Self-Adsorption Sites on a Close-Packed Surface: Ir on Ir(111)

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The binding sites for adsorption of a single iridium atom on a close-packed iridium (111) plane have been mapped out in the field-ion microscope by observing the location of one iridium atom after diffusion over the surface at $T \sim 100$ K. Both surface (hcp) and bulk (fcc) sites are found occupied, but the former are favored, with the free energy for adatoms $\sim$370 cal/mol lower on surface sites. This free-energy difference is small compared to the barrier of 6.2 kcal/mol which separates equivalent sites in surface diffusion.

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Thanks primarily to studies with LEED, and more recently with surface extended x-ray-absorption fine structure, there is now considerable information available about the structure of overlayers and the location of atoms in such layers in relation to the substrate.[1] In contrast, very little has been done to characterize the binding sites for isolated adatoms on crystals, even though such information is of considerable interest in understanding growth phenomena. Flahive and Graham[2,3] imaged single nickel as well as tungsten adatoms on tungsten (111) using the field-ion microscope[4] (FIM) and were able to directly observe the symmetry of the adsorption sites. They concluded that in the center of the (111) plane, nickel as well as tungsten adatoms sit at bulk sites, that is, at sites which continue the normal bcc structure. More indirect FIM studies of adatoms on tungsten have also been made, on (111),[5] (211), (321),[3] and on (110),[6] but no information at all is available on the binding of single adatoms on a close-packed surface. We wish to report here the first identification of binding sites for individual atoms on such a surface, the (111) plane of an fcc crystal, iridium.

LEED studies on a variety of clean fcc metals suggest that the (111) surfaces are not reconstructed,[1] and have the atomic arrangement of a plane in the bulk; detailed measurements by Chan *et al.*[7] have demonstrated that Ir(111) conforms to this pattern. In Fig. 1 a map is shown of atom locations in the outermost (111) layer of an fcc crystal. Within the unit cell there are two valley sites, each of threefold symmetry, but differing in their surroundings: There is a lattice atom directly underneath a surface site but not underneath a bulk site. Addition of an adatom to a bulk site continues the *abcabc* pattern of (111) planes characteristic of an fcc lattice and this location for atom binding will therefore also be referred to as an fcc site. Atoms placed at surface sites create a fault plane, with a local geometry characteristic of an hcp arrangement. Such a stacking fault in the interior of an iridium crystal raises the free energy per site by ≈ 2.75 kcal/mol.[8]

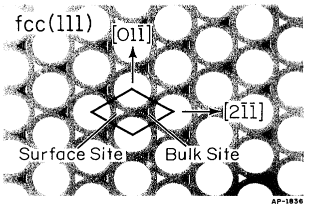

FIG. 1. Map of (111) plane for an fcc lattice, showing possible adsorption sites. The surface unit cell is indicated by heavy lines; the orientation shown is maintained throughout this work. Addition of atoms at bulk sites continues the fcc structure; atoms at surface sites create an hcp structure.

Which of the two sites, bulk (fcc) or surface (hcp), is actually occupied by an iridium atom on an Ir(111) plane? An FIM image of a [111]-oriented iridium sample is shown in Fig. 2, together with a hard-sphere model of an fcc crystal for comparison. A view of the (111) plane alone after deposition and equilibration of a single iridium atom on it is provided in Fig. 3. Observations on the iridium surface[9] have been made in one of our standard ultrahigh-vacuum FIM systems,[10] prepared by prolonged and intensive outgassing so that even after observations spanning more than an hour there is no trace of any contamination. All imaging is done with the sample at $T \approx 20$ K, using specially purified helium and a built-in microchannel plate image intensifier, itself conditioned by rigorous outgassing.

Although the added atom is clearly revealed in Fig. 3, the atomic arrangement of the underlying (111) plane remains in darkness with and without an adatom present, so that information about the geometry of the binding site must be obtained indirectly. However, the ability to see a single adatom on the surface and to accurately record its position makes it possible to map out the mesh of binding sites on (111). This is done by observing the adatom after it has been allowed to diffuse over the plane in the absence of applied fields, and repeating these observations until a reasonable fraction of the surface has been visited by the adatom.[11]

