterium sites determined by previous crystal structure studies. There are four different tetrahedral interstices available within the Zr₂Ni 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 Zr₄ sites, while Ni atom positions the corner of tetrahedron to make Zr₃Ni and Zr₂Ni₂ sites for *32m* and *16k*, respectively (see Fig. 1). Note that these Wyckoff positions will be

used to denote the interstitial sites in the deuteride, even if the space group symmetry is reduced to P_1^- due to a slight triclinic deformation on deuteration. Total of 68 sites are available in the unit cell for deuterium occupation, and our sample $Zr_2NiD_{4.8}$ then has 19.2 deuterium atoms occupied. In the literature, tetrahedral sites such as Zr_3Ni show 2H 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 2H MAS NMR data to deuterium in the Zr_3Ni site ($32m$). Addition or subtraction of Ni atom from the Zr_3Ni site is expected to move the 2H peak position similarly either to downfield or to upfield. Then, it is logical to assign the -4.0 ppm peak to the Zr_2Ni_2 ($16k$) while the further upfield peaks to the Zr_4 sites ($16l$ and $4b$). On the other hand, the site occupancy information of $Zr_2NiD_{4.5}$ [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 $Zr_2NiD_{4.8}$, 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 $Zr_2NiD_{4.8}$ formula. The intensity data is in good agreement with 10 site-filling of the Zr_3Ni ($32m$) 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_4 sites ($4b$ and $16ls$), which is noticeably different from the 2:6 of the $Zr_2NiD_{4.5}$ [13]. In addition, the Zr_2Ni_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 $Zr_2NiD_{4.5}$ 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. ($Zr_2NiD_{4.5} \rightarrow Zr_2NiD_{4.8}$) did appear to redistribute the deuterium filling somewhat. Overall, we believe that our 2H 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

2H 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 2H 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

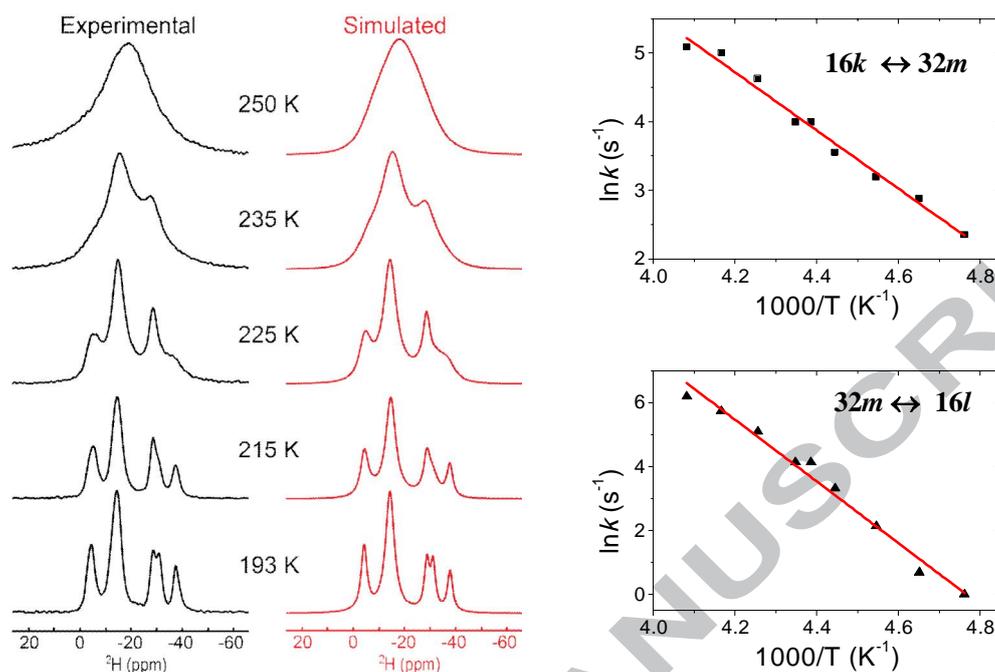


Figure 2. NMR data and site hopping rate calculations of $\text{Zr}_2\text{NiD}_{4.8}$. (a) Experimental ^2H VT MAS NMR spectra and ^2H MAS NMR spectra simulated with an exchange model proposed (see Fig. 1). The exchange rate constants (k) obtained for $16k \leftrightarrow 32m$ and $32m \leftrightarrow 16l$ site hopping, and the Arrhenius fit for activation energy calculation.

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 hopping 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_2NiD_x systems was the perturbed angular correlation (PAC) experiments performed by Baudry, et al [22] for $x \sim 5$. They reported an activation energy above room temperature for Zr_2NiD_5 that was similar to the value from PAC [21] and NMR [14] measurements on $\text{Zr}_2\text{NiH}_{4.8}$ with an additional lower value of ~ 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 ^2D 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 $\text{Zr}_2\text{NiH}_{4.8}$ system. There was non-site specific activation energy of 30.9 kJ/mol reported for $\text{Zr}_2\text{NiH}_{4.5}$ [14]. We saw no evidence during our study for motions with E_a of ~ 10 kJ 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 ($1.58 \text{ kJ/mol} \leq x \leq 1.98 \text{ kJ/mol}$) 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

Table II. Activation energies and correlation times for deuterium diffusion between two face-sharing tetrahedral sites.

