Hydrogen trapping at dislocation cores at room temperature in deformed Pd

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ABSTRACT

Small-angle neutron scattering (SANS) measurements of hydrogen segregation at dislocations in heavily deformed single crystal Pd have been performed at very low solute concentration ($PdH_{0.0016}$) at equilibrium with respect to hydrogen gas at 295 K. The net (the without-hydrogen measurement subtracted from with-hydrogen measurement) absolute differential macroscopic scattering cross section has been fit with a cylindrical form factor to represent the Cottrell atmosphere, yielding local trapped concentration $\delta \sim 0.06$ [H]/[Pd], local volumetric dilatation $f \sim 1.01$, and trapping radius $R \sim 4$ Å of the segregated hydrogen. This measurement augments SANS results below ambient temperature [B.J. Heuser, H. Ju, Phys. Rev. B 83 (2011) 094103]. The temperature dependence of the measured radius is confirmed by a Fourier transform of hydrogen occupation at dislocations based on an elastic continuum treatment [Trinkle et al., Phys. Rev. B 83 (2011) 174116]. The measured trapping parameters are consistent with a depopulation of weak long-range dislocation strain fields at ambient temperature; hydrogen binding to stronger core dislocation sites persists at 295 K and results in the measured net scattering. The local solute concentration and trapping radius (less than two Burgers vectors in Pd), are both too small to support optic mode dispersion due to inter-hydrogen interactions. This result supports the conclusion that trapped hydrogen undergoes a hydride to solid solution phase transformation between 200 and 300 K based on hydrogen vibration density of states measurements using incoherent inelastic neutron scattering [Trinkle et al., Phys. Rev. B 83 (2011) 174116, Ju et al., Nucl. Instr. Meth. Phys. Res. A 654, (2011) 522, and Heuser et al., Phys. Rev. B 78 (2008) 214101].

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Small-angle neutron scattering (SANS) is sensitive to hydrogen segregation at dislocations, providing local solute concentration, volumetric dilatation, and spatial information that cannot otherwise be obtained experimentally. Two groups have applied SANS to study hydrogen and deuterium trapping at dislocations in deformed Pd over the last two decades [1–4]. Our past work has demonstrated the SANS response from the trapped solute can be modeled with a cylindrical form factor [1,3,4], that single crystal Pd is required to eliminate strong Porod scattering from inclusions in polycrystalline Pd [4], and that the deformed PdH_x ($x \sim 10^{-3}$) system locally satisfies Vegard's law for the hydride phase ($PdH_{0.6}$) below 200 K [1]. Incoherent inelastic neutron scattering (IINS) has recently been used to measure the hydrogen optic mode vibrational density of states in the same PdH_x ($x \sim 10^{-3}$) system [5–7] The IINS measurements demonstrate hydrogen trapped at dislocations undergoes a hydride to solid solution phase transformation between 4 K and 295 K. The perturbing effect of the near-

core strain fields of dislocations on the phase behavior was studied with *ab initio* techniques [5,8]. The strain associated with dislocation cores in Pd breaks cubic symmetry, lifting the threefold degeneracy of the bulk octahedral interstitial site. The *ab initio* calculations did not include dispersion; a harmonic treatment of dispersion yielded good agreement with IINS results at 4 K [5]. Both the IINS measurements and *ab initio* results demonstrate solid solution behavior (that is, isolated hydrogen without dispersion effects) at ambient temperature in PdH_x ($x \sim 10^{-3}$). However, direct measurement of the local trapped concentration δ and volume dilatation f with SANS at 295 K at low hydrogen concentration in deformed Pd is difficult to quantify and therefore lacking in the published literature. We have performed this measurement and report the results here.

