Adatom Motion to Lattice Steps: A Direct View

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Observations of individual iridium atoms diffusing over Ir(111) planes with an iridium cluster at the center reveal an empty zone, ~3 nearest-neighbor spacings wide, around the cluster. In this zone adatoms are never seen. Quantitative studies of the probability of atom incorporation at the cluster, compared to the probability of being trapped at the plane edge, suggest that the empty zone comes about because in the vicinity of the cluster, diffusion toward an ascending step is much more rapid than on a flat terrace, so that adatoms are funneled to the cluster.

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Although crystal growth is of considerable current interest, the individual atomic events important in building a crystal still are poorly understood. For example, in the generally accepted picture of growth from the vapor at low supersaturation [1], atoms that have condensed on the substrate are assumed to migrate over the crystal terraces until they either reevaporate, or else they run into a lattice step, where incorporation can occur; only those atoms that condense within a diffusion distance of a step have a chance to incorporate. A few direct observations using the field ion microscope have been made of single metal atoms approaching ascending lattice steps [2,3]; they appear to be in rough accord with this view. Recently, however, we have carried out the first detailed examination of atomic transport to clusters formed on the close-packed (111) surface of iridium, an fcc metal. These studies suggest that atomic behavior in the vicinity of ascending steps differs from the traditional picture and is actually quite complicated.

Shown in Fig. 1 is a sequence of observations in the field ion microscope [4], giving the location of an iridium adatom around a cluster of 12 iridium atoms at the center of an Ir(111) plane. The cluster in Fig. 1(a) has been formed by field evaporation of the outermost layer of the iridium crystal at ~20 K. Thereafter, a single Ir atom is deposited on the (111) terrace in Fig. 1(b), and the adatom is repeatedly photographed after diffusing over the surface for 5 sec at 105 K. It is important to note that, as is always true in these experiments, atomic motion occurs in an ordinary thermal environment—the field is on only during imaging at low temperatures (~20 K), and brings about no observable lateral displacement of the adatom. After 118 diffusion intervals, the atom has incorporated [in Fig. 1(l)] into the cluster at the center of the plane; from this sequence, it appears that in its migration over the terrace the adatom avoids sites immediately around the cluster.

This impression is strengthened by mapping [5] the paths followed by adatoms as they move from one site to another on an Ir(111) surface with a central iridium cluster on it. In Fig. 2(a) are plotted the sites at which an Ir adatom has been observed prior to incorporating into a cluster of 10 iridium adatoms. Two other sequences on the same surface, but with clusters of 12 and 21 atoms, respectively, are shown in maps 2(b) and 2(c). These maps confirm the impression conveyed by the photographs in Fig. 1. In diffusing over the surface, the iridium adatom is *never* seen within a strip of sites ~3 nearest-neighbor distances l_0 deep around the cluster; that is, there is an empty zone devoid of adatoms around the cluster.

In diffusing over the (111) plane at some distance from the cluster under the conditions prevailing in Fig. 1, the rms displacement of an iridium adatom amounts to $\sim 0.6 l_0$ when the atom makes a displacement, it usually is from one site to the closest site of the same type. However, when incorporation finally occurs, the atom moves across the entire empty strip during one diffusion interval. Such an empty zone has been observed in hundreds of ex-

