

## NMR to determine rates of motion and structures in metal-hydrides

Mark S. Conradi<sup>a,\*</sup>, Michael P. Mendenhall<sup>a</sup>, Timothy M. Ivancic<sup>a</sup>, Erik A. Carl<sup>a</sup>,  
Caleb D. Browning<sup>a,1</sup>, P.H.L. Notten<sup>b,c</sup>, W.P. Kalisvaart<sup>c</sup>, Pieter C.M.M. Magusin<sup>c</sup>,  
R.C. Bowman Jr.<sup>d</sup>, Son-Jong Hwang<sup>e</sup>, Natalie L. Adolphi<sup>f</sup>

<sup>a</sup> Washington University, Department of Physics-1105, Saint Louis, MO 63130-4899, USA

<sup>b</sup> Philips Research Laboratories, Prof. Holstlaan 4, 5656 AE Eindhoven, NL, USA

<sup>c</sup> Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, NL, USA

<sup>d</sup> Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 79-24, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

<sup>e</sup> California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA 91125, USA

<sup>f</sup> New Mexico Resonance, Albuquerque, NM 87106, USA

Received 26 September 2006; accepted 16 November 2006

Available online 2 January 2007

### Abstract

Measurements of nuclear magnetic resonance (NMR) relaxation times allow the rates of H and D atomic hopping in metal-hydrides to be determined. A first example compares the rates of H hopping in  $\text{Mg}_{65}\text{Sc}_{35}\text{Pd}_{2.4}\text{H}_{220}$ , a promising new battery electrode and storage alloy, to  $\text{LaNi}_5\text{H}_x$  and to the end-members of the alloy system,  $\text{ScH}_2$  and  $\text{MgH}_2$ . The motion of  $\text{MgScH}$  is more rapid than in the metallic  $\text{ScH}_2$  and the ionic  $\text{MgH}_2$ , but slower than in  $\text{LaNi}_5\text{H}_x$ . Magic-angle spinning (MAS) NMR of metal-deuterides is a newer method that can resolve inequivalent D atoms and measure the rate of diffusive exchange between the sites. Examples include the tetrahedral and octahedral sites in  $\text{YD}_{2+x}$  and D in  $\text{ZrNiD}_x$ .

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Metal hydrides; Diffusion; Nuclear resonances

Nuclear magnetic resonance (NMR) is a powerful method for measuring the dynamics of atoms in solids and is particularly interesting for metal-hydrides and -deuterides. In this short review, two examples are discussed from the authors' groups.

### 1. MgSc hydrides

#### 1.1. Background

The research group at Philips/Eindhoven University has recently shown Mg–Sc alloys to be effective systems for hydrogen storage and metal-hydride battery electrodes [1–3]. The motivation behind this alloy system is to capture desirable features of both end-members. At one end,  $\text{MgH}_2$  has a high

hydrogen storage capacity of 7.6 wt%. However, the binding is of ionic character and this is believed to result in the very slow diffusion kinetics of H in  $\text{MgH}_2$ . At the other end is  $\text{ScH}_2$  with approximately 4.2 wt% storage but with the superior diffusion kinetics typical of interstitial metallic hydrides. The  $\text{H}_2$  equilibrium pressure [4] of the two-phase plateau region of  $\text{ScH}_x$  is very low at 1 Torr at 740 °C.

The Mg–Sc alloy hydrides take on the fluorite structure [3,5], as does  $\text{ScH}_2$ , for Mg fractions  $\leq 80\%$ . At higher Mg fractions the structure is rutile-like as for  $\text{MgH}_2$  and it appears the hydriding/dehydriding kinetics suffer markedly as a result. The fluorite-to-rutile structural transition may be driven by a change from metallic to ionic character. The fluorite-type MgSc hydrides show high storage capacity of 6.7 wt%, most of which is reversible, in approximate agreement with the view that the material can be hydrided up to an H-content equivalent to 2 H/Mg and 3 H/Sc. The expansion of the lattice is believed to allow partial occupation of the octahedral interstitial sites as the T–O distance in the fully hydrided state is roughly equal to the minimum of 2.1 Å dictated by the Westlake criterion [3]. Mg–Ti

\* Corresponding author. Tel.: +1 314 935 6292/6418; fax: +1 314 935 6219.

