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A new XPS/UPS study of the electronic structure of $PdH_{0.6}$

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Résumé. — Nous avons étudié la structure électronique de $PdH_{0,6}$ à 100 K au moyen de la photoémission en utilisant des sources de radiation MgKα et HeI, II. Nous observons dans $PdH_{0,6}$ un déplacement de la bande d par rapport à E_F et une diminution de $N(E_F)$. Contrairement à d'autres mesures, nous n'observons pas de bande d'émission aux environs de 5 eV. Par contre, nous voyons une faible émission à 8 eV probablement due aux états induits par l'hydrogène. Le déplacement chimique du niveau de cœur $3d_{5/2}$ est très faible ($+0,15 \pm 0,10$ eV).

Abstract. — We have studied the electronic structure of $PdH_{0.6}$ at 100 K by means of photoelectron spectroscopy using MgKα and HeI, II radiation. In $PdH_{0.6}$ as compared to Pd, the d-band is shifted away from E_F, and $N(E_F)$ is considerably decreased. In contradiction to earlier investigations we do not observe a band around 5 eV. However, we see weak emission at 8 eV probably related with the hydrogen induced states. The chemical shift of the $3d_{5/2}$ core level is very small ($+ 0.15 \pm 0.10$ eV).

At room temperature, Pd dissolves some hydrogen in the α-phase ($PdH_{0.01}$) and forms at the equilibrium pressure of ≈ 10 mbar the β-phase $PdH_{0.6}$. At higher pressure the hydrogen content of the β-phase increases towards stoichiometric PdH [1].

Many band structure calculations were performed for PdH_x. An overview on the different methods and the results was given recently by Switendick [2]. All the calculations have the following features in common, which can be tested experimentally :

1) The d-band of Pd is modified and shifted relative to E_F. The density of states $N(E_F)$ (one spin direction) at E_F decreases from 1.1 states/eV unit cell for Pd to 0.25 states/eV unit cell in PdH [3].

2) A new band is formed about 7 to 8 eV below E_F. It is mainly derived from s and d states of Pd.

3) A very small charge transfer seems to occur.

The decrease of $N(E_F)$ is in good agreement with results from specific heat and magnetic susceptibility measurements ([3] and references cited therein).

The electronic structure of PdH has been investigated by several groups by means of photoelectron spectroscopy using X-rays (XPS) or UV radiation (UPS) :

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Eastman *et al.* [4] exposed a Pd film at 350 °C to 5×10^{-6} torr of H_2 and subsequently at room temperature to 170 torr H_2 for 30 min. and analysed it with UPS. An additional peak was detected 5.4 eV below E_F and interpreted as the hydrogen induced band. No decrease of $N(E_F)$ was observed. The authors do not indicate at which hydrogen pressure and sample temperature the analysis was made, but probably at room temperature in ultrahigh vacuum.

Antonangeli *et al.* [5] charged a bulk Pd sample electrochemically with hydrogen and analysed it with XPS. They observed additional states from 5.5 to 8 eV which they related to the hydrogen induced states. No variation of $N(E_F)$ was observed. The Pd $3d_{5/2}$ core level is shifted from 334.8 eV in Pd to 334.9 eV in PdH. Again, sample temperature and hydrogen pressure during the analysis are not indicated.

Veal *et al.* [6] and Gilberg *et al.* [7] attempted to see the hydrogen induced states at room temperature by means of XPS and X-ray emission spectroscopy but failed because the hydrogen escaped through the clean surface.

The discrepancies between the experimental results of different groups about the new states and between theory and experiment about $N(E_F)$ led us to the reinvestigation of PdH by means of XPS and UPS.

The analysis was performed on a VG Escalab spectrometer using MgKα (1 253 eV), HeI (21.2 eV) and HeII (40.8 eV) radiation. The analyser was set to give an instrumental resolution of $\approx$ 1.0 eV for MgKα and $\approx$ 0.2 eV for HeI, II. E_F and the binding energy scale were calibrated on Au. Apart from the valence band we also investigated the Pd $3d_{5/2,3/2}$ core levels. The working pressure was 6×10^{-11} mbar before the inlet of He and before the desorption of hydrogen started.

Pd foils (0.125 mm thick, 99.99 %, Goodfellow), mounted on Cu sample holders, were cleaned in the spectrometer by Ar^+ bombardment and subsequently annealed at 300 °C for 1 hour. After the analysis of the Pd metal it was transferred into the high pressure autoclave of the spectrometer and kept for 30 min. at 15 bar hydrogen at room temperature. Before releasing the high pressures the sample was cooled to 100 K and then transferred on a cooled support to the precooled sample manipulator and analysed at 100 K.

The pressure in the analysing chamber rose to 5×10^{-9} mbar H_2 and dropped to 5×10^{-10} mbar H_2 within 10 min. A pressure increase was also observed when the power of the X-ray source was set to 200 W or more. Thus the XPS spectra were measured at 50 and 100 W. The residual gas was analysed with a mass spectrometer. All pressure variations were due to H_2 or He (He lamp on). The peaks at the masses 16, 18 and 28 (O_2, H_2O, CO) showed the same intensity as at 6×10^{-11} mbar total pressure.

