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Electronic structure and local atomic configurations of flat and stepped (111) surfaces of Ni and Cu

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Results of self-consistent linear-combination-of-atomic-orbitals calculations for ideal and stepped (111) surfaces of Ni and Cu are presented. They are related to catalytic activity by a simple physical picture. The *d* band is decomposed into a "local" *d* band at each site. The width, position, and occupancy of this local *d* band show simple trends as a function of site coordination. For Ni (and similarly, for Pt) sites of *highest* coordination tend to be the most active sites on a surface, provided they are accessible to adsorbate molecules. Copper shows little activity, regardless of site coordination.

I. INTRODUCTION

Catalysis is of great physical interest, and it is commercially important. In consequence, much effort has gone into the study of catalytic processes. Despite this, a detailed understanding of the behavior of catalysts is developing only slowly, for several interrelated reasons.

Foremost among these reasons is the complexity of the processes involved, especially for commercially important reactions. Several independent reaction steps may take place, each of which depends sensitively on a great number of circumstances, including temperature, partial pressure of each reactant, structure of the catalyst, and reaction time. Furthermore, the separate reaction steps may compete, one inhibiting the other. Thus it is often difficult or impossible to isolate the effect of a single reaction condition upon a single reaction step.

Theoretically, the full problem of a catalyzed reaction is intractable. The effect of a catalyst is to alter the rate at which a reaction proceeds. Reaction rates, however, are notoriously difficult to predict, and the treatment of reaction dynamics on even the simplest catalyst surface must be regarded for now as impossible.

One of the simplest effects one might study is the effect of steps on the electronic structure and, indirectly, on the catalytic activity of transition-metal surfaces. It is known that steps and kinks greatly increase the activity of the close-packed (111) surfaces of transition metals, but not of noble metals.[1–4] This effect has important implications on the design of practical catalysts. Moreover, it is conceptually simple, since only the geometry changes.

It is generally accepted that the usefulness of the group-VIII transition metals as catalysts is due to their almost-filled *d* bands. As one moves across the Periodic Table, transition metals with more filled *d* bands tend to bind adsorbates less strongly. A good catalyst must provide an optimal compromise between too strong binding, which results in irreversibly bound adsorbates, and too weak binding, where the surface is nearly inert.

The most generally useful catalysts fall in the last column of transition metals: Ni, Pd, and Pt. The next to last column of transition metals, Co, Rh, and Ir, are much less generally useful as catalysts, presumably because they are too chemically active, i.e., they bind adsorbates too strongly. The noble metals, on the other hand, are practically inert. Thus for Ni, Pd, and Pt, we see that the chemical properties must be an extremely sensitive function of the local electronic occupancy. It is this local occupancy, and its dependence on local geometry, which we wish to examine.

We find that sites of lower coordination, such as a step site, have a more completely filled local *d* band, and so are less chemically active. Sites of higher coordination than an ideal surface, such as the concave site at the bottom of a step, have more *d* holes, and so exhibit greater chemical activity. (This assumes that they are physically accessible to an adsorbate, as appears to be the case.) Erley and Wagner[2] have found that the binding energy of carbon atoms on Ni(111) is greater at step sites, leading to dissociative adsorption of CO.

The precise connection to catalytic activity necessarily remains conjectural at this point. It may simply be that the juxtaposition of sites of different chemical activity facilitates sequences of reaction steps, by providing sites with the proper bonding properties for each reaction step. However, because of the very nearly filled *d* band of Ni, and the consequent weak bonding of adsorbates, it is reasonable to suppose that for the stepped surface it is sites of stronger bonding which are responsible for the enhanced catalytic activity, relative to the ideal surface.

There is another, more subtle argument which also suggests that the concave site at the step plays a special role in catalysis. There is a long-standing conjecture that the catalytic activity is related to fluctuations in the local quasiatomic configurations.[5] If we imagine an adsorbate molecule interacting chemically with a single atom in the metal surface, that molecule has a finite probability of "seeing" the metal atom in any of a number of local atomic configurations. (We are speaking only of the *d* band here. For the less localized *s* and *p* orbitals it is probably too crude to speak of a local atomic configuration.) This flexibility on the part of the catalyst atoms explains qualitatively some of the most striking features of catalysts—their ability to catalyze widely disparate reactions, and their ability to interact chemically with a molecule, without binding any reactant so tightly as to poison the surface. Such fluctuations are stronger at a more bulklike site, where electrons have a more itinerant character. Fluctuations are suppressed at a site of low coordination. We characterize the degree of fluctuation at various sites by calculating the occupancies of individual *d* orbitals. In an atom each one-electron spin orbital has integral occupancy; the deviation from integral occupancy is a measure of the degree of fluctuation. We describe in Sec. II C how we choose the appropriate basis of *d* orbitals at each site.

