Diffusion of Large Surface Clusters: Direct Observations on Ir(111)

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To probe if cluster diffusion is possible without evaporation and condensation of atoms, observations with atomic resolution have been made on clusters on Ir(111) containing from 18 to 39 Ir atoms. For clusters which cannot assume a hexagonal structure, diffusion at $T \geq 550$ K takes place by atoms moving along the edges, changing the cluster shape. For Ir_{19}, with a compact hexagonal arrangement of atoms, no shape changes are observed. Nevertheless, diffusion occurs without loss of atoms, with the cluster frequently moving over distances larger than a nearest-neighbor spacing. [S0031-9007(97)04629-2]

That two-dimensional clusters of more than 50 metal atoms can diffuse over low-index planes of a metal has been known for some time from the work of Fink [1]. What has not been clear are the atomic mechanisms to account for this phenomenon, which is of interest in its own right as well as for its possible contributions to crystal and thin film growth. Over the years, various processes have been proposed that might be involved in the motion of large clusters, among them interface gliding [2–4], movement of dislocations [4–9], diffusion along the cluster edges [10–12], as well as atom evaporation and condensation [11,13–15]. Recently, however, it has been recognized that the dependence of cluster diffusivity upon size can reveal the atomic processes important in the migration of clusters [11,14–19]. From observations of Ag clusters containing more than 100 atoms on the Ag(100) plane at room temperature, Wen *et al.* [11] inferred that cluster movement depends upon the evaporation and condensation of adatoms at the periphery of the cluster. In experiments on clusters made up of vacancies as well as of Ag atoms on Ag(111) surfaces, Morgenstern *et al.* [15,20] came to a similar conclusion, based on quite detailed tests of the size dependence of the diffusivity.

Is atom evaporation and condensation the usual mechanism by which large clusters diffuse on metals, or are there other processes which take place at lower temperatures to facilitate cluster motion? To test if diffusion of large clusters is possible in the absence of adatoms, and *without* any evaporation, we have made direct observations on individual Ir clusters of a fixed size on Ir(111). For this purpose we have used a low-temperature field ion microscope [21] to reveal the cluster periphery with atomic resolution.

On an fcc(111) plane such as Ir(111), it is useful to distinguish two different categories of clusters, depending on the number of atoms in the cluster. If this number can be written as

$$n_c = 1 + 3x(x - 1), \qquad x = 2, 3, \ldots, \qquad (1)$$

then very stable clusters of hexagonal shape will be formed at equilibrium, with edges made up of x atoms. As an example, the hexagonal cluster assembled from 19 Ir atoms in Fig. 1 retains its hexagonal shape, with three atoms per edge, until it disappears at temperatures $T > 700$ K.

Clusters in which the number of atoms does not equal n_c must assume a less compact shape and exist in different forms. Iridium clusters made up of 18 atoms, which we examine first, exist in four energetically different forms, illustrated in Fig. 2; in all four forms the cluster atoms have the same number of nearest neighbors. Ir_{18} is significantly less stable than its larger neighbor, Ir_{19}. On heating to $T > 600$ K the cluster dissociates, and the freed adatom disappears from the surrounding terrace. However, when Ir_{18} is warmed repeatedly for 5 sec in an ordinary thermal environment but at a lower temperature, $T \sim 550$ K, it is clear from Fig. 3 that the cluster moves over the surface.

To ascertain how this cluster moves, its shape has been analyzed in detail after each heating interval, and the location of the atoms is plotted in Fig. 4. It should be noted that in *all* the clusters examined here, the atoms appear in fcc sites, as previously found for Ir_7 [22]. In going from frame 1 to 2, form I transforms to III as two atoms have moved from the left edge of the cluster to the long edge on the bottom. This move is indicated by the
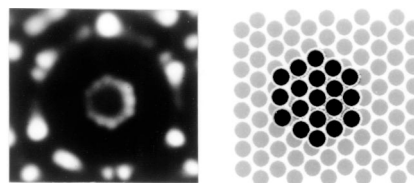

