PHYSICAL REVIEW B VOLUME 46, NUMBER 11 15 SEPTEMBER 1992-I

Inversion of the stability between normal and fault sites for transition-metal adatoms on (111) fcc and (0001) hcp transition-metal surfaces

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(Received 10 April 1992)

We present a theoretical study, in the tight-binding formalism, of the inversion of stability between normal and fault sites for transition adatoms on (111) fcc and (0001) hcp transition-metal surfaces. Results are in very good agreement with experimental data on Ir(111). Some predictions are made for transition adatoms on Ru(0001).

I. INTRODUCTION

The problem of crystalline growth is of a large interest in surface science. If the mechanisms of crystalline growth were completely understood, then a large number of new materials with specific applications (as, for example, in the world of magnetic recording) could be elaborated. In order to shed some light on these phenomena, we present here a study of the relative stability of different adsorption sites on a close-packed surface of a hcp or fcc transition metal. Indeed, the deposition of an overlayer of a transition metal M (hcp or fcc) on a close-packed surface of a transition metal M' (hcp or fcc) involves two types of threefold adsorption sites which are present in equal numbers (Fig. 1): the normal sites, which continue the bulk regular stacking or the fault sites, which introduce a stacking fault. In a preceding paper,[1] a study concerning stacking fault energies for a complete monolayer has already been reported. Now, we turn to the problem of the relative stability of the normal and fault sites when a single atom is deposited on a transition-metal surface.

An experimental study of this problem has been recently carried out[2] and leads to the conclusion that on Ir(111) the relative stability of the two sites varies with the nature of the adatom. The fault site is favored when a single atom of W, Re, or Ir is deposited on the surface. On the contrary, the normal site is more stable for a Pd adatom.

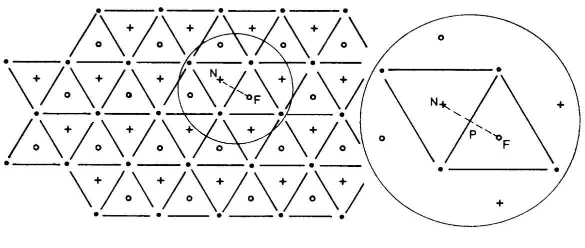

FIG. 1. Top view of a (111) fcc [or (0001) hcp] surface; solid lines outline grid formed by the surface atoms. An adatom may bind a normal (N) site (+) or at a fault (F) site (○). The diffusion path (N-P-F) has been enlarged in the inset.

In this paper, calculations of the binding energy of a single adatom on a (111) fcc surface are presented. Numerical results for Ir(111) are in good agreement with experiment. A similar investigation is carried out for a (0001) hcp surface and leads to predictions on the relative stability of the different adsorption sites for various adatoms on Ru(0001).

The method is briefly summarized in Sec. II. Section III presents a simplified calculation from which experimental trends can be understood. In Secs. IV and V, an accurate computation of binding energies at various sites of the (111) fcc and the (0001) hcp surfaces is reported.

II. THE METHOD

Let us consider an adatom at a normal or at a fault site on a (111) fcc or a (0001) hcp surface. For a better knowledge of the atomic processes that govern the growth on these surfaces, we must first determine the binding energies at the two possible adsorption sites and the activation energy that is involved during the migration of the adatom from one site to another. When diffusion by hopping occurs on this surface, the adatom is expected to follow the diffusion path indicated in Fig. 1, which is obvious when considering the atomic arrangement. Thus, at a normal site, a diffusing atom faces a barrier E_N in jumping into an adjacent fault site, whereas at a fault site it must pass over a barrier E_F to move to an adjacent normal site. The height E_N (resp. E_F) of the barrier is the difference between the binding energies of the adatom at the site N (resp. F) and at the saddle point P (Figs. 1 and 2). If we denote $E_B(S)$ the binding energy of the adatom at a site S, then