In Sec. II, we describe the calculation—the formalism, the physical approximations, and the quantities to be calculated. In Sec. III, we examine the results of our calculations, and the significance of these results for catalysis. In Sec. IV, we consider the usefulness of our results in understanding other transition- and noble-metal systems, particularly some recent experimental results for the (100) surfaces of Au with Pt overlayers and of Pt with Au overlayers.[6]

II. THE CALCULATION

The method which we use here has been described elsewhere[7,8] but we include a summary for completeness. For our Hamiltonian we use the usual tight-binding parametrization scheme of Slater and Koster.[9] We include 3*d*, 4*s*, and 4*p* orbitals, with interactions up to second nearest neighbors. Rather than calculate eigenstates for a thin film, as is often done, we prefer to consider a semi-infinite crystal. This is possible if we treat propagation between layers in a real-space Green's-function formalism, which has been developed elsewhere.[7,8] We first review the formalism for an ideal surface, and then make the simple extension to a stepped surface.

A. The Green's function

Let ϕ_{iR} denote the *i*th local orbital, centered on lattice site $\vec{R}$. Also let $\vec{R}_m$ denote a lattice vector lying in the *m*th plane of atoms from the surface. For our basis we take Bloch sums in a single plane,

$$\phi_{im}(\vec{k}) = N^{-1/2} \sum_{Rm} \phi_{iRm} \exp(i\vec{k}\cdot\vec{R}_m) ,$$

where $\vec{k}$ is a wave vector parallel to the surface, and N is the number of atoms in a layer.

The Green's function is defined by Dyson's equation, which for our one-electron Hamiltonian is simply $I = (\epsilon - H)G$. We handle the orbital indices implicitly in matrix notation, but write the layer indices explicitly as subscripts. For example, $\tilde{G}_{mn}(\vec{k},\epsilon)$ is a matrix such that

$$[\tilde{G}_{mn}(\vec{k},\epsilon)]_{ij} \equiv \langle \phi_{im}(\vec{k}) \,|\, G(\epsilon) \,|\, \phi_{jn}(\vec{k}) \rangle .$$

Then Dyson's equation leads to an infinite set of simultaneous equations involving different layers.

For example, with only neighboring layers interacting, we can write

$$\begin{aligned} \tilde{I} &= (\epsilon - \tilde{H}_{11})\tilde{G}_{11} - \tilde{H}_{12}\tilde{G}_{21} , \\ 0 &= (\epsilon - \tilde{H}_{22})\tilde{G}_{21} - \tilde{H}_{21}\tilde{G}_{11} - \tilde{H}_{23}\tilde{G}_{31} , \\ 0 &= (\epsilon - \tilde{H}_{33})\tilde{G}_{31} - \tilde{H}_{32}\tilde{G}_{21} - \tilde{H}_{34}\tilde{G}_{41}, \text{ etc.} \end{aligned} \tag{1}$$

To uncouple these equations we note that in the bulk, the relation between Green's-function matrix elements for successive layers must be independent of the particular layer. We therefore define the transfer matrix $\tilde{T} = \tilde{G}_{m+1,n}(\tilde{G}_{m,n})^{-1}$, which is independent of m and n, for m sufficiently large. The transfer matrices for each $\vec{k}$ and ϵ may be calculated once and stored.

In Eqs. (1) above, we include self-consistency only as a shift in the diagonal elements of the Hamiltonian for the first two layers; i.e., only H_{11} and H_{22} differ from the bulk value. (For a stepped surface, or a surface with an overlayer of another metal, the interaction H_{12} between the first two layers also differs from the bulk value.) Then $\widetilde{G}_{31}$ is related to $\widetilde{G}_{21}$ by an equation with only bulklike terms, and we can write $\widetilde{G}_{31} = \widetilde{T}\widetilde{G}_{21}$. Thus we uncouple the infinite set (1) of equations, and reduce it to two simultaneous matrix equations. For the ideal surface, we obtained accurate results with only one layer self-consistent. In that case (1) is reduced to a single matrix equation.

Once we have $\widetilde{G}_{mm}$ for the layers of interest, it is trivial to define the local density of states and local occupancy. For example, we can define a partial density of states $D_{md}(\epsilon)$ in which we project out the contribution from the d orbitals in layer m,

$$D_{md}(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\sum_{k}\mathrm{Tr}_d\widetilde{G}_{mm}(\vec{k},\epsilon)\ ,$$

where Tr_d denotes a partial trace, taken only over the indices corresponding to d orbitals. The d occupancy on a site in layer m is $n_d = \int_{-\infty}^{\epsilon_F} D_{md}(\epsilon)d\epsilon$. Later, in discussing local configuration fluctuations, we define a more general density matrix to include coherence between our basis orbitals.

B. Self-consistency

We treat the self-consistent change in the potential in a simple manner. For a given site, let n_{sp} and n_d denote, respectively, the total occupancy of the s and p orbitals and of the d orbitals, centered on that site. Also let $\Delta n_d \equiv n_d - n_d^{(\mathrm{bulk})}$, and similarly define Δn_{sp}. We assume that only the changes in the diagonal elements of the Hamiltonian are important. We neglect the relative shift of the s and p potentials, since the sp bands are very broad, with strong s-p hybridization. Then we must determine $\Delta\epsilon_s$ and $\Delta\epsilon_d$, where ϵ_s denotes $\langle\phi_s|H|\phi_s\rangle$ at the site, and we assume $\Delta\epsilon_s \approx \Delta\epsilon_p$.

