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# Structural stability of adatom islands on fcc(111) transition-metal surfaces

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The energetics of monomer, dimer, and triangular trimer adatom islands on the (111) surface of fcc transition metals of the same chemical species is calculated in the tight-binding scheme as a function of the *d* band filling. Both the adatom and their nearest neighbor substrate atoms are allowed to relax. We investigate all possible atomic configurations of the system arising from the existence of (a) two types of adsorption sites: normal (fcc) and fault (hcp) sites, and (b) both types of borders that may exist for triangles of adatoms: *A*, having (001), (010), and (100) facets and *B*, having $(11\bar{1})$, $(1\bar{1}1)$, and $(\bar{1}11)$ facets. It is found that there is an inversion of relative stability from fault to normal sites when the *d* band filling is larger than 8.2*d* electrons per atom for monomers, 7.85 for dimers, 7.5 for trimers of type *A*, and 7.6 for trimers of type *B*. There is also an inversion of stability for trimers from type *B* to type *A* when the *d* band filling is larger than 7.95. All these results are in very good agreement with experiments on Ir for which the *d* band filling is $\simeq 7.5--7.6$: monomers and dimers prefer to stick at fault sites while trimers settle at both sites. Furthermore, triangles of type *B* are energetically more favored than triangles of type *A*. The case of other transition metals is also discussed. [S0163-1829(96)03135-9]

## I. INTRODUCTION

The study and characterization of crystal growth[1] has, apart from its basic surface science interest, important implications in technology. The process of fabrication of very thin metal films is commonly used in electronics, optoelectronics, and the recording media industry. The more the growth is understood, the more controlled the fabrication processes can be made and, consequently, a better quality of the device performances can be obtained.

A possible scenario of layer-by-layer growth is the following: an atom adsorbs at the surface; it starts diffusing until it definitely sticks to a defect, e.g., a step or a vacancy; the step will ''flow'' and construct the new layer, or there will be adatom island formations if many adatoms cluster together before reaching a step site. A ''flow'' of steps is the desired, ideal two-dimensional growth, while a growth via adatom islands may result in a so called three-dimensional growth which gives rise to rougher surfaces. Moreover, it is desired that the growth also is epitaxial—the new layer should match the substrate and not introduce defects or stacking faults.

For growth on fcc(111) metal surfaces, there are two threefold adsorption sites: the normal (fcc) site which continues the stacking order of the fcc(111) and the fault (hcp) site which, if occupied by the adatoms during a growth process, will introduce the hcp stacking order instead and, thus, a stacking fault. Previous calculations[2] have shown that epitaxial monolayers always are energetically favorable on fcc(111). However, experiments[3] and calculations[4] show that for a single Ir adatom on Ir(111), the hcp, or fault, site is preferred. One may thus expect that for this element a transition from fault to normal site adsorption will occur when the adatom island size increases. Furthermore, adatom islands are expected to be limited by close-packed atomic rows corresponding to two different types of microfacets: (001) for type *A* and $(11\bar{1})$ for type *B*. These edges correspond, in other words, to the type of steps with dense edges existing on the fcc(111) surface.[5]

Wang and Ehrlich[6] have observed Ir clusters of various sizes on Ir(111). They find that there is indeed a transition from preferred fault site adsorption to normal site adsorption when the adclusters consist of at least four atoms and that triangles with type *B* borders are energetically favored over triangles with type *A* borders. Furthermore, experimental studies of the equilibrium shape of Pt clusters on Pt(111) have been performed by Michely *et al.*[7] They observed irregular hexagons, which have both *A* and *B* borders, and found that *B* edges are predominant. In view of the large size of the considered clusters, the equilibrium shape is dominated by the free energies of the steps limiting them. The calculation of the corresponding step energies has been presented elsewhere,[5] but it is not sure that the results still apply for small clusters where corner effects may be important. It is thus of interest to make a systematic investigation of the energy difference of monomers, dimers, and adatom triangles with different edges at the two possible adsorption

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sites on fcc(111) surfaces of the same chemical species as a function of the $d$ band filling.

In the following, we proceed with such an investigation within a tight-binding model. The paper is organized as follows. In Sec. II, we present the tight-binding model for $d$ electrons that is used for calculating the binding energies of transition metal adatom islands. The model is made explicit for application on adatom island adsorption on fcc(111) surfaces in Sec. III. In Sec. IV, our numerical results are presented and compared with experiments. Finally, a summary and our conclusions are given in Sec. V.

## II. TIGHT-BINDING MODEL

In a tight-binding semiempirical calculation, the binding energy $E_B$ of adatoms is usually expressed as the sum of an attractive and a repulsive contribution as[8]

$$E_B = \Delta E_{\mathrm{band}} + \Delta E_{\mathrm{rep}}, \tag{1}$$

where $E_{\mathrm{band}}$ is due to the broadening of valence electronic levels into a band and $E_{\mathrm{rep}}$ contains the ion-ion repulsion. The $\Delta$ indicates that we calculate the variation of band and repulsive energies relative to a reference system. For adatoms at a surface, the reference system is a surface and the free adatoms infinitely apart from each other and from the surface.

The repulsive energy is described by a Born-Mayer pairwise potential. Since we limit ourselves to the case where the adatoms and the substrate are transition metals of the same chemical species, it can be written as

$$E_{\mathrm{rep}} = \sum_{i,j<i} \mathcal{A} e^{-p[(R_{ij}/R_0)-1]}, \tag{2}$$

where $\mathcal{A}$ and $p$ are parameters characteristic of a given metal, $R_{ij}$ is the distance between atoms $i$ and $j$, and $R_0$ is the equilibrium interatomic distance in the bulk.

