# Atomic Behavior at Individual Binding Sites: Ir, Re, and W on Ir(111)

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(Received 7 October 1991)

It has for the first time become possible to make quantitative determinations of differences in energy and jump rate for adatoms at the two types of binding sites on a close-packed fcc (111) plane. For iridium on Ir(111), variations in the potential energy of an atom over the surface are found to be small. Binding energies are, however, strongly dependent upon the chemical identity of the adatom. For rhenium and tungsten, differences in binding at fcc and hcp sites are sizable. In contrast, the dynamics of jumps out of the two types of sites are similar for the same atom.

It has long been recognized that the properties of atoms adsorbed on a surface should depend upon the nature of the binding site [1]. However, because of the difficulty of establishing where atoms are actually held, little has been done so far to quantify these expectations [2]. On the close-packed (111) plane of the fcc metal iridium, for example, metal atoms are known to bind at two different sites, distinguished by the local geometry [3]. Addition of atoms at sites designated as fcc in the schematic in Fig. 1 continues the normal structure of the substrate crystal; in contrast, at hcp sites, atoms eventually create a fault plane. How does the behavior of an atom differ from one kind of adsorption site to another? Identification of the type of site at which an atom is held on fcc (111) has recently become very simple through the use of the field-ion microscope [4]. We have taken advantage of this newfound capability to carry out a quantitative examination of how kinetic and thermodynamic properties of metal atoms differ at the two types of sites, something not possible in the past.

An iridium atom at an hcp site on Ir(111) is readily identified [3]. It has a triangular image, with the apex pointing along [2$\bar{1}\bar{1}$], as in Fig. 1(b); at an fcc site, the orientation of the image triangle is reversed. After equilibrating an Ir(111) plane with a single iridium atom on it at $T \approx 100$ K in the absence of applied fields, both fcc and hcp sites are occupied when the surface is imaged at low temperatures (at which observations in a high field do not affect the distribution over the sites). For a system at equilibrium, the ratio of $N_f$, the number of times an atom is at an fcc site, to $N_h$, the number of times it is at an hcp site, immediately gives the free-energy difference through the standard relation [5]

$$\ln(N_f/N_h) = -\Delta F/kT = \Delta S/k - \Delta E/kT. \qquad (1)$$

Here $\Delta S$ is the entropy difference, $\Delta E$ the difference in the internal energy, and $\Delta F$ the difference in the free energy for the system with an atom at an fcc as compared to an hcp site; $k$ is Boltzmann's constant. The thermodynamic quantities can now be deduced from a plot of $\ln(N_f/N_h)$ against $1/T$.

Two practical problems must be surmounted to imple-

ment this simple idea. The number of sightings $N$ is subject to statistical fluctuations $\sigma^2(N)$, so that the equilibrium ratio $N_f/N_h$ is endowed with an appreciable uncertainty $\sigma^2(N_f/N_h) = N_f(N_f+N_h)/N_h^3$. To achieve statistically significant information therefore requires quite a large number of observations. Furthermore, to derive reasonable values of the energetics, measurements must be extended over as wide a temperature range as possible. At high temperatures, however, the possibility exists that during cooling from equilibration to imaging conditions, the distribution over the two types of sites may change. After all, it takes but a single jump to convert from one type of site to another. Provided $p_f$ and $p_h$, the probabilities of such a conversion for atoms initially at fcc and at hcp sites, are small, they can be measured by letting the heating period approach zero [6]. The populations at fcc and hcp sites corrected for conversion, $N_f$ and $N_h$, are then simply estimated from the observed quantities $N_f^0$ and $N_h^0$ using

$$N_f = [(p_h - 1)N_f^0 + p_h N_h^0]/(p_f + p_h - 1), \qquad (2)$$

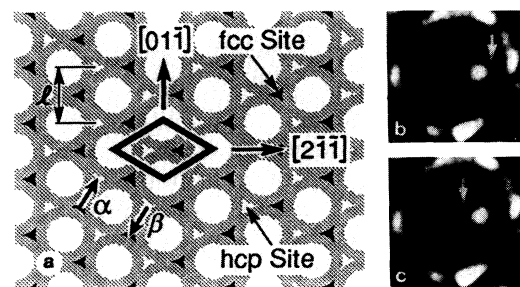$$N_h = [(p_f - 1)N_h^0 + p_f N_f^0]/(p_f + p_h - 1). \qquad (3)$$



FIG. 1. (a) Schematic of fcc plane, showing location of atoms in outermost layer. Surface unit cell is indicated by solid lines. $\alpha$ and $\beta$ designate jumps out of fcc and hcp sites, respectively. $l$ is the nearest-neighbor spacing. (b) Field-ion image of iridium adatom at hcp site on Ir(111). Apex of adatom image spot, indicated by arrow, is pointed to the right, along [2$\bar{1}\bar{1}$]. (c) Iridium adatom at fcc site. Apex of image spot (see arrow) points to the left.

