Theory of Alkali-Metal–Induced Reconstruction of fcc (110) Surfaces

K. W. Jacobsen[(a)]
NORDITA, DK 2100 Copenhagen, Denmark

and

J. K. Nørskov[(b)]
NORDITA, DK 2100 Copenhagen, Denmark, and
Haldor Topsøe Research Laboratories, DK 2800 Lyngby, Denmark

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The chemisorption energy and equilibrium configuration have been calculated for K adsorbed on Cu(110), by the effective-medium theory. At low coverages K is found to stabilize the (1×2) missing-row reconstructed surface, whereas it stabilizes the unreconstructed structure at higher coverages. The calculations form the basis for a general understanding of why adsorbed alkali-metal atoms induce a (1×2) reconstruction of fcc (110) surfaces.

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Adsorbed alkali metals and in particular potassium are known to induce a (1×2) reconstruction of the (110) surfaces of Ni, Cu, Ag, and Pd.[1-4] The experimental indications are[4] that the (1×2) structure is very similar to the (1×2) missing-row (MR) structure observed for clean Au(110), Pt(110), and Ir(110).[5-8] Here every second row of the close-packed [1$\bar{1}$0] rows is missing. The alkali-metal–induced reconstruction is observed for small adsorbate coverages ($\Theta_K \lesssim 0.1$). It is also observed that at the highest coverages the reconstruction is lifted even for a surface like Au(110), where there is a reconstruction of the clean surface.[4]

There has been considerable speculation as to the origin of the alkali-metal–induced reconstruction of fcc (110) surfaces. The many systems where the effect has been observed indicate that it is not particularly system specific, neither with respect to the substrate metal nor to the alkali-metal atom. The low coverages needed to observe the reconstruction have led to suggestions of long-range effects involving charge-density waves or phonon instabilities.[1] The variations with coverage have been taken as evidence that the amount of charge transfer is of importance.[1,4]

In the present Letter we show that the stabilization of the (1×2) MR structure at low alkali-metal coverages can be explained by a large increase in the alkali-metal chemisorption energy. The effect is local, but because of its magnitude only ∼0.1 monolayer of alkali-metal atoms is needed to reconstruct the whole surface. K chemisorption on the (1×2) MR surface is more stable than on the (1×1) unreconstructed surface mainly because the K atoms can get a larger effective coordination number here. At the highest coverages this is no longer possible because of K-K interactions and the K-induced reconstruction is lifted. The arguments are very general and should apply to all fcc (110) surfaces.

The basis for these conclusions is a calculation of the total energy and equilibrium configuration of K on Cu(110) as functions of coverage and surface structure. Large unit cells are needed to describe the low-coverage systems. Furthermore, we need to be able to minimize the total energy with respect to a large number of coordinates. This calls for an efficient way of calculating the total energy. We have used the effective-medium theory.[9] It has proven able to describe the cohesive properties of bulk metals,[9] surface energies and relaxations,[9,10] and adsorption of simple gasses on metal surfaces.[11]

The effective-medium theory is derived with direct use of the variational property of the total-energy functional: We make the *Ansatz* that the electron density of the system in question can be represented by the sum of atomic densities calculated when the atom is embedded in a homogeneous electron gas of a density given by the average of the densities from the neighboring atoms. This is a reasonable first approximation, which, for instance, includes the spherically symmetrical part of the screening effects. It also includes charge transfer, but again only in a spherically symmetrical way. The variational property then ensures that any errors in the *Ansatz* density relative to the true ground-state density will only show up to second order in the total energy of the system. The *Ansatz* allows us to write the total energy of the system as

$$E_{\mathrm{tot}} = \sum_i E_{c,i}(\bar{n}_i) + \Delta E_{1\mathrm{el}} + \Delta E_{\mathrm{AS}}, \tag{1}$$

where $\bar{n}_i$ is the average density in cell i from the neighbors:

$$\bar{n}_i(s_i) = \sum_{j \neq i} \Delta\bar{n}_j(s_i, r_{ij}), \tag{2}$$

$\Delta\bar{n}_j$ being the average of the jth atom density over the Wigner-Seitz sphere i with radius s_i,

$$\Delta\bar{n}_j(s_i, r_{ij}) = (\tfrac{4}{3}\pi s_i^3)^{-1} \int_{s_i} \Delta n_j(\mathbf{r} - \mathbf{r}_j)\, d^3r. \tag{3}$$

The energy function $E_{c,i}(\bar{n})$ is related to the energy of atom i in a homogeneous electron gas. It can be calculated once and for all within the local density approximation. For reactive atoms it shows a single minimum, indicating that atoms of this kind will tend to find surroundings providing a particular optimum density. This term describes the changes in energy of a close-packed metal with volume, and determines to a large extent the equilibrium lattice constant and bulk modulus.