E-mail address: [msc@wuphys.wustl.edu](mailto:msc@wuphys.wustl.edu) (M.S. Conradi).

<sup>1</sup> Present address: Leggett and Platt, Inc., Carthage, MO, USA.

alloys have similar behavior to Mg–Sc, but should be much less costly [6,7].

We report here proton NMR relaxation times for a MgSc alloy hydride, to directly determine the rate of H hopping. The results are compared to NMR-determined hopping rates in the end-members ScH<sub>2</sub> and MgH<sub>2</sub> as well as in the popular electrode material LaNi<sub>5</sub>H<sub>6.8</sub>.

## 1.2. Methods

Bulk Mg<sub>65</sub>Sc<sub>35</sub>Pd<sub>2.4</sub> was synthesized at Philips and loaded with H<sub>2</sub> to  $x = [H]/[M] = 2.2$  from the gas-phase. ScH<sub>2</sub> was also prepared at Philips and commercial MgH<sub>2</sub> was used to compare to the MgSc hydride. Samples were loaded into glass NMR tubes under 0.9 atm of N<sub>2</sub> and flame-sealed. RF field penetration into the powered metallic samples was judged to be good from measurements of rf pulse lengths for  $\pi/2$  and  $\pi$  nutations, compared to a water reference sample.

Relaxation times were measured with a homebuilt pulsed, superheterodyne NMR spectrometer with four transmitter phases and quadrature-detected receiver. The transmitted power to the probe was about 80 W peak. Pulse sequences were generated with a combination of TTL hardware and a Pulse Blaster card. The NMR acquisition and analysis software was written locally.  $T_1$  was determined with inversion-recovery and repeated-saturation-recovery schemes.  $T_2$  was measured from the decays of free induction signals ( $T_2^*$ ), two-pulse (Hahn) echoes, and CPMG echo trains. Continuous (not chopped) spin-locking with  $\gamma B_1/2\pi = 50$  kHz was used to measure  $T_{1\rho}$ . The relaxation of the dipolar-ordered state ( $T_{1D}$ , essentially  $T_{1\rho}$  in zero amplitude field) was measured using a phase-alternated version of the Jeener–Broekaert three-pulse method [8]. All measurements were made at 21.25 and 53.14 MHz at field strengths of 0.5 and 1.25 T, respectively.

## 1.3. Results

The relaxation times for Mg<sub>65</sub>Sc<sub>35</sub>Pd<sub>2.4</sub>H<sub>2.20</sub> are presented as functions of reciprocal temperature in Fig. 1. The data can be understood [9] by realizing that  $T_2$  begins to increase (motional averaging) when the H atomic hopping rate  $\omega_H$  is about  $10^5$  s<sup>-1</sup>. The  $T_{1\rho}$  minimum corresponds to  $\omega_H = 5 \times 10^5$  s<sup>-1</sup>, and a  $T_1$  minimum at 21.25 MHz would reflect  $\omega_H = 2 \times 10^8$  s<sup>-1</sup>, but

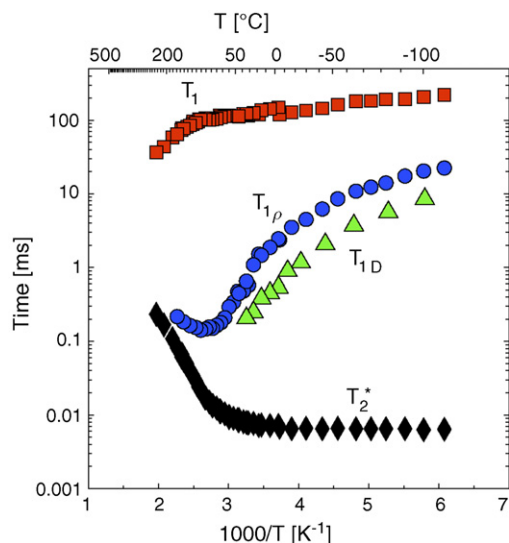


Fig. 1. Proton NMR relaxation times in Mg<sub>65</sub>Sc<sub>35</sub>Pd<sub>2.4</sub>H<sub>2.20</sub>.  $T_1$  was determined at 21.25 MHz and  $T_{1\rho}$  used a nutation frequency of 50 kHz.

