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A LOCAL VIEW OF BONDING AND DIFFUSION AT METAL SURFACES

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ABSTRACT

First-principles density functional calculations and corresponding experimental results underline the importance of basic chemical concepts, such as coordination, valence saturation and promotion-hybridization energetics, in understanding bonding and diffusion of atoms at and on metal surfaces. Several examples are reviewed, including outer-layer relaxations of clean hcp(0001) surfaces, liquid-metal-embrittlement energetics, separation energies of metal-adatom dimers, concerted substitutional self-diffusion on fcc(001) surfaces, and adsorption and diffusion barrier sites for adatoms near steps.

INTRODUCTION

Controlling the growth of thin films, for the sake of synthesizing "nanostructured" materials, and governing the relative rates at which surface chemical reactions proceed, to increase the yield of desired products, are two of the most important aims of surface science. Transport of atoms along a surface is a basic process in both cases. The rate at which adsorbed atoms diffuse on flat terraces affects the probability that they will find each other and nucleate a growth island, or that they will find and stick to a defect. The mechanism by which they diffuse determines whether the adatoms will stay on top of a surface or integrate themselves into it, an issue that is particularly

important in hetero-epitaxy. The chance that an atom arriving at a surface step will traverse it, determines whether growth will be "ideal", i.e. layer-by-layer, or whether 3-dimensional adsorbed clusters will nucleate.

Because it is fundamental to the outcomes of important surface processes, we want to develop a realistic, atomic-scale view of how surface diffusion works. From the theoretical perspective, to the extent that the Born-Oppenheimer approximation is valid, two developments are needed. One needs to know *what* forces are responsible for surface atom motion, and *how* they cause a given distribution of surface atoms to evolve in time. Most theoretical diffusion studies in the literature, based on molecular dynamics solutions of Newton's equations of motion or on Monte-Carlo simulations, focus on the second problem. Nonetheless, although the development of such simulation methods is vital to a complete understanding of the time evolution of surfaces, the reliability of their results is necessarily limited by the realism of the force laws that are used. For this reason it is important not to let our knowledge of the forces between surface atoms lag too far behind our ability to perform simulations. This thought is the motivation for the present review. The goal is a qualitative understanding of the forces that drive surface diffusion, one that is reliable by virtue of being based on "first principles" calculations.

Surface science lies at a crossroads of condensed matter physics and physical chemistry. Many surface phenomena of interest, diffusion certainly among them, involve the breaking and formation of interatomic bonds. This places the concerns of surface science squarely in the domain of physical chemistry. Nevertheless, because surface scientists are generally interested in samples large enough to make the distinction between "surface" and "bulk" meaningful, from clusters of hundreds of atoms up to solids comprised of 10^{23}, the physicist's perspective, based on translational periodicity and densities of closely-spaced electronic levels, would seem to be the appropriate starting point for a theory of the forces that determine surface atoms' behavior. These lectures are aimed at overcoming the sense that there is a discrepancy between the techniques appropriate for large, crystalline systems and the language that chemists use to describe interesting surface phenomena. The venue for the discussion is therefore not just surface diffusion, the focus of this workshop, but more generally, the potentials and forces that govern both the kinetic and the thermodynamic preferences of surface atoms.

The work I review is based on first-principles Local Density Approximation (LDA) calculations,[1-3] and focused on interpreting several unexpected results. These include the unusual outer layer relaxations of various hcp metals' close-packed surfaces,[4-8] the elemental dependence of liquid metal embrittlement,[9] the surprisingly low energy required to separate metal-adatom dimers on metals,[10] the unanticipated, substitutional-diffusion mode of metal adatoms on certain metal surfaces[11,12], and finally, the binding sites preferred by adatoms on vicinal surfaces.[13-15] I begin with some general remarks on why it is important to apply first-principles methods, even though they are costly, and on the meaning of the term "first-principles."

