

Structure and mechanism of alkali-metal-induced reconstruction of fcc (110) surfaces

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A comprehensive model for the interaction of alkali metals with fcc (110) metals is presented for the first time. It is based on a direct comparison of K on the *unreconstructed* Ni and the missing-row *reconstructed* Au(110) surfaces. Regardless of initial substrate structure, two processes may occur: *nonactivated* adlayer ordering or *local, activated* substrate reconstruction via island growth. Coverage-dependent electrostatic interactions determine the substrate structure. Low alkali-metal-atom coverages favor a corrugated, reconstructed substrate; high coverages favor a relatively flat, unreconstructed substrate.

Recent studies have reported that alkali-metal-atom adsorption can induce (1×2) reconstructions of the Ag(110), Pd(110), and Cu(110) surfaces.¹⁻⁷ The low coverage sufficient for the formation of the reconstructed phase was especially noted ($\Theta \leq 0.1$) which contrasts the expected ideal value of $\Theta = 0.5$ for a (1×2) overlayer structure.² Long-range effects were proposed to play a crucial role in inducing the reconstruction. These effects were attributed to the electronic charge donation into the metal which should induce a reconstruction of the surface even at relatively low alkali-metal-atom coverages.^{2,5}

In this Brief Report we present new experimental evidence for a comprehensive model of the structural and mechanistic aspects of the reconstructive interaction of potassium with the fcc (110) surfaces. This picture results from a comparison of potassium interaction with the (1×1) *unreconstructed* Ni(110) and the (1×2) missing-row *reconstructed* Au(110) surfaces.⁸⁻¹⁰ Our results point to a *local* rather than long-range mechanism, and are discussed in conjunction with other experimental observations on the interaction of alkali-metal adsorbates with the (110) faces of Cu, Pd, and Ag. Probable thermodynamic and mechanistic pathways are discussed. The experiments are performed in a standard UHV chamber; the crystals are prepared in the usual manner, details of the procedure will be published elsewhere.^{11,12}

Potassium adsorption on Ni(110) at 90 K leads to a disordered surface layer up to medium coverages, indicated by a general increase in the diffuse background of the low-energy electron diffraction (LEED) pattern. At $\Theta_K > 0.26$, beams of an ordered structure begin to emerge, which shift in position with increasing coverage, as indicated in Fig. 1(a). At saturation of the first K adlayer, the pattern of a slightly expanded $c(2 \times 2)$ structure [Fig. 1(c)] is exhibited. The corresponding saturation coverage, $\Theta_K = 0.48$, is used for calibration of the relative coverages determined by Auger-electron spectroscopy (AES). Further potassium exposure causes the LEED beams to fade due to the formation of disordered multilayers.

An entirely different set of ordered structures emerges

when annealing these adlayers, or adsorbing at higher temperatures. Adsorption at room temperature over a wide coverage range—results in LEED patterns dominated by half-order beams of (1×2) structure. However, additional faint streaks at the $(\frac{1}{2}, 0)$ position along the [01] direction reveals that the adlayer also has two-fold periodicity in the $[1\bar{1}0]$ lattice direction. At coverages of $\Theta_K < 0.2$ and $\Theta_K > 0.3$ the LEED patterns exhibit a coverage-dependent splitting and subsequent shift of the center streaks in the [10] direction and of the half-order spots in the [01] direction, as indicated in Fig. 1(b) and described in detail by Gerlach and Rhodin.¹³

