

Rate of hydrogen motion in Ni-substituted LaNi_5H_x from NMR

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Received 26 September 2006; received in revised form 18 December 2006; accepted 21 December 2006

Available online 12 January 2007

Abstract

Partial substitution of Sn, Ge, or Si for Ni in LaNi_5H_x greatly enhances the stability under repeated hydrogen-cycling. Proton NMR relaxation measurements are reported here to determine the rates of H hopping in the substituted metals $\text{LaNi}_{4.6}\text{M}_{0.4}\text{H}_x$ with $\text{M} = \text{Sn, Ge, and Si}$, for comparison to bare LaNi_5H_x . The relaxation times T_2^* (FID), T_2 (Hahn echo), T_2 -CPMG, T_1 , and $T_{1\rho}$ were determined from 130 to 375 K. The three substituents result in only small increases in the average rate of motion at a given temperature but with a broader distribution of rates over the many inequivalent H sites and hopping paths. Evidently, the average energy barriers along the paths for H motion are only little affected by these substituents. Changes of H content x produce only minor changes in the relaxation times.

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Keywords: Metal hydrides; Diffusion; Nuclear resonances

1. Introduction

The system LaNi_5H_x is the parent of metal-hydrogen systems currently employed as battery electrodes and for gas storage [1]. LaNi_5H_x has wide, constant-pressure plateaus corresponding to the α - β phase transition (α is dilute in H, $x < 0.5$, and β is concentrated, $x \sim 6$). The equilibrium pressure of H_2 is about one bar at 25 °C and the H_2 -storage capacity is about 1.5 wt%, adequate for many applications. Partial substitution of Al onto Ni sites reduces the plateau pressure, but also decreases the crucial diffusivity [2,3] of the H atoms by as much as a factor of 100. Poor resistance to degradation under charge/discharge cycling can be greatly improved by partial substitution of Sn, Ge, or Si onto Ni sites. This has been explained [4] in terms of the experimentally observed more uniform distribution of H (with Sn substitution) on the length scale of 4–15 nm, leading to reduced strain gradients in the partially discharged (two-phase) material. The structures [5,6] of the Sn- and Ge-substituted materials are the same (or nearly) as that of the parent LaNi_5H_x . Pressure-composition isotherms [7,8] indicate a reduction in H-storage capacity and a sloping “two-phase” plateau upon substitution,

which may be related to the more uniform spatial distribution of H atoms [4].

The kinetics of Sn-substituted materials have been investigated by transient gas-phase [9] and electrochemical methods [10]. The gas-phase work reports a decrease in hydrogen diffusivity with increasing tin content [9]. NMR relaxation measurements and pulsed-field gradient diffusion measurements of H motion in $\text{LaNi}_{4.8}\text{Sn}_{0.2}\text{H}_{5.8}$ were performed [11] and compared to results in LaNi_5H_6 . These NMR measurements show slightly faster diffusion and H-atom hopping in the Sn-substituted system. Clearly, new measurements are in order to address the rate of motion in the substituted materials. We report here NMR measurements of relaxation times to determine and compare the rates of H-atom hopping in $\text{LaNi}_{4.6}\text{M}_{0.4}\text{H}_x$, with $\text{M} = \text{Sn, Ge, or Si}$, as well as in the parent LaNi_5H_x .

Previous NMR relaxation measurements have shown that H-motion in LaNi_5H_x (x near 6, fully in the β -phase) is quite rapid, with line-narrowing [12,13] starting already at 170 K. Observation of a deep minimum [14,15] in $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame, at about 200 K demonstrates that H motion occurs at an average rate [16] of approximately $\tau^{-1} = 2\omega_1$, where $\omega_1 = \gamma B_1$ and B_1 is the rf field strength (so τ^{-1} of about $3 \times 10^5 \text{ s}^{-1}$). A minimum in the laboratory-frame spin-lattice relaxation time T_1 at 34.5 MHz is observed at about 300 K, showing that the average H hopping rate [16] is about $\tau^{-1} = 2\omega_0$, with $\omega_0 = \gamma B_0$ (so τ^{-1} of about $4 \times 10^8 \text{ s}^{-1}$). The T_1

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and $T_{1\rho}$ minima are broad functions of temperature, with more shallow slopes on the cold sides of the minima than on the hot sides. This implies that the motion of H atoms is described by a broad distribution of rates in the parent system LaNi_5H_x . Presumably this reflects the large number of hydrogen sites and the multitude of diffusion paths between them. In the substituted materials, one may expect the distribution of rates to be at least as large. The comparison of T_1 and $T_{1\rho}$ relaxation data with direct pulsed-field gradient determination of long-range diffusion concluded that the same motions are responsible for the relaxation and diffusion [11].

