

One-Dimensional Surface States (Chain States) on a Metal Surface: H on Ni(110)

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H adsorption on Ni(110) at sample temperatures $T_S > 200$ K is known to result in a one-dimensionally disordered surface exhibiting a missing/added row reconstruction with irregular row-to-row spacing but long range periodicity along the rows. Inverse photoemission shows an unoccupied surface state with wave vector perpendicular to the rows being completely quenched due to the one-dimensional disorder. In contrast, an unoccupied surface state propagating along the rows is not attenuated at all. This indicates that the latter is a one-dimensional chain state, localized to individual atom rows.

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The physics of electrons in low-dimensional systems is a topic of considerable current interest. The existence of two-dimensional electronic states on metal surfaces has been noted very early on the basis of theoretical considerations [1], but experimentally such surface states remained inaccessible until in the 1970's new techniques, such as angle-resolved photoemission [2] and, more recently, angle-resolved inverse photoemission [3,4] allowed detailed studies of surface states.

Surface states play a crucial role in several interesting physical phenomena, such as the nonadiabatic vibrational damping of adsorbate vibrations [5], adsorbate induced reconstructions [6,7], the magnetic properties of metal surfaces [8,9], and adsorbate-adsorbate interactions [10]. For the latter case it has been demonstrated that the reduced dimensionality of surface states leads to an oscillatory long range interaction falling off with r^{-2} as compared to the r^{-5} behavior resulting from an interaction mediated by bulk states [10]. In the presence of one-dimensional surface states adsorbate-adsorbate interactions are expected to scale with r^{-1} [11]. Thus, one-dimensional surface states would have important consequences for, e.g., the ordering, phase transitions, and the vibrational behavior of adsorbates.

To our knowledge, experimental hints for the existence of one-dimensional surface states on metal surfaces have been reported up to now for only two systems. The generally accepted signature of one-dimensional electronic states, i.e., dispersion in only one direction, was found on the Cu-O-Cu chains formed during the added row reconstruction of O/Cu(110) [12,13]. Similarly, Binns, Norris, and Gurman [14] interpreted their photoemission spectra from Tl/Cu(100) in terms of a one-dimensional Tl 6s band, although the situation there is complicated by the presence of two rotational domains.

In the present paper we investigate the surface state behavior in a one-dimensionally disordered system, namely, the H/Ni(110) missing/added row reconstructed surface. We show that the absence of a dispersion is a necessary but not in all cases a sufficient criterion for the localization of an electronic state. We therefore use the

quenching behavior of surface states to investigate their dimensionality. We demonstrate that the occurrence of one-dimensional surface states is not restricted to truly one-dimensional systems, but may be a common feature on all surfaces with a perturbed periodicity in one direction.

The experiments have been carried out on the system H/Ni(110). Low-temperature exposure of Ni(110) to H_2 leads to the formation of a (2×1) low energy electron diffraction (LEED) pattern at $\Theta_H = 1$ monolayer (ML). Further H exposure causes a (1×2) pairing row reconstruction. Saturation occurs at $\Theta_H = 1.5$ ML [15]. Room temperature exposure to H_2 causes a surface reconstruction already at coverages as low as $\Theta_H = 0.2$ ML. The corresponding LEED pattern shows the formation of a one-dimensionally disordered phase, i.e., streaks between the integral order spots in the [001] direction of the real space. Prolonged exposure to H_2 at room temperature or cooling from 400 to 240 K in ambient H_2 pressure ($\sim 2 \times 10^{-7}$ mbar) yields a saturation coverage $\Theta_H \approx 1.5$ ML [16,17]. The corresponding LEED pattern shows streaky half-order spots in a (1×2) structure indicative of a reconstruction with a strongly perturbed double periodicity in the [001] direction [15]. Recent ion scattering [18] and scanning tunneling microscopy (STM) [19] studies revealed that this reconstruction is of the missing row type. Actually, the STM data show that even at low H coverages Ni atoms are removed from the tightly packed rows in the Ni(110) surface and form added rows in the [110] direction on top of the terraces. Thus the reconstruction involves simultaneous formation of missing and added rows. At high coverages the rows tend to arrange themselves with an average separation of twice the lattice constant. However, this periodicity is strongly perturbed, with different distances appearing as well [19].

