# Energetics of Ir adatoms on Ir(111)

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**Abstract.**    The stability of Ir domains on Ir(111) is investigated theoretically by computing the relevant interaction energies. The study is based on a representation of the total energy in terms of a generalized Ising model containing effective cluster interactions which are determined from the electronic structure. A simple but realistic tight-binding Hamiltonian is used with configurational averages computed by a direct method. A transition from hcp (hexagonal close-packed) growth to fcc (face-centred cubic) growth as a function of adlayer concentration is observed and compact cluster formation is favoured, in precise agreement with experiment.

## 1. Introduction

The properties of homoepitaxially adsorbed atoms and clusters are important for an understanding of crystal growth and for the insight and control that they might bring to a wide range of technological devices and applications. Consequently a good deal of attention, theoretical as well as experimental, has now been devoted to this subject [1]. On the experimental side, much knowledge has been obtained through field ion microscopy (FIM) observations since this technique allows the visualization of individual metal atoms on metal substrates. This method was used, for example, to clarify the initial stages of the adsorption of Ir on the Ir(111) surface [2–9]. In this system two possible types of adsorption site, each of threefold symmetry but different in their surroundings, are present in equal numbers on the (111) plane: (i) the 'fcc' (or normal, or bulk) sites, at which an added atom continues the periodic fcc structure, and (ii) the 'hcp' (or fault, or surface) sites, at which continued growth introduces a stacking fault plane and the added atoms' environment is characteristic of the hcp lattice.

Observations of single adatoms of Ir on the Ir(111) surface have shown that, after equilibration at 100 K, both 'hcp' and 'fcc' sites are occupied, but with the adatom observed at 'hcp' sites in 85% of the cases [2]. The percentage of occupied 'hcp' sites decreases as the number of atoms $n$ of the adsorbed cluster increases: it falls to 50% for $n = 3$ and drops to zero for $n \geqslant 7$ [3, 4]. Thus a transition from preferential adsorption at 'hcp' sites (single atoms, dimers, and trimers) to preferential adsorption at 'fcc' sites ($n \geqslant 4$) is observed. Such a transition is not unexpected since the periodic stacking of the crystal is fcc, corresponding to entire monolayers occupying 'fcc' sites. Nevertheless, it is surprising that these sites are already preferred for relatively small clusters. It is also not immediately clear why single adatoms would preferentially occupy 'hcp' sites. An understanding of these phenomena must be sought in the material's electronic structure. It is also known from experiment that for clusters containing two to eight iridium atoms, the interatomic distances predominantly

correspond to nearest-neighbour spacings. For instance, if $n = 3$, the compact triangle is more stable than the linear chain. In these compact clusters, all atoms sit at the same type of site (i.e., all hcp or all fcc). No mixing of adsorption site types in a given cluster is observed [3, 5, 6].

At low temperature, diffusion on Ir(111) occurs primarily by jumps between nearest-neighbour sites, with the atom moving from one type of site to the other. Direct jumps from 'hcp' to 'hcp' site or from a 'fcc' site to a nearby 'fcc' site are much less likely [9]. A second experimental finding is that when single atoms are deposited at very low temperature (20 K) on a bare substrate, 'fcc' and 'hcp' sites are equally populated, demonstrating that the atoms localize immediately upon impact. However, if atoms are deposited close to an existing cluster they tend to migrate towards that cluster even at very low temperatures. Consequently, clusters tend to be surrounded by a depleted region [10].

The problem of homoepitaxial growth on transition metals in general and that of Ir on Ir(111) in particular have received a good amount of prior theoretical attention. Piveteau and collaborators [11, 12] used the tight-binding method to study the adsorption properties of adatoms and small clusters as a function of band filling. These authors determined the adsorption energies and activation barrier heights for a number of transition metals and obtained excellent agreement with experiment for the Ir system [11]. They found that for a single Ir adatom on Ir(111) the hcp site is the preferred one [11] and that for clusters the dimer still prefers the hcp site, while trimers are equally distributed over both types of site [12]. These authors did not work in the cluster expansion framework employed here, but rather calculated the energies directly. Thus it is not straightforward to relate their findings to a statistical model which can subsequently be used in simulations nor is it possible to disentangle the energy differences in separate contributions. On the other hand, their approach is better suited to studying a whole range of transition metals by sweeping in the band-filling parameter, while the present method needs to be performed on a case-by-case basis. Classical pair and many-body potentials have also been used to address these questions [13, 14]. The advantage of this approach is that it is ideally suited for molecular dynamics simulations. The main drawback is that the quantum mechanical origin of the interactions is tenuous at best. The kinetic picture that arises from these simulations is enlightening, but the barrier heights that are found are too small compared to experiment, which casts some doubt on the quantitative predictions of this methodology. The most accurate calculations to date for Ir on Ir(111) employ the full-potential linear-muffin-tin-orbital (FP-LMTO) method to calculate energy barriers for diffusion [15]. The comparison with experiment is excellent, but the method is very time consuming and is not well suited for treating problems with many inequivalent sites, such as that of adsorbed domains at finite concentration.