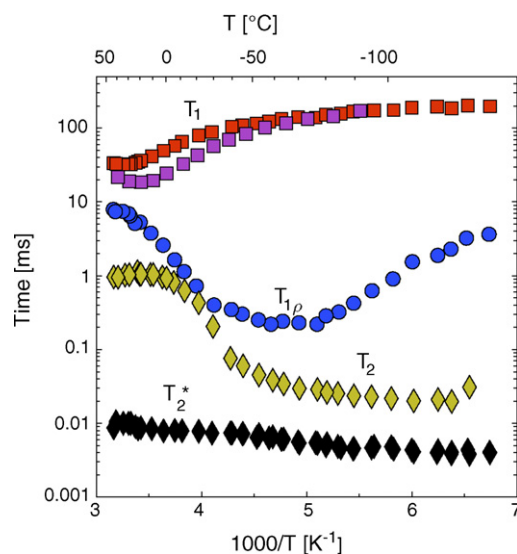


Fig. 2. Proton NMR relaxation times for LaNi<sub>5</sub>H<sub>6.8</sub>. The  $T_2$  data is from two-pulse spin echoes. The  $T_1$  data are from 53.14 MHz (upper) and 21.25 MHz (lower).

evidently the available temperature range is too low to reach such a fast rate of H motion. One sample was heated to 300 °C for about 1 h and suffered irreversible changes (e.g.,  $T_1$  was different upon returning to 25 °C). To within a factor of two, the time  $T_{1D}$  is equal to the mean hopping time,  $1/\omega_H$ , a strong-collision result [9].

For comparison, similar data for LaNi<sub>5</sub>H<sub>6.8</sub> are presented in Fig. 2. This material was synthesized at Ames Laboratory, Iowa State University, characterized by X-ray diffraction at JPL, and hydrided from the gas-phase at WU. Comparing Figs. 1 and 2, it is obvious that specific features such as the  $T_{1\rho}$  minimum occur at much higher temperatures in MgScH<sub>x</sub> than in LaNi<sub>5</sub>H<sub>6.8</sub>. Thus, at a given temperature the H motion in MgScH<sub>x</sub> is much slower (by a factor of  $\sim 3000$  near room temperature; see Fig. 3) than in LaNi<sub>5</sub>H<sub>6.8</sub>.

The relaxation map of Fig. 3 presents the log of  $\omega_H$  as a function of reciprocal temperature for the present samples of MgScH<sub>x</sub>, ScH<sub>2</sub>, MgH<sub>2</sub>, and LaNi<sub>5</sub>H<sub>6.8</sub>. The data points are from  $T_1$  minima (ScH<sub>2</sub> in Ref. [10] and LaNi<sub>5</sub>H<sub>6.8</sub>), the onset of motional averaging (ScH<sub>2</sub>, LaNi<sub>5</sub>H<sub>6.8</sub>, and MgScH<sub>x</sub>),  $T_{1\rho}$  minima (ScH<sub>2</sub>, MgScH<sub>x</sub> and LaNi<sub>5</sub>H<sub>6.8</sub>), and  $T_{1D}$  (using  $\omega_H = 1/T_{1D}$  in MgScH<sub>x</sub> and MgH<sub>2</sub>). In each case, the attempt frequency  $\omega_a$  is approximated as  $10^{13}$  s<sup>-1</sup>, corresponding to  $1000/T = 0$ , providing an additional point on each line. The straight line fits correspond to  $\omega_H = \omega_a \exp(-\Delta E/kT)$ , with the values of activation  $\Delta E/k$  given in the figure caption. The activation energies here agree with published values for LaNi<sub>5</sub>H<sub>x</sub> [11] and ScH<sub>x</sub> [12]. We believe this relaxation map approach to be more robust than determining activation energies from the temperature dependences of individual relaxation times, given the broad distribution of motion rates in some of these systems (LaNi<sub>5</sub>H<sub>6.8</sub> and MgScH<sub>x</sub>).

