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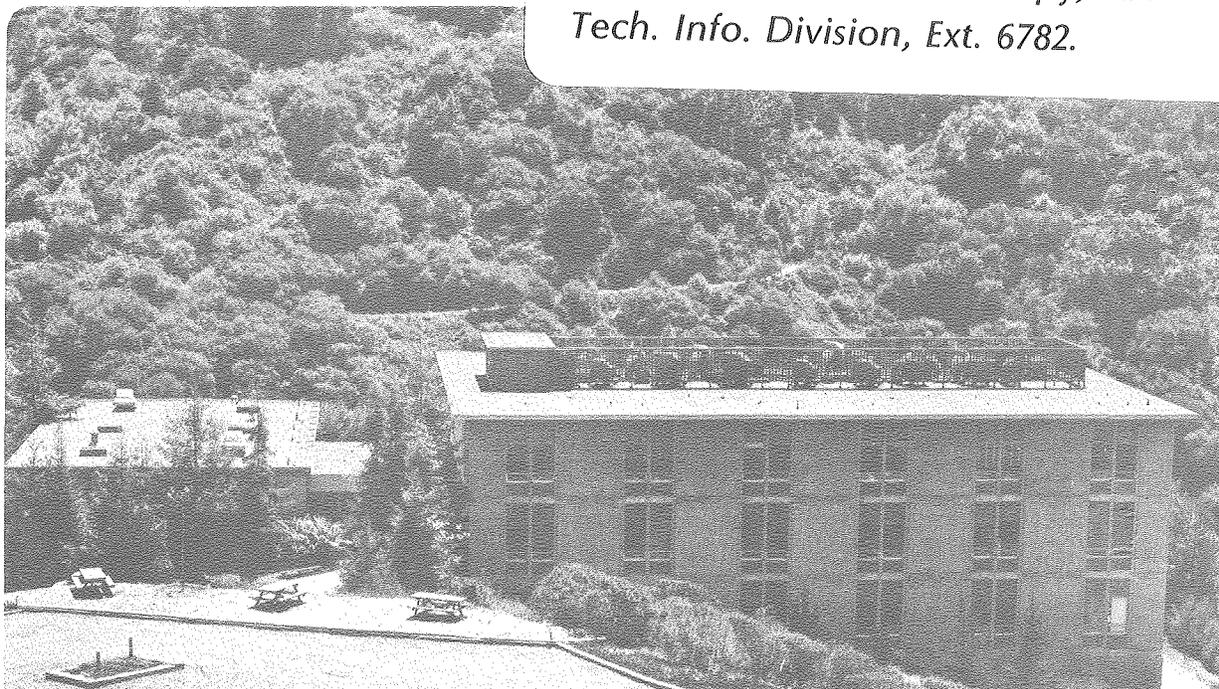
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SURFACES ON Ni AND Cu

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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 LCAO 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.

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1. 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 for noble metals $\sqrt{1-3}$. 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. The precise role of the d band is less clear, but there is a long-standing conjecture that the catalytic activity is related to fluctuations in the local quasi-atomic configurations $\sqrt{4}$. In an isolated atom, there is a series of one-electron orbitals, each of which has integral occupancy, either one or zero. In the solid, these orbitals broaden into bands and hybridize. The d orbitals in transition metals remain rather localized, but no longer have a well-defined energy or occupancy.

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.

Of course, it is imprecise to speak of the activity of a catalyst except with respect to a particular reaction. Whether the surface is stepped or smooth may be important for some reactions but not for others $\sqrt{5}$. Nevertheless, for close-packed transition-metal surfaces, the enhancement of catalysis by steps has been observed in a variety of reactions, and so we should be able to find a common causal factor in the catalyst alone.

Ultimately, the justification of our simplistic approach must lie in its relationship to the actual chemical processes at the surface, the formation of an "intermediate compound". Erley and Wagner $\sqrt{2}$ have found that the binding energy of carbon atoms on Ni (111) is greater at step sites, leading to dissociative adsorption of CO. A full d band is, energetically, not favorable to the formation of compounds. For a slightly less filled band, less energy needs be expended in promoting a d electron to a higher state. Thus for a nearly filled d band, an increase in the number of holes should favor the formation of bonds, and hence increase the chemical activity of the catalyst.

