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Identification of electronic bonding states of hydrogen on Ni(110)

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The electronic structure of hydrogen adsorbed on Ni(110) at 150 K has been studied using angle-resolved photoelectron spectroscopy with monochromatized He Iα radiation. At a saturation coverage of 1.5 monolayers, we observe a general shift of the spectral weight away from the Fermi level to higher binding energies indicating the hybridization of hydrogen levels with metal d states. Along selected Ni $3d$ bands the intensity shift is obvious whereas other bands remain unchanged. In addition, contrary to previous observations, a hydrogen induced state is visible at a binding energy of roughly 1.2 eV.

Heterogeneous catalysis is an important issue in surface science as is demonstrated in a recent article[1] where the (111) surfaces of Au, Pt, Cu, and Ni are compared theoretically by their hydrogen adsorption ability which is a test case for reactivity in general. It turns out that the filling of the metal d bands is crucial for the activation of the hydrogen bonding. For a transition metal like nickel, with partially filled d states at the Fermi level E_F, strong H $1s$-metal d bonding resonances should appear below the metal d bands. The antibonding states will lie above the Fermi energy, thus guaranteeing good adsorption. On the other hand, filled antibonding states like in noble metals cause repulsion of any adsorbate.[1] However, this model has not yet been experimentally confirmed for transition metals like Ni.

To our knowledge there are no recent photoemission experiments of hydrogen adsorption on Ni(110). Previous investigations on Ni(110) (Refs. 2 and 3) and on Ni(111) (Refs. 4–6) reported in great detail on the hydrogen-induced bonding states mentioned above. However, they could not unequivocally decide the debate which metal states are involved in the hydrogen bonding and what symmetry they have. Another uncertainty existed due to a lack of information on the geometrical positions of hydrogen adsorbed on the different Ni single crystal surfaces. This issue has been resolved in the last decade using more powerful diffraction methods, scanning tunneling microscopy, and electron energy loss spectroscopy.[7–16]

On Ni(110) two different pathways for the hydrogen adsorption have to be distinguished. At temperatures above 200 K, already at low hydrogen coverages a (2×1) missing row reconstruction of the Ni surface shows up which is completed at a saturation coverage of 1.5 monolayers (ML).[7–10] Another phase is observed at temperatures below 200 K. Different ordered lattice-gas structures on the unreconstructed Ni surface appear for coverages below 1 ML. These low-coverage phases consist of H zigzag chains along the close-packed Ni rows.[11,12] At coverages above 1 ML, the Ni surface reconstructs into a (2×1) pairing row structure which is saturated at 1.5 ML.[8,13–16] The hydrogen atoms are sitting in two different threefold symmetric sites located along the adjacent Ni rows on the topmost layer (see Fig. 4 of Ref. 14 or Fig. 7 of Ref. 16 for details). This phase referred to as low temperature (LT) phase will be studied by angle-resolved photoemission in this paper.

The LT phase can only be achieved by cooling the clean Ni crystal below 200 K before hydrogen is adsorbed. By warming up the saturated LT phase, half a monolayer hydrogen desorbs at 220 K and the Ni surface reconstructs into the (2×1) missing row structure. If the desorbed hydrogen is readsorbed again at higher temperatures (e.g., room temperature) the missing row reconstruction is saturated. This phase then also remains present if the crystal is cooled again below 200 K.[8]

This paper presents angle-resolved photoelectron spectroscopy results obtained for the low-temperature hydrogen adsorption on the Ni(110) surface. Angular cuts along $\bar{\Gamma}-\bar{X}$ of the surface Brillouin zone were performed for Ni(110) surfaces with and without adsorbed hydrogen and are compared to pure nickel band structure calculations adapted to our measurements. It is the aim of this study to identify the hydrogen induced changes in the electronic structure near E_F which are due to the adsorbate induced levels as well as due to the hybridization of the Ni bands.

The photoemission experiments were performed in a VG ESCALAB Mk II spectrometer with a base pressure $\leqslant 2\times10^{-11}$ mbar. The sample stage is modified for motorized sequential angle-scanned data acquisition over 2π solid angle[17,18] and can be cooled with LN_2 down to 140 K. SiK_α radiation (1740 eV) was used for X-ray photoelectron spectroscopy in order to check the cleanness of the sample. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with monochromatized He Iα radiation (21.2 eV). The setup of the plasma discharge lamp with the monochromator enabling the separation of different excitation lines from various gases such as He, Ne, and H_2, respectively, thus covering an energy range between approximately 10 and 50 eV, will be described elsewhere.[19] The energy resolution of the analyzer (angular resolution 1° full cone) for the UPS measurements was set to 50 meV.