We make the linear approximation

$$\begin{aligned}\Delta\epsilon_s &= \alpha\Delta n_s + \beta\Delta n_d\ ,\\ \Delta\epsilon_d &= \beta\Delta n_s + \gamma\Delta n_d\ ,\end{aligned} \tag{2}$$

which is good for small Δn. Changes in the interatomic terms are neglected. The parameters α, β, and γ in (2) were calculated in two independent ways. In the first, we took one-electron energies for the $3d$ and $4s$ orbitals in various atomic configurations from the atomic Hartree-Fock calculations of Clementi.[10] For the second approach we tried the valence orbital ionization potential (VOIP) scheme,[11] which uses spectral data.

Atomic data provide us only with energies at integral occupancies, $\Delta n = \pm 1$. For such a large range of occupancies, the linear equation (2) is inappropriate. To calculate the parameters we generalized (2) to a quadratic expansion. As expected, the quadratic terms are unimportant for the smaller values of Δn which occur in solids.

If one uses only available spectral data, one must expand about the positively ionized atom only. In that case, the d orbitals are more tightly bound than those in the neutral atom, and one finds values of $\Delta\epsilon_d/\Delta n_d$ which are far too large for the neutral solid. In order to have a sensible expansion about the neutral atom, we include the calculated ionization potential of the *negative* ion in the VOIP scheme, which was otherwise based strictly on spectral data.

With this precaution, we found values of α, β, and γ obtained by the two methods to be in excellent agreement. The parameters derived from the VOIP method were each about 20% larger than the corresponding parameter obtained using calculated one-electron energies.

For our final values we took the geometric means of the two sets. We find for Cu, in (eV/electron), $\alpha = 6.50$, $\beta = 7.77$, and $\gamma = 13.45$. This should be accurate to 10–20%, with the ratios between any two parameters considerably better than that.

For Ni, we could not calculate all three parameters independently since certain atomic terms were not available. However, those we could calculate agreed with the values for Cu to 5–10%, so we simply adopted for Ni the set of parameters obtained for Cu.

In general, there is also a change in the diagonal elements of the potential for sites with missing neighbors. We show in Sec. III that for Ni, this "chemical shift" merely causes a small charge transfer quite unimportant compared to the effects of altered local bandwidth. The position and width of the d band are practically unchanged. For Cu, however, the density of states at the Fermi level is small, charge transfer is less easily accomplished, and the local potential change shifts the local d band at the surface. Our neglect of this effect results in negligible error in the local occupancy, but gives the d band at too great a binding energy, compared to experiment[12] and to more sophisticated calculations for the ideal surface.[13] Since we are interested here primarily in local occupancies, not energies, and since for the more interesting case of Ni the effect of the chemical shift is slight, we make no attempt to incorporate this effect explicitly.

A more subtle question arises with respect to our neglect of the interatomic Coulomb interaction. Realistic calculations for the ideal surface[14] suggest that the charge deficit in the first layer is largely compensated by the net charge in the vacuum beyond the first layer, with a much smaller charge in the second layer. Since we are using a restricted basis, and cannot accurately describe the charge in the vacuum, it would be unphysical to impose charge neutrality on the surface within this model. To do so, without including the vacuum charge more realistically, would result in far larger errors than does neglect of intersite terms.

C. Analysis of local configuration

Thus far we have only stated broadly that we assume catalytic activity is related to fluctuations in the local quasiatomic configuration. We now proceed to explain how we define and quantify such fluctuations.

We define the usual probability density matrix

$$\widetilde{P}=\int_{-\infty}^{\epsilon_F} d\epsilon \sum_{v} |\psi_v\rangle\langle\psi_v|\,\delta(\epsilon-\epsilon_v) ,$$

where ψ_v are the one-electron energy eigenstates of our semi-infinite crystal, and the sum over v ranges over all eigenstates. It is trivially shown that

$$\widetilde{P}=-\frac{1}{2\pi}\sum_{k}\int_{-\infty}^{\epsilon_F} d\epsilon\,\mathrm{Im}[\widetilde{G}(k,\epsilon)-\widetilde{G}^{\dagger}(k,\epsilon)] .$$

The diagonal elements of $\widetilde{P}$, $[\widetilde{P}_{mm}]_{ii}$, give the probability that the orbital i on a site in layer m is occupied. Off-diagonal elements represent coherence effects. We neglect coherence between layers and between the *sp* and *d* bands, and focus on the (5×5) submatrix of $\widetilde{P}$ corresponding to the *d* orbitals on a given site. Since these are rather localized we can then speak comfortably of a local atomiclike configuration. The eigenvectors of this submatrix represent a basis of five orthonormal *d* orbitals whose occupancies are statistically independent, since in this basis all off-diagonal elements are zero. The eigenvalues give the probability of occupancy of the respective orbitals.

For noble and group-VIII transition metals, the *d* orbitals are usually occupied, and the probability of being unoccupied, i.e., occupied by a hole, is a good measure of the degree of occupancy fluctuation in a given orbital. We could also more generally characterize the degree of fluctuation[15] by $p(1-p)$, where p is the occupancy probability. But since we are restricting ourselves to Ni and Cu, we simply use the hole occupancy probabilities.

