

Surface Diffusion of Compact and Other Clusters: Ir_x on Ir(111)

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Quantitative measurements have been made of the diffusivity D of larger Ir clusters on Ir(111) to explore the mechanisms of motion. For noncompact Ir_{18} , migration occurs by changes in overall shape as atoms diffuse along cluster edges; in an Arrhenius plot, the prefactor D_0 is $\sim 10^{-3}$ cm²/s, comparable to that for single atom motion. For Ir_{19} and Ir_7 , clusters which exist as compact closed shells, diffusion by changes in overall shape is shown to be unlikely. Migration occurs by an entirely different mechanism, with prefactors D_0 being 3 or more orders of magnitude higher than for Ir_{18} . [S0031-9007(98)07759-X]

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During the past few years the important role played by clusters in the growth of films on crystals has become generally apparent; as one consequence, much attention has been focused on the mobility of clusters on metal surfaces [1–8]. The dependence of diffusivity upon cluster size has been extensively studied [1–3,9–14] in attempts to explore the atomic mechanisms by which large clusters move over surfaces, but recently it has been realized that this approach may not yield unequivocal information [3,4]. However, direct observations of single clusters in the field ion microscope (FIM) have established that, for other than compact Ir clusters on Ir(111), motion occurs exclusively by atoms diffusing along cluster edges [15]. Nevertheless, quantitative information about the diffusion of larger clusters is still quite limited; hardly anything is known about the kinetics of motion—for fcc metals, such information is so far available only for small clusters of five atoms or less [16]. Here we present the first quantitative studies of the diffusion parameters of larger clusters, which demonstrate the unique behavior of compact, closed-shell structures.

When a noncompact cluster such as Ir_{18} , illustrated in Fig. 1(a), is heated briefly to 550 K on an Ir(111) surface and then imaged again in a FIM [17], the shape of the cluster is seen to have changed as four atoms have moved along the edge of the cluster. By measuring the displacement Δx_i of each of the n atoms in the cluster, the displacement Δx_c of the center of mass is obtained as usual from $\Delta x_c = \sum_{i=1}^n \Delta x_i/n$. The diffusivity of the cluster center is derived by repeating this heating and measuring cycle roughly 100 times to obtain an estimate of the mean-square displacement, just as in diffusion studies of individual adatoms [18]. Figure 2(a) shows the diffusivity of Ir_{18} derived in this way at different temperatures, plotted according to the Arrhenius equation $D = D_0 \exp(-E_D/kT)$ at temperatures ranging from 520 to 580 K.

Noteworthy is the value of the prefactor, $D_0 = 7.8(\times 4.5^{\pm 1}) \times 10^{-4}$ cm²/s. It is of the same magnitude

as in the diffusion of single Ir atoms on Ir(111) [19], shown in Fig. 2(b). The activation energy E_D for the migration of Ir_{18} is, of course, much higher, 1.63 ± 0.07 eV compared with 0.290 ± 0.003 eV for Ir adatoms, but that is expected: in moving along the cluster edge, an atom is in much stronger interactions with its environment than an adatom on a bare (111) surface. There is little that is striking about the diffusion of Ir_{18} , except for the high temperature at which it occurs.

Clusters of 19 Ir atoms on Ir(111) behave quite differently. As is evident from the image in Fig. 1(c), Ir_{19} is a compact hexagonal cluster, with three atoms at each edge. The overall shape of the cluster before and after diffusion is the same and does not appear to ever change. How then does this compact cluster move over the surface? To explore this question, we have measured the distribution of the displacements [20] made by the cluster center during 10 s diffusion intervals at 690 K. Since the cluster does not change its shape, the center of mass is readily found once the location of the corner atoms is established. The displacements from the origin, mapped into the two upper quadrants of the (111) plane, are shown in Fig. 3,

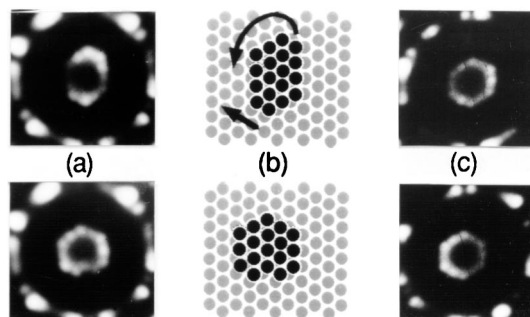


FIG. 1. Movement of Ir clusters over Ir(111). (a) Field ion image of Ir_{18} , a noncompact cluster, before (top) and after (bottom) 10 s heating at 550 K. (b) Schematic of Ir_{18} cluster in (a), with arrows indicating atoms that have moved. (c) View of compact Ir_{19} cluster before (top) and after (bottom) 5 s heating at 700 K has moved cluster to left.