We explored the behavior of unoccupied Shockley surface states on Ni(110) during hydrogen adsorption and H induced reconstruction by angle-resolved inverse photoemission (IPE). The photons were detected in Geiger-Müller counters featuring SrF_2 windows and an Ar/I_2 mixture as counting gas. This results in a photon detec-

tion energy of 9.4 eV with an overall resolution (including the thermal spread of the incident electron beam) of about 350 meV. The experimental setup has been described in more detail previously [20].

The surface states under investigation are located in the large sp band gaps of the projected bulk band structure at the boundary of the surface Brillouin zone (SBZ) of the Ni(110) surface, as shown in Fig. 1. On the clean Ni(110) surface these surface states have been observed previously by inverse photoemission [21,22]. Their dispersion, as measured on the clean surface, is given by the dots in Fig. 1. A transparent theoretical description of these surface states in terms of a multiple reflection model has been given by Echenique and Pendry [23]. The surface states can be interpreted as quantum well states trapped between the vacuum barrier (the $1/4z$ image potential; z is a coordinate normal to the surface) on the one and the bulk of the crystal on the other side. Penetration into the bulk is prohibited by the bulk band gap. True bound states in this "quantum well" may occur for "normal" energies $E_{\perp} < E_{\text{vac}}$ ($E_{\perp} = \hbar^2 k_{\perp}^2 / 2m$; E_{vac} is the vacuum energy). The energy and dispersion of these surface states can be calculated within the nearly free electron (NFE) approximation [24]. The solid lines in Fig. 1 show the result of such a calculation [22]. In the present study we will concentrate on the behavior of the surface states labeled $S_{\bar{X}}$ and $S_{\bar{Y}}$, respectively.

At first we investigate the behavior of the surface state $S_{\bar{Y}}$. Figure 2 shows inverse photoemission spectra of this state on the clean Ni(110) surface, on the same surface

saturated with hydrogen at a sample temperature $T_S = 100$ K ($\Theta_H = 1.5$ ML, low-temperature phase with pairing row reconstruction), and after cooling down in ambient H_2 pressure from 400 to 240 K ($\Theta_H = 1.5$ ML, streaky missing row reconstruction). The spectra have all been recorded at $T_S < 120$ K at a fixed angle of electron incidence ($\vartheta = 48^\circ$). At this angle final states with an energy of about 1 eV are located at \bar{Y} .

Low-temperature hydrogen adsorption is seen to shift the surface state $S_{\bar{Y}}$, as well as the next higher surface state, downwards by approximately 1.5 eV. Additional surface states appear in the band gap on the saturated surface. This has been described in detail in a previous publication [20]. A NFE model calculation could well reproduce the downshift and the dispersion of the surface states. According to the model, the adsorbed H increases the attractive potential at the surface and shifts the image plane slightly outwards [20]. It has to be emphasized that the $S_{\bar{Y}}$ surface state is somewhat attenuated, but neither the H adsorption nor the pairing row reconstruction leads to a quenching of the surface states.

If the Ni(110) surface is exposed to H_2 at elevated temperature, a one-dimensionally disordered missing/added row reconstructed surface is obtained, as described above. The surface states in the \bar{Y} band gap are completely quenched already at small coverages. The LEED pattern shows streaks in the [01] direction corresponding to the [001] direction in real space. The ordering is slightly improved if the coverage is increased to $\Theta_H = 1.5$

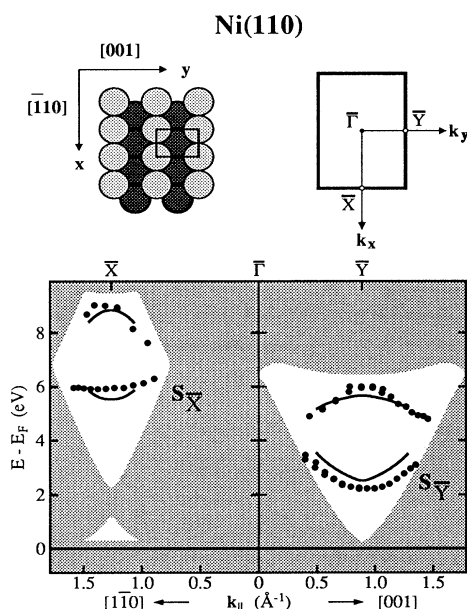


FIG. 1. The Ni(110) surface with a surface lattice unit cell, the corresponding surface Brillouin zone, and the projected bulk band structure. In the band gaps at \bar{X} and \bar{Y} , respectively, calculated and measured surface state bands are shown.