2. Experimental

The alloys $\text{LaNi}_{4.6}\text{M}_{0.4}$ with $\text{M} = \text{Sn, Ge, and Si}$ were prepared at the Ames Laboratory of Iowa State University by arc-melting the elements. The purities of the Ni, Si, Ge, and Sn were all 99.99% and the La purity was 99.96% including oxygen. The buttons were melted several times, inverting them after each melting. The arc-cast buttons were wrapped in Ta foil, sealed in an evacuated quartz tube, and annealed at 1223 K for 100 h. The alloy ingots were shown to be single phase from metallography and powder X-ray diffraction (XRD). Pieces of these ingots were mechanically crushed into powders and passed through 200-mesh for use in the NMR experiment. The parent metal compound, LaNi_5 , was prepared similarly at Ames.

The powdered metals were hydrided with research-grade H_2 in a clean Sieverts-apparatus at WU. The isotherms obtained were similar to published isotherms [7,8]. The samples were activated by heating with a hair dryer under 1 atm of H_2 and one subsequent hydride–dehydride cycle. After the last dehydriding, the samples were hydrided to the stoichiometries listed in Table 1, as deduced from gas volumetric measurements. The maximum stoichiometries in Table 1 for each metal-system correspond to H_2 pressures of about double the plateau pressure. The low equilibrium pressure for $\text{M} = \text{Sn}$ allowed the samples to be hydrided at 25 °C. The other samples were hydrided at 0 °C to maintain the pressure below atmospheric. After hydrogen loading, the samples were valved-off from the gas system and cooled with liquid nitrogen; then the glass sample tubes were sealed with a flame. Thus, the hydrided samples were never removed from their hydrogen atmosphere; the high equilibrium pressures and hydrogen diffusivities require this.

All NMR measurements were made in an iron-core electromagnet at 1.25 T (53.14 MHz proton frequency), equipped with F-19 NMR field stabilization, unless otherwise stated. The home-built spectrometer had quadrature phase-detection, four rf phases available for transmit, and an output power of about 100 W.

NMR measurements of the spin-dephasing time T_2 , the transverse or spin–spin relaxation time, were performed three ways. The duration of the free induction decay (FID), T_2^* , was measured by integrating the portion of the FID visible after the 5 μs receiver recovery time. Unavoidable, strongly magnetic Ni precipitates prevented T_2^* from increasing much above its low-temperature (rigid-lattice) value. The decay time T_2 of spin echoes (Hahn two-pulse echoes) was measured with a $\pi/2-\tau-\pi$ sequence with ~ 10 values of τ . The Carr–Purcell–Meiboom–Gill sequence, $\pi/2-\tau-\pi-2\tau-\pi\dots$, was used to form a train of echoes [16]. This sequence is known to reduce the effects of diffusion through the field gradients present in the somewhat magnetic sam-

ple particles [17]. The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, was measured with nutation frequency of 50 kHz and continuous (not chopped) spin locking. The laboratory-frame T_1 was usually measured with an inversion-recovery sequence $\pi-\tau-\pi/2$, using 10 values of τ . Some of the results were checked with a saturation-recovery sequence, with essentially identical results. Some T_1 measurements were also performed at 0.5 T (21.25 MHz), so that the T_1 minimum could be attained without heating the sample past an equilibrium H_2 pressure of about 3 atm, which might rupture the glass sample tube.

3. Results and discussion

All of the relaxation time data for $\text{LaNi}_{4.6}\text{Sn}_{0.4}\text{H}_{4.35}$ are presented in Fig. 1. These data are similar to the data from the other samples listed in Table 1, including the parent compound. The dephasing time T_2^* of the FID increases only weakly with temperature, reflecting the role of nickel precipitates in these materials. The appearance of some increase of T_2^* above -20 °C demonstrates that the magnetic Ni inclusions are on a sufficiently fine length scale that hydrogen atoms can diffuse from one to the next within time T_2^* . This permits a rough estimate of 20 nm for the length scale separating Ni inclusions. The T_2 derived from the decay of two-pulse echoes displays motional averaging up to 0 °C, beyond which temperature the echo- T_2 becomes limited by diffusion through the locally non-uniform field inside each particle. Above this temperature, the T_2 from CPMG echo trains (not shown) becomes longer than the two-pulse T_2 . These effects have been documented in other systems [17]. The rotating-frame time $T_{1\rho}$ and the laboratory-frame time T_1 both exhibit minima, as mentioned for LaNi_5H_x in the Introduction.