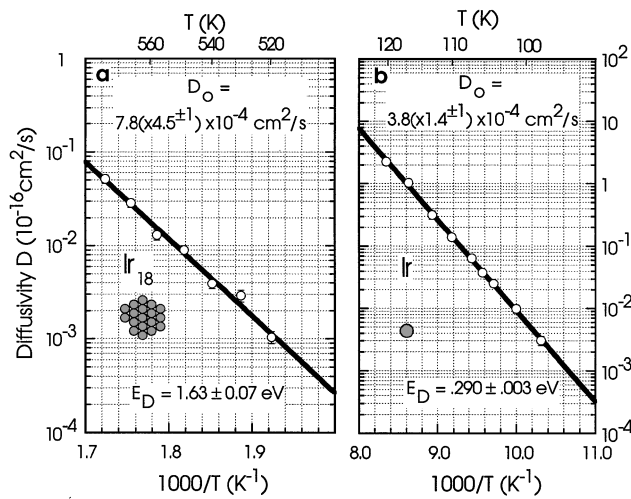


FIG. 2. Temperature dependence of diffusivities on Ir(111) derived from mean-square displacements. (a) Noncompact Ir₁₈ cluster. (b) Single Ir adatom.

compared with distributions obtained from kinetic Monte Carlo simulations [21] of different random walks of the center. It is clear that, if the center makes only transitions between adjacent fcc sites at a rate α , then the simulated distribution, listed under the heading “single” in Fig. 3, is not in satisfactory agreement with the experiments, given in bold numerals. To better represent the actual distribu-

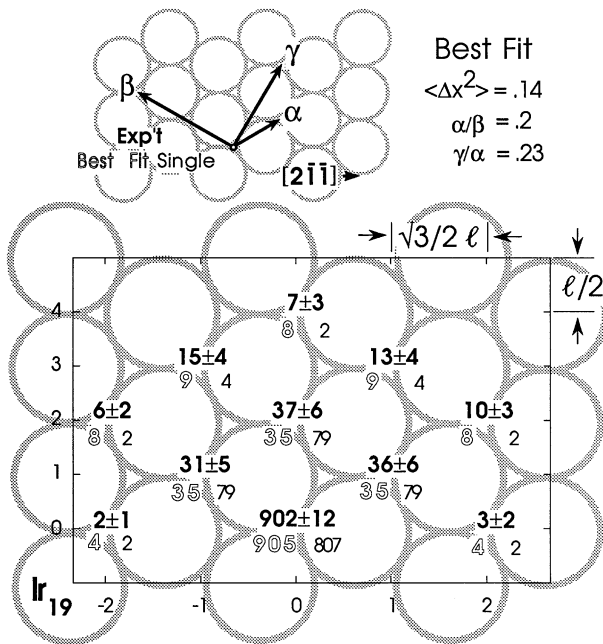


FIG. 3. Distribution of center-of-mass displacements for compact Ir₁₉ cluster during 10 s heating at 690 K. Types of jumps are indicated in the inset at top. The number of observed displacements is shown in bold numerals, best fit to the experiments in outline numerals just below and to the left. The fit assuming only nearest-neighbor transitions given in normal numerals is at bottom right. ℓ = nearest-neighbor distance.

tion, we also have to invoke double jumps, such as from (0, 0) to (-2, 2), at a rate β , as well as direct transitions from (0, 0) to (1, 3), at a rate γ . The best least-squares fit (in outline numerals) to the observed distribution of displacements is obtained for $\langle \Delta x^2 \rangle = 0.14$, $\beta/\alpha = 0.2$, and $\gamma/\alpha = 0.23$.

Transitions to other than nearest-neighbor fcc sites obviously play a significant role, contributing $\sim 60\%$ to the diffusivity of the compact Ir₁₉ cluster at 690 K [22]. This seems to eliminate the possibility that such compact clusters migrate by a Frenkel-Kontorova mechanism, as suggested by Hamilton [7]: This mechanism would not move the cluster through the distances observed.

The Ir₁₉ clusters are always found in the same compact, hexagonal shape; nevertheless there is a possibility that motion might still occur as a result of atoms diffusing along the cluster edges to change the shape. We need only postulate that the intermediate shapes formed in this way are of much higher energy than the compact hexagonal arrangement of atoms actually observed, so that the intermediates exist just briefly before reverting to the compact format. Of course, there is a limit: such intermediate structures cannot have an energy so high that atoms detach from cluster edges during diffusion. Ir₁₉ motion has been observed at temperatures from 650 to 700 K. At these temperatures, Ir₁₈ is not stable and dissociates rapidly [23]. The loss of even one atom from an edge during diffusion of the compact Ir₁₉ cluster would lead to the loss of the cluster rather than to diffusion.