THEORETICAL METHODS

Semi-empirical calculations

Surface science generally involves atoms in unsymmetrical, highly anisotropic environments. Guessing the nature of the bonds that are relevant to any particular surface phenomenon therefore takes more than a little self-confidence. Warranted or not, such confidence, does seem to be widespread -- the force laws typically used to simulate surface phenomena are computationally fast, and therefore useful, precisely because they derive from *a priori*, restrictive assumptions about the nature of bonding. In the *Embedded Atom Method* (EAM),[16] and *Effective Medium Theory* (EMT),[17] directional (covalent) bonding is either ignored completely or is incorporated via a crude approximation.[18] In tight-binding based energetics, the well-known correlation between coordination and bond strength[19] is typically absent. Semi-empirical schemes generally do not allow for charge transfer and the corresponding electrostatic forces.

First-principles calculations

This is not to say that the "first-principles" or *ab initio* methods used to treat surface problems, despite the self-congratulatory Latin, ever start from, or even approach solutions of the many-electron Schrödinger equation. The cost of methods that do, e.g., configuration interaction (CI) calculations, scales up unacceptably quickly with system size.[20] Thus, even in an age of "massively parallel" computers, and among quantum chemists with a characteristic devotion to high accuracy, CI calculations now give way to Density Functional (DF) methods;[1] they are not systematically improvable, but of reasonable accuracy[21] and enormously improved scaling.[22] The winning argument for DF methods is that even the most accurate computation for a surface represented by a small molecule is likely to be less reliable than the result of applying a decent approximation directly to the extended geometry of interest.

Though not "virtually exact," DF optimizations are *ab initio* in the modest but important sense that the DF variational equations are free to determine the nature of the bonds corresponding to a particular arrangement of atoms, independent of the theorist's preconceptions. If the DF energy is lowest with directional bonds, then they will be so. If there is charge transfer, the corresponding energy is included in the variational equations, and so forth.

Numerical methods

Until recently, all DF calculations have been based on a functional that relates the exchange-correlation energy density at any point in space to the electron density at the same point, so called Local Density Approximation (LDA) calculations.[1] It is their success, over many years, that has given confidence in the reliability of DFT as a tool for predicting molecular, surface and bulk, crystalline structure, and for illuminating observed bonding trends.[23] LDA calculations of phonon spectra[24] and of diffusion barriers,[25] i.e., of non-equilibrium phenomena, suggest that the potentials that describe the kinetics of extended systems might also be qualitatively reasonable in LDA. All results presented below are LDA-based.

This said, it is important to note that the interest of the chemistry community in DFT methods stems not from a sudden, new appreciation of LDA, but of a recent improvement called Generalized Gradient Approximations (GGA's).[26] The GGA version of DFT is based on using an exchange-correlation functional that depends not just on the local electron density, but also on its local derivative. As do LDA xc-potentials, GGA functionals come in various "flavors." (The least empirical of these is due to Perdew and Wang.[26]) Atomization energies of small molecules calculated using a GGA are often an order of magnitude closer to experiment, and often within "chemical accuracy" of a couple of kcal/mol of experiment.[21] The systematic reliability of these methods is less well established than that of LDA, and more in doubt when it comes to solids.[27] No GGA-based results are discussed here. But evaluating the performance of this new version of

DFT in the context of surface-atom potential energy surfaces is on many surface-scientists' near-term agendas.

In the work I discuss, several types of numerical basis have been employed. It is important to understand, however, that the basis set that one uses to solve a variational problem, assuming it embodies enough freedom to arrive at a converged answer, has no influence on the results or on their interpretation. Thus the fact that one uses plane waves as a basis set for the study of a surface atom arrangement, as against localized, atom-centered orbitals, does not preclude analysis via an angular-momentum decomposition of the wave functions in a sphere surrounding a particular nucleus, with "chemical-type" conclusions. The necessary overlap of the localized orbitals makes the usual Mullikan population analysis in a local-basis set calculation just as model-dependent, or independent, as the choice of projection sphere size does in the plane-wave case.