Since we are interested in computing band energies for transition metals, we use a tight-binding Hamiltonian, $H_{\mathrm{TB}}$, where only the $d$ electrons are explicitly taken into account. To its justification, it has been shown[9] that, at least for transition metals not too close to the extremes of the transition-metal series, the cohesive properties at equilibrium are by far dominated by the broadening and the occupancy of the valence $d$ levels.

When we deal with impurities, surfaces, etc., the effective atomic levels and local densities of states (LDOS's) are site dependent. Both quantities are interrelated since perturbations in LDOS's cause a change of the potential and, thus, of the atomic level at each site. Consequently, they should be calculated self-consistently. However, in metals, screening of charge takes place within an interatomic distance and the change of atomic levels may be obtained by requiring local charge neutrality.[8]

The band contribution, $\Delta E_{\mathrm{band}}$, to the binding energy of adsorbates can be split into two contributions: one which is coming from the broadening of the atomic levels of the adatoms ($\Delta E_{\mathrm{band}}^{\mathrm{ads}}$), and one which arises from the perturbation of the substrate due to the presence of the adatoms ($\Delta E_{\mathrm{band}}^{\mathrm{sub}}$). If we call $\varepsilon_a^*(\varepsilon_a)$ the atomic level of adatom $a$ in the adsorbed (free) state, $\Delta E_{\mathrm{band}}^{\mathrm{ads}}$ can be expressed as a sum of contributions of each adatom as

$$\Delta E_{\mathrm{band}}^{\mathrm{ads}} = \sum_a \left[ 10 \int^{E_F} E n_a(E) dE - N_d(\varepsilon_a^* - \varepsilon_a) - N_d \varepsilon_a \right], \tag{3}$$

where $n_a(E)$ is the LDOS's of adatom $a$ (normalized to unity) and $N_d$ is the number of valence $d$ electrons of the adatom and substrate atoms since they are assumed to be of the same chemical species. The second term in Eq. (3) arises from the double counting of electron-electron interactions responsible for the shift $(\varepsilon_a^* - \varepsilon_a)$, and Eq. (3) simplifies into

$$\Delta E_{\mathrm{band}}^{\mathrm{ads}} = \sum_a \left[ 10 \int^{E_F} E n_a(E) dE - N_d \varepsilon_a^* \right]. \tag{4}$$

For an atom at a substrate site $i$, the LDOS's $n_i'(E)$ is perturbed by the presence of the adsorbate(s) as $n_i'(E) = n_i(E) + \Delta n_i(E)$, where $n_i(E)$ is the LDOS's of atom $i$ in the clean substrate and $\Delta n_i(E)$ is the perturbation due to the adatoms. $\Delta E_{\mathrm{band}}^{\mathrm{sub}}$ is written as a sum of contributions from each substrate atom:

$$\Delta E_{\mathrm{band}}^{\mathrm{sub}} = \sum_{i \in \mathrm{substrate}} \left\{ 10 \int^{E_F} E \Delta n_i(E) dE - N_d \Delta V_i \right\}. \tag{5}$$

Here again the second term avoids the double counting of the change in electron-electron interactions responsible for the shift $\Delta V_i$ of the atomic level of substrate atom $i$ due to the presence of the adatoms.

The matrix elements of the Hamiltonian $H_{\mathrm{TB}}$ are the hopping integrals which have a finite range and are limited here to nearest neighbors, and the effective atomic levels. The hopping integrals are completely determined by three hopping parameters $dd\sigma$, $dd\pi$, $dd\delta$ (Ref. 10) and the direction cosines of the vector $\mathbf{R}_{ij}$ connecting sites $i$ and $j$. The variation of these parameters with distance is taken to be exponential $(\lambda = \sigma, \pi, \delta)$:

$$dd\lambda = dd\lambda_0 e^{-q[(R_{ij}/R_0-1]}. \tag{6}$$

The local density of states of a given atom is calculated using the Green operator:

$$G(z) = \frac{1}{z - H_{\mathrm{TB}}}, \tag{7}$$

as

$$n_i(E) = \frac{1}{5} \sum_\lambda -\frac{1}{\pi} \lim_{\varepsilon \to 0^+} \mathrm{Im} \langle i\lambda | G(E + i\varepsilon) | i\lambda \rangle,$$

$$n_i(E) = \frac{1}{5} \sum_\lambda -\frac{1}{\pi} \lim_{\varepsilon \to 0^+} \mathrm{Im} G_{ii}^{\lambda\lambda}(E + i\varepsilon),$$

$$n_i(E) = \frac{1}{5} \sum_{n,\lambda} |\langle \Phi_{i\lambda} | \Psi_n \rangle|^2 \delta(E - E_n), \tag{8}$$

where $\Phi_{i\lambda}$ is the atomic orbital of symmetry $\lambda$, centered at site $i$, and $\Psi_n$ is the eigenfunction of energy $E_n$.

