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(Ph.D. thesis)

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ABSTRACT

~~This thesis describes calculations~~ for a variety of nickel and copper systems, performed in order to develop a coherent picture of the electronic, magnetic and chemical properties of transition-metal surfaces, films and alloys. From the results of these calculations a unified picture of important physical mechanisms emerges. These results explain the magnetic behavior of such systems, and are also suggestive of important mechanisms affecting the surface chemical properties. In the latter case, however, no clear conclusion is possible, because of the complexity of the processes involved.

Among the detailed results presented are the following: for the Ni-Cu (100) interface, for Ni films on Cu (100) and (111) surfaces, and for (hypothetical) ordered Ni-Cu alloys, we give site-by-site magnetization and local density of states; and for flat and stepped paramagnetic Ni and Cu (111) surfaces, we give local density of states and local atomic configurations.

Experimental trends in thin-film and alloy magnetism are well explained. Results are in very good agreement

with previous theoretical results, in the few cases where such results are available.

The most striking result presented is the crucial role of hybridization between the nickel <u>d</u> band and the system's free-electron-like <u>sp</u> band in determining the Ni magnetization. This result is probably unique to Ni; for other ferromagnetic materials, this effect is not expected to be crucial. One implication is that the magnetic behavior of a Ni film is very sensitive to the degree of coupling to the substrate <u>sp</u> band, and hence to the structure and composition of the substrate. Our findings for films are thus similar to the familiar dependence of Ni alloy magnetism on the choice of nonmagnetic constituent.

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I. INTRODUCTION

Transition metals exhibit a number of remarkable properties which have presented fascinating puzzles throughout the history of solid state physics. Some of these metals are magnetic, and some exhibit surface chemical properties which make them uniquely useful as catalysts. In recent years novel behavior has been observed in a number of heterogeneous sytems composed of transition and noble (or normal) metals. This thesis describes our attempts to understand some of these effects.

Transition metals, like rare earths, occupy a special place in the periodic table because of the simultaneous filling, with increasing atomic number, of two very different sets of atomic levels. In the case of transition metals, these are the d shell (3d, 4d or 5d), and the s shell belonging to next higher principal quantum number.

When transition metal atoms are brought together into a solid, the s and d orbitals interact and form what may be thought of as distinct s and d bands, deriving from the respective shells of orbitals. As in "normal" metals, the s orbitals form a rather free-electron-like band. The more localized d orbitals however retain much of their atomic character (especially in the 3d series) even while combining into itinerant Bloch states.

This chapter introduces the reader to some aspects of transition metal behavior, and to the particular physical systems and effects which we have chosen to study. A more detailed discussion of each system, including experimental and theoretical background, is given in the respective sections.

A. Transition Metals

Transition metals have played a special role in solid state physics, because they combine free-electron-like behavior of the sp band with more or less atomic-like behavior of the d band. This mixed character gives rise to a wealth of fascinating behavior; of particular interest are the magnetic and chemical properties.

The magnetic transition metals are unique among magnetic materials in that the magnetization is due to highly itinerant electrons, which respond sensitively to changes in local environment. The magnetic behavior is therefore also drastically affected by such changes. Thus the magnetic and electronic properties are bound together in an intimate and intricate way.

Transition metals also possess remarkable chemical properties which make them uniquely useful as catalysts. Yet catalysis is not well understood even in principle; our current understanding of this important process is essentially phenomenological.

In recent years, there has been great interest in systems where transition metals are mixed with, or deposited on, noble or normal metals. This is natural, for such systems allow one to "tune" the mixture of atomic-like (d-shell) and free-electron-like (sp band) behavior. For example the magnetic moment per atom of Ni can be continuously varied by alloying with Cu. Also, alloys of Au with Pt have very different catalytic behavior than either metal alone.