Analysis of relaxation data is difficult in such systems with broad distributions of motion rates. The presence of ferromagnetic Ni inclusions only worsens the problem. Our preferred approach is to locate the temperatures of the T_1 and $T_{1\rho}$ minima, where the average hydrogen hopping rates are approximately $2\omega_0$ and $2\omega_1$. This “landmark” approach is more robust than analysis of the temperature dependences of individual relaxation times, because it is never clear whether all of the contributing

Table 1
Samples of $\text{LaNi}_{4.6}\text{M}_{0.4}\text{H}_x$

Ni-substituent, M	H-loading, x	$T_1 T$ (s K)
Ni (None)	6.8	31
Sn	4.35	29
Sn	3.6	29
Sn	2.9	29.5
Ge	4.8	26.5
Si	4.4	28.5

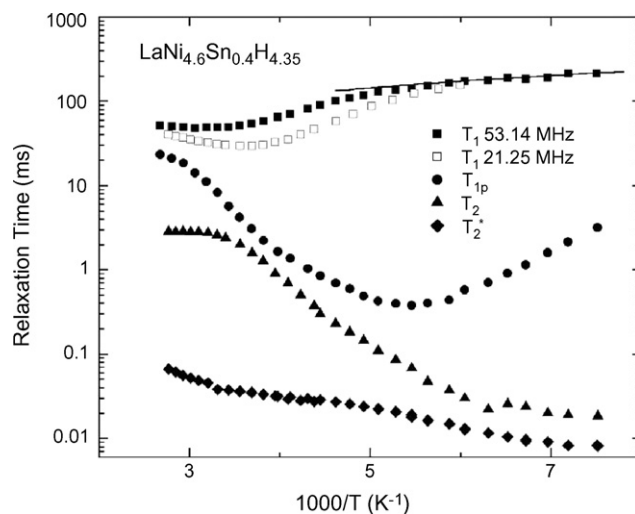


Fig. 1. Relaxation times measured in $\text{LaNi}_{4.6}\text{Sn}_{0.4}\text{H}_{4.35}$. T_2^* (diamonds) is from FIDs and T_2 (triangles) is from two-pulse echo envelopes. T_1 was measured at 21.25 and 53.14 MHz. $T_{1\rho}$ measured at 50 kHz appears as circles. The solid curve corresponds to relaxation from conduction electrons with $T_1 T = 29$ s K.

motions are in the fast or slow limit. We note that a very thorough temperature–frequency scaling approach has been developed for analysis of relaxation data in the LaNi_5H_x system [15].

At low temperatures, below -100°C , T_1 is determined by interaction with the conduction electrons, as evidenced by the good fit to the curve (see Fig. 1) $T_1 T = \text{constant}$. These constants, taken from fits to each data set, are reported for each sample in Table 1. Simple theoretical ideas of this Korringa relaxation mechanism [16] indicate that the $T_1 T$ value is proportional to the reciprocal of the square of the Knight shift. In turn, the Knight shift (difficult to measure directly for hydrogen nuclei because it is small) is proportional to the density of states at the Fermi level and the average probability density at the nucleus of the wave functions at this energy.

As the primary purpose of the present study is to compare the H hopping kinetics in the substituted and parent hydrides, T_1 and $T_{1\rho}$ data are presented in Fig. 2 for samples $M = \text{Sn}$, Ge , and Si as well as LaNi_5H_x . In the case of $M = \text{Sn}$, data are shown for the sample from Table 1 with the highest hydrogen loading, $x = 4.35$. The T_1 and $T_{1\rho}$ minima of the four samples appear at similar temperatures, with a small decrease (10%) of this temperature for $M = \text{Sn}$ similar to that found in Ref. [11] and suggesting a $\sim 10\%$ decrease in average activation energy. The minima are broader and less deep in the substituted systems, especially for $M = \text{Sn}$ and Ge , reflecting a broader distribution of H hopping rates. The distribution undoubtedly includes localized motions as well as motions contributing to long-range diffusion. Changes in the depth of the relaxation time minima will have contributions from variations in proton second moment [16] due to changes in hydrogen density (e.g., see H-loading x in Table 1). We conclude that the average activation energy for H hopping is unchanged or reduced only slightly with these substituents for Ni. The distribution of activation energies, already large in the parent LaNi_5H_x , becomes broader, especially for $M = \text{Sn}$ or Ge .