TABLE I. Tight-binding parameters used in the calculations are tabulated. The hopping integrals $dd\sigma_0$, $dd\pi_0$, and $dd\delta_0$ are expressed in units of the bulk bandwidth $W$. The parameters $p$ and $q$ are dimensionless.

| Parameter | Value |
|---|---|
| $p$ | 11.40 |
| $dd\sigma_0/W$ | -0.1300 |
| $dd\pi_0/W$ | 0.0586 |
| $dd\delta_0/W$ | -0.0073 |
| $q$ | 3.80 |

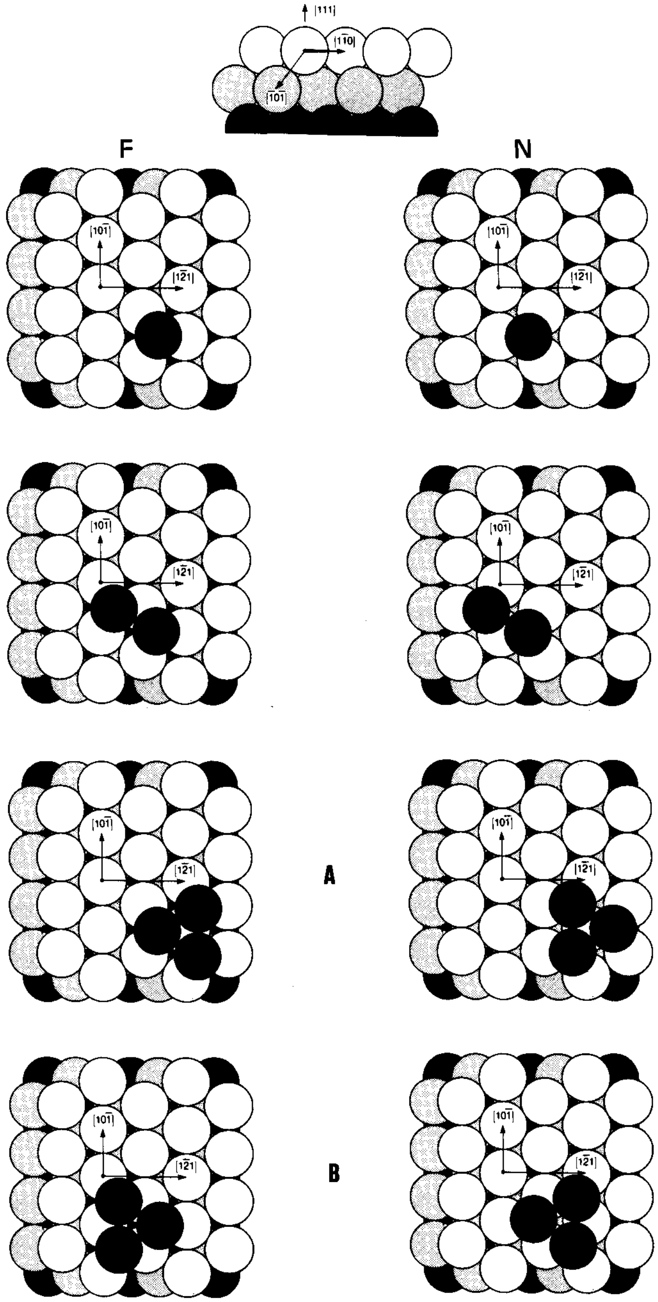

FIG. 1. Possible atomic configurations for monomers, dimers and triangular trimers on fcc(111) surfaces at normal ($N$) and fault ($F$) sites. Trimers of type $A$ with (001), (010), and (100) microfacets have their center above an atom in the surface layer. Trimers of type $B$ with (111), (111), and (111) microfacets have their center above an adsorption site. Four different configurations ($A_N,B_N,A_F,B_F$) are thus possible for triangular trimers.

The quantity $G_{ii}^{\lambda\lambda}$ can be expanded as a continued fraction.[8] When the corresponding coefficients are exact up to the level $n$, the LDOS's has $2n$ exact moments. The more accurate a calculation is required to be, the more exact moments $\mu_p^i$,

$$\mu_p^i=\int_{-\infty}^{+\infty}E^p n_i(E)dE, \tag{9}$$

need to be included.

In this work, the LDOS's of an atom in a system is evaluated by calculating exactly $n_c$ first levels in a recursion scheme and replacing the remaining part of the continued fraction by the usual square root terminator which corresponds to using the asymptotic values for the remaining coefficients.[8] The parameters $dd\lambda_0$ are fitted to band structure calculations at high symmetry points of the Brillouin zone. These parameters are given in Table I, in units of the bandwidth. They are derived for Ir, however, we have kept them constant as a function of the $d$ band filling since we do not expect that the ratios $dd\pi/dd\sigma$, and $dd\delta/dd\sigma$ vary substantially in other fcc transition metals. The values of $p$ and $q$ (Table I) have been derived from Ref. 11. The repulsive interaction energy of a pair of atoms is drawn from the bulk equilibrium condition, i.e.:

$$\mathcal{A}=-\frac{q}{6p}E_{\mathrm{band}}^{\mathrm{bulk}}(N_d), \tag{10}$$

where $E_{\mathrm{band}}^{\mathrm{bulk}}(N_d)$ is the bulk band energy at equilibrium (per atom).

## III. APPLICATIONS TO ADATOM ISLANDS AT fcc(111) SURFACES

We calculate the binding energies of monomers, dimers, and trimers on the (111) surface of fcc transition metals. In both cases, we determine the effective atomic levels and LDOS's on a cluster containing the adatoms, the surface atoms which are directly bound to them, and the nearest neighbors of the latter. The contributions to the binding energy of the adatoms from more distant neighbors are small and can be neglected. Monomers and dimers can adsorb with only two configurations: normal (fcc) or fault (hcp) (Fig. 1). For the trimers, there are six possible configurations of the adatoms: two linear and four triangular. The adatoms can be adsorbed either at both types of sites, and the triangles can have edges of type $A$ [with (001) microfacets] or $B$ [with $(\overline{111})$ microfacets]. We will not study the linear trimers since, in our model, correlation effects, which tend to stabilize atomic configurations with reduced coordinations,[12] are excluded. These effects would probably be important for calculating the energy difference between a linear and a triangular trimer since, in the latter case, all adatoms have five nearest neighbors while, for the linear trimer, the adatoms at both ends have only four nearest neighbors. Consequently, correlation effects will act to favor the linear trimer and thus compete with the increase of band energy resulting from the loss of one bond. We consider thus, in the following, only the triangular configurations which are shown in Fig. 1.

