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Compact surface-cluster diffusion by concerted rotation and translation

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First-principles calculations show that a pseudomorphic Ir monolayer on Ir(111) has an unexpected metastable on-top configuration only slightly above the stable fcc configuration. The energy required for any translation of the monolayer parallel to the surface is small. This opens the possibility that whole clusters can move by rotation and/or translation through configurations with many atoms in on-top sites. One such diffusion mechanism, the ''cartwheel shuffle'' could explain otherwise mysterious long jumps and high prefactors seen in the diffusion of 19-atom Ir clusters on Ir(111).

Island diffusion on surfaces has historically been explained by single-atom mechanisms including edge running and evaporation condensation. More recently, cooperative mechanisms for island diffusion including glide,[1] dislocations,[2] and dimer shear[3] have been proposed theoretically, although experimental evidence for some of these mechanisms remains limited. Island glide, defined as the nearly simultaneous translation of all island atoms parallel to the surface, could be related to friction,[4,5] since both phenomena require a layer of one material to slide past another material. The detailed atomic mechanisms for island glide and friction represent a challenging problem for theoretical and experimental investigation.

Field ion microscopy studies[6,7] of 19-atom Ir clusters on the Ir(111) surface have documented several remarkable diffusion behaviors as follows. (1) The clusters exhibit an excess of long jumps (i.e., beyond nearest stable fcc configurations) relative to single jumps. (2) The prefactor for diffusion is almost four orders of magnitude larger than the usual prefactors. (3) Edge running and evaporation condensation apparently can be ruled out as mechanisms for diffusion. These unusual experimental observations motivate a detailed theoretical examination of the possibility raised by Wang and co-workers[6,7] that the clusters glide by simultaneous translation of the cluster atoms over bridge sites.

The experimental results show that an 18-atom cluster moves by periphery diffusion, but that a compact hexagonal 19-atom cluster moves by some other mechanism. The compact hexagonal clusters are of special interest because of the high diffusion prefactors and unusual diffusion mechanisms. For this reason we will limit ourselves here to the motion of compact hexagonal clusters by collective mechanisms, including but not limited to, bridge glide. This paper has two main sections. First we consider the energy of a pseudomorphic monolayer of Ir on Ir(111). This is relevant since a compact 19-atom Ir cluster is a pseudomorphic island. We find, in dramatic contrast to a single adatom, that a pseudomorphic monolayer has a low-lying local energy minimum at the on-top position. This raises the possibility that on-top sites could easily be involved in island glide. In the second section we examine island glide in detail and propose a mechanism, the ''cartwheel shuffle,'' for island glide. This mechanism involves concerted rotation and translation of the cluster as a whole. We have investigated four possible glide mechanisms for long jumps of the 19-atom cluster. Of these, cartwheel shuffle has the lowest activation energy.

The first-principles energies presented here were calculated within the generalized gradient approximation (GGA).[8] We used the plane wave ($E_{\text{cut}} = 191\,\text{eV}$) and ultrasoft pseudopotential[9] based code, VASP, developed by Kresse and Furthmuller.[10] All activation energies for diffusion have been calculated using the nudged elastic band method.[11]

As mentioned previously, a 19-atom compact Ir island on Ir(111) is basically a hexagonal portion of a pseudomorphic Ir monolayer on Ir(111). The island will differ from a pseudomorphic film mainly at its perimeter where the atoms will relax inward slightly. Because of the similarity between island glide and monolayer shear, it is relevant to calculate the energies required to shear a pseudomorphic monolayer of Ir across an Ir(111) surface. In Table I, we contrast these energies for a pseudomorphic film with the energies for an adatom in the fcc, hcp, bridge, and on-top sites. All of the energies are expressed per atom in meV/atom and were calculated using first principles. For an adatom, the calculations of the relative fcc, hcp, and bridge energies are within about

TABLE I. Calculated relative energies (meV/atom) for a single adatom, for a pseudomorphic monolayer, and for four pseudomorphic layers in high-symmetry sites. Experimental values (adatom from Ref. 12, bulk from Ref. 18) are given in parentheses. All energies are referenced to the energy of the stable configuration. Note the remarkably low energy for the metastable on-top monolayer.

	fcc	hcp	Bridge	On top
Adatom	18 meV (22)	0 meV (0)	251 meV (269)	1565 meV
Monolayer	0 meV	81 meV	243 meV	113 meV
Bulk	0 meV (0)	120 meV (120)	234 meV	403 meV

