

## Oscillatory Behavior in the Size Dependence of Cluster Mobility on Metal Surfaces: Rh on Rh(100)

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The mobility of Rh clusters containing two to twelve atoms adsorbed on the Rh(100) plane is examined by field ion microscopy. The activation energy of surface diffusion exhibits an interesting, oscillatory behavior as a function of cluster size. Compact geometric structures (squares and rectangles) have a consistently higher activation energy than structures with extra atoms at the periphery. The atomic-level mechanism involved in cluster diffusion is inferred from a comparison of the measured activation energies to previous theoretical calculations.

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A fundamental understanding of how individual adatoms and small clusters move across single crystal terraces is essential to the development of microscopic models of crystal growth. Although a considerable amount of experimental information is now available on the energetics and mechanisms of single-atom diffusion [1], comparatively little is known about the details of cluster diffusion on surfaces. As a result, many growth models still assume that once a cluster is nucleated it remains immobile or, at best, its mobility simply decreases as the cluster grows [2,3]. However, it has been known for some time that clusters can migrate across surfaces without dissociation at typical growth temperatures [4]. Moreover, it has been shown both experimentally [5,6] and theoretically [7,8] that the mobility and stability of small clusters may exhibit a nonmonotonic dependence on cluster size. That such effects are important in crystal growth has recently been demonstrated in an investigation of homoepitaxy on Pt(111), where stable heptamers are believed to cause an anomalously high density of small clusters during the initial stages of growth [9]. These studies, as well as earlier molecular dynamics simulations of cluster diffusion [7], suggest that the size-dependence of the mobility and stability of clusters may be related to the geometric arrangement of atoms in the cluster. Direct experimental verification of this relationship, however, has been lacking.

In this paper I report the results of field ion microscope (FIM) experiments that show a definite correlation between the geometric structure (shape) of a cluster and its mobility across a single-crystal surface. Rh on Rh(100) is used as a model system for the investigation because clusters consisting of two to twelve atoms are found to migrate over the surface without dissociation. In addition, the diffusion of individual Rh adatoms on this crystal plane is found to take place by ordinary hopping displacements. For systems such as Pt on Pt(100) and Ir on Ir(100), displacements take place by an exchange process [10,11], leading to a more complicated mechanism of cluster migration, at least for dimers and trimers [12].

The present experiments indicate that for Rh clusters on Rh(100) compact structures (squares and rectangles of the cluster form  $\langle 110 \rangle$ ) have a consistently higher activation energy of surface diffusion than the same structures with extra atoms at the periphery (i.e., extra atoms along the close-packed  $\langle 110 \rangle$  edge). As a result, the activation energy of surface diffusion exhibits an oscillatory behavior as a function of increasing cluster size. This same behavior was predicted in earlier molecular dynamics simulations of Ag diffusion on Ag(100) [7]. As shown below, the results of these and more recent theoretical calculations [8] indicate why compact structures are less mobile than those with atoms at the periphery and provide considerable insight into the detailed mechanism of cluster motion. The agreement between experiment and theory supports models in which diffusion takes place by sequential displacements of edge atoms and is inconsistent with models in which the entire cluster glides as a unit across the surface [13].

The experimental methods used in field ion microscope studies of surface diffusion are well documented in several recent reviews [1]. Briefly, the procedure consists of taking snapshots of an atom or cluster as it performs a two-dimensional random walk across the surface. The snapshots are taken with the sample at 77 K. Migration occurs during 30 sec intervals at elevated temperatures with the field-ion imaging voltage turned off. An example of a Rh hexamer diffusing on the Rh(100) plane 394 K is shown in Fig. 1. The activation energy of surface diffusion is obtained by measuring the mean-square displacement of the cluster's geometric center (or center-of-mass) and following a standard Arrhenius-type analysis [1].

In this investigation, the temperature range over which reliable diffusion data could be obtained was too small to carry out a full Arrhenius analysis (mean-square displacement as a function of temperature). As a result, the activation energy for each size cluster was determined at a single temperature based on the assumption that the Arrhenius prefactor is independent of cluster size and is given by "standard value" for single atoms of  $10^{-3}\text{cm}^2/\text{sec}$  [1].



