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Neutron spectroscopic evidence for subsurface hydrogen in palladium

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The interaction of hydrogen with palladium black, a high-surface-area metal powder, has been investigated by incoherent inelastic neutron scattering. The vibrational spectrum associated with chemisorbed surface hydrogen occupying threefold sites has been identified. A vibrational mode at 58 meV, which is found to be inconsistent with either surface or bulk palladium-hydrogen species, is assigned to chemisorbed hydrogen occupying subsurface sites.

In recent studies of the chemisorption of hydrogen on palladium surfaces, evidence has been presented for the occupation of hydrogen in subsurface sites.[1-8] These sites are believed to be located in the region between the surface and second-layer palladium atoms. It has been suggested that hydrogen located in these sites provides an important link between strongly chemisorbed surface hydrogen and the more weakly bound hydrogen absorbed in the bulk. The experimental evidence for the occupation of subsurface sites, following the chemisorption of hydrogen on a variety of palladium surfaces, has been found by techniques such as thermal desorption,[1-4] photoemission,[5] low-energy electron diffraction,[2,3] and electron-stimulated desorption.[6] In addition, these studies have been supported by theoretical calculations.[2,7,8] For structural studies of hydrogen chemisorbed on Pd(111)[2,8] agreement between theory and experiment could only be achieved when a substantial fraction of the chemisorbed layer occupied subsurface sites. Evidence for subsurface hydrogen on Pd(111)[5] and Pd(110)[3,4] has been reviewed. We report here incoherent inelastic neutron scattering (IINS) measurements, which we believe provide the first vibrational spectroscopic evidence for the occupation of subsurface sites.

Unlike the vibrational spectroscopies [reflection-adsorption infrared and electron energy loss (EELS)] commonly used in surface science, IINS is neither limited by surface selection rules nor confined to the surface region. In IINS, the intensity of a vibrational mode is dependent primarily on the incoherent scattering cross section of the scattering nuclei and the mean-square amplitude displacement of the vibrating atoms. Additionally, integrated intensities allow direct estimates of the concentration of the hydrogen species present to be made. As the incoherent scattering cross section of hydrogen is 10–30 times greater than other nuclei, and modes involving hydrogen atoms have large mean-square amplitude displacements, IINS spectroscopy is very sensitive to those vibrational modes involving hydrogen motion, and has been used extensively in studies of hydrogen both absorbed in[9] and adsorbed on[10] metals. The IINS technique is thus a particularly suitable vibrational spectroscopic probe with which to investigate the interaction of hydrogen with palladium, as all forms of hydrogen (i.e., surface, subsurface, and bulk species) are, in principle, observable.

In the present Rapid Communication IINS has been used to probe the interaction of hydrogen with palladium black, a high-surface-area palladium powder. A sample of high-purity palladium black (27 g, initial surface area ca. 40 $m^2 g^{-1}$) was loaded into an aluminum, UHV compatible sample cell. The palladium surface was found to be essentially free of alkali-metal, alkaline-earth, and transition-metal impurities.[11] The sample was activated in the cell by hydrogen titration at 80 K to remove surface oxygen, followed by evacuation at ambient temperature and heating under high vacuum to 373 K for several hours. Three such hydrogen titration cycles were performed before the sample was finally heated under high vacuum to 373 K for 22 h. Under these conditions bulk hydride phases in palladium black are known to decompose spontaneously.[12] The resulting sample constituted hydrogen-activated palladium black.

Inelastic neutron scattering spectra were measured at 80 and 295 K on the BT-4 triple axis spectrometer at the National Bureau of Standards Research Reactor, using a liquid-nitrogen-cooled Be-filter analyzer. Over the energy range scanned, with 40-min collimation before and after a Cu(220) monochromator, an energy resolution of 5–6 meV below 90 meV and ~6% above 90 meV was obtained. Spectra were corrected for fast-neutron background contributions and differences in incident neutron counts.

The IINS spectra of hydrogen-activated palladium black at 295 and 80 K are shown in Figs. 1(a) and 1(b), respectively. These data show that no change in the spectral features occurs on cooling hydrogen-activated palladium black, other than a sharpening of the peaks due to a reduction in the multiphonon scattering. Intense resolved spectral features are observed in the spectrum at 58, 94, 101, and 120 meV, showing that a significant amount of strongly bound hydrogen remains after activation. Of these peaks, those observed above 75 meV have been assigned from normal-mode analysis coupled with neutron scattering intensity measurements,[11] to hydrogen adsorbed on surface threefold sites. These vibrational features and their assignment are in excellent agreement

