Theory of Adsorbate-Induced Surface Relaxations: Hydrogen on Cu(110)

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The effective-medium theory is used to study the chemisorption and incorporation of hydrogen on the Cu(110) surface. The hydrogen-induced relaxations of the Cu lattice and their role in stabilizing hydrogen just under the surface are studied in particular. We find that hydrogen induces local lattice distortions even when chemisorbed. The relaxations are largest when hydrogen is just under the surface, but not large enough to make this site more stable than the chemisorption site.

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In the present Letter we take issue with the recent proposals that hydrogen chemisorbed on many metals does not occupy a normal site outside the first metal plane but a site below the surface. The existence of such a subsurface state has been invoked to explain photoemission data for hydrogen on various Ni and Cu surfaces,[1] to explain the kinetics of hydrogen desorption from Ru(0001),[2] and to understand final-state distributions of hydrogen desorbed from Cu(100) and (111).[3] Most recently, Rieder and Stocker[4] suggested that subsurface hydrogen was responsible for their low-energy electron-diffraction (LEED) observation of a (1×2) reconstruction of Cu(110).

The existence of a stable subsurface hydrogen site on metals like Ni or Cu which have large and positive hydrogen heats of solution[5] would be remarkable. It would indicate that an interstitial site just beneath the surface should be substantially different from sites in the bulk. Since the screening length in metals is short, such an effect would most likely have to be associated with the coupling to the lattice.

We have studied this problem theoretically by calculating the total energy of ordered overlayers of hydrogen on Cu(110) including all relaxations of the metal lattice and the possibility that the surface reconstructs. We do indeed find that the subsurface site is considerably more stable than the bulk interstitial site and that this is connected with substantially larger relaxations of the Cu atoms. The subsurface site is, however, less stable than the normal chemisorption site by 0.3 eV. Outside the surface we find that the hydrogen can move almost freely along the surface as suggested by earlier calculations[6] and by recent LEED and high-resolution electron energy-loss spectroscopy (HREELS) experiments.[7] Calculated vibrational frequencies also agree with the measured ones. Hydrogen is found locally to induce relaxations of the Cu lattice even when outside the surface. The hydrogen-induced (1×2) reconstruction observed at high temperatures may be of the missing-row type. We find that this structure is stabilized by hydrogen and that the calculated vibrational frequencies again agree with HREELS experiments.[7]

To treat a problem like the present it is necessary to be able to optimize of the order 25 metal coordinates simultaneously for each adsorbate position. This calls for a very efficient and therefore approximate total-energy expression. We have used the effective-medium theory.[8] It has a number of advantages: The total-energy expression is derived from first principles, most of the parameters entering can be calculated within the local density approximation, and it is known to describe very accurately a number of properties of bulk metals,[8] metal surfaces,[8] and simple chemisorption systems where lattice relaxations do not play an essential role.[6]

The basis for the effective-medium theory is the variational property of the total-energy density functional. This allows us to make a simplified *Ansatz* for the electron density of the system in question and the error thus made will only show up to second order in the result. The *Ansatz* we make[8] is that the electron density is given by a superposition of atomic densities $\Delta n_i(\mathbf{r})$ calculated with the atom embedded in a homogeneous electron gas of a density given by the average $\bar{n}_i$ of the densities from all the neighbors to a given cell:

$$\bar{n}_i(s_i) = \sum_{j\neq 1} \Delta\bar{n}_j(s_i,r_{ij}), \tag{1}$$

where

$$\Delta\bar{n}_j(s_i,r_{ij}) = (\tfrac{4}{3}\pi s_i^3)^{-1}\int_{s_i} \Delta n_j(\mathbf{r})\,d^3r. \tag{2}$$

The average is over a sphere of radius s_i chosen so that the sphere is neutral. For a bulk metal, this definition of an atomic sphere coincides with the usual definition of the Wigner-Seitz sphere. This *Ansatz* is a reasonable first approximation which, for instance, includes the spherically symmetrical part of screening effects. It allows us to write the total energy of the system as[8]

$$E_{\mathrm{tot}}=\sum_i E_{c,i}(\bar{n}_i)+\Delta E_{1\mathrm{el}}+\Delta E_{\mathrm{AS}}, \tag{3}$$

where $E_{c,i}(\bar{n}_i)$ is given from the embedding energy of the atom i in a homogeneous electron gas of density $\bar{n}_i$. The E_c functions for Cu and H calculated within the local-density approximation both show a single minimum.[8,9] For bulk Cu, the density n_0 at the minimum determines the lattice constant so that the average density from the twelve neighbors in the fcc structure is equal to n_0. The depth of the minimum gives the cohesive energy and the curvature gives the bulk modulus.[8]