The deformed single crystal sample, surface polishing procedure, and hydrogen loading procedure and loading apparatus used here were identical our previous work [1]. The sample mass and thickness for the current SANS measurements were 4.3691 g and 3.01 mm, respectively, the volume of the loading system was 1.19 l, and the total H_2 pressure change during absorption was

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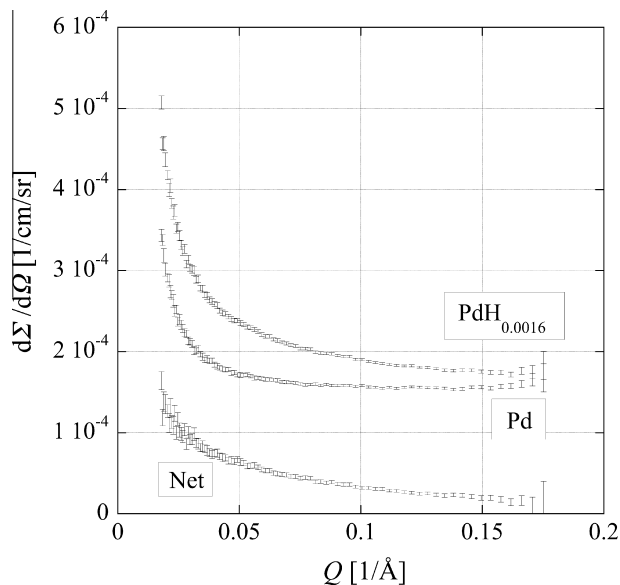 *E-mail address:* bheuser@illinois.edu (B.J. Heuser).

Fig. 1. Radial average SANS response from deformed single crystal Pd at 295 K at equilibrium with respect to H$_2$ gas. The net response is the subtraction of the without-hydrogen response from the with-hydrogen (with concentration 0.0016 [H]/[Pd]) response. The SANS measurements were corrected for empty cell scattering and area background.

Δp = 0.51 Torr. The corresponding hydrogen concentration using the ideal gas law was 0.0016 [H]/[Pd]. Equilibrium with respect to hydrogen gas is required for the SANS measurements at ambient temperature to prevent outgassing. A special environmental gas cell with sapphire windows described previously [3,9,10] was used to maintain equilibrium during the SANS measurements.

The General-Purpose CG-2 SANS instrument at the High Flux Isotope Reactor at Oak Ridge National Laboratory [11] was used for the measurements presented here. The configuration of the CG-2 instrument differed slightly from our previous experiments. The sample-to-detector distance was 3563 mm, the source-to-sample distance (SSD) was 4018 mm (seven guides inserted), and the incident neutron wavelength was 7.2 ± 1.1 Å ($\Delta\lambda/\lambda$ = 0.15). A 0.65 cm diameter Cd aperture defined the beam incident onto the sample and a 101 mm beam stop was used. The wave-vector transfer (Q) range for this instrument configuration was $0.02 \leqslant Q \leqslant 0.17$ Å^{-1}. The detector was not off-set to increase the high-Q limit. The net effect of this different configuration is an increase of ~2 in on-sample intensity compared to our previous measurement [1]; a factor 3.3 from the shorter SSD combined with a factor of 0.6 from the use of a smaller beam-defining aperture. The smaller beam aperture was required to ensure that stainless steel spacer and sample alignment elements within the environmental cell were not exposed to the neutron beam. In addition to the changes in the CG-2 instrument configuration, a new area detector was in use. The new detector combines the response of 192 linear position-sensitive tubes to form a 2-dimensional image and results in a much higher density of data points (better pixilation) across the entire Q range of a radial average. A total of five days of beam time were used, divided equally between the foreground (deformed sample with hydrogen), the sample background (deformed sample without hydrogen), empty beam (the environmental cell, including stainless steel spacer/alignment elements, with Cd aperture in place but without a sample), and the area or beam-blocked background measurements. Both sample measurements and the empty cell measurement were corrected for neutron transmission. The vitreous carbon standard was used to determine absolute differential macroscopic scattering cross sections.