What information about binding sites can be deduced

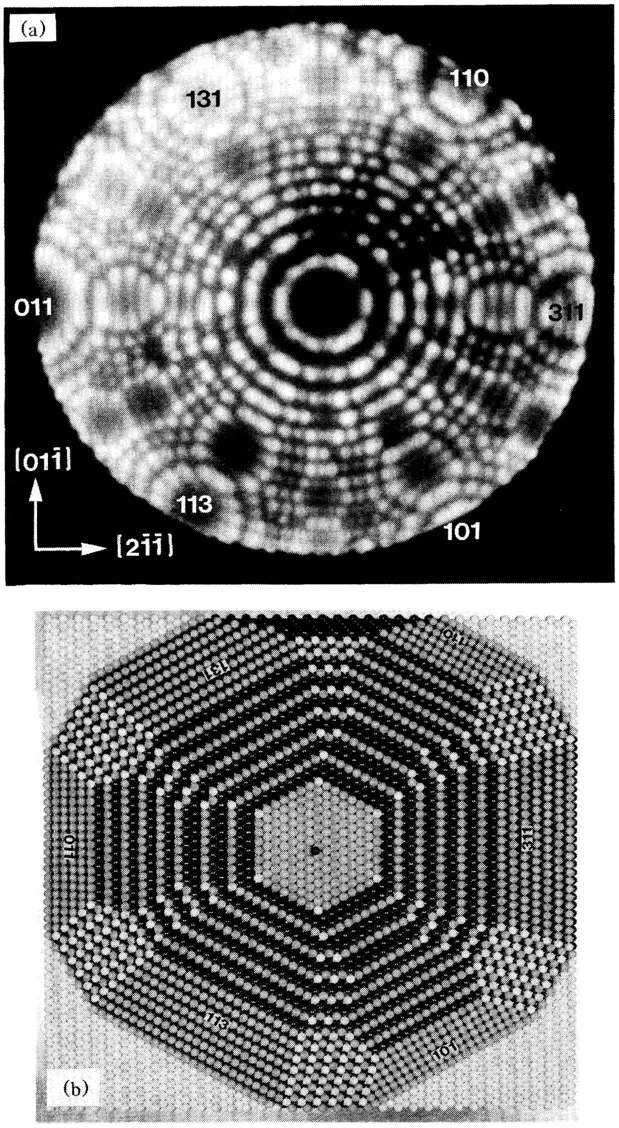

FIG. 2. (a) Field-ion micrograph of [111]-oriented iridium surface, obtained with helium image gas; surface field evaporated at $T \approx 20$ K. (b) Hard-sphere model of [111]-oriented fcc crystal, in same orientation as actual sample.

FIG. 3. Field-ion image of (111) region of an iridium surface. A single Ir atom has been evaporated onto (111), and has been equilibrated by diffusion for 10 sec at ≈ 100 K.

from such a grid? Shown in Fig. 4(a) is a map of the fcc (111) plane, with the bulk (fcc) sites connected by grid lines; a similar map of the surface (hcp) sites is given in Fig. 4(b). It is clear that if an iridium atom occupies only one type of site, be it either bulk or surface site, the grid obtained by plotting the observed atom positions will appear exactly the same. The relation of the grid to the substrate is of course different in the two cases. If bulk sites are occupied, and therefore mapped, then the other type of site appears toward the right of the unit cell drawn on the surface, that is toward $[2\bar{1}\bar{1}]$. If the surface sites are favored by the adatom, then the other type of site is located on the left of the unit cell. The differences in the two grids will be apparent provided sites of the other type are at least occasionally occupied by the adatom. If bulk and surface sites are equally favored by an adatom, then of course a hexagonal grid, as in Fig. 4(c), will be mapped out.

An example of the actual grid established by repeatedly observing the location of an iridium adatom on Ir(111) after diffusing for 10 sec at 102 K is given in Fig. 5. Three things are immediately evident. (a) Two

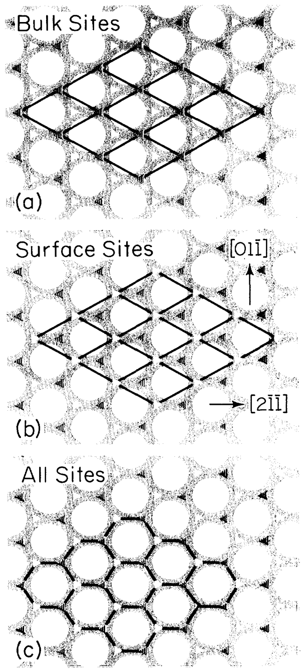

FIG. 4. Schematic of surface grids with adatoms in different types of adsorption sites on fcc (111). (a) Adatom at bulk (fcc) sites. (b) Grid for adatom at surface (hcp) sites. (c) For adatoms occupying bulk and surface sites with equal probability, a hexagonal grid is mapped out.

