

Relaxation and reconstruction on (111) surfaces of Au, Pt, and Cu

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We have theoretically studied the stability and reconstruction of (111) surfaces of Au, Pt, and Cu. We have calculated the surface energy, surface stress, interatomic force constants, and other relevant quantities by *ab initio* electronic structure calculations using the density functional theory in a slab geometry with periodic boundary conditions. We have estimated the stability towards a quasi-one-dimensional reconstruction by using the calculated quantities as parameters in a one-dimensional Frenkel-Kontorova model. On all surfaces we have found an intrinsic tensile stress. This stress is large enough on Au and Pt surfaces to lead to a reconstruction in which a denser surface layer is formed, in agreement with experiment. The experimentally observed differences between the dense reconstruction pattern on Au(111) and a sparse structure of stripes on Pt(111) are attributed to the details of the interaction potential between the first layer of atoms and the substrate.

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I. INTRODUCTION

The properties of close-packed noble and transition metal surfaces have been extensively studied in recent years. The research has made great advances since the introduction of new experimental techniques, in particular scanning tunneling microscopy (STM), and the improvement of first-principles computational methods based on the density functional approach. These surfaces show a wide variety of behavior with respect to reconstruction, preferred site, and strength of chemisorption of reactive species, adsorbate diffusion, etc.

Owing to the abrupt change of the electronic structure on metal surfaces the first layer of atoms may have rather different properties from the bulk. Often, a large intrinsic tensile surface stress appears, which is the driving force leading to compressive reconstruction on many close-packed metal surfaces. The stability of a particular surface is the result of the interplay of several physical quantities characteristic of surface, such as surface energy, surface stress, interatomic force constants, etc. The reconstruction is more likely to occur the larger the intrinsic stress and the smaller the energy for sliding the atoms of the first layers into positions out of registry with the substrate.

In this paper we consider (111) surfaces of copper, platinum, and gold. The Au(111) surface reconstructs, forming a uniaxially compressed layer, which can be seen in STM experiments.¹⁻³ The Pt(111) reconstructs only at high temperatures^{4,5} or in the presence of saturated Pt vapor,^{6,7} and Cu(111) does not reconstruct. We report on first-principles numerical calculations of the properties of these surfaces using the density functional theory (DFT). In Sec. II we first describe the generalities of the computation procedure. We then calculate the important physical quantities, such as the effective force constants in the first layer, the surface energies, and the intrinsic surface stress. In Sec. III we use these quantities in order to estimate the stability of the first layer of atoms with respect to a quasi-one-dimensional reconstruction, which can be treated theoretically by the Frenkel-Kontorova model. In the Sec. IV we discuss the results.

II. CALCULATIONS OF SURFACE PROPERTIES

The reconstructed phase of some close-packed metal surfaces may have a periodicity which involves many surface atoms. For example, the reconstruction of Au(111), one of the surfaces considered in this paper, involves a uniaxially compressed first atomic layer with a period of around 70 Å. Full first-principles calculations with such large supercells are not feasible. One instead evaluates the stability by calculating the relevant quantities of the unreconstructed surface and uses them in phenomenological models of reconstruction.

There have been a number of papers in which the stability of (111) surfaces of noble metals was evaluated using the Frenkel-Kontorova (FK) model⁸⁻¹⁰ of uniaxially compressive reconstruction. Ravelo and El-Batanouny (Ref. 11; see also references therein) have constructed effective potentials between surface atoms and performed molecular-dynamics simulations of the reconstructed phase. Mansfield and Needs¹² have derived conditions of stability of (100) and (111) surfaces towards a compressive reconstruction in the FK model and evaluated it for several metals. Apparently, their values of the parameters are not good enough, as they have found no reconstruction of Pt(111) and Au(111). In particular, the strength of the interatomic potentials seems to be overestimated. Takeuchi *et al.*¹³ have constructed a two-dimensional potential between first- and second-layer atoms of a Au(111) surface using the results of first-principles calculations. They have calculated the reconstruction pattern using simulation techniques in a two-dimensional FK model. Using the two-dimensional potential in a molecular-dynamics simulation, Narasimhan and Vanderbilt¹⁴ have concluded that the herringbone pattern of the reconstruction stripes observed on Au(111) is favored by the long-range elastic interactions mediated by the substrate. Recently, Narasimhan and Pushpa¹⁵ have studied a two-dimensional FK model of the Pt(111) surface for which the parameters have been obtained from *ab initio* calculations. They have obtained simulated STM images of the reconstruction stripes recombining and intersecting in various ways, similarly to the structures observed in STM experiments.