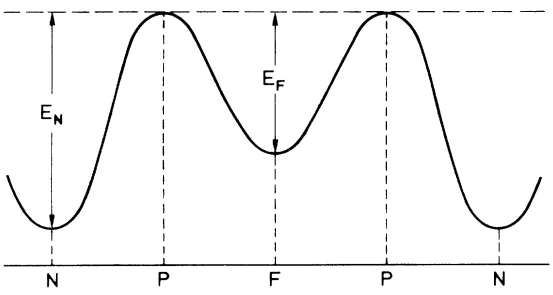

FIG. 2. Schematic of potential acting on an adatom in moving over fcc (111) [or hcp (0001)] along the diffusion path *N-P-F* indicated in Fig. 1.

$$E_N = E_B(P) - E_B(N) , \tag{1}$$

and

$$E_F = E_B(P) - E_B(F) . \tag{2}$$

The binding energy $E_B(S)$ is the difference between the total energy of the semi-infinite crystal with the adsorbed atom and that of the same system with the adatom far from the surface;[3] it can be expressed as

$$E_B(S) = \Delta E_b + \Delta E_{\text{rep}} , \tag{3}$$

where ΔE_b is the variation of the band energy and ΔE_{rep} is the variation of the repulsive energy.

The band contribution is computed using a self-consistent tight-binding scheme in which only the valence *d* electrons are taken into account. Hence, the effect of the valence *sp* electrons is neglected. We have largely justified this approximation in a preceding paper when considering the structural energy difference between the fcc and hcp structures.[1] The same arguments can be applied in the present case.

Provided that in the free state, the number of *d* electrons of the adatom is unchanged, ΔE_b can be written[3]

$$\Delta E_b = \sum_i \Delta E_{b,i} + \int_m^{E_f} E n_a(E)dE - N_a \varepsilon_a^* - E_f \left[\int_m^{E_f} n_a(E)dE - N_a \right] , \tag{4}$$

where $\Delta E_{b,i}$ is the variation of the *d*-band energy of an atom *i* of the substrate which is significantly perturbed by the presence of the adsorbate. The *d*-band energy $E_{b,i}$ of an atom *i* is given by the following formula:

$$E_{b,i} = \int_m^{E_f} E n_i(E)dE - N_d \delta V_i - E_f \left[\int_m^{E_f} n_i(E)dE - N_d \right] . \tag{5}$$

The problem of the convergence of the sum $\sum_i \Delta E_{b,i}$ will be discussed in the next sections. N_a, n_a, and ε_a^* are, respectively, the number of electrons of the adsorbate, its local density of states (LDOS), and its atomic level in the adsorbed state; n_i and δV_i refer to an atom *i* of the substrate and are, respectively, its LDOS and the perturbation of its atomic level (see below). E_f is the Fermi energy of the substrate and *m* denotes the lowest energy of the *d* band of the substrate (the energy of the five atomic *d* orbitals of the substrate is chosen as the origin of energies). Finally, N_d is the number of valence *d* electrons of the substrate.

An accuracy of about 10 meV is reached on the difference of these binding energies owing to a continued fraction technique with 14 exact coefficients and an analytical integration[4] of the LDOS on each atom. Moreover, the atomic potential δV_i [see (5)] on each atom *i* perturbed by the surface and/or by the presence of the adsorbate is calculated self-consistently by using a local charge neutrality condition accurate to 10^{-2} electrons per atom.

In order to calculate the total energy and to minimize it with respect to the atomic position, the tight-binding Slater-Koster parameters $dd\beta$ ($\beta = \sigma, \pi, \delta$) and their law of variation with the interatomic distance must be known. In practice, for any element,

$$\left| \frac{dd\sigma}{dd\pi} \right| \simeq 2 , \tag{6}$$

and $dd\delta$ is very small. As a consequence, it can be inferred that all transition metals having the same crystalline structure have the same band structure with a scaling factor determined by the *d*-band width *W*. Thus, in this work most of the calculated energies will be given in units of *d*-band width. For a quantitative comparison with experiments, the values of the *d*-band width will be derived from a compilation of *ab initio* band-structure calculations.