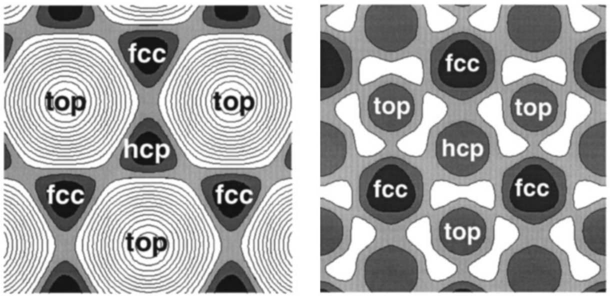

FIG. 1. Relative energy per atom as a function of position for a single Ir atom on Ir(111) (left plot) and for a pseudomorphic Ir monolayer on Ir(111) (right plot). This figure illustrates the dramatic difference between diffusing a single Ir atom on Ir(111) and shearing an Ir monolayer across Ir(111). For example, the top site is unstable for an adatom and metastable for the monolayer. Contour intervals are 100 meV/atom in both plots. The gray scale is choosen to emphasize the portions of the energy surface most likely to be visited during diffusion. Plots are Fourier fits to computed data.

10% of the experimental measurements.[12] This gives us considerable confidence in these first-principles calculations. As expected, the energy is a maximum at the on-top site and an adatom will avoid that site. The calculations for the pseudomorphic monolayer present a very different story. The energy required to place the layer in the on-top site is only slightly larger than the hcp energy and is much less than the bridge energy. Surprisingly, the on-top site is metastable for the pseudomorphic monolayer. To our knowledge this is the first time that this behavior has been reported for a transition metal. As shown here, it is different from the well-known behavior of a single adatom. It is also different from the well-known slip behavior of bulk fcc metals represented in Table I by a bulk calculation with five and four layers of iridium on the sides of a (111) slip plane, which reproduces the measured bulk stacking fault energy with fortuitously good agreement.

We have also performed semiempirical many-body calculations with two different iridium potentials.[13,14] These calculations fail to predict the important metastable on-top state and differ from first-principles calculations by almost an order of magnitude for the energy of this state.[15] Thus, relying on semiempirical calculations [e.g., embedded atom method (EAM), effective medium theory (EMT), or Finnis-Sinclair potentials] to provide even a qualitative understanding of Ir island glide on Ir(111) seems unwise. We did resort to semiempirical calculations to perform exhaustive preliminary searches for metastable states of rotated and translated clusters and to estimate prefactors for diffusion since such calculations are presently well beyond the capability of first-principles methods.

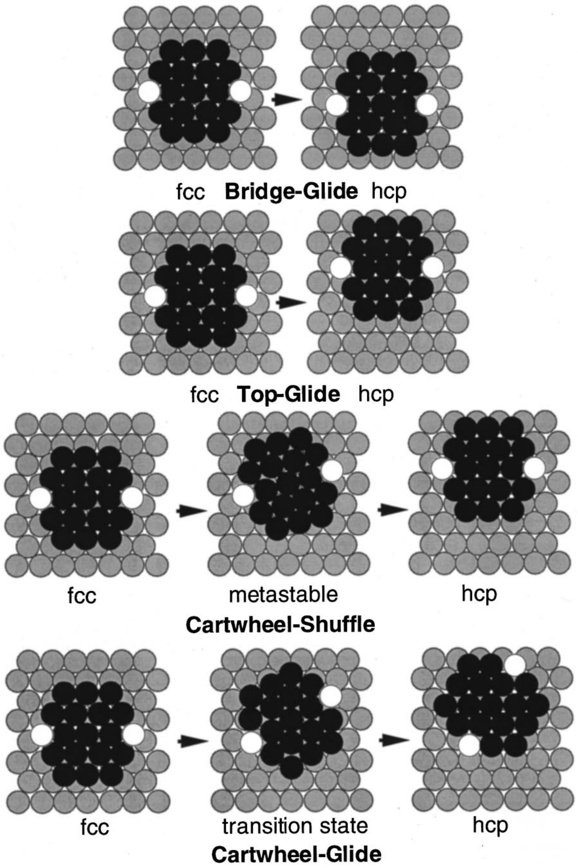

FIG. 2. Cluster glide mechanisms discussed in this paper. Bridge glide and top glide involve nearly simultaneous translation of all cluster atoms over the bridge and on top sites, respectively. Top glide was considered as one possible mechanism for long jumps. Cartwheel glide involves a simultaneous translation of the center atom over the on-top site while the cluster rotates by 60°. Cartwheel shuffle involves translation of the center atom to the on-top site while the cluster rotates by ~15° to form a metastable state. The cluster then translates to another hollow site while rotating back by ~15°.