Due to crystal-field effects, the total number of d holes per site is not the best indication of activity. A better indicator is the individual occupancies of d orbitals which are chosen to reflect the local field. At each site we find

the basis of five d-orbitals which are occupied independently, i.e. incoherently. The specific components of this basis depend on the local geometry. In the presence of a strong crystal field, these so-called crystal-field orbitals form a preferred basis; their individual occupancies are more physically significant than the total d-shell occupancy.

Whether one prefers the picture of local configuration fluctuations, or of the enhanced ability of less fully occupied d orbitals to form bands, the quantities to be calculated are the same.

We shall see that this physical picture, simple though it is, allows us to gain considerable insight into the effects of local geometry on catalytic surface sites. Specifically, we find that group VIII transition-metal atoms with fewer neighbors tend to have more completely filled d shells and hence are less active than atoms with higher coordination. The introduction of steps or other imperfections in a surface creates sites with coordinations different from those on an ideal surface. Sites with increased coordination are responsible for the catalytic activity of steps. Other effects are also discussed later.

In Section II, we describe the calculation--the formalism, the physical approximations, and the quantities to be calculated. In Section III, we examine the results of our calculations, and the significance of these results for

catalysis. In Section 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 overlayers⁶.

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 parameterization scheme of Slater and Koster⁹. We include 3d, 4s and 4p 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, $\phi_{im}(\vec{k}) = N^{-1/2} \sum_R \phi_{iRm} \exp[i\vec{k} \cdot \vec{R}_m]$, where \vec{k} is a wavevector 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 is sufficiently large. The transfer matrices for each \vec{k} and ϵ may be calculated once and stored.

In equations (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 \tilde{G}_{31} is related to \tilde{G}_{21} by an equation with only bulk-like terms, and we can write $\tilde{G}_{31} = \tilde{T} \tilde{G}_{21}$. 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) reduced to a single matrix equation.

Once we have \tilde{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 \underline{d} orbitals in layer \underline{m} ,

$$D_{md}(\epsilon) = -\frac{1}{\pi} \text{Im} \sum_{\vec{k}} \text{Trd} \tilde{G}_{mm}(\vec{k}, \epsilon) ,$$

where Trd denotes a partial trace, taken only over the indices corresponding to \underline{d} orbitals. The \underline{d} occupancy on a site in layer \underline{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 \underline{s} and \underline{p} orbitals, and

of the \underline{d} orbitals, centered on that site. Also let $\Delta n_d \equiv n_d - n_d^{(\text{bulk})}$, and similarly define Δn_{sp} . We assume that only the changes in the diagonal element of the Hamiltonian are important. We neglect the relative shift of the \underline{s} and \underline{p} potentials, since the \underline{sp} bands are very broad, with strong $\underline{s-p}$ 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 $3\underline{d}$ and $4\underline{s}$ orbitals in various atomic configurations, from the atomic Hartree-Fock calculations of Clementi¹⁰. For the second approach we tried the Valence Orbital Ionization Potential (VOIP) scheme¹¹, 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 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 Section III that for Ni, this "chemical shift" merely causes a tiny charge transfer quite unimportant compared to the effects of altered local bandwidth. For Cu, though, the density of states at the Fermi level is small, charge transfer is less easily accomplished, and so the local potential change shifts the d-band slightly at the surface. This results in little error for local occupancies, but could, for example, lead to confusion in comparisons with photoemission data.

C. Analysis of Local Configuration Fluctuations

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

We define the usual probability density matrix

$$\tilde{P} = \int_{-\infty}^{\epsilon_F} d\epsilon \sum_{\nu} |\psi_{\nu}\rangle \langle \psi_{\nu}| \delta(\epsilon - \epsilon_{\nu})$$

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

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

The diagonal elements of \tilde{P} , $[\tilde{P}_{mm}]_{ii}$, 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 (5x5) submatrix of \tilde{P} corresponding to the d orbitals on a given site. Since these are rather localized we can then speak comfortably of a local atomic-like 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 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.