The variation with distance of the tight-binding parameters is, as usual, assumed to be exponential:

$$dd\beta = dd\beta_0 e^{-qR} \quad (\beta = \sigma, \pi, \delta) . \tag{7}$$

We have used the values of the coefficients *q* tabulated in Ref. 5 for the different transition metals.

The repulsive energy between atoms is assumed to be pairwise and given by a Born-Mayer potential[6] which decreases with distance as $A_0 e^{-pR}$. As in Ref. 5, we adopt $p/q = 2.95$. The bulk equilibrium condition giving a relation between A_0 and the attractive part of the cohesive energy[7] allows the determination of A_0 and *p* for each transition metal. When the adatom and the substrate are not of the same chemical species, we assume that the Slater-Koster parameters as well as A_0, *p*, and *q* are equal to those of the substrate. The different nature of the adatom and the substrate is just mimicked by the perturbation of the atomic level ε_a^*, which is computed to achieve a *d*-band filling equal to N_a for the adatom.

Finally, at each site, the binding energy is minimized with respect to a displacement of the adatom perpendicular to the surface.

III. A QUALITATIVE APPROACH

In the tight-binding scheme, the problem of the relative stability of sites *N* and *F* can be qualitatively solved by considering the difference of the geometrical environment of the adatom at each site. Let us first assume that the adsorbate and the substrate are of the same chemical species and neglect all relaxation and self-consistency effects. Then, the first four moments $(\mu_0,\mu_1,\mu_2,\mu_3)$ of the total density of states are rigorously equal whether the adatom is on site N or F. This comes from the fact that the moment of order p is related to the paths of p jumps starting from the adatom and coming back to it. The moments μ_2 are obviously equal in the two structures, since each atom keeps the same coordination number. Since all the paths that are involved in the calculation of μ_3 are formed of equilateral triangles, μ_3 is proportional to their number. Clearly, this number is the same in both geometries. A well-known mathematical theorem states that if a function $f(x)$, defined on an x interval $[a,b]$, has its first n moments equal to zero, then $f(x)$ cancels at least n times in the interval $]a,b[$. When applied to the present case,[8] this theorem leads to the conclusion that the variation of the total density of states between the two geometries cancels at least for four values of the energies inside the band. Thus the associated variation of total energy, i.e., the difference of binding energy Γ $[\Gamma=E_B(F)-E_B(N)]$ between sites N and F cancels at least twice in the N_d interval: $0<N_d<10$.[8]

The results obtained for a (111) fcc surface shows the expected behavior (Fig. 3): Γ oscillates with N_d and cancels for two values of N_d, which we will denote N_{d_1} and N_{d_2}, $N_{d_2}>N_{d_1}$, in the following. In order to derive trends, we can mimic the different nature of the adatom and the substrate by imposing a nonvanishing value of ε_a^* [see (4)] in the computation of Γ. With a positive ε_a^*, which actually corresponds to $N_a<N_d$, the curve $\Gamma(N_d)$ has roughly the same behavior as previously (Fig. 3) but the values of N_{d_1} and N_{d_2} are slightly changed. In particular, the domain of stability of the fcc site [N site for a (111) fcc surface] for large values of N_d has been reduced (i.e., N_{d_2} has increased). Hence, we can expect that the relative stability of adsorption sites on a (111) fcc substrate at the end of the transition series may vary with the nature of the adatom. For N_a smaller than N_d, the hcp or fault site (F) may be favored. These qualitative conclusions are in agreement with the experimental data on Ir(111) (Ref. 2) (Table I). For a single adatom varying along the series from Ir to W, the stability of the hcp site increases. This comforting result, obtained with simplifying assumptions, has prompted us to compute Γ more precisely on a (111) fcc surface.