$\Delta E_{1\text{el}}$ is a one-electron energy difference which is important in the description of, e.g., the *d*-band formation in the transition metals. For the purposes of the present study it can be neglected.

Finally, ΔE_{AS} describes an extra electrostatic energy that must be included for systems where the Wigner-Seitz cell cannot be approximated by a sphere. This includes all situations where the system is not in a perfect close-packed arrangement. For such systems we choose still to work with atomic spheres and then correct for the regions that are double counted and those that are not included at all. The atomic spheres are chosen to be always neutral. In this way we avoid long-range Madelung-type contributions to the total energy. The atomic-sphere correction is generally repulsive when the neutral atomic spheres overlap. It is, for instance, this term which is responsible for the shear strength of a close-packed metal. The details of the calculational procedure are described in Ref. 9 and by Puska *et al.*[12] where the parameters calculated for Cu and K are also given.

Before we go on to describe the results we give a few words about the clean fcc (110) surface reconstruction. There is general agreement from a number of different theoretical methods that for Au(110) the energy difference between the (1×1) and (1×2) MR structure is rather small, of the order 25 meV per (1×1) unit cell.[10,13] For metals that do not reconstruct, like Ni, Cu, or Ag, it is calculated to be slightly negative or even slightly positive (∼5 meV).[10] The main point is that these surfaces are close to being unstable and only ∼25 meV extra is needed for them to behave like Au(110) which reconstructs.

We have calculated the total energy and equilibrium positions for one, two, and three K atoms in a (2×2), (3×2), and a (4×2) Cu(110) surface unit cell. This spans a K-coverage range between 0.12 and 0.5. At higher coverages multilayers begin to form. For each system the equilibrium geometry is found by minimization of the energy by a steepest-descent method. The calculations have been performed for both the unreconstructed and the missing-row reconstructed surface. The difference in the K chemisorption energy on the two structures is a measure of the tendency of K to induce the reconstruction.

The chemisorption energy difference per K atom is shown in Fig. 1 as a function of coverage. The sign convention is such that a negative energy difference means that the K atoms are most stable on the reconstructed surface. The tendency of K to stabilize the missing-row reconstruction at low K coverages is clearly seen. It is also seen that at the highest coverages it is the other way round, in complete agreement with experiment.[4] The stabilization at low coverages is so large that even at a K coverage of $\Theta_K = 0.12$ the stabilization of 0.17 eV per K atom corresponds to 0.02 eV per surface Cu atom. The adsorption of 0.12 monolayer of K on Cu(110) thus makes the energy change associated with a reconstruction of the Cu(110) surface similar to that of a free Au(110) surface.[10]

The origin of the variations in the K chemisorption energy difference is most easily illustrated by our looking at the equilibrium configuration of the K overlayers. This is shown in Fig. 2 for two coverages, $\Theta_K = 0.25$, where the chemisorption on the missing-row surface is still most stable, and $\Theta_K = 0.50$ where the effect has

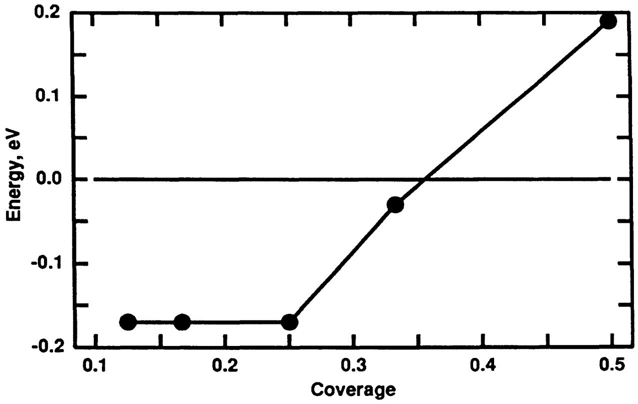

FIG. 1. Difference between the K chemisorption energies on a (1×2) missing-row reconstructed and an unreconstructed Cu(110) surface as a function of K coverage. At low coverages adsorbed K stabilizes the reconstruction whereas it destabilizes it at the highest coverages. The K chemisorption energy on the unreconstructed surface at low coverages is 2.0 eV.

