Photoemission Studies of Energy Levels in the Palladium-Hydrogen System[*]

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Photoemission studies of the Pd/H system show a band of hydrogen-induced energy states centered at 1 eV below the bottom of Pd-derived *d* bands of width 4.4 eV. These results show that the widely accepted simple "proton model" of Pd/H is misleading. Our augmented–plane-wave calculations of PdH, Pd_4H_3, and Pd_4H exhibit these low-lying states and also explain why the added number of electrons (0.6) in β-phase PdH exceeds the number of *d*-band holes (0.36) in Pd.

The Pd/H system has been perhaps the most extensively studied metal/gas system, and many studies have been reported concerning its hydrogen-diffusion characteristics, pressure-composition-temperature characteristics, and use as a hydrogenation catalyst.[1] Several interesting theoretical models for the electronic structure of metal hydrides and chemisorbed hydrogen have recently appeared. These include the one-electron augmented-plane-wave (APW) energy-band calculations for metal hydrides by Switendick,[2] the Anderson resonant bound-state model as applied to hydrogen chemisorption by Newns,[3] and the induced-covalent-band model of Gomer and Schrieffer.[4,5] However, little definitive experimental data have been published concerning the electronic structure of the Pd/H system. The simple "proton model" of Pd/H appears to be widely accepted.[1,6,7] In this model the hydrogen electrons simply fill up the *d*-band holes (and possibly *s* states) of Pd at the Fermi level E_F. This conclusion is supported by electronic specific-heat measurements[7] and magnetic-susceptibility measurements.[8]

We report the first photoemission spectroscopy measurements for a metal-hydrogen system and find that the name "proton model" is misleading for the Pd/H system. Photoemission measurements of β-phase PdH for photon energies of 16.8, 21.2, 26.9, and 40.8 eV show a band of hydrogen-induced energy states centered at about 5.4 eV below E_F in addition to Pd-derived *d* bands which extend from E_F to about 4.4 eV below E_F.

In contrast with the widely accepted "proton model," our APW calculations for PdH, Pd_4H_3, and Pd_4H indicate that these low-lying states are hybridized Pd-H bonding states that screen the added protons. Since these bonding states are modified Pd band states, rather than additional states, the added electrons in β-phase PdH fill the *d*-band holes at E_F as well as extra *s*-*p*-band states which our calculations show are pulled down below E_F. This latter result also explains why the number of added electrons (0.6) in β-phase PdH exceeds the number of *d*-band holes (0.36) in Pd (see Mueller *et al.*[9]).

High-energy ultraviolet photoemission spectroscopy measurements were made using a windowless system.[10] Energy-distribution curves for Pd and Pd/H are shown in Fig. 1 for $h\nu = 21.2$ eV. The Pd curve shows strong emission from *d*-band states within ~4.4 eV of E_F. As we have previously observed for the noble metals,[10] the

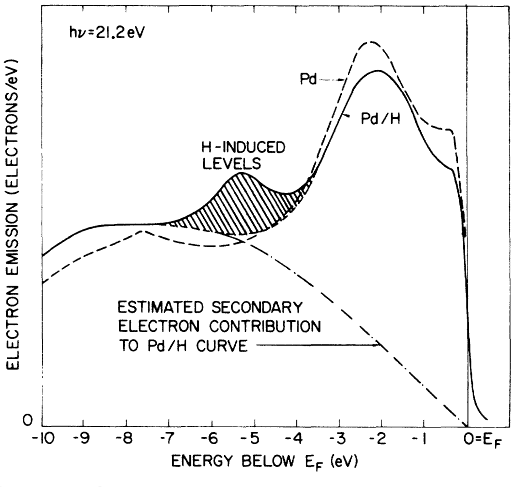

FIG. 1. Photoemission energy distribution for Pd (dashed curve) and a two-phase mixture of β-PdH and Pd (solid curve). The estimated secondary emission spectra are shown by the dashed-dotted line in the PdH curve. The initial energy scale places the highest occupied states at the Fermi level E_F.

energy-distribution curve for Pd reflects structure in the energy distribution of the joint density of states and is not equal to the band density of states. Structure is also seen in the secondary electron emission of Pd at about 7.5 eV below E_F which corresponds to inelastic scattering via plasmon excitation.[11] The Pd/H curve, which is for a two-phase mixture of Pd and β-phase PdH, shows new energy levels (shaded region) centered at 5.4 eV below E_F as well as the Pd d bands. Emission from these states near -5.4 eV is also seen for $h\nu = 16.8$ and 26.9 eV, and is very weak for $h\nu = 40.8$ eV. We associate these levels with hydrogen-palladium bonding states in β-phase PdH. Evidence for support of this suggestion and a description of our preparation technique follow.

While numerous contradictions and inconsistencies exist in the Pd/H literature, the following points germane to the present study seem fairly well established:

(1) Molecular hydrogen is dissociatively adsorbed on Pd and the atoms tend to diffuse into the bulk.