D. Steps and overlayers

Thus far, in discussing the calculation we have referred only to the ideal surface. The stepped surface is treated by defining periodic steps, and proceeding as before, with a supercell of several atoms in each plane parallel to the surface.

If we took a realistic, high-Miller-index stepped surface, we would have to work with high-index layers parallel to the surface. The interlayer separation between these sparse layers is very small, so that the nearest-neighbor coupling between atoms extends over a fairly large number of layers. This fact greatly increases the computational difficulty, since we thus have many simultaneous matrix equations to solve.

Instead, it is convenient to define up-then-down steps, so that the macroscopic surface is still in the [111] direction. Then, as for the ideal surface, we work with close-packed (111) layers, for which only nearest-neighbor layers interact. Moreover, the transfer matrices depend only on the average direction of the surface. In using (111) layers, we can relate the supercell transfer matrix to the ideal-surface transfer matrix by a simple canonical transformation.[8]

With a sufficiently large supercell, the steps would be essentially noninteracting, and the details of the periodicity would be irrelevant. However, practical computational considerations force us to take, in general, very small supercells. From experience with the ideal surface, we know that the screening length is quite short in Cu and Ni. The second layer is already very much bulklike, and this is especially true of integrated properties such as orbital occupancy.

We take, then, a supercell of three atoms, and form close-packed steps by removing every third row of atoms in the first layer, as shown in Fig. 1. Atoms *a* and *c* have the same local geometry as atoms at a close-packed step running in the $[1\bar{1}0]$ direction on a (111) surface. There are actually two distinct types of such steps. In the notation of Lang *et al.*,[16] atoms *a* and *c* define a $[n(111)\times 1(11\bar{1})]$ step, and atoms *b* and *d* define a $[n(111)\times 1(100)]$ step.

Since the atoms of the two upper-step edges are nearest neighbors, we can hardly assume that the steps are strictly noninteracting. However, the step

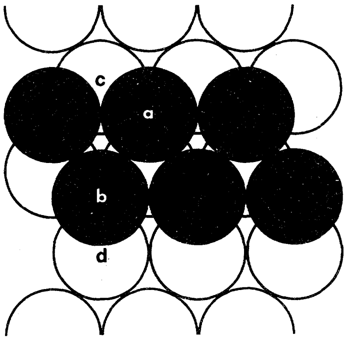

FIG. 1. Geometry for stepped (111) surface. Open circles are second layer, which is complete. Solid circles are first layer, of which every third row is removed to create steps.

atoms *a* and *b* each have the same number and arrangement of first- and second-nearest neighbors as those for an ideal step of the corresponding type. Moreover, the effect of local geometry on these two atoms is too drastic to be much affected by the artificial periodicity.

We find that the more interesting sites are the concave sites in the two inequivalent steps, labeled *c* and *d* in Fig. 1. These atoms have a realistic local geometry. They each have the correct arrangement of first- and second-nearest neighbors, except that atom *d* has one second-nearest neighbor which would be missing in a realistic geometry with larger terraces. The second-neighbor interactions are small in any case and negligible for the *d* orbitals, so no significant error is introduced.

In treating the occupancy fluctuations for atoms on a stepped surface, we neglect coherence between atoms in the supercell. The effect of such coherence in catalysis is probably nil; in any case it must depend sensitively on the particular adsorbate molecule and how it lies, and so is outside the scope of this paper.

For the handling of Cu overlayers on Ni or Ni overlayers on Cu, the discussion for the ideal surface is still applicable, though for the overlayer, as for the steps, we cannot uncouple the Green's-function equations at so early a stage as that for the ideal surface. We must, in addition, make an approximation for the interaction parameters between Cu and Ni. For these we simply take the geometric mean of the Cu-Cu and Ni-Ni interactions. Since the two sets are quite similar to begin with, the particular interpolation procedure used in handling the Ni-Cu interaction is actually of little importance.

There is also the possibility of charge transfer due to the different potentials of the two metals. We can either neglect this and take the bulk chemical potentials of Cu and Ni to be equal, or else estimate the difference in chemical potential. A simple estimate is provided by the electronegativity. Electronegativity can be expressed in units of energy, using the relationship (valid for certain elements) that the electronegativity equals the mean of the ionization energies of the positive and negative ions.[17] Using the Pauling scale, converted to units of energy per electron, Cu is roughly 0.3 eV more electronegative than Ni. We carried out the calculation both with and without this shift to see how important the relative potential difference is, since we do not have an accurate estimate of this difference.

E. Numerical technique and accuracy

While it is difficult to estimate the accuracy of our model, it is much simpler, and equally important, to consider how accurately we solve the model problem. We describe certain aspects of the calculational technique used, and briefly note the major sources of error and what limits they place on our accuracy.

A Green's-function technique poses a problem for surface calculations, because the one-dimensional density of states is singular at the band edges. This is circumvented by calculating the Green's function at complex energy. It is simple, but crucially important, to estimate *a priori* the error introduced by this approximation. We chose the imaginary part of the energy in each case so that the error in the total charge per atom is under 0.01, and the error in the individual orbital occupancies is at most $(1-2)\times 10^{-3}$.