The Ni(110) surface was prepared by repeated cycles of sputtering (1 keV Ar^+) and resistive heating to 700 °C. Dur-

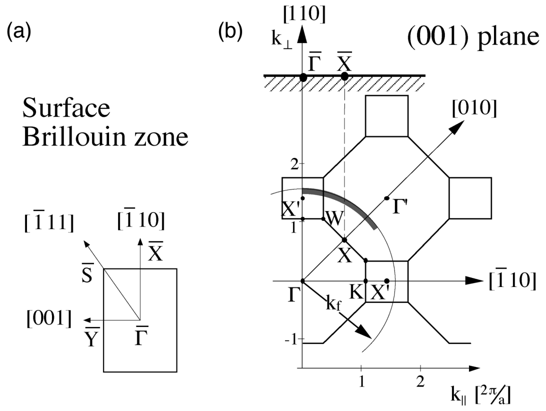

FIG. 1. Reciprocal space for the Ni(110) surface. (a) Surface Brillouin zone indicating high symmetry directions. (b) Brillouin zone boundaries in the (001) plane. The hatched zone represents the free electron final state wave vectors for angle-scanned photoemission with 21.2 eV.

ing annealing the pressure did not rise above 1×10^{-9} mbar. Typical contamination levels after this treatment were 0.01 ML O and 0.03 ML Ar. C and S amounts were too small to be quantified.

Hydrogen was adsorbed by exposing the cooled sample to 1×10^{-9} mbar partial H_2 pressure for one hour, thus reaching a total dose of 3.6 L (1 L$=$1 Langmuir$=10^{-6}$ Torr s). For the experiments on clean Ni(110) attention had to be paid to the hydrogen partial pressure p_H. Already within one hour at $p_H = 5 \times 10^{-11}$ mbar, the normal emission spectrum showed characteristic changes due to hydrogen adsorption. Before studying the clean Ni surface the remaining hydrogen partial pressure was minimized by activating a cerium sublimation pump. The reconstruction of the Ni surface after H adsorption was verified by low energy electron diffraction.

In Fig. 1 we present what is relevant for our study in reciprocal space. Figure 1(a) shows the (110) surface Brillouin zone (BZ) of an fcc lattice. Tilting of the emission angle from the surface normal towards $\overline{X}$ ($\overline{1}$10 direction) results in a cut through the (001) plane as is shown in Fig. 1(b). The octagons and squares indicate the bulk BZ boundaries for Ni in the extended zone scheme. Different high symmetry directions are labeled. The circular segment with the hatched zone represents the free electron final state wave vectors for emission from E_F down to 2 eV binding energy calculated for an excitation energy of 21.2 eV (He Iα), a work function of 4.7 eV and an inner potential of 10.7 eV.[20] Previous experiments have shown that the assumption of a free electron final state appears to be a good approximation.[21–23]

The angle-scanned photoemission spectra along $\overline{\Gamma} - \overline{X}$ in the (001) plane taken at 150 K before and after hydrogen adsorption are shown in Fig. 2. The individual spectra are measured in polar angle steps of 2°. Normal emission corresponds to 0°. Figure 2(a) shows the dispersion of the measured bands near E_F. The vertical lines indicate the peak positions fitted with a Lorentzian taking into account the Fermi-Dirac distribution and a Shirley background. A very general feature of adsorption is the shift in the spectral weight. High photoemission intensity is observed near 0 eV for the clean Ni surface. After H_2 exposure these sharp d states lose intensity near E_F and transfer weight to higher binding energies [very clearly observed for the spectra at $\Theta = 0°$ in Fig. 2(a)]. The behavior of the total density of states (DOS) is thus reflected in the shape of the 0° spectrum. The ratio of the d peak intensities near E_F to the background at higher binding energies is strongly decreased upon hydrogen uptake.