We note that the  $T_{1D}$  measurements reported in Fig. 3 are the only NMR measurements of diffusive motion in MgH<sub>2</sub>, to our knowledge. These involve long magnetization-recovery times

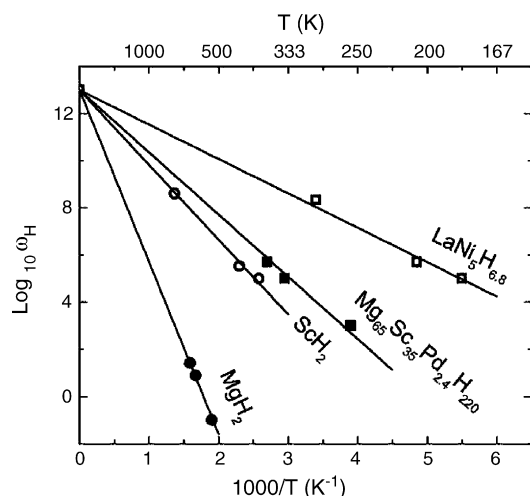


Fig. 3. Relaxation map showing rate  $\omega_H$  of H hopping as a function of reciprocal temperature in  $\text{MgH}_2$ ,  $\text{ScH}_2$ ,  $\text{MgScH}_x$ , and  $\text{LaNi}_5\text{H}_{6.8}$ . The data points correspond to  $T_1$  and  $T_{1p}$  minima and the onset of averaging (increasing  $T_2$  or  $T_2^*$ ); the smallest rates are from  $\omega_H = 1/T_{1D}$ . The approximate activation values  $\Delta E/k$  for the four systems are 16,800, 7300, 6100, and 3400 K, corresponding to  $\Delta E$  of 140, 61, 51, and 28 kJ/mol, respectively.

( $T_1$  is about 1000 s) and very slow H hopping ( $T_{1D}$  of 0.038 to 10 s is shown). This rate of H hopping is  $\sim 10,000$  times too slow to yield appreciable line narrowing [13]. The experiments were limited to  $T \leq 355^\circ\text{C}$  to avoid rupture of the sample tube from the  $\text{H}_2$  pressure [14].

The relaxation map of Fig. 3 demonstrates clearly the wide range of hydrogen mobility in these materials.  $\text{MgSc}$  alloy hydride has more rapid H motion than either end-member, with  $\text{MgH}_2$  being extremely slow. The motion of H in  $\text{LaNi}_5\text{H}_{6.8}$  is substantially more rapid than in  $\text{MgScH}_x$ .

## 2. Magic-angle spinning deuterium NMR

### 2.1. Background

High-resolution NMR methods have been developed for resolving inequivalent nuclei in a solid according to their chemical (or Knight) shifts [15]. However, these methods have found only sporadic application in metal-hydrides. The primary difficulty is that the H NMR lines in metal-hydrides typically have 40 kHz dipolar (H–H) linewidths in the absence of motion (while motional averaging will narrow the lines, the motion generally results in the H atoms exchanging sites and averaging away the desired site-specific information). Magic-angle spinning (MAS) alone cannot yet be performed with high enough rotation frequencies to sufficiently narrow the hydrogen lines; rotation frequencies much faster than the dipolar (homogeneous) linewidth are needed. Multiple-pulse narrowing (e.g., the cyclic irradiation of WAHUA-4 or MREV-8) schemes [15] do not work sufficiently well with metallic samples because of the rf field inhomogeneity resulting from the partial rf shielding (skin effect).

An underappreciated and simple solution to this problem is MAS-NMR of deuterium in metal-deuterides [16,17]. The MAS averages to zero the D–D and metal nuclei–D dipolar interactions and the electric quadrupole broadening. In addition, isotropic susceptibility distortions of the external dc field produced by the powdered sample are also averaged away. Often 4 kHz sample spinning is sufficient for good averaging, because the homogeneous D–D dipolar linewidth is no more than 1–2 kHz. To provide rf field penetration, a metallic sample must be powdered. To avoid dynamo currents in the rotating sample, the metal sample powder is generally mixed with an insulating powder such as  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ .

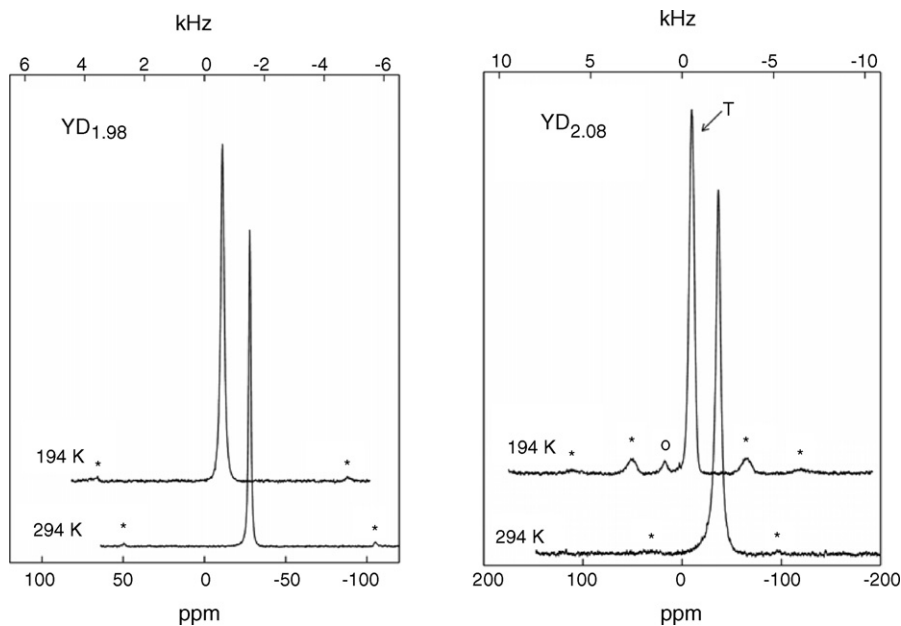


Fig. 4. MAS deuterium NMR spectra of  $\text{YD}_x$  with  $x$  slightly less than 2 (at left) and greater than 2 (at right). For  $x < 2$ , only T sites are occupied. For  $x > 2$ , a second, small line appears for the O-site D atoms at 194 K; at 294 K, the O and T resonances have merged by exchange averaging. The resonance frequency is 54.36 MHz. Spinning side bands are marked with asterisks (\*). In each panel, the higher temperature spectrum is offset for clarity.

A related technique is MAS-NMR of dilute (residual) H nuclear spins in metal-deuterides. The H–H dipole interactions responsible for homogeneous line breadth are reduced sufficiently by dilution to give good narrowing at modest MAS speeds; the larger H–D interactions generate inhomogeneous broadening and so average away even under slow MAS. We see no advantage of this H MAS-NMR technique—the higher per-spin sensitivity of H compared to D is cancelled by the required dilution of H. In fact, stray hydrogen contamination of the sample, MAS rotor vessels, or probe is expected to be a problem when using samples with dilute H.

## 2.2. Methods

These are single resonance deuterium NMR experiments. The MAS requirement of 4–8 kHz is easily met, even with older MAS probes. A simple test for the undesirable dynamo currents is to insert the probe with spinning sample into the dc field; dynamo currents produce drag and will reduce the spinning speed. The purpose of MAS-NMR is to identify and quantify separate resonance signals from inequivalent D atoms, so low temperatures are often required to slow the D-atom diffusion and avoid averaging of the resonances. MAS designs with a separate gas-flow for sample cooling (as opposed to bearing and spinning-drive flows) are particularly good at low temperatures.

## 2.3. Results in $YD_x$

The “simple picture” of D (or H) filling of the available sites in  $YD_x$  is that the tetrahedral (T) sites are lower energy and should fill first. At the nominal composition of  $YD_2$ , the T sites are filled, so further D atoms will locate on the sites of octahedral symmetry (O) [18,19]. At  $x$  of about 2.1, a phase transition (coexistence region) from the f.c.c. fluorite structure to the hexagonal structure of nominal  $YD_3$  begins [4]. However, neutron diffraction [20,21] and hydrogen NMR second-moment [22] evidence suggested that O-sites begin to fill well before the T sites are filled (i.e.,  $x < 2$ ).