In our previous papers [16, 17], we studied theoretically the initial stages of the adsorption of Ir on Ir(111) (isolated adatoms, dimers, and trimers), but only two particular cases were considered: (a) all adsorbed atoms located at 'fcc' sites, and (b) all adsorbed atoms located at 'hcp' sites. It was found that, in both cases, nearest-neighbour pairs stabilize adsorbed clusters and that the compact triangles are the most likely trimers. Monte Carlo simulations in the dilute limit showed the formation of small compact islands at low temperature, giving way, at intermediate temperature, to large domains, which where destroyed, leaving small irregular domains as the temperature was further increased. These overall trends are in good agreement with the FIM observations.

## 2. Model

In order to improve our understanding of the various cluster arrangements and diffusion mechanisms observed for the Ir/Ir(111) system, we now extend our study to the general case

where the Ir atoms can be adsorbed at *both* 'fcc'-type and 'hcp'-type positions on Ir(111) (figure 1). For this mixed lattice, we do not allow two Ir atoms to be first neighbours (i.e. with one atom at a 'hcp' site and a nearest neighbour at a 'fcc' site), because such structures have never been observed and the interatomic repulsion is very large at such close proximity. The coverage of the adlayer will always be given with reference to a 'pure' lattice (i.e., a sublattice composed of 'hcp' and 'fcc' sites). For the 'pure' lattice, the relaxation of the top layer versus the adlayer concentration is not exactly the same for both types of site. Therefore in the mixed lattice a small buckling might be anticipated. However, such effects are relatively small and outside the scope of the present work. Since we are mainly interested in studying the occupation of 'hcp' and 'fcc' sites as a function of the adlayer coverage, all calculations will be performed supposing no relaxation effects.
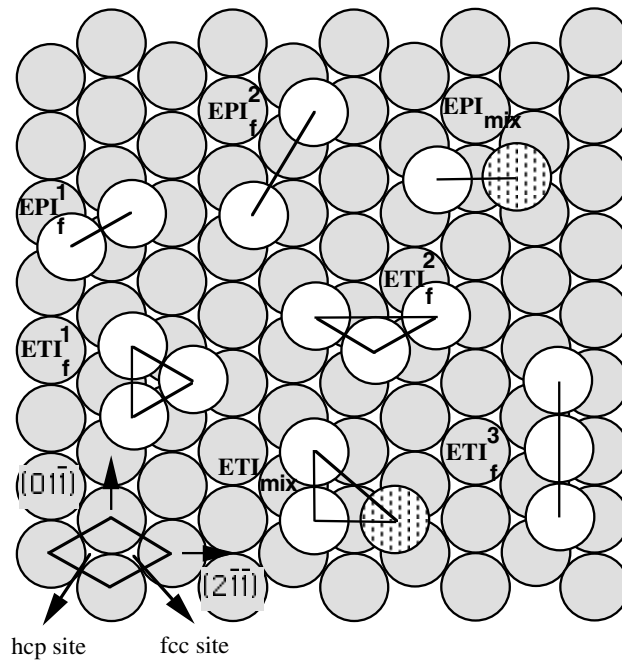


**Figure 1.** An illustration of the different effective cluster interactions considered in this work. The ECIs are of type 'hcp' or 'fcc' according to their position relative to the plane below the surface.

Statistical physics studies of adsorbed systems frequently rely on a representation of the system's energy in terms of a lattice gas (or, equivalently, Ising-model) Hamiltonian. The validity of such a decomposition is often postulated in an ad hoc manner with interaction parameters that are fitted to experiment. As will be shown here, it is actually possible to rigorously justify this methodology and to relate the various parameters to the underlying electronic structure. The starting point of our approach is an exact expansion discovered by Sanchez, Ducastelle, and Gratias [18]. These authors showed that a solid's total energy, $E$, may be expressed as

$$E = E_0 + \sum_\alpha V_\alpha \xi(\alpha) \tag{1}$$

where $E_0$ is a constant background term, irrelevant for the present purposes, $\alpha$ denotes the various configurational clusters, $V_\alpha$ is an effective cluster interaction (ECI), and $\xi$ is a multi-particle correlation function. This exact expression is very similar to a generalized Ising-model

Hamiltonian and has been the starting point for numerous studies of metallic alloys in the bulk [19] and near a surface [20]. Because the ECIs typically converge rapidly as a function of cluster size and interatomic separation, in practice the (infinite) sum in equation (1) may be truncated after a relatively small number of terms. The method has been applied very successfully to a wide range of systems and its value as a *computational* tool is now well established [20].