As modern experimental techniques have developed for depositing epitaxial films in ultra-high vacuum, new phenomena have been observed in such films. In some cases, the behavior of the film-plus-substrate systems are reminiscent of the corresponding alloys. For example, Ni films of only a few atomic layers, on normal-metal substrates, have their magnetic moment reduced relative to bulk Ni, just as occurs with alloying. At the same time, the surface and finite thickness of the film modify its magnetic properties, and there is a subtle competition between these various effects. The study of thin films moreover sheds light on the older problem of surface magnetism.

A surprising apparent enhancement of the chemical activity of a Pt surface after deposition of an atomic layer of Au has been observed, and here too an analogy may exist to the modifications in surface chemical activity which occur with alloying.

In order to elucidate the physical mechanisms underlying the effects described, and to provide a more unified understanding of such mixed systems, we have performed a number of calculations of electronic and magnetic properties of surfaces, films and alloys.

For conceptual and calculational simplicity, we have confined ourselves to nickel and copper systems. Ni and Cu crystallize in the fcc structure, with almost identical lattice constants (3.52 and 3.61 Å respectively). The two metals form ideal substitutional alloys and epitaxial films, so the structures of the heterogeneous systems are simple and well known.

Because of the large number of systems to be dealt with, we have employed the simplest possible calculational techniques consistent with the treatment of real materials. Where possible we compare our results with those of "state of the art" calculations.

In the remainder of this introduction we review the qualitative understanding of magnetic and chemical (catalytic) properties of transition metals. The main body of the thesis gives detailed background both experimental and theoretical, for the various problems which we have addressed, in addition to describing our own work.

B. Itinerant Ferromagnetism

Ferromagnetism may be understood either in terms of local moments or in an itinerant picture. In the Heisenberg, Ising and related models, one imagines local magnetic moments of fixed magnitude, with only orientational degrees of freedom, which are coupled to neighboring moments through some intersite exchange interaction. Such a model is appropriate for materials where the magnetic moment is due to an unpaired spin in an orbital which is extremely localized, compared to the distance of the nearest interacting spin.

The magnetic moment in transition metals however derives from the *d* shell, which is sufficiently non-localized that the *d* electrons form bands which are well described in terms of one-electron Bloch states. These *d*-like states are best pictured as linear combinations of local *d* orbitals. The dominant contribution to the exchange interaction between such states is the Coulomb repulsion between electrons which occupy orbitals on the same site[1]. The more localized the *d* orbitals, the stronger the interaction. Indeed, magnetism appears only among those transition metals with the most localized *d* shells. A comprehensive discussion of itinerant-electron magnetism is given by Herring[2].

The two crucial features of itinerant ferromagnetism, banding of the *d* states and the on-site Coulomb repulsion, are nicely captured in two simple models. Hubbard[3] suggested a Hamiltonian which incorporates both features explicitly,

$$H=\sum_{ij\sigma} t_{ij} C^{\dagger}_{i\sigma} C_{j\sigma} + U\sum_{i} C^{\dagger}_{i\sigma} C^{\dagger}_{i\bar{\sigma}} C_{i\bar{\sigma}} C_{i\sigma} \qquad (1)$$

where t_{ij} represents the hopping matrix element between sites i and j (usually taken to be non-zero only if i and j are nearest neighbors) and U is the on-site Coulomb integral. The main importance of this model is that its simplicity permits calculations which go beyond one-electron theory to include correlation effects. On the other hand, Stoner[4] proposed a mean field model,

$$H=\sum_{k\sigma} \varepsilon_k n_{k\sigma} + I \sum_{kk'\sigma} n_{k\sigma}\langle n_{k'-\sigma}\rangle \qquad (2)$$

where $n_{k\sigma}$ is the number operator and I is a phenomenological exchange parameter. This "rigid-band" approximation, in which the only effect of exchange is to shift the two spin-bands rigidly with respect to each other, precludes any explicit consideration of many-body effects. On the other hand the model permits a realistic density of states (DOS), and is very useful for understanding the role of the DOS in determining the magnetization. We will have occasion to use the Stoner model in the qualitative discussion of our results.