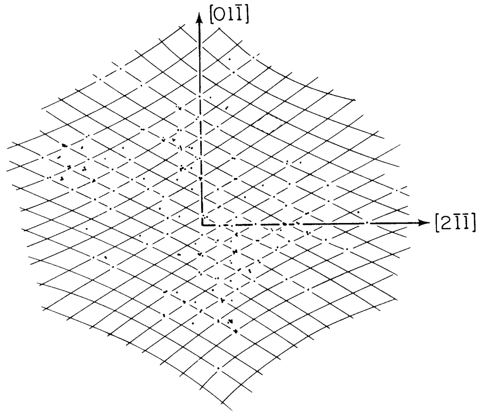

FIG. 5. Locations of a single Ir adatom on Ir(111) after diffusion at 102 K for 10 sec. Total observations, 455. Shaded area indicates unit cell.

types of sites are occupied by the iridium adatom: one at the intersections of the gridlines, the other in the interior of the unit cell. (b) The probability of occupation for the two sites differs significantly—in only 63 out of a total of 455 observations in Fig. 5 was the adatom observed at an interior site. (c) When the interior site is occupied it appears toward the left of the unit cell mapped out by the adatom positions. These are precisely the characteristics expected if the iridium adatom prefers to sit in surface (hcp) sites on Ir(111), but occasionally occupies a bulk (fcc) site as well, as modeled in Fig. 4(b). From the equilibrium distribution of iridium atoms over the two types of sites it appears that the free energy with an Ir atom at a surface site is 370 ± 30 cal/mol lower than for an Ir atom at a bulk site. This difference is quite small compared to the energy barrier separating equivalent binding sites from each other. In Fig. 6 we plot the diffusivity of a single Ir atom on Ir(111), as deduced from the mean-square displacement at different temperatures. The activation energy for atomic migration derived from these data, $E_A = 6.2$ kcal/mol, is more than an order of magnitude larger than the free-energy difference between the two types of binding sites.

The results of the mapping in Fig. 5 are quite reproducible. We have found similar plots in a dozen such determinations, on three different samples. Nevertheless, two possible reservations must be noted. The atomic positions mapped are those stable in the high field required for imaging. The field, however, does not appear to perturb the location of the adatom significantly. We have made repeated observations of an adatom at a given site. If the surface is not warmed between observations, then the position of the adatom remains unchanged in successive images of the surface, both at bulk and at surface sites. This eliminates the possibility of a shift in position at fields below those required for an image.

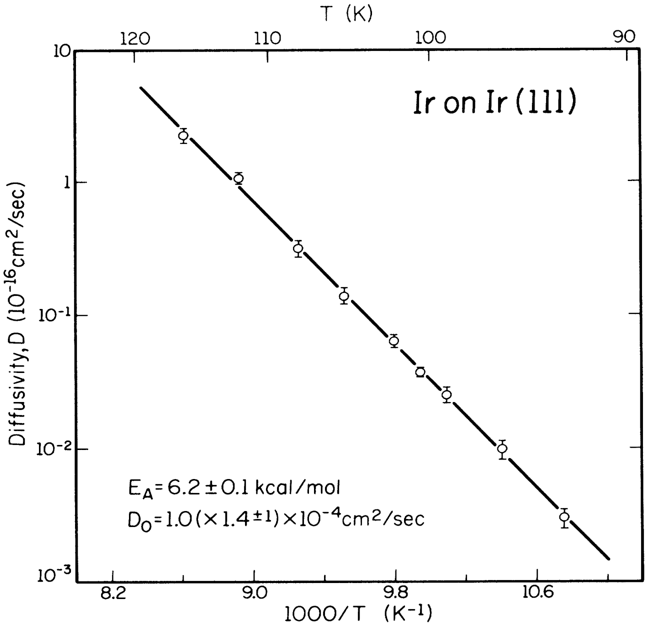

FIG. 6. Diffusivity of Ir adatoms on Ir(111), derived from mean-square displacement of a single atom at different temperatures.

Furthermore, it should be clear that we have ignored the possibility of adatoms sitting on top of the atoms forming the outermost lattice layer. This type of binding is highly unlikely for a metal adatom. Were it to occur, however, then the grid of binding sites mapped out by an adatom would resemble that in Fig. 1: Each unit cell would contain both a surface and a bulk site. In order to rationalize the site pattern actually seen in Fig. 5 on the assumption that the adatom sits on top of surface atoms, we would have to postulate that binding at surface sites is also possible, albeit not as favorable as on top of the lattice atoms, but that bulk sites cannot be occupied by atoms. This would be a most unusual combination of improbabilities. A similar argument can be made against the unlikely possibility of atoms being held at bridgehead sites.