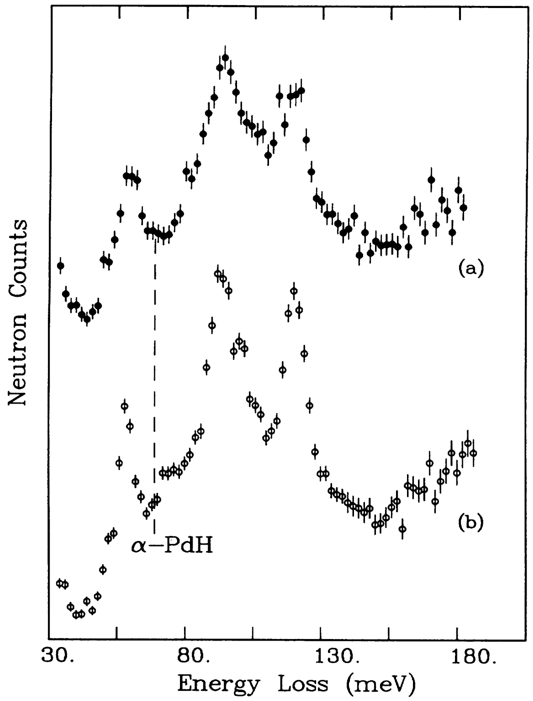

FIG. 1. The inelastic neutron scattering spectrum at (a) 295 K and (b) 80 K of hydrogen chemisorbed on activated palladium black. The position of the dominant peak in the density of states of α-phase palladium hydride is indicated for comparison.

with EELS results for hydrogen adsorbed on Pd(111).[13] The quantity of adsorbed surface hydrogen was estimated at between 0.5 and 0.7 monolayers, consistent with calculated surface coverages from the background pressure of 10^{-6} torr after activation. (A monolayer is defined by the BET surface area, assuming a Pd atom surface density of 1.2×10^{19} atoms m^{-2} and a H-Pd ratio of one at saturation coverage.) The remaining feature at 58 meV, whose relative intensity was found to be about 20% of the surface features, is of particular interest as it is inconsistent with both surface and bulk hydrogen. Evidence is presented in the following discussion which leads to the conclusion that this peak is associated with hydrogen located in subsurface sites below the palladium surface.

The 58-meV feature, we believe, cannot be assigned to a surface vibrational excitation for the following reasons. First, the vibrations of hydrogen bound in surface threefold sites have been identified at higher frequency, as discussed above.[11,13] Second, the vibration perpendicular to the Pd(100) surface of hydrogen adsorbed on a fourfold site has been observed at 64 meV in EELS measurements.[14] From this frequency we calculate, by normal-mode analysis,[11] that the degenerate parallel vibrations of a fourfold site are expected in the energy range 124–136 meV. Both the frequency of the perpendicular mode and the absence of a peak in the 124–136 meV region rule out an assignment of the 58 meV mode to a fourfold site. Third, similar normal-mode analysis arguments eliminate assignment of the 58 meV peak to vibrations at twofold sites.[11]

The concentration of hydrogen representing the feature at 58 meV is also inconsistent with this peak being due to a bulk hydride. When the estimated coverage of 0.14 ML for the 58-meV peak is converted to a stoichiometric concentration it yields $PdH_{0.005}$, which is well within the α-phase region of hydrogen in palladium at 295 K.[15] The IINS spectrum of hydrogen-activated palladium black at 295 K is shown in Fig. 1(a), with the position of the hydrogen vibration of the α-phase hydride measured by Rush, Rowe, and Richter[16] indicated. It is obvious from the figure that the 58 meV peak is not due to α-PdH, whose optical mode is observed at 69 meV. The observed peak energy is on the other hand close to that of the dominant vibrational peak of bulk β-phase palladium hydride observed at 59 meV.[16] However, at a hydrogen concentration of $PdH_{0.005}$ no β-phase hydrogen would be expected at 295 K, while essentially all of the hydrogen should be in the β-phase at 80 K, if it were in the bulk palladium. Thus if this peak were due to bulk hydrogen, its position should change from 59 meV at 80 K to 69 meV at 295 K. This temperature effect is clearly not seen in the data illustrated in Fig. 1. Additionally, previous studies have shown that the inelastic neutron scattering linewidth of the dominant density of states band of β- PdH is ≈ 10 meV (full width at half maximum) wide, after correction for instrumental resolution.[16] A similar width is obtained for α-PdH. Careful analysis of the peak observed in Fig. 1 reveals that its width is considerably narrower (6 meV) than that of the hydride features. This is strong evidence that the peak observed at 58 meV is not associated with bulk hydrogen.

In deuterium-hydrogen dilution experiments to be reported elsewhere[17] additional evidence was obtained that the feature at 58 meV is due to subsurface hydrogen. The 58 meV peak was found to remain selectively hydrogenated, whereas the surface features were deuterated more readily during deuterium-activation. There have been a number of reports of the selective adsorption of hydrogen into the subsurface region of the presence of deuterium.[3,18,19]

The evidence presented above clearly indicates that the 58 meV feature is due to nonsurface hydrogen species that is also not bulk in origin. In view of this evidence we believe that the 58 meV peak is due to hydrogen located in subsurface sites. As noted earlier the vibrational energy of the mode assigned to subsurface hydrogen is very similar to those observed for bulk hydrides. Such a mode frequency is reasonable, since the likely location for subsurface hydrogen is in the octahedral sites just below the surface metal atom plane. In both the α- and β-phase hydrides of palladium, hydrogen is found in such octahedral sites. The similarity in the vibrational peak energies observed here is thus consistent with a very similar coordination of metal bound to hydrogen in bulk species and in the proposed subsurface sites.

We thus conclude that the mode observed at 58 meV in the IINS spectrum of hydrogen-activated palladium black provides the first direct vibrational spectroscopic evidence for the existence and the nature of subsurface hydrogen in palladium.

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