

Interaction between adsorbed chalcogen and Al atoms on Al(001)

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First-principles, scattering-theory-based calculations for Al-S and Al-Te dimers adsorbed on a rigid Al(001) film show in both cases that the ad-Al and the chalcogen repel each other when forced to reside in neighboring hollows. This result, which stems from the fact that the through-metal effective repulsion is not compensated by a sufficiently attractive direct adatom interaction, indicates the importance of establishing whether there are any laws governing the nature of the interactions between surface additive atoms and various types of surface defects.

I. INTRODUCTION

A common observation in surface chemistry is that the presence of a small number of adsorbed "modifier" atoms drastically affects chemical activity.¹ Such an effect could be the result of modifier atoms migrating to and blocking the "defect sites" where chemical activity is concentrated.² This idea is plausible—defects are characterized by relatively low coordination numbers and therefore by unsaturated valence. These structural and electronic properties suggest (1) attractiveness to "modifiers" and "reactants," and (2) enhanced chemical activity.

There are, of course, many "structure-insensitive reactions" for which defects and thus the poisoning of defects are not important. For example, Goodman and collaborators have recently shown that S poisoning of CO methanation on Ni is explained by phenomena that have no relation to defect-site blocking.^{1,3} The effect of S in this reaction is the consequence of relatively long-ranged electronic perturbations of the surface. The evidence that defects are not important is that the methanation reaction on a per-surface-Ni-atom basis is as fast on a single-crystal surface, which has few defects, as on a highly dispersed "real-world" catalyst, which is essentially all defects.

In what follows, I take up part (1) of the plausibility argument: Regardless of whether the chemical activity of a surface is confined to defects, is it generally true that modifier atoms migrate to whatever defects are present? I make use of a new theoretical tool, the first-principles scattering theory of adsorption energies,⁴ to investigate whether a particular class of modifier atoms is attracted to a particular kind of defect. Specifically, I study the interaction between adsorbed chalcogen atoms and a defect comprised of a single self-adsorbed Al atom on the Al(001) surface. This work is obviously only the first step in an effort intended to yield a set of rules that tell what species of adatoms migrate to what sorts of defects on surfaces of interest. The reason for studying Al(001) is not that it is a "surface of interest," at least from the surface-chemistry viewpoint. Rather, it is that Al is a simple metal and therefore a good one for a baseline calculation using a new theoretical approach. However, the results of the calculation have fascinating implications:

Both adsorbed S-Al and Te-Al pairs on Al(001) are predicted to interact repulsively if the atoms of the pair are forced to reside in nearest-neighbor hollows. Despite the fact that an ad-Al is coordinated to only four nearest neighbors, while outer-surface-layer Al atoms have eight, the calculations indicate that it costs 0.25 eV to bring a S atom from a distant fourfold hollow to a hollow adjacent to an ad-Al. For a Te adatom the cost is 0.22 eV. (These numbers emerge from calculations in which substrate-atom positions are fixed. Relaxation of these positions in the presence of the adatoms might reduce the net repulsion somewhat.)

There are situations in which one would expect adatoms in adjacent hollows to repel. (1) If the sum of the radii of covalently adsorbed atoms is larger than the distance between the hollow sites, exchange repulsion pushes the adatoms apart. This should be the case for a pair of Pb atoms on Al(001). The Pauling electronegativities of Pb and Al are 1.8 and 1.5, respectively,⁵ suggesting covalent adsorption, while Pb atoms are significantly larger than Al atoms. (2) If two similar adatoms are adsorbed ionically, they repel electrostatically. This would be expected to happen, e.g., for two Na atoms (electronegativity 0.9) on an Al surface. Each Na⁺ together with its image gives rise to a dipole field that repels the dipole of its neighbor.