In Fig. 1 we show the energy per atom of an iridium adatom and of a pseudomorphic iridium monolayer plotted as a function of position. These plots are based on the calculations given in Table I and on calculations at intermediate positions. This figure emphasizes the dramatic difference between moving a single atom across a surface and moving a pseudomorphic overlayer over a surface. For a single atom, diffusion will occur from an fcc site to an hcp site and then to an fcc site. The probability of a long jump over the top site is insignificant. For a monolayer of iridium atoms (as in a pseudomorphic island), one can imagine other paths, such as diffusion from an fcc site to the metastable on-top site and then to the opposite hcp site. Since the energy surface is relatively flat for the monolayer, it also seems conceivable that an island could rotate in addition to translating across the surface. Simultaneous translation and rotation can produce a cartwheel-like motion. Cartwheel-like motion has been reported for gold nanocrystal diffusion on graphite,[16] but to find it possible in a homoepitaxial pseudomorphic island is unexpected.

In Fig. 2 we show four different collective diffusion mechanisms which we have studied using first-principles calculations of activation energies. (We have also considered a mechanism in which the cluster first rotates, then translates several times, then rotates again. Since this mechanism also has a high activation energy, we will not discuss it here.) The first two mechanisms, bridge glide and top glide, are almost pure translational mechanisms. The second two mechanisms, cartwheel shuffle and cartwheel glide, involve simultaneous translation and rotation. These mechanisms are shown for the 19-atom cluster. For the 7-atom cluster the mechanisms are

TABLE II. Calculated activation energies for glide by mechanisms shown in Fig. 2. For the 7-atom cluster, calculations should be reasonably accurate. For the 19-atom cluster, computational requirements limited calculation to a 19-atom cluster on a 3-layer slab with 2 fixed layers, limited lateral dimensions for the periodic cell, and limited *k*-point sampling. Thus 19-atom cluster calculations are only approximations.

Cluster size	Bridge glide	Top glide	Cartwheel shuffle	Cartwheel glide
7 atoms	1.54 eV	3.02 eV	1.92 eV	1.92 eV
19 atoms	3.2 eV	5.2 eV	3.6 eV	5.1 eV

similar except that cartwheel shuffle and cartwheel glide both involve a 30° rotation to reach a metastable state. For the 7-atom cluster, cartwheel shuffle and cartwheel glide are equivalent by symmetry if jumps in and out of the metastable state are uncorrelated. The first-principles activation energies for these glide diffusion mechanisms are given in Table II. In all cases the stable island configuration has all atoms near the fcc sites in agreement with experiment. The calculations suggest that bridge glide is the favored diffusion mechanism with an activation energy of 1.54 eV in excellent agreement with the 1.49 eV measured experimentally. The experimental data shows no excess of ‘‘long jumps.’’ Our calculations and the experimental data appear consistent with bridge glide as a cluster diffusion mechanism for the 7-atom cluster.

For the 19-atom cluster, the calculations show that top glide and cartwheel glide can be ruled out as diffusion mechanisms, since their activation energies of 5.2 and 5.1 eV, respectively, are much higher than for bridge glide and cartwheel shuffle. The experimental activation energy for diffusion of the 19-atom cluster is 2.54 eV. This is significantly lower than the 3.2 and 3.6 eV activation barriers calculated for bridge glide and cartwheel shuffle, respectively. The discrepancy between experiment and theory may be due to computational inaccuracies which we were forced to accept in order to perform first-principles calculations for such a large number of atoms. The intensive computational requirements limited the first-principles nudged elastic band calculation to a small unit cell and sparse *k*-point sampling. The errors associated with these compromises are difficult to quantify without exceeding all available computational resources. Since the calculations are not fully converged, we cannot make a definitive conclusion regarding whether bridge glide or cartwheel shuffle has the lower activation energy. It is also conceivable some other diffusion mechanism may exist which has a lower activation energy than bridge glide or cartwheel shuffle.

What theoretical conclusions can we draw with confidence regarding the glide mechanisms of a 19-atom cluster? First, we are sure that the cartwheel shuffle and bridge glide have a much lower activation energy than the on-top glide or cartwheel glide. The low activation energy of the cartwheel shuffle can be understood by noticing that several of the atoms in the cluster remain near the fcc sites during the transition from the fcc to the metastable configuration. The other atoms in the cluster move over on-top sites in an asynchronous fashion as the cluster moves in a cartwheel fashion from fcc to the metastable state. This means that only a portion of the atoms in the cluster will be in energetically unfavorable positions at any time during the cartwheel shuffle. We suspect that cartwheel shuffle has the lowest activation energy of all mechanisms involving glide of the center of mass of the cluster over the top site. Returning to the experiments on diffusion of 19-atom Ir clusters on Ir(111), we consider possible explanations for the long jumps. We are not able to understand how bridge glide could produce an excess of long jumps, since it moves a cluster from an fcc site to an adjacent hcp site (and then to an adjacent fcc site). For this reason we believe that cartwheel shuffle (probably in combination with bridge glide) should be given serious consideration as a possible explanation for the remarkable experimental observations.