The aim of this paper is to reevaluate with highest accuracy the properties of the surfaces which determine the stability towards reconstruction. In this section we report on such calculations for the (111) surfaces of Au, Pt, and Cu in the DFT approach. In the following subsections we describe, in order, the generalities of the numerical calculations, the calculation of surface energies, surface stress, surface spring constants, and the calculation of energy required to slide the complete first layer to various positions away from the most stable one. In the next section we use these results as input parameters in the (effectively one-dimensional) Frenkel-Kontorova model of uniaxially compressive reconstruction.

A. DFT calculations

We have performed first-principles calculations of the electronic structure of (111) surfaces within the density functional theory approach, using the DACAPO program.¹⁶ We have used the provided ultrasoft pseudopotentials for the Perdew-Wang exchange-correlation functional PW91 and the generalized gradient approximation (GGA).

We have first made calculations for bulk metal, in order to determine the lattice constant at which the energy per atom is minimum, using the primitive fcc unit cell. The lattice constant found often differs slightly from the experimental value: for example, our value is 4.00 Å compared with the experimental value 3.92 Å for Pt, 4.18 Å compared with the experimental value 4.08 Å for Au, and 3.66 Å compared with 3.61 Å for Cu. We have followed the common practice of using the computed value of the lattice constant in subsequent calculations, which ensures that no spurious bulk stresses appear.

The surfaces were described by a slab of five or more (up to 12 in some cases) hexagonal layers of atoms. Since the calculation assumes periodicity in all three dimensions, the metallic slabs were separated by typically five layers of vacuum. In addition to ideal surfaces, we calculated surfaces perturbed in various ways in order to deduce quantities like surface stress and surface energy, which can be used to estimate the stability of the surface. More details are given in the respective subsections.

In the case of a clean surface, the unit cell in the directions along the surface plane (x - y) consisted of one atom, and 56 k points in the two-dimensional first Brillouin zone were used. In some calculations described in the following subsections, e.g., when alternate rows of first-layer atoms were displaced in opposite directions, in order to probe the restoring forces within the first layer, unit cells with four atoms in each plane were used, and the number of k points was reduced to 18. In the z direction, perpendicular to the layers, only $k=0$ was considered, consistent with the assumption that the slabs, which repeat periodically because of the computational method, did not couple to each other. In most calculations, the two bottom layers were kept fixed at the bulk separation. We used an energy cutoff for the plane-wave basis set of 340 eV, and the electronic occupation was smeared by a pseudothermal distribution of $T=0.2$ eV. We performed some checks with a lower value $T=0.1$ eV and found that the changes of the calculated quantities were irrelevant.

TABLE I. Surface energy γ , surface stress τ , and force constants between nearest neighbors k_0 , for (111) surfaces of Au, Pt, and Cu. The two values of the surface energy γ have been obtained from a fully self-consistent DFT GGA calculation and from applying the LDA functional to the same electronic density; see text. The three values of the force constant k_0 have been calculated from the bulk modulus $B(k_{0B})$ and from the forces obtained in DFT calculations in which the first-layer atoms were slightly displaced “compressively” (k_{0C}) or “laterally” (k_{0S}); see Fig. 1.

	γ (eV/Å ²)		τ (eV/Å ²)	k_0 (eV/Å ²)		
	GGA	LDA		k_{0B}	k_{0C}	k_{0S}
Au	0.050	0.080	0.15	1.83	1.41	1.18
Pt	0.084	0.124	0.32	3.12	2.23	2.55
Cu	0.080	0.112	0.11	2.04	1.73	2.36

Next, we calculated the structure of clean (111) surfaces. The relaxation of the surface layers from truncated bulk positions was found to be rather small for the three metals considered. For gold, the first and second layers relax less than 0.3% of the interlayer distance in the $\langle 111 \rangle$ direction, with an energy gain of 1 meV, which is irrelevant considering the accuracy of the calculation. The first platinum layer relaxes outwards by about 1%, with an energy gain of 2.5 meV. This unusual expansion of the interlayer distance has been observed experimentally.¹⁷ On copper, the first three layers move inwards by less than 1%, and the energy gain is 4 meV.