The MAS deuterium NMR results [16,17] presented in Fig. 4 demonstrate that (i) for  $x \leq 2$ , only a single resonance is observed, from D atoms on T sites; (ii) for  $x > 2$  but still in the  $\beta$ -phase, the T sites resonance line below 210 K is augmented by a new resonance from occupied O-sites; and (iii) for  $x > 2$  and above 250 K, the O and T resonance lines merge, indicating diffusion that exchanges atoms between the two kinds of sites. Careful measurements of the relative resonance intensities (areas) in case (ii) are in accord with the simple picture above.

Once distinct D-atom sites are resolved in the MAS-NMR spectrum, the rate of exchange between them can be measured by use of exchange NMR spectroscopy. As presented in Fig. 5, the T resonance can be selectively inverted (see spectrum taken 10 ms after inversion). Subsequent T–O atomic exchange, the most elementary diffusion step, carries the inverted deuterium magnetization over to the O resonance (see 180 ms spectrum). The time constant for this process, determined by inspecting the NMR spectrum at several times after the selective inversion, is exactly the mean time for a D atom initially on an O-site to jump to a T site. These exchange results extend the previous measurements of D-atom hopping to slower rates by several orders of magnitude [16,17].

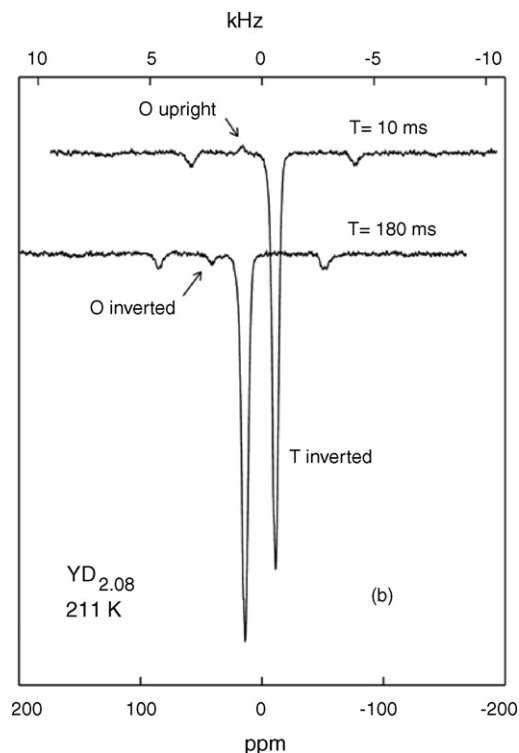


Fig. 5. Deuterium MAS-NMR spectra taken 10 and 180 ms after selective inversion of the T-site resonance. At 180 ms, exchange between the sites has carried inverted spin magnetization to the O resonance.

In the  $YD_{2+x}$  system, it was also possible to distinguish D atoms in two kinds of T sites: those with *versus* those without an occupied O-site nearest neighbor. The picture from MAS deuterium NMR has been confirmed with deuterium static-sample quadrupolar-broadened lineshapes [16,17,23] and by  $^{89}\text{Y}$  MAS-NMR [24].

## 2.4. Results in $ZrNiD_x$

Deuterium MAS-NMR reveals [25,26] two MAS lines for  $x = 2.99$  (see Fig. 6). From the spinning sideband intensity pattern, the stronger resonance has a small quadrupolar interaction, while the weaker line has large quadrupole coupling. This is in accord with static sample measurements; the 2:1 intensity ratio (intensities include all spinning sidebands) agrees with the numbers of  $Zr_3Ni$  and  $Zr_3Ni_2$  sites in the known crystal structure. The two resonances merge due to deuterium diffusion (and the  $Zr_3Ni_2$  site spinning sidebands broaden) at about 324 K.