FIG. 1. Field ion micrographs illustrating the migration of a Rh hexamer on the Rh(100) plane. The images were recorded in  $2 \times 10^{-4}$  Torr Ne at 77 K. Between each photograph the sample was heated to a temperature of 394 K for 30 sec. Superimposed circles indicate atomic positions. From (a) to (b) the rectangular cluster changes orientation by  $90^\circ$ . From (b) to (c) the orientation changes back to that in (a) displaced by one lattice position. From (c) to (d) the cluster changes to a highly metastable configuration (observed only once in 75 heating intervals).

This assumption is justified to a certain extent by previous measurements of Pt cluster diffusion on W(110) [14] and Ir cluster diffusion on Ir(111) [5], where the prefactor is found to be relatively insensitive to cluster size. It is important to emphasize, however, that the qualitative conclusions concerning the relationship between cluster structure and mobility are evident from the measured mean-square displacements and are not dependent on this assumption.

With the exception of trimers, the most stable configuration for Rh clusters on Rh(100) is a two-dimensional island. For the compact shapes (four, six, nine, and twelve atom) the cluster form is  $\langle 110 \rangle$ . Others have the same form, but with extra atoms at the  $\langle 110 \rangle$  edge. Configurational stability is determined by simply noting the number of times a diffusing cluster is observed in a particular configuration. For example, the rectangular configuration of atoms for the hexamer seen in Fig. 1(a) and 1(c) is observed in 74 out of 75 diffusion cycles. The metastable configuration seen in Fig. 1(d) is observed just once. Of the ten different clusters examined, only trimers are found to be more stable in a linear-chain configuration than a two-dimensional island configuration (44 out of 50 cycles). This result is quite different than that from previous studies of Ir on Ir(100) [15] and Pt on Rh(100) [6], where chain configurations are more stable for clusters up to five atoms. It is also different from results for Pt on Pt(100) [16], where the stable configuration actually oscillates between chains and islands. The reason for these interesting differences is still uncertain, although some insight is being gained through theoretical modeling [17]. In this Letter the focus

is on the mobility of the clusters—questions concerning their configurational stability in relation to other systems are addressed in a separate publication [18].

Table I lists the experimental parameters, measured mean-square displacements, and calculated activation barriers for single atoms and clusters consisting of two to twelve atoms. The statistical errors in the activation energies are approximately 0.01 to 0.02 eV. All measurements are taken from observations on the same sample tip using the same temperature calibration and imaging conditions. Data are not displayed for an eleven-atom cluster because the tip “jumped” (field stresses sometimes cause a tip to fracture) while the cluster was being prepared. Fortunately, the absence of results for an eleven-atom cluster does not affect the general conclusions of the study.

The nonmonotonic behavior of cluster mobility as a function of cluster size is apparent from inspection of the mean-square displacements listed in Table I. Consider, for example, clusters consisting of three to seven atoms. The mean-square displacement of a trimer at 366 K is  $9.6 \text{ \AA}^2$ . The mean-square displacement of a tetramer at the same temperature is  $4.1 \text{ \AA}^2$ —a factor of two smaller than that for the trimer. Thus, as one might expect, the tetramer is less mobile than the trimer. However, the mean-square displacement of a pentamer is  $15.7 \text{ \AA}^2$ —a value larger than that for both the trimer and the tetramer. This indicates that the addition of an atom to the periphery of the square tetramer *increases* the overall mobility of the cluster. Upon addition of another atom to form a hexamer, the cluster becomes totally immobile at 366 K. Even at 394 K, the mean-square displacement of the hexamer is only  $2.9 \text{ \AA}^2$ . One more atom added to the hexamer again increases the cluster’s mobility resulting in a mean-square displacement at 394 K of  $59.5 \text{ \AA}^2$  for the heptamer. This oscillatory behavior continues for clusters up to twelve atoms.