Two types of atomic relaxation have been considered: first the adatoms are allowed to relax perpendicularly to the surface, each bond inside the adatom island remaining parallel to the surface. Second, atomic displacements of surface atoms parallel to the surface are allowed in the following way: each adatom is assumed to give rise to an isotropic dilatation (or contraction) of the equilateral triangle formed by its three first neighbors in the surface and the displacements produced by two different adatoms on the same surface atom are supposed to be additive. Under these conditions the symmetry of the unrelaxed system is preserved: threefold for monomers and trimers, twofold for dimers. Even though these conditions may seem rather restrictive, we do think that the main effects of atomic relaxation is accounted for in these schemes. Indeed, lateral relaxations of adatoms are not detected in experiments[6] and *ab initio* calculations on Al(001) (Ref. 13) have shown that the displacements of the neighbors of the adatoms into the bulk are negligible. The assumption of additive displacements is obviously not rigorous but should be valid as a first approximation. The energy minimization has been carried out with respect to both displacements. In the following, the perpendicular relaxation will be given in the percentage of the bulk (111) interplanar distance $d$ $(10^2\Delta d/d)$, while the lateral relaxation of the neighbors will be referred to the height $h$ of the equilateral triangle formed by three nearest neighbors in the bulk $(10^2\Delta h/h)$.

In order to reach sufficient accuracy in the calculated energies and energy differences of various adatom islands, we use $n_c=10$ exact levels in the continued fractions — which amounts to 20 exact moments. In the following calculation we have varied the $d$ band filling from $N_d=6.8$ to $N_d=9.2$ $e^-$/atom. This range of band fillings includes all fcc transition metals.

It is well known that in bulk crystals there are inversions of relative stability between the hcp and the fcc stucture as a function of the $d$ band filling. It has been shown that these inversions follow from the equality of the first three moments $(\mu_1,\mu_2,\mu_3)$ of the total density of states in both structures.[14] Then it can be easily proved that the difference in energy between the two phases cancels at least twice in the interval $N_d \epsilon [0,10]$. In particular, in the range of $d$ band fillings considered here, we find, using the tight-binding parameters given in Table I, that there is an inversion of stability from the hcp phase to the fcc one when $N_d$ is larger than $\simeq 7.5$ $e^-$/atom, in agreement with what is indeed observed. In the case of the same cluster of adatoms adsorbed either at fcc or hcp sites on a (111)fcc surface at the same distance from the surface, and when the renormalization of atomic levels is neglected, a similar behavior is also expected since the total densities of states have again the same $\mu_1$, $\mu_2$, $\mu_3$ in both geometries. Indeed, it is well known[15] that $\mu_2$ and $\mu_3$ are, respectively determined by the number of bonds and of triangular paths on the lattice involving three jumps between nearest neighbors. It has been shown that for a whole layer the inversion of stability occurs at roughly the same band filling as in the bulk, so that a stacking fault is never stable at the surface.[2] However, the particular value of band filling at which the inversion occurs may be dependent on the considered clusters (size and geometry). The same behavior is also expected when comparing $A$ and $B$ triangles. We will see in the following that the above qualitative trends remain valid when the model is improved by taking into account the renormalization of the atomic levels of the adatoms, its neighbors, and of the first layers of the substrate and when atomic relaxation is allowed.

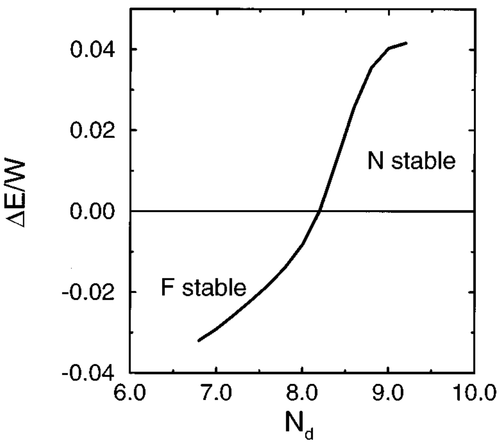

FIG. 2. Difference, $\Delta E = E_B(F) - E_B(N)$ (in units of the substrate bandwidth $W$), of the binding energy of a monomer between the fault and the normal adsorption site on fcc(111) transition-metal surfaces as a function of the $d$ band filling $N_d$.

## IV. RESULTS AND DISCUSSION

### A. Single adatoms

In a previous work using exactly the same model,[4] we have been able to explain the inversion of stability between fault and normal sites on Ir(111) when the $d$ valence shell of the adatom fills. In particular, it was found that an Ir adatom was more stable at a fault site with an increased stability when the neighboring surface atoms were allowed to relax. However, no full minimization with respect to both this relaxation and the vertical relaxation of the adsorbate was carried out.

In the present work we limit ourselves to the case of homoepitaxy, but a systematic study is performed as a function of the $d$ band filling. Furthermore the total energy is fully minimized as a function of the two allowed displacements. The difference of adsorption energy between the fault and the normal site is shown in Fig. 2. It is seen that an inversion of stability from the hcp to the fcc site occurs at $N_d=8.2$ $e^-$/atom. This value is significantly larger than the value found when the substrate relaxation is neglected. Thus the substrate relaxation acts in favor of the hcp site when $N_d$ is smaller than about 8.2 $e^-$/atom. This is clearly related to the different behavior of the atomic relaxations found as a function of the $d$ band filling for the two types of sites (Fig. 3). As expected the normal displacement $\Delta d/d$ of the adatom is directed towards the surface, while the neighbors are laterally displaced away from the adatom.

