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Vibrational density of states measurement of hydrogen trapped at dislocations in deformed $PdH_{0.0008}$

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The vibrational density of states (DOS) of hydrogen trapped at dislocations in deformed $PdH_{0.0008}$ has been measured at 4 and 295 K with incoherent inelastic neutron scattering. The vibrational DOS at 4 K exhibits features characteristic of the low-temperature β-Pd hydride phase while the characteristic peak in the 295 K DOS corresponds to the solid-solution α-Pd phase. This is evidence of a $\alpha \rightarrow \beta$ transition at low temperature within the distorted environment of dislocations.

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I. INTRODUCTION

Although the first measurement of the dynamics of hydrogen in Pd using inelastic neutron scattering (INS) techniques dates to 1961,[1] the majority of the work in this area occurred in the 1970s and 1980s.[2–12] Rowe *et al.*[4] were the first to measure the frequency-wave vector dispersion relations in the Pd-H (-D) system with coherent INS while Chowdhury and Ross[2] recorded the first vibrational density of states (DOS) with incoherent INS. More recently, Ross *et al.*[13] and Kemali *et al.*[14] investigated directional-dependent anisotropy at high-energy transfer as it relates to the anharmonicity of the potential well. Except for one measurement discussed below, all studies to date involved one of three phases—the high-concentration high-temperature ($T > 50$ K) disordered α' hydride phase, the high-concentration low-temperature ($T < 50$ K) ordered β hydride phase, or the solid-solution α phase—and were designed to characterize the local environment of hydrogen in the regular octahedral interstitial lattice site. The vibrational DOS of hydrogen trapped at dislocations, more difficult to isolate and quantify, is presented here. As explained below, the hydrogen vibrational DOS can serve as a probe of the local environment of the dislocation trapping sites, albeit perturbed by the presence of interstitial hydrogen. These measurements, in addition to characterizing the phase behavior of the trapped hydrogen via comparison to the known α and β phase DOS spectra, represent an initial examination of the local octahedral interstitial trapping environment through consideration of peak location and width.

II. EXPERIMENTAL

Approximately 21 g of 0.25-mm-thick 99.98% pure (metals basis) polycrystalline Pd sheet material cut into 0.5 by 5 cm pieces was used for the INS measurements. This sheet material, supplied by Alpha Aesar, was cold rolled in the as-received condition and then cycled twice across the Pd hydride miscibility gap at ~60 °C prior to the INS measurement. Cycling is known to generate significant dislocation density in Pd.[15,16] The vibrational DOS was measured at three global hydrogen concentrations (0.0008, 0.015, and 0.63 [H]/[Pd]) using the filter-analyzer neutron spectrometer (FANS) (Ref. 17) at the NIST Center for Neutron Research. The deformed $PdH_{0.0008}$ sample was measured at 4 and 295 K, the $PdH_{0.63}$ sample at 4 K, and the well-annealed $PdH_{0.015}$ sample at 295 K. FANS measures the incoherent inelastic neutron-scattering response by detecting down-scattered neutrons that pass through a Be-Bi-graphite low-energy band-pass filter [~1.2 meV average final energy and ~1.1 meV full width at half maximum (FWHM) energy resolution[17]] as the energy of the incident beam is scanned. The instrument was configured with a Cu (220) monochromator and with $60'/40'$ collimation. The overall energy resolution varies from 3 meV (FWHM) at 65 meV energy transfer to 8 meV (FWHM) at 130 meV in this configuration. The $PdH_{0.63}$ INS measurement was performed in the fully saturated state of the second hydride cycle with a corresponding equilibrium H_2 gas pressure of approximately 340 Torr. The hydrogen concentration (0.63 [H]/[Pd]) was measured directly by the total pressure reduction during loading. A final 130 °C 3 h annealing step under vacuum was then used to complete the second hydride cycle prior to the $PdH_{0.0008}$ INS measurement. The residual trapped hydrogen after this annealing step accounts for the final global hydrogen concentration. This concentration was determined by scaling the area under the measured INS curve after background subtraction (see below) over an energy range of 40–100 meV to the known concentration of the $PdH_{0.63}$ sample. The result of this scaling is $[H]/[Pd]=0.0008$ and $[H]/[Pd]=0.0006$ at 4 and 295 K, respectively. It is possible that some hydrogen escaped the sample during the extended (3 d) 295 K measurement. It is also possible these concentrations are equivalent since the error associated with the concentration determination is estimated to be 1×10^{-4} [H]/[Pd]. For simplicity, we refer to all low-concentration measurements as $PdH_{0.0008}$.