To probe the possibility of changes in overall shape as the mechanism underlying the mobility of Ir₁₉, we have examined the stability of intermediate structures that arise when adatoms move around the edges. These intermediates cannot be created by heating Ir₁₉. Instead, they have been made up in a two-step process. An Ir₁₈ cluster is first produced by partial field evaporation of the outermost (111) plane followed by annealing at ~ 550 K to create one of four different allowed forms. A single Ir atom is then deposited on the surrounding terrace, which is held at ~ 100 K until the atom joins up with the central Ir₁₈ cluster to form the metastable Ir₁₉ clusters shown in Fig. 4. After heating at temperatures in the range of 675–700 K at which diffusion occurs, these intermediates either convert into the stable compact form or else disappear from the (111) plane entirely. The probability of these two events varies from one structure to another, as indicated in Fig. 4, but for all of the metastables tested there is a finite probability of the cluster disappearing during heating, rather than continuing to diffuse. Changes in overall shape as atoms diffuse around the cluster periphery therefore do *not* appear likely as the means by which migration of compact Ir₁₉ takes place.

The mechanism by which compact clusters such as Ir₁₉ diffuse is clearly different from that operating for noncompact structures; this difference should also reveal itself in the kinetics of diffusion. We have therefore

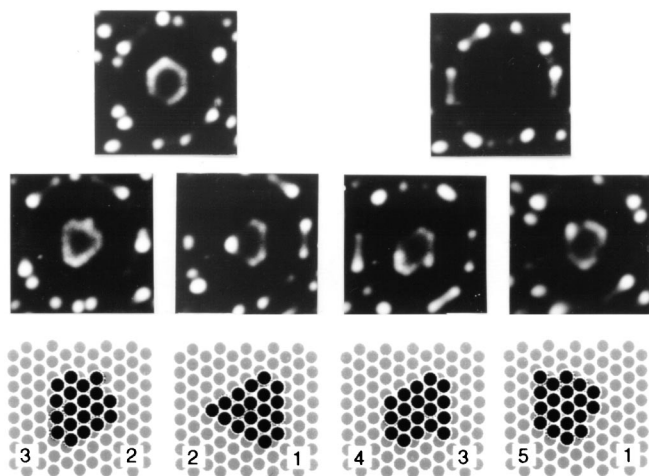


FIG. 4. Stability of metastable Ir₁₉ clusters on Ir(111). Field ion images of metastable forms are shown in the center, with schematics of their structure below. After heating for 5 s at temperatures from 675–700 K, either a compact Ir₁₉ forms (top left) or else the cluster disappears from Ir(111) (top right). In the schematics of metastable structures, the number of trials resulting in the formation of a compact cluster is shown at the left, compared to the disappearance at the right.

measured diffusivities of Ir₁₉ at temperatures ranging from 650 to 700 K. The results in Fig. 5(a) are surprising indeed. The prefactor, $D_0 = 13(\times 2.6^{\pm 1}) \text{ cm}^2/\text{s}$, is 4 orders of magnitude greater than for Ir₁₈; the diffusion barrier $E_D = 2.54 \pm 0.06 \text{ eV}$ is 1.5 times that found for Ir₁₈. What a difference one atom makes. Is this type of behavior characteristic of the diffusion of compact, closed-shell clusters? Could this unusually high prefactor be associated in some way with the occurrence of long jumps, which characterizes the diffusion of Ir₁₉? Is this perhaps some artifact of the temperature measurements,

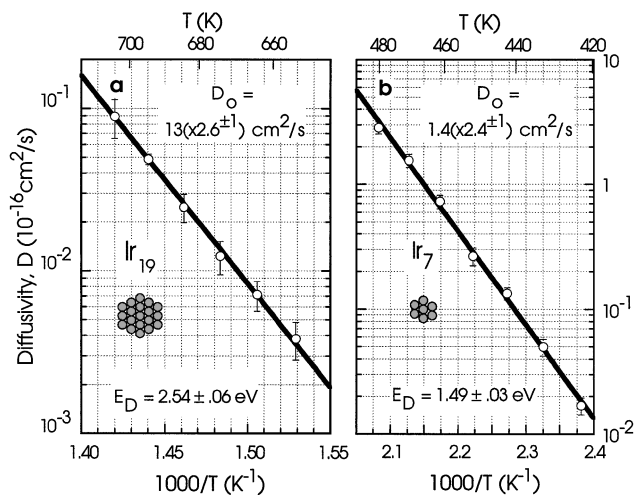


FIG. 5. Temperature dependence of diffusivities for compact Ir clusters on Ir(111) [(a) Ir₁₉ and (b) Ir₇]. Prefactors are more than 3 orders of magnitude higher than for noncompact Ir₁₈ in Fig. 2.

or possibly just a consequence of the high temperatures, higher than in any other direct observation of single particle diffusion?