If we are correct in expecting that catalytic activity increases with increasing fluctuations in a drastic, non-linear manner, then the observed activity is due mainly to the one or two most highly fluctuating orbitals. However, in presenting our results, we give in each case all five 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 inter-layer 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 non-interacting, 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 bulk-like, 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 Figure 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; atoms b and d in Figure 1 have the same local geometry as the second type of step.

Since the atoms of the two upper-step edges are nearest neighbors, we can hardly assume that the steps are strictly non-interacting. However the step atoms a and b each have the same number and arrangement of first and second nearest neighbors as for an ideal step of the corresponding type. Moreover, the effect of local geometry on these two atoms is not 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, labelled c and d in Figure 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; and 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 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. 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, re-calculating 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 Section 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 Figure 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 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 wavefunction is "stiffer" than 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 Wertheim¹⁴. The same effect occurs at step sites, more or less dramatically depending on the coordination of the site.

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 3d 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.

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, non-local 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.

Citrin and Wertheim¹⁴ 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 Section 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 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 metal in the same row of the periodic table had 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 metal 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 Section 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 of. 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 al⁶. 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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REFERENCES

1. G.A. Somorjai, R.W. Joyner and B. Lang, Proc. Roy. Soc. A331, 335 (1972);
B. Lang, R.W. Joyner and G.A. Somorjai, J. Catal. 27, 405 (1972).
2. W. Erley and H. Wagner, Surface Sci. 74, 333 (1978).
3. M.A. Chesters and G.A. Somorjai, Surf. Sci. 52, 21 (1975).
4. Y.W. Tsang and L.M. Falicov, J. Phys. C 9, 51 (1976).
5. M. Boudart, Advanc. Catal. 20, 153 (1969).
6. J.W.A. Sachtler, M.A. Van Hove, J.P. Bibérian, and G.A. Somorjai, Phys. Rev. Lett. 45, 1601 (1980).
7. L.M. Falicov and F. Yndurain, J. Phys. C 8, 147 and 8, 1563 (1975).
8. V.T. Rajan and L.M. Falicov, J. Phys. C 9, 2533 (1976).
9. J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954).
10. Enrico Clementi, Tables of Atomic Functions, Supplement to IBM Journal of Research and Development 9, 2 (1965).
11. O. Bisi and C. Calandra, Nuovo Cimento 38B, 81 (1977).
12. P. Thalmeier and L.M. Falicov, Phys. Rev. B 20, 4637 (1979).
13. Linus Pauling, The Nature of the Chemical Bond, Third Edition (Cornell Univ. Press, Ithaca, N.Y., 1960), p. 93.
14. P.H. Citrin and G.K. Wertheim, Phys. Rev. Lett. 41, 1425 (1978).

TABLE I

Electronic Properties of Atoms at Flat and Stepped (111) Surfaces

Site	z	Δn_{total}	Δn_{sp}	Δn_{d}	$\Delta \epsilon_{\text{sp}}$	$\Delta \epsilon_{\text{d}}$
Ni Bulk	12	0.	0.	0.	0.	0.
Ni Surface	9	-0.11	-0.29	0.18	-0.025	0.017
Ni Steps						
atom \bar{a}	7	-0.18	-0.49	0.31	-0.047	0.028
atom \bar{b}	7	-0.18	-0.50	0.32	-0.047	0.025
atom \bar{c}	11	-0.04	-0.08	0.04	-0.017	0.003
atom \bar{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 \bar{a}	7	-0.19	-0.34	0.15	-0.066	-0.050
atom \bar{b}	7	-0.19	-0.36	0.17	-0.060	-0.041
atom \bar{c}	11	-0.03	-0.05	0.02	-0.013	-0.005
atom \bar{d}	10	-0.04	-0.11	0.07	-0.015	0.002

z = Coordination number

Δn = Change in total electron occupation (with respect to the bulk)