Several of the results discussed (notably the exchange-diffusion barriers) were obtained using an unusual, "scattering-theory" or Green's function approach to LDA that makes it possible to evaluate the energy of an *isolated* adatom (or cluster of them) on an otherwise perfectly periodic surface.[3] This elegant approach to surface "defect" problems is, unfortunately, rather slow as implemented, and requires writing and maintaining a rather complex computer code. The method has therefore never been widely used, and seems to be passing from the scene.

The O/stepped-Pt(111) calculations described below were performed using QUEST, a Linear Combination of Atomic Orbitals (LCAO) implementation of LDA designed to run efficiently on a massively parallel computer. With this code, on 1024 processors of an Intel Paragon, one can routinely investigate the geometries of unit cells involving 50 - 100 Pt or Ir atoms, plus adsorbed O's.[28]

A QUALITATIVE PICTURE OF BONDING AT SURFACES? -

Chemistry is the science of breaking and forming interatomic bonds. According to this definition, more of surface science is a branch of chemistry than one is typically trained to think. Cleaving a crystal to expose a perfect surface self-evidently involves the breaking of interatomic bonds. The energetics of perfect surfaces, and of fracture, therefore merit attention from a chemical perspective. Surface diffusion, the subject of this workshop, involves the breaking of an adsorbed atom's bonds to some of its neighbors and forming new bonds with others. Thus a diffusion step should be viewed a chemical reaction, and understanding the forces that govern surface diffusion is in principle only a more difficult version (because of lower symmetry) of the problem of understanding the structure of a perfect surface. To begin, here are two examples of the chemical approach to the simpler problem:

Role of valence in surface relaxation

Recall the widely-accepted, "physical" picture of surface relaxation due to Finnis and Heine (FH.)[29] The idea is that when one cuts a crystal to form a surface, electrons reduce their total kinetic energy by displacing in a way that reduces charge density corrugation in the near vacuum region. This "Smoluchowski charge smoothing"[30] moves electrons from above surface atoms to the hollows between them, and thus provides a rationale for the fact that outermost surface layers typically relax inward: The displacement of negative charge from the vacuum *toward* the solid attracts the outer layer of (positive) ion-cores toward the rest of the crystal. The FH picture also predicts larger contraction on more open surfaces and little contraction on close-packed ones. Here the idea is that charge smoothing and inward relaxation should both be bigger effects when zeroth-order corrugation is larger. On close-packed surfaces, whose electronic corrugation is slight even in the absence of Smoluchowski smoothing, only subtle effects are anticipated.

In light of this model, what can we make of the unusual case of clean Be(0001).[4-6] Contrary to conventional wisdom, the separation of the outer two layers of this crystal face is *substantially expanded* relative to bulk hcp Be (by 6% according to the original LEED analysis[4,31]) rather than contracted. As it happens, conventional wisdom fails to consider the effect of shell closure (i.e. valence), which is the source of the unusual surface geometry. This idea is confirmed by LAPW calculations[2,4] that show a demotion of *p*- to *s*-electrons in the outer Be layer. The energy cost of $2s$- to $2p$-electron promotion is not adequately recompensed by a gain in hybridization, for the outer-layer Be's, because of their reduced coordination. Thus the surface atoms are closer to being in a noble gas configuration and move away from the rest of the crystal.

Recent calculations for Ti(0001) and Zr(0001) predict large inward relaxations of 7.8% and 6.3%.[8] These results conflict with the common observation that the relaxation of close-packed surfaces should be small.[4,32] But they do agree with the chemical notion that because the $d \rightarrow s$ promotion energy in these atoms is small, the outer layers of their crystals gain much more in increased *d*-bonding if they contract than if they expand away from the metal and return toward their atomic s^2d^2 ground state electronic configurations.

