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Energetics of vicinal surfaces of fcc (111) transition metals

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We investigate vicinal surfaces of fcc (111) transition metals with close-packed step edges in the tight-binding model. There are two types of such vicinals, A and B, since there exist two types of steps with close-packed edges obtainable on fcc (111) surfaces. We calculate energies and energy differences of these vicinal surfaces, their steps, and the interaction between steps for a number of terrace widths. It is seen that steps of type A are preferred for metals with high d band fillings (e.g., Pt) while for lower d band fillings (e.g., Ir), steps of type B are more stable. Finally, the interaction energy between steps is shown to be a (decaying) oscillatory function with both terrace width and band filling. Its magnitude is found to be comparable to the elastic interaction energy between steps at short distances and low temperatures.

I. INTRODUCTION

The study of vicinal surfaces is a handy tool in the quest of finding reliable models of various surface processes. They provide well-defined defects (steps) for understanding, among many other situations, diffusion at surfaces, roughening transitions, surface growth, and chemical reactions such as chemisorption and catalysis.

One specific example is the equilibrium shapes observed at Pt(111) — hexagons with two different edge sizes.[1] This is explained by the existence of two types of dense steps on fcc (111) surfaces having different energies. The ratio between their free energies gives the ratio between the lengths of the hexagon edges. Equilibrium shapes of Ir clusters on Ir(111) have also been studied[2] where the above-mentioned differences in step energies manifest in a similar way. It is thus of interest to make a systematic investigation of the energy differences of the two kinds of dense steps encountered on fcc (111) transition metals.

Furthermore, steps have been shown to modify the adatom motion at surfaces.[3] It is thus of importance also for understanding diffusion at surfaces to chart the energetics of steps. We emphasize that both possible growth shapes and atom diffusion are crucial ingredients in industrial growth of metals, which make their study all the more interesting to pursue.

Finally, the existence of interactions between steps plays an important role in some physical phenomena. Indeed such interactions are a crucial mechanism for roughening transitions at surfaces[4] and the stabilization of vicinals. The interstep interactions can have various sources. There are elastic interactions[5] due to atomic relaxations around the steps. The deformation fields around each step, in an elastic continuum model, interact repulsively with each other[6] and give rise to an interaction energy varying as $1/d^2$ with distance d. Then, there is an entropic interaction[7] coming from the fact that meandering steps cannot cross each other. This interaction is also repulsive and varying as $1/d^2$. Thirdly, there exist dipole-dipole interactions between steps. Due to charge redistribution at the steps, similarly to a metal surface, dipoles are formed that interact either repulsively or attractively with each other.[8,9] Also these interactions vary as $1/d^2$.

Several theoretical investigations have been made of interacting steps where elastic and/or dipolar interactions are present.[4–6,8,10] There have though, to our knowledge, been much fewer considerations of conduction electron-mediated interactions,[11,12] although some electronic structure calculations have been performed on Al stepped surfaces[13,14] not discussing step interactions.

In our analysis, we will concentrate on electronic effects at the temperature $T=0$ K. This means that no entropic term will be present and since we study unrelaxed structures, no elastic deformation contribution will be present either. Nevertheless, since the electronic contribution is seldom considered in step interactions, it is of interest to give an estimate of its magnitude and sign.

The paper is organized as follows. In Sec. II, we present the tight-binding model used for calculating total energies of transition metals. The model is made explicit for application on vicinals of fcc (111) surfaces consisting of the two possible kinds of dense steps that exist on such surfaces. Simple analytical models for total energies are also presented in order to illuminate and discuss certain aspects of step and interaction energies. In Sec. III, our numerical results are presented and discussed in detail. Finally, our conclusions and a summary are presented in Sec. IV.

II. MODEL

A. Tight-binding model

Our aim is to compute the total energies of different crystal configurations in order to compare them and find the most

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stable ones. In a tight-binding (TB) model, the crystal energy is usually expressed as being composed of an attractive and a repulsive part as

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

where E_{band} is due to the broadening of valence electronic levels into a band and E_{rep} would be any other effect, notably the ion-ion repulsion.

The repulsive energy will be described by a Born-Mayer pairwise potential limited to first nearest neighbors:

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

where $\mathscr{A}$ and p are parameters that may be fitted, e.g., to bulk properties, R_{ij} is the distance between atoms i and j, and R_0 is a reference distance, usually the equilibrium interatomic distance in the bulk.

Since we are interested in computing band energies for transition metals, we use a tight-binding scheme where only the d electrons are taken into account. It has been shown[15] that, at least for transition metals not too close to the extremes of the transition-metal series, the cohesive properties are by far dominated by the valence d electrons. The bulk band energy is written as

$$E_{\mathrm{band}} = \int_{-\infty}^{E_F} E \mathscr{N}(E)\, dE, \tag{3}$$

where $\mathscr{N}(E)$ is the (total) density of states and E_F is the Fermi energy of the system. The zero energy is chosen to be at the center of gravity of $\mathscr{N}(E)$.

When our system deviates from a bulk crystal, i.e., we deal with impurities, surfaces, etc., it is convenient to introduce the notion of local density of states (LDOS), which will be defined more precisely in the following. To each atomic site i, we assign a local density of states $n_i(E)$. For an atom at a site different from the bulk, the LDOS will be perturbed compared to a bulk atom: $n_i(E) = n(E) + \delta n_i(E)$ where $n(E)$ is the bulk density of states per atom and $\delta n_i(E)$ is the LDOS perturbation. The perturbation $\delta n_i(E)$ causes a perturbation δV_i of the potential at site i. Both perturbations are interdependent and should be calculated self-consistently. However, in metals, screening of charge takes place within an interatomic distance and the change of the potentials δV_i may be obtained by requiring local charge neutrality.[16] The band energy becomes

$$E_{\mathrm{band}} = \sum_i \left\{ \int_{-\infty}^{E_F} E n_i(E, \delta V_1, \delta V_2, \ldots, \delta V_j, \ldots)\, dE - N_i \delta V_i \right\}, \tag{4}$$

where N_i is the number of d electrons at site i and the second term in the brackets avoids the double counting of the change in electron-electron interactions responsible for the shift δV_i.[16]

The density of states of a system is calculated using a tight-binding Hamiltonian H_{TB}. It is assumed that the set of d orbitals, $\Phi_{i\lambda}$ ($\lambda = xy, yz, zx, x^2-y^2, 3z^2-r^2$) centered at all sites i, provides a complete orthonormal basis on which we can expand the electronic wave functions Ψ_n of energy E_n. The matrix elements of the Hamiltonian in this basis will be determined by the hopping integrals $\langle \Phi_{i\lambda} | V_i | \Phi_{j\mu} \rangle$, usually limited to nearest neighbors, and the effective atomic levels $\langle \Phi_{i\lambda} | H_{\mathrm{TB}} | \Phi_{i\mu} \rangle = \delta V_i \delta_{\lambda\mu}$.

