Photoemission from H adsorbed on Ni(111) and Pd(111) surfaces

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The electronic states of H chemisorbed onto the Ni(111) and Pd(111) surfaces are investigated as a function of H concentration using angle-resolved photoelectron spectroscopy and synchrotron radiation as the light source. Exposure of either crystal surface to molecular H_2 results at low temperature in adsorption of approximately one monolayer of atomic H. This saturation coverage of H is characterized by a H-induced band split off from the bulk bands with 1×1 dispersion and by dramatic changes in the d-band surface states. As the H concentration is decreased, the split-off state moves upwards towards the bulk bands at all $\bar{k}_{\|}$ until it disappears at a H concentration of ~ 0.5 [0.3] of the saturation coverage for Ni(111) [for Pd(111)]. In contrast to the behavior of the split-off state the substrate surface states shift continuously with H concentration. We propose that the split-off state results from the attractive H potential but its dispersion is dictated by the substrate symmetry.

I. INTRODUCTION

The adsorption of H onto a transition-metal surface or the absorption into the bulk constitute two very important areas of research activity in materials science.[1,2] The interaction of H with a transition metal has been viewed for many years as a simple prototype system for understanding chemisorption. Yet after more than a decade of both theoretical and experimental studies of H adsorption, there are many glaring inconsistencies as well as a few clear successes. To illustrate this point, consider the history of spectroscopic measurements and their interpretations for H adsorbed on single-crystal faces of Ni. Angle-integrated photoemission measurements for adsorption at room temperature onto a Ni(111) surface showed a H-induced peak ~ 6 eV below the Fermi energy.[3,4] This peak was originally interpreted as the H—Ni bonding level. But Himpsel et al.,[5] using the variable photon energy available at a synchrotron, demonstrated that the peak at 5.8 eV below the Fermi energy was not a H bonding level but instead an enhancement of the direct transition from the bulk sp band of Ni. Himpsel et al.[5] believed that they had observed a "new type of chemisorption bond" on a transition metal, where the bonding was predominantly with the free-electron-like sp band. However, measurements at lower temperatures on Ni(111) clearly showed the existence of a two-dimensional H—Ni split-off state,[6] in contrast to the room-temperature measurements.[3–5] This H-induced band had the correct dispersion to be an ordered (1×1) overlayer of H. The dramatic change in the photoemission spectra as a function of H concentration in going from ~ 1 monolayer adsorbed onto a surface cooled to 80 K to $\sim \frac{1}{2}$ of a monolayer adsorbed at room temperature led us to speculate that the room-temperature "invisible" H was in a subsurface site.[6] Neither the sub-

surface site hypothesis or the speculation about its invisibility have received any theoretical support,[7–9] yet no other explanation has been presented.

The vibrational data for H adsorbed onto Ni surfaces seemed to give a consistent picture of a localized H-metal bond. On the Ni(100) surface Anderson[10] observed a 74-meV dipole allowed mode and DiNardo[11] has seen a 135-meV nondipole mode which are presumably the symmetric and asymmetric stretch of H bound in a fourfold site. H on Ni(111) exhibits at low temperature two nondipole active modes at ~ 90 and 140 meV, which were interpreted as being the asymmetric and symmetric stretches, respectively, of a H atom bound in a threefold site.[12] H adsorbed onto Ni(110) in the low-coverage—low-temperature lattice gas regime exhibits modes at 71 and 131 meV which are interpreted as the asymmetric and symmetric stretch of a threefold site composed from Ni atoms in the first and second planes.[13,14] All of these modes are consistent with a nearest-neighbor harmonic force constant model[13] and are justified by theoretical calculations by Muscat.[15] Then calculations[16,17] based on effective-medium theory appeared and produced results for chemisorption energies of all of the 3d, 4d, and 5d metals in very good agreement with experimental data.[16] This theoretical approach however showed that the force-constant model for determining vibrational energies of H was not appropriate. Instead one must consider the dispersion and anharmonicity of the specific levels before the observed frequencies can be interpreted.[17] At present the interpretation of all H vibrational data is in limbo.

In contrast to the above, theoretical calculations compared to experimental angle-resolved photoemission data for saturated H on Pd(111) (Ref. 18) and Ti(0001) (Ref. 19) show remarkably good agreement and give a detailed picture of the H-metal surface bond.

The photoemission observations reported in this paper clear up the issue[6] of the disappearance of the H-induced split-off state for room-temperature adsorption on Ni(111) and Pd(111). The energy position of the split-off state with respect to the Fermi surface depends upon H concentration. For a concentration of H below ~ 0.5 [~ 0.3] of a saturated coverage on Ni(111) [on Pd(111)] the split-off state merges into the bulk bands, making it a resonant state which is very difficult to observe. This observation is consistent with calculations for the electronic structure of β-phase palladium hydrides, where it was found that the energy position of the H-induced state was a function of H concentration.[20] The metallic surface states on Ni(111) and Pd(111) are observed to shift continuously with H concentration, consistent with a previously reported observation of H adsorption on Cu(111).[21] All of these observations indicate that the effect of H adsorption is to change the surface potential in a very delocalized fashion, dependent upon H concentration. However, we still do not have a clear picture of the concentration-dependent H-bonding site or the H mobility, both of which are crucial for a realistic model.

In Sec. II we describe the experimental procedure, while Sec. III reports our observations. Section III is subdivided into four parts. In Sec. III A we describe the saturated H coverage results for Ni(111) equivalent to the measurements for Pd(111) which have already been reported.[18] In Secs. III B and III C the dependence of the photoemission spectra upon H concentration is described. Finally, Sec. III D describes preliminary results for H adsorbed onto Co(0001).

II. EXPERIMENTAL PROCEDURE

These experiments were performed primarily at the Synchrotron Radiation Center of the University of Wisconsin. The synchrotron light was dispersed by a dual toroidal grating monochromator which operated in the 10^{-10}-Torr vacuum range. The angle-resolved spectrometer is a 2.5-cm mean radius hemispherical analyzer with an angular resolution of $\pm 2.5°$. The combined resolution of the monochromator and analyzer was usually set at a few tenths of an eV. The main vacuum chamber operated in the low 10^{-10}-Torr range. The sample was mounted onto a Dewar with a two-axis rotation and x,y,z translation. With liquid-N_2 cooling, the crystal could be cooled to ~ 100 K or heated to ~ 1000 K. The temperature was measured by a thermocouple, spot welded to the sample.

The crystals were cleaned by Ne ion bombardment, accompanied with chemical treatment when necessary. The surface cleanliness was monitored by Auger spectroscopy and the appearance of surface states. The orientation of the crystal with respect to the analyzer was first checked with low-energy electron diffraction (LEED) and finally adjusted using symmetry-related angle-resolved photoemission measurements. Work-function changes were measured by recording the shift in the cutoff of the secondary electrons in the photoemission energy distribution. For these work functions measurements the sample was biased by several volts to avoid any problems originating from work-function differences between the sample and analyzer. Our thermal desorption spectra were obtained by measuring the change in the H_2 signal in the mass spectrometer as a function of crystal temperature for a constant heating current. The measured temperature versus time was nearly linear in the temperature range of interest.