	$16k \leftrightarrow 32m$	$32m \leftrightarrow 16l'$	$32m \leftrightarrow 16l$	$16l' \leftrightarrow 4b$	$16l \leftrightarrow 4b$
E_a (kJ/mol)	35.2 ± 1.6	80.2 ± 4.1	62.2 ± 3.5	28.7 ± 1.8	75.4 ± 20
τ_c (s) at 245 K	5.4×10^{-3}	1.3×10^{-3}	2.8×10^{-4}	6.7×10^{-3}	4.6×10^{-4}

Zr₃Ni sites. Furthermore, comparable activation energies were also found from ZrNiD_{3.0} (59.8 kJ/mol) for jumps involving the Zr₃Ni and Zr₃Ni₂ sites in the γ -phase [8].

On one hand, we observe that the hopping between $16l' \leftrightarrow 4b$ showed the lowest activation energy of 28.7 kJ/mol in our Zr₂NiD_{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 Zr₂NiD₅ [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 Zr₂NiD_{4.8} crystalline phase via ²H 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 Zr₂Ni₂ ($16k$), Zr₃Ni ($32m$), and Zr₄ ($16l$, $4b$). 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 Zr₂NiD_{4.8} phase when compared to the ordered Zr₂NiD_{4.5} phase. The activation energies and the correlation times for hopping among 5 different sites were measured from the line shape analysis of ²H 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 Zr₂NiD_{4.8} phase contains more highly mobile deuterium than observed for the ZrNiD_x phases [10] as indicated by low activation energy for the $16k \leftrightarrow 32m$ hopping.

Acknowledgements

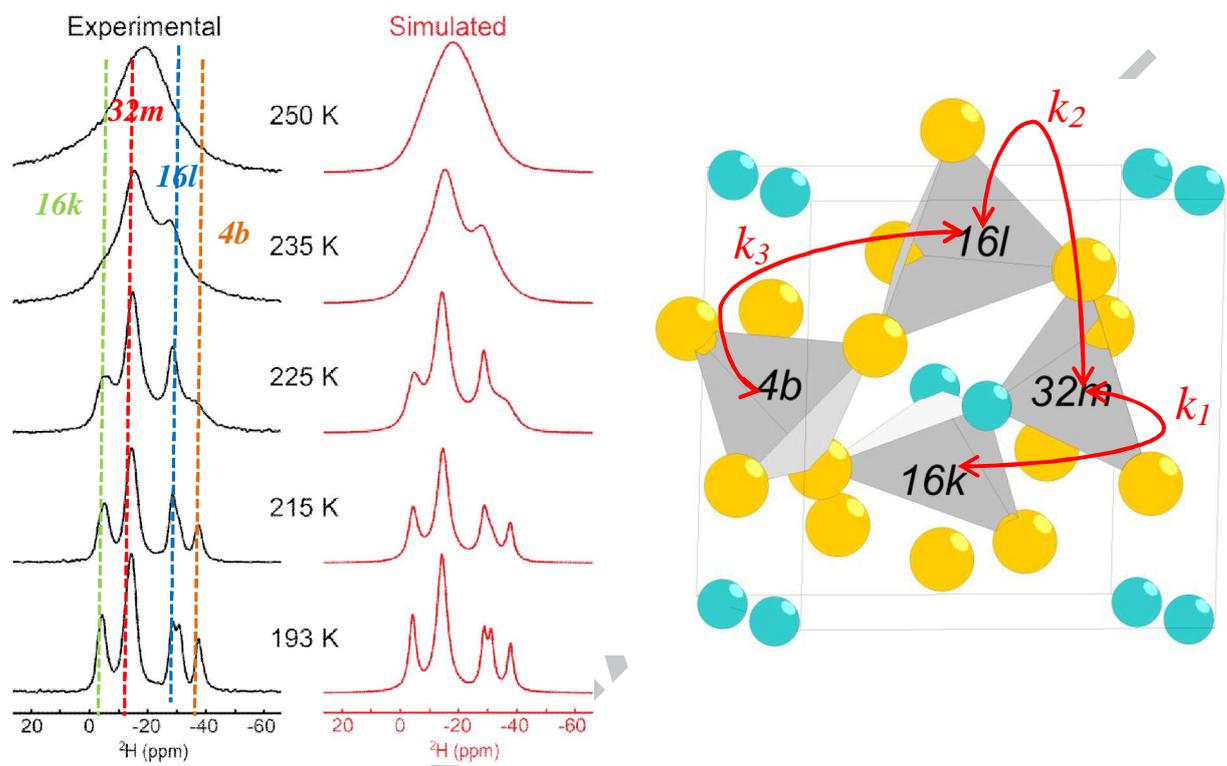
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^2H VT MAS NMR determines the site occupancies and hopping motions of deuterium atoms among Zr_4 ($4b$, $16l$), and Zr_3Ni ($32m$), and Zr_2Ni_2 ($16k$) interstices in $\text{Zr}_2\text{NiD}_{4.8}$.