Lattice Relaxation near Isolated Adsorbates

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Self-consistent calculations show that S and Al adatoms form directional bonds to Al(001) in fourfold hollows. If substrate nearest-neighbor nuclei are allowed to move, each adatom approaches the surface, as its square of neighbors expands and moves slightly into the metal. These relaxations approximately preserve adatom-Al bond lengths. They open Al-adatom-Al bond angles slightly, and *shorten* the bonds between first- and second-neighbor atoms in the outer Al layer, as expected for a surface under tensile stress.

Barrier heights for surface diffusion on and absorption into a solid are key elements of any theory of surface kinetics. Such barriers are expected to depend strongly on the local lattice relaxations which adatoms induce.[1,2] It is therefore important to know what general principles determine how a substrate relaxes when adatoms are present. Bond-order–bond-length correlations,[3] for example, might be expected to govern the relaxation of covalently bonded substrates. Thus, when a covalent surface contributes bonding electrons to an adsorption bond, each adatom nearest neighbor must bind less strongly to *its* neighbors. The bonds between an adatom's first- and second-nearest neighbors should therefore lengthen. Similarly, in ionic adsorbate bonding to metals, charge transfer from metallic bonds to the adsorbate is understood to be the source of repulsive forces between an adatom's nearest substrate neighbors.[4,5] However, several results imply that the principles which govern adsorbate-induced lattice relaxation at metal surfaces must go beyond simple bond-order–bond-length ideas. Recent semiempirical work predicts that O adsorption on Al *shortens* the bonds between the O atom's first and second Al neighbors.[1] More generally, since the very formation of a surface implies cutting bonds, bond-order–bond-length ideas imply that every unreconstructed, clean metal surface must relax inward, which is simply not true.[6] In what follows, I report *ab initio* calculations of local lattice distortions on Al(001) induced by isolated S and Al adatoms. The results are consistent with the idea that relief of surface stress, rather than bond-order–bond-length correlation, governs the nature of the distortions. In particular, although adsorption weakens the bonds between each adatom's nearest neighbors, it strengthens and shortens those between the first and second shell of its surface-plane neighbors. This is just what one would expect if the surface layer were under tensile stress.

That Al surfaces are subject to tensile stress has recently been shown by Needs.[7] The lattice parameter of a nearly free-electron metal is determined in a competition between the expansion pressure of the kinetic energy and the compressive forces associated with electrostatic and exchange-correlation potentials. Needs's calculations show that at the surface of such a metal, electron spillout into the vacuum reduces the pressure associated with the kinetic energy. The consequence is that the bulk lattice parameter, in the surface plane, is too large for the surface Al's. They are consequently under tensile stress. If a surface atom were removed, to create a vacancy, one would expect its neighbors to relax away from the vacant site. Similarly, I assert, since an adatom creates an environment below it that is similar to what exists between a clean slab's outermost and subsurface layers, an adatom tends to relieve the tension in the bonds between its nearest neighbors. This allows the bonds between the adatom's first and second neighbors in the surface plane to shorten, relieving their tensile stress and lowering the system's total energy.

Computations were carried out using the self-consistent, matrix Green's-function (or "scattering-theory") method,[8,9] which has previously been used to compute adsorption energies and geometries in the absence of substrate relaxation,[9-11] and also to evaluate restoring forces on displaced atoms of a clean surface.[12] In the present work, adsorption and substrate-atom displacement are combined, with the focus on Al and S atoms adsorbed on Al(001), the subject of earlier studies.[11,13]

The matrix Green's-function approach to the surface-point-defect problem is particularly well suited to the treatment of substrate lattice relaxation.[14] In this approach, Kohn-Sham (KS) one-electron Schrödinger equations[15] for the perfect surface plus adatoms that are not allowed to interact with it, and for the fully interacting adsorption system, are projected into local bases at the outset. The basis orbitals of the perfect and adsorption systems are required to be in one-to-one correspondence, and to be identical far from the adsorbate, where its effects are negligible. Near the adsorbate, however, the basis functions can differ. This enables one to take account of substrate-atom lattice relaxation by moving basis orbital centers with substrate nuclei. Since the basis-projected KS equations are algebraic equations, they can be solved by straightforward matrix manipula-

tions that require no reference to the basis orbitals in coordinate space. This is the essence of how the matrix method simplifies computation of substrate lattice relaxation effects.