Let us emphasize that the second-moment potential:[16]

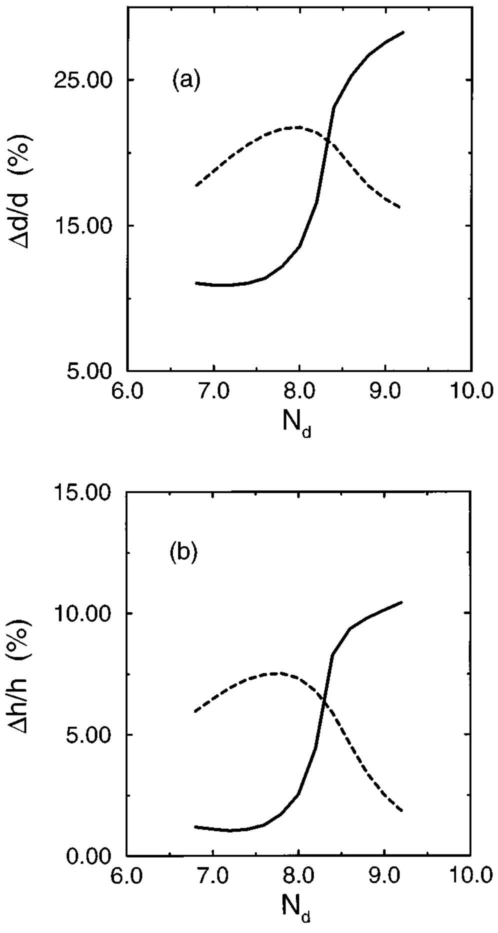

FIG. 3. Atomic relaxations for a monomer at a normal site (solid line) and at a fault site (dashed line) as a function of the $d$ band filling $N_d$: (a) normal displacement of the adatom towards the surface in percentage of the bulk (111) interplanar distance $d$, (b) lateral displacement of the neighbors away from the adatom in percentage of the height $h$ of the equilateral triangle formed by three nearest neighbors in the bulk.

$$E_{\rm tot}=\sum_i\left(\sum_{j<i}\mathcal{A}e^{-p[(R_{ij}/R_0)-1]}-\mathcal{B}\sqrt{\sum_{j\neq i}e^{-2q[(R_{ij}/R_0)-1]}}\right), \qquad (11)$$

when limited to first nearest neighbors, would lead to atomic displacements independent of the $d$ band filling. Indeed, in this approximation, $E_{\rm band}^{\rm bulk}(N_d)=\mathcal{B}\sqrt{12}$ and consequently $\mathcal{B}$ is proportional to $\mathcal{A}$ [see Eq. (10)]. Nevertheless, for the purpose of comparison, we have also performed calculations using this scheme. Contrary to the above complete calculation, the results are very similar for both sites. This can be qualitatively explained as follows. The second-moment approximation only takes into account the variation of nearest neighbor distances. Consequently, it gives usually the right sign and order of magnitude of the atomic displacements when all nearest distances are increased (or decreased), as in the case of normal relaxation of flat surfaces. This is corroborated by a calculation with the present model (using 20 moments) but allowing vertical displacements of the adatom only, since this relaxation is then almost independent of the type of adsorption site and roughly equal to that obtained with the second-moment potential. However, in the case of the lateral relaxation, such as the substrate relaxation studied here, some distances are expanded whereas some others are compressed and the net effect on the second-moment may nearly cancel. This explains qualitatively why the second moment calculation gives almost no lateral relaxation of the surface atoms. In these conditions angular distortions which are taken into account in the third and higher moments play the dominant role. These distortions are obviously dependent on the adsorption site which explains the different behavior of the lateral relaxation of the adatom neighbors between fault and normal sites. In addition, it is clear that if the triangle of neighbors expands, the adatom moves towards the surface to compensate for the increased bond length, so that finally both relaxations vary in the same way.

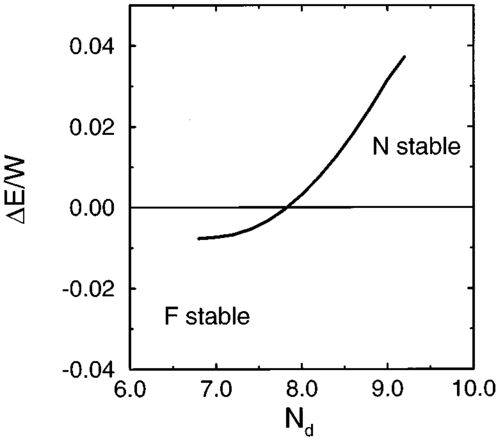

FIG. 4. Difference, $\Delta E=E_B(F)-E_B(N)$ (in units of the substrate bandwidth $W$), of the binding energy per atom of a dimer between the fault and the normal adsorption site on fcc(111) transition-metal surfaces as a function of the $d$ band filling $N_d$.

### B. Dimers

The difference of adsorption energy per atom between the dimers at fault and normal sites is shown as a function of the $d$ band filling in Fig. 4. The same type of behavior as for the monomer is found. However, on the one hand, this difference is smaller than for the monomer. On the other hand, the range of $d$ band fillings for which the dimer at fault sites is more stable than at normal sites is narrower than in the case of the monomer since the inversion of stability occurs now at $N_d\simeq 7.85$ $e^-$/atom. The relaxations corresponding to both geometries are given in Fig. 5. It is seen that the relaxations are larger at fault sites than at normal sites until $N_d\simeq 8.2$ $e^-$/atom. Consequently, as for the adsorption of a single adatom, relaxations act in favor of the fault site in the lower part of the range of $d$ band fillings considered here. Actually, when the relaxation of the neighbors of the adatom is neglected, the inversion of stability is found for $N_d\simeq 6.8$ $e^-$/atom.