While the calculations presented here employ only one-electron theory, much work has gone into understanding the role of correlation (many-body) effects in itinerant ferromagnetism. One major change is the reduction of the effective exchange interaction[2]. Electron correlations may also play a crucial role in determining the degree of localized or itinerant behavior in the system[5].

Recently, there has been great progress in understanding the behavior of itinerant ferromagnets at finite temperature. For finite temperature, the excitation of spin-waves reduces the average magnetic moment. Such excitations are difficult to describe self-consistently within a band picture. Recently simple models have been studied[6,7] which correctly describe the finite temperature behavior of itinerant ferromagnets, including the presence of local spin fluctuations above the Curie temperature. However, the realistic microscopic description of finite-temperature magnetic properties of real materials is still out of reach. We confine ourselves here to the case of $T=0$.

In the case of heterogeneous systems, there are aspects of itinerant ferromagnetism which are not easily described by any simple model. The magnetism originates in itinerant electrons, whose behavior is very sensitive to local environment. If an atom has some neighbors removed or replaced with atoms of a different element, the electronic states and local magnetic properties may be drastically altered. We must ask to what extent these effects may be understood within a simple qualitative picture.

There is a natural first extension of our knowledge of homogeneous magnetic systems to inhomogeneous ones.

We can calculate the (paramagnetic) local DOS projected at a site, and then apply the Stoner model to this local DOS as we would to the total DOS of a pure metal. This proves to be a very fruitful approach for gaining qualitative insights, and we make use of such an analysis several times in this work.

There are however two shortcomings of this approach which warrant comment here. The first is that the effective exchange interaction depends on the characters of the wavefunctions, which are not reflected directly in the DOS. The most important consideration here is hybridization between the sp and d bands. The less d character in a state, the smaller the effective exchange potential which it feels. We have attempted to quantify this effect so as to get some idea of its importance.

The second problem with a strictly local picture is that the actual wavefunctions are extended, so that neighboring sites are coupled. The local DOS gives no insight into the role of intersite coupling and associated kinetic energy and screening effects. The most severe obstacle to a simple understanding of non-local effects is the presence of two different length scales in the problem. The d bands have much greater effective masses, and much shorter screening lengths, than the sp band. Of course, such effects are fully included in the actual calculation.

C. Surface Chemical Activity

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 ge regarded for now as impossible.

Among the simplest effects one might study are the effects of steps and metallic overlayers 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[8-10]. This effect has important implications for the design of practical catalysts. Moreover, it is conceptually simple, since only the geometry changes. Enhancement of the chemical activity of transition metals has also been observed in metallic overlayer system, specifically Pt-on-Au and Au-on-Pt films[11].

It is not know to what extent these effects can be understood in terms of the electronic structure of the clean surface or film. The relationship between our electronic-structure results and catalysis therefore remains conjectural, and a more detailed discussion is deferred until Chapter III.

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II. ITINERANT FERROMAGNETISM OF Ni-Cu ALLOYS AND EPITAXIAL FILMS

The magnetization of metallic Ni may be drastically reduced by alloying with a non-magnetic metal such as Cu or Al[1], by deposition in the form of thin films on non-magnetic substrates[2-5], or by sandwiching Ni films between layers of a normal metal[6]. The similarity of these effects suggests a common physical origin.

We have performed a series of calculations for these related systems in order to understand the cause and the nature of the reduction in Ni magnetization. In this chapter we discuss results for progressively more complex systems: the Cu-Ni alloys, a Cu-Ni interface, and finally, thin Ni films on a Cu substrate. From these results emerges a coherent picture of the complex interplay between electronic structure and itinerant ferromagnetism in these systems. In particular, we follow Anderson[7] in stressing the importance of *sp-d* hybridization in suppressing the magnetization of Ni.

A. Ni-Cu Alloys

1. Introduction

For almost half a centuray the magnetic behavior of Ni-Cu alloys has been a model problem in itinerant ferromagnetism. The magnetic and electronic properties of these alloys have been extensively studied both experimentally[8,9] and theoretically[10-13]. The most striking feature is that the magnetic moment *per Ni atom* of the alloys decreases approximately linearly with Cu concentration, from 0.616 μ_B for pure Ni to zero at about 60 at.% Cu.