FIG. 1. Hexagonal Ir_{19} cluster on Ir(111) plane. Field ion image, taken at $T \sim 20$ K, is at the left, a schematic of the cluster is at the right. The cluster retains its shape until it disappears after heating at $T > 700$ K. In this and subsequent images, the $[2\bar{1}\bar{1}]$ direction points to the right.
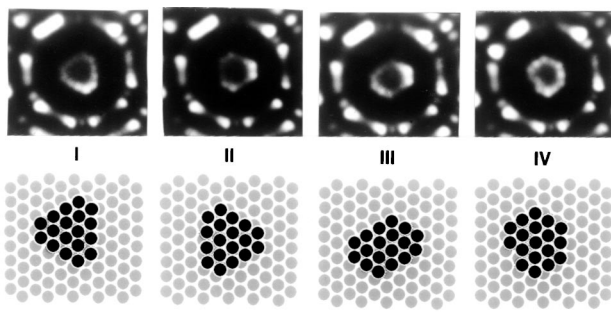
FIG. 2. Four nonequivalent forms of Ir_{18} cluster on Ir(111), observed after equilibration at $T \sim 550$ K. Field ion images of the cluster are at the top, schematics of the atomic arrangement below. Only one configuration is shown for each form, but III and IV can exist in six equivalent configurations.

arrow in frame 1; subsequent changes in atom positions are highlighted in a similar fashion. The arrows are not intended to show actual atomic jumps—rather they mark *where* overall changes have occurred: the heating intervals are too long to isolate individual jumps. In all but six of the heating intervals the cluster undergoes changes. These always seem to involve the transfer of at least two atoms from one place on the cluster periphery to another, so the total number of nearest neighbors remains the same throughout this sequence.

As a result of these rearrangements, Ir_{18} passes through the various forms in Fig. 2 and the center of the cluster moves over the substrate. That this is not just an oscillatory motion, as atoms circle around the periphery of an otherwise stationary core, but a repeatable long-distance displacement, is apparent by examining the cluster in frames 11 and 68 of Fig. 4: Compared to its location in frame 11, the center of the cluster in frame 68 is displaced by $\Delta x = \sqrt{3}\,\ell/2$ and $\Delta y = -3\ell/2$, where ℓ is the distance between neighboring atoms. As expected for random motion, the mean displacement per diffusion interval evaluated from the overall sequence in Fig. 4 differs from zero by less than a standard deviation. The mean-square displacement $\langle \Delta R^2 \rangle$ amounts to $(0.097 \pm 0.015)\ell^2$, which gives a diffusivity $D = (3.6 \pm 0.6) \times 10^{-2}$ Å^2/sec. Migration over the surface has occurred *without* loss of any atoms from the cluster, merely by shape changes as atoms move along the cluster periphery.
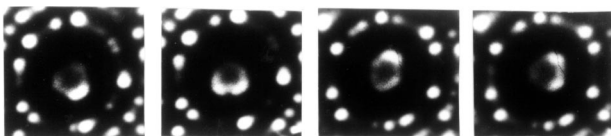

FIG. 3. Movement of Ir_{18} over Ir(111) after heating at $T \sim 550$ K without any electric fields applied. Field ion images record changes after four, five, and one heating intervals of 5 sec duration each. In this series, the cluster center has moved up and to the right.

The same general events also appear to participate in the motion of larger Ir clusters over the (111) plane. In Fig. 5 are mapped the configurations of an Ir_{36} cluster after 5 sec heating intervals at $T \sim 650$ K. There is one difference from the behavior of the smaller cluster: In contrast to the movement of Ir_{18}, shape changes now always involve the transfer of three edge atoms, as is necessary in order to maintain the number of nearest neighbors constant. It is worth noting that Ir_{36} starts to evaporate at $T > 680$ K, but movement over the surface already takes place at significantly lower temperatures, without any loss of atoms from the cluster, merely by repeated rearrangement of the shape as atoms are repositioned at the periphery of the cluster.

How do Ir clusters with the correct number of atoms n_c to form a compact structure behave on Ir(111)? Once in a hexagonal form, these clusters do *not* change their shape at temperatures below that at which they disappear. Nevertheless, movement over the surface *does* take place. In Fig. 6, a compact cluster of 19 atoms has been brought to 690 K for 10 sec; after heating, the cluster has moved
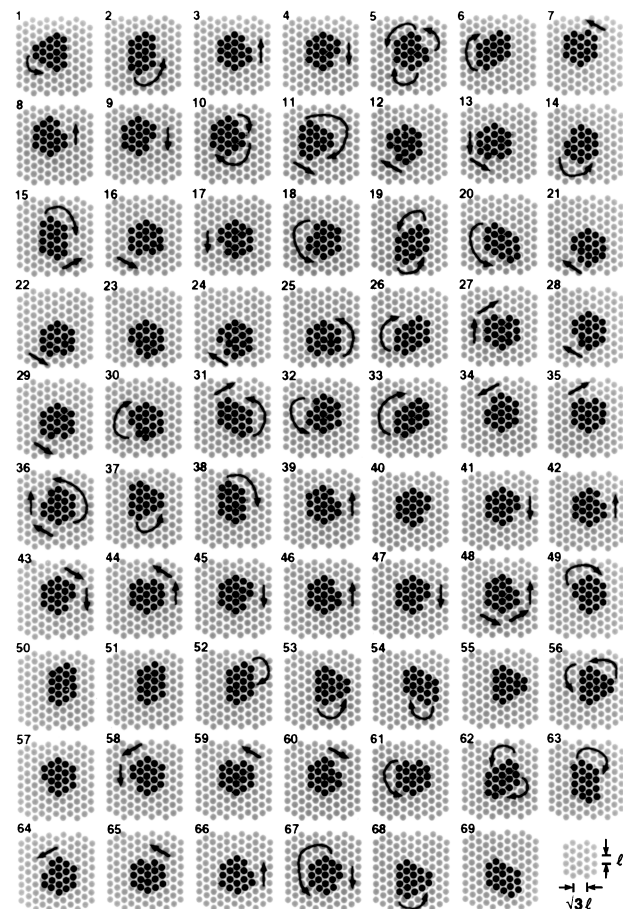