To check out the different possibilities, we have also examined the diffusion of Ir₇, the next smaller compact cluster, with only two atoms per side. As appears from the plot of the temperature dependence [in Fig. 5(b)] the activation energy for diffusion of Ir₇, $E_D = 1.49 \pm 0.03 \text{ eV}$, is quite close to that for the diffusion of the noncompact Ir₁₈. However, the prefactor $D_0 = 1.4(\times 2.4^{\pm 1}) \text{ cm}^2/\text{s}$ is more than 3 orders of magnitude larger—despite the fact that the temperature range for the Ir₇ measurements is $\sim 100 \text{ K}$ below that for Ir₁₈. It is clear that an unusually high prefactor is characteristic of the motion of compact clusters; it is *not* connected with the high temperatures of the measurements.

To learn more about the diffusion of Ir₇, the distribution of cluster displacements has also been measured, at $T = 450 \text{ K}$. From the comparisons of observed and simulated distributions in Fig. 6, it appears that the contribution from the two types of long jumps is small, each amounting to only 4% of the rate α of jumps between nearest-neighbor fcc sites. Evidently the high prefactor found for both compact clusters, Ir₁₉ and Ir₇, is *not* intimately tied to the participation of long jumps in diffusion. It is rather a characteristic of the unique mechanism by which compact clusters migrate over the (111) plane. The high prefactor is certainly not consistent with diffusion by dislocation motion—for this mechanism, molecular dynamics simulations suggest a prefactor similar to that for single atom motion [7].

How then do compact clusters migrate over the Ir(111) plane? One remaining possibility is that, in diffusion, the atoms in a cluster move over bridge sites on the (111) plane at much the same time, preserving the overall shape as the cluster glides over the surface

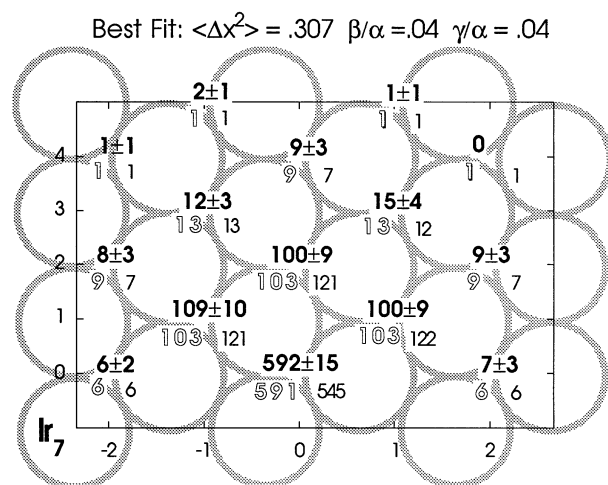


FIG. 6. Distribution of displacements in diffusion of compact Ir₇ during 5 s heating intervals at 450 K. Conventions are as in Fig. 3. The contributions of β and γ are small.

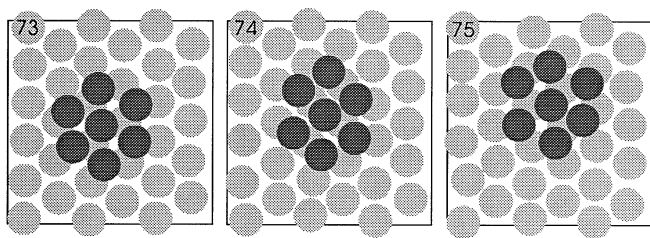


FIG. 7. Molecular dynamics simulations of Ir_7 diffusion on $\text{Ir}(111)$. Adjoining frames show the location of cluster (dark) and surface atoms (light) after 0.5 ps at 1350 K. In this sequence, the cluster moves up and to the right, undergoing small distortions while retaining its overall shape.

while it undergoes small structural distortions. Molecular dynamics simulations of the diffusion of Ir_7 on $\text{Ir}(111)$ using a Sutton-Chen potential [24] give indications of cluster gliding. Such motion is illustrated by the sequence in Fig. 7, taken from simulations on a 12×12 (111) surface. In ~ 1000 snapshots taken immediately after 0.5 ps intervals at 1350 K (to enhance the number of interesting events), six transitions of this type, and no others, were detected. Gliding therefore seems a likely mechanism for the migration of compact clusters, but we still do not understand the remarkably high prefactors which characterize the diffusivity of both Ir_7 and Ir_{19} .

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