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NMR study of the nanocrystalline palladium–hydrogen system

J.W. Hanneken[a,1], D.B. Baker[b,*], M.S. Conradi[c], J.A. Eastman[d]

[a]University of Memphis, Physics Department, Memphis, TN 38152, USA
[b]William Jewell College, Department of Physics, 500 College Hill, Liberty, MO 64068, USA
[c]Washington University, Department of Physics-1105, St. Louis, MO 63130-4899, USA
[d]Argonne National Laboratory, Materials Science Division, Argonne, IL 60439, USA

Abstract

Proton nuclear magnetic resonance spectra of nanocrystalline n-$PdH_{0.7}$ at room temperature reveal two distinct, motionally-narrowed peaks, attributed to crystallite interstitial and interfacial hydrogen populations. In addition, proton spin-lattice relaxation measurements show enhanced relaxation rates. Both results are qualitatively consistent with a previously-observed hydrogen concentration enhancement in grain boundaries of α-phase n-PdH_x. Magnetization recovery data for n-$PdH_{0.7}$ also reveal that the separate populations of hydrogen do not exchange on time scales of up to order 0.1 s, a surprising result considering the correlation time associated with spin-lattice relaxation, of order 10^{-8} s. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polycrystalline materials are composed of atoms which reside in one of three types of environments: within crystallites, within grain boundaries between crystallites, or at free surfaces. A special class of polycrystals called nanocrystalline materials possess small grain sizes (1–100 nm), resulting in relatively large fractions of atoms at interfaces between grains or at free surfaces, and, in turn, leading to many of their unique properties [1,2]. For our purposes, interstitial atoms are located within the interior of grains; interfacial atoms are located in grain boundaries or at free surfaces.

In the present study proton nuclear magnetic resonance (NMR) data are obtained for a nanocrystalline metal–hydrogen system, n-$PdH_{0.7}$, for comparison with previous results for conventional (large polycrystalline grains) $PdH_{0.7}$ [3,4]. The conventional PdH_x system is ideal for comparison since it is probably the most widely-studied of the metal–hydrogen systems [5–8]. Recent results for nanocrystalline PdH_x indicate that compared to conventional PdH_x, n-PdH_x exhibits an enhanced solubility of H [9–12], narrowing of its miscibility gap [9,11], and an increased chemical diffusion coefficient for H [9]. The only NMR study of n-PdH_x is for α-phase n-$PdH_{0.037}$ [13].

NMR data for metal–hydrogen systems typically include proton spin-lattice relaxation rates R_1 and proton spectra. Spin-lattice relaxation is induced by magnetic field fluctuations with frequency components at the proton NMR frequency [14]; hence, R_1 reflect both the strength of the fluctuating fields and the rate of the atomic motions responsible for the fluctuations. Proton spectra can reveal the presence of chemically distinct populations of hydrogen from chemical shifts. Proton linewidths reveal the strength of proton–proton dipolar interactions and the rate of atomic motions, in the regime of motional narrowing [14].

2. Experimental

Nanocrystalline palladium (10 nm grain size as determined by transmission electron microscopy, TEM) was prepared by gas condensation, as described previously [11]; the prepared metal sample was kept in powder form to allow for penetration of radio frequency (RF) fields in the NMR experiments. Hydrogen was loaded into the sample by introducing research grade H_2 gas into an evacuated 5 mm NMR tube containing the powdered

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*Corresponding author. Tel.: +1-816-7817-700 ext. 5665; fax: +1-816-4155-027.

E-mail addresses: jhannekn@memphis.edu (J.W. Hanneken), bakerb@william.jewell.edu (D.B. Baker).

[1] Co-corresponding author. Tel.: +1-901-6782-417; fax: +1-901-6784-733

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sample at ambient temperature. The hydrogen content of the sample was determined from the pressure change in the calibrated volume of the system and found to be [H/Pd]= 0.72±0.01.

NMR data at 21 and 53 MHz were obtained using a superheterodyne pulsed spectrometer with associated electromagnet; data at 200 MHz were obtained using a commercial system. Temperatures were controlled using flowing nitrogen gas and monitored using a thermocouple. Spin-lattice relaxation rates were determined from the observed recovered magnetization as a function of the waiting interval, following saturation of the spin system. Reported values of R_1 were taken from single exponential fits to the data for time intervals out to about 2–3 times the determined relaxation time. However, plots for longer waiting times revealed nonexponential magnetization recovery.