B. Surface energy

We obtained the surface energy per atom as the difference of the energy of the bulk and of a slab. In order to minimize the influence of the computational details, we calculated the energy of the bulk using a slab consisting of the abc stacking sequence of the $\langle 111 \rangle$ fcc direction repeated 2–4 times, i.e., 6–12 layers of metal atoms, with no layers of vacuum. After that, we changed the configuration by introducing four layers of vacuum which created two (111) surfaces and calculated the energy, allowing both surfaces to relax. The surface energies γ , one-half of the difference of the energies obtained in the two calculations, are given in the GGA column in Table I. These values are consistently smaller by about one-third than those calculated recently by Vitos *et al.*¹⁸ and Galanakis *et al.*^{19,20} and various experimental values reported therein. One possible source of the discrepancy are the different pseudopotentials and exchange-correlation functionals used. We therefore also report the surface energies calculated using the local density approximation (LDA) functional for the electronic densities obtained in the GGA calculations, in the column labeled as LDA in Table I. These electronic densities are, of course, non-self-consistent with respect to the LDA functional. They are always larger than the GGA results, in better agreement with Refs. 18–20. In order to analyze the influence of the slab thickness and of the choice of the pseudopotential, we made calculations for Pt using the standard 10-electron pseudopotential with 6 layers (the values in Table I) and with

TABLE II. The parameters of the Frenkel-Kontorova model of uniaxial compressive reconstruction. A is the area per surface atom, and a is twice the distance between the fcc and hcp hollow sites on the (111) surface. The other parameters were determined from the DFT calculations as described in the text. These are the surface stress τ , the non-self-consistent LDA value of the surface energy γ_{LDA} , the force constant $\mu = 3/2k_{0C}$, and the average amplitude of the corrugated potential of the second layer W . The quantities α and β defined in Eq. (4) determine the stability of the surface in the Frenkel-Kontorova model.

	$A(\text{\AA}^2)$	$a(\text{\AA})$	τ (eV/ \AA^2)	γ_{LDA} (eV/ \AA^2)	μ (eV/ \AA^2)	W (eV)	α	β	Reconstruction
Au	7.57	3.41	0.15	0.080	2.12	0.038	23	-24	Compressive
Pt	6.93	3.27	0.32	0.124	3.35	0.061	22	-35	Compressive
Cu	5.79	2.99	0.11	0.112	2.60	0.056	18	-3.6	No

12 layers and using a new improved 18-electron pseudopotential with 12 layers. The results for γ_{LDA} are, in order, 0.124 eV/ \AA^2 , 0.130 eV/ \AA^2 , and 0.133 eV/ \AA^2 ; i.e., they agree within 7%. The difference is not relevant to the discussion of the surface stability in the following sections. In the bulk calculation (i.e., without vacuum) we used only one k point in the z direction, in order to keep similarity with the surface calculations. This implies that long-distance contributions in the z direction have an effective cutoff corresponding to the number of atomic layers used. The fact that γ_{LDA} changes little when going from 6 to 12 layers shows that they are sufficiently well taken into account. Our approach also ensures that the problems of poor convergence of the bulk energy discussed by Boettger²¹ do not occur. Also, we used the equilibrium lattice constants obtained self-consistently in our GGA calculations which were larger than the experimental values and those obtained by other authors from LDA calculations.

In the following section, when discussing the stability of the surfaces, we shall use the LDA results, which seem to agree well with the best values reported in the literature.

C. Surface stress

The surface stress can be found by considering the change of energy when the lattice constant in the x and y directions (i.e., in the surface plane) is varied. In the bulk calculations the leading correction to the energy when the lattice constant is varied around the equilibrium value is quadratic by construction, since we used the lattice constant corresponding to the energy minimum. Owing to the reduced coordination, the optimum interatomic distance in the surface layer is smaller than the bulk lattice constant, as already mentioned, causing an intrinsic tensile surface stress.^{22,23} Therefore, the surface contribution to the energy has a leading linear term if the lattice constant in the x and y directions is varied.