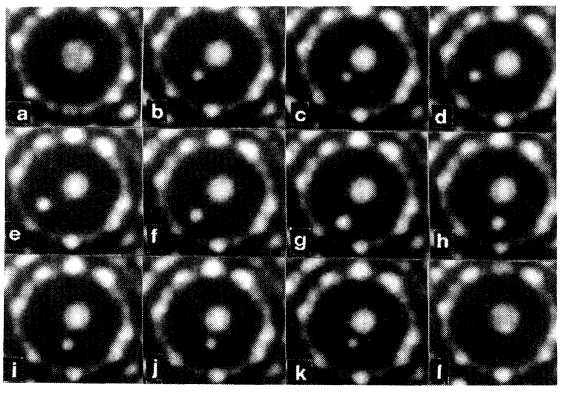

FIG. 1. Diffusion of Ir adatom on Ir(111) plane at 105 K prior to incorporation into Ir_{12} cluster at the center. Images are taken at ~20 K. (a) Central cluster, formed by field evaporation. (b) Ir adatom has been deposited on terrace surrounding cluster. (c) After diffusion interval of 30 sec. (d) 90 sec. (e) 55 sec. (f) 65 sec. (g) 30 sec. (h) 110 sec. (i) 80 sec. (j) 20 sec. (k) 40 sec. (l) After diffusion for another 65 sec, atom has incorporated into cluster.

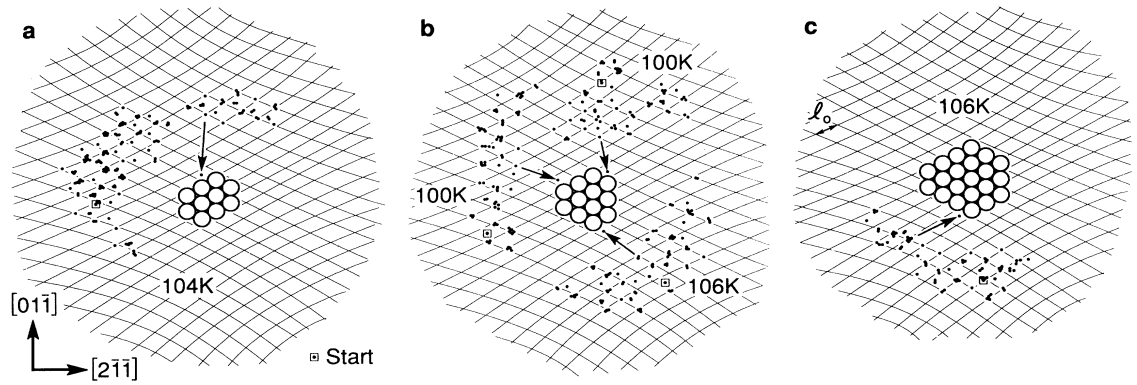

FIG. 2. Map of iridium atom positions prior to incorporation into clusters, formed on Ir(111) by field evaporation. Location of atom upon deposition marked by square; arrow indicates incorporation. Hcp sites are at intersections of grid lines. Observations after 5-sec diffusion intervals at indicated temperatures. (a) Ir_{10} at center. (b) Incorporation into Ir_{12}. (c) Cluster of 21 Ir adatoms at center. l_0 is nearest-neighbor distance.

periments in which an adatom is deposited on the (111) plane with a cluster on it and its subsequent movement followed in detail. This phenomenon is not limited to clusters of 12 iridium atoms, on which this study has concentrated; it has also been observed with larger clusters, made up of 18 and 21 atoms, as well as with clusters of 10 atoms, and appears to be a general effect.

Could the empty zone just be an imaging artifact, brought about by distortion of the paths of the helium ions, which form the image, in the vicinity of the central cluster [6]? To check this, we plot in Fig. 3 the positions observed for atoms on an Ir(111) plane with a central Ir_{12} cluster on it. Thereafter, the cluster is removed by field evaporation, and the binding sites are mapped out in the usual way by allowing an atom to diffuse over the now flat surface. The grid drawn in Fig. 3 is that obtained from observations of the sites on the *bare* Ir(111).

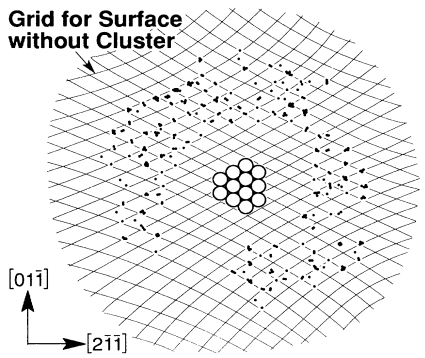

FIG. 3. Location of Ir adatoms after diffusing over Ir(111) with Ir_{12} cluster at the center. Plot obtained by combining observations for different depositions, always of a single atom, on the same plane. Grid lines have been obtained after these observations, by field evaporating the cluster and mapping out binding sites on the bare (111) plane [5].

