Diffusion Path for an Al Adatom on Al(001)

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The barrier to self-diffusion on Al(001) by concerted displacement in a (100) or (010) direction is predicted to be smaller than $\frac{1}{3}$ that for ordinary Al-adatom hopping over bridges between fourfold hollows. The transition state for the concerted motion corresponds to an Al ad-dimer symmetrically located above a surface site vacated by one of the dimer atoms. Covalent bonding in this configuration is favorable because each of the (trivalent) Al atoms above the surface bonds to the other, and to two surface atoms.

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In considering diffusion on a surface, it is natural to begin by assuming that an adatom sees a static corrugated potential, whose ridges and hollows determine the adatom's diffusion rate. A more sophisticated approach includes substrate elasticity. Noting that formation of adatom-surface bonds affects the electron density between the adatom's neighbors, one expects to have to refine a diffusion-barrier calculation by allowing for relaxation of the adatom's neighbors' positions both in equilibrium and in the barrier geometry.

Experimental evidence indicates, however, that even this more sophisticated picture is inadequate to describe surface diffusion in general. Field-ion-microscope studies of self-diffusion on fcc(110) surfaces show that motion along channels need not be more facile than across ridges, in contradiction to expectations based on pair-potential summations.¹⁻⁴ Wrigley and Ehrlich's atom-probe study of a W atom on Ir(110) shows directly that what initially appears to be diffusion of W across ridges actually proceeds via replacement of an Ir atom by the W, followed by Ir self-diffusion.³ Kellogg and Feibelman have found that individual displacements of Pt atoms occur exclusively in (100) and (010) directions on Pt(001) at low temperatures (as low as 175 K).⁵ Chen and Tsong have observed similar behavior for selfdiffusion on Ir(001).⁶ Since ordinary hopping along (100) or (010) directions on a rigid fcc(001) surface requires passing through atop sites, where the binding energy is expected to be small and the barrier to diffusion correspondingly high, it is reasonable to assume that something more complicated, i.e., a replacement mechanism, is at work.

The key to developing a correct model of surface selfdiffusion is to think of it as a chemical phenomenon rather than in terms of a hard sphere moving on a bumpy plane. Just as in the dissociation of a diatomic molecule at a surface, a minimum-barrier diffusion path corresponds to motion in which new bonds can form *at the same time as* old ones are broken.⁷ As an adatom moves from a hollow to a bridge site on a fcc(001) plane, four bonds are replaced by two. To some degree each of the two bonds at the bridge will be stronger than each of the

four bonds was in equilibrium. But Pauli repulsion limits the strength of bonds, and this limitation fixes the minimum barrier energy for passage over a bridge. With this in mind, for the case of Al diffusion on Al(001), I have considered a "concerted displacement" (see Fig. 1), in which an Al adatom replaces a substrate Al atom, as the latter becomes an adatom in a second-neighbor fourfold hollow. I find that the barrier to this motion is less than $\frac{1}{3}$ that for ordinary, single adatom hopping over a bridge. The reason for the low barrier energy is that in the concerted motion, neither Al atom's coordination drops below 3. Since Al is trivalent, this coordination is desirable. Thus, the energy gained in forming three strong covalent bonds largely compensates the cost of extracting an Al atom from the surface layer. (An essential point, here, is that since an Al atom only possesses three valence electrons, the eight "metallic bonds" of a surface-layer Al atom are relatively weak.)



FIG. 1. Barrier configurations corresponding (a) to ordinary hopping over a bridge on Al(001) and (b) to the concerted displacement mechanism described in the text. The solid circles represent nuclear positions. The open circle in (b) is the vacancy created when atom B emerged from the surface and which will be filled by adatom A.

I calculate the energetics of diffusion by using the local-density-functional- (LDF-) theory-based, matrix-Green's-function scattering method.⁸⁻¹¹ This method makes it possible to evaluate the electronic structure of a spatially compact defect (a "surface point defect") on an otherwise perfect, crystalline surface. The inputs to the calculation are the species and locations of all nuclei, norm-conserving pseudopotentials¹² describing the effects of the atomic cores on the valence electrons, and a local exchange-correlation potential.¹³ Outputs include the change in valence-electron energy due to adsorption, and its gradient with respect to changes in nuclear positions. The size of each calculation is determined by the number of (localized) basis orbitals that overlap the unscreened defect-induced potential. Thus, the method differs from a conventional cluster calculation mainly in that the wave functions are Bloch waves of the perfect system scattering off the defect region, rather than molecular orbitals that drop to zero beyond the cluster edges. The scattering calculations are performed by projecting the Euler-Lagrange equation of LDF theory into the localized basis at the outset. This means that the scattering problem involves solution of simultaneous linear equations (hence the name "matrix" scattering method), a fact that makes it particularly straightforward to allow for changes in substrate nuclear postions,⁸⁻¹⁰ including the creation of a vacancy.¹¹