III. RESULTS AND DISCUSSION

We have separated the presentation of the data into four sections. In Sec. III A we describe for Ni(111) the effect of saturated H adsorption at $T < 170$ K, which corresponds to 1 monolayer of atomic $\tilde{H}$.[6,22] The same data
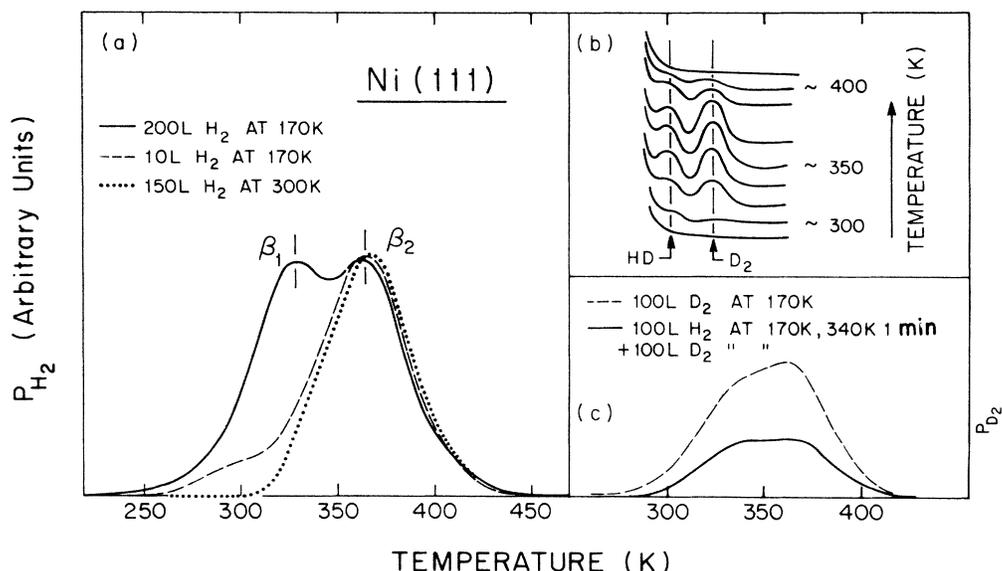

FIG. 1. Thermal desorption spectra (TDS) of H_2 and D_2 from Ni(111); (a) TDS of H_2, (b) mass spectrometer analysis of HD and D_2 signal versus crystal temperature for exposure conditions described in text, (c) TDS of D_2 from D_2 saturated surface ($- - -$) and from surface co-exposed first to H_2 and then to D_2 after desorbing the β_1 state.

for Pd(111) has already been published together with a comparison to theoretical calculations.[18] In Sec. III B (C) we describe the changes in the photoemission spectra as a function of H concentration for H adsorbed on Ni(111) [Pd(111)]. Finally, Sec. III D presents first data on the Co(0001) surface.

A. Saturated adsorption on Ni(111) at low temperature

Figure 1 displays thermal desorption spectra as well as isotopic mixing experiments. The main point of this figure is to calibrate our data with others previously reported.[23,24] The thermal-desorption spectra show two nearly equal peaks centered at 325 and 365 K. This should be compared to the data of Winkler and Rendulic,[24] which gives equivalent temperatures of 310 K and 380 K. Christmann et al.[23] report desorption peak temperatures of ~345 and 390 K. Considering the differences in heating rates and the slight nonlinearity of our heating rate we consider that our data is as consistent with the data of Winkler and Rendulic,[24] and Christmann et al.[23] as they are consistent with each other. The right-hand side of Fig. 1 shows that the adsorbed hydrogen is *atomic*. In the lower right panel the dashed curve shows the thermal desorption of D_2 following 100 L exposure at 170 K. [1 langmuir (L) $\equiv 10^{-6}$ Torrsec.] The solid curve is the thermal desorption of D_2 following 100 L of H_2 adsorbed at 170 K, heated for 1 min to 340 K to desorb the β_1

state, and then exposed to 100 L of D_2 to populate the β_1 state by D_2. D_2 is desorbed from both the β_1 and β_2 states. The top set of curves shows the time evolution of the mass spectra of HD and D_2 as a function of desorption temperature for the same co-exposure procedure and proves that there is complete mixing. The saturation coverage of H atoms has been measured to be 1 monolayer for low-temperature adsorption.[22]

Figures 2 and 3 reproduce the photoemission spectra for exposures of H where the crystal temperature is held below the temperature where H will desorb. You can easily see (tic marks) the H-induced split-off state, which shows 3—4 eV dispersion as a function of $\bar{k}_{\parallel}$ both in the $\bar{\Gamma}$ to $\bar{K}$ direction seen in Fig. 2 or the $\bar{\Gamma}$ to $\bar{M}$ direction of Fig. 3. At $\bar{\Gamma}$ we already know that the sp-like (Λ_1 symmetry) surface state at 0.25 eV below E_F is quenched by H adsorption.[5,6] Figure 2 shows that there are dramatic changes in the region of the Ni d band in the $\bar{\Gamma}$ to $\bar{K}$ direction, while Fig. 3 indicates much less pronounced changes at $\bar{M}$. The huge intensity in the emission from
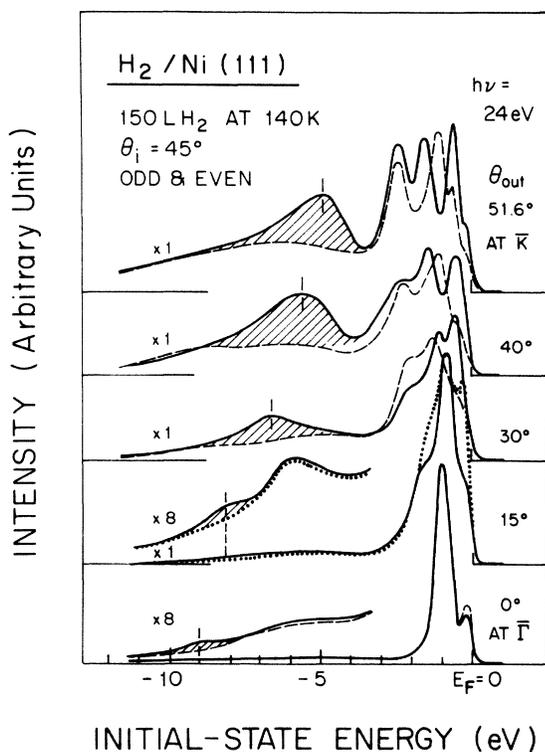