The radial-averaged absolute differential macroscopic scattering cross sections dΣ/d$\Omega(Q)$ of deformed single crystal Pd with

hydrogen, without hydrogen, and net (without hydrogen response subtracted from the with-hydrogen response) measured at 295 K are shown in Fig. 1. The least square best-fit of the net SANS response to a cylindrical form factor [1], yielding cylinder radius $R = 4 \pm 1$ Å, cylinder length $L = 100 \pm 10$ Å, and amplitude factor $A = 367 \pm 9$ l/cm^2, is shown in Fig. 2. The high-Q behavior of the net SANS response is nearly identical to a perfect Q^{-1} power law (shown as the straight solid line in Fig. 2), indicating the trapped radius at 295 K is of order $R \sim 0$.

The SANS response from solute loaded, deformed Pd is comprised of four components [4]; solute–solute correlation scattering, solute-dislocation correlation scattering, dislocation–dislocation correlation scattering, and incoherent scattering from Pd and the solute. The SANS response from dislocations in heavily deformed Pd is very weak, is expected to have a ~Q^{-3} dependence [4], and is observed below $Q \sim 0.02$ Å^{-1} [3,4]. These observations are confirmed by the reference single crystal Pd SANS data shown in Fig. 1 and in Ref. [3]. Given that the SANS response from dislocations is weak and occurs below ~0.02 Å^{-1}, the cross-correlation solute-dislocation SANS response will likewise be very weak (or non-existent) and occur at lowest Q.

The measured value of the absolute differential cross section of the without-hydrogen sample at high Q, the invariant incoherent response (see Fig. 1), disagreed with the expected value (5.0×10^{-4} l/cm/sr) by approximately at factor of 3. A similar (~10^{-4} l/cm/sr) incoherent cross section for Pd was observed previously on the same instrument and same calibration standard [1]. This was attributed to poor counting statistics (~10^{-2} relative error) for the transmission measurement, the very low absolute cross section, and an unknown offset error related to the absolute calibration. The resolution of the incoherent cross section at high Q is enhanced in the present measurement because of the larger on-sample intensity and improved transmission counting statistics (~10^{-4} relative error). The greater detector pixilation adds visual support to this statement. Analysis of the net absolute cross section is not affected by this offset error.

We follow the same procedure as before to determine the local concentration of trapped hydrogen δ and volumetric dilatation f from the shape factor R and amplitude A [1]. The result of this analysis is shown in Fig. 3 and includes the known $\delta(f)$ dependence for
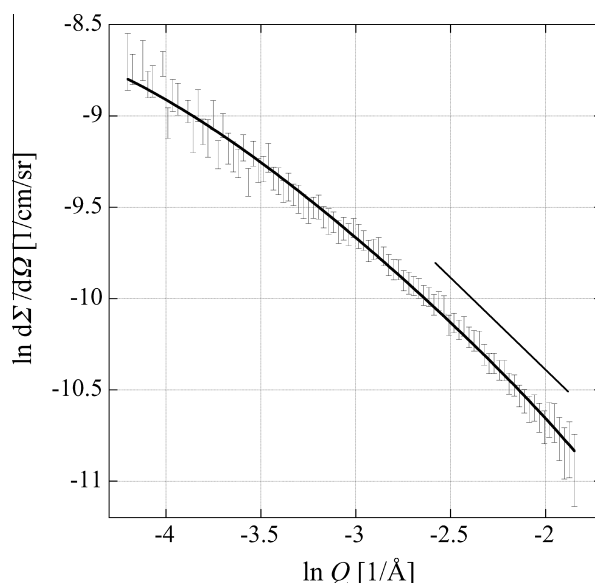