The hopping integrals are completely determined by three hopping parameters $dd\sigma$, $dd\pi$, $dd\delta$,[17] 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:

$$dd\lambda = dd\lambda_0 e^{-q(R_{ij}/R_0 - 1)}, \quad \lambda = \sigma, \pi, \delta. \tag{5}$$

The parameters $dd\lambda_0$ and q are usually fitted to band-structure calculations at high-symmetry points in the Brillouin zone.

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

$$G(z) = \frac{1}{z - H_{\mathrm{TB}}} \tag{6}$$

as

$$\begin{aligned} n_i(E) &= 2\sum_{\lambda} -\frac{1}{\pi} \lim_{\varepsilon \to 0^+} \mathrm{Im} \langle i\lambda | G(E + i\varepsilon) | i\lambda \rangle \\ &= 2\sum_{\lambda} -\frac{1}{\pi} \lim_{\varepsilon \to 0^+} \mathrm{Im} G_{ii}^{\lambda\lambda}(E + i\varepsilon) \\ &= 2\sum_{n,\lambda} |\langle \Phi_{i\lambda} | \Psi_n \rangle|^2 \delta(E - E_n). \end{aligned} \tag{7}$$

The quantity $G_{ii}^{\lambda\lambda}$ can be expanded as a continued fraction.[16] When the corresponding coefficients are exact up to the level n, the LDOS has $2n$ exact moments. The more accurate a calculation is required to be, the more exact moments μ_p^i:

$$\mu_p^i = \int_{-\infty}^{+\infty} E^p n_i(E)\, dE \tag{8}$$

need to be included.

In this work, the LDOS 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 square-root terminator, which corresponds to using the asymptotic values for the remaining coefficients.[16] In practice, a cluster of atoms is built around the atom i for which we wish to calculate the LDOS. The number of atoms in the cluster is determined by the requirement that all atoms should be reached from i within n_c jumps. A great advantage of this technique is that we do not need to assume any periodicity of the system.

Sometimes, for simplicity, only the first three moments (μ_0, μ_1, μ_2) are used for computing the LDOS. In this case, the total energy of a system (relative to the energy of the free atoms) can be written as[18]

$$E = \sum_i \left(\sum_{j<i} \mathscr{A} e^{-p(R_{ij}/R_0 - 1)} - \mathscr{B} \sqrt{\sum_{j \neq i} e^{-2q(R_{ij}/R_0 - 1)}} \right), \tag{9}$$

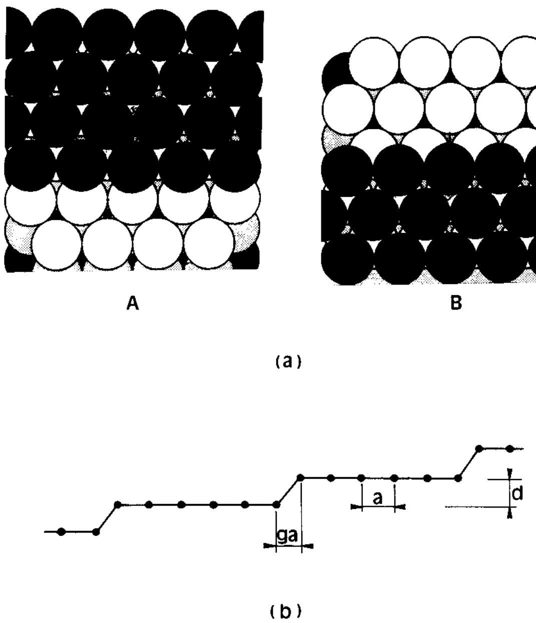

FIG. 1. Atomic structure of vicinal surfaces of fcc (111). (a) The differences of the steps A and B on fcc (111) surfaces are shown. (b) Schematic view from the side of a fcc (111) vicinal surface. The various distances, used in our analysis, are indicated: a, the normal distance between terrace rows (the full terrace width is thus ma on this vicinal), d, the normal distance between (111) atomic planes, and ga, the horizontal distance between inner and outer step edges ($g=2/3$ for fcc $(m,m,m+2)$ or type A vicinals, $g=1/3$ for fcc $(m+1,m+1,m-1)$ or type B vicinals).

where $\mathscr{B}$ is a constant depending on the band filling and the $dd\lambda_0$. This form of writing the energy goes under the name "second-moment approximation."

B. Application to vicinal surfaces

1. Free energies of vicinal surfaces

Our purpose is to calculate energies of vicinal surfaces of fcc (111) transition metals. We choose dense-step vicinal surfaces, i.e., such that two consecutive atoms along the step edges are nearest neighbors in the crystal. For fcc (111) metals, such step edges run in the $\langle 110\rangle$ direction. However, there are two ways to cut the crystal to obtain the desired orientation of step edges. If we, e.g., choose to cut at an angle θ that will give a dense-step vicinal, the angle $-\theta$ will also give a dense-step vicinal but of a different structure. In Fig. 1, the two different types A and B of resulting (111) vicinals are shown. The type A vicinals can be described by the Miller indices $(m,m,m+2)$, where $m+1$ gives the number of rows at the terraces that are parallel to the step edges (including the inner edge of the steps). The type B vicinals are described by the Miller indices $(m+1,m+1,m-1)$. Another way to describe these vicinals is to note that the atoms at the inner edges of the steps have 10 nearest neighbors for type A vicinals while the corresponding atoms for type B vicinals have 11 nearest neighbors. Finally, we note that these vicinals also can be characterized by the orientation of their microfacets: (001) and $(11\bar{1})$ for type A and type B, respectively.

It is interesting to find out if the small structural difference for fcc (111) dense steps will manifest in different stabilities between them. To this aim, we compute the energy (per unit area) of the vicinal surfaces neglecting possible atomic relaxations.

The vicinal surface energy per unit area, γ, as a function of m is usually expressed as

$$\gamma(m)=\gamma^{(111)}\cos\theta(m)+\frac{\beta_0}{d}\sin\theta(m)+E_{\mathrm{int}}(m), \tag{10}$$

where $\gamma^{(111)}$ is the surface energy (per unit area) of the flat surface, $\theta(m)$ is the misorientation angle, β_0 is the step energy per unit length, d is the normal distance between (111) atomic planes, and $E_{\mathrm{int}}(m)$, also in eV per unit area, is due to the interactions between steps. This term not only includes the interaction between pairs of steps at all possible distances, but also many-body contributions. Consequently, we have not tried to express it as a sum of pairwise interactions. As usually done in the literature, $E_{\mathrm{int}}(m)$ is written as

$$E_{\mathrm{int}}(m)=\beta_{\mathrm{int}}(m)\frac{\sin\theta(m)}{d}, \tag{11}$$

where $\beta_{\mathrm{int}}(m)$ is called the step interaction energy per unit length.