Δn_{sp} = Change in s and p-electron occupation

Δn_{d} = Change in d-electron occupation

$\Delta \epsilon_{\text{sp}}$ = Self-consistent shift in on-site potential for s and p electrons (Rydbergs)

$\Delta \epsilon_{\text{d}}$ = Self-consistent shift in on-site potential for d electrons (Rydbergs)

TABLE II
Hole Occupancy for Local
Crystal-Field d-Orbitals

Site	Occupancies*				
Ni Bulk	.165	.165	.165	.065	.065
Ni Surface	.153	.153	.138	.045	.045
Ni Steps					
atom <u>a</u>	.148	.117	.108	.055	.044
atom <u>b</u>	.155	.117	.102	.060	.037
atom <u>c</u>	.194	.161	.119	.067	.060
atom <u>d</u>	.179	.137	.131	.068	.054
Cu Bulk	.041	.041	.041	.013	.013
Cu Surface	.031	.028	.028	.008	.008
Cu Steps					
atom <u>a</u>	.026	.021	.021	.006	.004
atom <u>b</u>	.024	.019	.012	.008	.008
atom <u>c</u>	.047	.043	.025	.016	.008
atom <u>d</u>	.036	.031	.027	.011	.009

*in decreasing order

TABLE III

Electronic Properties of Atoms at (111)
Surfaces With Single Overlayer

Site	Z	Δn_{total}	Δn_{sp}	Δn_{d}	$\Delta \epsilon_{\text{sp}}$	$\Delta \epsilon_{\text{d}}$
Ni on Cu						
layer 1 (Ni)	9	-0.12	-0.32	0.20	-0.030	0.017
layer 2 (Cu)	12	0.01	0.	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

Meaning of column headings is as for TABLE I.

TABLE IV

Hole Occupancy for Local
Crystal-Field d-Orbitals

Site	Occupancies*				
Ni on Cu					
layer 1 (Ni)	.155	.155	.138	.038	.038
layer 2 (Cu)	.040	.040	.040	.014	.014
Cu on Ni					
layer 1 (Cu)	.031	.026	.026	.008	.008
layer 2 (Ni)	.165	.165	.147	.065	.065

*in decreasing order

FIGURE CAPTIONS

Figure 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.

Figure 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.

Figure 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.