FIG. 2. Angle-resolved photoemission spectra for 150 L of H_2 adsorbed onto a Ni(111) crystal at $T = 140$ K. The photon energy is 24 eV and the light is p polarized in the plane of $\bar{\Gamma}$, $\bar{M}$, and the surface normal. The angle of incidence of the light θ_i is 45°. The dashed or dotted curves are for clean Ni(111).
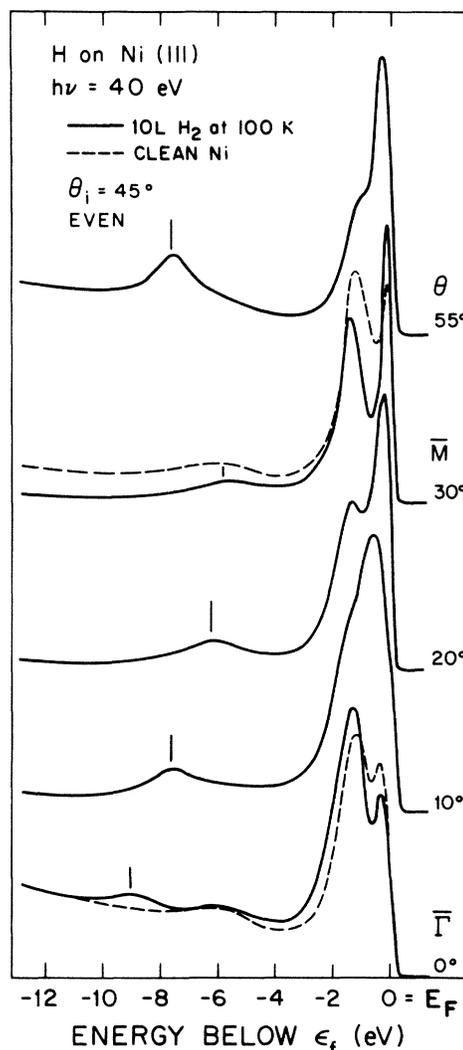

FIG. 3. Angle-resolved photoemission spectra along the $\bar{\Gamma}$ to $\bar{M}$ direction for H adsorbed on Ni(111) at 100 K.
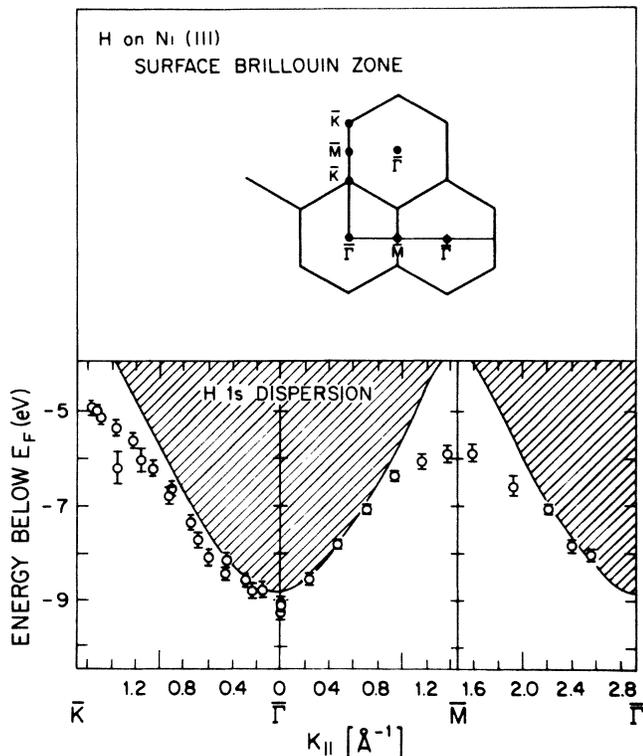
FIG. 4. Measured dispersion of the H-induced split-off band for saturation H adsorbed on Ni(111) at low temperature. The shaded region is the projection of the bulk band structure (Ref. 25).

the split-off state around $\bar{K}$ indicates a strong admixture of Ni $3d$ states into this H-induced level at certain symmetry points in the surface Brillouin zone (SBZ). The measured dispersion of the H split-off state is plotted in Fig. 4 as a function of $\bar{k}_{\parallel}$ in the SBZ of Ni(111). The

shaded regions are the projection of the bulk band structure onto the SBZ. The dispersion of the H state exhibits the correct periodicity for a (1×1) structure. Notice that at $\bar{\Gamma}$, the H-induced state is very close to the bottom of the bulk bands.[25]

In Table I we compare the observations for the H-induced split-off bands on Ni(111) and Pd(111) with those observed on other crystal surfaces. Ni, Pd, and Pt(111) surfaces all show a H split-off state for a one monolayer H concentration. The magnitude of the observed dispersion is related to the H density, being the largest for the largest concentration [H on Ni(111)]. There is no correlation between the position of the H split-off state and the H adsorption energy.[6] Instead it appears that the position of this band at $\bar{\Gamma}$ is dictated instead by the bulk bands. The H level is only 0.2 eV off from the Ni bulk band for Ni(111) and 0.9 eV for Pd(111). Notice that for Pt(111) the H band is slightly above the bottom of the bulk bands. This latter observation may however be vague since in the case of Pt we have used the theoretical bulk bands for the projection.

The next section is introduced in Fig. 5 where we have plotted the dependence of the energy position of the H-induced split-off state as a function of H exposure. The saturation curve shows the same split-off state seen in Figs. 2 and 3, but at lower exposures the H state moves up toward the Fermi energy disappearing into the Ni bulk emission features. It was this identical behavior for H on Pd(111) that we explained as the consequence of the removal of dispersion in the H level as the concentration of H decreases. When the average H-H spacing increases, the magnitude of the dispersion should decrease if the dispersion is a consequence of H-H direct or indirect interaction and there is no island formation. This means that the binding energy of the state at $\bar{\Gamma}$ will decrease while the average binding energy at the SBZ boundaries should increase.

TABLE I. Energy position and width of H split-off band. FWHM represents the full width at half maximum.

Crystal (face)	Energy at $\bar{\Gamma}$ (eV)	Peak width FWHM (eV)	Bottom of s band	Dispersion (eV)	H density in 1 monolayer
Ni(111)	9.0	1.4	8.8	$3.2\bar{\Gamma}-\bar{M}$ $4.2\bar{\Gamma}-\bar{K}$	0.186 atoms/Å^2
Pd(111)[a]	7.9	1.2	7.0[b]	$1.4\bar{\Gamma}-\bar{M}$ $2.0\bar{\Gamma}-\bar{K}$	0.153 atoms/Å^2
Pt(111)	9.4	1.4	9.8	yes ~ 2	0.150 atoms/Å^2
Co(0001)	7.2	$\lesssim 2$[c]		yes	0.183 atoms/Å^2
Cu(111)[d]	6.3	1.2	9.0	no	0.177 atoms/Å^2
Ni(100)[e]	no split-off state seen				0.162 atoms/Å^2
Ni(110)[f]	8.2	1.3			0.114 atoms/Å^{2g}

[a]See Ref. 18.
[b]See Ref. 28.
[c]Poor angle resolution.
[d]See Ref. 21.
[e]See Ref. 8.
[f]See Ref. 26.
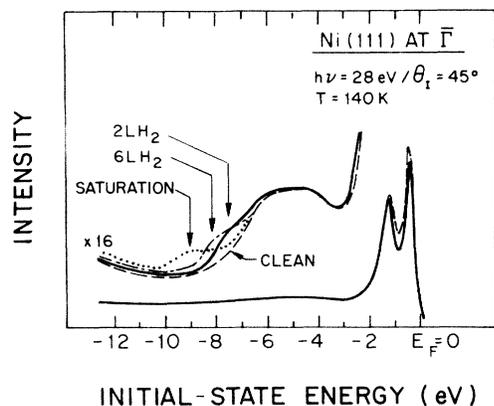[g]The saturation concentration is 1.5 monolayers (Ref. 27).