3. Results and discussion

Fig. 1 shows a typical 200 MHz proton spectrum for n-$PdH_{0.7}$ at room temperature, revealing the presence of two distinct proton resonances. This result is remarkable since coarse-grained $PdH_{0.7}$ is known to exhibit only a single proton NMR line [3]. Absolute chemical shifts for the peaks are unavailable since the sealed sample did not contain a chemical shift reference. Measured intensities (areas) of the peaks indicate that the lower frequency peak, A, represents about 30–40% of the total intensity of the spectrum. The measured splitting of the peaks in Fig. 1 at 200 MHz is 22±2 ppm; the splitting of the spectrum at 53 MHz is the same in ppm units. Thus, the shift in Hz units scales linearly with the field, consistent with the shift being a chemical and/or Knight shift [15]. Half-height full linewidths of the peaks are in the range 400–600 Hz, indicating substantial motional narrowing of the proton spin populations.

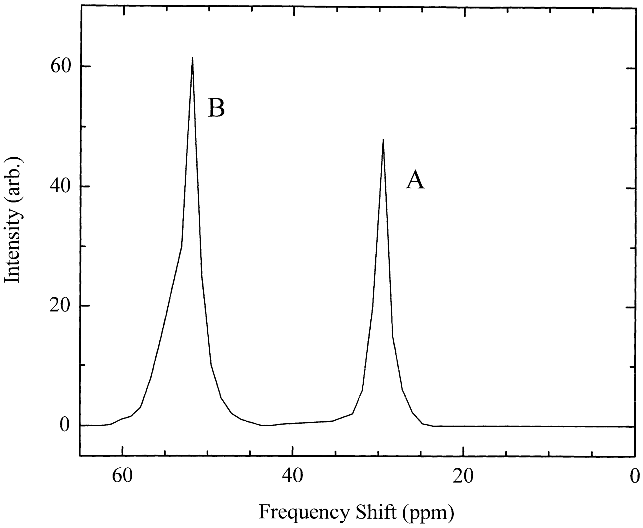

Fig. 1. 200 MHz proton NMR spectrum for n-$PdH_{0.7}$, revealing the presence of two distinct hydrogen resonances. The peaks are attributed to interstitial crystallite (peak A) and interfacial (peak B) hydrogen populations. Note the sign convention for the spectrum is increasing frequency to the left.

In conventional metal–hydrogen systems, motional narrowing of proton NMR lines results from averaging of proton dipole–dipole interactions to zero when the correlation time for hydrogen diffusion is much less than the inverse of the NMR linewidth [14]. Typical rigid-lattice (i.e. at temperatures too low for motional averaging on the NMR time scale) linewidths for metal–hydrogen systems are of order 10 kHz [14], corresponding to time intervals of 10^{-4} s. Therefore we conclude that diffusive motions with correlation times much less than 10^{-4} s are responsible for motional narrowing here, in agreement with the observation of rapid H diffusion in α-phase n-PdH_x [16].

Previous NMR studies of metal–hydrogen systems have revealed the presence of multiple hydrogen peaks when systems exhibit two simultaneous structural phases (α and β phases, for example) [17]. In the present case, however, the system is expected to exhibit only the beta phase due to its high concentration of hydrogen (H-to-Pd ratio of 0.72) and the range of experimental temperatures [8]. A possibility is that the separate resonance lines result from physically-separated regions of α- and β-phase populations due to the enhanced concentration of hydrogen in interfacial regions. However, the experimental hydriding behavior of nanocrystalline PdH_x indicates the entire system transforms to the β phase upon exposure to pressures of hydrogen used in our sample preparation [11].

Multiple hydrogen peaks also arise when interstitial hydrogen occupies multiple sites (tetrahedral and octahedral sites, for example) in metal–hydrogen systems [18]. In polycrystalline $PdH_{0.7}$, however, hydrogen is known to occupy only octahedral sites [19], thus yielding a single NMR line. For completeness we note also that multiple ^1H (^2D) NMR lines have been observed for conventional PdH_x, NbH_x, and PdD_x systems in which sizable numbers of dislocations, domain boundaries, or interstitial impurities are present [20–24].

Finally, the possible presence of a contaminant was considered to account for multiple proton resonance lines. Contaminants such as water are not expected to be present in large enough quantities to form monolayer coverage of the sample, as required to produce either of the proton. NMR signals observed. Furthermore, no proton NMR signal was observed in the nonhydrided sample.