In order to find the intrinsic surface stress, we calculated the energy of slabs consisting of 6 or 12 layers, as in the preceding subsection, both unperturbed and with the unit cell compressed or expanded along the coordinates x and y (i.e., in the directions in the surface plane) in steps of 0.1%, not allowing any additional relaxation in the z direction. We also calculated similar configurations without vacuum layers, in order to subtract the quadratic bulk term, as discussed earlier. The diagonal element of the surface stress tensor τ , which is the relevant quantity for the surface reconstruction, is

$$\tau = \frac{\Delta E}{2\Delta A}, \quad (1)$$

where ΔE is the change of energy when the lattice constant is varied (after subtracting the quadratic bulk term) and ΔA is the associated change of the surface area. The numerical values are given in Table II. The calculations were performed using three values of the distortion, $\pm 0.1\%$ and 0, but in the case of Pt we made extensive checks using two different pseudopotentials, 12 layers instead of 6, and 9 values of the distortion, up to $\pm 0.4\%$. The values of the surface stress agree within a few percent, as was the case with surface energy in the preceding subsection. We have found that in this case there is almost no change if the non-self-consistent LDA values of the energy are used instead of the GGA values.

D. Surface spring constants

The simplest atomic-scale model of the lattice dynamics of fcc metals is to assume central harmonic forces between nearest-neighbor atoms. In this model there is a universal scaling of phonon spectra and different elements of the elasticity tensor, which is obviously an oversimplification. Nevertheless, this model is sufficient for the purpose of this work. The force constant k_{0B} of the nearest-neighbor bond in the bulk can be found from the bulk modulus²⁴ $B = 1/3(C_{11} + 2C_{12})$:

$$k_{0B} = \frac{1}{2a_0B}, \quad (2)$$

where a_0 is the lattice constant of the conventional fcc unit cell.

However, the effective force constant between the atoms in the first surface layer can differ from the value in the bulk, since the lower coordination can substantially alter electronic properties, and an *ab initio* DFT calculation is necessary. (Note that this force constant also contributes to the quadratic energy term in the preceding subsection, where we did not consider the possibility that it was modified within the first layer. However, the possible error which this introduces in the calculation of the surface stress is negligible.)

We made slab calculations (with relaxation turned off) in which rows of atoms in the first layer were displaced by about 0.05 \AA either in the direction of the rows or perpendicularly to it, as shown in Fig. 1. Unlike other calculations

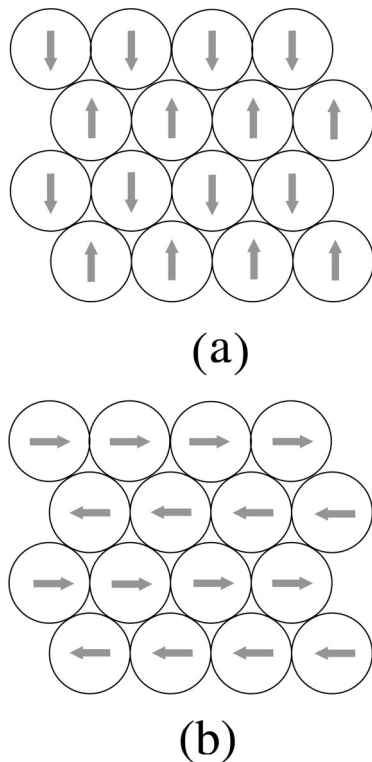


FIG. 1. The calculation of the force constants between the atoms in the surface layer of (111) surface. The atoms in the top layer of the slab were displaced by around 0.1% of the interatomic distance, and the restoring forces were calculated. Assuming that only central nearest-neighbor restoring forces exist, the force constants are $k_{0C} = (1/6)(F/\delta y)$ for “compressive” displacements (a) and $k_{0S} = (1/2)(F/\delta x)$ for “lateral” displacements (b).