S-Al and Te-Al pairs fit neither of these descriptions. Judging from the positions at which I find isolated S, Te, and Al atoms to adsorb, there is no impediment to bonding of S, Te, and Al atoms at distances of 4.79, 5.32, and 5.09 bohrs from (their substrate) Al nearest neighbors. Comparing these bond lengths to the minimum distance between nearest-neighbor fourfold-hollow sites on Al(001), 5.42 bohrs, one sees that the overlap of filled shells is not the reason for the S-Al or Te-Al repulsion. At the same time, two facts imply that the ad-Al is covalently adsorbed: (1) that the adsorbed and substrate Al atoms obviously have the same electronegativity, and (2) that the covalent radius of Al, 2.38 bohrs, equals the effective radius of the ad-Al. Therefore dipole-dipole electrostatic repulsion between the screened chalcogen atom and the screened ad-Al is eliminated from consideration.⁶

An alternate and more plausible explanation of the

repulsion found for Al-chalcogen dimers follows from a consideration of recent total-energy calculations for an Al-Al dimer on Al(001).⁷ In qualitative agreement with field-ion-microscope observations for various examples of metal-dimer adsorption,⁸ these calculations show that the energy to separate an ad-Al dimer is small, only about $\frac{1}{8}$ the cohesion per bond of bulk Al. The explanation of this striking fact is that dimer separation involves the *compensation* of two energies. The energetic price of rupturing the direct ad-Al—ad-Al bond is almost entirely regained in strengthening the individual ad-Al bonds to the surface. One indication that this is true is that the adsorbed dimer sits considerably higher (0.3 bohr) off the surface than either ad-Al does when isolated.

The fact that the bonds between the ad-Al atoms and the surface weaken as the dimer bond forms is not surprising. Charge neutrality limits the number of valence electrons in the neighborhood of each Al to three. Therefore valence electrons from each ad-Al that go into the direct dimer bond must come out of Al-surface bonds, weakening them. This is a standard argument explaining “bond-order–bond-length” correlations. However, it does not address the interesting issue, namely, *why* it is preferable to form the dimer bond and weaken the bonding to the surface. The reason is that two adatoms in adjacent hollows have a pair of nearest-neighbor surface atoms in common, and must compete for valence electrons from this pair (see Fig. 1, in which the adsorption geometry is illustrated). Because of this

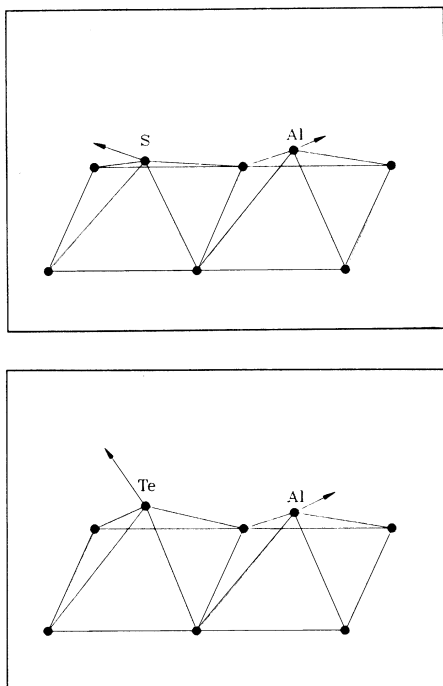


FIG. 1. Diagrams indicating relative locations and forces on S-Al and Te-Al dimers adsorbed on Al(001). Each adatom is at the height above the surface where it would reside if isolated from its partner. Arrows indicate relative directions and magnitudes of calculated forces for the dimer geometries shown.

competition, neither adatom can bond as effectively to the shared surface atoms as it could if the other adatom were absent. The result is that when two adatoms are forced to reside in neighboring hollows, each must solve an optimization problem—how best to rehybridize its valence electrons as a result of not being able to bond as strongly to the two substrate-Al neighbors that it must share with the other adatom. In the case of the adsorbed Al dimer, the optimization problem is solved by forming a direct dimer bond. In the case of the chalcogen-Al dimers, because of atomic size as well as valency differences, the optimization problem is solved differently, and evidently not quite as well. Thus instead of the weak attraction found in the case of the Al dimer, there is a weak repulsion instead. Of course, this repulsion is not weak on the scale of room temperature, 25 meV. Thus the implications for chemistry are significant.

The rest of this article is organized as follows. In Sec. II, I review the formalism of the scattering theory of adsorption, which was used to obtain numerical, first-principles results for adatom binding energies and forces. In Sec. III the specifics of the numerical calculations are reported. Section IV is a presentation and discussion of the results calculated for the S+Al/Al(001) and Te+Al/Al(001) systems.