Consequently the step energy per unit length β_0 is obtained as the limit when $m\to\infty$ of the function:

$$\beta(m)=d\,\frac{\gamma(m)-\gamma^{(111)}\cos\theta(m)}{\sin\theta(m)}, \tag{12}$$

and

$$\beta_{\mathrm{int}}(m)=\beta(m)-\beta_0. \tag{13}$$

2. Consideration on simple models

We first consider simple models in which the contribution E_i of a given atom i to the total energy is only a function of its coordination: $E_i=E(Z_i)$, where Z_i is the coordination number.

On the vicinals A and B, the atoms at the surface, save for the outer and inner step edges, have the coordination Z_F of the flat surface. The atoms at the outer and inner step edges have coordination Z_O and Z_I, respectively. All other atoms have the bulk coordination Z_B. The inner and outer step edges are horizontally shifted with respect to each other (see Fig. 1 for the illustration), parallel to the terraces and normal to the step edges. This shift is denoted ga, where a is the interrow spacing on the terrace in the direction normal to the step edge. It can be shown then that the step energy is

$$\beta(m)=\frac{1}{l}[E(Z_O)+E(Z_I)-(1+g)E(Z_F)-(1-g)E(Z_B)], \tag{14}$$

where l is the interatomic distance along the edge, here $l=R_0$. Since $\beta(m)$ is found to be independent of m, the interaction between steps vanishes in these models for *any* choice of $E(Z_i)$. Thus, we have $\beta(m)=\beta_0$.

It can also be shown that the shift parameter g is written as

$$g=\frac{Z_B-Z_I}{Z_B-Z_F}. \tag{15}$$

We are interested in the difference $\beta^B-\beta^A$ of step energy between type A and type B steps. Several energy functions depending on the coordination number Z have been proposed in the literature. If nearest-neighbor pairwise interactions are assumed, then

$$E(Z_i)=Z_i\frac{\mathscr{A}}{2}, \tag{16}$$

where $\mathscr{A}$ is the pair interaction between nearest neighbors. Substituting Eq. (15) and Eq. (16) for g and $E(Z_i)$ in Eq. (14), we find

$$\beta_0=\frac{1}{l}(Z_O-Z_F)\frac{\mathscr{A}}{2}. \tag{17}$$

Consequently, in this model, steps of type A and type B have the *same* energy since the atoms at their respective outer edges have the same coordination number, which is 7.

A more complex choice for $E(Z_i)$ can be derived from a form of the effective-medium theory (EMT),[19] mostly appropriate for simple metals. Neglecting relaxations and including density contributions to the atom i in a system only from its nearest neighbors, we can write this atom energy relative to a bulk atom as[19]

$$E(Z_i)-E(Z_B)=C\left[1-\left(\frac{Z_i}{12}\right)^{\eta/b\eta_2}\right]^2+\alpha_i n_0\left[\left(\frac{Z_i}{12}\right)^{\eta/b\eta_2}-\left(\frac{Z_i}{12}\right)\right], \tag{18}$$

where the parameters C, η, η_2, α_i, and n_0 are extracted from self-consistent calculations of an atom embedded in a homogeneous electron gas and b is characteristic of the fcc lattice: $b=(16\pi/3)^{1/3}/\sqrt{2}$.

Using Eq. (14), we get

$$\beta_0^B-\beta_0^A=\frac{1}{l}\left(E(Z_I^B)-E(Z_I^A)+\frac{1}{3}E(Z_F)-\frac{1}{3}E(Z_B)\right). \tag{19}$$

The parameters in this model are material dependent and we will arrive at different values for $\beta_0^B-\beta_0^A$ depending on the system at hand. As an example,[20] using appropriate parameters for Pt,[21] the difference $\beta_0^B-\beta_0^A$ amounts to ~ -0.7 meV, which is to say that the B step is slightly more stable on Pt. The difference is so small though that the result seems indecisive. Using parameters for Al (Ref. 19) gives a similar value for $\beta_0^B-\beta_0^A$: ~ -0.5 meV.

Another possible choice for $E(Z_i)$ is the so-called "second-moment approximation" [Eq. (9)] which yields

$$E(Z_i)=Z_i\frac{\mathscr{A}}{2}-\mathscr{B}\sqrt{Z_i}. \tag{20}$$

The first term comes from E_{rep} and the second from E_{band}. Also here, the steps A and B have different energies. It is found that

$$\beta_0^A=\frac{1}{l}\left(-\mathscr{A}+\frac{\mathscr{B}}{3}[5\sqrt{9}+\sqrt{12}-3(\sqrt{10}+\sqrt{7})]\right),$$
$$\beta_0^B=\frac{1}{l}\left(-\mathscr{A}+\frac{\mathscr{B}}{3}[4\sqrt{9}+2\sqrt{12}-3(\sqrt{11}+\sqrt{7})]\right), \tag{21}$$

so that:

$$\beta_0^B-\beta_0^A=\frac{\mathscr{B}}{3l}(-\sqrt{9}+3\sqrt{10}-3\sqrt{11}+\sqrt{12})\approx\frac{\mathscr{B}}{l}3.53\times10^{-4}. \tag{22}$$

From the treatment of the above simple pairwise model, it was in fact clear beforehand that only the band energy could contribute to the energy difference — the repulsive part being of pairwise form not giving rise to any difference. Since $\mathscr{B}$, the band energy parameter, is positive for all band fillings, step A is always more stable than step B in this model.

Let us look at the order of magnitude of β_0^A, β_0^B, and $\beta_0^B-\beta_0^A$ in the "second-moment approximation." The ratio $\mathscr{A}/\mathscr{B}$ can be obtained from the equilibrium condition with respect to a small variation of the lattice parameter. From Eq. (9), we find that

$$\frac{\mathscr{A}}{\mathscr{B}}=\frac{1}{\sqrt{3}}\frac{q}{p}, \tag{23}$$

and

$$E_{\text{coh}}(R_0)=\left(1-\frac{q}{p}\right)\mathscr{B}\sqrt{Z_B}. \tag{24}$$

Using the value $p/q=3$ derived from universal potentials,[22] we obtain

$$\beta_0^A l\approx 6.6\times10^{-2}E_{\text{coh}}(R_0), \tag{25}$$

and

$$\beta_0^B l-\beta_0^A l\approx 1.7\times10^{-4}E_{\text{coh}}(R_0). \tag{26}$$

Since $E_{\text{coh}}(R_0)$ is of the order of a few eV,[15] $\beta_0^A l$ and $\beta_0^B l$ are of the order of a few tenths of an eV, while $\beta_0^B l-\beta_0^A l$ is only of the order of 1 meV. Thus, if we expect that such a model gives a reasonable order of magnitude of $\beta_0 l$, the energy difference between steps A and B is so small that the influence of higher-order moments may drastically change, not only the numerical values, but also the general behavior as a function of band filling. Moreover, higher-order moments introduce indirect long-range interactions between steps. This can be shown qualitatively before any numerical calculations, which we proceed to do in the following.