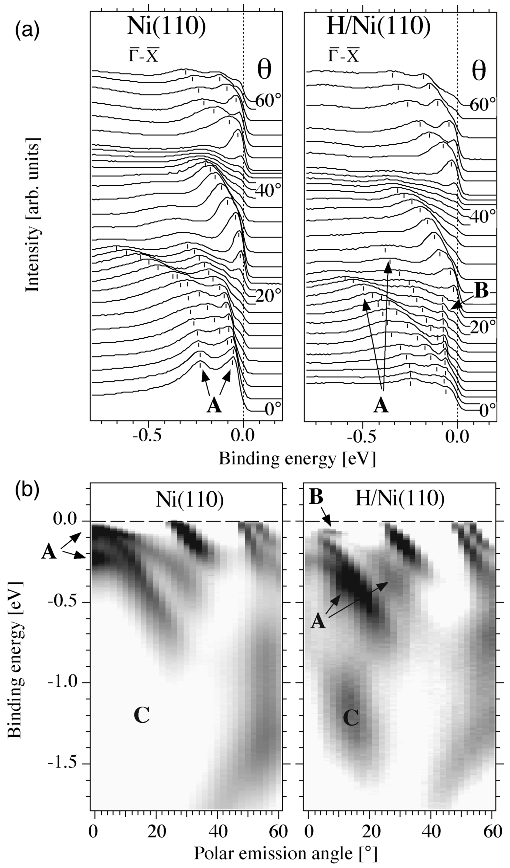

FIG. 2. (a) He Iα photoemission spectra near E_F along $\overline{\Gamma} - \overline{X}$ for clean and hydrogen saturated Ni(110) at 150 K. Normal emission corresponds to $\Theta = 0°$. (b) The same spectra in a grayscale dispersion plot down to 1.8 eV binding energy. Different features are labeled (see text).

This can be understood in terms of hybridization of the adsorbate-induced levels with the metal d bands as described by Hammer and Nørskov.[1] As the Ni $3d$ bands are not completely filled the antibonding states lie above the metal d states and are therefore not occupied. This results in an extra attraction of the hydrogen atoms and a stabilization of the hybridized Ni d states on the surface. However, this stabilization is not completely uniform as can be seen in Fig. 2(b) where the measured spectra are represented in a gray scale dispersion plot. The spectra from 0° to 60° polar angle are shown from left to right. Black means high intensity. This representation is complementary to the one in Fig. 2(a) since here it is easier to decide which bands experience the strongest changes. On the other hand, the dispersion of bands with weak intensities is better seen in the upper panel. Notice that the different bands shown in Fig. 2 are individually labeled in a blown up section in Fig. 3.

Label A in Fig. 2 marks the striking intensity shift along two parallel bands (labeled 1 and 3 in Fig. 3) whereas the

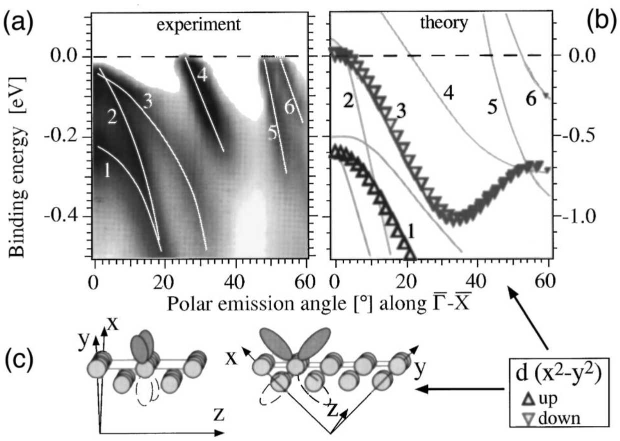

FIG. 3. Comparison of the measured (a) and the calculated (b) dispersion of clean Ni(110) along $\overline{\Gamma}-\overline{X}$. Labels 1 to 6 mark the identified bands. Features 1 and 3 are the exchange-split Ni $d_{x^2-y^2}$ bands which are schematically sketched in (c).

intensity distribution of the band crossing between them (labeled 2 in Fig. 3), as well as of the other bands crossing E_F, remains unchanged. The dispersion of the bands is not altered except for a slight shift due to the work function change of $+0.6$ eV during hydrogen adsorption. The work function was determined by the intensity cut-off for low kinetic energy in the photoemission spectra. Its increase may be explained as a consequence of the filling of the H $1s$/Ni $3d$ bonding states. Per bond, in addition to the H $1s$ electron, one Ni electron can be taken up and be stabilized in energy. Since the hydrogen is localized at the surface this results in additional negative charge at the surface and is therefore consistent with the measured higher work function.