II. FORMALISM

The results reported here were obtained using the “matrix Green’s-function” formulation of the recently developed first-principles scattering theory of adsorption energetics.⁴ This method of solving the local-density-functional (LDF) electronic-structure variational problem⁹ makes it possible to study situations in which a spatially compact adsorbate, i.e., an adatom or several of them not far from one another, resides on an otherwise perfect crystalline surface. Details of the method have been published in Refs. 4. Briefly, the idea is to make use of the fact that the adsorbate-induced potential is screened to zero within an atomic distance or two of the adatoms. As a result, the one-electron wave functions of the adsorption problem are Bloch waves incident from the unperturbed region of the solid and scattered off the adsorbate-induced potential. One takes advantage of the localization of the adatom potential due to screening, by representing the wave functions as linear combinations of a set of localized orbitals, $\{\phi_i(\mathbf{r})\}$. In such a representation, the Euler-Lagrange equation for the minimization of the LDF energy can be cast as a self-consistent matrix scattering equation in which the potential responsible for the scattering has only a finite number of non-negligible matrix elements, those involving orbitals that overlap the adsorbate potential appreciably. As a result, the scattering problem involves the solution of a *finite* number of simultaneous linear equations. With a good choice of orbital basis, this number is roughly the number of orbitals on the adatoms and on two or three shells of neighbors. The unknown in the scattering-theory matrix problem is the one-electron Green’s function, $G_{ij}(\mathbf{Z})$, defined by

$$\sum_k (\mathbf{Z}S_{ik} - H_{ik})G_{kj}(\mathbf{Z}) = \delta_{ij}, \quad (1)$$

where H_{ik} and S_{ik} are the one-electron Hamiltonian and the overlap matrices in the localized-basis representation, δ_{ij} is the Kronecker delta, and Z is a complex number with the dimensions of energy. Because the one-electron Hamiltonian matrix H_{ik} depends on the electron charge density $n(\mathbf{r})$ through the exchange-correlation potential of the LDF theory, $G_{kj}(Z)$ must be determined self-consistently. Specifically, the $n(\mathbf{r})$ used to determine H_{ik} must agree with that which is calculated via the formula

$$n(\mathbf{r}) = \sum_{i,j} \rho_{ij} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}), \quad (2)$$

where ρ_{ij} is the one-electron density matrix obtained by integrating $G_{ij}(Z)$ on a contour in the Z plane that surrounds the electron levels that lie below the Fermi energy. This self-consistency problem is solved by a conventional iterative relaxation scheme.¹⁰ Once input and output charge densities agree to a fine enough tolerance, observables of interest can be calculated from the self-consistent ρ_{ij} . These generally include the energy change produced by adsorption and the forces on the nuclei in the problem. Knowledge of the forces facilitates the discovery of an adsorption geometry in which the forces vanish and the binding energy is maximized. In principle, not only the positions of the adatoms but also those of the neighboring substrate atoms should be relaxed. However, in the present work this has not been done. Studies of the contribution of local lattice relaxation to adsorption energies are in progress.

III. SPECIFICS OF THE NUMERICAL CALCULATIONS

As noted above, the scattering-theory method is founded on the use of the local-density-functional description of exchange and correlation.⁹ The results reported here were obtained using the local exchange-correlation potential parametrized by Perdew and Zunger¹¹ (PZ) on the basis of electron-gas simulations of Ceperley and Alder.¹² The effects of atomic cores were represented via the norm-conserving pseudopotentials, described by Bachelet *et al.*,¹³ whose numerical values were derived using the PZ exchange-correlation potential.

It is particularly important to choose a local basis set carefully in the scattering theory of adsorption. An obvious reason is that computational expense grows rapidly with the size of the matrix of scattering equations that must be solved. Thus orbitals are chosen to be as short ranged as possible. A less obvious reason is that a scattering-theory calculation of adsorbate electronic structure actually represents the difference between two variational problems and thus does not benefit from the usual quadratic convergence property of variational methods. In particular, if the zeroth-order description of the clean surface has insufficient variational flexibility, then the clean-surface charge density will not be fully relaxed and will make use of adsorbate orbitals to relax further. In this case what appears to be a calculated heat of adsorption will include a measure of clean-surface relaxation energy, and will be systematically too large. Improving the basis in the adsorbate problem will not improve

this situation.