I model the Al(001) surface as a five-layer slab, set the Al-Al separation in the surface plane to 5.42 bohrs, and choose pseudo-orbitals for Al and S atoms as in Ref. 11. I allow each adatom and its four nearest substrate neighbors to seek their equilibrium positions. All other nuclear positions are frozen. To permit a study of adsorbate-induced surface relaxation, the undisturbed surface must be in equilibrium. In Ref. 12 I found that a 0.38% contraction of the outer layer spacing relative to the ideal bulk value corresponds to an outward normal force on a surface Al of only 0.012 eV/bohr, i.e., effectively zero. I adopt this contraction in the present work. For adsorption in a fourfold hollow, I assume that the orbitals affected by the adatom and its relaxed neighbors include those centered at the adatom's four nearest neighbors, each of their first two shells of neighbors in the surface layer, each of their first two shells of neighbors in the subsurface layer, and their nearest neighbors in the second subsurface layer. I also include floating p orbitals above the surface Al's and floating s orbitals above the subsurface-layer atoms. With this choice, the

matrix Dyson's equation for S/Al is 523×523 in size; for Al/Al the matrix is 522×522. Since the cluster of affected orbitals in the present problem is larger than that of Ref. 12, the force on an atom of the clean, undisturbed, but 0.38%-contracted surface need not equal 0.012 eV/bohr outward, and in fact changes to 0.031 eV/bohr inward. This change indicates the level of convergence with respect to the size of the set of "affected orbitals." In evaluating surface Al relaxation along the surface normal, with an adsorbate present, I subtract the residual 0.031 eV/bohr from the normal force on the surface atoms. I then seek relaxed geometries for which the forces on the adatoms and their nearest neighbors are less than 0.05 eV/bohr in magnitude. For the following qualitative analysis, this is adequately "relaxed to equilibrium." Results for the two adatom species are similar. Both Al and S form directed bonds to the surface. In each case the effect of freeing the substrate neighbors is that the adatom moves 0.10 bohr closer to the surface while the square of nearest-neighbor Al's expands, the side increasing by 0.11 bohr, and moves into the slab, by <0.01 bohr for Al and about 0.02–0.03 bohr for S. These relaxations approximately preserve the adatom-substrate-neighbor bond distance. They open Al-adatom-Al bond angles slightly, and *reduce* the length of
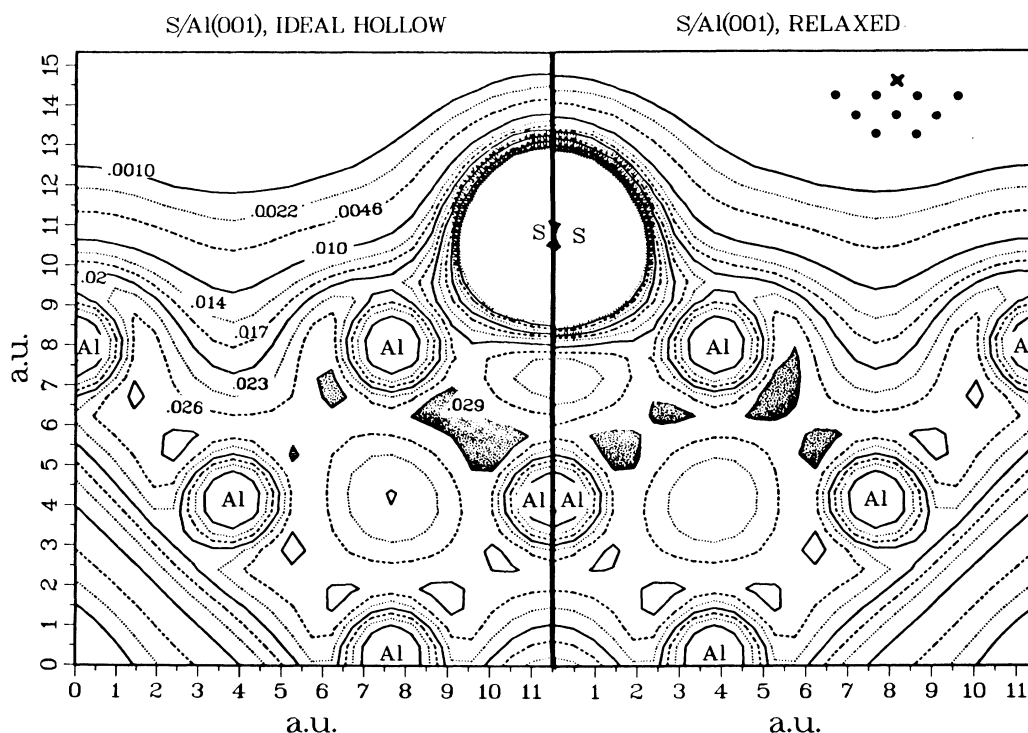