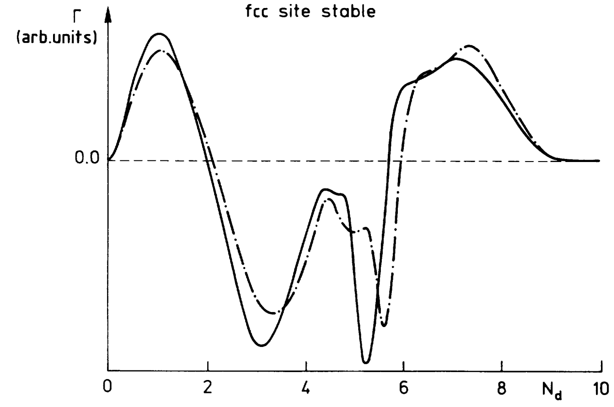

FIG. 3. Simplified calculation of Γ for an adatom on a (111) fcc surface as a function of the number of d valence electrons of the substrate (N_d): ——, adatom of the same chemical species as the substrate; —·—·—·, adatom and substrate of different chemical species. This case is mimicked only by imposing an atomic level of the adsorbate (ε_a^*) different from the substrate. ε_a^* is chosen so that $N_a<N_d$. A negative Γ means that the F (or hcp) site is the most stable.

TABLE I. Atom condensation of W, Re, Ir, and Pd on Ir(111) (from Ref. 2). E_N and E_F are the barrier heights faced by the adatom at sites N and F (see Sec. II). Since bulk Ir has the fcc structure, the N site is the fcc one, while the F site is the hcp one.

Adatom	W	Re	Ir	Pd
The most stable site	hcp	hcp	hcp	fcc
E_N-E_F (kcal/mole)	-4.35	-3.27	-0.5	1.0
E_N-E_F (meV/atom)	-187	-141	-21.5	43

IV. CHEMISORPTION ON A (111) fcc SURFACE

The preliminary calculations presented in the preceding section clearly show that a tight-binding scheme can account for the variation of stability of the different adsorption sites on a (111) fcc surface. In this section an accurate computation of Γ and of the surface diffusion activation energies (extrapolated at 0 K) is performed. This accuracy depends on the number of atoms of the substrate which are considered to be perturbed by the presence of the adatom. In this study, we have taken into account the perturbation of 22 atoms of the substrate, all located inside a sphere centered on the adatom (assumed nonrelaxed) and of radius $R_c=2.39R_1$, R_1 being the bulk first-nearest-neighbor distance. When the adsorbate relaxes, it may occur that some bulk atoms come inside this sphere. Nevertheless, we will neglect their contribution, as it would introduce an unrealistic discontinuity in the binding energy as a function of the adatom relaxation. Let us stress here that the value chosen for R_c can only slightly affect the numerical results. The trend followed by the relative stability of the adsorption sites cannot be modified by selecting another value of R_c, as it is largely dominated by the adatom and its first nearest neighbors (Sec. III).

Let us first consider an adatom of the same chemical nature as the substrate ($N_a=N_d$). We computed Γ for two values of N_d.

For $N_a=N_d=7.5$, $\Gamma/W\cong-1.7\times10^{-3}$ (W denotes the d-band width of the substrate). The hcp site is slightly more stable than the fcc one, but the energy difference is just at the limit of accuracy of our computation.

For $N_a=N_d=8.3$, $\Gamma/W\cong7.6\times10^{-3}$. The fcc site is more stable than the hcp one.

The existence of an inversion of stability between the two adsorption sites was expected from Fig. 3. It is interesting to note here that in the domain of d-band filling ($7.5<N_d<10$) the quantity Γ, the bulk energy difference between the hcp and the fcc structures, and the bulk and surface stacking fault energies have the same behavior.[1]

The experimental data of Ref. [2] show that the inversion of stability of sites occurs for a d-band filling close to that of Ir. Our computation is in full agreement with these experiments. If we assume $N_d = 7.5$ and $W = 8.3$ eV for bulk Ir, we obtain $\Gamma \cong -14$ meV, a value which is in good agreement with the experimental one (Table I).