in this paper, here we were not interested in the total energy, but rather in the restoring forces appearing owing to the non-equilibrium configurations. We analyzed the results assuming central harmonic interactions (“springs”) between nearest neighbors, neglecting the coupling to the second layer. Taking into account the number of nearest-neighbor bonds and the angles, we calculated the force constants k_{0S} . The results for both the bulk values obtained from Eq. (2) and the surface DFT calculations are shown in Table I. We note once again that this approach does not attempt to give a complete description of the lattice dynamical properties of the first surface layer. In general, even if the interactions with subsurface atoms are not taken into account, a set of force constants between second and further neighbors and/or angular force constants would be necessary in order to reproduce accurately the lattice dynamics—i.e., the phonon spectra. The present approach is a simplification to be used only in an estimation of the stability of the surface layer. One may further object that the reconstruction has a large wavelength, while the displacements shown in Fig. 1 correspond mainly to short-wavelength modes around the edge of the Brillouin zone, and the estimated k_S need not be the same. Also, there is a possibility that there are significant anharmonicities in the interatomic potential in the first layer. In our opinion, the calculated values are sufficiently accurate for a qualitative

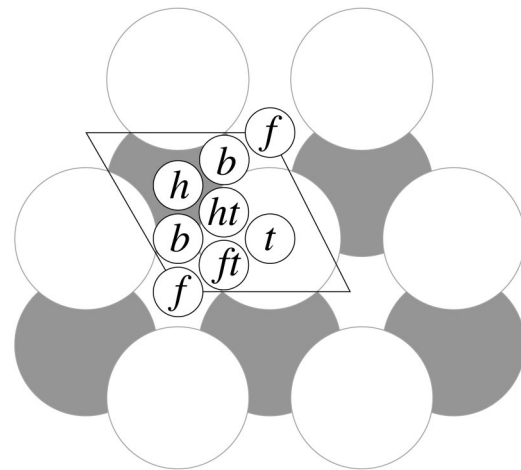


FIG. 2. Various positions of the first-layer atoms (small circles) on a (111) surface, relative to the second layer (large circles) and the third layer (gray). In the unreconstructed phase, all first-layer atoms are in the fcc positions (f). Upon reconstruction, the atoms are found in various positions along the path $f-b-h-b-f$.

discussion of the surface reconstruction, but the spring constants are the least reliable of all the quantities used in the estimates in Sec. III and may deserve further considerations.

E. Potential between the top layer and the bulk

When reconstruction occurs, some first-layer atoms are displaced to energetically less favorable positions with respect to the second layer. The last quantity which we need for an estimate of the stability is the amount of energy lost by the atoms when displaced to various nonoptimal positions. Since the periodicity of the reconstruction pattern is large compared with the substrate periodicity [e.g., by a factor of around 22 on Au(111)], the position of each subsequent atom along the reconstruction direction with respect to the second layer changes only slightly. A good estimate of the energy involved can be obtained by considering structures in which all atoms in the first layer are simultaneously displaced by the same vector. We performed DFT calculations of such configurations, keeping the displacement in the x - y plane fixed and allowing the atoms to relax in the z direction.

We first calculated the energy of the regular fcc configuration, denoted by f in figures and tables, which is energetically the most favorable. Next, we considered the configuration with the first-layer atoms in the hcp hollows of the second layer (h), which is also a local energy minimum. We furthermore calculated the energy of some other configurations which are not local energy minima, keeping the x and y coordinates fixed, so that the algorithm for the atomic relaxation ignored the lateral forces acting on the first-layer atoms. These are (see Fig. 2) the “bridge” position (b) in which the first-layer atoms are halfway between fcc and hcp hollows, the on-top configuration (t), the configurations (ft) and (ht) halfway between (f) and (t), and (h) and (t), respectively, etc. (Not all calculations were performed for all three metals.) For the quasi-one-dimensional compressive reconstruction, the relevant configurations are along the path

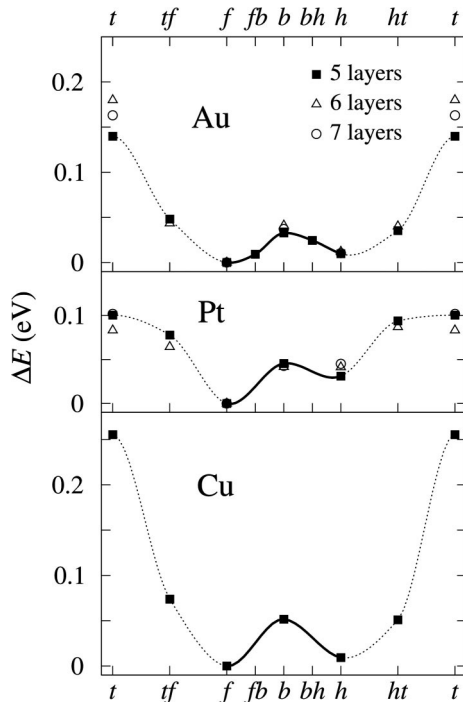


FIG. 3. The energy needed in order to move the complete first atomic layer away from the optimum fcc into other configurations. The various positions are depicted in Fig. 2, and the energies are expressed in eV/atom.