TABLE I. Diffusion parameters for Rh clusters on Rh(100)

Cluster size (atoms)	Temperature (K)	Number of observations	Mean-square displacement ( $\text{\AA}^2$ )	Activation energy <sup>a</sup> (eV)
1	296	70	$6.2 \pm 1.0$	0.84
2	352	57	$14.7 \pm 1.0$	0.97
3	366	50	$9.6 \pm 1.5$	1.02
4	366	50	$4.1 \pm 1.5$	1.05
5	366	50	$15.7 \pm 2.4$	1.01
6	394	75	$2.9 \pm 0.5$	1.14
7	394	36	$59.5 \pm 11.3$	1.04
8	394	45	$3.0 \pm 1.0$	1.14
9	440	80	$10.6 \pm 1.9$	1.22
10	380	50	$6.1 \pm 1.1$	1.07
12	455	40	$26.6 \pm 5.4$	1.23

<sup>a</sup>Calculated assuming  $D_0 = 10^{-3} \text{ cm}^2/\text{sec}$

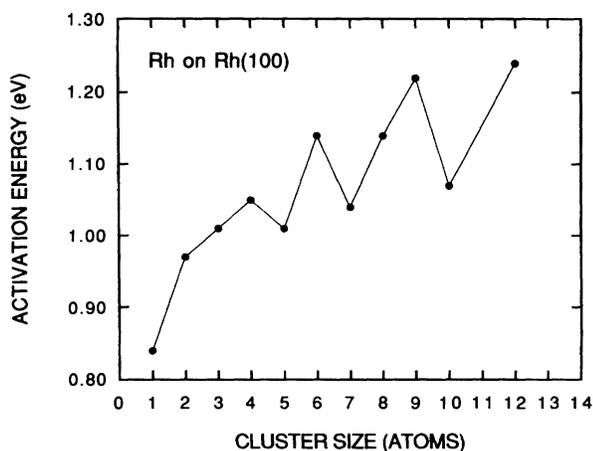


FIG. 2. A plot of the measured activation energy of surface diffusion for Rh clusters on Rh(100). The low mobility of clusters with compact geometric shapes cause the activation energy to oscillate as a function of cluster size.

Figure 2 shows a plot of the calculated activation energies of surface diffusion as a function of cluster size. Although subject to the assumption of a size-independent Arrhenius prefactor, calculations of the activation energies are useful in that they permit one to examine the mobilities of different-sized clusters measured at different temperatures on a single plot. The oscillatory nature of cluster mobility as a function of cluster size is evident in Fig. 2, as is the fact that clusters whose atoms are in compact configurations (i.e., four-, six-, nine-, and twelve-atom clusters) have higher activation barriers than less compact structures. As indicated below, this behavior provides compelling evidence that movements of the individual edge atoms are of critical importance in defining the overall mobility of a cluster.

Insight as to why clusters with compact shapes are less mobile than clusters with extra atoms at the periphery can be gained from theoretical calculations of cluster diffusion. Molecular dynamics simulations of Ag cluster diffusion on Ag(100) by Voter [7] indicate that diffusion occurs by sequential displacements of individual atoms at the edge of the cluster, or by a process he calls "edge-atom running." The calculations predict the same oscillatory size dependence of cluster mobility as observed experimentally for Rh on Rh(100). The mobility of clusters with compact geometric shapes, referred to as "stable blocks" by Voter, is found to be lower because the activation energy required to break an edge atom free from the cluster is higher. A comparison of the calculated detachment energies for atoms from tetramers and pentamers illustrates this point. The displacements are shown schematically in Fig. 3. The calculations indicate that to detach an atom from the corner of a square tetramer [Fig. 3(a)] requires an energy of 0.81 eV. To detach the