However, it is clear that the atom positions observed on the surface *with* an Ir_{12} cluster in the center fall quite well on this grid of sites. Even at the boundary with the empty region, only small displacements from the sites on the bare (111) plane can be detected. The empty zone is evidently real, and *not* due to image distortion around the cluster. Contrary to the traditional view, in the vicinity of a step, adatoms do *not* diffuse as they do on a flat surface.

A possible way to account for the unexpected behavior of adatoms in the proximity of a cluster is to postulate a higher diffusion barrier, which keeps atoms from moving closer toward the cluster. Once an adatom does penetrate into the empty region, however, jumps toward the cluster take place more rapidly, over reduced barriers, until the atom is captured at the step. To examine this possibility, it is useful to first look at the behavior of atoms approaching the *descending* step delimiting the (111) plane.

In the temperature range from 100 to 128 K, atoms wandering to the vicinity of the descending step are trapped close to but generally not at the very edge, just as found in the diffusion of atoms on large clusters on the (111) plane [3]. This is clear from Fig. 4, showing the positions of adatoms, on a (111) plane without a central cluster, that eventually come to rest in the vicinity of the descending step. Even at the lowest temperature (100 K), atoms are able to diffuse into the region bordering on the descending step. Any additional barrier to the movement of atoms toward the strip of sites adjacent to the step would have to be small, $< \frac{1}{10}$ the activation energy of $\sim$6 kcal/mol for diffusion of Ir atoms on Ir(111). Once in this strip, however, the atoms are trapped; that is, the potential binding the atom is deeper close to the edge than in the interior of the plane.

We can now view the migration of an iridium atom over a (111) plane with a central cluster on it as a random walk between an absorbing boundary, in the vicinity of the descending step, and a partly reflecting energy bar-

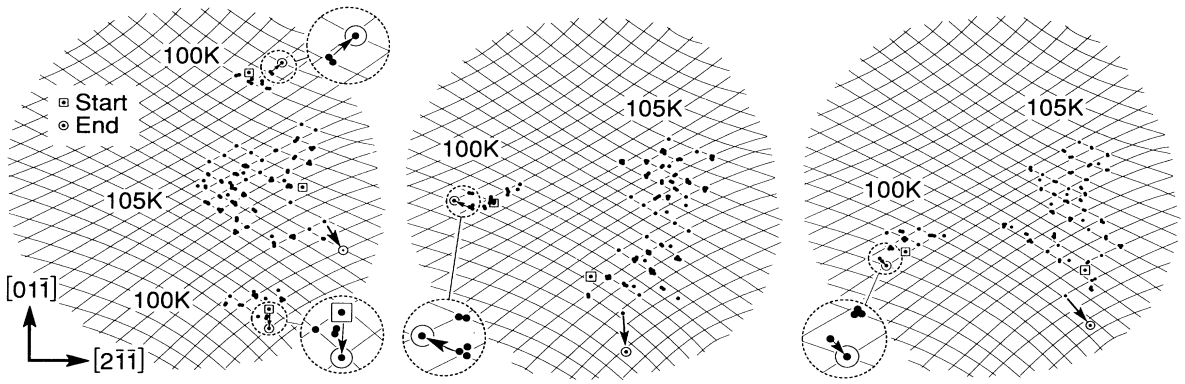

FIG. 4. Behavior of Ir adatoms near descending step which terminates the otherwise flat (111) plane. Shown are positions of adatom after 5-sec diffusion intervals at indicated temperature. Insets give magnified view of final transition.

rier, of unknown height, which separates the plane from the empty region around the cluster. Once an atom surmounts this barrier, it can immediately move across the empty zone, in which diffusion barriers are much reduced, to be captured by the cluster. An atom which instead moves into the zone around the descending step will be trapped there. If this description is appropriate, then at low temperatures we expect most atoms diffusing over the surface to eventually be captured in the region around the descending step. At higher temperatures, however, at which the thermal energy is large enough to permit atoms to pass over the barrier into the empty region, an increasing fraction of the atoms should be incorporated at the central cluster. In Fig. 5 is shown the ratio of the number of atoms N_i incorporated into the cluster compared to the number N_t trapped near the descending step, observed at different temperatures. This ratio is close to unity, independent of temperature. If there is a barrier to incorporation, it is the same as the barrier to trapping within ± 150 cal/mol.