3. Qualitative discussion on the influence of higher order moments

To this aim, we will keep the pairwise form of the repulsive energy but go beyond the second-moment approximation for the band energy. We will also neglect all δV_i ($\delta V_i=0$) and ensure the conservation of total charge by a small variation of the Fermi level,[23] i.e., we impose global charge conservation instead of local charge neutrality. Thus we write the variation of the total band energy due to a variation $\delta\mathcal{N}(E)$ of the total density of states as

$$\delta E_{\text{band}} = \int_{-\infty}^{E_F} (E-E_F)\,\delta\mathcal{N}(E)\,dE. \tag{27}$$

When the first p moments $(\mu_0,\ldots,\mu_{p-1},p\geqslant 3)$ of $\delta\mathcal{N}(E)$ vanish, a mathematical theorem[23] states that δE_{band} changes sign at least $p-2$ times when E_F varies in $]b,B[$, b and B being the bottom and the top of the d band, respectively.

For the interaction energy between steps, similarly to the case of interactions between adatoms,[24] it is easily seen that the first moment that is modified by the presence of several steps is the moment that includes the shortest closed paths starting from a step edge, going to the next step edge and coming back. This moment is μ_{2m+2}. Note that, since $m\geqslant 2$ in order to meaningfully speak about vicinal surfaces, the very first moment that can be altered is μ_6. Any calculation with fewer moments than $2m+2$, meaning of course TB calculations employing global charge neutrality, will fail to reproduce interaction energies.

The consequences due to the theorem cited above for the interaction energy are that, for a given value of m, $E_{\text{int}}(E_F)$ changes sign at least for $2m$ values of E_F. Furthermore, for a given value of E_F, E_{int} will also change sign as a function of m since the positions and the number of zeroes of $E_{\text{int}}(E_F)$ depend on m. As a conclusion, E_{int} oscillates as a function of both E_F and m and may thus be either attractive or repulsive depending on the considered transition metal and on the actual width of the terraces.

We consider now the implications of the theorem on the difference in step energies $\beta_0^B-\beta_0^A$. To this aim, we need to be able to express this difference as an integral similar to the right-hand side of (27). The moment μ_3 of the local density of states $n_i(E)$ is completely determined from the knowledge of the number and location of the first nearest neighbors of atom i. This means that, in the present case, the band energy, also when μ_3 is taken into account, can be written as a function of the coordination number. Thus the quantity $\beta_0^B-\beta_0^A$ can, in a straightforward way, be expressed as in Eq. (19) when all the LDOS are calculated with exact μ_0,μ_1,μ_2,μ_3. In this "third-moment approximation," the difference of step energies is given by

$$\begin{aligned}\beta_0^B l-\beta_0^A l &= \int_{-\infty}^{E_F} dE(E-E_F)\frac{1}{3}[3n_I^B(E)-3n_I^A(E)\\ &\quad +n_F(E)-n_B(E)]\\ &= \int_{-\infty}^{E_F} dE(E-E_F)\,\delta\mathcal{N}_{BA}(E),\end{aligned} \tag{28}$$

where $n_I^{A[B]}(E)$ is the LDOS of an atom at the inner edge of step $A[B]$, and $n_F(E)[n_B(E)]$ is the LDOS of an atom in the flat surface [bulk]. It can be shown analytically that the moments μ_0,μ_1,μ_2,μ_3 of $\delta\mathcal{N}_{BA}(E)$ cancel. If a larger number of exact moments are taken into account in the calculation, an expression similar to Eq. (28) for $\beta_0^B-\beta_0^A$ can be derived, but $\delta\mathcal{N}_{BA}(E)$ will include additional LDOS coming from the atomic rows, which are farther from the inner step edge. In this case we can no longer express the band energy as a function of coordination number. We have verified numerically that the moment μ_4 of $\delta\mathcal{N}_{BA}(E)$ does not cancel. Consequently, $\beta_0^B-\beta_0^A$ cancels at least twice when E_F varies in $]b,B[$. We conclude thus that the calculation of E_{band} must include at least five exact moments in order to describe the difference between step A and step B for any band filling.

Let us emphasize that on the one hand the approximation (27), which ensures a global neutrality rather than a local neutrality, tends to overestimate the number of zeroes of $\delta E_{\text{band}}(E_F)$ and displace their position.[25] On the other hand, the so-called second moment approximation, which implicitly assumes local neutrality, gives a constant sign for $\beta_0^B-\beta_0^A$ as a function of E_F, but with a very poor description of the LDOS.

In the above discussion the atomic relaxation effects have been completely disregarded. A calculation including these effects is, in principle, possible in the tight-binding theory since the laws of variation with distance of all the parameters entering into the Hamiltonian are known. However, such a calculation is a formidable numerical task if the LDOS are computed with a large number of exact moments but remains accessible in the framework of the second-moment approximation of Eq. (9). This has recently been carried out on vicinal surfaces of Cu.[26] In this study the step-step interaction comes from the interference between the deformation fields induced by the atomic relaxation at each step since, as shown above, this interaction vanishes on a rigid lattice in this approximation. Consequently, this work substantially improves the description of the elastic interactions since the discrete nature of the lattice is taken into account contrary to the previous studies based on the elasticity theory of continuous media. It is found that at large terrace width this interaction decreases as $1/m^2$. Moreover the relative energies of steps A and B have been compared and it was found that relaxation effects do not modify qualitatively the results of the second-moment approximation with a rigid lattice at least for Cu: step A is preferred by $\simeq 1$ meV.

From this discussion, we can deduce that it is instructive to calculate β_{int} and $\beta_0^B-\beta_0^A$ with LDOS calculated using a large number of exact moments with the local charge neutrality condition, even when relaxation effects are neglected. Indeed, on the one hand, such a calculation should give a reasonable estimate of the conduction electron mediated step-step interaction to compare with the elastic one and, on the other hand, to determine if the step B can be stabilized by a better description of the LDOS in the domain of band filling of fcc crystals.