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

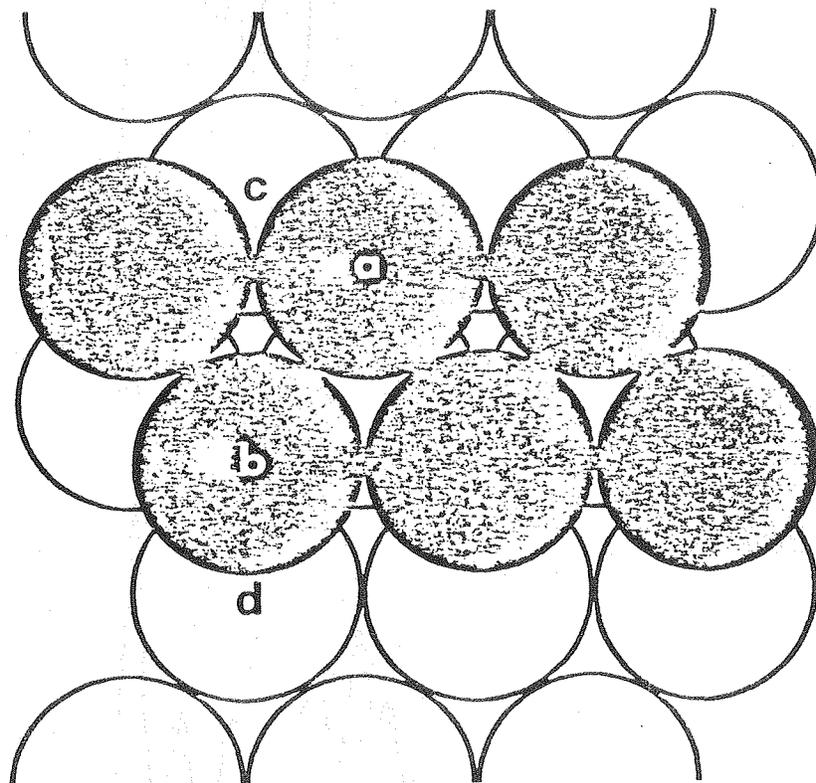