The present study is restricted to adsorption strictly in the first monolayer, i.e. all adatoms are confined to occupy sites in the first plane directly above the substrate. The interesting questions occurring as regards the transition to three-dimensional growth (clumping, mound formation, etc) are deferred to a future investigation. Thus, as far as the configurational statistics is concerned, the problem is a purely two-dimensional one. Of course, in the electronic structure calculation the full three-dimensional system (adsorbates plus substrate) is taken into account. Moreover, in the present work, all calculations are performed at fixed concentration. As a consequence the ECIs are concentration dependent and equation (1) must also be interpreted at fixed concentration. It is in fact possible to reformulate the theory with concentration-independent ECIs (the constraint of fixed concentration in equation (1) is then lifted). The two types of ECI are related by a renormalization procedure [21]. However, for the present purposes, the first formulation is physically most transparent.

The starting point of the calculations is a tight-binding (TB) Hamiltonian, in which only the 5d orbitals are retained, which is a standard approximation for transition metals. Although the TB formalism cannot compete in accuracy with the methods based on density functional theory (such at the FP-LMTO method), it tends nevertheless to give an adequate description of the band structure, whilst providing one with the flexibility of treating non-periodic systems [22]. It is also particularly suited to calculate ECIs, especially when combined with the recursion method and the direct configurational averaging (DCA) procedure [23]. In the latter approach, the ECIs are computed directly, rather than as a difference of large terms, and the averaging needed to sample the various configurations at fixed concentration is performed by a Monte Carlo procedure. Here, except in the dilute limit, all quantities were averaged over 50 independent configurations. The Hamiltonian matrix elements are described following the Harrison prescription [24]: the general form of the Slater–Koster parameters $dds(d_{ij})$, $ddp(d_{ij})$, and $ddd(d_{ij})$ is derived from the muffin-tin-orbital theory by means of the expressions

$$dd l(d_{ij}) = h_{dd l}(h^2/m)(r_d^3/d_{ij}^5) \qquad (2)$$

where the constants $h_{dd l}$ ($l = $ s, p, d) are the same for all transition metals ($h_{dds} = -16.2$; $h_{ddp} = 8.75$; $h_{ddd} = 0$) and where the length $r_d$ is characteristic of the pure element. This equation has the advantage of reducing the number of parameters characterizing the hopping integrals to only one parameter ($r_d$) and of providing a law of variation with distance for the hopping integrals. The number of 'd' electrons considered for Ir is 8. For ion–ion repulsion energy, we adopt the Born–Mayer approach given by Rosato *et al* [25]. Charge transfer in the surface region is taken into account approximately by a rigid shift of the on-site matrix elements until local charge neutrality is obtained for each adatom and surface layer. Effects were only noticeable for the four topmost surface planes. We consider a cluster corresponding to seven shells and apply the recursion method with ten levels in the continued fraction and a Beer–Pettifor quadratic terminator [20, 23].

The lowest-order ECIs, called point energies, are those for the single-site cluster. In cases where all lattice sites are equivalent they can simply be absorbed in the background term, since they do not affect the configurational dynamics. However, in situations with broken symmetry (as in the present case) they frequently provide the dominant contribution to the observed behaviour. In the case under study there are only two inequivalent sites ('hcp' and

'fcc'). Therefore two point energies need to be considered and it is the competition between them that will dominate the statistical physics. The adsorbed system is a bit more delicate than a surface alloy problem and some care is needed in the treatment of the ECIs. For a binary alloy at the surface the concentration can be very different from that in the bulk owing to segregation effects [20]. Thus, concentration-dependent interactions have to be considered but the numerical effort to compute such interactions, assuming reasonable concentration profiles and minimizing the total energy, is feasible. In the present case the situation is much more delicate, since the two different concentrations (at 'fcc' and 'hcp' sites) are not known *a priori*. The point energies corresponding to fcc and hcp sites will be denoted as $V_f$ and $V_h$ respectively. Likewise, the concentration of atoms at 'hcp' sites and 'fcc' sites will be denoted as $c_h$ and $c_f$. The same subscripts will be used for the other ECIs, with superscripts (1, 2, . . . ) indicating the nature of the cluster (see figure 1).