For a given imaginary part of the energy, the sharpest possible structure in the density of states is a Lorentzian of corresponding width. This allows us, trivially, to determine the necessary energy grid to calculate $G(\vec{k},\epsilon)$. This makes numerical integration a negligible source of error.

For self-consistent calculations, the rate of convergence is a major determinant of the cost of a calculation. After some experimentation we found a particularly efficient convergence scheme appropriate to our simplified treatment of the self-consistent potential. First, for an initial potential, we calculate the individual orbital components of the density of states. Then we assume that the component for each orbital at each site is rigidly and independently shifted by a change in the corresponding diagonal element of the Hamiltonian. Within this crude approximation we achieve self-consistency by calculating the local potential, shifting the various density-of-states components, recalculating the local potential, and iterating. The resulting potential is then used as the input potential for the second "true" calculation. This procedure is repeated until the change in individual orbital occupancies is less than 2×10^{-3}.

For the ideal surface we sampled nine special points in the irreducible surface (two-dimensional) Brillouin zone (ISBZ). This sample should give integrated quantities such as occupancy and bandwidth quite accurately. In particular, simple convergence tests indicate that occupancies of individual orbitals have converged to better than 10^{-3} for this sample.

For the stepped surface of Ni, we sampled four points in the supercell ISBZ. Simple tests suggest that for the stepped surface, total *d* occupancy per atom is accurate to about 0.02, but individual orbital occupancies are only reliable to about 8×10^{-3}. This is the dominant source of error for the stepped surface, but it is still a small fraction of the effects we are studying.

For the stepped Cu surface, which is of less interest, we sampled only two points in the ISBZ. We have no good estimate of the accuracy here, but because of the full *d* band, the $\vec{k}$ sample is far less crucial for Cu, and the accuracy may well be comparable to that for Ni.

III. RESULTS

In discussing the results of our calculation we first describe the general effect of local geometry on the local density of states and net charge. Then we specifically consider the effect on the local configuration fluctuations and the implications for catalysis. Later, in Sec. IV, we see how these results shed light on recent experimental findings for Au-Pt systems.

Table I gives the following information for surface sites on ideal and stepped surfaces of Cu and paramagnetic Ni: the coordination of the site, the net calculated charge, the change in the local *s*, *p*, and *d* occupancies, and the self-consistent shift in the local potential for *s*, *p*, and *d* orbitals. Figure 2 shows the projected *d*-orbital component of the local density of states for Ni surface and bulk sites. Figure 3 gives the same for Cu, and Fig. 4 for selected Ni step sites. The densities of states shown are actually the sum of one-dimensional densities of states, and so contain spurious structure due to one-dimensional Van Hove singularities. Integrated

TABLE I. Electronic properties of atoms at flat and stepped (111) surfaces. z is the coordination number, Δn is the change in total electron occupation (with respect to the bulk), Δn_{sp} is the change in *s*- and *p*-electron occupation, Δn_d is the change in *d*-electron occupation, $\Delta\epsilon_{sp}$ is the self-consistent shift in on-site potential for *s* and *p* electrons (rydbergs), and $\Delta\epsilon_d$ is the self-consistent shift in on-site potential for *d* electrons (rydbergs).

Site	z	Δn_{total}	Δn_{sp}	Δn_d	$\Delta\epsilon_{sp}$	$\Delta\epsilon_d$
Ni bulk	12	0	0	0	0	0
Ni surface	9	−0.11	−0.29	0.18	−0.025	0.017
Ni steps						
atom *a*	7	−0.18	−0.49	0.31	−0.047	0.028
atom *b*	7	−0.18	−0.50	0.32	−0.047	0.025
atom *c*	11	−0.04	−0.08	0.04	−0.017	0.003
atom *d*	10	−0.08	−0.19	0.11	−0.023	0.008
Cu bulk	12	0	0	0	0	0
Cu surface	9	−0.10	−0.19	0.09	−0.039	−0.017
Cu steps						
atom *a*	7	−0.19	−0.34	0.15	−0.066	−0.050
atom *b*	7	−0.19	−0.36	0.17	−0.060	−0.041
atom *c*	11	−0.03	−0.05	0.02	−0.013	−0.005
atom *d*	10	−0.04	−0.11	0.07	−0.015	0.002

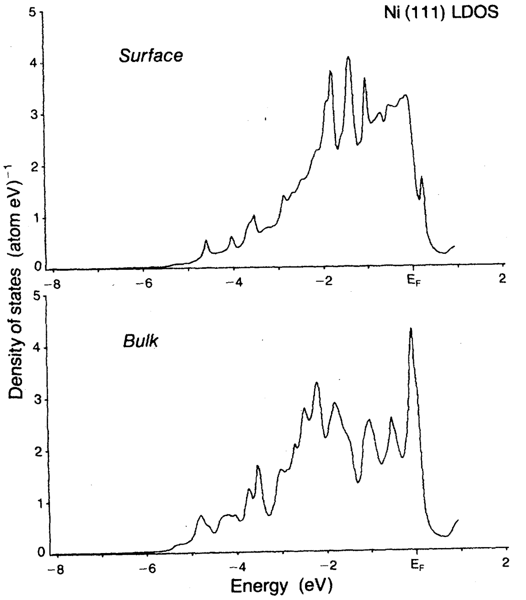

FIG. 2. *d*-orbital component of local density of states of Ni, for surface and bulk layers. Sample of nine points in irreducible section of two-dimensional surface Brillouin zone.