(2) Two distinct solid phases can coexist at room temperature below about 300°C. Near room temperature, the equilibrium concentrations expressed as atom ratios are $\mathrm{H/Pd} \simeq 0.005$ (α phase) and $\mathrm{H/Pd} \simeq 0.6$ (β phase), and the pressure of molecular hydrogen in equilibrium with the two solutions is about 10 Torr.[12] According to Lewis,[1] it has been the general finding that below 200°C the rate of equilibration is very slow for direct pressure-concentration studies. It is frequently found that the β phase when once formed may be very stable at room temperature even at very low hydrogen pressures.

(3) Neutron-diffraction studies[13] have shown that both hydrogen and deuterium atoms in β-phase PdH and PdD are located in the octahedral positions of the fcc Pd lattice. Thus stoichiometric PdH in the β phase would have the full sodium-chloride lattice.

Film specimens of Pd were prepared by evaporation onto a smooth Mo substrate using an electron beam gun. Pressures of approximately 5×10^{-9} Torr were maintained in the sample chamber with the lamp on. The pressure rose to about 1×10^{-7} Torr during evaporation of the Pd films and then rapidly recovered to $<10^{-8}$ Torr within 1 min.

The Pd/H sample was prepared by evaporating Pd at a rate of a few angstroms per second onto a substrate heated to 350°C in the pressure of 5×10^{-6} Torr of H_2. We then exposed the Pd/H film to 170 Torr of H_2 at room temperature for about 30 min. This caused the intensity of the hydrogen-induced states near -5.4 eV to increase by a factor of 2. Subsequently, heating of the substrate in 10^{-8} Torr to about 350°C caused a decrease in intensity. The energy position of these new states was found to be insensitive to a variety of hydrogen pressures and substrate temperatures during preparation of the Pd/H film. The use of deuterium gas in place of hydrogen resulted in an identical emission spectrum. All of these observations are fully consistent with the phase diagram of the Pd/H system[1] and the postulate that the observed states centered at -5.4 eV arise from β-phase PdH in the bulk of the film. Also, we rule out that the observed structure is due to chemisorbed molecular or atomic hydrogen since a very small effect was obtained when clean films were exposed to hydrogen at pressures of 10^{-5} Torr for several minutes (i.e., thousands of monolayer times). The possibility that the observed states at -5.4 eV are due to adsorbed O_2, CO, etc., is ruled out since exposure of Pd films to these gases for about 10^{-4} Torr sec caused negligible effects.

Previous calculations of the energy bands of metal hydrides have been reported for the rare-earth dihydride and trihydride systems[2] for which the anion model has particular relevance. In this previous work,[2] it was stated that no new low-lying bands are added for monohydrides such as VH, NiH, and PdH. In order to apply this band-model approach to our photoemission results for nonstoichiometric β-phase PdH, we have performed APW calculations for Pd and hypothetical PdH, Pd_4H_3, and Pd_4H.

Our results are summarized in Fig. 2, where we show calculated densities of states for Pd and PdH. These curves were obtained from our APW calculations using a tight-binding interpolation scheme with a nonorthogonal linear combination of atomic orbitals. The results clearly show a new set of states for PdH about 5-6 eV below E_F, i.e., centered about 1.5 eV below the bottom of the Pd d bands. The appearance of these new states is seen to be in agreement with our measurements for β-phase PdH in Fig. 1. These states are formed by the strong interaction of the hydrogen 1s electron states and the low-lying Pd states. Consequently, a modified band with strong hydrogen-palladium bonding character is developed below the Pd d bands. Charge-density calculations show that these

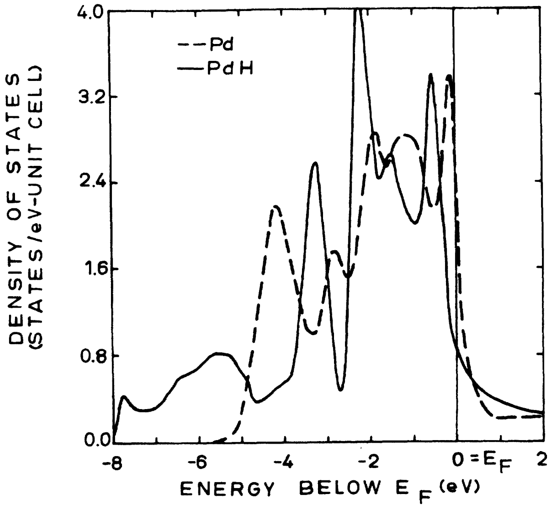

FIG. 2. Calculated densities of states for Pd and PdH. The Fermi levels for Pd and PdH were determined by filling 10 and 10.6 electron states, respectively.

states are hybridized bonding states with greater than 0.6 electron of 1s character inside the hydrogen APW sphere (radius = 0.704 Å). This charge is larger than the 0.5 electron inside the same size sphere for the hydrogen atom. Thus the proton is well screened in PdH and has about the same negative charge as it does in neutral hydrogen.