## 3. Results

Using the TB-DCA technique described above, the point energies were computed for various concentrations. In a first step, the point energies corresponding to the two types of site were determined assuming the same concentration for each type (i.e. $c_f = c_h$). A clear trend was obtained: in the dilute limit the 'hcp' point energy is lower than that for the 'fcc' sites, while at larger concentration the opposite behaviour is observed. In order to determine the crossover point, a systematic study was performed which indicated some very interesting trends. Figure 2 shows the variation of the point energies as a function of the concentration at 'fcc' sites with the 'hcp' concentration fixed at 0.1. As can be seen, when the 'fcc' concentration changes, the 'hcp' point energy remains almost constant, whereas the 'fcc' point energy varies strongly upon changing the 'fcc' concentration. Even at lower 'hcp' concentration a similar
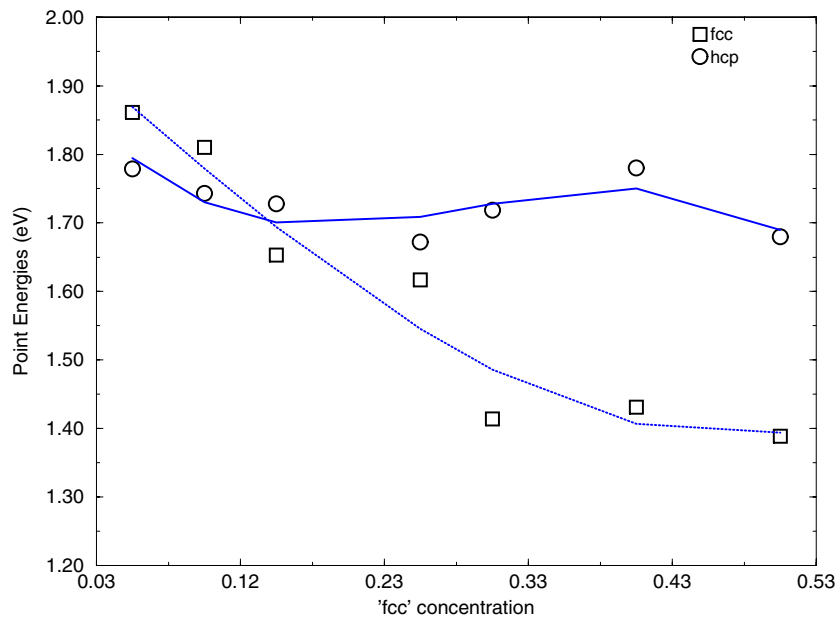


**Figure 2.** Point energies for 'fcc' (solid squares) and 'hcp' (solid circles) sites as a function of 'fcc' concentration at a fixed 'hcp' concentration of 0.1.

behaviour was obtained. Thus the general crossover can be expected for a total ('hcp' plus 'fcc') concentration slightly below 10%. Such a variation in point energy (with a consequent change in site occupancy) is a genuine electronic structure effect, associated with the filling of the d band, and cannot be understood in a classical potential model. It is important to emphasize that the crossover from hcp to fcc stacking occurs as a function of the *overall* concentration, i.e. it is a collective effect, rather than being observed in isolated clusters.

The higher-order ECIs were mostly found to be attractive, leading to compact cluster formation. For these configurations only results for identical 'hcp' and 'fcc' concentrations were considered. The nearest-neighbour effective pair interactions (EPIs) listed in table 1 are large. Since no nearest 'fcc' and 'hcp' sites can be occupied simultaneously, the first EPIs (i.e. with the shortest possible distance) are connecting two atoms of the same type. At very low coverage, the relatively large, negative value of these EPIs reinforces the stability of pairs with two 'hcp' sites or two 'fcc' sites. The very small difference between $EPI_h^1$ and $EPI_f^1$ favours both types of site. In fact, if the point energies were absent, the EPIs alone would favour occupation of 'fcc' sites even in the dilute limit. However, this tendency is counteracted by the much larger point energy which favours 'hcp' site occupation in this regime. When the coverage increases, the EPIs decrease in absolute value but surprisingly the difference between the two types of EPI remains almost constant. The first pair configuration with one 'hcp' and one 'fcc' atom corresponds to a distance which is 1.15 times that between nearest neighbours of the same type. As table 1 shows, the value of the corresponding 'mixed' EPI is smaller in magnitude than that for the nearest-neighbour EPI between like sites. It should be noticed that at low coverage this EPI is negative, leading to an attraction between atoms at 'hcp' and 'fcc' sites. However, this effect is overwhelmed by the stronger attraction between nearest-neighbour sites of either type. It may play an important role, though, in assisting atoms as they diffuse around the surface. For larger coverage the absolute value of $EPI_{mix}$ decreases, but it always remains smaller than those of $EPI_h^1$ and $EPI_f^1$. This explains why mixed pairs are not favoured [3,5,6]. Further-neighbour effective pair interactions were found to be much smaller than nearest-neighbour EPIs. However, they were usually negative, which contributes, once again, to the formation of compact clusters.