A zero-hydrogen-concentration Pd blank background measurement was performed at 4 and 295 K as well. These measurements were performed using the same Pd sample after annealing in vacuum at 900 °C for 4.5 h. This annealing procedure was performed after the deformed-sample INS measurements. Although not confirmed, annealing likely resulted in recrystallization of the deformed Pd sample. Finally, the annealed sample was loaded to 0.015 [H]/[Pd] from the gas phase (concentration determined from the total pressure reduction during loading) and the vibrational DOS was measured at 295 K. This sample was annealed at 130 °C for 30 min under H_2 gas and then slowly cooled to 295 K to ensure homogeneity. The hydrogen concentration in the $PdH_{0.015}$ sample is just at the $\alpha-\alpha'$ miscibility gap boundary at room temperature; the vibrational DOS measurement therefore represents the dilute α phase in our sample material. Both the $PdH_{0.63}$ and $PdH_{0.015}$ spectra will serve as points of comparison to the $PdH_{0.0008}$ measurements as discussed below.

The fast neutron background was measured by scanning the incident-beam energy with the $PdH_{0.63}$ sample in place and with the detector bank blocked downstream of the sample using 0.6-mm-thick Cd sheet. All measurements were performed with the sample loaded in a thin-wall Al sample cell sealed with an indium gasket. This cell was placed in a top-loading He closed-cycle refrigerator (CCR) for all measurements except for the 295 K $PdH_{0.015}$ sample. This measurement was done with the Al sample can placed on the spectrometer table without the CCR. The data presented here required approximately 10 d of beam time.

III. RESULTS AND DISCUSSION

The incoherent INS measurements of the $PdH_{0.0008}$ sample at 4 and 295 K, corrected for the fast neutron background, are shown in Fig. 1. Generally, the background measured by FANS is sample and temperature dependent. In particular, the background between 40 and 50 meV is enhanced at 295 K in both the $PdH_{0.0008}$ and Pd blank measurements. The higher sample temperature leads to more populated acoustic and optic modes, which in turn activate multiphonon INS processes that increase the background.

The net incoherent INS measurements are shown in Fig. 2. The $PdH_{0.63}$ and $PdH_{0.0008}$ data have been normalized by the area under each curve between 40 and 100 meV after background subtraction. Two background components were subtracted from the $PdH_{0.63}$ and $PdH_{0.0008}$ spectra: (1) the Pd blank measurement and (2) a constant intensity level ($400/1.5\times10^6$ monitor and $600/1.5\times10^6$ monitor at 4 and 295 K, respectively) representing an energy-independent background attributed to multiphonon processes. Only the 295 K Pd blank measurement was subtracted from the $PdH_{0.015}$ spectrum, with the area normalization between 50 and 80 meV performed after this subtraction.

The Pd blank measurements are not perfectly uniform between 50 and 90 meV, a fact especially true at 4 K. Two possible contributions to this intensity exist: optic phonon down-scattering events resulting from residual hydrogen or spurious background intensity, as described by Udovic *et al.*[17] It is doubtful that residual hydrogen remained after the 4.5 h 900 °C vacuum anneal. This statement is supported by temperature-programmed desorption analysis of the $PdH_{0.0008}$ sample shown in Fig. 3, which demonstrates that all hydrogen are evolved below approximately 700 °C. The evolution of hydrogen from the sample at 900 °C (inset of Fig. 3) also provides proof of complete outgassing. The likely source of the excess scattering is therefore spurious intensity from elastically scattered neutrons undergoing inelastic events within the filter material. In fact, vibrational DOS of Be has features between 50 and 80 meV (Ref. 17) that are similar to those evident in the 4 K Pd blank measurement. Stuhr *et al.*[18] observed similar features from zero-hydrogen-concentration nanocrystalline Pd at 10 K using FANS, albeit before the installation of the Bi filter component. As explained by Udovic *et al.*,[17] Bi was added to the FANS filter to eliminate the predominate portion of the spurious intensity between 50 and 80 meV.