$\Delta E_{1\mathrm{el}}$ is a one-electron-energy difference which is important in describing the d-band formation in the transition metals and other effects involving large changes in density of states around the Fermi level.[8] For the H/Cu system it is a good approximation to neglect it.

The last term in Eq. (1) corrects for the error implicitly made above in treating each atom as inscribed in a neutral atomic sphere. In general, these spheres will overlap thus leading to double counting in some regions and the neglect of other regions. To correct for this we must include[8]

$$\Delta E_{\mathrm{AS}}=-\tfrac{1}{2}\int O(\mathbf{r})n(\mathbf{r})\phi(\mathbf{r})d^3r, \tag{4}$$

where the overlap function $O(\mathbf{r})$ is defined to be $n-1$ if $\mathbf{r}$ is in n spheres, and $n(\mathbf{r})$ and $\phi(\mathbf{r})$ are the total density and the corresponding electrostatic potential, respectively. Dividing n and ϕ up into an adsorbate and a metal part, we can write Eq. (4) as

$$\Delta E_{\mathrm{AS}}=\Delta E_{\mathrm{AS}}^{\mathrm{MM}}+\Delta E_{\mathrm{AS}}^{\mathrm{AA}}+\Delta E_{\mathrm{AS}}^{\mathrm{AM}}. \tag{5}$$

The adsorbate-adsorbate part $\Delta E_{\mathrm{AS}}^{\mathrm{AA}}$ can be neglected at the coverages of interest here. The metal-metal part is calculated as in Ref. 8. For the adsorbate-metal part, we evaluate Eq. (4) directly keeping only the overlap regions where the integrand is much larger than in the "holes." There are exchange-correlation and kinetic-energy analogs to Eq. (4), but they are much smaller and will be neglected here.[8] ΔE_{AS} generally acts to prevent the neutral spheres from overlapping. It is, for instance, this term that dominates the phonon spectrum.[8]

The inputs to the calculation are the energy functions in Fig. 1 and the densities $\Delta n(\mathbf{r})$ of the atoms in a homogeneous electron gas.[8,9] We have found it necessary to adjust the Cu densities slightly in order to get a reasonable bulk shear modulus C_{44}.[9] This only affects the details of the Cu density, and can be regarded as finding an even better *Ansatz* density.

Before addressing the problem of subsurface hydrogen, let us explore the description of hydrogen outside and far inside Cu(110). Figure 1(a) shows a contour map of the energy of hydrogen outside the surface. The metal atoms are not allowed to relax here. The results are therefore very close to those found with the simpler version of the effective-medium theory where the metal-metal interactions are not included.[6] The lowest-energy point in the surface unit cell is at the long-bridge site, but the quasithreefold site marked with a dot in the figure is only 20 meV higher in energy. The hydrogen atom is, however, much less confined in the direction perpendicular to the close-packed rows in the sites shown in Fig. 1(a) than in the long bridge sites. We estimate that the zero-point energy is about 50 meV higher in the long-bridge site making it slightly less stable overall. These small energy differences should not be taken too seriously; the main conclusion to be drawn from this is that the potential is very flat. Hydrogen will be delocalized on the surface.[10] This picture is in close agreement with recent LEED and HREELS experiments.[7] A complete evaluation of the vibrational spectrum of this system is complicated by the large anharmonicities and the flatness seen in Fig. 1(a).[6,10] We estimate the frequency for the motion perpendicular to the surface to be 70 meV in the long-bridge site and 95 meV in the quasithreefold site. This is in good agreement with the experimentally found frequencies which lie in the range 68 to 81 meV.[7]

In terms of the energy expression Eq. (3), the depth, position, and curvature of the chemisorption minimum