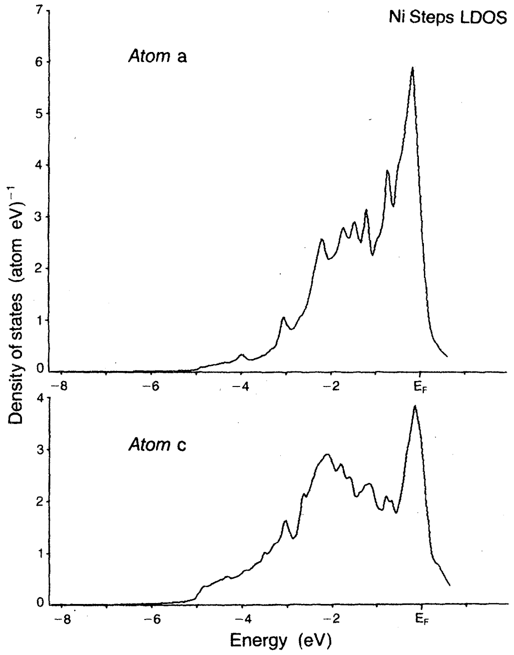

FIG. 4. *d*-orbital component of local density of states for Ni, at upper and lower atoms of step (labeled *a* and *c*, respectively, in Fig. 1). Sample of four points in irreducible section of two-dimensional Brillouin zone of surface supercell.

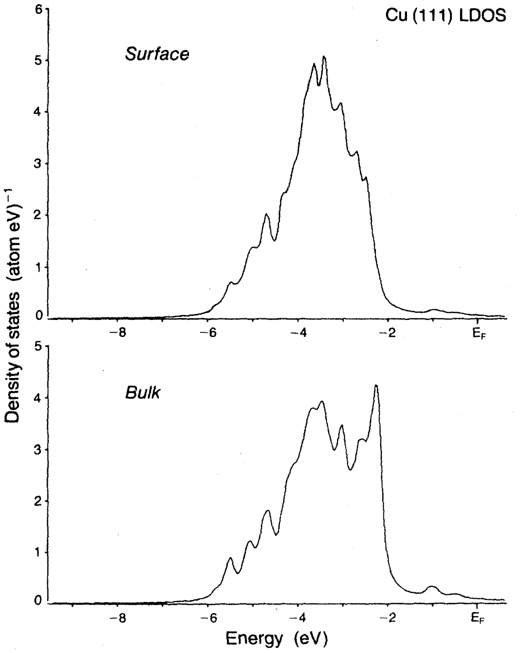

FIG. 3. *d*-orbital component of local density of states of Cu, for surface and bulk layers. Sample of nine points in irreducible section of two-dimensional surface Brillouin zone.

properties, such as occupancy and bandwidth, are accurately represented, however.

First we note that, while there is a net deficit of electrons at the surface for both metals, the number of *d*-like electrons increases. The physical picture is simple. The *d* band is centered well below the Fermi energy. As we reduce the coordination of an atom, the local *d* band narrows and hence becomes more nearly filled. (Even for Cu the *d* band is not completely filled, if we define the *d* band as the *d*-orbital component of the bands, due to *s*-*d* hybridization.) The opposite applies to the *sp* band. The wave function is "stiffer" than that for the *d* orbitals, due to the longer range of the interaction, and kinetic energy considerations cause a charge deficit in the surface layer. Thus, at the surface, electrons are shifted from the *sp* band to the *d* band, whether we include self-consistency or not. This effect has been observed experimentally by Citrin and Wertheim.[12] The same effect occurs at step sites, more or less dramatically depending on the coordination of the site. This effect is unfortunately exaggerated by our use of orthogonalized basis orbitals. We found that this choice somewhat increases both the net surface charge and the *s*-*d* charge transfer, but does not affect the trend in *d*-orbital occupancy.

Already we see the main feature of importance for catalysis. At sites of reduced coordination, the local *d* band becomes narrower and fuller, and hence more nearly inert. For a stepped surface, there are some atoms with higher coordination than that of ideal-surface atoms, and these must show substantially enhanced activity.

Table II shows our results for the (hole) occupancy of the five 3*d* orbitals on various sites. The orbitals are chosen so as to have statistically independent occupancies, as discussed above. We see that the edge atoms at the steps, atoms *a* and *b*, have greatly reduced hole occupancies compared to the ideal surface, and should be relatively inactive. The atoms at the concave sites, atoms *c* and *d*, show enhanced hole occupancy, especially atom *c*.