f - fb - b - bh - h and back to b and f . (The on-top configuration, which is not occupied in the reconstruction, was calculated with the aim to obtain a better insight into the difference between various metals.) In practice, the calculations were performed so that initially, all layers except the top one were kept fixed at the bulk configuration, the top layer had fixed x and y coordinates, and the z coordinate was allowed to relax. In a second step, the bottom two layers were kept fixed, the intermediate layers were allowed to relax in all directions, and the top layer was allowed to relax in the z direction only. The second step produced only minor changes for the symmetrical configurations (f), (h), (t), and (b), but the non-symmetric configurations changed significantly, as the atoms in the second layer (and to a lesser degree in deeper layers) relaxed laterally under the force exerted by the first-layer atoms.

In Fig. 3 we show the calculated energies, measured with respect to the energy of the fcc configuration, which was the lowest for all three metals. The “bridge” position, midway between fcc and hcp hollows, is approximately a saddle point. All points were calculated for five layers (first one fixed in x and y , two free, two fixed), and some points were also calculated for six and seven layers. It was found that the energies changed by several meV, but the qualitative behavior remained similar, and the estimates of stability towards reconstruction in the following section are not affected. Generally, the energies of symmetric configurations (h , b , t) increase with increasing number of layers, while those of non-symmetric configurations, like (fb) or (ht), decrease. This can be attributed to the fact that in the latter case there are

more atomic layers which are free to relax laterally, leading to a more complete relaxation.

The first-layer atoms in positions other than the regular fcc one (f) are also protruding further out. For all three metals, the values are similar—namely, around 0.1 Å for the bridge (b), 0.02 Å for the hcp (h), and 0.3–0.4 Å for the on-top position (t).

The relevant quantity for the stability estimate is the average energy W along the path f - b - h - b - f , in the approximation of making a Fourier expansion and keeping only the two lowest terms:

$$W = \Delta E(b) + \Delta E(h)/2. \quad (3)$$

III. STABILITY AND RECONSTRUCTION

In this section we use the calculated quantities to discuss the stability of the surfaces of platinum, gold, and copper. We first introduce the one-dimensional Frenkel-Kontorova model and then discuss, in order, each of the considered surfaces, calculating the stability criteria and comparing the results with the known experimental findings.

A. Reconstruction of (111) surfaces

As already said, the electronic structure of closed-packed metal surfaces is very different from that in the bulk, with an abrupt decrease in density of conduction electrons. The consequences may be a change of the length of the bonds between surface atoms, occasionally accompanied by a reconstruction which involves a change of the number of atoms in the first surface layer.

The reconstruction of the fcc (111) surface involves a large number of atoms in inequivalent positions with respect to the underlying layer of atoms. In scanning tunneling microscopy experiments, the reconstruction of the Au(111) surface can be clearly seen as bright stripes,^{1,3,25} owing to the increased height of atoms which are out of registry with the second layer. On a larger scale, the stripes form a herringbone pattern, as the quasi-one-dimensional reconstruction proceeds along three equivalent directions on the surface. A typical size of the reconstructed Au(111) supercell is 70 Å × 280 Å. The reconstruction of the Pt(111) surface is similar, but occurs only at high temperatures^{4,5} or in the presence of saturated Pt vapor.^{6,7} STM micrographs show that the stripes do not form continuous patterns, but are instead well separated, with various types of intersections.⁷ The stripes in both systems consist of quasi-one-dimensional compressive reconstruction^{1,2} and can be treated as solitonic solutions of the Frenkel-Kontorova model.^{13,14} The large-scale two-dimensional structure of the reconstructed phase depends upon details of the interactions and will not be discussed here.