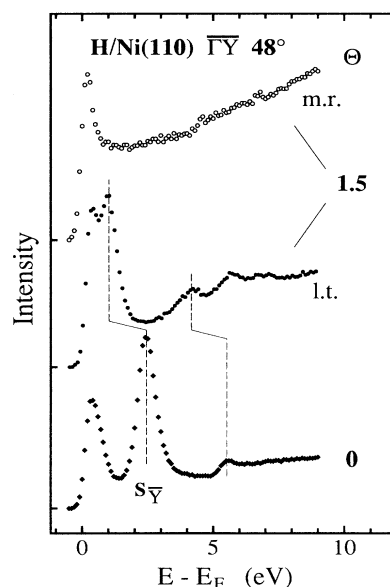


FIG. 2. Inverse photoemission spectra of the surface state $S_{\bar{Y}}$ for the clean Ni(110) surface (bottom), for the H saturated, pairing row reconstructed surface (low-temperature phase: LT) (middle), and for the H saturated, streaky missing row reconstructed surface (MR) (top). Note the complete quenching of $S_{\bar{Y}}$ in the streaky missing row phase.

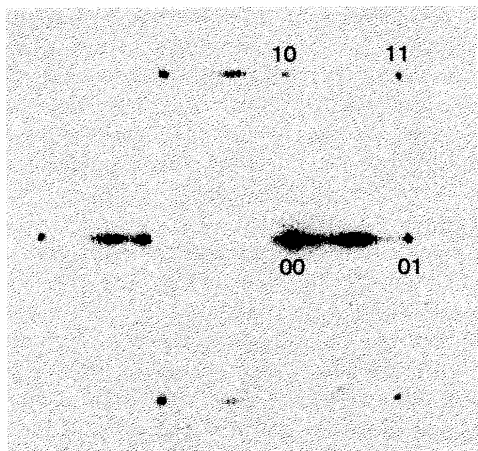


FIG. 3. Low energy electron diffraction pattern of the streaky missing row phase with $\Theta_H = 1.5$ ML. Indices are given for some of the integral order spots. The elongation of the half-order spots indicates one-dimensional disorder.

ML by cooling from 400 to 240 K in ambient H_2 pressure. In the LEED pattern a (1×2) superstructure is clearly recognizable, but due to persisting one-dimensional disorder, the half-order spots are still elongated in one direction as shown in Fig. 3. Even for this streaky (1×2) reconstructed surface the IPE spectrum (topmost spectrum in Fig. 2) shows a virtually complete quenching of the surface states in stark contrast to the (1×2) pairing row reconstructed surface formed after low-temperature exposure. Thus, because of the one-dimensional disorder, the surface states in the \bar{Y} band gap are completely suppressed throughout the H coverage range where the missing row reconstruction takes place.

We now turn to the $S_{\bar{X}}$ surface state in the band gap around the \bar{X} point. Figure 4 shows the coverage dependent shift of this surface state on the low-temperature phase of the H/Ni(110) surface as well as on the streaky phase prepared at elevated temperatures. The IPE spectra presented in Fig. 4 have been recorded at an angle of incidence of $\vartheta = 52^\circ$, which ensures that final states with an energy around 6 eV lie at the \bar{X} point of the SBZ. In the spectra obtained from the H/Ni(110) low-temperature phase $S_{\bar{X}}$ shows the familiar downshift, although it is only about half as large as for $S_{\bar{Y}}$, namely, 0.7 eV. On the streaky missing row reconstructed surface the surface state is upward shifted by about 0.2 eV. Most notably, however, the formation of the streaky missing row phase *does not quench, not even attenuate* the surface state $S_{\bar{X}}$.