Figure 1

Ni (111) LDOS

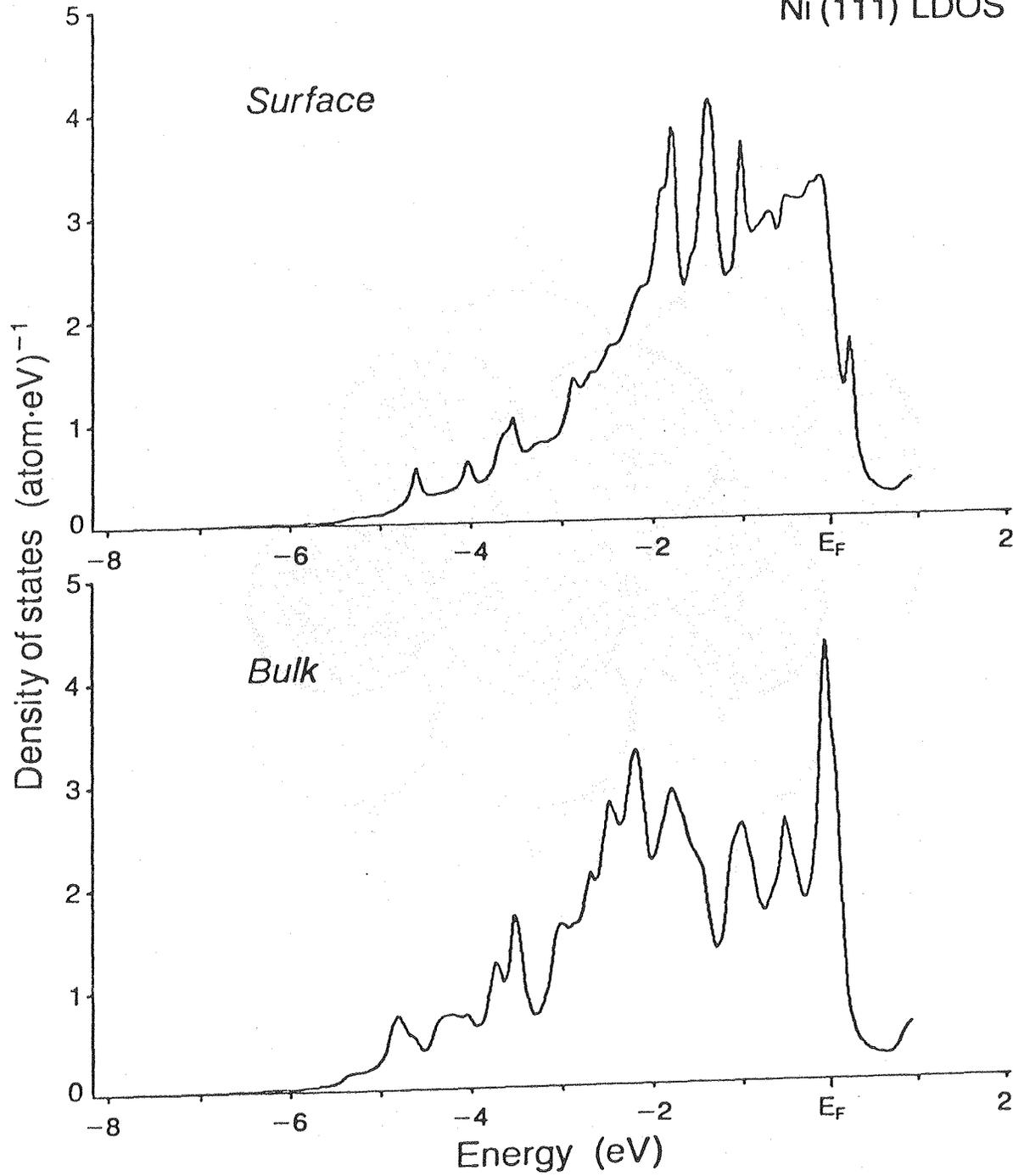


Figure 2