The contamination of the sample was checked by the analysis of the 1s levels of carbon and oxygen before and after the hydrogenation and again after desorption. No carbon could be detected. The oxygen 1s level overlaps with the Pd $3p_{3/2}$ peak. However, from the comparison of the peak areas divided by theoretical cross section of the $3d_{5/2}$ and $3p_{3/2}$ peaks we conclude that within the accuracy of the background subtraction and of the cross sections no oxygen was present.

From the thermodynamic properties of the Pd-H system [1] we estimate that we charged our samples to the concentration slightly above $PdH_{0.6}$. At 100 K the equilibrium pressure should be of the order of 10^{-10} mbar H_2 and the kinetics very slow. Thus we estimate that our samples, after some initial desorption during the first 10 min., correspond to $PdH_{0.6}$.

At temperatures above 150 K and ultrahigh vacuum all our $PdH_{0.6}$ samples with clean surfaces desorbed very quickly their hydrogen at least within the escape depth of XPS ($\approx$ 25 Å for the VB and Pd $3d_{5/2}$). Electrolytically charged samples kept the hydrogen under similar conditions, but their surface was contaminated.

In figure 1 the HeI and HeII spectra are shown for $PdH_{0.6}$ at 100 K and 5×10^{-10} mbar H_2 (curves A), for PdH_x after the beginning of the desorption ($\approx$ 200 K, 1×10^{-6} mbar H_2, curve B) and for Pd at the end of the desorption (250 K, 5×10^{-7} mbar, curves C). In $PdH_{0.6}$ the d-band is displaced relative to E_F and accordingly $N(E_F)$ is rather small. No peaks appear between 5 and 6 eV. With increasing desorption (B) the displacement becomes smaller and at the end of the desorption (C) the d-band begins at E_F and $N(E_F)$ is large. The HeI and HeII spectra of $PdH_{0.6}$(A) as compared to those of Pd (C) exhibit a weak additional emission around 8 eV.

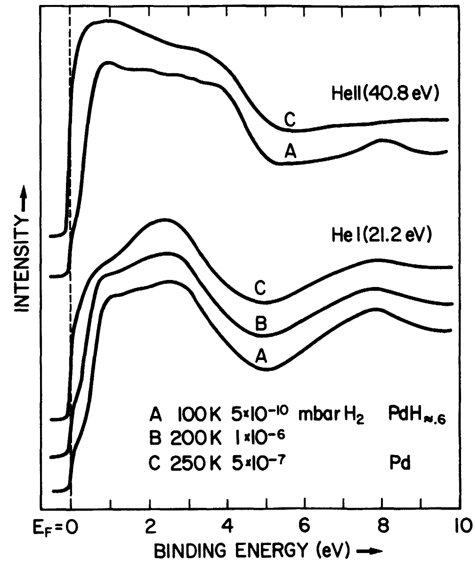

Fig. 1. — UPS spectra of PdH_x before (A), during (B) and at the end (C) of hydrogen desorption.

The XPS valence band spectrum of $PdH_{0.6}$ (Fig. 2) as compared to that of Pd shows the same features as the He spectra show : A small displacement of the d-band relative to E_F together with the decrease of $N(E_F)$, no peak between 5 and 6 eV, but some additional emission around 8 eV. The d-band intensity of $PdH_{0.6}$ at 3 eV is slightly larger than in Pd. The chemical shift of the $3d_{5/2}$ core level (Fig. 2) to higher binding energy is very small (0.15 ± 0.10 eV).

In conclusion, we have shown that the XPS and UPS spectra of $PdH_{0.6}$ differ from those of Pd in the following points : The d-band of $PdH_{0.6}$ is displaced relative to E_F and $N(E_F)$ is considerably reduced in agreement with theory. A weak emission around 8 eV is probably due to the

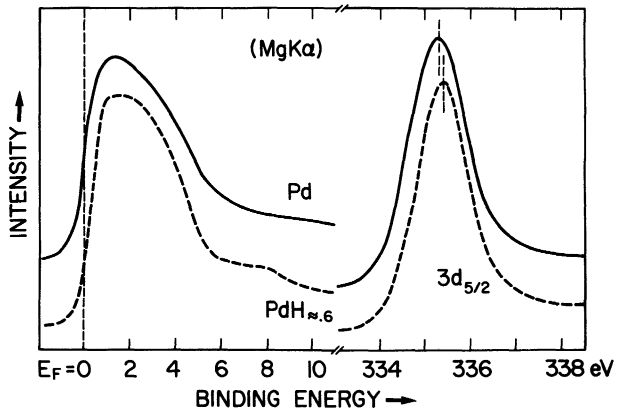

Fig. 2. — XPS spectra of the valence band and of the $3d_{5/2}$ core level of $PdH_{0.6}$ and Pd at 100 K.

hydrogen induced states. We do not observe, however, hydrogen induced states between 5 and 6 eV. The $3d_{5/2}$ core level is shifted not more than 0.15 ± 0.10 eV.

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