The different quenching behavior of the surface states $S_{\bar{X}}$ and $S_{\bar{Y}}$, respectively, indicates a different sensitivity towards the one-dimensional disorder: $S_{\bar{Y}}$, which propagates perpendicular to the tightly packed rows, is strongly perturbed by the random distribution of the missing and added rows on H/Ni(110); in contrast, the intensity of $S_{\bar{X}}$, which propagates along the tightly packed rows, is

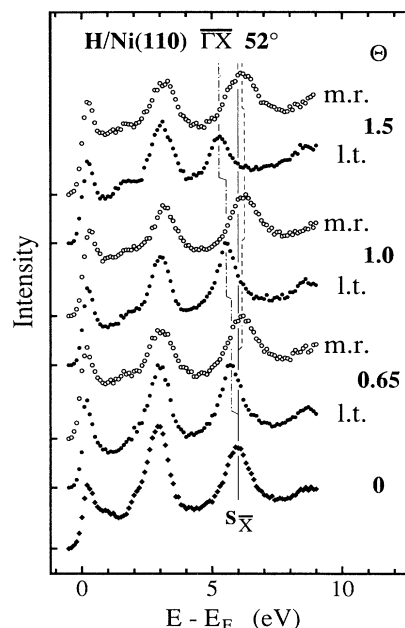


FIG. 4. Inverse photoemission spectra of the surface state $S_{\bar{X}}$ as a function of H coverage for the low-temperature phase (LT; dots) and the missing row reconstructed room temperature phase (MR; circles) of the H/Ni(110) system. Note the virtually constant intensity of $S_{\bar{X}}$ throughout the whole coverage range.

not influenced by the irregular spacing in the $[001]$ direction. This immediately leads to the conclusion that the surface state $S_{\bar{X}}$ is localized with respect to this direction. In other words, $S_{\bar{X}}$ is a one-dimensional surface state extending along the densely packed Ni rows in the $[1\bar{1}0]$ direction. Accordingly, it may appropriately be termed a one-dimensional "chain state."

The slight upward shift of $S_{\bar{X}}$ on the missing row reconstructed surface shown in Fig. 4 is consistent with a similar shift of $S_{\bar{Y}}$, which we observed upon the alkali-metal induced missing row reconstruction of fcc (110) surfaces [25–28]. In that case we explained the upshift in terms of a less attractive surface potential due to the reduced surface atom density on a missing row reconstructed surface. This could also apply for the present case.

The surface state $S_{\bar{X}}$ shows virtually no dispersion around \bar{X} . This, however, does *not* prove its localized nature: The dispersion of a surface state lying in a band gap is determined by a balance between the dispersion of the bulk bands forming the upper and the lower gap edge and the parabolic dispersion of the escape threshold $E_{\text{esc}} = E_{\text{vac}} + \hbar^2 k_{\parallel}^2 / 2m$, as discussed by Smith [29]. Accordingly, the sign of the dispersion of a surface state in the sp band gaps at the SBZ boundary depends on its energy position within the gap. $S_{\bar{X}}$ is located close to the middle of the \bar{X} band gap, where the dispersion happens to be at

its minimum. Thus the absence of an observable dispersion of $S_{\bar{X}}$ is a consequence of the topology of the gap rather than an indication of the localized character of this state.

We have shown in a recent paper how simple symmetry considerations can be applied to obtain a description of the surface states in terms of a linear combination of atomic orbitals (LCAO) [28]. Both surface states, $S_{\bar{X}}$ and $S_{\bar{Y}}$, have sp_z hybrid character with respect to the topmost substrate atoms. $S_{\bar{X}}$ has Ni-Ni antibonding character along the Ni atom rows. Vice versa, $S_{\bar{Y}}$ is bonding along the rows, but row-to-row antibonding.

In summary, we have investigated surface states on the H/Ni(110) surface, which exhibits a one-dimensionally disordered missing/added row reconstruction. During the H induced reconstruction tightly packed Ni atom rows are formed with periodicity in the $[1\bar{1}0]$ direction, but with irregular spacing in the $[001]$ direction. A surface state in the \bar{Y} band gap of the projected bulk band structure, i.e., propagating into the $[001]$ direction, is immediately quenched by the reconstruction-induced disorder. In contrast, a surface state in the \bar{X} band gap, i.e., propagating along the tightly packed rows, is not attenuated at all. This indicates that the surface state at \bar{X} does not experience the perturbed periodicity in the $[001]$ direction, thereby proving its one-dimensional character as a chain state localized along the tightly packed rows in the $[1\bar{1}0]$ direction.

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