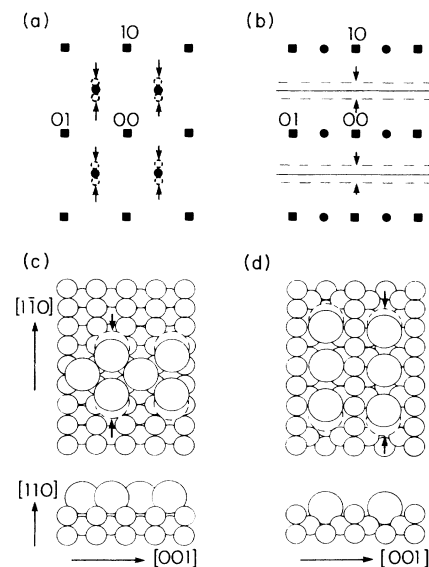


FIG. 1. LEED patterns [(a),(b)] and real-space structures [(c),(d)] of $c(2 \times 2)$ -like structures on a (1×1) [(a),(c)] and (2×2) -1D-like structures on a (1×2) [(b),(d)]. \circ , K; \circ , Ni(110) or Au(110); \blacksquare , integral-order beams; \bullet , (1×2) fractional-order beams; — — —, extra beams at lower coverages; arrows indicate beam shift or structure compression as coverage is increased.

(These authors have interpreted the patterns in terms of a series of one-dimensionally incoherent structures on an *unreconstructed* substrate.) The pattern, displayed in Fig. 1(b), can thus be assigned to a (2×2) -1D structure as it shall be called henceforth.

Titration experiments, performed by exposing a K-precovered Ni(110) surface at 320 K to oxygen, reveal that at $\Theta_K > 0.14$ the entire surface is covered with a uniform K adlayer (i.e., a mixed phase containing K and O atoms in the unit cell). However, at *lower* K precoverages oxygen adsorption leads to the formation of the (2×1) O structure, with simultaneous compression of the K adlayer into islands of (2×2) -1D phase, thus locally inducing the reconstruction.¹¹

Au(110) differs from Ni(110) in that the clean surface exhibits a (1×2) reconstruction which has been assigned as a missing row.⁸⁻¹⁰ As expected, the adsorption behavior of K on Au(110) is quite different from that on Ni(110). The resulting LEED patterns are, however, closely related. Adsorption at 90 K on the reconstructed surface yields no extra features at low coverages, while at medium coverages ($\Theta_K \sim 0.2-0.3$) central streaks are formed similar to those observed on Ni after annealing. The half-order spots, originally visible for the clean surface, are not affected. Upon higher exposures (into the multilayer range) the LEED pattern again fades away on an increased background.

Annealing the K-covered Au surface just beyond the multilayer desorption temperature causes major structural rearrangements of the surface. Small and medium coverages produce patterns comparable to those of the (2×2) -1D related structures on Ni(110). At $\Theta_K > 0.3$, a $c(2 \times 2)$ pattern develops, which eventually remains as the only existing pattern at saturation of the first adlayer. This phase, which also forms by adsorption to saturation at ~ 480 K, provides the calibration of the absolute coverage ($\Theta_K = 0.5$) for the AES-based coverage determination.

The sequence of various (2×2) -1D-like structures we observe for K on the *reconstructed* Au not only parallels the K interaction with the *unreconstructed* Ni, but also closely resembles the sequence reported for K/Pd(110),⁵ K/Cu(110),⁷ and K/Ag(110).² All these systems exhibit the coverage-dependent formation of (1×2) patterns and streaked intermediates between (1×2) and (1×3) . A distinct (1×3) pattern has been observed on Ag and Cu. For K/Cu(110) the additional streaks reported in the present study were also found.⁷ This suggests that (2×2) -1D-like structures are common to all these surfaces. A missing row substrate reconstruction [Fig. 1(d)] is highly plausible in these systems for various reasons: (a) results of recent ion scattering structure analyses of the (2×2) -1D structure of K/Ag(110) (Ref. 3) and Li/Cu(110) (Ref. 6) favor a missing-row substrate reconstruction; (b) a LEED intensity analysis of the same structure on Pd(110) provides evidence for the same model;⁵ (c) we observe that these structures are readily formed at 100 K on the missing-row reconstructed Au(110) surface, while formation on the nonreconstructed surfaces requires annealing to at least 300 K. This points to an *activated* process for the alkali-metal-

induced reconstructions.