Promotion-hybridization energetics in liquid metal embrittlement

In numerous cases, including Ga/Al, Au/Mo, Hg/Zn, and Cd/Fe, a solid metal sample weakens dramatically when a liquid metal is deposited on its surface.[33] In the example of Ga/Al, a droplet of Ga causes an otherwise ductile single-crystal Al specimen to cleave under tension, exposing (001) surfaces.[34,35] Consistent with the idea that there is a thermodynamic basis for this phenomenon,[36] LDA calculations by Stumpf and myself show that Ga lowers the surface energy of the Al(001) surface considerably more than of the close-packed (111) plane or of the open (110).[9] We also find that because Ga binds more strongly to Al than to itself, a second Ga layer on Al(001) lies relatively high above the first layer, and is bound to it rather weakly. The result is that the second Ga layer sees a weakly corrugated substrate potential, and can thus be estimated to diffuse with a barrier of 10-20 meV. This is essential if Ga is to diffuse rapidly to a propagating crack tip.

The Ga/Al system is particularly interesting from a chemical perspective because Ga and Al are neighbors in column IIIA of the periodic table, whose chemistry "ought to be" similar. Why then does Ga not *weld* a crack in an Al crystal rather than promoting its propagation? A good starting point for an answer is the idea is that embrittling agents are species that do not form many bonds. Hydrogen is an obvious example. The low-temperature, orthorhombic Ga crystal structure α-Ga, provides a hint that Ga is another. In α-Ga, each atom has one neighbor only 2.44Å away and six others 0.27 to 0.36Å more distant. Liquid Ga also shows evidence for the presence of Ga dimers.[37] Why is there a tendency toward dimerization in Ga and not in Al? A reasonable assumption is that what distinguishes the chemistry of Ga and Al is their different $s \rightarrow p$ promotion energies.[38] In both atomic Ga and Al, the electronic ground state configuration is s^2p. Thus, since the valence s-shell is closed, there is only a single p-electron available to form a bond. In order to make many bonds, an *s*-electron must be promoted to a *p*-state, such that the excited atom has three unpaired electrons.[39] If the energetic cost of this promotion is relatively high, and the compensation in the form of hybridization energy is not equally high, $s \rightarrow p$ promotion will not occur. In this case, there will be a tendency to form few bonds.

Atomic spectroscopy reveals that the minimum $s \rightarrow p$ promotion energy in Ga is 4.71 eV. In Al it is 3.60 eV.[40] Thus Ga is more stable than Al in singly relative to multiply bonded states. The reason for the higher promotion energy is that *s*-electrons of any principal quantum number spend an appreciable fraction of their time close to the nucleus, because they are not subject to a centrifugal barrier. When a Ga *s*-electron is inside the n=3 shell, it is attracted by an effective nuclear charge of 21 instead of only 3. But a 3*s*-electron in Al sees a nuclear charge of 11 when it is inside the n=2 shell, not 21, because there is no 2*d* shell. The upshot is that the 4*s*-electrons in Ga are bound more tightly than the 3*s*'s are in Al, and Ga is less able to form strong multiple bonds.

Ad-dimer separation energies and diffusion

The interaction energy versus separation of metal adatoms on metal surfaces has been measured using Field Ion Microscopy, for numerous combinations of adatom and substrate.[41] A general result of such measurements is that the energy required to dissociate an ad-dimer is smaller, often by a factor of 6 or 7, than the "bond energy" that one obtains by dividing the cohesive energy of a solid comprised of the two atoms by the number of bonds per atom. First-principles calculations explain this mystery.[10] The energy cost of rupturing the bond between the adatoms is partially paid back by an increase in the adatom-substrate bond strength. The compensation between bond-order and bond-strength is a basic feature of the molecular bond,[19] and is equally important in understanding the binding of adatoms on metal substrates.