Fig. 2. The net SANS response at 295 K in ln–ln format. The solid line through the data is the best-fit of a cylindrical form factor as discussed in the text. The straight solid line represents a Q^{-1} scattering response (that is, with $R = 0$). The falloff from the Q^{-1} response at lower Q is due to a non-infinite cylinder length.
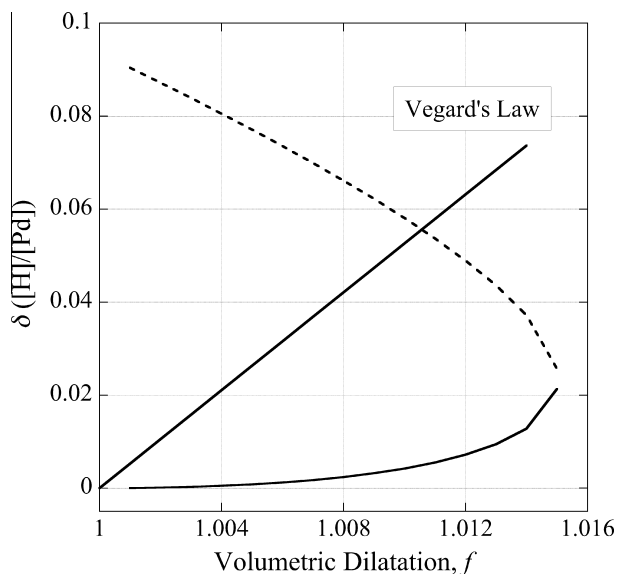
Fig. 3. Analysis of the 295-K SANS response using the amplitude factor A and shape factor R to determine the local trapped concentration δ and volumetric dilatation f. The dotted and solid curves represent two solutions to the quadratic equation discussed in Ref. [1]. The known $\delta(f)$ dependence for hydrogen in bulk Pd (Vegard's law) is shown as well. The intersection of Vegard's law and the dotted line gives the local trapped hydrogen δ–f phase behavior in $PdH_{0.0016}$ at 295 K.

Fig. 4. Dependence of trapped hydrogen radius R versus temperature T determined from the fit of the cylindrical form factor to the measured net SANS response (open boxes) and from the Fourier transform of the calculated hydrogen occupancy (closed boxes). The 15, 100, and 200 K measured radii are from Ref. [1].

hydrogen in bulk Pd (i.e., Vegard's law), $f-1 = 0.19\delta$ [12]. The intersection of Vegard's law with the loci of points satisfying the A–R criteria derived from the measured net scattering response [1] in Fig. 3 yields $\delta \sim 0.06$, local volumetric dilatation $f \sim 1.01$. For comparison, local concentration $\delta \sim 0.6$ and local volumetric dilatation $f \sim 1.1$ were derived from the measured $PdH_{0.0013}$ net SANS response at and below 200 K, consistent with $PdH_{0.63}$ hydride formation at dislocations at low temperature [1]. Optic mode vibrational density of states measurements of trapped hydrogen in deformed Pd at low temperature were also consistent hydride phase formation [5–7]. The measured temperature dependence of the trapped hydrogen radius $R(T)$ is shown in Fig. 4. This includes radii from Ref. [1] and the current 295 K value.

The elastic continuum model of hydrogen occupation at dislocations developed by Trinkle et al. [5] can be used to predict the $R(T)$ dependence. This model indicates the long-range dislocation strain field trapping sites depopulate between 100 and 200 K, with core trapping persisting at room temperature [5]. Our measured $R \sim 4$ Å at 295 K presented here is consistent with such core trapping. The hydrogen occupancy at each strain site associated with the dislocation was determined for $PdH_{0.0013}$ at 15, 100, 200, and 300 K using the continuum model, and includes the hydrogen–hydrogen interaction energy. The $d\Sigma/d\Omega(Q)$ dependence was obtained by performing a numerical Fourier transform of the occupation model and then integrating over the dislocation orientation and length to acquire the spatially-averaged scattering behavior. We then fit the continuum-model $d\Sigma/d\Omega(Q)$ with same form factor used for the SANS response [1,3,4] to determine the trapping radius R at each temperature T. The absolute magnitude of R magnitude at low T, relative insensitivity of R below 200 K, and the small trapping radius at 295 K are all confirmed by the calculated response, as shown in Fig. 4.