In the same manner as previously, we have computed the barrier heights E_N and E_F for Ir. We obtain

$$E_N = 241 \text{ meV} \quad \text{and} \quad E_F = 255 \text{ meV} .$$

These values compare very favorably with the experimental ones:

$$E_N = 246 \pm 3 \text{ meV} \quad \text{and} \quad E_F = 267 \pm 3 \text{ meV} .$$

These surface diffusion activation energies are rather small, as expected for a (111) fcc surface.[9]

We have also studied some other cases, keeping $N_d = 7.5$ and varying N_a, in order to investigate the variation of relative stability of adsorption sites with the nature of the adatom. For $N_a = 7.0$, $\Gamma/W = -5.6 \times 10^{-3}$ and for $N_a = 6.5$, $\Gamma/W = -11.6 \times 10^{-3}$. In both cases, the hcp site is favored. On the contrary, for $N_a = 8.5$, $\Gamma/W = 4.8 \times 10^{-3}$, i.e., the fcc site is preferred. For an Ir substrate ($W = 8.3$ eV), the variation of Γ with N_a is shown and compared with experiment in Fig. 4. We do find that there is an inversion of stability between the hcp and fcc sites when the number of valence d electrons of the adsorbate decreases, the hcp site being the most stable when $N_a < N_d$. This result confirms the trend that was derived from the simplified calculations (Sec. III) and is in perfect agreement with experiment.

In the case where $N_a = 6.5$, we have evaluated the barrier heights E_N and E_F, which the adatom faces on Ir(111). We obtain

$$E_N = 300 \pm 10 \text{ meV} \quad \text{and} \quad E_F = 400 \pm 10 \text{ meV} .$$

Although there is no experimental determination of E_N and E_F for this exact d-band filling of the adatom, these values are in good agreement with experimental data for W and Re adatoms (Fig. 5).

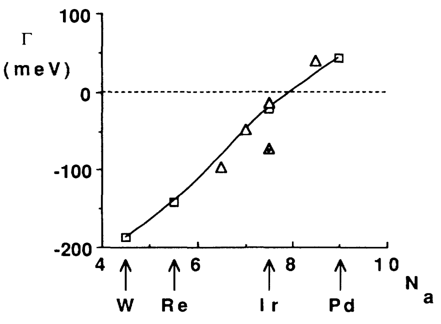

FIG. 4. Comparison between the experimental (□) (from Ref. 2) and the computed (△) values of Γ for various adatoms chemisorbed on Ir(111). ▲ is the value of Γ for an Ir adatom when taking into account a surface relaxation near the adsorbate.

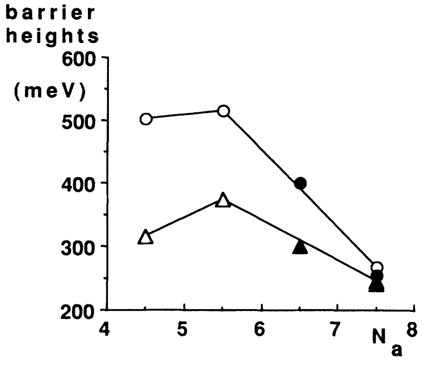

FIG. 5. Comparison between the experimental values of E_N and E_F (from Ref. 2) and the computed ones for various adatoms on Ir(111). △, E_N from Ref. 2; ○, E_F from Ref. 2; ▲, E_N from computation; ●, E_F from computation.

A relaxation of the surface in the presence of an adatom has been reported.[10,11] On the (111) fcc surface, we expect these effects to be rather small, since the surface is close packed. However, one may wonder if such an effect could reverse the stability of the adsorption sites. To answer this question, we assume that the relaxation of the surface does not affect the symmetry of the problem, i.e., that the relaxation is limited to an isotropic dilatation (or contraction) of the equilateral triangle formed by the three first nearest neighbors of the adatom at sites N and F (Fig. 6). These assumptions are justified by a preceding study[11] on Al(001), which has shown that the relaxation results in a simple expansion of the square formed by the four first nearest neighbors of the adatom, while their displacement into the Al slab is negligible.