We present T_1 , T_2 , and $T_{1\rho}$ data in Fig. 3 for two samples with different H-loading x for $\text{LaNi}_{4.6}\text{Sn}_{0.4}\text{H}_x$. The differences

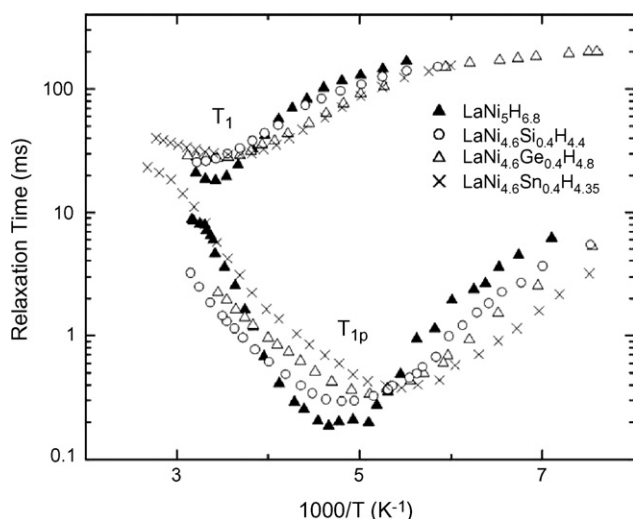


Fig. 2. Comparison of $T_{1\rho}$ and T_1 (at 21.25 MHz) data for $\text{LaNi}_{4.6}\text{M}_{0.4}\text{H}_x$ with $M = \text{Sn}$, Ge , and Si and for LaNi_5H_x .

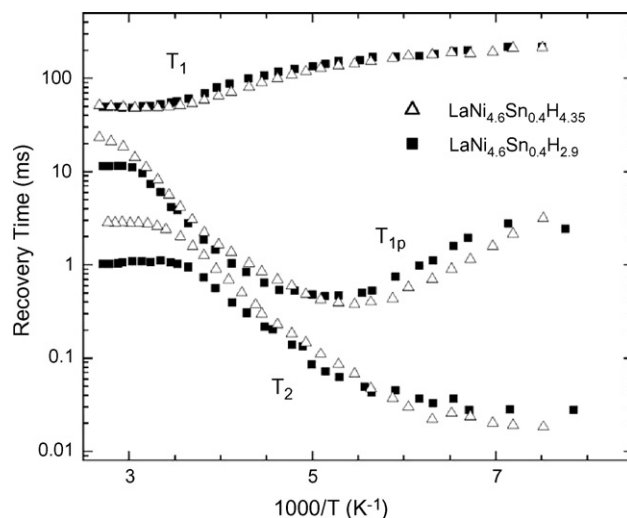


Fig. 3. $T_{1\rho}$, T_2 (two-pulse echo) and T_1 (at 53.14 MHz) data for two samples of $\text{LaNi}_{4.6}\text{Sn}_{0.4}\text{H}_x$ with $x = 2.9$ and 4.35 .

with different H-loading are small, demonstrating that such differences are not the source of the changes with Ni substitution evident in Fig. 2. The absence of substantial variation with x is expected because of the two-phase equilibrium and the small H-content of the α -phase.

4. Conclusions

A full set of NMR relaxation times has been measured in the substituted hydrides $\text{LaNi}_{4.6}\text{M}_{0.4}\text{H}_x$ for $M = \text{Sn}$, Ge , and Si , and compared to results for the parent hydride, LaNi_5H_x . The temperatures of the T_1 and $T_{1\rho}$ minima show that there is only a slight increase in the average H-atom hopping rate at a given temperature in the substituted hydrides. This change is greatest for $M = \text{Sn}$, with a decrease in the temperature of the $T_{1\rho}$ minimum of about 10%; for $M = \text{Si}$, the temperatures of the minima are essentially unchanged from the parent hydride. For the substituted hydrides, especially for $M = \text{Sn}$ and Ge , the minima are broader in temperature and less deep, indicating that the distribution of H-atom hopping rates is broader than in the parent LaNi_5H_x . Thus, the distribution of site and/or barrier energies is increased somewhat with these substituents. Overall, the effects on the H hopping rate with $M = \text{Sn}$, Ge , or Si are small.

Comparison of results from samples with $M = \text{Sn}$ loaded with different amounts of hydrogen (from $x = 2.9$ to 4.35), but still almost entirely in the β -phase, show only very small differences.

Acknowledgments

The authors acknowledge NSF support through grant DMR-0400512. The research was partially performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautical and Space Administration. We thank T. Ellis and T.M. Riedemann of Ames Laboratory for preparing the metal samples.

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