Because of the interplay between the adatom-adatom and adatom-substrate interactions, the diffusion barrier seen by a dimer is lower than might be anticipated. There are two reasons:[10] The first is that a dimer sits higher above the substrate than either adatom would if isolated. But higher above the substrate, the potential that opposes diffusion is less corrugated, which translates into a reduced barrier. The second effect operates if dimer diffusion proceeds by a two-step process wherein first one atom moves and then the other "catches up." The idea is that while the first atom is surmounting a barrier, and at the same time moving away from the second atom, the latter responds by rehybridizing and strengthening its bonds to the substrate. The energy it gains via this "rebonding" reduces the *total* energy necessary for the first atom to complete its diffusive step.

Valence saturation in single-atom self-diffusion on a metal

In metal-adatom diffusion on a metal surface, a good way to discover the low-energy diffusion mechanism is to ask what path minimizes bond breaking. Such thinking guided Schwoebel and Shipsey (in 1966!),[42] as they tried to imagine the minimum energy path for transport over step edges, in crystal growth. It seemed clear to them that the reduction in coordination necessary for an adatom simply to move over a step-edge could be energetically prohibitive. A concerted process whereby a step-edge atom moves out onto the terrace, while the adatom on the upper terrace replaces it, was, plausibly, more favorable.

This idea makes good sense, in the case of transport over a step edge, because step-edge atoms are relatively weakly attached to the rest of the solid. (Since their relatively few neighbors are not uniformly distributed in the 4π steradians around each edge atom, their bonding electrons must be closer to each other than optimal.) That is, the barrier to concerted interlayer transport is plausibly low, but only if pulling a step-edge atom out onto a terrace is relatively inexpensive, energetically. That this should be the case for interlayer Al diffusion on stepped Al surfaces has been verified via LDA calculations by Stumpf and Scheffler,[43] almost three decades later.

Because outer layer atoms at smooth surfaces are better coordinated, and thus better bound than step-edge atoms are, the idea of concerted diffusion on such surfaces was not considered until I discovered,[11] via "scattering theory" based LDA calculations,[3] that ordinary hopping for an Al adatom on Al(001) is energetically rather costly. The calculated barrier is roughly 2/3 eV, which is comparable to measured barriers for transition metal adatoms on transition metal surfaces. The reason for the relatively high barrier is that to hop from one fourfold hollow to the next, the trivalent Al adatom must pass through a bridge site where it has only two neighbors, i.e., a site where it is poorly bonded to the solid.

This notion leads directly to the thought that, even on as smooth a surface as Al(001), a concerted process must be considered. Such a process is illustrated in Fig. 1. In a concerted diffusion step, what initially is the Al adatom plunges into the surface, replacing an outer-layer Al. The latter simultaneously emerges onto the surface, becoming the new adatom. It is particularly significant that in this process, both the initial Al adatom and the final one never have fewer than three near neighbors at any point along the diffusion path. This is an obvious benefit for the initial adatom, which would otherwise have to move through a twofold coordination site. Nevertheless, it is not *a priori* clear how disadvantageous the threefold transition geometry is for the initially eightfold coordinated surface atom.

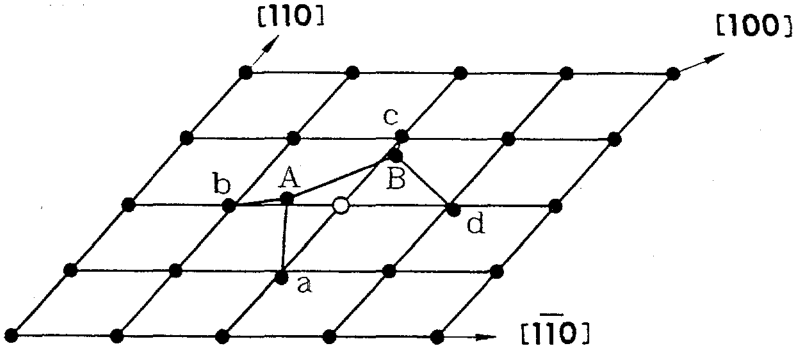

Fig. 1. Schematic illustration of the barrier configuration corresponding to the substitutional diffusion process described in the text. The open circle marks the location of the vacancy created when atom B emerged from the surface. At the end of the diffusion process this site will be filled by the initial adatom, A. Notice that A and B are both coordinated to three near neighbors.