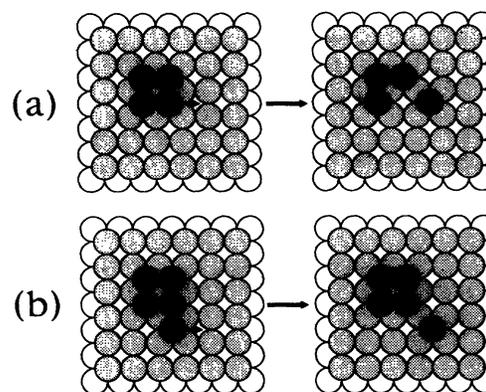


FIG. 3. (a) and (b): schematic drawings illustrating the rate-determining displacements for the diffusion of tetramers and pentamers on fcc(100) surfaces.

peripheral atom of a pentamer [Fig. 3(b)], however, requires only 0.56 eV. Similar results (2.0 vs 1.4 eV) were found even earlier for the system of Rh on Rh(100) [19], but these results are probably not as reliable because a less-sophisticated interaction potential (Lennard-Jones) was used. More recent molecular statics calculations using embedded atom method (EAM) potentials for Ni on Ni(100) [8] yield values of 1.0 and 0.68 eV. In all cases the energy to move the peripheral atom from the pentamer away from the cluster is significantly less than the energy required to remove a corner atom from a tetramer.

The calculations also indicate that the initial detachment-type displacements shown in Fig. 3 are rate limiting. The remaining steps required to produce a net motion of the cluster involve either the return of the initially displaced atom to a site adjacent to the cluster or displacements of atoms along the cluster's periphery. The activation energies associated with these displacements, especially those for diffusion along the edges, are quite low. The calculated values of these barriers along with the optimal diffusion paths for tetramers and pentamers on the (100) surfaces of Rh, Ag, and Ni are given in the original articles [7,8,19]. It is expected that the same arguments will hold for the enhanced mobility observed for heptamers versus hexamers and larger clusters.

The low activation barriers for atoms to move along the edge of a cluster predicted in the calculations mentioned above are also observed in the present experiments. As an example, Fig. 4 shows field ion micrographs of an octamer, whose stable configuration is a square with one of the corner atoms missing. Between each photograph in Fig. 4, the temperature is raised to 277 K. It is apparent that the corner vacancy (indicated by the arrow) moves from corner to corner during the heating intervals. This indicates that the peripheral atoms are moving around the cluster at 277 K. The observation of displacements at this temperature corresponds to an activation

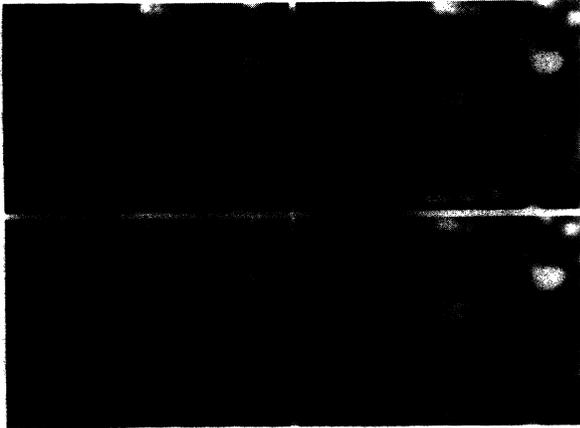


FIG. 4. (a)–(d): field ion micrographs showing displacements of a “corner vacancy” for a Rh octamer on Rh(100). Between each photograph the sample was heated to a temperature of 277 K for 30 sec. Net displacements of the entire cluster occur only when the temperature is increased to 390 K.

energy of  $\sim 0.78$  eV. A net displacement of the entire cluster, however, does not occur until the temperature is increased to 390 K, corresponding to an activation energy of 1.14 eV. Thus, consistent with the theoretical predictions, it is possible for atoms to migrate along the edge of a cluster at temperatures well below those required for net motion of the entire cluster. This observation further supports the argument that the detachment of an atom from the edge is the rate-limiting step in cluster diffusion.