Mott[1] proposed a rigid-band model in which conduction electrons are shared equally among Cu and Ni sites. This results in charge transfer from Cu to Ni, with filling of the Ni minority-spin band, and consequent reduction of magnetization. The theory gives excellent results for the magnetic moment as a function of concentration. However, the very different behavior of alloys of Fe and Co with non-magnetic metals[14] suggests that the success of the rigid-band model for Ni is fortuitous. More recent experiments[8,15] moreover suggest that d-band filling is less important than local environment effects in reducing the alloy magnetization.

Unfortunately, the fully self-consistent calculation of electronic properties of random transition-metal alloys is not yet feasible, despite recent progress[16]. Some magnetic CPA calculations have been performed for simple model Hamiltonians[10-12] but these have not included hybridization between the sp and d bands. Such hybridization is crucial for a realistic physical description, as we see below.

In order to examine the basic physical mechanisms responsible for the extinction of ferromagnetism in the Ni-Cu alloys, and to gain some idea of their relative importance, we have therefore calculated the electronic and magnetic properties of some ordered Ni-Cu alloys. Specifically, we consider those geometries which can be represented with a four-atom supercell, the conventional cubic cell for the fcc lattice. These structures are entirely artificial for the Ni-Cu alloy, and in interpreting our results we try to distinguish between those effects which are sensitive to the precise geometry, and those which are not.

We find three distinct effects which are important: the effective exchange interaction is reduced in the alloy, relative to pure Ni, by hybridization of the Ni d band with the conduction band, which increases the partial sp character of the d-like states at E_F; the magnetization is further reduced by changes in the shape of the density of states (DOS) projected at the Ni sites; and there is some d-band filling, though it cannot be described in a rigid-band model such as Mott's.

2. Calculation

We take our Hamiltonian to be the sum of a one-electron term H_0 and an electron-electron interaction term H_{ee}. For H_0 we choose the parameterized tight-binding scheme of Slater and Koster[17]. The Hamiltonian H_0 is written in terms of one and two-center integrals, which are treated as parameters chosen to fit the bulk band structure. We include s, p and d orbitals, with interactions up to second-nearest neighbor. For the matrix elements between Ni and Cu in the alloy, we take the geometric mean of the respective Ni-Ni and Cu-Cu matrix elements. The two sets of intersite matrix elements are very similar, so the results are insensitive to the precise scheme for choosing the Ni-Cu matrix elements.

The electronegativities of Ni and Cu are the same to within about 0.1 eV[18], so we choose the zeros of energy for the two metals so as to line up their bulk Fermi levels. However the final self-consistent results is not sensitive to physically reasonable (∿0.2 eV) differences in the respective Fermi levels.

For the electron-electron interaction we use a single-site approximation, which has been extensively discussed[19],

$$H_{ee} = \sum_{i\sigma\sigma'} \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta}\, c^{\dagger}_{i\alpha\sigma}\, c^{\dagger}_{i\beta\sigma'}\, c_{i\gamma\sigma'}\, c_{i\delta\sigma} \quad , \tag{1}$$

where $c^{\dagger}_{i\alpha\sigma}$ creates an orbital of symmetry α and spin σ at site $\underline{i}$. Intersite Coulomb terms can be neglected here, since results for the single-site approximation are already essentially charge-neutral at each site.