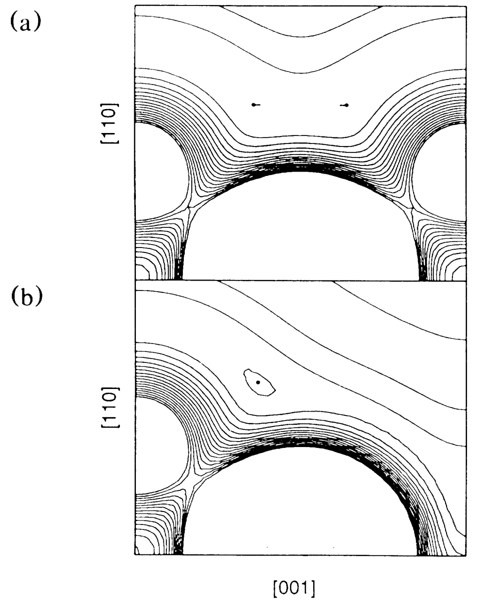

FIG. 1. Contour plots of the binding energy of half a monolayer of hydrogen atoms at a Cu(110) surface. At this coverage the H-H interactions are negligible. In both cases the cut shown is perpendicular to the surface and along the [001] direction between two short-bridge positions of the unreconstructed surface, and the Cu lattice is kept fixed at the bulk terminated positions. (a) The unreconstructed surface; (b) the (1×2) missing-row reconstruction. The smallest contour value shown is −2.4 eV and the energy difference between contours is 0.2 eV. The minima are indicated by dots.

are largely given by the E_c function for hydrogen. Outside the surface the hydrogen atoms tend to find the site where the density is equal to the value where E_c has its minimum. This picture has also been confirmed by larger calculations.[11] We generally find bond lengths that are too long by a few tenths of an angstrom. This we tentatively ascribe to the neglect of nonspherical contributions to the hydrogen electron density. The asymmetrical surroundings at the surface will polarize the hydrogen atom and pull it closer to the surface.

For the clean Cu(110) surface there is a contraction of the first interlayer spacing. It is driven by the E_c term of the metal energy. The surface atoms have fewer neighbors than the bulk atoms, and a surface atom with the perfect bulk interatomic distance to its neighbors will therefore feel a lower than optimum density. To compensate for this, it can move closer to the second layer. This is opposed by the ΔE_{AS} term and the magnitude of the contraction is determined by a balance between the two terms. The contraction of 4% that we calculate is on the small side of the experimental values which range from 5.4% to 9.6%.[12] Again we suspect the slightly too large bond length at the surface to be a result of the neglect of polarization effects.

The presence of chemisorbed hydrogen tends to lift the contraction. This is very simple to understand in the present picture. The hydrogen atoms simply donate charge to the surface Cu atoms, which therefore need not be so close to the second-layer atoms in order to try to optimize the density. Clearly, only the Cu atoms that are nearest neighbors to the hydrogen atoms are affected substantially. One hydrogen neighbor gives rise to a 4% expansion and two to a 6% expansion. This means that the average interlayer spacing increases continuously as a function of the hydrogen coverage and that the contraction of the clean surface is lifted at a hydrogen coverage of half a monolayer. This is in good agreement with recent LEED experiments.[7]

In the calculation, an ordered overlayer of hydrogen has been considered for computational convenience. The H-H interaction is, however, found to be very small for coverages less than half a monolayer, and the hydrogen cannot be expected to order on the surface.

Movement of a chemisorbed hydrogen atom to a bulk interstitial site is associated with a large (0.6 eV) cost in energy. This is related to the fact that inside the metal the electron density is much higher than the optimum value for hydrogen thus increasing the value of E_c considerably. The chemisorption energy that we calculate is -2.4 eV (cf. Fig. 1), and the binding energy at an interstitial site is thus -1.8 eV, which compares favorably with the value deduced from the experiment heat of solution (-1.7 eV).[5] Since the chemisorption energy is also in good agreement with the experimental value,[13] the energy difference between the interstitial and chemisorption sites is well described by the theory. In order to diminish the density from the surroundings, an interstitial hydrogen atom pushes away the six nearest Cu atoms around the octahedral site by 0.06 Å. The energy gain associated with this relaxation is 0.2 eV. It comes from a smaller ΔE_{AS} (the overlap is smaller), and because the density in the hydrogen cell is smaller, i.e., closer to the value where E_c has its minimum.