III. RESULTS AND DISCUSSION

The question is how many moments should be included in the computation of the LDOS. The convergence requirements are set by the minimum energy differences that we calculate which are of the order of 1 meV. In order to reach sufficient accuracy in the calculated energies, we use 10 exact levels in the continued fractions — i.e., 20 exact moments — for (111) vicinals. In terms of cluster sizes, this translates to at most 3871 atoms per cluster. We assume that potential perturbations occur on all atoms that can be reached in 10 nearest-neighbor jumps from the central atom of the system (chosen to be an atom at the inner step edge). We need thus to calculate the LDOS on all geometrically inequivalent atoms and, consequently, to construct as many clusters. The number of such atoms is a function of terrace width. For (111) vicinals, it is $n_c(m+1)+1$, where n_c is the number of levels used in the continued fraction. As an example, for a vicinal with $m=4$, we need to construct 51 clusters.

We calculate energies of unrelaxed structures and use the parameters

$$dd\sigma=-0.798\ \text{eV},\ dd\pi=0.317\ \text{eV},\ dd\delta=-0.0367\ \text{eV} \tag{29}$$

for finding the band energy. The repulsive energy parameter $\mathscr{A}$ is determined from the condition that the total bulk energy is at a minimum at equilibrium $(R_{ij}=R_0)$. This gives the relation

$$\frac{E_{\text{band}}(R_0)}{E_{\text{rep}}(R_0)}=-\frac{p}{q}. \tag{30}$$

As above, we use the value $p/q=3$.

A. Vicinal surfaces of type A

As already discussed, the vicinal surfaces of type A on fcc (111) metals have steps with (001) facets and they are denoted by the Miller indices fcc $(m,m,m+2)$ where $m+1$ also denotes the number of rows at the terraces that are parallel to the steps.

For these vicinals, using Eq. (10), γ_A as a function of m is given by

$$\gamma_A(m)=\gamma^{(111)}\frac{3(m+2/3)}{\sqrt{9(m+2/3)^2+8}}+\frac{\beta_0^A+\beta_{\text{int}}^A(m)}{l\sqrt{2/3}}\,\frac{2\sqrt{2}}{\sqrt{9(m+2/3)^2+8}}. \tag{31}$$

Here and in the following, the units of γ and $\gamma^{(111)}$ will be in eV/unit area and the units of β and β_{int} in eV/unit length. The interatomic distance is chosen as the length unit. The figures will be presented in eV, i.e., γl^2, βl, and $\beta_{\text{int}}l$ in order for them to be independent of the lattice parameter. For purposes of comparing directly with experiments, the appropriate band filling and interatomic distance should be chosen.

In Fig. 2(a), we present the vicinal surface energies $\gamma_A l^2$ as a function of m for several d band fillings f and compare them to the flat surface energies. Since the intra-atomic potentials δV_i are determined from the local charge neutrality condition, the number of electrons N_i on each site is a constant that is set equal to f. The vicinal surface energies, γ_A, and the flat surface energies $\gamma^{(111)}$ are obtained directly by integrating the local density of states of the different representative atoms and subtracting the double counting terms and the bulk energy. Since we are interested in fcc transition metals, the band fillings are chosen to be representative of those, i.e., since the fcc metals are situated at the end of the transition-metal series, we choose band fillings larger than 6.8.

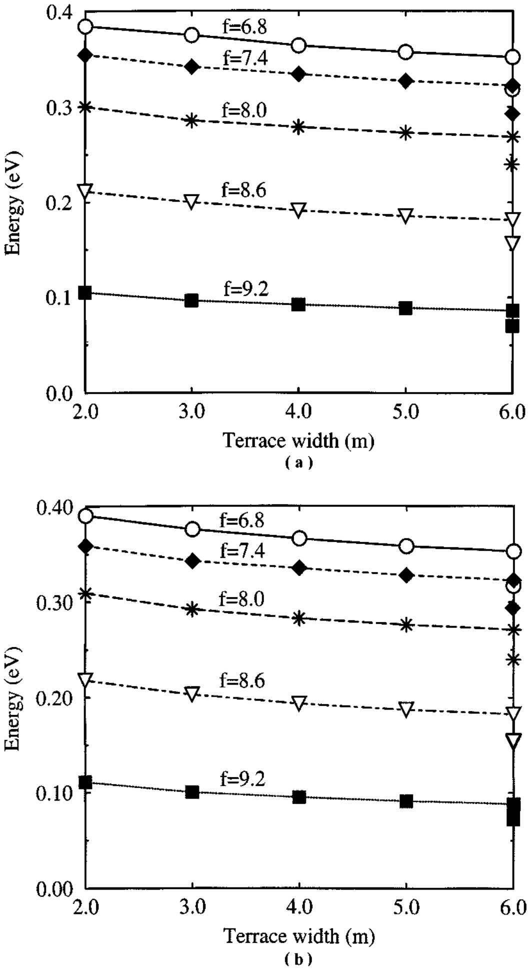

FIG. 2. Vicinal surface energies $\gamma(m)l^2$ (in eV), where l is the nearest-neighbor distance as a function of the terrace width m and for several band fillings f. The flat (111) surface energy for each band filling is shown at the vertical rightmost axis in corresponding symbols. (a) fcc $(m,m,m+2)$ vicinals, i.e., with steps of type A. (b) fcc $(m+1,m+1,m-1)$ vicinals, i.e., with steps of type B.

The vicinal surface energies are seen to decrease smoothly with m and with band filling. The difference between vicinal and flat surface energies is in the range $0.01-0.1$ eV and decreases with increased band filling and with m. The energy difference between subsequent vicinal surfaces is in the range 0.002–0.02 eV — the largest differences being for low band fillings and between $m=2$ and $m=3$ and the smallest ones for high band fillings and between $m=5$ and $m=6$. In terms of ratios, we have, e.g., $\gamma_A(6)/\gamma^{(111)}\approx 1.1$ for $f=6.8$, but this ratio increases with band filling and is ≈ 1.2 for $f=9.2$.

In order to extract β_0, the single step energy, we examine the behavior of $\beta(m)$. In Fig. 3, the step energy $\beta^A(m)l$ as a function of terrace width is shown for a band filling of 7.6. We note that $\beta^A(m)l$ converges rapidly with m. The interaction energy becomes unimportant already for $m=6$. This means that, for our purposes, $\beta_0=\beta(6)$.

