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# Angle-resolved photoemission study of the electronic structure of chemisorbed hydrogen on Ni(111)

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The electronic structure of hydrogen chemisorbed on Ni(111) has been studied using angle-resolved polarization-dependent photoelectron spectroscopy with synchrotron radiation. For coverages from ~ 0.01 to ~ 0.1 monolayer, we observe a shift of the $p_z$-type Ni(111) surface state towards increased binding energies. At saturation coverage, direct transitions from *sp*-type bands are enhanced, whereas *d*-like interband transitions remain unchanged. We observe no split-off hydrogen-derived state. Since hydrogen is observed to bond only to *sp*-type orbitals, a simple metal (jellium) model is qualitatively applicable and can account for the lack of a split-off adsorbate state.

## INTRODUCTION

Hydrogen chemisorption on transition metals is of widespread interest, e.g., in various (de-) hydrogenation processes in catalytic reactions. Traditionally, transition metals have been thought to interact with adsorbates such as H mainly via their *d* orbitals. This has made a theoretical description of the crystal-adsorbate system complicated and prevented *ab initio* treatments of realistic systems. Calculations for greatly simplified models (see Ref. 1) give no unique answer to the role of *sp* electrons versus *d* electrons in chemisorption. uv-photoemission experiments have suggested that for Ni-H- (Ref. 1) and Ni-O- (Ref. 2) chemisorption, *d* orbitals play a minor role since *d*-band photoemission is unaffected by these adsorbates. This would contrast Ni to the corresponding 4*d*- and 5*d*-transition metals, Pd and Pt, respectively. However, other authors[3] have reported changes for Ni 3*d* levels upon hydrogen chemisorption.

We have investigated the system Ni(111) + H using angle-resolved photoelectron spectroscopy, and find that *sp* orbitals dominate in the bonding of H to Ni(111). Observed spectral changes in the *d*-band region can be accounted for by a quenching of an intrinsic Ni(111) *sp* surface state (0.25 eV below $E_F$) and by enhancement of transitions from an *sp*-type bulk band which hybridizes with the *d* bands. A weak feature observed in spectra at 5.9 eV below $E_F$ cannot be attributed to a hydrogen level[1,3] because we observe a dispersion with photon energy at fixed momentum parallel to the surface $\vec{k}_{\parallel}$. Rather, this feature is an adsorbate-enhanced interband transition from the lowest *s*-like Ni band, as shown by its dispersion and polarization behavior.

The lack of a localized adsorbate-derived energy level renders the Ni(111) + H system a model for a new type of chemisorption bond. Ni can be characterized approximately by a free-electron-like jellium model for the *sp* bands since *d* bands are weakly involved. *Ab initio* calculations for the hydrogen-jellium system are available[4-7] and show, for metallic bond lengths, that hydrodgen

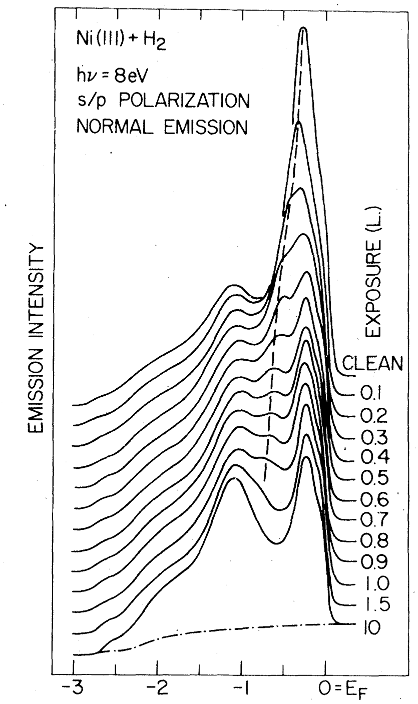

FIG. 1. Angle-resolved energy distribution curves (AREDC's) for normal emission from Ni(111) showing a shift of the Ni(111) surface state (dashed line) upon hydrogen chemisorption. The lowest curve is for saturation coverage.