The $c(2 \times 2)$ -like, high-coverage structures on Ni(110) and Au(110), which we predict to exist on the other fcc (110) surfaces, are incompatible with a missing row reconstructed substrate, but may be attributed to densely packed adlayers on an unreconstructed surface [Fig. 1(c)]. This structural assignment agrees well with the observation that these structures are readily formed on unreconstructed Ni(110) at 100 K, but need thermal energy on the reconstructed Au(110) in order to rearrange the underlying substrate. The different activated and nonactivated structural transformations due to K adsorption on fcc (110) surfaces may be placed into two categories: all steps involving a rearrangement of the substrate are activated, while adlayer ordering itself is not activated.

The fcc (110) surfaces discussed here are inherently unstable, i.e., energy differences between different configurations of the same surface are small. Recent calculations for Pt(110) show the (1×2) missing row is indeed only slightly more stable than the unreconstructed (1×1) phase,^{14,15} but this small energy difference is directly evident from the large number of adsorbate-induced reconstructions of these surfaces. The interaction of adsorbed K is characterized by this structural ambivalence as well: only minor modifications—e.g., coverage variations—suffice to make either the unreconstructed or the missing-row reconstructed substrate surface more stable. This is depicted in Fig. 2, in which the difference in adsorption energy of K on a reconstructed ($E_{ad,II}$) or unreconstructed substrate ($E_{ad,I}$) at a given

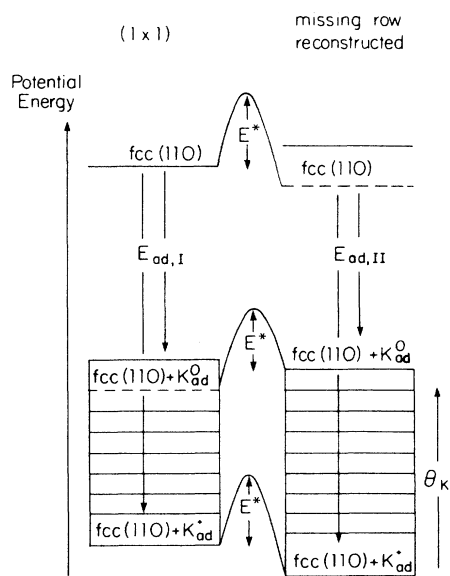


FIG. 2. Schematic potential energy diagram of the interaction of alkali-metal atoms with fcc (110) surfaces. Energy levels for clean and potassium-covered surfaces at low (K_{ad}^+) and high (K_{ad}^0) coverages for the bulklike (1×1) (left) and the missing-row (1×2) (right). E^* , activation barrier for adsorbate-induced substrate reconstruction; E_{ad} , Θ -dependent adsorption energy of potassium on respective substrate phases; —, Ni(110); — —, Au(110).

coverage determines the thermodynamically stable substrate structure.

The term “adsorption energy” reflects a thermodynamic property only, and does not specify its physical origin. For alkali-metal-induced reconstructions, the energetic driving force is certainly related to electronic charge donation into the metal, as has already been suggested by Hayden *et al.*² We observe that at higher coverages, where work-function measurements show that K_{ad} exhibits predominantly metallic character, the bulk-like (1×1) phase is stabilized. In contrast, at lower coverages, where K_{ad} may be described as mostly ionic, the missing row is thermodynamically favored. In this case, electrons donated from the adsorbate increase the tendency of the substrate to arrange in a close-packed surface,¹⁶ which indeed is developed on the reconstructed surface in the form of (111) microfacets. In addition, the K-ion cores in the missing row are much closer to the metal than on the unreconstructed (1×1) substrate [Figs. 1(c) and 1(d)]. Due to interaction between K^+ and its image charge, the reconstructed phase is further stabilized. At higher coverages both of these contributions decrease because of depolarization. Also, the adsorbate-substrate bond becomes more covalent, which is often stronger on more open crystal planes.¹⁶ This supports the observation that the (110) (1×1) phase is favored at high coverage. It is the potassium coverage which determines the strength of these interactions, which ultimately dictates the substrate structure.