The orbital basis that I use to describe the electronic structure of the substrate in the present work, a five-layer Al(001) film, includes s -, p -, and d -like radial functions, one of each, centered on each Al nuclear site (see Table I). The s - and p -like functions are linear combinations of Gaussian ("Gaussian contractions") chosen to fit the $3s$ and $3p$ pseudo-wave-functions of an isolated Al atom from the nucleus out to a distance of 3.5 bohrs. Because of this fit, little variational flexibility is wasted in reproducing near-nucleus wave-function behavior in calculations involving an Al crystal. By restricting the attenuation constants of the Gaussians in the linear combinations to equal 0.18 bohr^{-2} or greater, I make the range of the basis orbitals short enough that the adsorbate-induced-potential matrices do not have to be impossibly large. I take the radial d functions to be of the form $r^2 \exp(-0.18r^2)$, where r is expressed in bohrs. Their inclusion is necessary in order to obtain an accurate representation of the Al wave functions at point \bar{M} in the surface Brillouin zone (SBZ), which have significant d -like components.

In addition to Al-nucleus-centered functions, the basis includes floating orbitals in the vacuum: p -like orbitals of the form $r \exp(-0.19r^2)$ atop the Al surface atoms and s -orbitals proportional to $\exp(-0.19r^2)$ above the four-fold hollows, both at a height of 3.5 bohrs above the outer-layer Al nuclei. These floating orbitals provide the flexibility necessary to describe electron spillout into the vacuum and the smoothing of charge-density corrugations associated with the Smoluchowski effect.¹⁴

The adequacy of this orbital basis was verified by a series of calculations involving a clean five-layer Al(001) slab. Specifically, as reported in a series of earlier articles,¹⁵⁻¹⁷ I showed the following.

(1) That the linear combination of atomic orbitals (LCAO) work function and one-electron energy-level dispersions over the entire SBZ agree to no worse than 0.15 eV with corresponding results from a highly converged and completely independent linearized-augmented-plane-wave (LAPW) calculation^{15,16} for the same five-layer Al(001) film.

(2) That the LCAO equilibrium separation of the outer two layers of the five-layer Al(001) film is close to ideal [actually it is contracted by about 0.3% (Ref. 15)], in agreement with the LAPW calculation,¹⁶ and with experiment.¹⁸

(3) That scattering-theory-based calculations of restoring forces on surface-layer Al atoms displaced from their equilibrium positions¹⁷ agree with expectations based on conventional, well-converged, force-constant calculations for periodic displacements of surface-layer atoms.¹⁹

I use the same Al-centered basis orbitals for the adsorbed Al atom as for the Al atoms of the substrate. In addition, I include a set of floating p orbitals centered 2.75 bohrs above the ad-Al. The ad-S or ad-Te atom is represented by two s -, two p -, and one d -radial functions. As in the case of Al, the valence s and p orbitals of S are chosen by fitting contractions of Gaussians to the valence pseudo-wave-functions of an isolated S or Te atom from the nucleus out to a distance of 3.5 bohrs. The additional

TABLE I. Coefficients c and attenuation constants α (in bohr⁻²) for the contractions of Gaussians used to represent the orbitals of Al, S, and Te atoms. The values correspond to radial functions $R_l = r^l \sum_{\alpha} c_{\alpha} \exp(-\alpha r^2)$ normalized to $4\pi/(2l+1)$, where l is the orbital-angular-momentum quantum number. The superscripts of the c 's for the S and Te atoms correspond to the two different s functions and the two different p functions that were included in the basis for these atoms.

Al-centered radial functions							
α_s	c_s		α_p	c_p		α_d	c_d
0.18	1.999 218 6		0.19	1.102 230 2		0.18	0.129 794 5
0.25	-2.203 909 3		0.25	-1.483 388 0			
0.44	1.230 277 1		0.40	1.043 053 0			
1.05	-2.047 651 3		0.60	-0.401 933 9			
1.40	1.183 289 2						
S-centered radial functions							
α_s	$c_s^{(1)}$	$c_s^{(2)}$	α_p	$c_p^{(1)}$	$c_p^{(2)}$	α_d	c_d
0.222	0.723 620 4	-1.169 659 3	0.178	0.222 194 8	0.391 643 1	0.18	0.129 794 5
0.850	1.261 773 2	0.695 921 7	0.590	0.670 439 2	-1.953 506 1		
1.550	-2.129 715 4	-5.795 953 4	2.400	-0.175 817 9	0.512 292 9		
3.800	0.416 885 4	1.134 541 4					
Te-centered radial functions							
α_s	$c_s^{(1)}$	$c_s^{(2)}$	α_p	$c_p^{(1)}$	$c_p^{(2)}$	α_d	c_d
0.165	0.613 503 4	0.249 445 9	0.160	0.259 342 1	0.378 033 2	0.19	0.145 470 1
0.590	1.301 850 5	-5.594 168 6	0.530	0.379 136 5	-3.842 119 4	0.65	-0.149 147 0
1.030	-3.113 691 2	13.379 811 0	1.150	-0.899 270 0	9.113 083 4	1.00	0.344 421 5
1.660	1.290 211 8	-5.544 156 2	1.700	0.442 406 5	-4.483 289 2		