As mentioned earlier, atoms *c* and *d* correspond to two distinct types of close-packed steps. The implication here is that one type of step should be substantially more active catalytically than the other. We do not know of any experimental results for transition-metal catalysts which have distinguished between the two types of steps. We believe, however, that the experiment is a feasible one.

We have pointed out the effect of coordination on total *d*-band occupancy. But in addition, at a step or other imperfection, the local symmetry is reduced. The surface atoms have lower symmetry than the bulk, and the occupancies in each case show the appropriate degeneracy. The step sites have still lower symmetry and show no degeneracy. This results in one of the least filled orbitals becoming still less full and more active (at the expense of another), even without a net change in total occupancy.

While it is impossible to relate the hole occupancies directly to reaction rates, we should make some observations regarding the magnitude of the effect. Experimentally, the catalytic activity of the Ni(111) surface is dramatically increased for many reactions by the presence of steps. If we are correct in attributing this to local orbital fluctuations, then our results for Ni give us an idea of the scale of occupancy changes involved. We see that the difference between hole occupancies for Ni and Cu is far greater than the difference between Ni sites of drastically different activity. It is to be expected, therefore, that Cu will not display significant catalytic properties regardless of the presence or absence of steps.

We should point out that, since we are using orthogonalized orbitals as our basis, the *d*-like orbital already includes a small component from *s* orbitals centered on neighbor sites. Thus the value of n_d (and similarly n_{sp}) has a small degree of arbitrariness. However, this only affects the value of Δn_d, the change in occupancy, as a slight second-order effect which we may neglect.

Thus far we have not discussed the orientation of the "crystal-field" *d* orbitals we have defined. It would be awkward to plot the directional dependence of each orbital on each site, but we have ex-

TABLE II. Hole occupancy for local crystal-field *d* orbitals.

Site	Occupancies[a]				
Ni bulk	0.165	0.165	0.165	0.065	0.065
Ni surface	0.153	0.153	0.138	0.045	0.045
Ni steps					
atom *a*	0.148	0.117	0.108	0.055	0.044
atom *b*	0.155	0.117	0.102	0.060	0.037
atom *c*	0.194	0.161	0.119	0.067	0.060
atom *d*	0.179	0.137	0.131	0.068	0.054
Cu bulk	0.041	0.041	0.041	0.013	0.013
Cu surface	0.031	0.028	0.028	0.008	0.008
Cu steps					
atom *a*	0.026	0.021	0.021	0.006	0.004
atom *b*	0.024	0.019	0.012	0.008	0.008
atom *c*	0.047	0.043	0.025	0.016	0.008
atom *d*	0.036	0.031	0.027	0.011	0.009

[a] In decreasing order.

TABLE III. Electronic properties of atoms at (111) surfaces with single overlayer. Meaning of column headings is the same as for Table I.

Site	z	Δn_{total}	Δn_{sp}	Δn_d	$\Delta\epsilon_{sp}$	$\Delta\epsilon_d$
Ni on Cu						
layer 1 (Ni)	9	-0.12	-0.32	0.20	-0.030	0.017
layer 2 (Cu)	12	0.01	0.00	0.01	0.004	0.006
Cu on Ni						
layer 1 (Cu)	9	-0.09	-0.19	0.10	-0.034	-0.010
layer 2 (Ni)	12	-0.01	-0.05	0.04	-0.003	0.005

amined the results and can make a simple generalization. Despite some hybridization at sites of low symmetry, the two most fully occupied d orbitals in each case have primarily e_g symmetry, and the three less fully occupied orbitals have primarily t_{2g} symmetry.

The t_{2g} orbitals each have four lobes directed at four nearest-neighbor sites. Of the three t_{2g}-like orbitals at each site at the top or bottom of a step, the ones which are least filled are those which overlap the greatest number of neighbor atoms. Those orbitals which overlap unoccupied neighbor sites (where an adsorbate could sit) are more filled. One may think of holes as being bound away from the vacuum, into the solid, to reduce the antibonding character of the bonds between metal atoms. It is important to recognize, however, that this property of the bare stepped surface is drastically changed if an adsorbate is present. On the other hand, the characteristic difference in d occupancy between sites of different coordination should not be altered by the presence of an adsorbate, since the *difference* in the number of neighbors for the respective sites is unchanged.

As we mentioned above, we treated the case of a monolayer of Ni on Cu and a monolayer of Cu on Ni for two values of the chemical potential difference between the two metals. In Tables III and IV we give the results for the case of identical chemical potentials (i.e., neglecting charge transfer). The outstanding feature of the results is the insensitivity of the local electronic structure to modest changes in the character of neighboring sites. A comparison of Tables II and IV reveals that any atom is little affected by whether neighboring layers are Cu or Ni. This is to be expected, since the band structures of Cu and Ni are similar except for a more or less rigid shift. Of course, if we were interested in the sp electrons, nonlocal effects would then play a much greater role.

Inclusion of the estimated potential difference of 0.3 eV resulted in a change of net charge on an atom of no more than 0.02 electrons, a change in total d occupancy of no more than 0.01, and a change in individual d-orbital occupancies of no more than 2×10^{-3} in any case. Even if we underestimated the potential difference, its effect on charge transfer is certainly minor on the scale of changes induced by altered site coordination.