The LDA calculations I performed indicate that it is not very disadvantageous. The barrier for the concerted diffusion step is predicted to be about a third of the barrier for a simple hop. The reason, presumably, is that a threefold bonding configuration saturates the valence of the trivalent Al atom. As a surface layer atom, in the initial state, this Al had 8 weak, "metallic" bonds, while in the transition state it has 3 strong, covalent ones. Unfortunately, the concept of valence saturation is hard to apply in the case of transition metal atoms and surfaces. Therefore, a systematic statement of what atoms should move by concerted diffusion, on what fcc(001) surfaces, is not yet available.[44]

The key to proving that concerted diffusion actually occurs (on any surface!) is the realization that this mechanism should only be energetically inexpensive for motion in certain crystallographic directions. Those directions are such that bond angles never have to be too small. In the case of concerted diffusion on a fcc(001) surface, as illustrated in Fig. 1, the easy directions for the concerted process are [100] and [010]. Note that for motion in these directions the initial and final adatoms are bonded to each other and to *two substrate atoms that are second neighbors to each other.* This means that in the transition geometry, the bond angles are all in the neighborhood of ideal tetrahedral angles. For displacement along [110], for example, the substrate atom neighbors of the moving atoms would be nearest rather than second neighbors to each other, and the bond angles in the transition geometry would be considerably smaller. The consequence is that adatom motion along [100] and [010] directions is a *signature* of concerted diffusion, and a map of sites visited by a diffusing atom is just the data required to learn if this diffusion mode is dominant. Such data, obtained via Field Ion Microscopy,[12] provided the original evidence that concerted substitutional self-diffusion actually occurs on Pt(001) and Ir(001).

Although it is not easy to state "laws" of the elemental dependence of concerted vs. hopping diffusion on fcc(001) surfaces [e.g., why Rh does diffusion on Rh(001) proceed by hopping, while immediately below it in the periodic table, Ir diffuses by substitution on Ir(001)[44]], one can make qualitative statements regarding crystal-face dependence. On fcc(111) surfaces, in particular, one would not expect concerted substitutional self-diffusion. These close-packed surfaces are very smooth, and an adatom, only threefold-coordinated at most, sits higher above a (111) surface than above a (001). As a result, the potential that governs hopping diffusion on a (111) surface can be expected to be only weakly corrugated. (FIM measurements for Ir/Ir(111)[45] and Pt/Pt(111)[46] yield barriers of 0.27 eV and 0.25 eV, respectively.) At the same time, the geometry of a (111) surface inhibits concerted substitution. Atoms attempting a substitutional step must bind to surface atoms that are nearest neighbors to each other. This means that the bond angles must be quite small, driving up the barrier energy. Given that hopping is relatively easier and substitution more costly, hopping is expected to dominate on (111) surfaces.

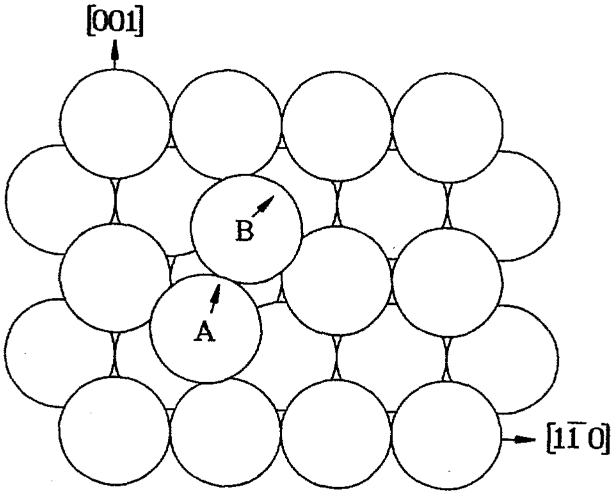

Fig. 2. Example of a diffusion mechanism, for the fcc(110) surface, that minimizes bond breaking: Adatom A and channel wall atom, B, move together in such a way that at worst each has the other and two channel wall atoms as near neighbors. The result is apparent cross-channel diffusion.