s and p functions are obtained by orthogonalizing the longest-ranged Gaussian in each valence function to that valence function. The d -like radial function for S is taken to be of the form $r^2 \exp(-0.18r^2)$, as for Al, while that for Te is a Gaussian contraction fitted to the Te-ion d -like pseudo-wave-function used in obtaining the Te d -like pseudopotential. A list of the orbital coefficients and attenuation constants for the S, Te, and Al orbitals is given in Table I.

Because the minimum Gaussian attenuation constant in any orbital of the basis was 0.18 bohr⁻², orbitals farther than two Al lattice spacings from an adatom could be presumed not to overlap the adsorbate-induced potential. This presumption leads to a 392×392 scattering-theory matrix problem when both S and Al atoms are on the surface. This is not a small matrix problem, but it is tractable on modern supercomputers.

A previous article outlined a method by which electrostatic matrix elements and energies can be calculated accurately even when the pseudo-charge-density near certain nuclei varies rapidly.²⁰ This method was used in the present calculations to treat the electrostatic contributions from the neighborhood of the adsorbed S. Integrals involving the slowly varying components of the one-electron potential were performed on an equally spaced mesh with points roughly 0.6 bohr apart.

Integrals of the Green's function with respect to the complex parameter Z were performed numerically by sampling 40 points in the upper half- Z -plane. These include 24 points on the line between E_F and $E_F + i2.72$ eV and 16 points on the circle that intersects $E_F - 27.2$ eV and $E_F + i2.72$ eV, where E_F is the Fermi energy.

Surface-brillouin-zone integrals, which are necessary both in the self-consistent calculation of the properties of the clean Al film, as well as to convert from the k -space description appropriate to the clean film to the coordinate-space representation appropriate to the impurity problem, were performed via a sample of 21 equally spaced k vectors in the irreducible $\frac{1}{8}$ of the Al(001) SBZ.

IV. RESULTS AND DISCUSSION

As a reference for calculations of an adsorbed Al-chalcogen dimer, it is necessary to consider the adsorption of the Al and of the chalcogen atoms separately on the five-layer Al(001) substrate. Previous experience⁴ suggests that an Al adatom will sit in a fourfold symmetry position, roughly 3.35 bohrs above the outer Al layer. I carried out a calculation adopting this adsorption geometry, with the following results: The force on the adsorbed Al is along the surface normal and equals 0.023 eV/bohr toward the surface. Judging from previous force-constant calculations,¹⁶ this means that the height above the surface where the force vanishes and the ad-Al is in equilibrium is only 0.01–0.02 bohr closer, i.e., the initial guess for the ad-Al geometry was a good one. The binding energy of the ad-Al is calculated to be 3.09 eV.²¹

For the adsorbed S atom two fourfold-hollow-site geometries were considered, corresponding to S heights above the outer Al layer of 2.75 and 3.00 bohrs. The calculated forces along the surface normal in these cases

were 0.253 eV/bohr away from the surface and 0.279 eV/bohr toward the surface, respectively. Assuming the force to vary linearly between the two heights, this implies that at equilibrium the ad-S sits 2.87 bohrs above the surface. Its binding energy is calculated to equal 4.90 eV.²¹ Finally, for the adsorbed Te, calculations corresponding to heights of 3.55 and 3.75 bohrs above the surface yielded forces of 0.316 eV/bohr away and 0.131 eV/bohr toward the surface. Thus the Te atom resides at a height of 3.69 bohrs above the outer Al plane. Its binding energy is found to be 3.82 eV.²¹