The likely scenario is that the two peaks arise from crystallite interstitial and interfacial hydrogen populations with a large fraction of hydrogen preferentially located within interfacial regions. Based on our grain size (diameter of 10 nm) and an assumed interfacial zone thickness of 1 nm (equivalent to a few lattice spacings), the volume fraction occupied by interfacial regions is approximately 50% for spherical grains. Previous studies reveal hydrogen concentrations within grain boundaries that exceed those within grains by factors of 2–3 for α-phase n-PdH_x [16]. Measurements of relative intensities (spectral areas) in Fig. 1 yield ratios of approximately 2:1 (B:A) for peak B relative to peak A, in reasonable agreement with the study cited [16]. In such a scenario peak A and peak B represent interstitial crystallite and interfacial hydrogen populations, respectively.

Proton spin-lattice relaxation rates R_1 versus temperature are shown in Fig. 2 for n-Pd$H_{0.7}$ at two resonance frequencies. For comparison previous R_1 data for coarse-grained Pd$H_{0.7}$ (at 11 MHz) are indicated by a solid line [4]. Inspection of the data reveals that relaxation rates in the nanocrystalline system are significantly greater than those in the coarse-grained system. For example, at 155 K the measured R_1 for n-Pd$H_{0.7}$ (at 21 MHz) is 33 s^{-1}, as compared with 4.6 s^{-1} for coarse-grained Pd$H_{0.7}$ at 11 MHz.

This enhancement is actually more dramatic, because the plot reports measurements at different NMR frequencies. On the low temperature side of the relaxation rate maximum, the rates vary inversely with NMR frequency, ω. The variation ranges from $R_1 \propto \omega^{-2}$ in systems described by a single correlation time τ_c to $R_1 \propto \omega^{-1}$ in many systems described by a distribution of correlation times [25]. Comparing the present n-Pd$H_{0.7}$ 21 and 53 MHz data we find that R_1 scales as ω^{-1}. Using this frequency dependence, the 11 MHz relaxation rates for n-Pd$H_{0.7}$ are expected to exceed those at 21 MHz by factors of 1.9. Hence after correction for frequency dependence, the observed 21 MHz relaxation rates for n-Pd$H_{0.7}$ display an enhancement of approximately 14, compared to the coarse-grained Pd$H_{0.7}$.

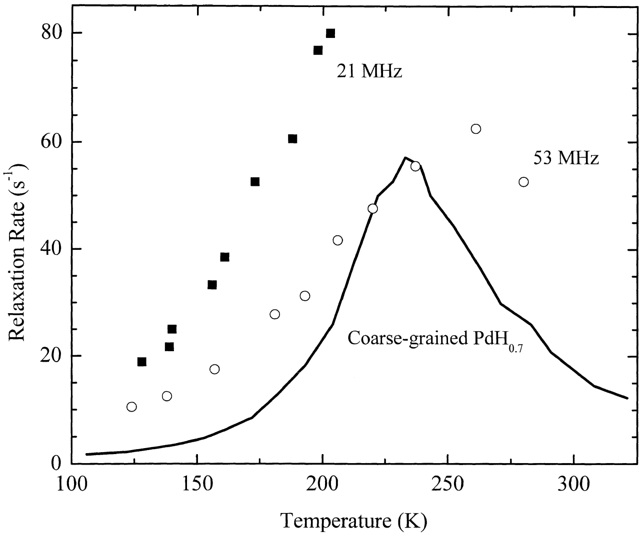

Fig. 2. Proton spin-lattice relaxation rates R_1 versus temperature for n-Pd$H_{0.7}$ at 21 MHz (closed squares) and 53 MHz (open circles). For comparison the solid line indicates the data of Cornell and Seymour at 11 MHz for coarse-grained Pd$H_{0.7}$ [4].

An interesting issue in our data is the exchange rate concerning the hydrogen atoms of peaks A and B. Because two separate NMR resonances are resolved, the exchange lifetime is at least as long as the reciprocal of the individual peaks' linewidths, approximately 1 ms. The presence of nonexponential, longitudinal magnetization recovery in the R_1 data suggests the exchange is at least as slow as the spin-lattice relaxation time scale, of order 0.1 s. If the exchange was faster, both resonances would relax longitudinally at the same average rate. This rather slow exchange time is remarkable since correlation times associated with spin-lattice relaxation are of order 10^{-8}–10^{-9} s near the R_1 maximum at 53 MHz. Thus, the interstitial and interfacial hydrogen atoms both move rapidly (as indicated by motional averaging and by the proximity of the R_1 maximum) but do not interchange even on time scales longer by a factor of 10^7.