FIG. 4. Map of Ir_{18} cluster on Ir(111), derived from field ion images taken after 5 sec diffusion intervals at $T \sim 550$ K. Arrows indicate how the cluster shape will change in the next frame. Tail of arrow points to atoms that will move; head shows where atoms will appear in next frame.
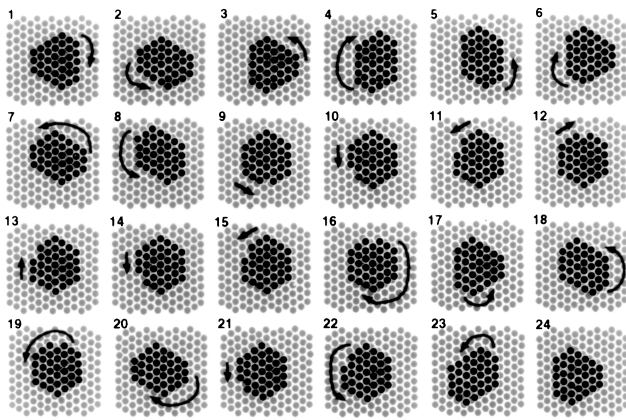
FIG. 5. Position of atoms in Ir_{36} cluster on Ir(111), observed after 5 sec heating interval at $T \sim 650$ K. Arrows point to location where atoms will appear after the next diffusion interval. Cluster has moved from upper right in frame 6 to lower left in frame 24.

over the surface. That it has done so without loss of atoms is clear. Movement continues at 690 K, a temperature at which a cluster with less than 19 atoms would long have evaporated. Dissociation followed by recombination with an adatom from the surrounding terrace is not a possibility. Ir atoms on an Ir(111) surface have been observed to incorporate into descending lattice steps on a time scale of seconds even at temperatures below 200 K [23]. When other than compact clusters, for example, Ir_{39} or Ir_{18}, are dissociated, the freed atoms disappear from the surrounding terrace, and only the diminished cluster remains behind.

Observations have been made after each of more than a thousand heating intervals in order to probe how Ir_{19} migrates over the surface. The displacements of the cluster center have been mapped out, yielding a mean-square displacement $\langle \Delta R^2 \rangle = (0.28 \pm 0.02)\ell^2$. That the movement of the center cannot be described as a simple random walk between nearest-neighbor fcc sites on the (111) plane becomes clear on closer examination.
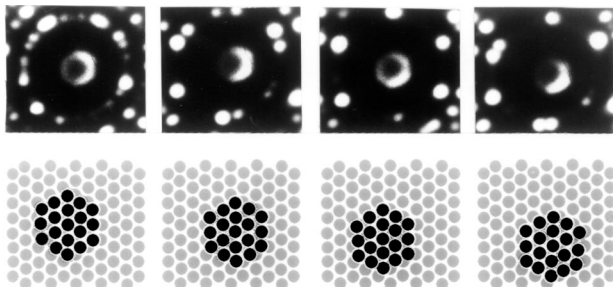

FIG. 6. Compact hexagonal Ir_{19} cluster moving over Ir(111) after heating at $T \sim 690$ K. Field ion images on top, schematics of cluster below. Changes are shown after 6, 14, and 10 heating intervals of 10 sec duration each. As the cluster moves away from the center, there are changes in the image intensity, but not in the number of cluster atoms.