The energy of the actual step, $\beta_0^A l$, as a function of band filling is shown in Fig. 4(a). Its band and repulsive parts are shown separately in order to compare their respective importance. The value of $\beta_0^A l$ is smoothly decreasing with increas-

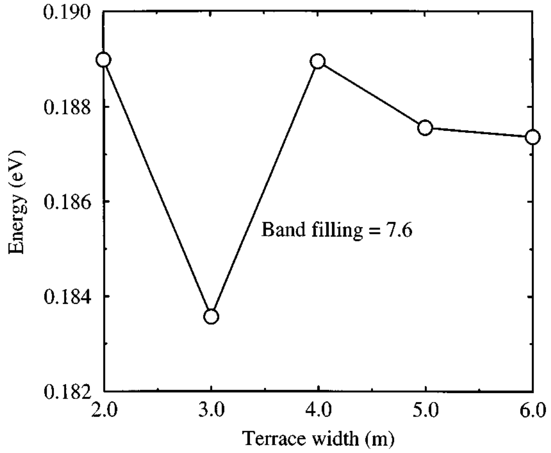

FIG. 3. Energy $\beta^A(m)l$ (in eV per step atom, l being the nearest-neighbor distance) needed for creating a step of type A at vicinal surfaces of fcc (111) crystals as a function of the number m of interrow spacings at the terraces. The band filling is $f=7.6$. The value of $\beta^A(m)$ is seen to converge rapidly when m tends to infinity towards the value β_0^A, which corresponds to noninteracting steps.

ing band filling with a slight flattening in the region 7.4−8.0. This has to do with the way that the band and repulsive energy contributions interplay. The band energy part of β_0^A is decreasing at about a constant rate up to a band filling of 8.6 and decreases even faster after that, whereas the repulsive energy part is less and less negative with increasing band filling.

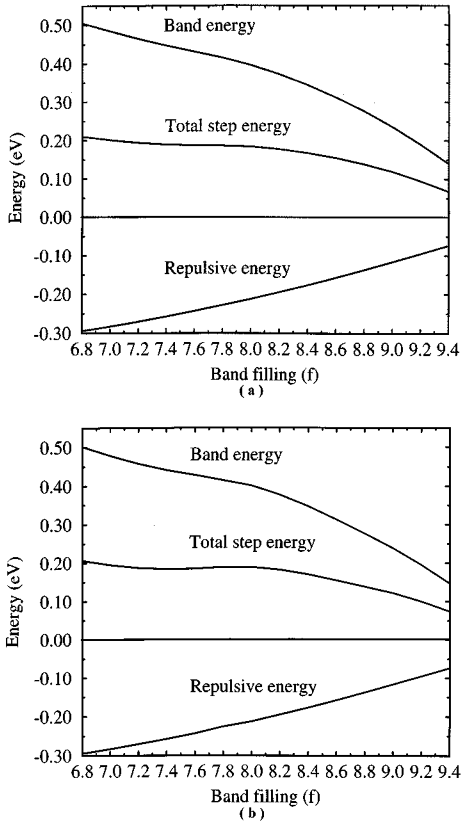

FIG. 4. Energy $\beta_0 l$ (in eV per step atom, l being the nearest-neighbor distance) needed for creating an isolated step on an a fcc (111) surface as a function of the band filling f. The energy is decomposed in its band and repulsive contributions in order to compare their respective importance. (a) step of type A (b) step of type B.

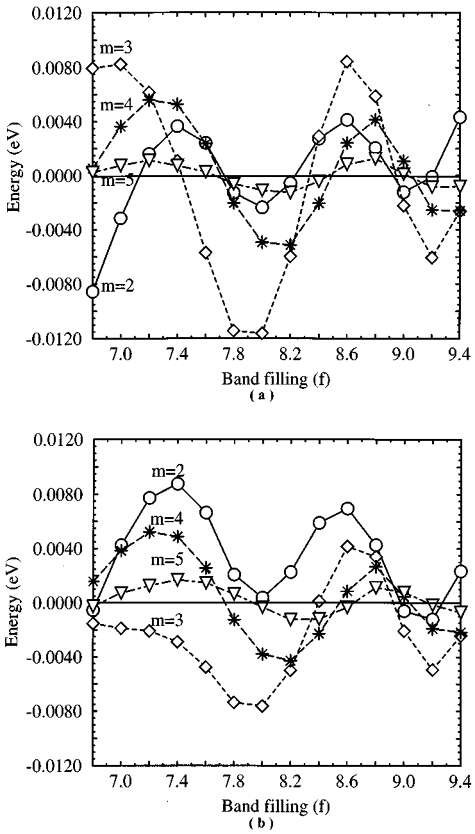

FIG. 5. Interaction energy $\beta_{\mathrm{int}}l$ (in eV per step atom, l being the nearest-neighbor distance) between steps on vicinal surfaces of fcc (111). It is given as a function of band filling and for terrace widths of $m=2-5$ where m denotes the number of interrow spacings at the terraces. (a) fcc $(m,m,m+2)$ vicinals, i.e., with steps of type A. (b) fcc $(m+1,m+1,m-1)$ vicinals, i.e., with steps of type B.

Once β_0^A is known, we can extract the value of the step interaction energy per unit length β_{int}^A from Eq. (31). In Fig. 5(a), we present the step interaction energy again as a function of band filling for $m=2-5$. As seen, the interaction between steps of type A is oscillating and exhibits changes of sign 3–5 times as a function of band filling for all terrace widths. The oscillatory behavior is solely caused by the band energy contribution and as such, illustrates the theory of moments discussed in Sec. II. We note that inclusion of δV_i's and local charge neutrality requirements do not affect the qualitative trends predicted by the theorem. As stated in Sec. II, the step interaction for a given m may thus be either attractive or repulsive depending on the band filling of the material.

In Fig. 6(a), the step interaction energy as a function of terrace width is presented for several band fillings. We have oscillations in the curves and changes of sign just as for β_{int}^A as a function of band filling save for the $f=9.2$ curve where β_{int}^A is always attractive. For the same metal, at least for band fillings less than 9.2, the electronic part of the step interaction energy may thus be either attractive or repulsive depending on the width of the terraces.

The magnitude of $\beta_{\mathrm{int}}^A l$ is a few meV and diminishes dras-

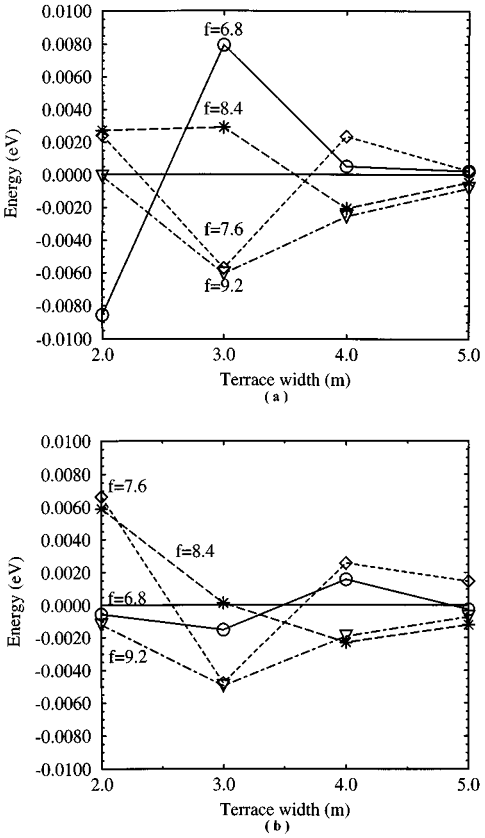

FIG. 6. Interaction energy $\beta_{\rm int}l$ (in eV per step atom, l being the nearest-neighbor distance) between steps on vicinal surfaces of fcc (111) as a function of terrace width m for several band fillings f. (a) fcc $(m,m,m+2)$ vicinals, i.e., with steps of type A. (b) fcc $(m+1,m+1,m-1)$ vicinals, i.e., with steps of type B.