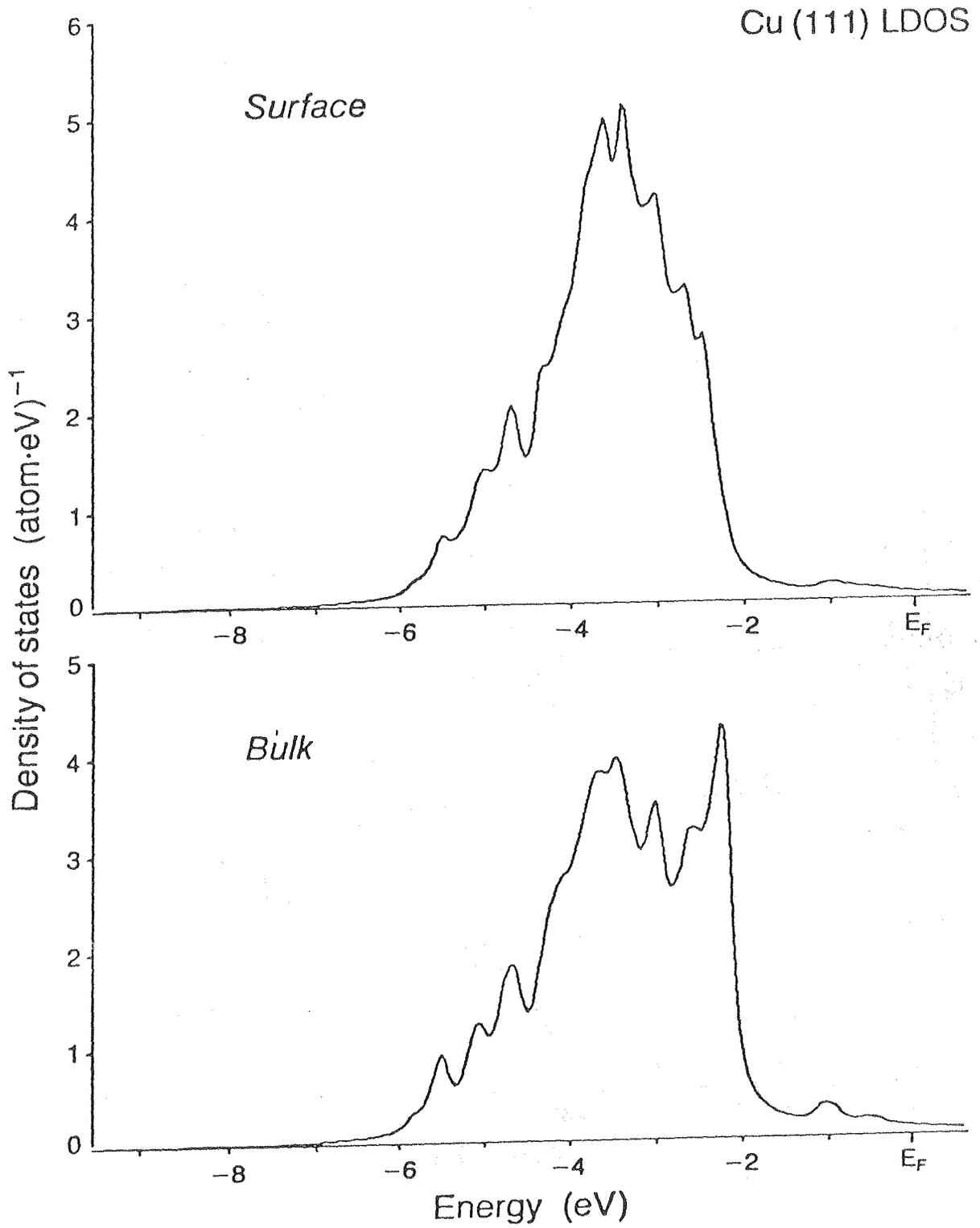


Figure 3

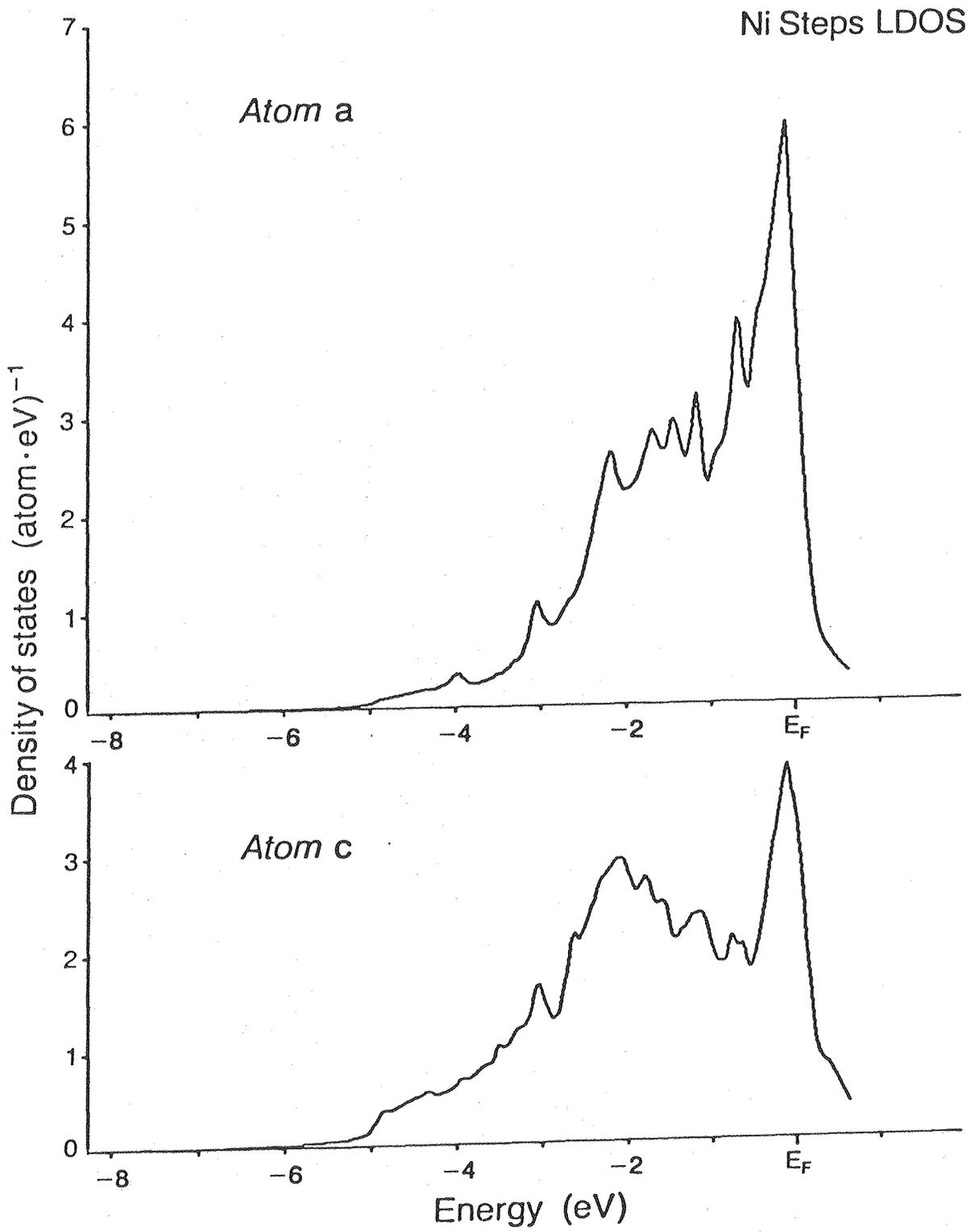


Figure 4