On fcc(110) surfaces, matters are very different (see Fig. 2). Here a metal adatom occupies a fivefold coordination site in equilibrium that lies low over the surface. Hopping diffusion is over two fold bridges, and thus one expects a highly corrugated potential energy surface. On the other hand, for concerted diffusion to occur, with an adatom pushing a surface layer atom into a neighboring $[1\bar{1}0]$ channel, the energetics should be quite favorable. Now the neighbors to the initial and final adatoms are third neighbors to each other, implying large bond angles, and as noted above in the discussion of diffusion over steps, the surface layer atoms are not especially strongly bound. The consequence is that concerted substitution should be preferred on (110) surfaces. There are strong experimental indications that this is the case.[47]

Binding site preferences on a stepped surface

The behavior of gas fragments near defects on transition metal surfaces is central to scientific issues from the interpretation of scanning tunneling micrographs[48] to the energetics of reconstructive phase transitions.[49] The way that light adspecies interact with surface defects is also the key to important technological questions, including the mechanisms and performance of "surfactant" species in promoting layer-by-layer crystal growth,[50] and the nature of heterogeneous catalytic reactions.[51] Early LDA calculations for Al, H and S adatoms on the intrinsically stepped, Al(331) surface revealed the relationship of adatom site preferences to atomic radius and valence.[13,14] Whereas an Al adatom prefers to occupy the epitaxial growth site at a step bottom, step edge sites are optimal for H and S, because at such sites, these smaller, low-valence atoms can passivate the surface Al's that are most poorly coordinated while satisfying their own valence requirements.

More recent LDA calculations concern O on surfaces vicinal to Pt(111), a system for which much experimental information is available.[15] O is known to prefer binding to steps on Pt(111).[52,53] Pre-adsorbed O has been shown to promote layer-by-layer growth of Pt(111),[50] and at higher temperatures, ad-O causes a "step-doubling" reconstruction.[49] Thus O/vicinal-Pt(111) exhibits many phenomena that one would like to understand.