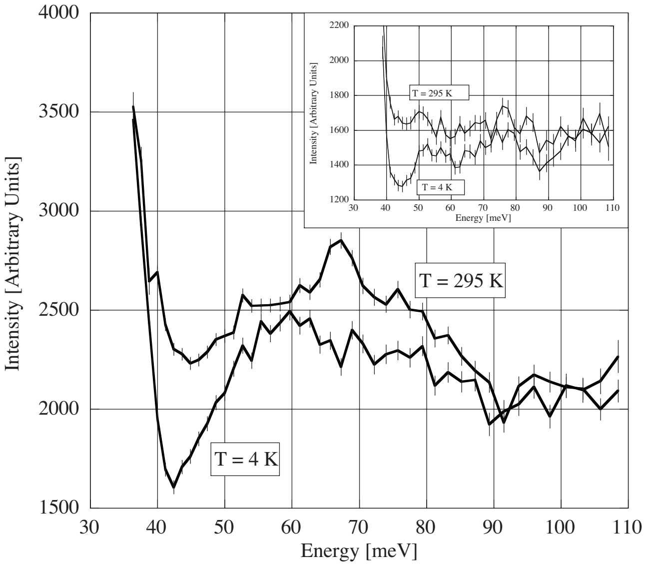

FIG. 1. Incoherent INS spectra from the deformed $PdH_{0.0008}$ at 4 and 295 K. The abscissa is the neutron energy loss during down-scattering events. The fast neutron background has been subtracted from all measurements. Inset shows the Pd blank measurement at 4 and 295 K. All data sets, including those in the inset, are normalized to 1.5×10^6 monitor counts and therefore can be directly compared. Error bars indicate $\pm1\sigma$ derived from counting statistics. The increasing intensity below 40 meV is due to acoustic modes associated with the sample and Al can.

Discussion of the vibrational DOS measurements begins with the peak energies associated with the data in Fig. 2. The two 4 K spectra are asymmetric, exhibiting high-energy shoulders, and were fit with a two-Gaussian model (not shown). The location and standard deviation of the primary peaks obtained from these fits are listed in Table I, as are the peak locations from the $PdH_{0.0008}$ and $PdH_{0.015}$ measurements at 295 K. The 4 K $PdH_{0.63}$ peak position and the shape of the high-energy shoulder observed here are similar to past measurements by others.[8,13,14,19] Thus, the 4 K $PdH_{0.63}$ measurement serves to validate the experimental procedure, provides the normalization for the hydrogen concentration of the $PdH_{0.0008}$ sample, and serves as a direct comparison to the deformed $PdH_{0.0008}$ 4 K spectrum. The high-energy shoulder in the $PdH_{0.63}$ 4 K DOS is typically attributed to the