### C. Adatom triangles

The four possible types of triangular trimers at an fcc(111) surface which are depicted in Fig. 1 are denoted in

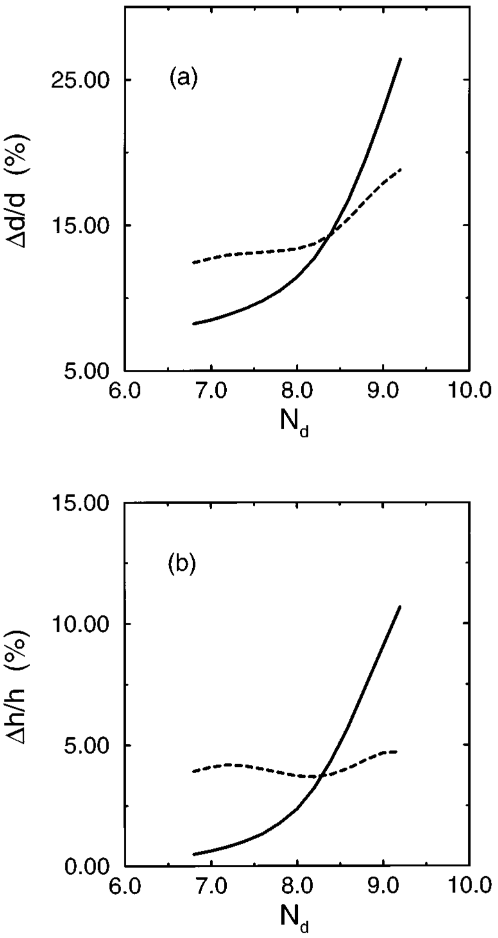

FIG. 5. Same caption as Fig. 3 but for the dimer.

the following; $A_N$ for the type $A$ triangle at normal sites, $A_F$ for the type $A$ triangle at fault sites, $B_N$ for the type $B$ triangle at normal sites, $B_F$ for the type $B$ triangle at fault sites.

We have calculated the energy (per atom) of adatom triangles in the previously mentioned configurations as a function of the *d* band filling. The adsorption energy difference (per atom) between fault and normal adsorption sites for *A* and *B* triangles is shown in Fig. 6. It exhibits the same qualitative behavior as for monomers and dimers, but its magnitude is again decreased. As expected, there is a change of sign of this difference around $N_d = 7.5$ $e^-$/atom for *A* triangles and $N_d = 7.6$ $e^-$/atom for *B* triangles, the normal sites being preferred beyond these values of the band filling. Thus there is always an inversion of stability between hcp and fcc sites when $N_d$ crosses a critical value $N_d^c$. However, when the size of adatom islands increases from 1 to 3 atoms, $N_d^c$ decreases and, for triangles, it is very close to the critical value of $N_d$ for which the transition hcp-fcc occurs in the bulk, i.e., $N_d^{c,\mathrm{bulk}} = 7.5$ $e^-$/atom.

The relaxations obtained for the 4 types of triangles are shown in Figs. 7 and 8. As in monomers and dimers, the relaxations are larger at fault sites than at normal sites when $N_d \leq 8$ $e^-$/atom. Thus, in this range of $N_d$, they act in favor of the fault site by displacing $N_d^c$ to larger band fillings but just enough to obtain a very narrow range of band fillings above $N_d^{c,\mathrm{bulk}}$, where the fault and normal triangles have about the same energy. On the contrary, when $N_d \leq 8$ $e^-$/atom, the relaxations around *A* and *B* triangles are almost the same provided that the adatoms occupy the same type of sites. Consequently, one can infer that the relaxations have little influence on the relative stability of triangles *A* and *B*.

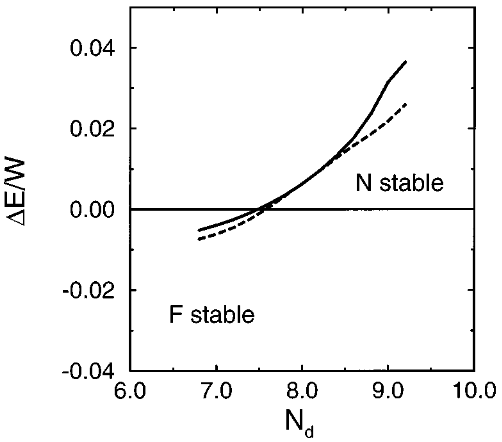

FIG. 6. Difference, $\Delta E = E_B(F) - E_B(N)$ (in units of the substrate bandwidth $W$), of the binding energy per atom of a trimer between the fault and the normal adsorption site on fcc(111) transition-metal surfaces as a function of the *d* band filling $N_d$. Solid line: *A* triangles; dashed line: *B* triangles.