Since these "new" low-lying states in PdH are modified states which already existed (and were occupied) in Pd metal, the additional electrons associated with the hydrogens must fill previously unoccupied states. Our calculations show that these states are of three classes. The first class is the ~0.36 hole in the *d* bands. The second class is a group of states located around the *L* point in the Brillouin zone. These states originally were associated with the unoccupied top of the lowest *s*-*p* band in Pd and have L_2' symmetry character. Upon the addition of hydrogen, these states take on hydrogen *s* character and fall below the top of the *d* bands. Approximately 0.5 of an electron is taken up upon filling these states for PdH.[14] The third class of states is the remaining *s*-*p* band states above the top of the *d* bands. We can now understand why β-phase PdH forms with an average hydrogen-to-palladium ratio greater than the number of *d*-band holes (0.36). It is energetically favorable to fill the first two classes of states, which cause only a slight increase in the Fermi energy relative to the Pd *d* bands. However, the low state density of the *s*-*p* band states above the top of the *d* bands means that the energy increase per added electron to these states is substantial, and thus they do not fill.

We have confirmed that these occupied *s*-*p* states around *L* in β-phase PdH are due to hydrogen-hydrogen interactions by an APW calculation for Pd_4H. This calculation was also undertaken to simulate the effects of nonstoichiometry. The structure we have assumed for Pd_4H is a cubic unit cell containing four palladiums in the original face-centered cubic positions with a single hydrogen in one of the octahedral sites, namely, the center of the cube. The results again show hybridized hydrogen-palladium bonding states below the bottom of the Pd *d* bands, but of a somewhat decreased magnitude due to the sharing of the hydrogen by four palladiums. The rest of the band structure resembles very closely that of Pd mapped four times into the smaller Brillouin zone of the cubic cell. In particular, the states at *R* in this reduced zone which come from *L* in the fcc zone are only slightly modified and the top of the Pd *s*-*p* band remains above the *d* bands. This calculation in a sense represents an isolated hydrogen atom in the lattice and shows the hydrogen-palladium interaction with only a slight hydrogen-hydrogen interaction.

These calculations for PdH, Pd_4H_3, and Pd_4H show that nonstoichiometric β-phase PdH, which has an average of 2.4 hydrogens in the cubic cell, should have strong hydrogen-hydrogen interactions as well as hydrogen-palladium interactions. Only nearest-neighbor palladiums are essential for the hydrogen-palladium interaction which results in the formation of bonding states at the bottom of the palladium *d* bands, whereas nearest-neighbor hydrogens are necessary for lowering a significant number of *s*-*p* states below the top of the *d* bands.

In summary, photoemission measurements for β-phase PdH have shown new hydrogen-induced energy states about 1 eV below the bottom of the *d* bands in β-phase PdH. These low-lying states have been explained via energy-band calculations for PdH and Pd_4H. The calculations indicate that hydrogen is more electronegative than palladium in β-phase PdH, and also explain the limiting composition in terms of filling *s*-*p* hydrogen-hydrogen bonding states which are pulled down below the top of the *d* bands as well as filling the Pd *d*-band holes. A fruitful extension of this study would appear to be the measurement of other metal-hydrogen systems, including the rare-earth, group-IV, and group-Va metals which occlude hydrogen more strongly than Pd.

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Sign of the Nuclear Quadrupole Interaction in Rhenium Metal

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The sign and magnitude of the nuclear quadrupole splitting in rhenium metal have been determined by heat-capacity measurements down to 19 mK. We find an average coupling constant $e^2qQ/h = -246 \pm 2$ MHz for the two rhenium isotopes. This gives an electric field gradient at the nucleus of $q = -100\,q_{\mathrm{lat}}$, where q_{lat} is the source gradient produced by the Re^{7+} ion cores in the hcp lattice.

In recent years hyperfine quantities, such as the electric field gradient (EFG) at the nucleus, have become increasingly important as a means of studying the spatial behavior of conduction electrons in metals. The EFG originating from the charged ion cores in a noncubic lattice experiences a major enhancement from the screening effect of the conduction electrons, which involves the total electron charge density and thus all the states in the occupied volume within the Fermi surface. This effect has been shown[1] to produce considerable antishielding in the only case fully calculated, that of antimony, where the semimetallic nature allowed the small Fermi-surface overlaps to be ignored and only filled Brillouin zones to be considered. On the other hand, the calculations of Watson, Gossard, and Yafet[2] predict that in heavy metals with high densities of states at the Fermi level the free carriers will contribute a gradient which may be two orders of magnitude greater than the source gradient and which will have the opposite sign, i.e., a shielding rather than an antishielding effect.

While there exists a great deal of experimental data on quadrupole coupling constants and nuclear quadrupole moments, which allow the magnitude of the EFG at the nucleus to be obtained with fair accuracy in many metals, the lack of knowledge of the sign of the EFG is apparent. Obviously in treating a quantity such as the EFG which is made up of several canceling contributions, it is as desirable to know the sign as it is to know the magnitude. Except for γ resonance experiments involving transitions between different nuclear excitation levels, the sign of the quadrupole interaction can only be determined directly if some means are available for producing nuclear alignment. This is not straightforward as the splittings are of the order of 1 mK.

In the present work we report results from nuclear heat-capacity measurements on rhenium metal down to 19 mK, from which the sign of the quadrupole coupling has been unambiguously obtained. The net contribution to the EFG from the conduction electrons turns out to be one of substantial shielding, which is in agreement with the