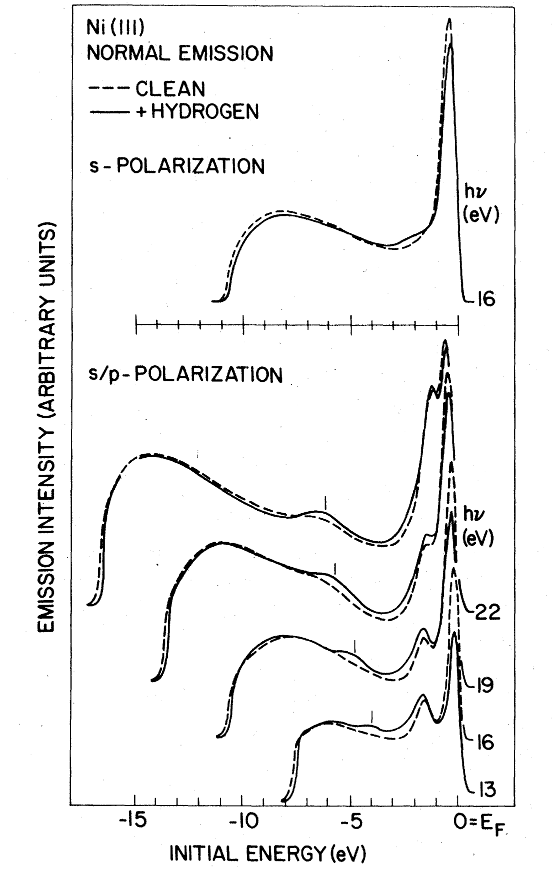

FIG. 2. Normal emission AREDC's from Ni(111) (dotted lines) and Ni(111) + saturation coverage of hydrogen (full lines) for different photon energies $h\nu$ and different polarizations ($h\nu = 16$ eV). The ticmark shows transitions from the lowest $s$-like $\Lambda_1$ band enhanced by hydrogen chemisorption.

forms a broad resonance with the metallic states rather than a split-off level.

A uv photoelectron spectrometer with a double pass cylindrical mirror analyzer having a drum-type angle resolver[8] was used at the Synchrotron Radiation Center of the University of Wisconsin, Madison. A Ni(111) crystal was cleaned by sputter annealing in the usual way at a working pressure of $< 5 \times 10^{-11}$ Torr. Auger-electron spectroscopy (AES) was used to check cleanliness of the sample, but photoemission from the intrinsic Ni(111) surface state[9] proved to be more sensitive to contaminants than AES. All measurements were done at room temperature, where hydrogen is known to form a disordered atomic overlayer on Ni(111).[10] For the data shown in Fig. 1, the angular acceptance was $\delta\theta = 4°$ (full angle) and the overall energy resolution was $\delta E = 0.15$ eV. For Fig. 2, the settings were $\delta\theta = 12°$ and $\delta E = 0.2$ eV. Reducing $\delta\theta$ to 4° changed the spectra only at 0.25 eV below $E_F$, where emission from the Ni(111) surface state[9] occurs which is strongly peaked in the normal direction.

## RESULTS

We have observed two "regimes" which depend on the amount of chemisorbed hydrogen on Ni(111). At coverages small compared to one monolayer (Fig. 1), we observe a shift of the Ni(111) $\Lambda_1$ surface state[9] towards higher binding energy (dashed line in Fig. 1) with increasing coverage. This shift $\Delta E$ is proportional to the work function increase $\Delta\Phi$, with $\Delta E / \Delta\Phi \sim 4$. For clean Ni(111), the $\Lambda_1$ surface state lies $0.25 \pm 0.05$ eV below $E_F$ (at $\vec{k}_{\parallel} = 0$) and the work function is $\Phi = 5.15 \pm 0.1$ eV. The binding energy of the shifted surface-state peak does not depend on the photon energy $h\nu$. This is characteristic for a surface-state feature since bulk interband transitions would show an energy dispersion.[11] An interesting effect is that the surface-state intensity is already strongly reduced for <0.1 monolayer coverage, which implies that there is effectively a long-range interaction between adsorbate atoms and the surface state.

For saturation coverage ($\Delta\Phi = 0.15$ eV at room temperature), the surface-state disappears completely (Fig. 1, last curve; Fig. 2). The remaining peak at about 0.3-eV initial energy is due to a transition from a $d$-like $\Lambda_3$ symmetry initial band.[11] This can be concluded from the polarization behavior of its intensity. According to dipole selection rules,[11] only $\Lambda_1$ initial states can be seen in normal emission with the electric field vector $\vec{E}$ perpendicular to the surface and only $\Lambda_3$ initial states can be seen with $\vec{E}$ parallel to the surface ($s$- polarization). We observe that the $\Lambda_3$ transition remaining after chemisorption is stronger for $s$ polarization (Fig. 2, $h\nu = 16$ eV), whereas the difference between the clean and H-covered spectrum is smaller for $s$ polarization. This latter corresponds to the $\Lambda_1$ symmetry of the surface state and shows that the $\Lambda_3$ transition is hardly affected by the hydrogen. At lower initial energies $E_i$ (Fig. 2, $E_i \sim -1.5$ eV, $E_i - \sim -5$ eV), two $\Lambda_1$ bulk interband transitions are observed (as determined by their polarization behavior and their dispersion with $h\nu$). The lower transition is hardly visible for the clean Ni spectra (Fig. 2), but can be seen with a larger $\vec{E}$ component perpendicular to the surface (Ref. 11). Both transitions are enhanced by hydrogen chemisorption. Finally, hydrogen enhances the region $-3 \text{ eV} \lesssim E_i \lesssim -2$ eV, which corresponds to a band gap between the two $\Lambda_1$ bands mentioned above (compare also

Ref. 11).