Based on the low coverages at which the reconstruction occurs, a long-range mechanism has been previously suggested.^{2,5} Our LEED data show for the first time that the adsorbate structure resembles a (2×2) -1D rather than a (1×2) structure, which reduces the “ideal” coverage from $\Theta_K = 0.5$ to 0.25. In addition, our oxygen coadsorption experiments demonstrate that for $\Theta_K \leq 0.14$ on Ni(110) *only part* of the surface is reconstructed. In view of these results there is no obvious discrepancy between ideal and actual coverage. Therefore, the implication of a long-range mechanism for the alkali-metal-induced reconstruction of these fcc (110) surfaces on the basis of coverage arguments is *not* justified. Similarly, electronic arguments give little evidence for a long-range mechanism. Tomanek *et al.* have concluded, from linear combination of atomic orbitals (LCAO) calculations on the clean Pt(110) surface, that a specific electronic origin of the reconstruction, such as surface states just below E_F , is absent.¹⁵ Accordingly, Hayden *et al.* could not find any such states in angle-resolved ultraviolet photoemission spectroscopy experiments on K/Ag(110).^{2,17}

First hints on the mechanism are gleaned from comparison with other adsorbate induced structural transformations on these surfaces. The estimated activation barrier (E^* , Fig. 2) for the K-induced (1×2) reconstruction, derived from the transition temperature (~ 300 K), is comparable to those found for the O-induced (2×1) and the H-induced (1×2) reconstructions on

Ni(110),^{18,19} which occur via a “nucleation and growth” mechanism, i.e., island growth of the reconstructed phase surrounded by unreconstructed area. The higher local binding energy of the adsorbate in the reconstructed phase is the energetic driving force. A similar mechanism is also probable for the present alkali-metal-induced reconstructions on Ni(110). The proposed assignment is based not only on structural and kinetic arguments, but is also supported by our observation of an island growth mode for the reconstructed (2×2) -1D phase, as shown by the oxygen coadsorption experiments.

As for the microscopic mechanism, which describes the progress of the structural transformation, a phonon-driven (“soft mode”) process² may certainly be ruled out, since reconstruction requires mass transport of 0.5 monolayers of substrate atoms rather than just local displacement of metal surface atoms. The modification of metal-metal bonds, reflected by a change in phonon frequencies, may, however, play an important role. Similar to the CO-induced structural transformation on Pt(100) (Ref. 20) we expect a two-step mechanism: In a first step substrate atoms (e.g., those adjacent to an already reconstructed area) are removed from their lattice sites and expelled into the next layer. In a second step these atoms may diffuse away on the smooth substrate surface. While the removal of a single atom from a (110) plane is energetically unfavorable²¹ the displacement of atoms near K_{ad} must be energetically less costly such that this step may now occur already at 300 K.

In summary, a comprehensive model for the interaction of alkali metals with fcc (110) metals such as Ni, Cu, Pd, Ag, and Au is presented for the first time. A comparative study of K with the *unreconstructed* Ni(110) and the missing-row *reconstructed* Au(110) shows that identical structures form in both cases, i.e., regardless of initial substrate structure. The mechanisms of formation do, however, depend on initial structure and are identified as the nonactivated ordering within the adlayer, and the alkali-metal-induced reconstruction of the metal surface which proceeds via *local*, thermally activated, island growth. The thermodynamic stability of the system is a function of coverage, depending mainly on the strength of electrostatic interactions induced by charge transfer from the alkali-metal-atom adlayer. For Ni and Au we observe that low coverages favor the more-corrugated missing-row reconstruction, whereas higher coverages favor the relatively flat (1×1) . We predict this trend to hold true for all the fcc (110) metals.

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