tically beyond $m=4$. Various experimental and theoretical[26,27] extractions of step interaction magnitudes at different vicinals show that the elastic interaction energy decreases from about 10 to 1 meV when the terrace width increases from 2 to 5 interrow spacings. Furthermore, the dipolar interaction is about a factor of 10^3 smaller. For low temperatures, entropic interactions are small and can be discarded. The order of magnitude of indirect electronic interactions for small terrace widths is then seen to be comparable to the elastic interactions and may thus, due to its oscillating nature, give rise to attractive step interactions. Evidence to that effect is claimed to have been seen for vicinals of Ag.[9,12]

B. Vicinal surfaces of type *B*

The type B vicinal surfaces of fcc (111) metals have $(\bar{1}11)$ facets. Their Miller indices are fcc $(m+1,m+1,m-1)$. Analogous to Eq. (31), we can express the B vicinal surface energy as a function of terrace width m as

$$\gamma_B(m)=\gamma^{(111)}\frac{3(m+1/3)}{\sqrt{9(m+1/3)^2+8}}+\frac{\beta_0^B+\beta_{\rm int}^B(m)}{l\sqrt{2/3}}\,\frac{2\sqrt{2}}{\sqrt{9(m+1/3)^2+8}},\qquad(32)$$

where notations are as in Eq. (31).

In Fig. 2(b), the surface energies of the type B vicinals are shown for several band fillings. The behavior of these curves is similar to the type A curves — they decrease smoothly with band filling. The energy difference between vicinal and flat surfaces as well as the difference between vicinal surfaces with different m's are analogous to the type A case — the vicinal surfaces have energies 0.01–0.1 eV larger than the surface energy and there are energy differences of 0.002–0.02 eV between subsequent vicinals. The ratios $\gamma_B(m)/\gamma^{(111)}$ behave similarly to the corresponding ratios for the vicinals of type A: they increase slightly with band filling and their values are around the ones for the type A vicinals.

The value of the step energy β_0^B is extracted in the same way as β_0^A and is shown as a function of band filling in Fig. 4(b). Its band and repulsive part are shown separately. β_0^B resembles β_0^A but exhibits a local minimum in the region $7.2-7.8$ instead of just flattening, which comes from the less pronounced decrease of the band energy part of β_0^B compared to β_0^A. This will allow the repulsive energy part to dominate more in β_0^B for band fillings less than 7.8.

The step interaction energy $\beta_{\rm int}^B l$, obtained in the same manner as $\beta_{\rm int}^A l$, is shown in Fig. 5(b) as a function of band filling for $m=2-5$. The form of the step interaction curves for vicinal surfaces of type B is similar to the type A curves — we have oscillations and changes of sign 2–4 times as a function of band filling.

The step interaction energy $\beta_{\rm int}^B l$ as a function of interstep distance is shown in Fig. 6(b). The curves oscillate slightly differently from the corresponding $\beta_{\rm int}^A l$ curves in Fig. 6 but the overall behavior is exactly analogous. We notice also here changes of sign for band fillings less than 9.2.

$\beta_{\rm int}^A$ and $\beta_{\rm int}^B$ resemble each other closely (see Fig. 5) but are far from identical. A noteworthy example is for the low band fillings in the case $m=3$ where $\beta_{\rm int}^A$ is repulsive whereas $\beta_{\rm int}^B$ is attractive. We note that the magnitude of $\beta_{\rm int}^B$ for short terrace widths is a few meV which, similarly to the analysis for type A interactions, may be comparable to the magnitude of elastic interaction energies.

C. Energy difference between *A* and *B*

As we found in the previous subsections, there are noticeable differences between energies of fcc (111) vicinal surfaces of type A and B. We will here examine these differences in more detail.

Firstly, we show the difference of vicinal surfaces energies γ_A and γ_B as a function of band filling. In Fig. 7 the difference $(\gamma_B-\gamma_A)l^2$ is shown for terrace widths of $m=2-6$. The shapes of the curves are similar for all m, but the amplitudes differ. For $m\geqslant 4$, the amplitudes are very similar but the curves exhibit quasirigid shifts towards a "zero" level. The energy is always larger for γ_B, which is the effect of the contribution of the band energy. It is thus the band energy that is responsible for the stability of type A vicinals in our calculations.

In Fig. 8, the energy difference $(\beta_0^B-\beta_0^A)l$ between the isolated steps of type B and A is shown as a function of d band filling. This energy difference is less than 10 meV and

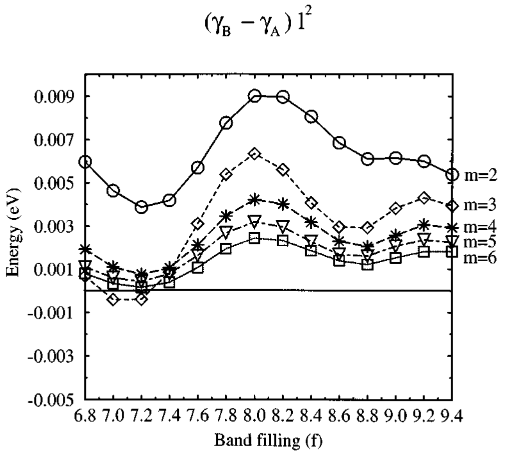

FIG. 7. The difference in free energy $(\gamma_B - \gamma_A)l^2$ (in eV) between vicinal surfaces of type A [fcc $(m,m,m+2)$] and type B [fcc $(m+1,m+1,m-1)$] is shown as a function of band filling, f, for terrace widths $m=2-6$. The number m denotes the number of interrow spacings at the terraces and l is the nearest-neighbor distance.

shows a change of sign at a band filling of 7.6. We have thus the range of band fillings divided into two regions: for band fillings $\leqslant 7.6$, steps of type B are preferred while for band fillings >7.6, steps of type A are preferred. There is though an uncertain region for band fillings 8.6–8.8 where the energy difference is very small.