We treat H_{ee} in the Hartree-Fock approach; we can, with some approximations, reduce H_{ee} to a simple form for the on-site potential shifts,

$$\Delta E_{d\nu\sigma} = -\frac{1}{2}(U-J)\langle m_{d\nu\sigma}\rangle - \frac{1}{2} J\langle m_{d\sigma}\rangle + V_{sd}\langle n_s - n_s^{\circ}\rangle + V_{dd}\langle n_d - n_d^{\circ}\rangle \tag{2}$$

$$\Delta E_{s\sigma} = V_{ss}\langle n_s - n_s^{\circ}\rangle + V_{sd}\langle n_d - n_d^{\circ}\rangle$$

Here $\Delta E_{d\nu\sigma}$ is the on-site potential shift for a d orbital of symmetry ν and spin σ, measured relative to the value for the pure paramagnetic metal. By $m_{d\nu\sigma}$ we denote the spin polarization $(n_{d\nu\sigma}-n_{d\nu\bar{\sigma}})$ in the d orbital of symmetry ν at a given site, and $m_{d\sigma} \equiv \sum_{\nu} m_{d\nu\sigma}$. The total d occupancy at the site is denoted by $\left(n_d \equiv \sum_{\nu\sigma} n_{d\nu\sigma}\right)$, and the value for the respective pure metal is n_d^o. Quantities for s and p orbitals are similarly defined. In (2), s refers to the entire sp complex.

We define U as the on-site direct Coulomb integral between d orbitals of the same symmetry (rescaled by correlation effects, see below); U' is the integral between d orbitals of different symmetry; and J is the exchange integral. We define $V_{dd} \equiv U'-\frac{1}{2}J$, which give the effective (repulsive) interaction between d electrons, aside from magnetic effects. We similarly define an effective interaction V_{ss} among sp electrons, and V_{sd} between sp and d electrons. We neglect the on-site exchange integrals other than between d orbitals. The ratios U:U':J are taken to be 5:3:1 as suggested by Herring[19]; this incidentally allows us to cancel a term involving U+J-2U'. These ratios are not crucial. Similar results are obtained for J=0 or J=U as long as the absolute magnitude is scaled to give the correct[20] bulk Ni magnetization, $\mu=0.616\mu_B$. Such scaling is necessary in any case when we work in the Hartree-Fock approximation, since the effective interaction is reduced by correlation effects[19].

For the spin-independent part of the potential, we can rewrite (2) as

$$\Delta\varepsilon_s = V_{ss}\,\Delta n_s + V_{sd}\,\Delta n_d \quad ,$$
$$\Delta\varepsilon_d = V_{sd}\,\Delta n_s + V_{dd}\,\Delta n_d \quad . \tag{3}$$

The parameters V_{ss}, V_{sd} and V_{dd} 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[21]. For the second approach we tried the Valence Orbital Ionization Potential (VOIP) scheme[22], 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 (3) is inappropriate. To calculate the parameters we generalized (3) 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 $(\Delta\varepsilon_d/\Delta n_d)$ 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.

The description of the calculation thus far has applied equally to all sections of this work. However for the Ni-Cu alloy (and by analogy the Ni-Cu interface) it has been supposed that charge transfer plays an important role, as we discuss below. Large values for V_{dd} etc. tend to suppress charge transfer. Since we will argue that this is not an important effect in any case, we wish to choose the smallest plausible values of V_{dd} etc., so as not to prejudice the issue. For the alloy and interface calculations we therefore replace V_{dd} with the (screened) Auger values (4 and 8eV for

Ni and Cu, respectively)[23], and scale V_{ss} and V_{sd} accordingly.

Note that in all cases the parameters for the spin-dependent and spin-independent parts of the electron-electron interaction are chosen independently. This is because renormalization of the effective interaction by correlation effects is very different for the two sets of terms.

We tested this Hamiltonian for pure Ni, and found excellent agreement with theory and experiment[24] for the band structure, Fermi surface and DOS. The calculated spin-splitting was about 0.06 Ry for states of t_{2g} symmetry, somewhat larger than the experimental value, but in good agreement with that obtained[24] with the Kohn-Sham potential, which neglects correlation effects. We then calculated the electronic properties of the ordered Ni-Cu structures described above. Our Ni_3Cu and $NiCu_3$ structures are generated by replacing one of the four atoms in the conventional cubic cell of Ni or Cu with the other metal. Our NiCu structure consists of alternating (100) layers of Ni and Cu on the underlying fcc lattice. We restrict consideration to only ferromagnetic and paramagnetic states.