We have minimized the total binding energy with respect to the displacement of the adatom nearest neighbors, keeping the adatom at the position previously determined. When $N_a = N_d$, we find that the triangle of neighbors of the adatom expands slightly at both sites N and F. However, this expansion is very small, and the subse-

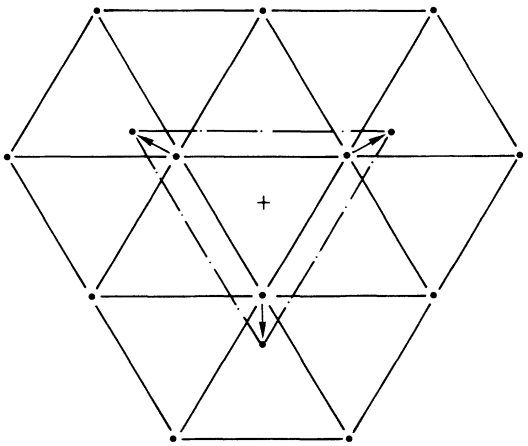

FIG. 6. The assumed relaxation of the (111) fcc surface in the presence of an adsorbate at a threefold site. The displacement of the surface atoms are indicated by arrows. + is the projection of the adatom of the surface; ● are the surface atoms.

quent variations of binding energies reach the limit of accuracy of our computation. The most significant expansion was found for $N_a = N_d = 7.5$ at the hcp site: the side of the triangle increases by $\cong 5\%$ and the binding energy of the adatom varies by $\cong 2\%$. These expansions are of the same order of magnitude as for an Al adatom on a Al(001) surface. However, in our case, we find that the adatom-substrate bond length remains slightly smaller than the bulk interatomic distance. For instance, when $N_a = N_d = 7.5$ at the hcp site, the adatom-substrate bond length is equal to $0.94R_1$.

These surface relaxations lead to a new value of Γ for Ir(111) equal to $\cong -72$ meV. This value remains in reasonable agreement with the experiments (Fig. 4). An accurate computation of Γ should allow the adatom to move again after this surface relaxation. Nevertheless, such a procedure would go beyond the limit of accuracy of a tight-binding scheme. Let us recall that the aim of this surface relaxation study was only to investigate if such effects could reverse the relative stability of adsorption sites. This is clearly not the case, and, in the following, we will neglect these effects. However, we must stress that there is no contraction of the triangle of the first nearest neighbors of the adatom: even a slight contraction ($\cong 1\%$) involves a cost of energy that is significant tin our computation.

V. CHEMISORPTION ON A (0001) hcp SURFACE

We now consider the chemisorption of a single adatom on a (0001) hcp surface. The computation of the binding energy is carried out using the same method as for the (111) fcc surface. Preliminary calculations of Γ, performed with the same assumptions as in Sec. III, show that Γ oscillates with N_d. However, there are two domains of N_d for which the hcp bulk structure is stable: $1 < N_d < 3.5$ and $6 < N_d < 7.5$ (while the fcc structure is stable only for $N_d > 7.5$).[1] Consequently, we can expect a more diversified behavior for the hcp metals than for the fcc ones. In particular, it is interesting to know if an inversion of stability between the two adsorption sites can occur in each N_d interval. As in Sec. III, the variation of the chemical nature of the adsorbate is mimicked by a variation of its atomic level ε_a^* [see (4)] and we find that a positive ε_a^* ($N_a < N_d$) favors the N (hcp) site in the N_d interval $6 < N_d < 7.5$, while no obvious trend emerges from this calculation when N_d lies in the interval $1 < N_d < 3.5$.