Several mechanisms are possible to account for the more rapid proton spin-lattice relaxation in the nanocrystalline system, compared to the coarse-grained system. One such mechanism is proton cross-relaxation [26] to palladium nuclear spins. However, cross relaxation is ruled out because motional narrowing also averages the Pd–proton dipole interaction, eliminating cross-relaxation effects.

Another possible mechanism for enhanced proton relaxation is unusually rapid H diffusion [16]. While an increased rate of motion is possible, it (alone) cannot account for the relaxation rates observed here. Spin-lattice relaxation rates reach their maximum values when $\omega\tau_c$~1. On either side of the spin-lattice relaxation rate maximum, R_1 values decrease as the correlation time moves away from ω^{-1}. Generally, temperature determines the correlation time such that increases in temperature produce decreases in correlation time according to an Arrhenius relation. Thus, the overall result of an enhanced rate of diffusion should be to simply decrease the temperature at which the maximum relaxation rate occurs, without affecting the magnitude of the maximum relaxation rate. Since several of our reported low temperature relaxation rates for the nanocrystalline system exceed the R_1 maximum for the coarse-grained system, the observed (enhanced) relaxation cannot be due simply to enhanced diffusion. We also note that the R_1 maximum in n-Pd$H_{0.7}$ at 53 MHz (see Fig. 2) occurs at an only slightly higher temperature than the R_1 maximum at 11 MHz in coarse-grained Pd$H_{0.7}$, indicating that the rate of motion in the nanocrystalline system is similar to that in the coarse-grained system.

A third possibility for enhanced relaxation is increased interactions among protons in the nanocrystalline system. Proton spin-lattice relaxation rates, due to like-nuclear-spin-dipole interactions, are directly proportional to the proton second moment, which varies inversely as the sixth power of the separation of the hydrogen atoms. Thus, small decreases in the average separation of nuclear spins can yield dramatic increases in relaxation rates.

Hydrogen concentrations within grain boundaries are known to be higher than those within the grains themselves, by factors of 2–3 for α-phase n-PdH_x [16]. This presumed increased concentration of hydrogen within interfacial regions must be accompanied by a corresponding decrease in the separation of hydrogen atoms, resulting in enhanced second moments and enhanced R_1 relaxation rates. For the special case of randomly diluted systems of spins, the second moment is linearly proportional to the spin (hydrogen) concentration [27]; thus, for this case the second moment (and R_1) in n-Pd$H_{0.7}$ interfacial regions is expected to be enhanced by a factor of 2–3.

To determine if this is in reasonable agreement with our R_1 data, maximum relaxation rates for the two systems are compared. Such a comparison is more appropriate than comparisons at fixed temperatures, because the R_1 maximum in nanocrystalline and conventional systems will not necessarily occur at the same temperature (see above). The R_1 maximum should scale as the inverse of the NMR frequency (R_1 maximum$\propto\omega^{-1}$), approximately true even in disordered systems, so that the 11 MHz maximum should exceed that at 53 MHz by approximately 4.8. However, from Fig. 2, the maximum R_1 for n-Pd$H_{0.7}$ (at 53 MHz) is approximately 62.5 s^{-1}, as compared to about 57 s^{-1} for Pd$H_{0.7}$ at 11 MHz. This implies that the enhancement of the maximum R_1 in n-Pd$H_{0.7}$ is just over 5, larger than the factor of 2–3 expected. We regard this very rough agreement as supporting the enhanced concentration of interfacial hydrogen. However, the assumption of random dilution in the above argument may not be justified.

In addition to enhancements of H concentrations in grain boundaries, H diffusion in grain boundaries is found to be at least partially restricted in α-phase n-PdH_x [16]. As a result, exchange between the interfacial and interstitial sites may be partially inhibited, giving rise to nearly independent spin-lattice relaxation pathways for the two hydrogen spin populations. This is a plausible explanation for the non-exponential magnetization recoveries observed in the present studies.

4. Conclusions

Proton NMR spectra for n-Pd$H_{0.7}$ reveal the presence of two distinct proton resonances, indicating two populations of hydrogen within the nanocrystalline system. Further, proton spin-lattice relaxation data for n-Pd$H_{0.7}$ show enhanced relaxation rates as compared with conventional Pd$H_{0.7}$. Both observations are qualitatively consistent with enhanced H concentrations within interfacial regions.

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