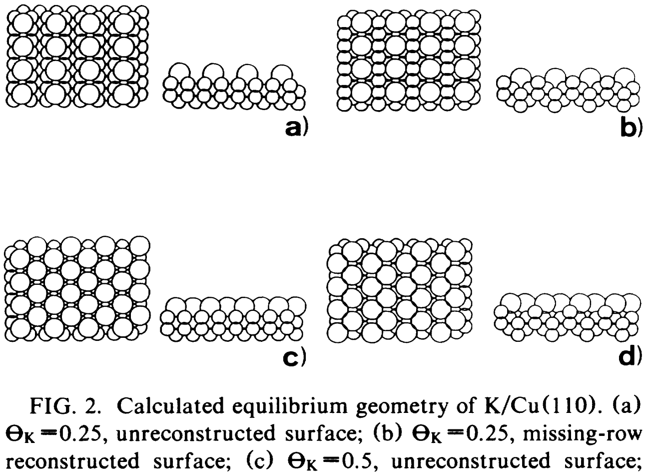

FIG. 2. Calculated equilibrium geometry of K/Cu(110). (a) $\Theta_K = 0.25$, unreconstructed surface; (b) $\Theta_K = 0.25$, missing-row reconstructed surface; (c) $\Theta_K = 0.5$, unreconstructed surface; (d) $\Theta_K = 0.5$, missing-row reconstructed surface.

changed sign.

On both the unreconstructed and the reconstructed surfaces the adsorbed K atoms tend to occupy the site of highest coordination number. This can be understood in the present framework as follows: The E_c term requires the K atoms to find a particular electron density outside the Cu surface. This can be found at any position in the surface unit cell, but at varying distances from the surface. The higher the coordination number is, the further away from the Cu atoms the K atoms will tend to be. Since ΔE_{AS} is larger the larger the overlap between the atomic cells is, this term will clearly favor the highest-coordination-number site. Likewise, the Cu atoms prefer as large a number of neighbors as possible. One can say that adsorption of the K atoms relieve some of the strain the unsaturated Cu atoms in the surface feel, and one can think of part of the K chemisorption energy as the surface energy of the free surface. Together these two effects give adsorption in the highest-coordination-number sites. This is a general rule, which is expected to hold whenever the one-electron energy term is not important.

Now that we have established that the K atoms prefer to occupy the fourfold sites on both the surfaces, the same arguments as above explain why the chemisorption energy is largest on the reconstructed surface. The K atom is very large, or, in the present language, the K atom prefers a position where the electron density from the neighbors is very small. That means that the K atom is so far outside the surface that it is close to seven Cu atoms on the reconstructed surface, but only five on the unreconstructed.[14] Adsorbed K therefore gets a larger effective Cu coordination number on the reconstructed surface, but since the Cu densities fall off rather rapidly the extra two Cu atoms contribute only little to the K energy. The K density is much more spread out and consequently the Cu atoms on the ridge of the missing-row structure are significantly stabilized by the adsorbed K. This is the main effect behind the stabilization of the missing-row reconstruction by adsorbed K. It is mainly electrostatic, since it mainly stems from ΔE_{AS}. Clearly, these arguments are not particular to Cu nor to K. It must be expected that other "large" atoms will have the same effect on all the fcc (110) surfaces. The unique property of the alkali-metal atoms in reconstructing the fcc (110) surfaces is thus, according to this picture, their size.

At the higher coverage it is no longer possible for all the K atoms to find the optimum site on the reconstructed surface. K-K interactions prevent the atoms from getting to the bottom of the troughs. On the unreconstructed surface this is not the case. Here the K atoms arrange in a $c(2\times2)$ pattern as observed experimentally.[4] It is thus adsorbate-adsorbate interactions which prevent the reconstruction at the highest coverages. These stem from ΔE_{AS} or the overlaps of the atomic spheres that can be seen in Fig. 2, and are therefore mainly of an electrostatic nature.

In conclusion, we have shown that the alkali-metal-induced reconstruction of fcc (110) surfaces can be explained by a considerably higher chemisorption energy of large atoms on the more open missing-row structure. At high coverages, on the other hand, adsorbed K stabilizes the unreconstructed structure because the electrostatic K-K repulsion is smaller there. The calculations and the analysis have been made within the effective-medium theory. Refinements of the treatment, like the inclusion of nonspherically symmetrical K densities, may change the energies involved somewhat, but are not expected to add qualitatively new features.

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[a] Present address: Laboratory for Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853.

[b] Present address: Laboratory for Applied Physics II, Technical University of Denmark, DK2800 Lyngby, Denmark.

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[14] The equilibrium nearest-neighbor K-Cu distance is found to be 3.0 Å at 0.25 monolayer coverage on both the reconstructed and unreconstructed surface. The distance to the ridge Cu atoms on the reconstructed surface is found to be 4.4 Å.