We conclude that there is no significant energy barrier keeping atoms out of the region immediately around the central cluster. On the contrary, atoms which in their random migration over the surface enter this zone find the barrier to diffusion toward the cluster lowered; they migrate rapidly toward the cluster and are incorporated there. The fact that in our experiments adatoms are never observed in the empty zone, even at temperatures as low as 100 K, is consistent with a lowering of the diffusion barrier in the direction toward the cluster on the order of 10% below the diffusion barrier on the flat Ir(111); a schematic illustrating this effect is given in Fig. 5. The actual course of the potential does not emerge from the present observations, but from other experiments it appears that binding of atoms in the empty region may in fact differ profoundly from binding on a perfect (111) plane.

What is the cause of the unusual behavior of atoms close to the lattice step? The traditional view of crystal growth ignores the disturbance of the lattice brought about by the presence of steps. At steps on metals the distribution of electrons is altered: electrons fill in depressions to create a dipole layer with its positive end away from the surface, lowering the work function [7]. However, the dipole on both a step and on an adatom is expected to have the same sign [8], leading to a small net repulsion rather than the attraction needed to explain high mobility toward the cluster. A more likely cause of the phenomena we have observed is the change in the atomic positions around a step attendant upon the redistribution of electrons [9]. Estimates of the structure of steps and clusters [10–13], made in different approximations, all point to significant realignments in the location of lattice atoms, which are bound to affect the behavior of adatoms in the immediate vicinity of a step.

No matter what the exact cause, our experiments indicate that transport of adatoms to lattice steps is quite different from ordinary diffusion over perfect crystal facets: within a few nearest-neighbor spacings of an ascending step, that is, within the empty region, adatoms move rapidly toward the step to become incorporated; the region immediately around a cluster thus serves to funnel

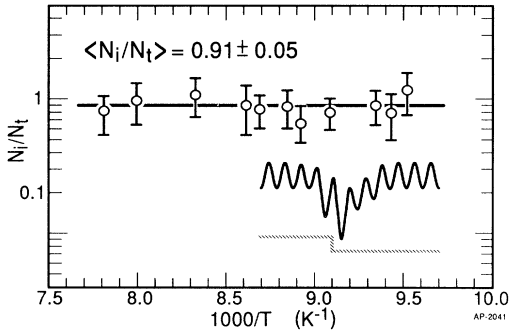

FIG. 5. Ratio of number of Ir atoms N_i incorporated into central Ir_{12} cluster on Ir(111), compared to N_t, the number trapped close to the edge of the (111) plane. At the lower right is a sketch of the potential, consistent with our data, for an adatom moving across a step.

atoms toward the step. In the capture of atoms migrating over the surface the effective radius of the cluster must therefore be taken as the actual radius increased by the width of the empty zone.

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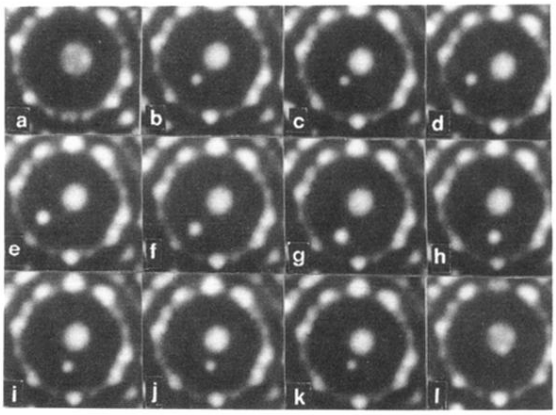

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