A comparison of the activation barriers for Rh clusters on Rh(100) to earlier FIM measurements of Pt clusters on Rh(100) [6] provides additional evidence for the connection between cluster shape and mobility. For Pt on Rh(100) it was found that trimers, tetramers, and pentamers all diffuse with the same activation energy of 1.03 eV. This result is entirely different than that for Rh on Rh(100) (see Table I). The difference can be explained by the fact that trimers, tetramers, and pentamers of Pt on Rh(100) are more stable as one-dimensional chains than two-dimensional islands. The rate-determining step for migration of chain structures apparently involves the displacement of an end atom, which is insensitive to the length of the chain. The smallest size cluster for which a Pt cluster is stable as an island is a hexamer, which, like Rh, is stable in the shape of a rectangle. Consistent with the present results, the activation energy of surface diffusion for the Pt hexamer is considerably higher – 1.16 eV. In fact, the activation barrier for Pt hexamers on Rh(100) is essentially the same as that for Rh on Rh(100).

In summary, a close connection between the geometric shape of clusters on surfaces and their mobility is established from (i) measurements of the size-dependence

of the diffusion rate for Rh clusters on Rh(100) and (ii) a comparison of these results to Pt clusters on Rh(100). The general agreement between the experimental results presented here and previous theoretical predictions [7,8] provides compelling evidence that the mechanism of cluster diffusion involves sequential displacements of edge atoms. Oscillations in the activation energy of surface diffusion as a function of cluster size would not be expected if the cluster were to glide across the surface as a unit [13]. The relatively low mobility of clusters having compact geometries is attributed to the higher activation energy required to detach an atom from the cluster’s periphery. The resulting size dependence of cluster mobility is expected to play an important role in defining the nature of crystal and epitaxial growth processes.

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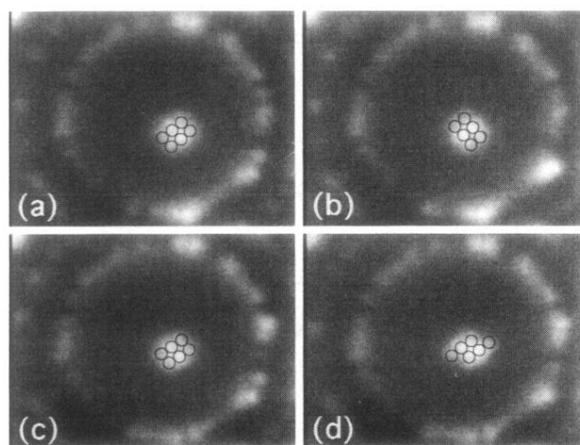


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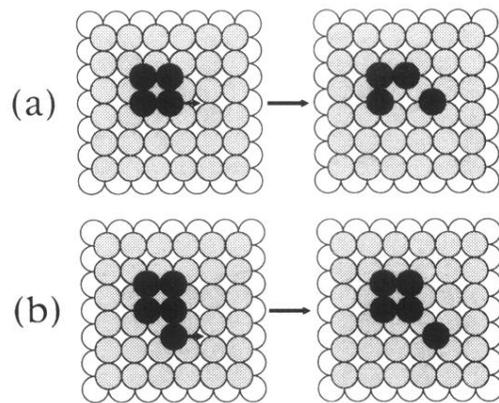


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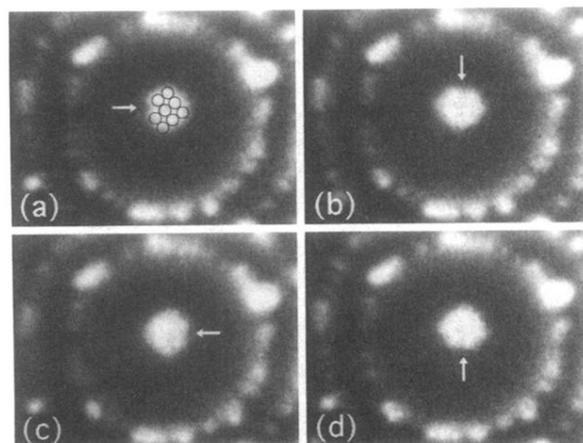


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