FIG. 5. Normal-emission photoemission spectra as a function of H_2 exposure at $T = 140$ K.

The next section will show that, as the H concentration decreases, the split-off band does not exhibit the expected behavior, because the dispersion is not a consequence of H-H interaction alone.

B. H concentrations less than 1 monolayer [Ni(111)]

The variations in the photoemission spectra as a function of exposure condition, subsequent heating and/or cooling all appeared to be only a function of H concentration. Therefore we will present only two types of experiments in this section. The first class of experiments involves exposure of the Ni crystal to H_2 at a temperature below any desorption ($T < 200$ K), subsequently warming to a temperature T and cooling back down before a photoemission spectra was accumulated. The second set of experiments involved exposure of the crystal held at room temperature. The amount of H remaining on the crystal was determined from the work-function change (see Fig. 8 below) which was calibrated by Christmann et al.[23] or from the thermal-desorption spectra.

Figure 6 shows a set of angle-resolved spectra taken at $\bar{K}$ in the SBZ. The bottom two curves compare clean Ni(111) and Ni(111) after 150 L exposure at a crystal temperature of 140 K. There are two features in these spectra that change as the H concentration is decreased. The first is the H-induced split-off state at ~ 5 eV below the Fermi surface and the second is the surface state in the clean spectrum at an initial-state energy of -1.0 eV. The saturated exposure of H shifts this surface state to -1.36 eV. The second set of curves is obtained when the crystal is heated for 1 min to 295 K and then cooled to 140 K. The split-off state has almost disappeared, but the clean surface state is still shifted. Note also that, while at $\bar{\Gamma}$ the split-off state has shifted up by ~ 0.6 eV, at $\bar{K}$ the weakly resolved H 1s-derived state has hardly shifted at all, despite an expected downward shift at $\bar{K}$ of ~ 0.9 eV. The peak in the clean Ni(111) spectrum due to an intrinsic surface state at -1.0 eV appears at -1.2 eV after warming to 295 K. This is ~ 0.2 eV lower than in the clean spectra but ~ 0.15 eV higher than the equivalent state for saturation H coverage. Our work-function measurements
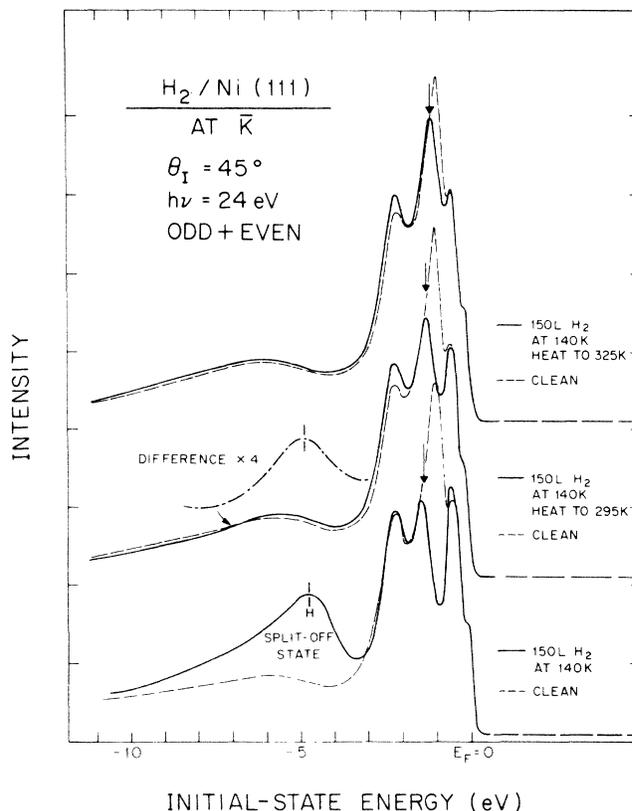

FIG. 6. Angle-resolved photoemission spectra at $\bar{K}$ of the Ni(111) SBZ. The sets of spectra show the evolution as a saturated H layer adsorbed at 140 K is heated (desorption temperature held for 1 min, measurement taken again at 140 K).

indicate that there is ~ 0.6 of a monolayer of H left on the surface after heating to 295 K for 1 min. The strong reduction in the photoionization cross section around $\bar{K}$ indicates that the character of the wave functions for the H-bonding state is significantly different in this new phase. The top set of curves in Fig. 6 shows that after heating to 325 K for 1 min the energy distribution has almost returned to the clean spectrum. The surface state is only shifted by ~ 0.1 eV with respect to the clean counter part. The H coverage is ~ 0.3 of a monolayer. To summarize Fig. 6 we have observed that the surface state at -1.0 eV at $\bar{K}$ shifts almost linearly with H coverage obeying the equation $E = -1.0 - 0.036\Theta$ (eV) (Θ is coverage in monolayers). In stark contrast, the H split-off state at $\bar{K}$ is only visible for coverages $1 < \Theta \lesssim 0.5$.