Yamashita et al[25] have calculated the densities of states for the ordered alloys considered here, and also for the corresponding random alloys (within the coherent potential approximation) without spin-polarization. The similarity between the ordered and disordered cases is strong, supporting our claim that disorder introduces only quantitative modifications here.

We note that more accurate calculational methods than those used here are currently available. However, since we are treating an artificial system, and one for which the tight-binding approximation is well suited, there is little point of applying such demanding methods here.

3. Results

Our results are summarized in Table I and Figure 1. For each alloy, Table I gives the number z_{Ni-Ni} of Ni neighbors at a Ni site; the magnetization μ at a Ni site; the change Δn_d in total d-orbital occupancy at a Ni site, relative to pure ferromagnetic Ni; $D_d(E_F)$, the d component of the DOS at E_F at a Ni site; and α, a measure of hybridization effects, which is defined and discussed below, and is proportional to the "effective" Stoner exchange parameter.

For the geometries considered, all Ni sites are equivalent. In all cases, the moment at a Cu site is negligible, in agreement with experimental results of Medina and Cable[8]. All sites are essentially charge neutral. We omit further discussion of quantities projected at the Cu sites.

In Figure 1 we show the contribution to the alloy DOS from d orbitals at a Ni site for each spin. This projected DOS is based on a finite wavevector sample (i.e. 5832 points in the full simple-cubic Brillouin zone of the four-atom cell for Ni_3Cu). The DOS is smoothed by convolution with a Gaussian of full-width at half-height equal to 0.01 Ry.

Some simple trends are immediately evident from Table I. The magnetization of course decreases with increasing Cu concentration. Our results for the Ni magnetic moments of the two ferromagnetic alloys are in excellent agreement (within 0.04 μ_B per Ni atom) with experimental results of Medina and Cable[8], interpolated to 25% and 50% Cu. This agreement may be regarded in part as fortuitous, though, in view of the artificial geometries used here.

There is a significant filling of Ni d orbitals in the alloy, relative to pure Ni. This filling Δn_d is approximately linear in the number of Cu neighbors. The d-band filling is due to narrowing of the projected Ni d-band with reduced Ni-Ni coordination. The d band is centered well below E_F, so as it narrows, it pulls below E_F and becomes fuller. This is possible because charge neutrality can be maintained at only moderate cost in energy by transferring electrons from the sp band to the d band at the Ni site. This mechanism for d-band filling is suggested by results of calculations for the random paramagnetic Ni-Cu alloy[13] using a non-selfconsistent potential. We find that this effect is modified by self-consistency, but not eliminated, as it would be in a calculation which omitted the sp band. Note that this is completely unrelated to the Mott rigid-band picture. Charge transfer is between sp and d band projected at the Ni site, not between Ni and Cu. Also, the driving force for charge transfer is band narrowing, which is absent in a rigid-band model. Most important, the d-band filling accounts for only a fraction of the change in magnetization.

A major cause of the reduced magnetization is evident in Fig. 1. In the alloy, the upper edge of the d-band becomes rounded, for reasons discussed below. This reduces the DOS at E_F, and hence the magnetization. In the Stoner rigid-band model, a ferromagnet with a "square" band (constant DOS with sharp cutoff) is always saturated at T=0, i.e. for an almost full band there are no majority-spin holes left. With a rounded upper band edge some majority-spin holes can remain, reducing the magnetization. We believe this DOS "shape" effect to be a crucial factor for magnetism in Ni alloys, and the failure to mimic the detailed shape of the alloy DOS is the major barrier to relating our results quantitatively to the random alloy.