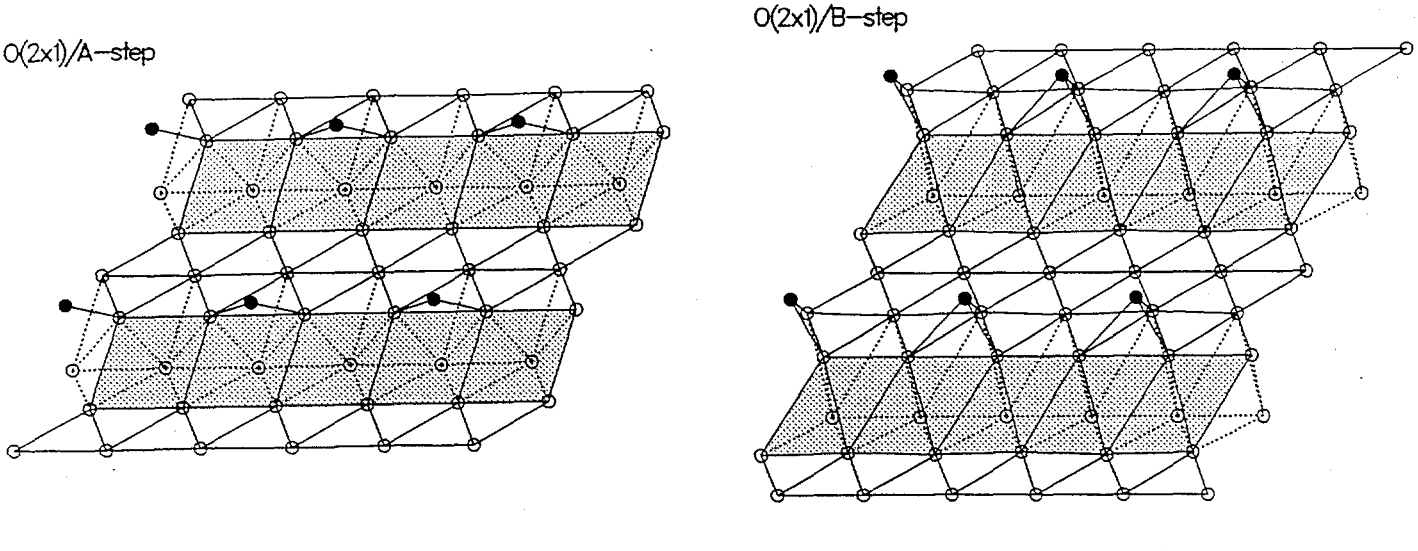

Fig. 3. Schematic illustrations of an O-saturated A-step (left) and a B-step (right). In each case, the O atoms (filled circles), and the Pt atoms (open circles) are located in their optimal binding sites.

Using the QUEST LDA code,[28] it has been possible to compute the energies of O adatoms in various arrangements on Pt(211), (221) and (322) films, which have (111) terraces and monoatomic steps. The (211) and (322) surfaces have "A-type" steps, whose risers are (100) microfacets while the (221) surface has "B-type" steps, whose risers are (111) microfacets (cf., Fig. 3). The results of the calculations, in which the 2x1 rows of O adatoms were aligned parallel to the steps, either mid-terrace or in various sites near the step edges, follow two simple rules:

1) Bonding in *fcc* sites is preferred to *hcp* by ~0.4 eV. Here, the concept of "*fcc* site" includes the edge-bridge at an A-step, where there is no Pt atom directly below the O adatom on the lower terrace in front of the step. Similarly, the idea of *hcp* binding is extended to the edge-bridge at a B-step, where there is a Pt atom on the lower terrace in front of the step, below the ad-O.

2) An O adatom gains binding energy in rough proportion to the number of its nearest neighbors that are step-edge atoms. The gain is about 0.25 eV if the O atom has only one step-edge neighbor, it is ~0.4 eV if the O atom's nearest neighbors are one terrace and two step-edge atoms, and it is ~0.6 eV if the ad-O hangs off the step edge, coordinated only to two step-edge Pt atoms.[9]

The consequence of these local bonding rules is that the preferred geometry is very different at the A and B steps. In the former case the O's optimally reside in two-fold sites, bridging a pair of step-edge atoms and "hanging out" over the lower terrace. In the latter, the O's prefer the three-fold fcc hollows of the upper terrace that are closest to the step edge. This difference provides a direct, simple interpretation of differences evident in STM micrographs of O-saturated steps bounding monolayer height Pt islands on Pt(111).

The large structural energy differences governing the O/Pt system, and the evidence that LDA accounts correctly for the observed O geometries near step edges,[15] strongly imply that this system can help us understand how an additive modifies metal-atom transport near step edges. The results to date suggest that a qualitative picture based on local bonding concepts will be a valuable guide to the answer.

SUMMARY

Using elementary chemical concepts to interpret the results of first-principles calculations of surface energetics is evidently a very fruitful endeavor. It has yielded explanations of the unexpected relaxations of hcp(0001) surfaces,[4,9] and of the fact that ad-dimer separation energies are often roughly an order of magnitude smaller than corresponding "bond energies."[5] It has led to the discovery of a novel mode of diffusion on metal surfaces[6,7] and to the prediction of an unexpected binding sites for low valence atoms at steps.[8]

Because of the great expense of first-principles computations of force-laws for atoms at surfaces, simulations of surface processes often rely on "educated guesswork" to provide the necessary information. The surprise in each of the first-principles results reported here dramatizes the importance of using elementary chemical concepts as a "reality check" for such guesswork.

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