In Fig. 7 we illustrate the behavior of the angle-resolved spectra at $\bar{M}$ in the SBZ. There are very few changes in the d-band states (0 to -3 eV) upon H adsorption, but the split-off state of even symmetry at -5.9 eV is very visible. The middle set of curves were recorded after heating the saturation layer to 280 K for 1 min. There are very few changes in the spectrum compared to saturation coverage. There is still 0.8 to 0.9 of a monolayer of H present. The top curve is obtained after 1 min heating to 315 K. The split-off state has moved up to -4.9 eV, instead of moving down by ~ 1 eV as expected from the
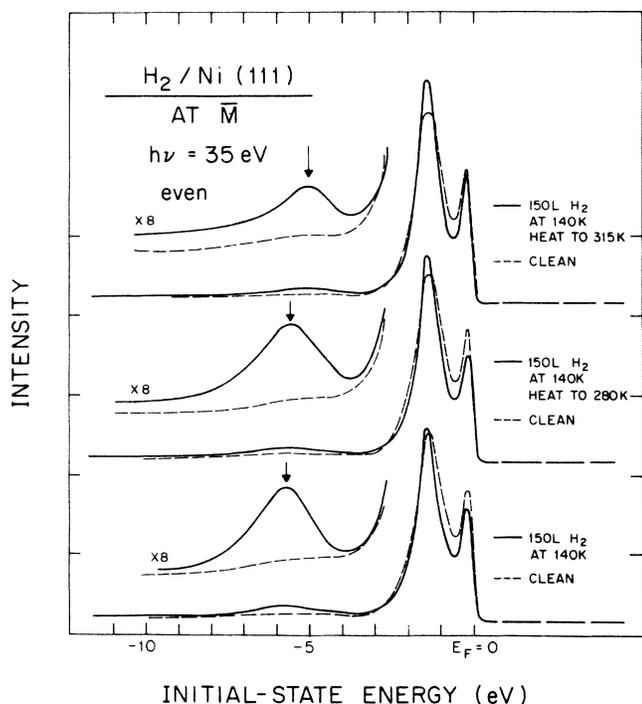
FIG. 7. Angle-resolved photoemission spectra at $\overline{M}$ of the Ni(111) SBZ. As in Fig. 6, the spectra show the evolution when a saturated H layer adsorbed at 140 K is heated.
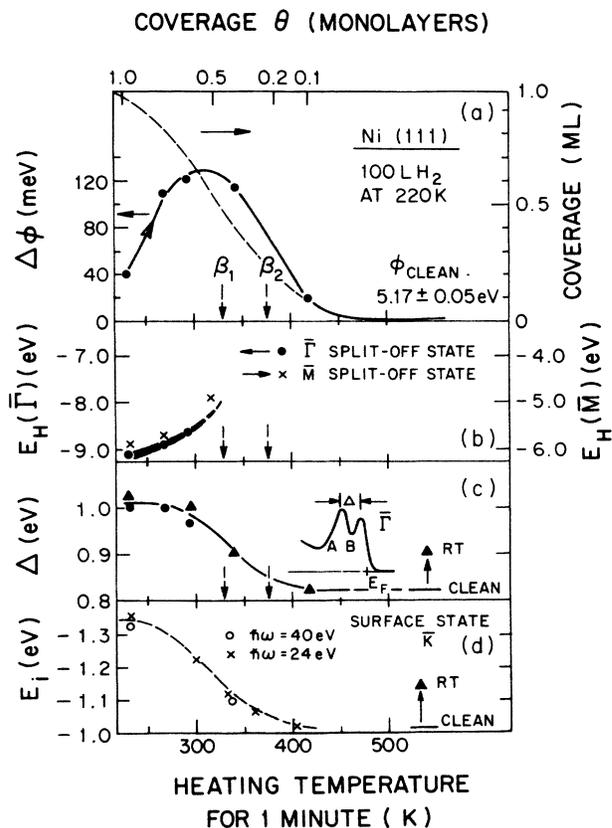

FIG. 8. Properties of the H-Ni(111) system as the adsorbed H is thermally desorbed. (a) shows the correlation between work function change and H coverage. (b) is a plot of the dependence of the energy position of the H split-off level at $\overline{\Gamma}$ (left) and $\overline{M}$ (right) upon the heating temperature after saturation adsorption at ~ 100 K. (c) displays the splitting in the two peaks observed at $\overline{\Gamma}$. (d) is a plot of the energy of the surface state at $\overline{K}$.

behavior at $\overline{\Gamma}$, and has decreased in amplitude. The coverage is $\sim 0.5-0.6$ monolayer. The split-off state at $\overline{M}$ has lost about $\sim \frac{1}{2}$ of its intensity at this coverage. When the coverage is reduced below ~ 0.5 the split-off state disappears at $\overline{M}$. The detailed heating treatments summarized in Fig. 8 reveal that the split-off state has an intensity variation roughly proportional to coverage for $1 < \Theta < 0.5$, but that it shifts toward E_F as the coverage decreases. The split-off state is not visible at $\overline{\Gamma}$, $\overline{M}$, or $\overline{K}$ for $\Theta \leq 0.5$.

Figure 8 tries to condense the findings from the photoemission spectra taken at $\overline{\Gamma}$, $\overline{K}$, and $\overline{M}$ of the Ni(111) SBZ as a function of H concentration. The top panel shows our measurement of the work-function change after heating for 1 min at the temperatures indicated by the horizontal scale. Our work-function—versus—heating curve looks very similar to the work-function—versus—coverage curve published by Christmann et al.[23] There is no quantitative agreement since our saturation work-function change is ~ 40 meV while theirs is extrapolated to be ~ 70 meV and the maximum change observed by Christmann et al.[23] is 180 meV compared to 130 meV in our experiment. If we scale our curve to fit theirs then we can calculate the H coverage versus heating temperature. This curve is shown by the dashed line in panel (a). The coverage ordinate is on the right. Panel (b) shows the behavior of the $\overline{\Gamma}$ and $\overline{M}$ split-off states as a function of heating temperature or H concentration. The energy scale for the $\overline{\Gamma}$ state on the left has been shifted up by 3 eV compared to the $\overline{M}$ scale on the right. This panel shows that the split-off band moves up as the H coverage decreases until it disappears for $\Theta < 0.5$ of a monolayer. Qualitatively

our observations indicate that the magnitude of the dispersion in the $\overline{\Gamma}$ to $\overline{M}$ direction is independent of coverage and the periodicity of the dispersion is always (1×1).

The normal emission spectra always show two peaks, which are reproduced in the insert of panel (c), and the separation of these two states versus the heating temperature or the H concentration is given in (c). The splitting for the H-saturated surface is ~ 1.1 eV and decreases continuously with coverage to ~ 0.82 eV for clean Ni(111). Panel (d) shows the shift in the surface state at $\overline{K}$. This surface state starts at -1.0 eV and shifts to -1.36 eV for saturation H exposure. All of the surface states in the d-band region of Ni seen in the $\overline{\Gamma}$ and $\overline{K}$ spectra shift continuously with H concentration. The sp-like surface state at 0.25 eV below E_F at $\overline{\Gamma}$ behaves very similar with respect to the H concentration as the same state on Cu(111).[21] It is only fully restored above ~ 450 K, where all of the hydrogen is desorbed.

Note that the existence of the split-off state in the photoemission spectra for $\Theta > 0.5$ monolayer is accompanied by a change in sign of the surface dipole moment as manifested in the work-function change.
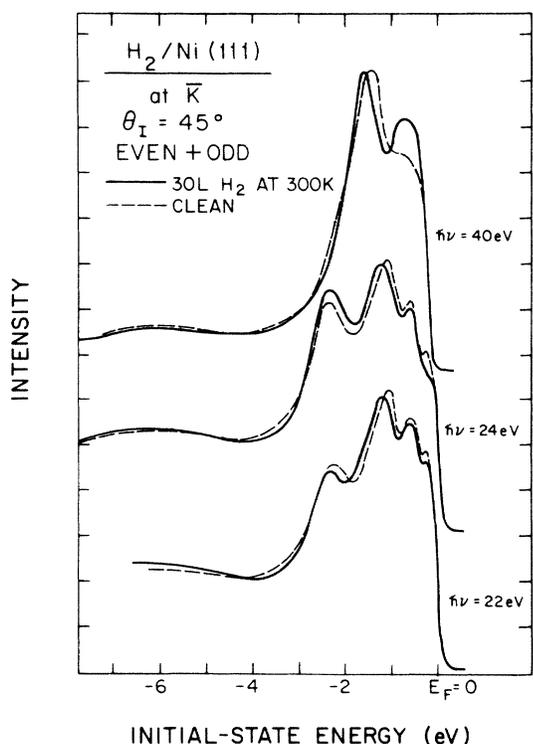
FIG. 9. Clean and H_2-exposed Ni(111) at room temperature.