For a random walk [24], the mean-square displacement $\langle \Delta R^2 \rangle$ is given as

$$\langle \Delta R^2 \rangle = NL^2 = 4Dt, \qquad (2)$$

where N is the mean number of jumps during the diffusion interval t, and L is the root-mean-square jump distance. If transitions of Ir_{19} always take place between adjacent fcc sites, at a distance ℓ from each other, then the mean number of jumps N during the interval t, estimated from Eq. (2), is just 0.28. For uncorrelated jumps, the actual number during any given heating interval is governed by a Poisson distribution. With N as estimated here, the likelihood of more than a single jump occurring is small, less than 1/30; should jumps be longer, this probability would be smaller still.

A plot of the displacements actually observed, such as the one for a run of 140 observations shown in Fig. 7, is therefore to a reasonable approximation a plot of the distances covered in single jumps. If we compare these displacements with distances between fcc sites on the (111) plane, shown in the inset of Fig. 7, it is immediately clear that the cluster center does *not* execute a random walk just between nearest-neighbor fcc sites. There are many heating intervals in which no displacements are observed at all; when a displacement is eventually observed, it is frequently longer than a nearest-neighbor distance ℓ. The distribution of nonzero displacements derived from all the observations is shown in Fig. 8. Long displacements are common; more than $\frac{1}{3}$ exceed the distance ℓ between adjacent fcc sites on Ir(111), which is the most probable of the displacements.

Although the mechanism by which these movements occur is not immediately obvious, diffusion of Ir_{19} is best described as an occasional displacement over a significant distance, large by comparison with the separation between
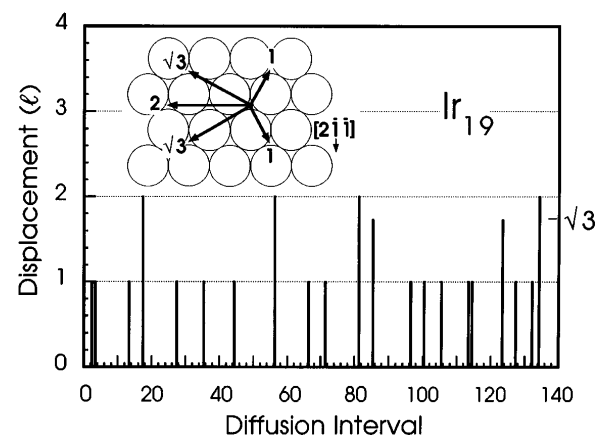

FIG. 7. Movement of Ir_{19} over the Ir(111) plane. Absolute value of the displacement of the cluster center after 10 sec intervals at 690 K is plotted in units of the spacing ℓ between nearest-neighbor fcc sites. Inset shows relevant distances (in the same units) on an fcc(111) plane.
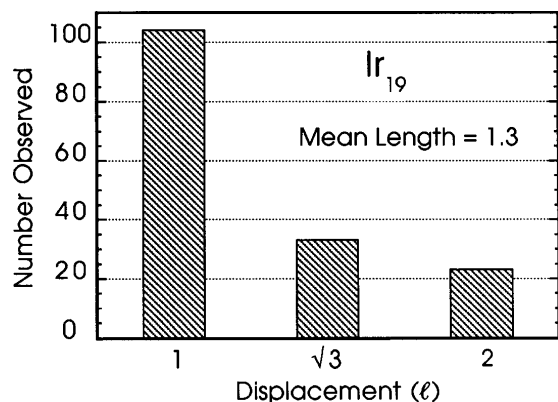
FIG. 8. Frequency of nonzero displacements of Ir_{19} cluster observed after 10 sec heating intervals at 690 K. Displacements longer than the distance ℓ between nearest-neighbor fcc sites make up 35% of the jumps.

adjacent fcc and hcp sites on the (111) plane. We note that this picture is at variance with what is expected for motion of compact clusters by a dislocation mechanism. As a dislocation passes through a cluster, the atoms move between adjacent sites on the surface [7], certainly not through distances long by comparison with ℓ which are observed.

What the present studies have shown is that on the close-packed Ir(111) plane, clusters made up of 18 or more Ir atoms are able to diffuse in the absence of any adatoms on the surface, and without evaporation of atoms from the clusters. For clusters in which the number of atoms does not permit a compact shape, diffusion over the surface takes place by cluster atoms migrating along the edges to change the shape of the cluster. For compact, hexagonal clusters, diffusion is possible even though changes in the shape of the cluster are not observed. The mechanism of this motion is not yet established. However, for Ir_{19}, the example studied quantitatively, dislocation motion does not appear likely, and neither diffusion of atoms around the edges of the cluster nor atom evaporation and condensation are observed. A possibility that remains is that diffusion occurs by clusters as a whole gliding over the surface.

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