



実験報告書様式(一般利用課題・成果公開利用)

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課題番号 Project No. 2015A0260 実験課題名 Title of experiment Vibrational states of H atoms in nanocrystalline palladium hydride 実験責任者名 Name of principal investigator Maiko Kofu 所属 Affiliation Institute for Solid State Physics, University of Tokyo	装置責任者 Name of responsible person Ryoichi Kajimoto 装置名 Name of Instrument/(BL No.) 4SEASONS (BL01) 実施日 Date of Experiment 2015/10/30 – 2015/11/6

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form. Bulk PdH _{0.73} Nanocrystalline Pd Nanocrystalline PdH _{0.42}

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons. <p>The behavior of hydrogen in metals has attracted considerable attention in fundamental and applied research areas. Palladium hydride PdH_x is an ideal metal-hydrogen system and has been intensively studied for many decades. Pd has remarkable abilities to absorb plenty of hydrogen and to catalyze a broad range of reactions. Metal nanoparticles are of current interest owing to their unique properties as compared with bulk materials. We have investigated the thermodynamic property by an adiabatic calorimetry [1], structure by a neutron diffraction (ND) [2], and diffusion dynamics by a quasielastic neutron scattering (QENS) [3] for both bulk and nanocrystalline PdH_x with a size of 8 nm. In bulk PdH_x, the H atoms occupy the interstitial octahedral (O) sites (1/2, 1/2, 1/2) in the face-centered cubic (fcc) Pd lattice. Interestingly, our ND work on nanocrystalline PdH_x demonstrated that some of H atoms, probably in the subsurface (a few layers below the surface), are accommodated at tetrahedral (T) sites (1/4, 1/4, 1/4) [2]. It was also found from the QENS study that an additional fast diffusion process of the H atoms appeared in nano-PdH_x [3]. The results suggest that the H atoms diffuse fast near the surface, via the T sites.</p> <p>In this work, we have performed inelastic neutron scattering (INS) measurements to examine vibrational states of H atom in the Pd lattice in a wide energy region $0 < \hbar\omega < 300$ meV. The measurements were done using the Fermi chopper spectrometer 4SEASONS. Figure 1 shows colormaps of dynamical structure factor, $S(Q, \omega)$, for bulk PdH_{0.73} and nano-PdH_{0.42}, obtained with $E_i = 331$ meV at 10 K. Vibrational excitations are</p>
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2. 実験方法及び結果(つづき) Experimental method and results (continued)

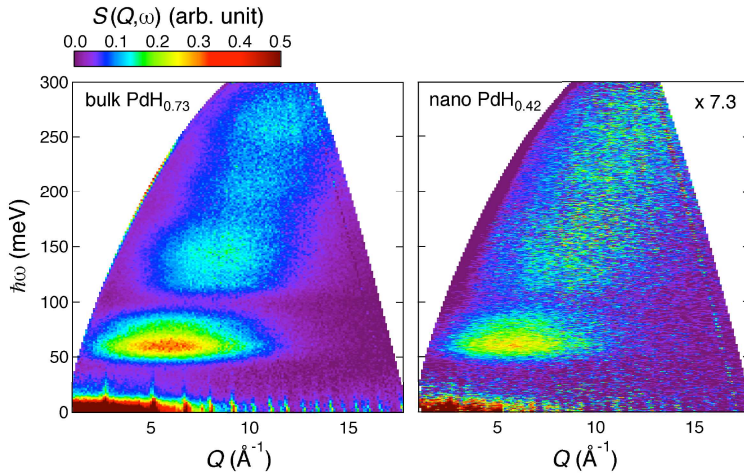


Fig. 1: $S(Q, \omega)$ maps of bulk $\text{PdH}_{0.73}$ and nano- $\text{PdH}_{0.42}$ at 10 K.

clearly visible at around 70, 140, 210, and 280 meV in bulk $\text{PdH}_{0.73}$. On the other hand, the $S(Q, \omega)$ map of nano- $\text{PdH}_{0.42}$ exhibits a clear excitation at 70 meV and a continuum above 120 meV. The excitations observed above 50 meV correspond to multiphonon processes that originate in the vibrations of H atoms.

To evaluate the excitation energies and intensities, the excitation peaks were fitted with multiple Gaussian functions. The vibrational spectrum of bulk $\text{PdH}_{0.73}$ was roughly reproduced by a quantum harmonic oscillator (QHO) model. In nano- $\text{PdH}_{0.42}$, in addition to the excitations which closely resemble those observed in bulk $\text{PdH}_{0.73}$, the excess excitations were found at higher energies (see Fig. 2). Our analyses demonstrated that the excess states were not explained by QHO but reasonably described as vibrations in a highly anharmonic trumpet-like potential. The excess excitations are attributed to the H vibrations at the T sites in the subsurface region stabilized by surface strain/distortion effects.

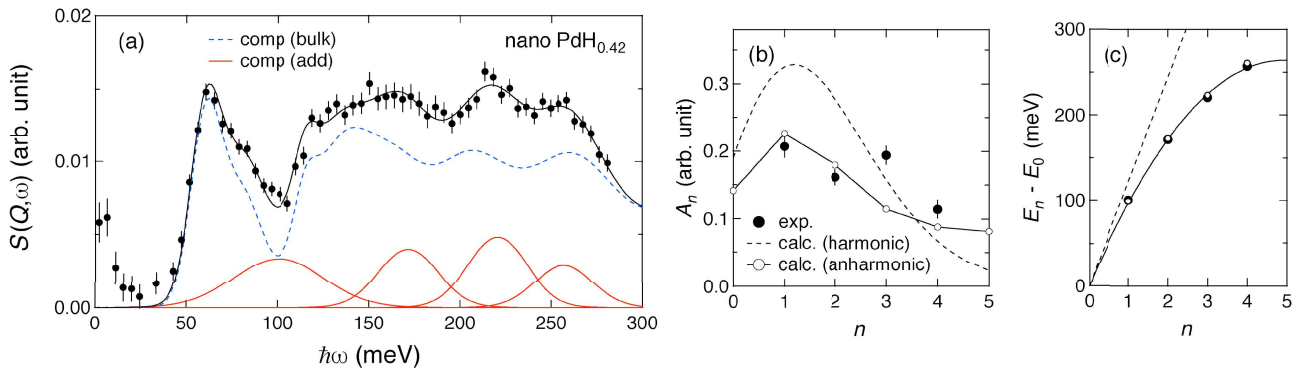


Fig. 2: (a) A constant- Q cut at $Q = 10 \text{ \AA}^{-1}$ of nano- $\text{PdH}_{0.42}$. (b) Excitation intensity and (c) energy against a quantum number.

- [1] H. Akiba, H. Kobayashi, H. Kitagawa, M. Kofu and O. Yamamuro, *Phys. Rev. B*, **92**, 064202 (2015).
 [2] H. Akiba, M. Kofu, H. Kobayashi, H. Kitagawa, K. Ikeda, T. Otomo, and O. Yamamuro, *J. Am. Chem. Soc.* **138**, 10238–10243 (2016).
 [3] M. Kofu, N. Hashimoto, H. Akiba, H. Kobayashi, H. Kitagawa, M. Tyagi, A. Faraone, J. R. D. Copley, W. Lohstroh, and O. Yamamuro, *Phys. Rev. B*, **94**, 064303 (2016).