FIG. 10. Normal emission EDC's for clean Pd(111) and with a saturated monolayer of hydrogen. The angle of incidence of the light θ_i is varied to show the polarization dependence of various features in the spectra.

The second set of experiments were done with the Ni crystal held at room temperature. In general, our observations showed that the features in the photoemission spectra were determined solely by the H concentration, as determined by the work-function change and the thermal desorption spectra, and not by the crystal temperature. At $\overline{M}$ we saw almost no change in the d bands and no split-off state. At $\overline{\Gamma}$, the Λ_1 symmetry surface state was attenuated and at lower photon energies there was an enhancement in the sp-band direct transition intensity as reported by Himpsel et al.[5] In Fig. 9 we show spectra taken at $\overline{K}$ for three photon energies. All three sets of spectra show a shift in the clean surface state at -1.0 eV. This shift is ~ 0.13 eV and is indicated by the triangle on the right of Fig. 8(d). Figure 8(c) also shows the energy separation of the two peaks at $\overline{\Gamma}$ for room-temperature adsorption. Both of these measurements indicate approximately 0.5 of a monolayer of H present on the surface which is consistent with the thermal desorption spectra.

C. H on Pd(111)

Results for saturated hydrogen coverage on Pd(111) at 90 K and at room temperature were reported earlier.[6,18] The earlier paper also included an exposure sequence at 90 K.[18] At the time however we did not have experimental data showing the symmetry of the surface states involved. Recently Chan and Louie[7,29] predicted a change in symmetry of the surface states of the Pd surface at $\overline{\Gamma}$ when H occupies a subsurface location.[6]

Figure 10 shows normal emission spectra of clean Pd(111) and with a saturated hydrogen layer at two dif-
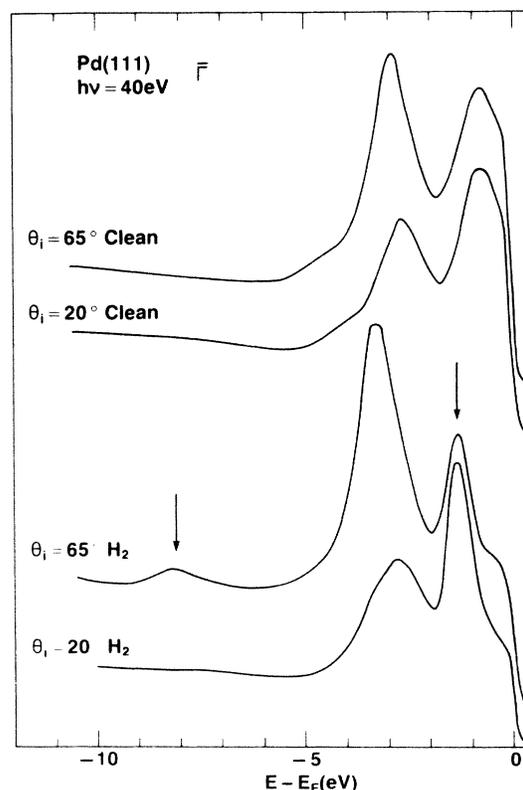
ferent angles of incidence of the light. Thus, we are able to detect which features are excited by the component of the polarization vector normal to the surface (Λ_1 symmetry initial states) or by the component parallel to the surface, which excites initial states of Λ_3 symmetry. Comparing the energy-distribution curves (EDC's) in Fig. 10, we find that the H split-off state has Λ_1 symmetry, as predicted.[18,29] The H induced state at -1.2 eV on the other hand, has Λ_3 symmetry. In order to determine the symmetry of the clean surface state near E_F we have to use the difference curves between spectra of the clean and H-covered surface. This eliminates the contribution from the underlying bulk interband transitions. From the difference curves it becomes obvious that this surface state also has Λ_3 symmetry, again as predicted.[18,29] However we have not observed a symmetry change in this surface state when the surface was exposed to H_2 at room temperature. This change in symmetry was predicted by theory,[7,29] if H occupied a full monolayer of subsurface octahedral sites.

We now turn to the coverage dependence of the H-induced features on the Pd(111) surface which is illustrated in the spectra in Figs. 11—13 and summarized in Fig. 14. The hydrogen coverage was determined using thermal desorption measurements. The various coverages were prepared in the same way as for Ni(111) by heating a low-temperature saturated crystal surface to a certain
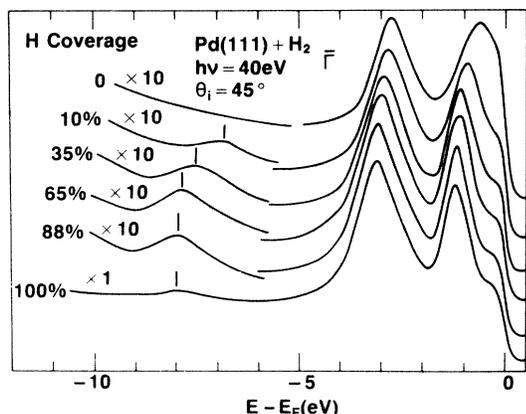
FIG. 11. Normal emission EDC's for various coverages of hydrogen on Pd(111) obtained by heating the saturated low-temperature phase to different temperatures. All spectra are taken at $T = 90$ K. The hydrogen coverage was determined by thermal desorption.

temperature. All photoemission spectra were taken at 90 K. The thermal desorption curves do not exhibit two distinct maxima as for Ni(111) (Fig. 1) but rather a peak at 250 K with a shoulder at 190 K. The shoulder (β_1 state) is either present in the desorption spectra or not, depending on the coverage, whereas the main desorption peak shifts with coverage from 250 K to a maximum of 310 K at low coverages. A distinct hysteresis in the thermal desorption was observed similar to the results of Christmann et al. for H on Pt(111).[30]

The intrinsic Pd(111) surface states at $\bar{\Gamma}$ and $\bar{K}$ shift linearly with hydrogen coverage to higher binding energy (see Figs. 11—13). In all three cases the total shift is approximately 0.5 eV. The H $1s$ split-off state however does not shift at all at $\bar{K}$ and $\bar{M}$ with changing coverage, whereas at $\bar{\Gamma}$, a shift of more than 1 eV is observed. Nevertheless the 1×1 periodicity of the dispersion of this state is maintained down to $\sim 30\%$ of saturation coverage.

How do we reconcile a 1×1 dispersion at less than monolayer coverage with a continuous shift of the intrinsic surface states? We know from the latter observation that there is probably no island formation on the surface, otherwise we would observe that the surface state with low H concentration was a composite of the clean surface state and the saturated monolayer surface state. Moreover, island formation is also precluded by a rather strong H-H repulsion in a hydrogen monolayer.[2] Therefore our observations are more consistent with an expansion of the mobile hydrogen atoms to form a uniformly dense layer across the surface. The intrinsic surface states feel a potential change linear with hydrogen coverage and the apparent 1×1 dispersion of the "H $1s$ band" is caused by predominantly d admixture into this band from the substrate states. This d admixture imprints the 1×1 dispersion since it has the substrate periodicity by nature.