We can thus conclude that the theory provides a good description of hydrogen outside the surface and in the bulk. We can then go on to study the subsurface region. Figure 2 shows the hydrogen binding energy as a function of distance from the surface calculated both with a rigid lattice and where the lattice has been allowed to relax for each H position. It can be seen from Fig. 1 that the lowest-energy path into the solid involves considerable motion of the hydrogen atom parallel to the surface. In Fig. 2 we therefore show the lowest-energy point of a cut like in Fig. 1 for each distance of the H atom from the surface. Two things are apparent from Fig. 2. First of all, the effect of relaxations for H positions under the surface is enormous. The stabilization of the subsurface octahedral site is considerably larger than in the bulk. This is mainly due to large (0.37 Å) shifts of the surface Cu atoms out from the surface. The second-layer Cu atoms shift out by 0.05 Å, but also move away from the H atoms parallel to the surface by 0.05 Å. Secondly, in spite of the large relaxations, the subsurface site is still considerably less stable than the chemisorption site. On the other hand, it is possible that for metals where the heat of solution is smaller than for Cu the subsurface site could be at least as stable as the chemisorption site. This is, for instance, proposed to be the case for Pd surfaces.[14]

An energy difference of 0.3 eV as found here between the surface and subsurface sites would exclude occupation of these sites under normal conditions. It then re-

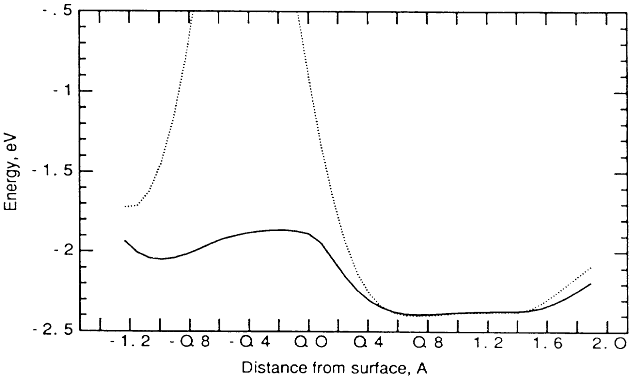

FIG. 2. The binding energy of a hydrogen atom as a function of distance from a Cu(110) surface. Both the static (dotted line) and relaxed (solid line) lattice results are shown. For each distance outside the surface, the energy value plotted is the lowest in the cut shown in Fig. 1. The curves end at the subsurface octahedral site of the unrelaxed surface.

mains to explain the occurrence of a (1×2) reconstruction at high (300 K) temperature as observed by Rieder and Stocker[4] and by Baddort *et al.*[7] We notice that a similar structure has been reported for hydrogen on Ni(110).[15] One possibility is that it is the missing-row structure observed on, e.g., clean Au(110).[16] This is tempting because clean Cu should be very close to making such a transition. Calculations based on the effective-medium theory indicate that the stability of the (1×2) structure relative to the (1×1) structure is only 20 meV larger for Au(110) than for Cu(110).[17] We have also studied the chemisorption of hydrogen on the missing-row structure of Cu(110). The results are shown in Fig. 1(b). The equilibrium chemisorption site is now the threefold site, which is more stable than the similar site on the unreconstructed surface by 20 meV. This is an energy of a sufficient order of magnitude to make the missing-row structure stable,[18] but also so small that the accuracy of the calculation could be questioned. At coverages higher than one, the energy gain in the missing-row structure might be larger because the (1×2) facets have more chemisorption sites. The vibrational frequency for hydrogen motion perpendicular to the (111) facets of the reconstructed surface is estimated to be 120 meV. A shift to higher frequencies in connection with the (1×1) to (1×2) reconstruction has been observed experimentally.[7] In spite of this we cannot make any definite conclusions about the nature of the (1×2) reconstruction. The missing-row model, for instance, does not *a priori* explain why the (1×2) structure is not observable with He diffraction.[4]

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[18] The present calculation actually shows the missing-row reconstruction to be stable by 10 meV even for the clean surface. The adsorption of hydrogen increases the stability by 20 meV.