Measured values of the equilibrium ratio corrected in this way are plotted in Fig. 2 at two-degree intervals from 96 to 106 K [7]. To compensate for the limited range of temperatures, special circuitry has been installed ensuring temperature reproducibility of ±0.1 K; to reduce the statistical scatter, roughly 300 observations have been made at each temperature. That the system was thoroughly equilibrated even at the lowest temperatures was established by introductory experiments as well as by Monte Carlo simulations.

At the highest equilibration temperature, $T = 106$ K, iridium atoms are at fcc sites in ≈ 15% of the observations. This proportion increases only very slowly; even around room temperature the two sites would still be equally populated. From the data in Fig. 2, we find that the internal energy for an iridium atom at an fcc site exceeds that of an atom on an hcp site by 499 ± 34 cal/mol; that is, for a self-adsorbed atom, binding at the two sites differs by only $\frac{1}{270}$ of the heat of vaporization. The entropy for iridium at an fcc site is $(0.64 \pm 0.17)k$ higher than at an hcp site. This difference is in keeping with expectations. For atoms at fcc sites, where they are more weakly bound, the vibrational frequency should be less and the entropy therefore larger than at hcp sites. A roughly 30% difference in just two vibrational modes at a frequency of ≈ $1.5 \times 10^{12}$ s$^{-1}$ would account for the measured results.

With this information in hand, it is now also possible to examine the diffusive jumps of iridium atoms at the two kinds of sites. From the mean-square displacement $\langle \Delta x^2 \rangle$ measured along the $x$ axis during time $t$, the diffusivity $D$ is derived in accord with the Einstein relation $\langle \Delta x^2 \rangle$

$= 2Dt$. At low temperatures, migration of iridium on Ir(111) is known to occur by transitions between adjacent sites [3]. The diffusivity $D$ must therefore involve both the jump rate $\alpha$ from fcc to hcp sites, and the rate $\beta$ for the reverse process; $D$ has in fact been shown to be of the form [8]

$$D = \beta l^2 / 2(1 + \beta/\alpha) = D_0 \exp(-\Delta E_D / kT), \qquad (4)$$

where $l$ is the nearest-neighbor spacing, $\Delta E_D$ the activation energy, and $D_0$ the prefactor for the diffusivity. In an equilibrium system, detailed balance ensures that the ratio of the rates $\beta/\alpha$ is equal to the equilibrium ratio $N_f/N_h$ measured above [9]. The individual jump rates $\alpha$ and $\beta$ can therefore be derived by combining data from diffusion studies with measurements of the equilibrium distribution of iridium atoms over fcc and hcp sites; this has been done in Fig. 3.

From this analysis it appears that the frequency factor for $\beta$ jumps, $v_\beta = 4.07 \times 10^{11}$ s$^{-1}$, is somewhat on the small side, amounting to only a fifth of the often-cited value of $kT/h$. The frequency factor out of fcc sites is smaller still. In the rate-limiting $\beta$ jumps out of hcp sites, iridium atoms have to overcome a barrier of 6.22 ± 0.07 kcal/mol in order to move to an adjacent fcc site. This is only 0.046 of the heat of vaporization. Variations in the potential energy as an iridium atom moves over the close-packed Ir(111) surface are evidently quite small compared, for example, with what is known about diffusion on the densest plane of a bcc metal, such as W(110) [10]. On this surface, the ratio of the diffusion barrier to the heat of sublimation is ≈ 0.11.