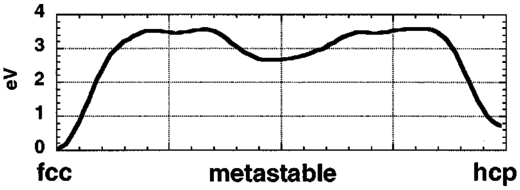

FIG. 3. Calculated energy as a function of translation and rotation during cartwheel shuffle shown in Fig. 2. Note that the curve is very flat near the maxima (transition states), and steep near the fcc and hcp minima.

Finally we consider the high prefactors measured experimentally for diffusion of compact clusters. Prefactors for diffusion can be calculated from the harmonic approximation to transition state theory using the result derived by Vineyard,[17]

$$\nu = \prod_{n=1,m} \nu_{\mathrm{fcc}} \Bigg/ \prod_{n=1,m-1} \nu_{\mathrm{ts}},$$

where ν_{fcc} are the phonon frequencies at the fcc configuration and ν_{ts} are the phonon frequencies at the transition state. Unfortunately, calculation of the phonon frequencies is well beyond the capability of first-principles calculations for systems of this size. Figure 3 shows the energy as a function of position during the cartwheel-shuffle diffusion process. In this plot the energy rises abruptly from the global minimum at the fcc cluster configuration. However, the energy varies very slowly in the vicinity of the maxima (the transition states) on this curve. This is consistent with the type of flat energy surface shown in Fig. 1(b) and suggests that some of the phonon modes (other than the reaction coordinate) at the transition state may have lower frequencies than the phonon modes at the fcc state, thereby producing a high prefactor.

In order to estimate the prefactors for diffusion of Ir clusters on Ir(111) we used two semiempirical potentials. The calculated prefactors for various mechanisms and two different potentials are given in Table III. We also compare these results to the experimental values for diffusion of single-atom, 7-atom, and 19-atom clusters. One can only hope for a qualitative prediction here, both because of the inaccuracies involved in the semiempirical approach and possible errors associated with the harmonic approximation. Nonetheless, we find that the prefactors for cartwheel shuffle and bridge glide are much larger than for single atom diffusion. We also performed this prefactor calculation for Au, Ag, Cu, Ni, Pd, and Pt using 18 different commonly used EAM and EMT potentials. For a 19-atom cluster, the prefactors for bridge

TABLE III. Prefactors calculated using semiempirical potentials from Refs. 13 and 14. All prefactors are in Hz. Values from experiments are also given.

	1 atom	7 atoms	19 atoms
Hopping (Ref. 13)	2×10^{12}		
Hopping (Ref. 14)	3×10^{12}		
Bridge glide (Ref. 13)		7×10^{13}	2×10^{16}
Bridge glide (Ref. 14)		1×10^{14}	7×10^{16}
Cartwheel shuffle (Ref. 13)		7×10^{14}	8×10^{16}
Cartwheel shuffle (Ref. 14)		5×10^{14}	1×10^{17}
Experiment (Ref. 7)	7×10^{11}	3×10^{15}	2×10^{16}

glide ranged from 1×10^{12} to 2×10^{15}, whereas the prefactors for cartwheel shuffle ranged from 1×10^{14} to 1×10^{18}. This shows that the high theoretical prefactors for these cooperative mechanisms are not just an artifact of the particular iridium potentials used.

To summarize, we find that a monolayer of Ir on Ir(111) is metastable in the on-top configuration. This low on-top energy suggests that some cluster atoms may pass close to on-top sites during diffusion by a glide mechanism. In particular, a cartwheel-shuffle mechanism is proposed which may be competitive with other diffusion mechanisms. This mechanism, probably in combination with bridge glide, appears capable of explaining the long jumps and high prefactors observed in diffusion experiments. In view of the complexity of this problem, additional theoretical and experimental investigation (perhaps examining the intermediate-sized, compact 12-atom cluster and/or other field ion microscope metals) will doubtless be required to determine a definitive diffusion mechanism.

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