For the real metal or alloy, the d bands hybridize with the sp band. The effective exchange field felt by a state is approximately proportional to the magnetization, and to the degree of d character of the state. For the

Ni-Cu alloy, the magnetization is localized at the Ni sites, so the effective exchange potential felt by a state is proportional to its d character at the Ni sites. We therefore define a quantity α which measures the average fraction of a state, at the Fermi level, which is derived from d orbitals at Ni sites. To be precise, we define

$$\alpha \equiv \left(\sum_\nu W_\nu^2 \delta(E_F - E_\nu)\right) \div \left(\sum_\nu W_\nu \delta(E_F - E_\nu)\right) \quad , \tag{4}$$

$$W_\nu \equiv \sum_{im} |\langle\phi_{im}|\nu\rangle|^2 \quad , \tag{5}$$

where $|\nu\rangle$ is an eigenstate of the system (either spin) of energy E_ν, normalized to unity in the unit cell; and ϕ_{im} is a d orbital of symmetry m at Ni site i in the cell.

A more obvious parameter might have been

$$\left(\sum_\nu W_\nu \delta(E_F - E_\nu)\right) \div \left(\sum_\nu \delta(E_F - E_\nu)\right) \quad .$$

However this is simply the fraction of the DOS at E_F which derives from Ni d orbitals. Such a definition would give no measure of the degree of hybridization between sp and d band. Our parameter α defined by (4) is equal to 1 if the Ni d-band at E_F uncouples from the conduction band, regardless of the relative magnitudes of the components of the DOS (the Cu d-band contribution at E_F is negligible).

On the other hand, if $D_d(E_F)$ derives from states with only partial d character, α is reduced.

In fact, it is easy to show that for the Stoner rigid-band model, given a d-band hybridized with a conduction band (whose spin polarization and exchange interaction may be neglected), the Stoner susceptibility formula

$$\chi = 2\mu^2 N(1-IN)^{-1} \tag{6}$$

should be replaced by

$$\chi = 2\mu^2 N_d(1-\alpha I N_d)^{-1} \quad , \tag{7}$$

where N_d is the d component of N, the one-spin DOS at E_F, I is the Stoner exchange parameter for the d-band alone, and α is defined by Eq. (4). Thus α is the correct measure of the reduction in the effective exchange interaction due to hybridization, at least in the paramagnetic case where (6) holds.

Returning to Table I, we see that the Ni_3Cu structure has a moment per Ni atom which is 23% less than the Ni bulk. The change in α is modest, and for the pure Ni DOS (Fig. 1a) this reduction in the effective exchange strength would probably result in little change in magnetization. Half the loss of magnetization results from d-band filling, if we assume all the extra d electrons go into the minority-spin band.

Another effect which reduces the magnetic moment is easily seen in Fig. 1b. The projected DOS at the Ni site has become rounded relative to pure Ni. The large DOS at the top edge of the d band, characteristic of the ideal fcc structure, is greatly reduced in the alloy. This effect is clearly seen in non-selfconsistent calculations for the random paramagnetic alloy[13], and we have mentioned how this DOS rounding tends to reduce magnetization. The change in the DOS has two causes: the reduced local order, and the fact that the Cu d band is lower in energy than the Ni d band. The latter factor results in energy-dependent narrowing of the projected Ni d band. The states at the top of the Ni d band interact least with the Cu d band, (due to the larger energy denominator), so these states are the most "narrowed" towards the band center, relative to pure Ni, reducing the DOS at the top of the band. In fact, near E_F the interaction with the Cu d band can almost be neglected; only the effect of the conduction band remains. If we artificially remove the Cu d orbitals from the Hamiltonian, the shape of the Ni DOS well below E_F changes, but the behavior near E_F, the magnetization and the charge transfer are all affected surprisingly little. Thus as regards magnetism, the Cu d level may be considered crudely as an almost inert core.

The effect of reduced local order is drastic. For the ideal fcc structure, the sharp features at the upper edge of the d band are caused by the very flat bands encountered along various lines (e.g. WX and WL) in the Brillouin zone faces. Any reduction in symmetry (and, a fortiori, any disorder) lifts this degeneracy, and in general suppresses that sharp peak at the top of the fcc d band, which is so conducive to ferromagnetism in pure Ni.