In order to compute an adatom's diffusion barrier one must first evaluate its adsorption energy in equilibrium, as a reference. For a single Al adatom in a fourfold hollow on Al(001), this energy is 2.90 eV if the surface is assumed to be rigid, and 2.93 eV if the four nearestneighbor Al atoms on the surface are allowed to move.^{14,15} I obtained these numbers using an orbital basis for the model substrate [a five-layer Al(001) slab] that yields bands in good agreement with a wellconverged linearized-augmented-plane-wave calculation.¹⁰ The slab's outer-layer separation is 0.38% contracted so that the force on an Al atom of the perfect surface is zero to within calculational error. To obtain the diffusion barrier for ordinary hopping, I compute the energy of the ad-Al at a bridge. Holding the substrate rigid, the maximum binding energy of a bridging ad-Al is 2.25 eV, when the adatom is 4.30 bohrs above the surface plane. Allowing the adatom's two nearest neighbors to move increases this energy to 2.28 eV, corresponding to a configuration in which the ad-Al has moved 0.15 bohr closer to the substrate and the two neighbors have moved away from the adatom by 0.10 bohr (along the $\langle 110 \rangle$ and $\langle \overline{1} \overline{1} 0 \rangle$ directions), and into the substrate by 0.08 bohr [see Fig. 1(a)]. (Note in passing, that the nature of neighbors' relaxation at the bridge is similar to that which is found in the fourfold hollow. In both cases the adatom's nearest neighbors move away from each other and toward the second-neighbor shell, to relieve surface tensile stress.¹⁴)

A number of interesting conclusions follow from these

results. The diffusion-barrier energy, assuming a rigid substrate, is 0.65 eV, and allowing for elasticity makes no difference, to two-place accuracy. It is not surprising that small relaxations of the substrate nuclear positions have a small effect on the barrier height. Elastic relaxation involves phonon energies, which are on the order of tens of meV. Besides, since the barrier height is the difference in energies in equilibrium and at the bridge, the gains in binding in the two geometries tend to cancel. Thus unless one wishes to obtain a very precise barrier height for motion over a bridge, one need not consider further refinements of the relaxed geometry. For example, one need not ask whether binding at the bridge might be somewhat better if the bridged atoms rotate by some angle as they separate in response to the adatom. This might affect the barrier energy by some tens of meV but not more.

The reason that a precise description of motion over a bridge is not necessary here is that the self-diffusion onset temperatures measured for various planes of Al [unfortunately not including (001)] all correspond to diffusion-barrier energies of about 0.45 eV, assuming a normal prefactor.⁴ This cannot be explained, obviously, by reducing the calculated value of 0.65 eV by 10 or 20 meV. In addition, observed self-diffusion onsets for motion along channels and across ridges on Al(110) are roughly the same.⁴ This says that replacement mechanisms merit consideration.

Although pure Al is a metal with a nearest-neighbor spacing of 5.42 bohrs, Al also can bond covalently-its covalent radius is 2.38 bohrs. This value is smaller than (5.42 bohrs)/2 because in bonding covalently, Al has a lower coordination than in its metallic form and thus has stronger, shorter bonds. This suggests that replacement diffusion might occur if an Al adatom can enlist the participation of a substrate Al atom in such a way that the price of extracting the latter from the surface plane is largely recouped by the formation of strong covalent bonds. A diffusion-barrier geometry designed to test this idea is schematized in Fig. 1(b). It corresponds, effectively, to two Al atoms adsorbed above a vacancy. In the figure, A and B are moving in the (100) direction. Adatom A was originally in the fourfold hollow to its lower left and is heading toward the vacancy that B left behind when it emerged from the surface. At the conclusion of the diffusion event, B will become the adatom in the hollow to its upper right and A will fill the vacancy. Since Al is trivalent the geometry of Fig. 1(b) satisfies the bonding requirements of both adatoms, if the various bond lengths and angles can assume appropriate values without incurring too large a cost in strain energy.

I determine the optimal geometry of the form schematized in Fig. 1(b) by relaxing the forces on the six labeled atoms to less than 0.08 eV/bohr.¹⁶ This corresponds to moving atom a by (-0.14, -0.36, -0.16)bohr relative to its location on the perfect surface, while b, c, and d move symmetrically, and to placing atoms A and B 5.00 bohrs apart, at a height of 1.70 bohrs above the outer surface layer. In this geometry, the adsorption energy is 2.73 eV which implies a diffusion barrier of only 0.20 eV, i.e., *less than* $\frac{1}{3}$ *the barrier for ordinary hopping* over a bridge.