Having explained the shifts of the intrinsic surface states and the persistence of the 1×1 dispersion, we still
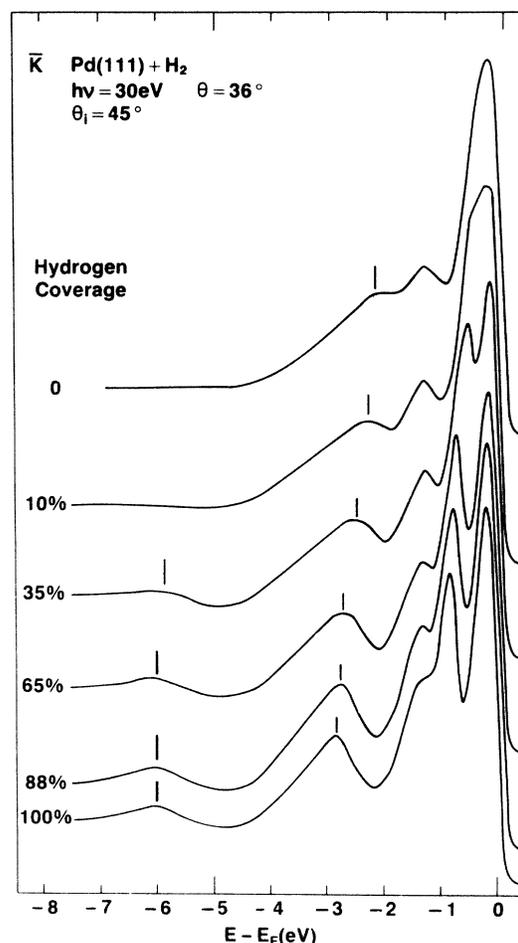

FIG. 12. Same as Fig. 11 but at a polar angle setting of the detector corresponding to the $\bar{K}$ point of the SBZ.
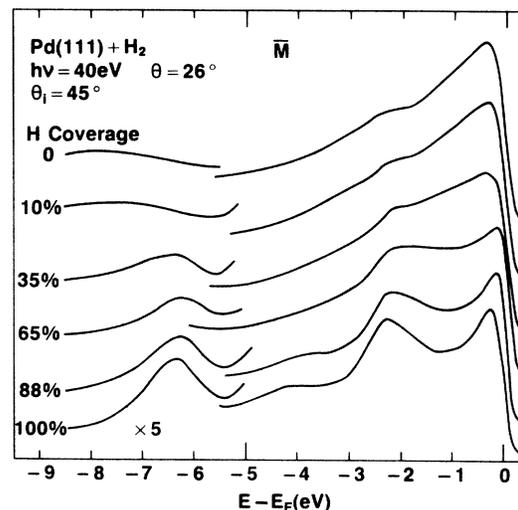

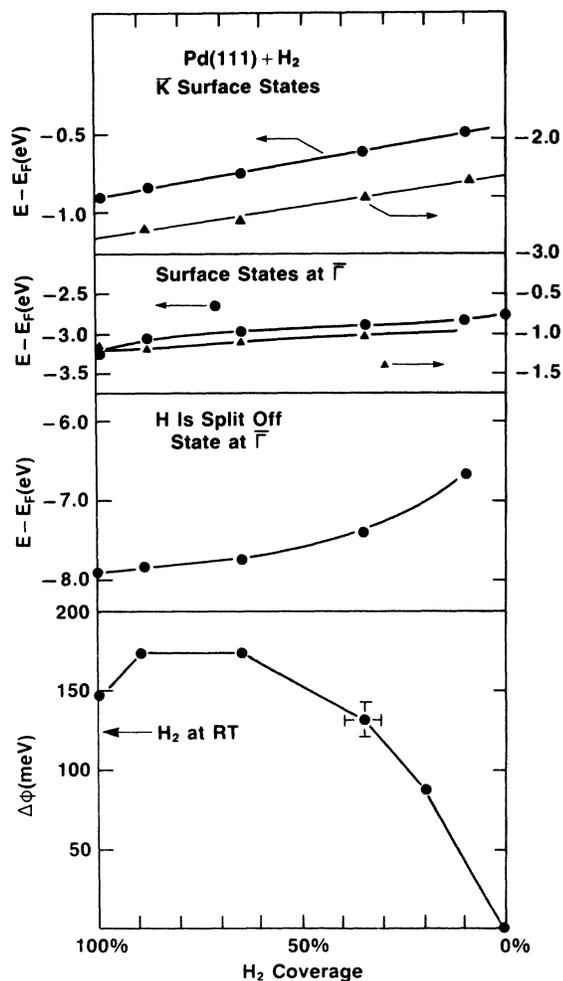FIG. 13. Same as Fig. 11 but taken at the $\bar{M}$ point of the SBZ.

FIG. 14. Work function and peak positions of various extrinsic and intrinsic Pd(111) surface states as a function of hydrogen coverage.

split-off state near the zone boundary.

Lowering the hydrogen concentration affects both, the center and SBZ boundary part of the H split-off band on Ni, whereas the split-off state on Pd only is affected in the center. The zone boundary part of this state is pinned by the Pd bulk band because of the avoided level crossing.

D. H on Co(0001)

The system $H_2/Co(0001)$ qualitatively shows the same behavior as was observed before for the other dense packed surfaces of Cu, Ni, Pd, and Pt.[6,18,21] Only a few preliminary results are reported here. At low temperatures, the H split-off state is observed at ~ 7.2 eV below E_F near the center of the SBZ (Fig. 15). This band was observed to show some dispersion, the exact dependence however could not be measured due to the experimental restrictions in part of these measurements. Upon heating to room temperature (and subsequent cooling back to ≤ 170 K), the split-off state disappears together with the first peak in the thermal desorption spectrum (TDS) [Fig. 16(a)] and with the H-induced structure in the Co d bands at ~ 1.7 eV below E_F [Fig. 16(b)]. The sp-like surface state at E_F, which is clearly seen at low photon energies [Fig. 16(b)], is quenched as long as any hydrogen is present on the surface. Saturation adsorption at room temperature produces the same results as heating the low-temperature phase up to room temperature for approximately 1 min, followed by subsequent cooling. Even with a standing H_2 pressure of 10^{-5} Torr in the system, none of the low-temperature characteristics could be enforced at room temperature. From TDS we estimate a coverage of ~ 0.6 monolayers for room temperature. The origin of the third peak in TDS at $\sim 60\,°C$ is not clear at