To see whether an ad-Al and an ad-S attract or repel each other, I place these atoms in neighboring fourfold-hollow sites at the heights where they would reside if they were far apart. Thus taking the origin at a fourfold-hollow site in the outer Al(001) plane, I place the S nucleus at (0.0,0.0,2.87) bohrs and the nucleus of the ad-Al at (5.42,0.0,3.35) bohrs. The following results then emerge from a self-consistent scattering-theory calculation: The binding energy of the dimer to the Al(001) substrate is 0.30 eV less than if the Al and the S were adsorbed at sites far from one another. The force on the ad-S equals (-0.19,0.0,0.09) eV/bohr, while that on the ad-Al is (0.12,0.0,0.07) eV/bohr. These results indicate that the net interaction between the adatoms is repulsive; more specifically, that each adatom would prefer to move away from the bridge adjacent to its partner, away from the surface, and towards the bridge on the opposite side of its hollow (see Fig. 1). An obvious interpretation of this preference is that the bonding of each adatom to the pair of substrate Al atoms between them is weakened by the fact that these same substrate atoms must bond to its partner. The S atom is apparently unable to compensate for this by forming a strong direct bond with the ad-Al. Therefore the net adatom-adatom interaction is repulsive, and the adatoms move toward the bridges on the opposite sides of their respective hollows, where they do not have to compete with each other for substrate valence electrons. A second calculation in which the S and Al atoms have been moved to (-0.14,0.0,2.93) and (0.09,0.0,3.40) bohrs, respectively, results in a repulsion energy of 0.26 eV and forces on the S and Al atoms of (-0.05,0.0,0.8) and (0.02,0.0,0.0) eV/bohr, respectively. Assuming that the decrease in repulsion energy is proportional to the reduction in the square of the magnitude of the residual forces, one can expect that further relaxation of the ad-Al and S nuclear positions within the adjacent hollows will lead to a metastable S-Al dimer repulsion energy of roughly 0.25 eV.

Two factors must be considered in interpreting the repulsive interaction between adsorbed S and Al adatoms, in contrast to the attraction found earlier for two ad-Al atoms: (1) that the valence of S atoms is 2, while that of the Al atoms is 3, and (2) that S atoms are smaller than Al atoms (depending, of course, on charge states). The fact that S has a valence of 2 suggests that when the S atoms bonds to the common pair of surface atoms are weakened by the presence of an adatom neighbor the S can satisfy its valence requirements simply by moving toward its other pair of surface-atom nearest neighbors, thereby strengthening its bonds to them. In contrast, an

ad-Al, having a valence of 3, moves toward its adatom neighbor, so that in addition to strong bonds to its two unshared surface atom neighbors, it can form a third strong bond at the same time. The atomic-size interpretation of the S-Al effective repulsion is that since the S atom is small, as evidenced by the fact that it sit 0.5 bohr closer to the surface than an ad-Al, it cannot simultaneously form strong bonds to a neighboring ad-Al and to the pair of surface atoms not shared with this neighbor.

By performing calculations for a Te-Al ad-dimer, since Te atoms are as large or larger than Al atoms, the atomic-size interpretation can be evaluated. In particular, if the Te is thought of as a "large S," then the size argument implies that a Te-Al dimer should interact attractively. As in the S-Al case, I determine the nature of the Te-Al interaction by placing Te and Al nuclei in neighboring fourfold-hollow sites at the heights they would adopt if isolated from each other. Thus I place Te and Al adatoms at (0,0,0,3.69) and (5.42,0.0,3.35) bohrs, respectively. In this configuration I find that the total energy of the system is repulsive by 0.27 eV relative to that of isolated adatoms, while the forces on the Te and Al equal (-0.15,0.0,0.29) and (0.15,0.0,0.10) eV/bohr (see Fig. 1). These results show that, again, atomic-size effects notwithstanding, the chalcogen and the ad-Al repel one another. The fact that both atoms are repelled from the surface suggests that the source of the effective repulsion is again the weakening of the bonds between the adatoms and the pair of surface-atom neighbors that are shared. The conclusion is, therefore, that although chalcogen-size effects may be important regarding the details of the repulsive forces, the dominant cause of the different interactions of chalcogen-Al and Al-Al ad-dimers is related to valency. Relaxing the positions of the Te and ad-Al nuclei, respectively, to (-0.11,0.0,3.90) and (0.11,0.0,3.42) bohrs, the forces on the Te and ad-Al become (0.0,0.0,-0.12) and (-0.07,0.0,-0.04) eV/bohr, with a corresponding repulsion energy of 0.23 eV relative to large separation. Assuming that this energy lowering is proportional to the reduction in the square of the magnitude of the residual forces, one can expect that further relaxation of the ad-Al and Te nuclear positions within the adjacent hollows will lead to a metastable Te-Al dimer repulsion energy of 0.22 eV. The fact that this repulsion is weaker than that for the metastable S-Al dimer is not surprising given that the Te bonds to Al(001) start out weaker than those of S.