For  $ZrNiD_x$  with  $x = 0.88$  and  $x = 1.0$ , two MAS resonances of equal intensity appear [25,26], as shown in Fig. 6 for  $x = 0.88$ . This is remarkable, as the accepted diffraction-determined structure has only a single kind of D-atom site. The MAS evidence is unambiguous, however, so a reexamination of neutron scattering and diffraction was performed carefully on this material. Neutron vibrational spectroscopy confirms the existence of at least two kinds of D atoms [26]. The new structure determined by neutron powder diffraction does have, in fact, two inequivalent sites for D atoms [27].



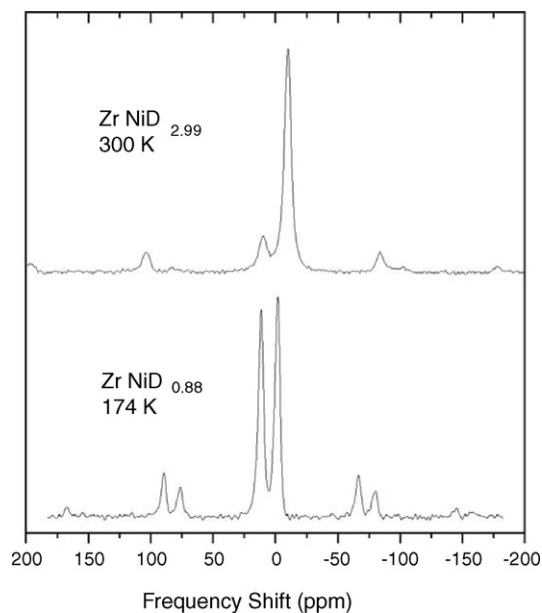


Fig. 6. Deuterium MAS-NMR of  $\text{ZrNiD}_x$ . For both the  $\gamma$  ( $x=2.99$ ) and  $\beta$  ( $x=0.88$ ) phases, two distinct deuterium sites are evident. Spinning sidebands are spaced away by about 80 ppm.

The D MAS-NMR spectra were used to map out the phase boundaries in the  $\text{ZrNiD}_x$  system [26]. The rate of D hopping is readily determined at the temperature where the two lines in the MAS spectrum coalesce due to hopping between inequivalent sites. The observation of coalescence provides an unambiguous measure of the motion rate at the specific temperature and can thus be included on a relaxation map [26] (like Fig. 3) together with relaxation time minima measured with non-spinning NMR [28].

### 3. Conclusions

Measurement of relaxation times in  $\text{MgScH}_x$  allows the rate  $\omega_H$  of H atom hopping to be determined over a wide temperature range. At any given temperature, the rate is faster than in  $\text{ScH}_2$  and much faster than in the ionic  $\text{MgH}_2$ , but slower than in  $\text{LaNi}_5\text{H}_{6.8}$ . Measurements of  $\omega_H$  as functions of H-loading  $x$  and Sc/Mg ratio should shed light on the factors controlling H motion in  $\text{MgScH}_x$ .

Deuterium magic-angle spinning NMR is a simple yet powerful method for resolving inequivalent sites in metal-deuterides. In  $\text{YD}_x$ , MAS-NMR demonstrates the clean sequential filling of first T sites and then O-sites. In  $\text{ZrNiD}_x$ , the observation of two resonance lines for  $x=0.88$  showed the existing crystal structure to be incorrect, as confirmed by recent neutron diffraction and neutron vibrational spectroscopy.

### Acknowledgments

The authors acknowledge support from NSF grant DMR-0400512 and DOE grants DE-FG02-05ER46256 and DE-AI-01-05EE11105. The  $\text{ZrNiD}_x$  work was performed under NSF

grant DMR-9804094 and Research Corp. grant CC4705. The research was partially performed at Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. The effort of the Caltech NMR facility was supported under NSF grants 97243240 and DMR-0080065 (MRSEC program). We thank T.J. Udovic and the authors of Ref. [26] for use of their data. The research on  $\text{MgSc}$  hydrides was performed as part of the Sustainable Hydrogen Program of Active Chemical Technologies for Sustainability (ACTS).