have to discuss the bandwidth of the split-off state and the differences in this state between Ni and Pd as listed in Table I. The large difference in bandwidth (see Table I) of the split-off state between Ni(111) and Pd(111) cannot be explained solely by the 10% increase in lattice constant from Ni ($a = 3.52$ Å) to Pd ($a = 3.88$ Å). Moreover, an isolated H monolayer in the correct spacing to match the Pd surface has a calculated bandwidth of 4 eV.[31] In general this bandwidth could increase upon contact of the monolayer with the substrate because of the additional through substrate interaction. We also note that the H split-off state has a normal sp-like dispersion on Ni(111) (Fig. 4), whereas on Pd(111) we observe a strong deviation about halfway out in the SBZ.[6,18] The explanation for both, the unusual dispersion and the rather small bandwidth, lies in the interaction with the Pd d electrons. Because of this interaction with underlying substrate electrons the H 1s band is repelled from the substrate bands and therefore becomes rather flat in the outer parts of the SBZ and has a smaller bandwidth. On Ni, the d band is smaller than on Pd [3.5 eV (Ref. 25) versus 4.7 eV (Ref. 32)], therefore we do not see as much distortion of the
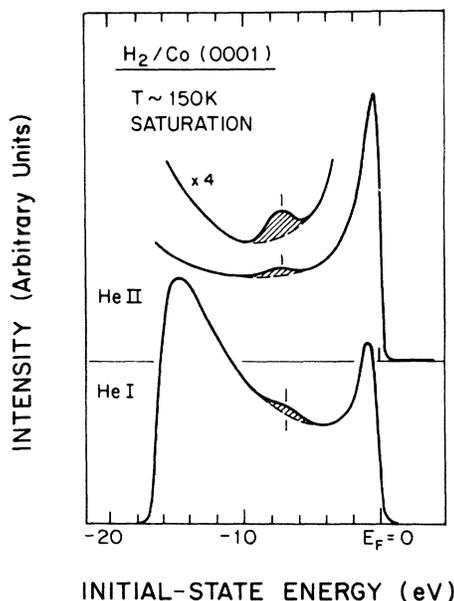

FIG. 15. Spectra for the low temperature adsorption of H_2 on the Co(0001) surface. The data as taken on a VG Instruments ESCALAB spectrometer with poor angular resolution.
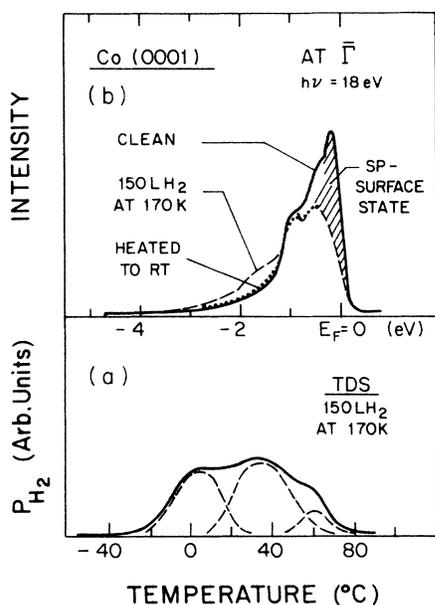
FIG. 16. (a) Thermal-desorption spectrum and (b) normal emission spectra for clean and hydrogen covered Co(0001).

present and might possibly be related to crystal defects for this surface, which is rather difficult to prepare due to the hcp-fcc phase transition.

IV. CONCLUSIONS

Our results for hydrogen adsorption on Ni(111) and Pd(111) indicate that the H layer acts as a uniform attractive potential, with the strength of the potential depending upon the H concentration. All intrinsic d-derived surface states on both crystal surfaces shift to higher binding energy (away from E_F) as the hydrogen concentration is increased. This shift is nearly linear with hydrogen coverage. The (H 1s)-derived split-off state seen in photoemission has a large admixture of substrate d character, especially near the zone boundary. The position and shape of this split-off band changes with H coverage, in a fashion consistent with the picture of a uniform H surface potential. In general, the H 1s split-off band shifts up toward the Fermi energy as the H concentration is decreased. At a concentration of ~0.5 [0.3] monolayers of H on Ni(111) [Pd(111)] this band merges into the bulk bands and loses its identity. On Pd(111) the H induced split-off band has a smaller dispersion than on Ni(111) because of the repulsive interaction with the Pd d bands near the zone boundary. This also causes the position of this band on Pd at the zone boundary to maintain a nearly constant binding energy throughout the coverage range where it can be observed.

The calculated and measured dispersion of the (H 1s)-induced split-off band for a monolayer of H on Pd(111) are in very good agreement.[6,18] Recently Chubb and Davenport[31] have calculated the dispersion of a $p(2\times2)$

H overlayer of H on Pd(111). This $\frac{1}{4}$ monolayer of H creates a split-off band much closer to the bulk Pd bands than was the case for a 1 monolayer film. These authors conclude that there is an upward shift in the H-induced state at $\bar{\Gamma}$ as the coverage is decreased, shifting by 1.3 eV from 1 monolayer to $\frac{1}{4}$ monolayer. This is consistent with our observation of a ~1-eV shift shown in Fig. 14.

There is still the unresolved question of subsurface H. The theoretical calculations addressing this issue indicate that the electronic structure of H above and below the surface plane of Pd are very similar.[7,18,31] Therefore it is difficult to extract a definitive answer based only on the photoemission spectra. The behavior of the H split-off band, in particular its intensity versus coverage variations, as well as the observed work function changes, however, clearly demonstrate that the bonding configuration changes upon reducing the coverage. A detailed analysis of the H bonding to these surfaces has to include not only the H-H and H-substrate interaction, but also the possibility of a temperature- and coverage-dependent mobility of the adsorbed (absorbed) H atoms. Hence dynamic aspects, such as the mean residential time at a given bonding site, and a certain degree of disorder must be treated in a successful microscopic description. It is possible that the low-coverage configuration consists of random vacancies.

There seems to be more direct evidence for subsurface H on a Pd surface than there is for H on Ni. Behm et al.[33] have summarized the evidence for "subsurface" H on Pd(110) and in a recent paper, Felter et al.[34] present both experimental and theoretical evidence for H bound in the octahedral site between the first and second plane of Pd(111). In the latter paper two ordered H graphiticlike structures were observed with LEED at $\frac{1}{3}$ and $\frac{2}{3}$ of a monolayer. The two ordered phases produce the same LEED pattern $(\sqrt{3}\times\sqrt{3}R\,30°)$ and disorder at 85 and 105 K, respectively.[34] Theoretical calculations using the embedded-atom method[35] predict that H in the surface threefold site is slightly more strongly bound than in the octahedral site (2.67 eV compared to 2.65 eV) for an isolated H atom. But the strong H-H repulsion makes the subsurface site more favorable for higher coverages. This theoretical work predicts that at temperatures above the critical temperatures of ~100 K the H moves in and out of the surface quite freely. When the H is on the surface the strong H-H repulsion coupled with the two types of triangle sites causes a disordered H film. Therefore it is most likely that we are looking at a disordered H film at all coverages both on Ni (Ref. 36) and Pd, with evidence for the Pd case that the H is also moving in and out of the surface plane.

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