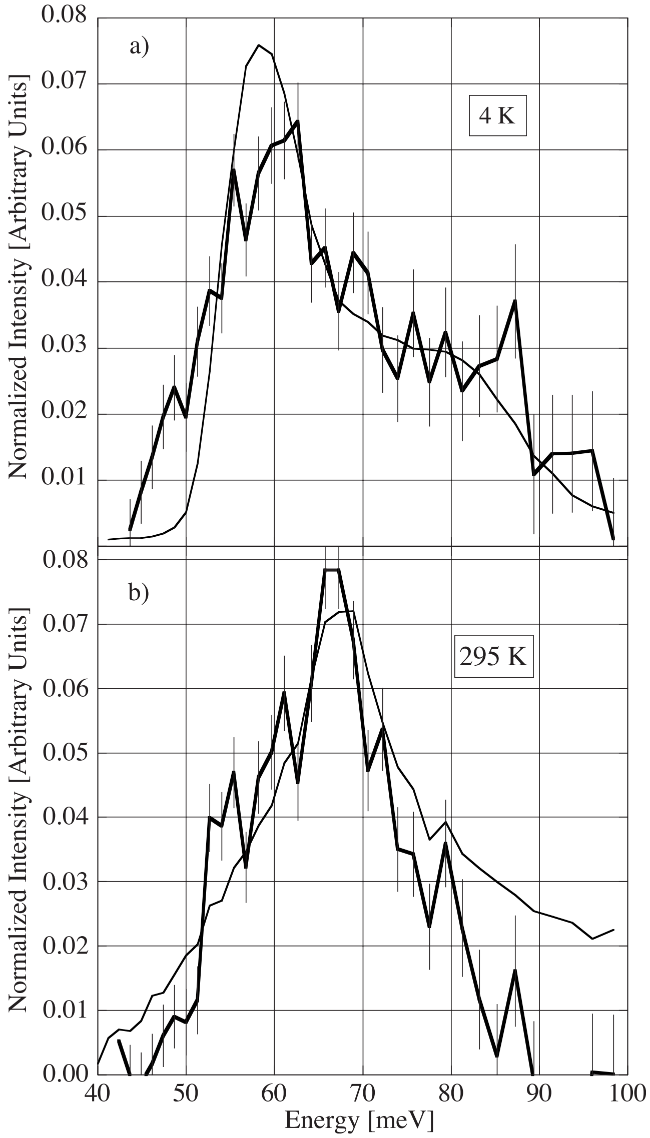

FIG. 2. (a) Comparison of the $PdH_{0.63}$ spectrum (thin solid line) to the deformed $PdH_{0.0008}$ spectrum at 4 K and (b) comparison of the $PdH_{0.015}$ spectrum (thin solid line) to the deformed $PdH_{0.0008}$ spectrum at 295 K. Error bars indicate $\pm 1\sigma$ after subtraction of the Pd blank and normalization as discussed in the text. The corresponding error for the $PdH_{0.63}$ and $PdH_{0.015}$ spectra are very small by comparison and not shown.

longitudinal-optic mode of the hydride phase,[4] although an alternative explanation based on a Franck-Condon transition has been proposed.[14] The 4 K $PdH_{0.0008}$ measurement also has a high-energy shoulder similar in relative magnitude (compared to the primary peak) to that of the 4 K $PdH_{0.63}$ measurement. Less-defined high-energy shoulders are observed in dilute α-Pd DOS spectra, such as the $PdH_{0.015}$ measurement presented here, and are generally attributed to a multiphonon process involving the local hydrogen modes and the acoustic modes of the Pd lattice.[8]

The relevant aspects of the Fig. 2 data are the characteristic peak locations (see Table I) in the $PdH_{0.0008}$ spectra at 295 and 4 K compared to the known first harmonic of dilute hydrogen in a regular octahedral site in α-Pd [68.5,[5] 69,[8] and 69 meV (Ref. 20)] and to the transverse optic (TO) mode in β- or α'-Pd [57,[3] 58,[8] and 56 meV (Ref. 19)], respectively. The agreement is good and our $PdH_{0.63}$ and $PdH_{0.015}$ measurements add further confirmation. These observations suggest that a $\alpha \rightarrow \beta$ phase transformation occurs upon cooling from 295 to 4 K in deformed $PdH_{0.0008}$. Given the very low hydrogen concentration and heavily deformed state of the $PdH_{0.0008}$ sample, it is reasonable to assume this behavior is representative of hydrogen trapped near dislocations.

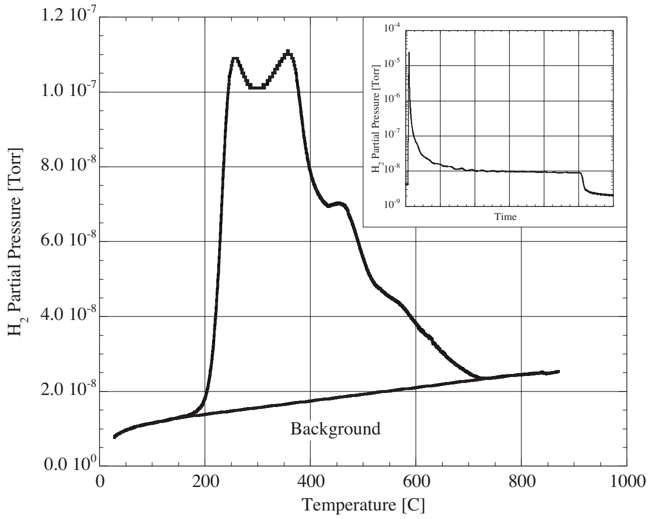

FIG. 3. Temperature-programmed desorption analysis of the deformed $PdH_{0.0008}$ sample showing the evolution of hydrogen (H_2 partial pressure) versus temperature under a constant heating rate of 7.1 °C/min. Approximately 1 g of material was used for this measurement. Inset shows the evolution of hydrogen from the balance of the 21 g sample over the 4.5 h 900 °C annealing procedure used to prepare the blank specimen. The sharp falloff near the end of the evolution curve corresponds to the furnace being powered down.

It is difficult to determine from our data if this phase transformation is influenced by the local lattice distortion associated with dislocations. Lattice dilatation associated with trapping sites at or near the dislocation core would in principle lead to softer optic modes and a corresponding shift of the TO peak to lower energy transfer. However, the peak locations at 4 K, a temperature at which the strongest dislocation-core trapping sites are expected to preferentially fill, are nearly identical and agree with the expected β-phase value. On the other hand, peak broadening is present in the $PdH_{0.0008}$ spectra at 4 K that may signal a loss of degeneracy. A loss of degeneracy is expected when strains perturb the

TABLE I. Vibrational DOS peak energies and standard deviations measured in this work.