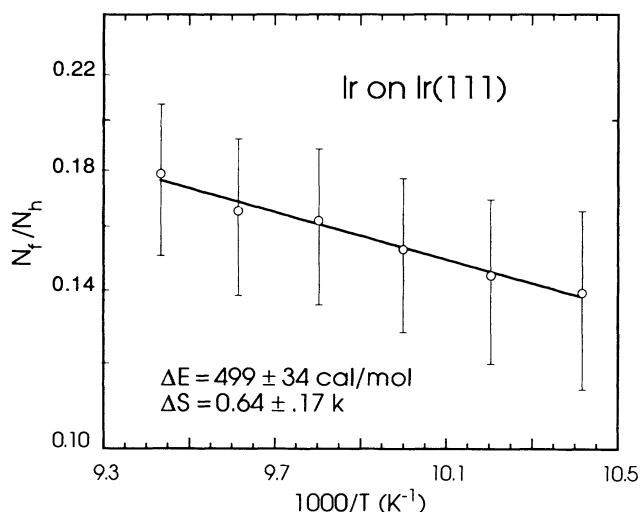For the other metal atoms we have examined on Ir(111), the approach that was successful in characteriz-



FIG. 2. Ratio $N_f/N_h$ of iridium adatoms at fcc and at hcp sites on Ir(111) after equilibration at different temperatures $T$. Values are derived from experiments in accord with Eqs. (2) and (3). In this, as in other plots, only statistical uncertainties are indicated; uncertainties in the absolute temperature calibration of ≈ 2 K may shift energies by 4%.
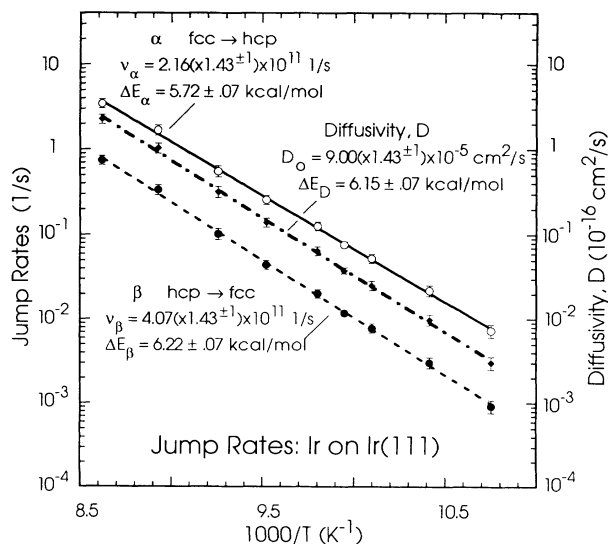


FIG. 3. Arrhenius plot for the diffusivity $D$ of iridium adatom on Ir(111). Also shown is the jump rate $\alpha$ out of fcc sites and the jump rate $\beta$ out of hcp sites.

ing the behavior of iridium atoms fails, as only one type of site is populated at reasonable temperatures. Palladium, a group-VIII platinum metal which on Ir(111) is already mobile at $\approx 65$ K, is always observed at fcc sites after equilibration. The situation is just the reverse for refractory metal atoms, such as group-VIB tungsten and -VIIB rhenium. Tungsten and rhenium become mobile on Ir(111) at much higher temperatures, $T \approx 200$ K; when they do, they are found to occupy only hcp sites. Nevertheless, for these atoms it is possible to compare the thermodynamics of binding at hcp and fcc sites by resorting to detailed diffusion studies. For both tungsten and rhenium, the ratio of the jump rates $\beta/\alpha$ (which equals the occupation ratio $N_f/N_h$) amounts to $< \frac{1}{100}$ at temperatures around 200 K, and can be safely neglected in Eq. (4). Measurements of the diffusivity $D$ therefore provide quantitative values of the rate $\beta$ at which atoms jump from hcp to fcc sites. We write the jump rate in terms of transition-state theory [9] as

$$\beta = v_\beta \exp(-\Delta E_\beta/kT), \quad v_\beta \equiv v_0 \exp(\Delta S_\beta/k), \quad (5)$$

where $v_0$ is a temperature-independent frequency factor and $\Delta E_\beta$ is the energy of activation which is available from the temperature dependence of the rate.

To measure the rate constant $\alpha$ for an atom jumping from fcc to hcp sites is more difficult, as neither tungsten nor rhenium atoms occupy fcc sites after equilibration. However, when these metals are deposited on the (111) plane maintained at low temperature, atoms are randomly distributed over fcc and hcp sites [11]. A determination of the time $\tau_\alpha$ an atom spends at an fcc site before jumping to the thermodynamically favored hcp position then leads to the desired rate $\alpha$ and to the activation energy $\Delta E_\alpha$ for the transition from fcc back to hcp sites. Information about the difference $\Delta E$ in internal energy for an atom at fcc and hcp sites also becomes available from the energies of activation through

$$\Delta E = E_f - E_h = \Delta E_\beta - \Delta E_\alpha. \quad (6)$$

This approach yields direct information about jump rates for atoms at specified sites but there is also a drawback: The internal energy difference $\Delta E$ is obtained as the difference between two large quantities, and is therefore subject to greater uncertainties than values derived directly from equilibrium measurements.