### References

- [1] P.H.L. Notten, M. Ouwerkerk, H. van Hal, D. Beelen, W. Keur, J. Zhou, H. Feil, J. Power Sources 129 (2004) 45–54.
- [2] R.A.H. Niessen, P.H.L. Notten, J. Alloys Comp. 404–406 (2005) 457–460.
- [3] W.P. Kalisvaart, R.A.H. Niessen, P.H.L. Notten, J. Alloys Comp. 417 (2006) 280–291.
- [4] W.M. Mueller, J.P. Blackledge, G.G. Libowitz, Metal Hydrides, Academic, New York, 1968.
- [5] M. Latroche, W.P. Kalisvaart, P.H.L. Notten, J. Solid State Chem. 179 (2006) 3024.
- [6] R.A.H. Niessen, P.H.L. Notten, Electrochem. Solid State Lett. 8 (2005) A534–A538.
- [7] P. Vermeulen, R.A.H. Niessen, P.H.L. Notten, Electrochem. Commun. 8 (2006) 27–32.
- [8] J. Jeener, P. Broekaert, Phys. Rev. 157 (1967) 232–240.
- [9] C.P. Slichter, Principles of Magnetic Resonance, Springer-Verlag, New York, 1996.
- [10] L.-T. Lu, M.S. Thesis, Iowa State University, unpublished, 1982.
- [11] G. Majer, U. Kaess, R.C. Bowman Jr., Phys. Rev. B 57 (1998) 13599–13603.
- [12] M. Jerosch-Herold, L.-T. Lu, D.R. Torgeson, D.T. Peterson, R.G. Barnes, Z. Naturforsch. 40a (1985) 222–228.
- [13] M. Stiovi, A. Grayevsky, A. Moran, S. Kreitzman, N. Kaplan, D. Shaltiel, J. Less-Common Met. 104 (1984) 119–124.
- [14] J.F. Stampfer Jr., C.E. Holley Jr., J.F. Suttle, J. Am. Chem. Soc. 82 (1960) 3504–3508.
- [15] E.O. Stejskal, J.D. Memory, High-Resolution NMR in the Solid-State: Fundamentals of CP/MAS, Oxford, New York, 1994.
- [16] N.L. Adolphi, Ph.D. Thesis, Washington University, unpublished, 1995.
- [17] N.L. Adolphi, J.J. Balbach, M.S. Conradi, J.T. Markert, R.M. Cotts, P. Vajda, Phys. Rev. B 53 (1996) 15054–15062.
- [18] P. Vajda, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 20, Elsevier, Amsterdam, 1995 (Chapter 137).
- [19] J.N. Daou, P. Vajda, Phys. Rev. B 45 (1992) 10907–10913.
- [20] J.A. Goldstone, J. Eckert, P.M. Richards, E.L. Venturini, Solid State Commun. 49 (1984) 475–478.
- [21] D. Khatamian, W.A. Kamitakahara, R.G. Barnes, D.J. Peterson, Phys. Rev. B 21 (1980) 2622–2624.
- [22] D.L. Anderson, R.G. Barnes, D.T. Peterson, D.R. Torgeson, Phys. Rev. B 21 (1980) 2625–2626.
- [23] O.J. Zogal, A.H. Vuorimaki, E.E. Ylinen, Eur. Phys. J. B 10 (1999) 201–207.
- [24] X. Helluy, J. Kummerlen, A. Sebald, O.J. Zogal, Solid State Nucl. Magn. Reson. 14 (1999) 225–230.
- [25] N.L. Adolphi, S. Badola, L.A. Browder, R.C. Bowman Jr., Phys. Rev. B 65 (2001) 024301, and erratum: Phys. Rev. B 69 (2004) 149901(E).
- [26] R.C. Bowman Jr., N.L. Adolphi, S.-J. Hwang, J.G. Kulleck, T.J. Udovic, Q. Huang, H. Wu, Phys. Rev. B 74 (2006) 184109.
- [27] T.J. Udovic, private communication.
- [28] C.D. Browning, T.M. Ivancic, R.C. Bowman Jr., M.S. Conradi, Phys. Rev. B 73 (2006) 134113.