B. Frenkel-Kontorova model

The one-dimensional Frenkel-Kontorova model^{8–10} consists of a linear chain of atoms, subject to two competing interactions with different intrinsic periodicities. The atoms interact via a nearest-neighbor harmonic coupling with a pre-

ferred lattice constant b . In addition, there is an external periodic potential (i.e., the potential of the second atomic layer) of a periodicity a . Depending on the strength of the external potential and the magnitude of the spring constant μ , various stable solutions are possible. At small “pressures” (i.e., small difference of a and b , small μ) the external periodic potential dominates and all atoms are in potential minima, forming a commensurate phase. As the “pressure” increases, the natural periodicity of the atomic chain becomes more important. If, say, $b < a$, solitons appear in which the atoms are closer to each other, thus gaining energy from the harmonic interaction but paying the cost of increased potential energy in the external potential. Finally, when the external potential is weak compared with the elastic energy needed to stretch the atomic chain, the atoms follow the periodicity b , forming an incommensurate phase.

Mansfield and Needs¹² have applied the Frenkel-Kontorova model to the reconstruction of (111) surfaces of the fcc metals. They have found that the relevant quantity is

$$P = \frac{A(\gamma - 4\tau/3)}{2\sqrt{2\mu}Wa^2} = \frac{W\beta}{W\alpha}, \quad (4)$$

where the parameters of the Frenkel-Kontorova model have already been expressed in terms of the physical properties of real (111) surfaces. Thus, γ is the surface energy, τ is the surface stress, μ is 3/2 of the surface force constant, and W is the average potential energy. (The factors 4/3 in the stress term and 3/2 in the definition of μ appear because the path f - h - f is not straight.) a is twice the distance from the fcc hollow site to the nearest hcp hollow site on the (111) surface, and A is the surface area per atom. These quantities are the same (or closely related to) those calculated in the preceding section for real metal surfaces. There is no reconstruction for $|P| < 1$; the reconstruction is compressive for $P < -1$ and expansive for $P > 1$. The quasicontinuum approach is valid if the magnitudes of the dimensionless quantities α and β defined in Eq. (4) are large—say, larger than 5.

In the following subsections we apply this analysis to the (111) surfaces of gold, platinum, and copper. The relevant quantities derived in Sec. II are summarized in Table II, and the resulting α and β are given.

C. Au(111)

In our calculations the first layer of an ideal Au(111) surface relaxes outwards by about 0.005 Å, less than 0.3%, which is at the limit of accuracy of the calculations. The energy per surface atom of the hcp configuration is higher than that of the ideal (fcc) structure by around 10 meV per atom and that of the bridge by 33 meV (Fig. 3). This is in excellent agreement with the calculations of Takeuchi *et al.*¹³ and Galanakis *et al.*,^{19,20} who used a density functional approach with a mixed basis set. These energies are the smallest of all metals considered here. The surface energy is also small, and owing to a moderately large tensile surface stress we obtain that β is slightly larger than α , indicating that the surface reconstructs. Experimentally, the surface appears par-

ticularly prone to reconstruction, and a dense pattern of stripes of $23 \times \sqrt{3}$ reconstruction is observed at room temperature with STM.^{1,3,25}

D. Pt(111)

Our calculations show that the first atomic layer on Pt(111) relaxes outwards by 0.023 Å or 1%. This somewhat exceptional behavior has also been found in other calculations and confirmed experimentally.¹⁷ It has been attributed to an outward pointing electrostatic force on the positively charged atoms of the first layer owing to the kind of spill-out of electrons away from the surface.²⁶ The energy of the bridge configuration is around 46 meV larger than that of the regular fcc surface. The energy of the hcp configuration is only slightly smaller than the bridge (even less so in calculations with six and seven layers), which is different from the other surfaces considered. The force constant k_{0C} calculated assuming that a “longitudinal” displacement of rows of first-layer atoms is reduced by about 30% compared with that derived from the bulk compressibility. The intrinsic tensile surface stress is large, more than twice larger than in the other two metals considered. Although the surface energy is also quite large, the quantity β is much larger than α , predicting a strong tendency to reconstruct.

A large value of the surface stress compared to the surface energy on Pt(111) has also been found in other DFT calculations. In a recent study employing different program and pseudopotentials¹⁵ a value of 0.124 eV/Å² for the surface energy, which agrees completely with our LDA result, and of 0.40 eV/Å² for the surface stress, which is 25% larger than ours, were calculated.