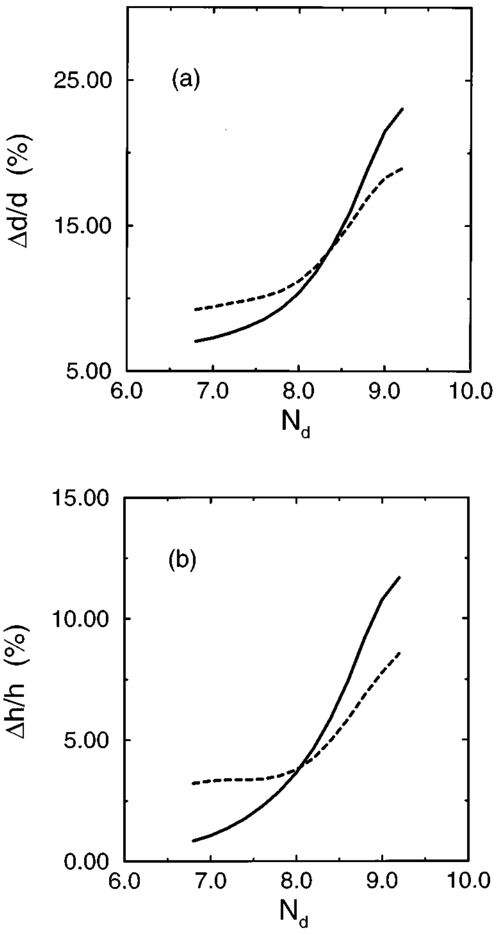

FIG. 7. Same caption as Fig. 3 but for a trimer of type *A*.

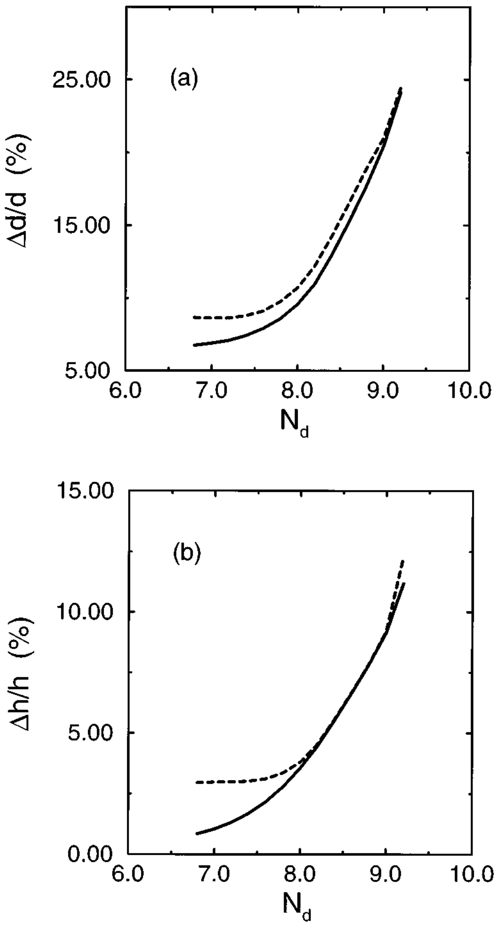

FIG. 8. Same caption as Fig. 3 but for a trimer of type *B*.

In Fig. 9, the energy differences (per atom) of adatom triangles of type *A* and *B* at normal and fault sites on fcc(111) surfaces are shown. There is a change of sign of this energy difference at a band filling around 7.95 $e^-$/atom. For metals with a *d* band filling less than 7.95 $e^-$/atom, the type *B* adatom triangle is more stable than the type *A* adatom triangle irrespective of the site. The reverse is true for *d* band fillings larger than 7.95 $e^-$/atom except for the fault triangles where a second inversion of stability from *A* to *B* triangles occurs at $N_d \simeq 8.85$ $e^-$/atom. Let us note that, as expected from the above discussion on relaxations, the critical value corresponding to the first inversion of stability is not very sensitive to relaxation. Indeed, when relaxation is completely neglected, the critical value is found at $N_d = 8.2$ $e^-$/atom for both types of sites. Thus it increases slightly the range of stability of *A* triangles. Finally, the energy difference between *A* and *B* triangles is larger at fault than at normal sites for low band fillings, the reverse being obtained at high band fillings.

### D. Comparison with experiments

Let us now compare our results with the findings of Wang and Ehrlich[6] on Ir clusters. These authors, using field ion microscopy, have been able to examine Ir clusters containing from 1 to 13 atoms held on the close-packed Ir(111) plane. They have found that in all the clusters examined, atoms sit in nearest neighbors sites. Furthermore, triangular trimers are found to be slightly more stable that the linear ones although this difference is at the limit of the capability of the experimental method. By mapping all the sites occupied by an adatom after repeated diffusions, they have been able to show that the fault sites are preferred for the monomers and dimers while normal sites are much favored over fault ones for tetramers and larger clusters. For triangular trimers both types of sites are roughly equally stable. In addition, triangles *B* are significantly more stable than triangles *A*.

From our calculations, it can be deduced that there exist a domain of *d* band fillings $N_d \epsilon [7.5,8.2]$ for which the hcp site is more stable than the fcc site for one adatom on a fcc(111) surface of the same chemical species. This domain narrows very rapidly when the cluster size increases. Consequently, outside this domain and in the range of stability of bulk fcc, i.e., $N_d > 8.2$ $e^-$/atom, we predict that cluster adatoms sit always at normal sites irrespective of the size of the cluster. On the contrary for $N_d \epsilon [7.5,8.2]$ a transition from fault to normal site is expected for clusters containing 2 or 3 atoms. Taking $N_d \simeq 7.5-7.6$ $e^-$/atom for Ir,[4] we find, in accordance with experiments, that Ir monomers and dimers occupy fault sites, whereas fault and normal triangular trimers have almost the same adsorption energy, but *B* triangles are significantly more stable than *A* triangles. If we note that Rh has the fcc structure and that its band filling must be close to that of Ir since they belong to the same column in the Periodic Table, we predict the same kind of behavior for this element. It would be interesting to have experiments performed on this metal.