The changes in local trapped solute phase behavior (δ–f) and radius R from $T < 200$ K to $T = 295$ K are significant. The SANS results at 295 K presented here indicate a considerable reduction in both local trapped concentration and volumetric dilatation relative to that expected for Pd hydride ($PdH_{0.6}$). While a local trapped hydrogen concentration of 0.06 [H]/[Pd] is within the Pd–H miscibility gap at 295 K, this concentration would correspond $\sim$10% hydride
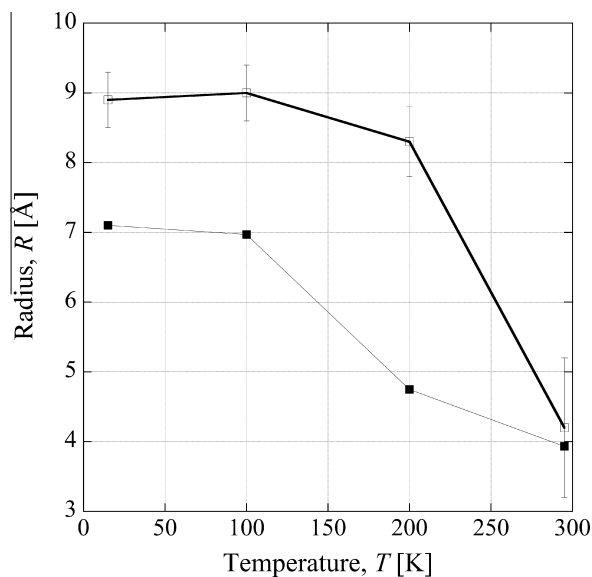
volume fraction in bulk. The radial extent R of the segregated solute is small, less than two Burgers vectors b ($b = 2.75$ Å in Pd). The octahedral interstitial site nearest-neighbor distance in Pd is also 2.75 Å. As discussed by Rowe et al., the large longitudinal optic mode dispersion observed from $PdH_{0.63}$ requires strong first and second like nearest-neighbor interactions [13]. The small trapping radius and low local hydrogen concentration derived from the SANS measurements presented here suggest hydride formation necessary for optic mode dispersion does not occur at dislocations at 295 K. Further, the volumetric dilatation induced by trapped hydrogen is small at 295 K and will not lead to significant mode softening from lattice expansion. Accordingly, the 295-K SANS results presented here confirm our recent IINS measurements; namely, the dispersion and optic mode softening associated with the Pd hydride phase are not present in the trapped hydrogen vibrational density of states at 295 K [5–7].

References

[1] B.J. Heuser, H. Ju, Phys. Rev. B 83 (2011) 094103.
[2] M. Maxelon, A. Pundt, W. Pyckhout-Hintzen, J. Barker, R. Kirchheim, Acta Mater. 49 (2001) 2625.
[3] B.J. Heuser, J.S. King, J. Alloys Comp. 261 (1997) 225.
[4] B.J. Heuser, J.S. King, G.C. Summerfield, F. Boue, J.E. Epperson, Acta Metall. Mater. 39 (1991) 2815.
[5] D.R. Trinkle, H. Ju, B.J. Heuser, T.J. Udovic, Phys Rev. B 83 (2011) 174116.
[6] B.J. Heuser, T.J. Udovic, H. Ju, Phys. Rev. B 78 (2008) 214101.
[7] H. Ju, B.J. Heuser, D.L. Abernathy, T.J. Udovic, Nucl. Instr. Meth. Phys. Res. A 654 (2011) 522.
[8] H.M. Lawler, D.R. Trinkle, Phys. Rev. B 82 (2010) 172101.
[9] W.C. Chen, B.J. Heuser, Phys. Rev. B 65 (2001) 014102.
[10] B.J. Heuser, J.S. King, W.C. Chen, J. Alloys Comp. 292 (1999) 134.
[11] K.C. Littrell, K.M. Atchley, G. Chengm, Y.B. Melnichenko, G.D. Wignall, Neutron News 19 (2008) 20.
[12] H. Peisl, in: G. Alefeld, J. Volkl (Eds.), Hydrogen in Metals I: Basic Properties, Topics in Applied Physics, Springer-Verlag, Berlin, 1978, p. 70.
[13] J.M. Rowe, J.J. Rush, H.G. Smith, M. Mostoller, H.E. Flotow, Phys. Rev. Lett. 33 (1974) 1297.