Experimentally, the reconstruction of Pt(111) is observed only at high temperatures or in the presence of saturated platinum vapor.⁴⁻⁷ The nature of the reconstruction is similar to that of Au(111), but the stripes of compressive “solitons” do not form a dense pattern. Instead, they are sparse, and occasionally intersect in several distinct ways.^{7,15}

E. Cu(111)

Unlike the other two metals considered, we find that the first layer on an ideal (fcc) Cu(111) surface relaxes inwards by 0.014 Å. The contraction of the interlayer distance is usual for close-packed surfaces of many transition metals. The hcp configuration is a clear local energy minimum, and the energy of the on-top configuration is found to be exceptionally large at about 250 meV. The intrinsic surface stress is again tensile, but rather small. The calculated β is clearly smaller than α , indicating that the surface does not reconstruct. Indeed, no reconstruction has been observed experimentally.

F. Discussion

The use of the stability condition of (111) surfaces derived in the one-dimensional Frenkel-Kontorova model, Eq. (4), gives correct qualitative answers—namely, that the surfaces of gold and platinum reconstruct compressively and the sur-

face of copper does not. From a quantitative point of view, the agreement between theory and experiment is less satisfactory. We find that the condition for reconstruction, $|\beta| > \alpha$, is barely satisfied for the Au(111) surfaces, while in experiments a dense pattern of reconstruction stripes is always found on this surface. On the other hand, we obtain that the condition of Eq. (4) is amply fulfilled for the Pt(111) surface, while, experimentally, reconstruction is observed only under favorable thermodynamic conditions, at high temperatures, or in the presence of Pt vapor. It has already been noticed that calculations predict only a marginal tendency for reconstruction on Au(111), at variance with experiment. It has been suggested that the ordering of the reconstruction stripes into a herringbone pattern is indeed an essential contributing factor to the stability of the reconstructed phase.^{14,25} Furthermore, a large anharmonicity of the interatomic potential in the first Au layer may play a role in the reconstruction. The theoretical overestimate of the tendency to reconstruct in the case of Pt(111) may be due to the large value of the surface energy, which makes it unfavorable to bring additional atoms to the surface once the surface stress has been reduced by the formation of a few sparse reconstruction stripes.

The approach used in this paper can also give relevant parameters for other physical properties. We have calculated relaxations around adatoms of the same species on the surfaces considered in this paper and found that the force-relaxation ratio is consistent with the model of elastic constants calculated in Sec. II. Surprisingly, in our calculations (one adatom per four surface atoms) the adsorption into a hcp hollow site was slightly more favorable than into a fcc hollow site for all three metals considered. We have not found any conclusive experimental data about this property.

The approach can also be applied to relaxation around defects and chemisorbates of different species, energetics of self- and heterodiffusion, and other properties of (111) surfaces.

IV. CONCLUSIONS

Using the density functional theory approach we have calculated key properties of (111) surfaces of several metals and evaluated the stability towards reconstruction into a uniaxially compressed reconstructed layer using a one-dimensional quasicontinuum Frenkel-Kontorova model. The intrinsic surface stress is tensile for all surfaces; i.e., the atoms in the first layer prefer a denser packing than dictated by the potential of the second layer, which reflects the bulk periodicity. On the opposite side of the energy balance is the energy required to bring an extra atom into the surface layer and the energy lost owing to the fact that surface atoms in a reconstructed phase are no longer in the minima of the potential of the second layer. We have found that Pt(111) reconstructs owing to a large intrinsic tensile surface stress. The stress on Au(111) is considerably smaller, but the surface energy is also smaller and the reconstruction criterion is satisfied. The intrinsic surface stress in Cu(111) is somewhat smaller than that in Au(111), but other quantities are unfavorable, and the surface does not reconstruct, in agreement with experimental observations. Experiments show that Au(111) has the largest tendency to reconstruct, and dense reconstruction patterns are observed using STM, while Pt(111) reconstructs only under favorable conditions, and only a small fraction of the surface is reconstructed. This is the opposite from what our reconstruction criteria suggest, where Pt(111) is much deeper in the reconstruction regime. The reason may be further stabilization of the reconstruction of the gold surface by the formation of a two-dimensional herringbone structure,^{14,25,27} which is not included in the one-dimensional model used in the derivation.

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