Studies of the diffusivity $D$ and of the lifetime $\tau_\alpha$ of atoms at fcc sites have been done for both tungsten and rhenium atoms on Ir(111) at different temperatures. The techniques for diffusion measurements are well established. To determine the lifetime, observations of the surface are made after short time intervals until an atom at an fcc site moves into an adjacent hcp site. The average of about 25 such determinations is taken as the mean lifetime. In Fig. 4 the results for rhenium are shown. From the temperature dependence of the diffusivity we find an activation energy for $\beta$ jumps out of hcp sites of
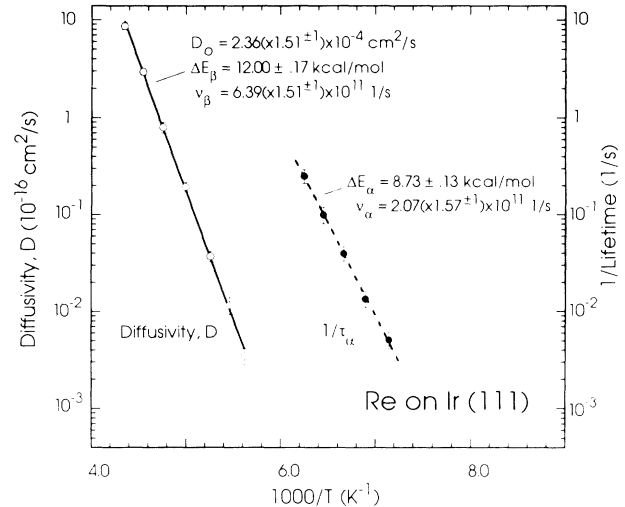


FIG. 4. Temperature dependence of the diffusivity $D$ and of the lifetime $\tau_\alpha$ of a rhenium adatom at an fcc site on Ir(111).

$12.00 \pm 0.17$ kcal/mol. The barrier to $\alpha$ jumps from fcc sites back to hcp, deduced from the lifetime $\tau_\alpha$ of a rhenium atom at an fcc site, amounts to only $8.73 \pm 0.13$ kcal/mol. On Ir(111), the binding of rhenium at hcp sites therefore is $3.27 \pm 0.21$ kcal/mol stronger than at fcc sites. The ratio of jump prefactors at the two types of sites amounts to $\approx 3.1$; on the assumption that $v_0$ is site independent, this is equivalent to an entropy difference $\Delta S = (1.13 \pm 0.61)k$, with the entropy at the more weakly binding fcc site again the larger. In view of the sizable statistical error and the arbitrary assumption about $v_0$, little significance is attached to the fact that $\Delta S$ is about twice as large as for iridium atoms. The frequency factor for jumps from fcc to hcp sites is identical with that for iridium atoms. It is somewhat on the small side, as of course is the term $D_0$ in the diffusivity, which differs by a factor of 4 from the value of $10^{-3}$ cm$^2$/s often ascribed to $D_0$.

For tungsten on Ir(111), the results in Fig. 5 are in many ways similar. The activation energy for $\beta$ jumps out of hcp sites, deduced from diffusivity measurements, is $11.69 \pm 0.27$ kcal/mol. In contrast, the barrier to the reverse $\alpha$ jumps, found from lifetime studies at fcc sites, is only $7.34 \pm 0.19$ kcal/mol. The internal energy difference of $4.35 \pm 0.33$ kcal/mol for tungsten atoms at hcp as compared to fcc sites is larger than for any of the other atoms we have studied on Ir(111). The ratio of prefactors of $\approx 2.2$, or equivalently the entropy difference $\Delta S = (0.78 \pm 0.94)k$, is comparable to that for iridium atoms; the uncertainty is again too large for a closer analysis. More interesting is the value of the prefactor for the diffusivity, $D_0 = 2.85(\times 1.89 \pm 1) \times 10^{-5}$ cm$^2$/s, which is an order of magnitude smaller than for rhenium, even though diffusion takes place in the same temperature range. For W atoms, $D_0$ is a factor of 35 below the
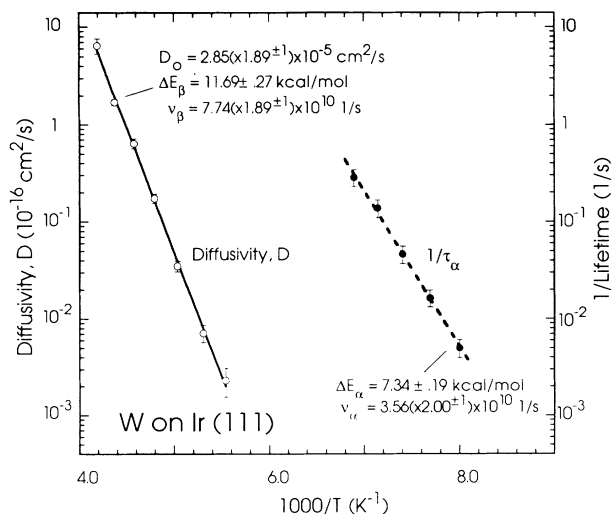
FIG. 5. Diffusivity $D$ and lifetime $\tau_a$ of tungsten adatom at fcc sites on Ir(111).