**Table 1.** Effective pair interactions as a function of total coverage. The subscripts $h$ and $f$ denote all 'hcp' sites and all 'fcc' sites, respectively, while the subscript '*mix*' denotes a mixed pair, consisting of one 'hcp' site and one 'fcc' site. For the mixed pairs, the interatomic distances are of course larger than for the corresponding 'hcp' and 'fcc' pairs. Nearest-neighbour effective pair interactions are as defined in figure 1.

| Nearest-neighbour-effective pair interactions (EPI$^1$) | | | |
|---|---|---|---|
| Concentration | $EPI_h^1$ (meV) | $EPI_f^1$ (meV) | $EPI_{mix}$ (meV) |
| 0.024 | −263 | −270 | −115 |
| 0.05 | −240 | −247 | −104 |
| 0.30 | −121 | −128 | −57 |

| Next-nearest-neighbour effective pair interactions (EPI$^2$) | | |
|---|---|---|
| Concentration | $EPI_h^2$ (meV) | $EPI_f^2$ (meV) |
| 0.024 | −1.0 | + 0.6 |
| 0.05 | −4.0 | −4.5 |
| 0.30 | + 0.1 | −13 |

In table 2 are reported some effective trimer interactions, which play for this system a small role. Nevertheless, the largest absolute values obtained for the ETIs correspond to triangular clusters. Therefore the stability of such compact arrangements is enhanced, as

**Table 2.** Effective triplet interactions (in meV) as a function of total coverage for various basic clusters (see figure 1). The subscripts $h$ and $f$ denote all 'hcp' sites and all 'fcc' sites, respectively.

|  | $c = 0.024$ | $c = 0.05$ | $c = 0.30$ |
|---|---|---|---|
| $ETI_f^1$ | −26 | −31 | −3.8 |
| $ETI_h^1$ | −13 | −6 | −2.3 |
| $ETI_f^2$ | −29 | −24 | −8 |
| $ETI_h^2$ | −30 | −22 | −7 |
| $ETI_f^3$ | −0.7 | −5.2 | −14 |
| $ETI_h^3$ | −1.3 | −1.4 | −18 |
| $ETI_{mix}$ | −18 | −12 | −3 |

experimentally observed.

As we have seen, the effects of the 'mixed' lattice are subtle and sensitive. In the present case the difference between the pairs of the same type and pairs at different sites was large. However, systematic studies, confirmed by simple moments arguments [20, 23], indicate that the effective cluster interactions display a minimum number of nodes when the d-band filling varies from 0 to 10. Since for fcc bulk materials, 'hcp' and 'fcc' sites are, *a priori*, in competition during the growth along the (111) direction, one may wonder whether, in some cases, a cancellation of the point energies might not occur leading to the growth mechanism being driven by the effective cluster interaction between two different types of site. The conditions under which this interesting effect might be observed will have to await further study. One advantage of the approach developed in this work is its ability to consider inequivalent sites treated on an equal footing in the presence of a changing alloy concentration. This approach provides a clear identification of the relevant physical quantities which can be used in numerical simulations.

## 4. Conclusions

Summarizing, the relative stabilities of Ir adatoms on a smooth Ir(111) surface (at 0 K) have been calculated for a lattice presenting 'surface' and 'bulk' sites. An inversion in stability is found as a function of adatom concentration, the hcp site being favoured at low concentrations, but the fcc site having a lower energy at higher concentrations. This is a consequence of changes in the band structure and mimics the same phenomenon observed as a function of band filling [11, 12]. The method used is efficient and leads to results that are qualitatively and quantitatively in good agreement with experiment. The findings also compare well with those of other quantum mechanical treatments. The various contributions to the binding energies are decomposed in a unique way as a lattice gas Hamiltonian. This is both numerically advantageous (since it avoids subtractive cancellation problems) and physically insightful. Work in progress aims at extending these calculations to deal with ledges and kinks. These are known to exhibit some very interesting effects [7, 27].

## Acknowledgments

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