Since the energy difference between step B and step A at $T=0$ K is very small one can wonder if at high temperature (for instance, $T \simeq 900$ K) the vibrational contribution to the difference in the free energies of step B and step A may play a significant role. To estimate the order of magnitude of this contribution we have used the Einstein model with a force constant κ limited to first nearest neighbors. In this model the contributions of the surface vibrational internal energy, δU^{B-A}, and entropy, δS^{B-A}, to $(\beta_0^B - \beta_0^A)l$ are given by[16]

$$\delta U^{B-A} = \int_0^{\omega_{\max}} \frac{\hbar\omega}{2} \coth \frac{\hbar\omega}{2k_BT}\, \delta\mathcal{N}_{BA}(\omega)\, d\omega, \tag{33}$$

and

$$\delta S^{B-A} = k_B \int_0^{\omega_{\max}} \left[\frac{\hbar\omega}{2k_BT} \coth \frac{\hbar\omega}{2k_BT} - \ln\left(2\sinh \frac{\hbar\omega}{2k_BT} \right) \right] \delta\mathcal{N}_{BA}(\omega)\, d\omega, \tag{34}$$

with

$$\delta\mathcal{N}_{BA}(\omega) = \frac{1}{3}[3n_I^B(\omega) - 3n_I^A(\omega) + n_F(\omega) - n_B(\omega)]. \tag{35}$$

Indeed, when considering phonons the electronic LDOS appearing in $\delta\mathcal{N}_{BA}(E)$[Eq. (28)] should simply be replaced by the corresponding local spectral densities of phonons.

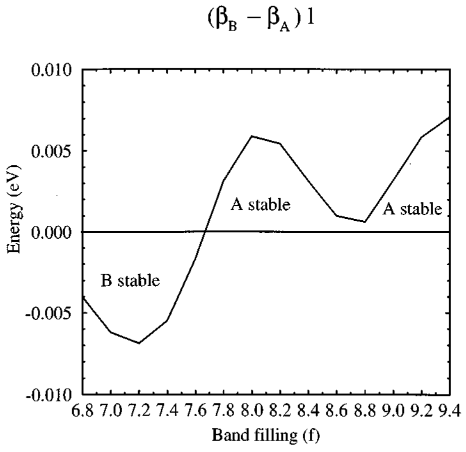

FIG. 8. The difference in energy $(\beta_0^B - \beta_0^A)l$ (in eV per atom, l being the nearest-neighbor distance), between steps of type B and steps of type A of fcc (111) surfaces is shown as a function of the band filling f. The domains where step B and step A are more stable are indicated, respectively.

In the Einstein model it is found that

$$\delta\mathcal{N}_{BA}(\omega) = (1/3)[3\delta(\omega - \sqrt{3}\omega_0) - 3\delta(\omega - \sqrt{5/2}\omega_0) + \delta(\omega - \sqrt{2}\omega_0) - \delta(\omega - \sqrt{7/2}\omega_0)], \tag{36}$$

with $\omega_0^2 = \kappa/M$, M being the mass of an atom. In the high-temperature limit, δU^{B-A} vanishes and

$$\delta S^{B-A} = 2.1 \times 10^{-3} k_B. \tag{37}$$

More specifically at $T=900$ K, $\delta U^{B-A} \simeq 10^{-9}$ eV and the contribution of the surface vibrational free energy to the difference of energy between step B and step A is

$$\delta F^{B-A} \simeq -T\delta S^{B-A} \simeq -1.6 \times 10^{-4} \text{ eV}. \tag{38}$$

Consequently vibrational effects, at least for straight steps, favor step B for any element but are one order of magnitude smaller than electronic effects.

In order to compare with experimental findings, we may look at Ir, which has ~7.5 electrons per atom in the d band and Pt, which has around one more electron. We find that type B steps would be more stable than type A steps on Ir, which seems to be the case also in experiments.[2] For Pt, we find that steps of type A are very slightly more stable than steps of type B. However, the band filling of Pt falls in the above-mentioned uncertain region. Experimentally[1] it is found that for this metal the B steps are more stable. There may be several reasons behind this apparent discrepancy. First the influence of atomic relaxation and the spin-orbit coupling effect may distort the curve $(\beta_0^B - \beta_0^A)l$ but we do not expect drastic changes.[26] A more serious approximation may be the neglect of s electrons at the end of the series, i.e., for Pt. Indeed, they may play a dominant role since the effects of d electrons for this metal do not favor clearly one type of step relative to the other. According to the calculations performed on Al(111) steps,[14] s electrons favor the B steps: this could be the reason why B steps are energetically more favorable in Pt. In these numerical calculations,[14] the difference between type A and type B steps on Al is found to be 16 meV with the type B step being more stable than the type A step, which is more in line with what was found for Pt. This energy difference seems larger than the energy differences we find, but the comparison cannot be immediately done since Al is a free-electron metal and the calculations in Ref. 14 also include relaxation effects. In view of these calculations and from our estimates within EMT, it might be said that the effect of s electrons could well be to render B type steps energetically more favorable at the end of the series.

Other semiempirical calculations[28] have also found the B type steps energetically more favorable than the A type steps on Pt, the so-called equivalent crystal theory being closer to experimental values than the so-called embedded-atom method. To what extent one may distinguish the s and d electron contributions in those calculations is, however, not clear to us.

IV. SUMMARY AND CONCLUSIONS

The properties of vicinal surfaces with dense steps of fcc (111) transition metals have been investigated within a tight-binding model where the local densities of states are calculated from a continued fraction expansion of the Green function with 10 exact levels.

The (111) surfaces of fcc metals can have two types of dense steps, A and B (see Fig. 1), which give rise to two different types of vicinals. We have calculated the energies of A and B vicinal surfaces of various terrace widths, the energies of their single steps, and the step interaction energies.

We have first investigated simple models for describing the energies. It is found that models where the energy of an atom in a system is written as a function of its coordination number cannot produce the interaction energies between steps at vicinal surfaces. We have shown that, within the tight-binding model, at least $2m+2$ moments (where $m+1$ gives the number of rows at the terraces) have to be included in order to sense the electronic interactions between steps. Furthermore, we have proved that a "second-moment approximation" to the energy cannot give the correct answer for all d band fillings for the energy differences between steps of type A and B.

The interaction energies between steps is seen to oscillate as a function of both band filling and terrace width and can be either attractive or repulsive, depending on the particular metal and the particular terrace width. This oscillatory behavior is consistent with the predictions of the theorem of moments, as demonstrated in Sec. II. The magnitude of the interaction energy is compared to experimental and other theoretical findings and is seen to be comparable to the elastic energy for short distances. Since entropic contributions are small for low temperatures and dipolar contributions have been estimated to be three orders of magnitude smaller than the elastic interaction, we conclude that the important effects for the interaction between steps on vicinal surfaces are elastic and electronic at low temperatures and short terrace widths.

The energy difference between steps A and B exhibits a clear change of sign as a function of d band filling. For d band fillings $\leqslant 7.6$, the B step is energetically favored while for band fillings >7.6, the A step is more stable. However, the region around 8.7 electrons per atom is so uncertain that the effects of s electrons may be dominating for this range of band fillings.

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