These results justify our neglect of another source of change in the local potential, the chemical shift at one site, due to the altered local potential at a neighboring site with a different element or a vacancy. However, this neglect would not be justified in all cases if we were concerned with the details of the local density of states. The inclusion of an *ad hoc* 0.3-eV shift in the local potential at the surface for Ni resulted in minute charge transfer, and in a shift of only 0.06 eV in the final self-consistent local potential at the surface. For Cu, the charge transfer was again minute, but the final self-consistent potential changed by 0.20 eV.

TABLE IV. Hole occupancy for local crystal-field d orbitals.

Site	Occupancies[a]				
Ni on Cu					
layer 1 (Ni)	0.155	0.155	0.138	0.038	0.038
layer 2 (Cu)	0.040	0.040	0.040	0.014	0.014
Cu on Ni					
layer 1 (Cu)	0.031	0.026	0.026	0.008	0.008
layer 2 (Ni)	0.165	0.165	0.147	0.065	0.065

[a] In decreasing order.

Citrin and Wertheim[12] find experimentally that the local surface d bands of Au are narrower than the bulk and shifted to slightly lower binding energy. We indeed find this for Ni; but for Cu the calculated d band was shifted to slightly higher binding energy. We attribute this error to our neglect of the chemical shift at the surface caused by the three missing nearest neighbors. As we have seen, the corresponding error for Ni should be much smaller. For both metals, the error in occupancies due to neglect of this chemical shift are clearly unimportant.

These results are useful in Sec. IV, where we consider recent experiments with Au overlayers on Pt and Pt overlayers on Au. They also suggest a test of the claim that we can understand the effect of steps in terms of the activity of individual sites of increased coordination. If we were to deposit Cu on the (111) face of Ni, this should, for small coverages, increase the catalytic activity of the surface as we create inner step sites. The active site at the lower layer should behave much as that for a pure Ni step. Of course, for higher coverages the loss of Ni surface sites would become important, and the activity might start to fall off, even before coverage reached half a monolayer.

IV. APPLICATION TO OTHER SYSTEMS

While thus far we have carried out calculations only for the (111) surfaces of Cu and Ni systems, our results can be qualitatively applied to other elements, and indirectly to other geometrics. In particular, the general effects we have described should apply equally to other noble and group-VIII transition metals. The crucial features were simply that the d band is narrow and nearly filled, and that there is significant s-d hybridization around the Fermi energy. Also, for mixed overlayers it was important that the transition and noble metals in the same row of the Periodic Table have similar band structure.

We cannot hope to make quantitative comparisons between metals in different rows of the Periodic Table, since we have considered only configuration fluctuations. However, for a given row, the respective transition and noble metals should show the same basic behavior when we introduce steps, overlayers, etc., as we found here for Ni and Cu.

Having a clear physical picture of how local geometry affects catalytic activity, we would like to test it on other systems. Sachtler *et al.*[6] have reported very interesting experimental results for the catalytic activity of the (100) surface of Pt with various coverages of Au, and Au with overlayers of Pt. Specifically, they measured the rate of cyclohexene dehydrogenation to benzene as a function of coverage. For Au on Pt, the reaction rate increased sharply with increasing Au coverage up to one monolayer, and then dropped rapidly, falling nearly to zero at two monolayers of Au. For Pt on Au, the reaction rate increased with increasing Pt coverage until about two monolayers, at which point the reaction rate reached a stable plateau.

The reaction rate for two or more layers of Pt on Au and for a monolayer of Au on Pt were both much higher than that on the ideal Pt surface. Throughout the region of greatest interest, from half a monolayer to a few monolayers, the surface is unreconstructed and the overlayer is in register with the substrate crystal.

The (100) surface is quite open, and crude bond-length estimates suggest that a carbon atom, or other smaller atom, could fit into the hollow site and interact with the second layer. Atoms in the first layer of the (100) surface have only eight nearest neighbors, whereas atoms in the second layer have twelve. Thus we expect the second layer to be much more active in catalysis than the first layer. As we saw in Sec. III, we may assume, to a first approximation, that the behavior of a given layer is independent of which metal the other layers are composed. From this perspective, it is obvious why the activity of Au on Pt falls off rapidly after one monolayer. At one monolayer, the second layer is still Pt, but at two monolayers the second layer is, ideally, all Au, and hence inactive. Why the activity increases up to one monolayer is a more difficult question, but several possibilities are suggested in the article, notably the observed elimination of carbon poisoning of the surface by a gold monolayer. If the second layer is the crucial one, poisoning of the surface by carbon atoms in the hollow sites should be particularly detrimental to catalysis. Similarly, Pt on Au reaches its peak activity at about two monolayers and then levels off once the second layer is completely Pt.

All the mechanisms mentioned here, as well as others, are suggested by Sachtler *et al.*[6] What we have done here is to suggest that in catalysis on the (100) surface, our picture implies that the second layer is not only significant, but dominant. This immediately accounts for several salient features of the results. A more detailed calculation for the (100) surfaces of Cu and Ni, with and without overlayers, is therefore of considerable interest and should be carried out.

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