In the optimal geometry, aA and AB assume the values 4.81 and 5.00 bohrs, respectively, which are both close to twice the Al covalent radius. Charge buildup between the ad-Al and its nearest neighbors, seen in Fig. 2(a), shows that even in equilibrium the ad-Al is co-



FIG. 2. Electron-number-density contour plots (labeled in bohr⁻³) for an Al adatom (a) in its equilibrium fourfold hollow on Al(001) and (b) in the barrier configuration for diffusion by concerted displacement. In panel (a) the cut is a (100) plane, passing through the Al adatom and two of its substrate nearest neighbors. The vacuum is toward the top of the plot. Only contributions to the density are included which correspond to basis orbitals that overlap the adatom-induced potential. This accounts for the linear contours in the lower corners of the plot. In panel (b) the plot is in the plane of atoms a, A, B, and d as defined in Fig. 1(b). Notice that the charge buildup between atoms a and A (or B and d) exceeds that between the Al adatom and its neighbors in panel (a). Also note the relatively small charge buildup between first- and second-layer atoms in panel (a).

valently bonded to the surface. The stronger charge buildup in the aA and Bd bonds in Fig. 2(b) confirms the idea that the barrier to concerted-displacement diffusion is low because it permits the formation of still stronger covalent bonds. It is worth noting, in Fig. 2(a), that the charge between first- and second-layer Al neighbors is less than that between the ad-Al and the surface. It is the weakness of the bonds of substrate Al atoms to their neighbors that makes extracting one from the surface energetically possible.

The bond angles aAb and aAB are respectively 121° and 108°, compared to the ideal tetrahedral angle of 109.5° and the ideal sp^2 bond angle of 120°. This indicates that the bonding is somewhere between sp^3 and sp^2 , owing to competition between the ad-Al's desire to form sp^2 hybrids and resistance to compressive strain in the surface.

A key feature of the barrier configuration of Fig. 1(b) is that it is an intermediate step in diffusion along a surface (100) (or (010)) direction. Motion in the (110) and $\langle 1\overline{10} \rangle$ directions is not abetted by a similar concerted displacement because of unfavorable lattice geometry, and therefore can only occur via hopping over a higher barrier. The consequence is that an Al adatom sees the surface as a checkerboard-facile diffusion for an atom on a "black square" only occurs to other "black squares." Recent experiments by Kellogg and Feibelman⁵ for selfdiffusion on Pt(001) and by Chen and Tsong⁶ on Ir(001)see just such diffusion, and at rather low temperatures (175 K in the case of Pt). A concerted-displacement mechanism similar to that described here for Al is almost certainly necessary to explain these results. The alternative is to suppose that the minimum barriers for self-diffusion on these group-VIII metal surfaces correspond to ordinary hopping over onefold-coordination ("atop") sites. Since Pt and Ir are fcc metals, they evidently favor high coordination. This makes it unlikely that bonding at a onefold site could be stronger than at a twofold bridge.

In assessing the numerical significance of the results presented here, it is important to recognize two sources of systematic error. The first is that nuclear positions beyond those of the adatoms' first neighbors have been relaxed neither for the equilibrium state nor for barrier geometries. This deficiency can be expected to have introduced errors smaller than, but of the order of, the elastic relaxation energies quoted above for nearestneighbor motion, i.e., 10-20 meV. The second source of error is associated with a technical problem related to the matrix-Green's-function method, namely, that in this method it is natural to treat substrate atoms and adatoms asymmetrically.^{9,11} This is a problem because the transition configuration for the concerted displacement diffusion mechanism is symmetric; i.e., in the barrier configuration it is not clear which is the diffusing atom and which is the surface atom [see Fig. 1(b)]. In order to maintain this symmetry the barrier energy reported

here was evaluated by treating the diffusion problem as though it involved two adatoms and a surface vacancy. This introduces a systematic error because the reference equilibrium configuration ought then to involve one "adatom" in the vacancy and another in the adsorption site. A measure of the magnitude of the error is the calculated excess binding energy of an Al "adatom" in an Al surface vacancy. This quantity, which ought to equal zero, actually equals -52 meV,¹¹ given a reasonable level of numerical convergence. Thus the diffusion barrier for the concerted displacement might actually be as small as 0.15 eV in a more accurate calculation.¹⁷

The most important result reported here is that via concerted displacement, low-temperature diffusion of trivalent Al is expected in $\langle 100 \rangle$ and $\langle 010 \rangle$ directions on Al(001). The fact that low-temperature self-diffusion in these directions has been observed for Pt(001)⁵ and Ir(001),⁶ however, suggests that the replacement mechanism does not depend strictly on trivalency. The systematics of diffusion by concerted displacement is thus an interesting and important area for further study.

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¹⁶Further refinement of the barrier geometry will improve the barrier energy by an amount that is considerably less than expected systematic error, as discussed below.

¹⁷An "adatom" need not be in equilibrium at the site vacated by a "substrate atom." One may therefore question whether the full 53-meV "binding energy" of the adatom in a vacancy should be subtracted from the calculated diffusion barrier. The only answer to this sort of question is to avoid it by improving numerical convergence to the level warranted by the experimental situation.