The flat feature labeled B in Fig. 2 which is strongly amplified upon hydrogen adsorption or, alternatively, set free by the intensity shift in the other bands cannot be explained by bulk calculations which will be presented below in Fig. 3. As it does not lie in a band gap we assume that it is either a surface resonance, due to indirect transitions from a flat band within the (001) plane having a very high DOS,[24,25] or it is a hydrogen derived state which necessarily is a surface state. Other possibilities are a cross section change or observation of a bulk band via a 2×1 surface Umklapp process.

A completely new state, labeled C in Fig. 2, appears at approximately 1.2 eV binding energy after hydrogen exposure. Its nonexistence for the hydrogen-free surface and the fact that it is localized below the strong metal d states (label A) is an indication that we actually observe a hydrogen-induced level. The formerly observed H induced split-off state for saturation coverage (1 ML) on Ni(111) (Ref. 6) lies much deeper ($E_B=9.0$ eV at $\overline{\Gamma}$) in the bulk band gap. A similar split-off state at 8.2 eV should exist on the Ni(110) surface (after Horn, unpublished reference in Ref. 6). However, our measurements did not show any hydrogen-induced state in this energy region.

In order to distinguish clearly between hydrogen-induced and hybridized Ni states we compared our results to a bulk band structure calculation of pure Ni using the full potential linearized augmented plane wave method[26] within the generalized gradient approximation.[27] The lattice parameter of the Ni fcc lattice was chosen to be $a_0=3.52$ Å. In order to simulate the dispersion plots we assumed a free electron final state for the photoelectron using a work function of 4.7 eV and an inner potential of 10.7 eV [see Fig. 1(b)]. The calculated structure of the (001) plane cut is shown in Fig. 3. The white lines in the experimental plot represent the peak positions as fitted in the energy distribution curves. All the measured bands between 0 and 0.5 eV binding energy can be identified in the calculation although the energy scale is overestimated by a factor of 2.5 in the theory. This may be attributed to electron correlation effects[28] which are not explicitly incorporated in our simulation. Two calculated bands near the one labeled 1 in Fig. 3(b) as well as the expected upward bending of band 3 are not observed in the measurements. A possible reason for this is the simplicity of our calculation, not including a proper final state or matrix element effects.

The bands showing no intensity shift in Fig. 2 upon hydrogen adsorption are labeled 2, 4, 5, and 6, respectively. The bands marked 1 and 3, however, are strongly involved in the hydrogen bonding. By projection onto a basis of spherical harmonics we can identify these bands (big markers in the simulation) as having $d_{x^2-y^2}$ character. The corresponding orbitals [schematically sketched in Fig. 3(c)] lie in the (001) plane which is orthogonal to the displacement direction of the Ni rows during the pairing row reconstruction. For the clean and unreconstructed surface they can overlap forming antibonding orbitals along the close-packed rows. During hydrogen adsorption the $d_{x^2-y^2}$ orbitals may now build up bonds to the H atoms in the threefold symmetric sites between the rows resulting in lower energies for the involved Ni electrons. This might indeed be the driving force for the pairing row reconstruction.

In conclusion, we have presented angle-scanned photoemission spectra of clean and hydrogen adsorbed Ni(110) near E_F at 150 K. A general shift in the spectral weight of the photoemission intensity towards higher binding energies indicates the H $1s$/Ni $3d$ band hybridization by which electrons from the metal d states are stabilized by the hydrogen-induced bonding levels. The comparison with a Ni bulk band structure calculation identifies the Ni $d_{x^2-y^2}$ bands as the ones that are mostly affected by the hydrogen bonding whereas other bands remain unchanged. In addition, one of the corresponding adsorbate-induced states below the metal d states could be observed at 1.2 eV binding energy.

Finally, our observations are consistent with the following picture: hydrogen atoms adsorbed on the surface are interacting with the Ni d states near the surface forming unoccupied antibonding and occupied hybridized bonding levels. The bonding levels are, as yet, only occupied by the H $1s$ electron. Therefore, selected d bands may participate, thereby lowering their energy. As a consequence, more electronic charge is accumulated at the surface going well along with the measured increase of the work function.

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