Angle-integrated photoemission experiments[1,3] have reported an enhancement of the emission intensity around $E_i = -5.8$ eV, and attributed this to a hydrogen-induced level. In normal emission, we also see an enhancement in this energy range, but the peak in the difference spectrum disperses from $E_i \sim -4.1$ eV at $h\nu = 13$ eV to $E_i \sim -6.2$ eV at $h\nu = 22$ eV (ticmark in Fig. 2). This dispersion clearly contradicts the interpretation of this $-5.8$ eV structure[1,3] as being due to a hydrogen-induced surface state, since such a surface state should always have the same binding energy at fixed $\vec{k}_\parallel$ ($\vec{k}_\parallel = 0$ in normal emission). The observed enhancement of intrinsic Ni bulk transitions indicates that a hydrogen surface resonance exists which affects (e.g., hybridizes with) only the tail of the bulk wave functions near the surface and therefore influences the matrix element and surface transmission probability. We have also looked at a $\vec{k}_\parallel$ near the boundary of the surface Brillouin zone ($k_\parallel = 1.68$ Å$^{-1}$ in $[1\bar{1}0]$-direction), where the bulk bands do not extend as far down in energy as at $\vec{k}_\parallel = 0$; no structure was seen near $E_i = -6$ eV in the difference spectrum for a saturation coverage of hydrogen.

From our observations we draw two main conclusions: (i) Hydrogen bonds to Ni(111) mainly via the $s,p$ orbitals. This conclusion is supported by the fact that emission from the two $sp$-like $\Lambda_1$ bands is enhanced by hydrogen chemisorption but not from the $d$-like $\Lambda_3$ band. The $s$, $p_z$-type $N_i$ (111) surface state plays a role in the initial adsorption of hydrogen, as indicated by the chemical shift of this state. (ii) There is no localized hydrogen-induced surface state near $E_i \sim -6$ eV, but rather a hydrogen surface resonance spread out over the whole range of the Ni $s,p$ bands ($-7$ eV $\lesssim E_i \lesssim -1$ eV).

Different calculations[12-15] disagree upon the role of $sp$ vs $d$ electrons in the Ni-H bonding. As pointed out in Ref. 1, the more localized character of the $3d$ wave functions as compared to the $4d$, $5d$ wave functions could explain why hydrogen seems to interact with Ni(111) mainly via the $s$, $p$ orbitals but with Pd(111) via $d$- orbitals. We add to this argument the observation that the $sp$-like $\Lambda_1$ surface state is occupied for Ni(111)(Ref. 9) but lies above the Fermi level for Pd(111).[16,17] Knowing that $d$ electrons are not active for the Ni(111) + H system, we suggest that *ab initio* atom-jellium treatments[4-7] give an approximate description of the character of the hydrogen bonding. The lowest $s$-like band in Ni disperses like a free electron band except for small regions near the zone boundary, as *ab initio* band-structure calculations[18] and the experimental energy-band dispersions[11] show. Experimentally, we find free-electron-like behavior for $-6.5$ eV $< E_i < -4$ eV,[11] i.e., for the range where the existence of a hydrogen level has been claimed.[1,3] Using the lowest Ni $s$ band in a jellium model,[4-7] the bottom of this band at $E_i \sim -9$ eV (Refs. 11 and 18) corresponds to $r_s \sim 2.4$. For any reasonable hydrogen-jellium distance, atom-jellium calculations[5,7] predict a wide resonance, not a separate hydrogen level. Since the energy position of this resonance depends on the jellium-adatom distance, in principle one might try to determine the position of hydrogen in the Ni lattice by fitting the H-Ni distance to experimental data using a structural model[10] together with a calculation which reintroduces the crystal lattice.[5,7] However, our results show that uv photoemission spectra may not approximate the density of states close enough, because there are strong angular and polarization effects. Namely, we have taken spectra integrating over the acceptance of a double pass cylindric mirror analyzer, and find that the shape of the difference spectra depends so strongly on the photon energy and sample orientation (several broad maxima are seen) that the center of gravity of the hydrogen resonance cannot be located.

## ACKNOWLEDGMENTS

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