Accurate values of Γ are presented in Table II for $N_a = N_d$. In this study we have not considered the metals with small values of N_d, as it can be expected that the sp-d hybridization can significantly affect the values of Γ for such d-band fillings. Furthermore, such values of N_d would correspond to rare-earth metals for which surface studies have been scarcely carried out.

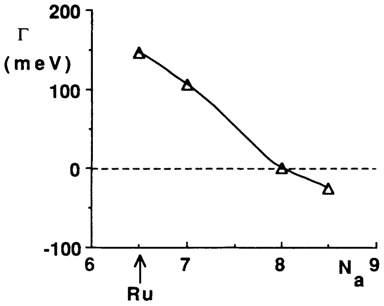

FIG. 7. Variation of Γ with the number of valence d electrons (N_a) of an adatom chemisorbed on Ru(0001).

When $1 < N_d < 3.5$, there is clearly an inversion of stability between the two adsorption sites. At small values of N_d, the N (or hcp) site is the most stable, while for $N_d = 3.40$, the F (or fcc) site is favored. A linear interpolation between $N_d = 2.54$ and 3.40 leads to a cancellation of Γ around $N_d = 2.70$. This value is slightly larger than the d-band filling of Ti. We can thus predict that the difference between the barrier heights E_N and E_F should be small for Ti, and slightly in favor of the hcp sites.

When $6 < N_d < 7.5$, the hcp site is always more stable than the F (or fcc) one (Table II). These d-band fillings correspond to metals such as Re, Ru, or Os. We have investigated more particularly the case of Ru, for which $N_d \cong 6.5$. Assuming a d-band width of about 8.5 eV for this metal, we obtain $\Gamma \cong 150$ meV and values of barrier heights E_N and E_F equal to

$$E_N \cong 364 \text{ meV} \quad \text{and} \quad E_F \cong 214 \text{ meV} .$$

As for Ir, we have studied the variation of relative stability of sites N and F with the number of valence d electrons of the adsorbate. When N_a increases from 6.5 to 8.5, Γ/W decreases monotonically and cancels around $N_a = 8.0$ (Fig. 7). Hence, for $N_a > 8.0$, the fcc site is more stable than the hcp one. Accordingly, we find that on Ru(0001), Co, Rh, or Ir adatoms should be more stable at the hcp site, while the fcc site should be favored for Ni, Pd, or Pt adatoms. It would be then very interesting to perform such an experiment, which to our knowledge, has never been carried out presently.

VI. CONCLUSION

We have shown that a simple tight-binding scheme accounts for the relative stability of the two ternary adsorption sites that are present on a (111) fcc or a (0001) hcp surface. Our calculated results are in perfect agreement with the experimental data on Ir(111) and the behavior of adatoms on Ru(0001) is predicted.

These results raise some questions about the mecha-

TABLE II. Difference of the binding energies of an adatom at sites N and F on a (0001) hcp surface. N_d ($=N_a$) is the number of d valence electrons of the substrate and the adsorbate. W is the d-band width of the substrate. A negative Γ means that the F (or fcc) site is the most stable.

N_d ($=N_a$)	1.65	2.54	3.40	6.32	6.52	7.30
Γ/W	18×10^{-3}	3×10^{-3}	-11×10^{-3}	19.5×10^{-3}	17.5×10^{-3}	7×10^{-3}

nisms of crystalline growth. A preceding paper[1] has shown that the deposition of a complete atomic monolayer on a (111) fcc surface is always in epitaxy at 0 K with the substrate. In particular, there is no spontaneous surface stacking fault for an Ir monolayer on Ir(111). On the contrary, a single Ir atom prefers the fault site on Ir(111). Thus, as has already been pointed out,[12] it will be of interest to see if a transition from fault to normal sites occurs when the adatom concentration increases. The difference between the binding energy of the adatom at the two sites being small, it can be inferred that this transition may be driven by the adatom-adatom interaction.[12]

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