Let us now discuss the case of Pt. At larger cluster sizes (several hundreds Å wide), Michely *et al.*[7] have found that the cluster exhibits an irregular hexagonal shape with *A* and *B* borders, the *B* borders being predominant. At these sizes, the shape of the cluster is completely determined by the step energies of the borders. The energies of steps *A* and *B* have been studied in a previous work,[5] neglecting relaxation effects. It was shown that in the range of *d* band fillings corresponding to Pt, *A* borders were slightly energetically fa-

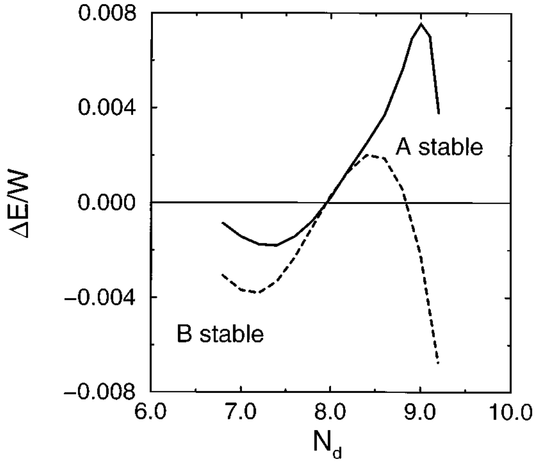

FIG. 9. Difference, $\Delta E = E_B(B) - E_B(A)$ (in units of the substrate bandwidth *W*), of the binding energy per atom between type *B* and type *A* trimers on fcc(111) transition-metal surfaces as a function of the *d* band filling $N_d$. Solid line, trimers at normal sites; dashed line, trimers at fault sites.

vored but the corresponding energy difference was so small that it might be overcome by relaxation effects and/or the influence of $s$ electrons. In the present calculation, the difference in energy between $A_N$ and $B_N$ triangles is larger by one order of magnitude even when the relaxations are neglected so that it is not clear that the equilibrium geometry of very small Pt adatoms islands will be the same as in experiments of Michely *et al.* on large adatoms islands. Consequently, it would be also highly interesting to study the very first stages of growth of Pt on Pt(111). Experiments on Pd, which is also fcc and in the same column as Pt, would be also welcome.

## V. SUMMARY AND CONCLUSIONS

The binding energies of monomers, dimers, and trimers at normal and fault sites on fcc(111) surfaces of the same chemical species have been calculated within a tight-binding model for $d$ electrons in order to investigate trends for cluster adsorption along the transition-metal series of a fcc structure ($d$ band fillings of $6.8-9.2\ e^-$/atom).

Vertical relaxation of the adatom(s) as well as lateral relaxation of its (their) nearest neighbors have been taken into account. We have shown that, contrary to the predictions of the second-moment potential, these relaxations are quite different between the hcp and the fcc sites, and given the reason for this discrepancy. This has an important consequence since the width of the domain of $d$ band fillings for which the hcp adsorption site on the (111)fcc surface is preferred increases.

Our results give a coherent interpretation of the field ion microscopy observation of Ir clusters on Ir(111) by Wang and Ehrlich.[6] We predict the same trends for the early stages of the growth of Rh on Rh(111). It would also be very interesting to carry out similar experiments on Pt and Pd to see if there is really an inversion of relative stability of $A$ and $B$ triangular trimers when going from the Rh and Ir column to that of Pd and Pt.

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[1] *Kinetics of Ordering and Growth at Surfaces*, edited by M. G. Lagally (Plenum, New York, 1990); Phys. Today **46** (11), 24 (1993).

[2] B. Piveteau, M. C. Desjonquères, and D. Spanjaard, J. Phys. (France) I **2**, 1677 (1992).

[3] S. C. Wang and G. Ehrlich, J. Chem. Phys. **94**, 4071 (1991); Phys. Rev. Lett. **68**, 1160 (1992).

[4] B. Piveteau, M. C. Desjonquères, and D. Spanjaard, Phys. Rev. B **46**, 7121 (1992).

[5] S. Papadia, D. Spanjaard, and M. C. Desjonquères, Phys. Rev. B **53**, 4083 (1996).

[6] S. C. Wang and G. Ehrlich, Surf. Sci. **239**, 301 (1990).

[7] T. Michely, M. Hohage, M. Bott, and G. Comsa, Phys. Rev. Lett. **70**, 3943 (1993).

[8] M. C. Desjonquères and D. Spanjaard, *Concepts in Surface Physics* (Springer-Verlag, Berlin, 1993).

[9] J. Friedel, *The Physics of Metals*, edited by J. M. Ziman (Cambridge University Press, Cambridge, 1969), p. 340; C. D. Gelatt, Jr., H. Ehrenreich, and R. E. Watson, Phys. Rev. B **15**, 1613 (1977); D. G. Pettifor, CALPHAD, **1**, 305 (1977).

[10] J. C. Slater and G. F. Koster, Phys. Rev. B **94**, 1498 (1954).

[11] D. Spanjaard and M. C. Desjonquères, Phys. Rev. B **30**, 4822 (1984).

[12] J. P. Bourdin, M. C. Desjonquères, D. Spanjaard, and J. Friedel, Surf. Sci. **157**, L345 (1985).

[13] P. J. Feibelman, Phys. Rev. Lett. **63**, 2488 (1989).

[14] F. Ducastelle, *Order and Stability in Alloys* (North-Holland, Amsterdam, 1991), Vol. 3, Chap. 6.

[15] F. Cyrot-Lackmann, J. Phys. Chem. Solids **29**, 1235 (1968).

[16] V. M. Rosato, M. Guillopé, and B. Legrand, Philos. Mag. A **59**, 321 (1989).