FIG. 1. Charge-density contours (labels in e/bohr^3), for S/Al(001), in a plane through the S nucleus and two of its nearest-neighbor Al nuclei. Left panel: S at its equilibrium height above a rigid Al surface. Right panel: S and nearest-neighbor Al's allowed to relax their nuclear positions. Inset: Geometry of the plot with the S represented as an × and the Al's as dots. Shading indicates bonds between nearest-neighbor and farther Al's. Continuity of the contours across the center of the plot at the bottom indicates excellent screening of the adsorption-induced charge.

the bonds between first- and second-shell substrate Al's, as expected for a surface under tensile stress. At equilibrium, the S adatom resides 2.77 bohrs from the undisturbed Al surface layer, while the Al chooses a height of 3.25 bohrs. The energies associated with the local lattice relaxations are roughly 0.03 eV for the Al adatom and 0.05 eV for S. These values are small on the scale of the Al and S heats of adsorption on Al(001), which are several eV in magnitude, but are comparable to adatom-adatom interaction energies on this surface.[10,11]

Figures 1 and 2 show how S bonds to Al(001), and the consequences of nearest-neighbor Al positional relaxation. Results for Al adsorption are similar. The plotted quantity is $\sum_{ij}\rho_{ij}\phi_i(r)\phi_j^*(r)$, where ρ_{ij} is the one-electron density matrix that emerges from the self-consistent calculations, and $\{\phi_i(r)\}$ is the set of basis orbitals used. The sum on i and j is restricted to orbitals that overlap the adsorption-induced potential. Thus, the figures represent the electron charge density near the adsorbate, but are meaningless far from it. In particular, the linear contours in the lower corners of Fig. 1 and in the lower left corner of Fig. 2 should be ignored.

Figure 1 shows a cut normal to the surface plane, through the S adatom and two of its surface-layer

S/Al(001), RELAXED

FIG. 2. Charge-density contours (labels in e/bohr^3), for S/Al(001), in the plane of Al nuclei which are nearest neighbors to the ad-S. The S resides above the upper right-hand corner of the plot as indicated in the inset, which shows the S atom as an × and the Al's as dots. The square in the inset indicates the region of the contour plot. Lower panel: S at its equilibrium height above a rigid Al surface. Upper panel: S and nearest-neighbor Al's allowed to relax their nuclear positions. Shading indicates bonds between nearest- and next-nearest surface-layer Al's. Continuity of the contours across the diagonal in the lower-left corner indicates excellent screening of the adsorption-induced charge.