The most important lesson of the work reported here is the understanding that since the separation energy of two neighboring adatoms is typically a small difference of large numbers, i.e., the energy losses associated with the weakening of some adatom-surface bonds and the energy gains attendant on the formation of the adatom-adatom bond and on the strengthening of other adatom-surface bonds, it is not trivial to predict whether the dimer interaction will be strong or weak or even whether it will be attractive or repulsive. As a consequence, one must be skeptical of the idea that surface impurity atoms should *generally* be expected to migrate to a defect—laws governing impurity-defect interaction need to be determined.

In this regard it should be noted that the present results are not the last word even for chalcogen-Al interactions on Al(001), because they do not include the effects of substrate-nucleus positional relaxation. The absence of these effects implies that both the isolated adatom and dimer binding energies calculated here are somewhat too high. How much too high is a matter of great interest, as is the consequent effect of including local lattice relaxa-

tions on the nature of the interadatom interaction. These issues are a focus of ongoing work.

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- ¹D. W. Goodman and M. Kiskinova, *Surf. Sci.* **105**, L265 (1981).
²The defect-controlled behavior of NO/Pt is a particularly well documented case. See J. A. Serri, M. J. Cardillo, and J. C. Tully, *J. Chem. Phys.* **79**, 1530 (1983).
³See D. W. Goodman, R. D. Kelley, T. E. Madey, and J. T. Yates, Jr., *J. Catal.* **63**, 226 (1980), Fig. 9.
⁴P. J. Feibelman, *Phys. Rev. B* **35**, 2626 (1987); A. R. Williams, P. J. Feibelman, and N. D. Lang, *ibid.* **26**, 5433 (1982).
⁵L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, 1960).
⁶The Pauling electronegativities of Al, S, and Te are, cf. Ref. 5, 1.5, 2.5, and 2.1. This implies that neither S nor the Te will be adsorbed via a strongly ionic bond. The charge transfer to the S, to the extent that such a quantity can be defined, will be larger than that to the Te. However, the S resides 0.82 bohr closer to the image plane than the Te does. Thus neither chalcogen adsorbate should be expected to give rise to a large dipole moment.
⁷P. J. Feibelman, *Phys. Rev. Lett.* **58**, 2766 (1987).
⁸T. T. Tsong and R. Casanova, *Phys. Rev. B* **24**, 3063 (1981); R. Casanova and T. T. Tsong, *ibid.* **22**, 5590 (1980); D. Bassett, *Surf. Sci.* **53**, 74 (1975); H. W. Fink and G. Ehrlich, *J. Phys. F* **4**, L212 (1974).
⁹*The Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).
¹⁰I use the second method of C. G. Broyden, *Math. Comput.* **19**, 577 (1965), as implemented by G. P. Srivastava, *J. Phys. A* **17**, L317 (1984).
¹¹J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
¹²D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
¹³G. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
¹⁴R. Smoluchowski, *Phys. Rev.* **60**, 661 (1941).
¹⁵P. J. Feibelman, *Phys. Rev. B* **38**, 1849 (1988).
¹⁶P. J. Feibelman and D. R. Hamann (unpublished).
¹⁷P. J. Feibelman, *Phys. Rev. B* **38**, 7287 (1988).
¹⁸M. van Hove, S. Y. Tong, and N. Stoner, *Surf. Sci.* **54**, 259 (1976); Groupe d'Etudes de Surface, *ibid.* **62**, 567 (1977); N. Masud, R. Baudoing, D. Aberdam, and C. Gaubert, *ibid.* **133**, 580 (1983); P. E. Viljoen, B. J. Wessels, G. L. P. Berning, and J. P. Roux, *J. Vac. Sci. Technol.* **20**, 204 (1982).
¹⁹K. M. Ho and K.-P. Bohnen (unpublished).
²⁰P. J. Feibelman, *J. Chem. Phys.* **81**, 5864 (1984).
²¹Binding energies were obtained by reference to isolated atom calculations using the spin-polarized, local-density-functional approach. For each adatom species, such a calculation was carried out, yielding a value of the total valence-electron energy of the isolated atom. (The computer code for these calculations was kindly provided by D. R. Hamann.)