standard value of $10^{-3}$ cm$^2$/s, well outside the effects expected from random errors; for Re and Ir the prefactor is much closer to normal. There appears to be a distinct chemical specificity in the dynamics of diffusion on Ir(111), and it will be important to explore the underlying reasons for this.

Our experiments make it clear that the behavior of atoms on the two different sites of the (111) plane of iridium varies strongly with the chemical identity of the adatom. For self-adsorbed iridium atoms, binding is somewhat stronger at hcp than at fcc sites, but this difference is quite subtle on the scale of the cohesive energy. The barriers to motion of Ir atoms are small also, allowing diffusion over the (111) plane at a temperature $T < \frac{1}{25}$ of the melting point. For the other atoms, the thermodynamics of binding on Ir(111) are rather different: Both W and Re atoms strongly favor hcp sites. Even at room temperature, fcc sites should be occupied by a Re atom in less than 1.5% of the observations; for W, this figure drops to $<0.15\%$. The barriers to atom

jumps are much larger also; they are almost twice as high as in the self-diffussion of Ir over this surface. However, for a given metal atom, the frequency factors for jumping out of hcp and fcc sites are comparable. It appears that the chemical identity of the adatom has a profound effect upon how strongly it is bound at fcc as compared to hcp sites; nevertheless, the dynamics of jumps out of hcp versus fcc sites are much the same.

[1] See, for example, G. Ertl, in The Nature of the Surface Chemical Bond, edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979), p. 313.

[2] For early attempts, see P. G. Flahive and W. R. Graham, Surf. Sci. 91, 463 (1980).

[3] S. C. Wang and G. Ehrlich, Surf. Sci. 224, L997 (1989); 246, 37 (1991).

[4] The technique is examined by E. W. Müller and T. T. Tsong, Field Ion Microscopy Principles and Applications (American Elsevier, New York, 1969); K. M. Bowkett and D. A. Smith, Field Ion Microscopy (North-Holland, Amsterdam, 1970); J. A. Panitz, J. Phys. E 15, 1281 (1982); T. T. Tsong, Atom-Probe Field Ion Microscopy (Cambridge Univ. Press, Cambridge, 1990).

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[7] Factors dictating the temperature range accessible in experiments with adatoms are discussed by G. Ehrlich, Scanning Microsc. 4, 829 (1990).

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[9] C. P. Flynn, Point Defects and Diffusion (Clarendon, Oxford, 1972), Chap. 7.

[10] D. W. Bassett, in Surface Mobilities on Solid Materials, edited by V. T. Binh (Plenum, New York, 1983), p. 63.

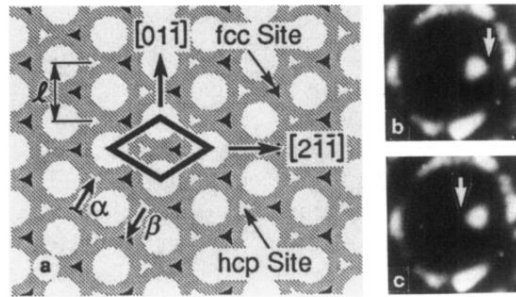[11] S. C. Wang and G. Ehrlich, J. Chem. Phys. 94, 4071 (1991).

FIG. 1. (a) Schematic of fcc plane, showing location of atoms in outermost layer. Surface unit cell is indicated by solid lines. $\alpha$ and $\beta$ designate jumps out of fcc and hcp sites, respectively. $l$ is the nearest-neighbor spacing. (b) Field-ion image of iridium adatom at hcp site on Ir(111). Apex of adatom image spot, indicated by arrow, is pointed to the right, along $[2\bar{1}\bar{1}]$. (c) Iridium adatom at fcc site. Apex of image spot (see arrow) points to the left.