nearest neighbors. The directionality of the S-Al bond is manifest as a bulge in the charge density along the line joining the S and the nearest Al, and also via the charge-density *minimum* lying on the surface normal between the S nucleus and the nearest subsurface Al (located at the center of the two quasielliptical contours shown). The minimum shows that there is no bond between the S and its subsurface second neighbor. This implies that the relaxation of the S toward the surface, when the nearest-neighbor Al's are free to move, it is not motivated by strengthening the interaction between the S and the subsurface Al. On the contrary, comparing the two panels of Fig. 1, one sees that the charge-density minimum between the S and the subsurface Al deepens as the S moves into the slab. At the same time the relaxation diminishes the strength of the bond between the nearest surface and subsurface Al's, while the bond between the nearest surface Al and the second-nearest subsurface Al gets stronger. Relaxation of the nearest-neighbor Al's thus depletes charge between the S and the surface in the neighborhood of the surface normal and increases it in the vicinity of the lines joining the S and its nearest neighbors.

Figure 2, representing a cut in the plane of the S-adatom's nearest-neighbor Al's, tells a similar story. As the inset shows, the surface normal through the S passes through the upper right-hand corner of the plot. At this point the charge density is at a relative maximum in the plane of the figure. That this maximum is reduced in the relaxed adsorption geometry is indicated by the fact that the contour labeled 0.026 is reached sooner, moving down along the diagonal, than in the case of the ideal geometry. At the same time, the local lattice relaxation strengthens and shortens the (shaded) bond between the first- and second-neighbor Al's in the surface plane.

These results are consistent with Needs's calculations[7] showing Al surfaces to be under tensile stress. The adsorbates studied weaken the bonds between their nearest neighbors. As a consequence, bonds between the adatoms' first and second neighbors in the surface plane strengthen and shorten, the adatom is pulled toward the surface, and presumably,[1] the adatom absorption barrier is reduced. It is of great interest to know if this scenario is a general one, and moreover, to know whether surface stress plays a comparable role in surface diffusion barriers,[10] adsorbate interactions,[16] and other key energies underlying surface chemical phenomena. If the nature of the surface stress at clean surfaces is widely predictive of adsorbate energetics, one will have made an important stride toward the goal of tailoring surfaces for desired applications.

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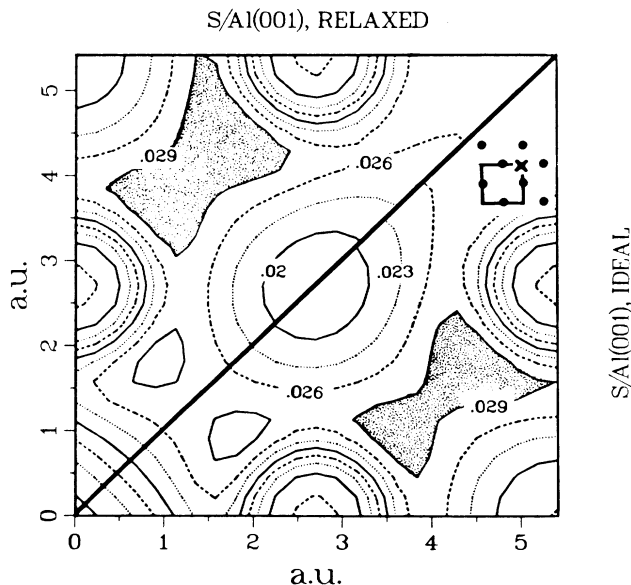[1]M. Limbäck and U. Yxklinten, "Calculations on the Initial

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[16]See, e.g., P. R. Schwoebel, S. M. Foiles, C. L. Bisson, and G. L. Kellogg (to be published), for evidence that local lattice relaxation is important in determining the shapes of Pt clusters on Pt(001).