Our observations on Ir(111) suggest that single iridium atoms are bound preferentially at surface (hcp) rather than bulk (fcc) sites. This result is quite the opposite of what has previously been found for self-adsorption on W(111).[3] That, of course, is a bcc lattice, for which the (111) plane is atomically rough, and comparisons are therefore inappropriate. A more important questions is how does a new crystal layer form on Ir(111) if surface sites are favored for adsorption of single atoms? Here it is important to note that the free-energy difference for binding in the two types of positions is only on the order of kT. Small perturbations should therefore be enough to change the balance. Formation of a new layer involves interactions among many adatoms, and these may very well be favorable to adsorption on bulk sites. It clearly will be of interest to see if a transition from surface to bulk sites is in fact observed as the adatom concentration is increased.

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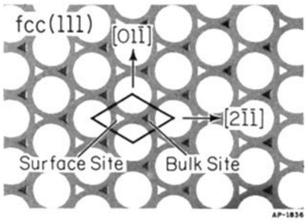

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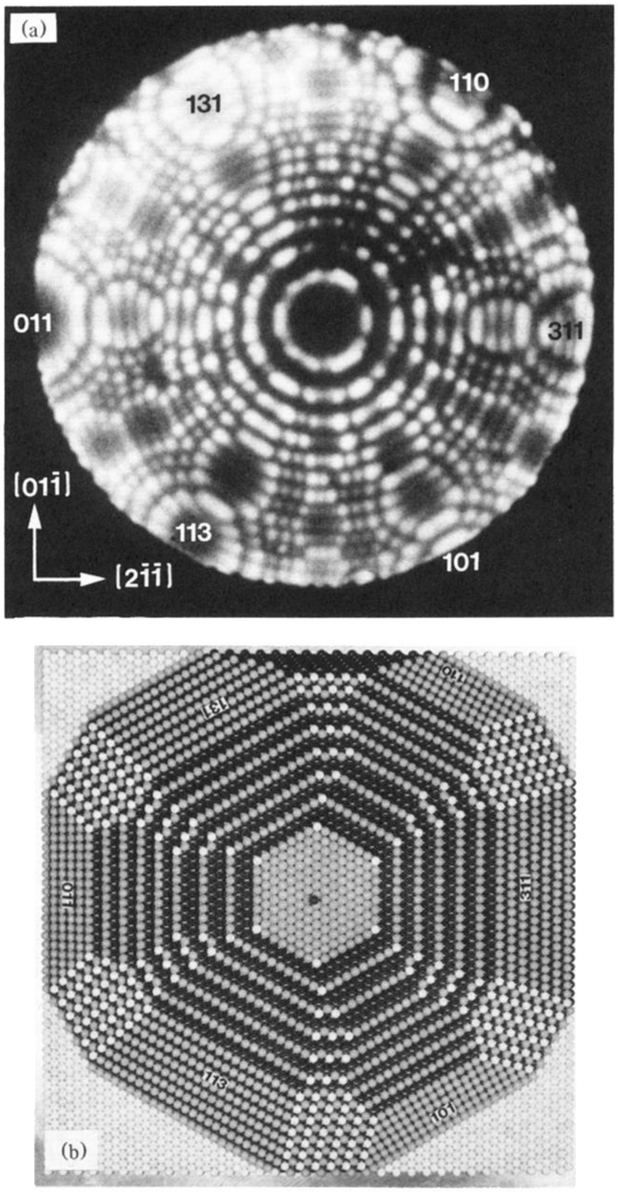

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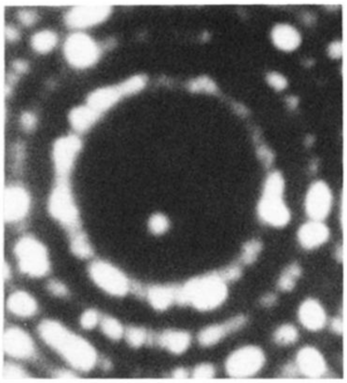

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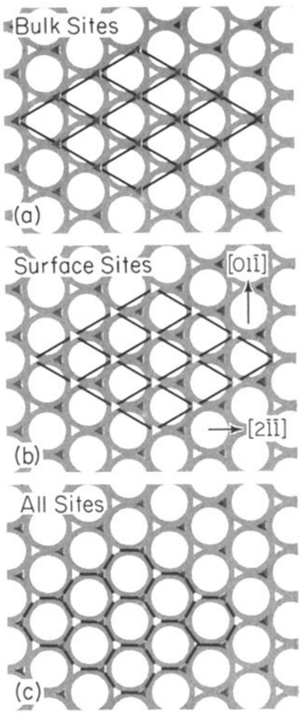

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