Sample	E (meV)	σ (meV)
$PdH_{0.63}$ (4 K)	58.6	4.0
$PdH_{0.0008}$ (4 K)	59.0	5.8
$PdH_{0.015}$ (295 K)	68	
$PdH_{0.0008}$ (295 K)	66	9

threefold point symmetry of the octahedral interstitial site in an fcc lattice.

A difference in peak energy is observed at 295 K between deformed $PdH_{0.0008}$ and well-annealed $PdH_{0.015}$ (66 vs 68 meV, respectively). It is likely that hydrogen resides in the weaker trapping sites associated with the elastic strain field of (edge) dislocations at 295 K. The inherent strain perturbation at these sites will be smaller than the core trapping sites; this will act to preserve the cubic point symmetry and degeneracy associated with the octahedral interstitial site. The difference in peak energy at 295 K may then be attributed to the local lattice dilatation induced by the presence of trapped hydrogen. This statement is substantiated by a simple calculation using the measured peak positions. Assuming the peak shift from 68 to 58 meV as the hydrogen concentration changes from low (the solid-solution $PdH_{0.015}$ α phase) to high (the hydride $PdH_{0.63}$ β phase) can be used to estimate the local concentration, a linear interpolation yields 0.12 [H]/[Pd] trapped at dislocations in deformed $PdH_{0.0008}$ at 295 K. This concentration agrees with the local concentration of 0.15 [D]/[Pd] estimated from small-angle scattering measurements of trapped deuterium in single-crystal Pd at ambient temperatures.[16] This local concentration is beyond the normal solubility limit of hydrogen in Pd at room temperature. The question then remains as to why the vibrational DOS of the solid-solution α phase is observed. One possible answer would be that the lattice strain associated with the trapping sites decreases the interaction energy between hydrogen and Pd atoms, resulting in a suppression of the critical temperature. Further measurements are planned to identify the phase transformation temperature.

The investigation of trapped hydrogen with incoherent INS has been attempted previously in Pd (Ref. 20) and in other metals.[21,22] Most relevant is the experiment by Kirchheim *et al.*[20] in which the hydrogen vibrational DOS in cold-worked and well-annealed $PdH_{0.008}$ were measured at room temperature. This concentration is below the solubility limit at room temperature; trapping at dislocations was anticipated to increase the local concentration beyond the solubility limit, thereby resulting in DOS features characteristic of the high-concentration α' hydride phase. No such evidence was found. Kirchheim *et al.*[20] estimated that 30% of the hydrogen was trapped at dislocations; the balance residing regular interstitial sites. This may have reduced the sensitivity of the measurement to hydride DOS features because of superposition onto the primary 69 meV α peak. However, the spectrum from the deformed $PdH_{0.008}$ sample was, except for a slight broadening, identical to the annealed spectrum. The broadening observed in the deformed sample was attributed to a possible loss of degeneracy due to local lattice distortion.[20]

The spatial extent of trapped hydrogen (deuterium) has been characterized with small-angle neutron scattering at room temperature, at equilibrium with respect to the gas phase, and at bulk concentrations below the terminal solid-solution solubility.[15,16,20,23] The spatial profile of the trapped solute was modeled with a cylindrical geometry,[15,16] leading to a direct measurement of the Cottrell atmosphere radius of approximately 10 Å and a length exceeding 50 Å. The regions of trapped hydrogen (deuterium) are therefore large enough to undergo a phase transformation and result in the associated vibration DOS spectrum.

Very low overall hydrogen concentration was employed in the present work to ensure that all hydrogen were trapped, in effect isolating the influence of the distorted dislocation environment on the measured hydrogen vibrational DOS. While this was the case, it led to much lower hydrogen inventory (0.15 mg here compared to ~7 mg for Ref. 20, for example). The primary objective of our measurements was to observe changes in the vibrational DOS upon cooling without crossing into the hydride miscibility gap in the bulk. We therefore believe the observed shift in primary peak energy from 66 to 59 meV is the direct result of a hydride phase transformation near dislocations upon cooling from room temperature to 4 K. Peak broadening at 4 K in the deformed sample is attributed to a loss of degeneracy induced by local lattice strain associated with the core and near-core trapping sites. The 66 meV peak location of 295 K, shifted slightly from the expected (and observed) 68–69 meV value of α phase, is attributed to hydrogen-induced dilatation of the interstitial site in the elastic portion of the dislocation strain field. An estimate of the local trapped hydrogen concentration from this peak shift is consistent with a direct measurement of the deuterium concentration in deformed Pd obtained by small-angle neutron scattering.

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