The sp-d hybridization produces a related but more subtle effect, a "smearing" of the d-orbital component of the DOS. Some d holes are hybridized into high-energy states of mostly sp character, which cannot contribute significantly to the spin-polarization. In the alloy this effect is stronger than in bulk Ni, because of the larger sp DOS per Ni atom at E_F. The number of "effective" d holes per Ni atom is thus reduced. This behavior is analogous to that found in Anderson's model[7] for a magnetic impurity.

For the 50-50 alloy, consisting of alternate (100) layers of Ni and Cu, each Ni atom has only four Ni neighbors and the magnetic moment has almost vanished. In fact, it is surprising that any moment remains, since experimentally the moment vanishes at 60 at.% Cu, with each Ni atom having about five Ni neighbors on the average. The reason for this apparent discrepancy can be seen in Fig. 1c. Because of the highly ordered geometry, the projected d-band DOS at the Ni site shows sharp peaking at the top of the band. The small Ni-Ni coordination also narrows the band, further increasing the DOS at E_F, which is anomalously large (Table I). Even so, this structure is only precariously magnetic. For a less symmetric structure, with the same Ni-Ni coordination, the upper band edge would be less sharp, $D(E_F)$ would be smaller, and the system would be paramagnetic.

To illustrate this point, we note that in another calculation[26] using the same Hamiltonian, we found that a Ni atom at a (100) Ni-Cu interface has a moment 0.28 μ_B. In that case the Ni-Ni coordination at the site is 8, as for the Ni_3Cu structure here, yet the high-symmetry Ni_3Cu alloy has a much larger Ni moment, 0.47 μ_B. We should add that the local symmetry of the structure may affect not only the DOS, but also the degree of hybridization of the local sp and d bands.

For the $NiCu_3$ structure, the Ni atom has no Ni neighbors, and the situation is similar to the low-Ni-concentration limit. The Ni DOS is extremely narrow, but E_F lies in the high-energy tail of the DOS, so $D_d(E_F)$ is quite small, and the alloy is paramagnetic. Also the very small value of α (Table I) indicates that the small $D_d(E_F)$ derives from states with a large sp character, i.e. highly hybridized states.

A final comment is in order concerning the effect of the filling of the Ni d band. For small Cu concentration, it is reasonable to think of these extra electrons as going primarily into the minority-spin d-band, reducing μ by roughly Δn_d. Near the critical concentration, however, the spin-splitting is small, and $D_\uparrow(E_F) \approx D_\downarrow(E_F)$, so the extra charge is shared nearly equally between the two spins. The notion that the majority-spin d-band is full in Ni arises from neglect of hybridization, and is misleading in this context. In the alloy, the notion loses all validity.

To the extent that d-band filling is important in the near-critical regime of concentration, it is because such filling pushes E_F further into the high-energy tail of the d band, where the DOS is quite small, even for a very narrow band, as in Fig. 1d.

4. Conclusion

By calculating the electronic and magnetic structure of some artificially ordered Ni-Cu alloys, we have distinguished three mechanisms responsible for the reduced magnetic moment per Ni atom in the Ni-Cu alloy, relative to pure Ni. These are d-band filling due to band narrowing;

changes in the shape of the site-projected local DOS; and sp-d hybridization, which reduces both the effective exchange interaction, for states at E_F, and the number of "effective" d holes, as the Cu concentration is increased. All three factors are important. The shape of the DOS is the factor most sensitive to the disordered nature of the real alloy; however a self-consistent potential is required to position correctly the d band, which is crucial in determining both d-band filling, and hybridization, i.e. the effective exchange interaction strength.

B. The Ni-Cu (100) Interface

1. Introduction

Recently, there have been exciting advances in the understanding of thin magnetic film systems, both experimentally[3] and theoretically[27]. When a thin layer of Ni is deposited on a non-transition-metal substrate such as Cu or Al, the magnetic moment per Ni atom is reduced. Physically, it is of great interest to distinguish, as far as possible, the effect of the free film surface from that of the metal-metal interface. For computational reasons, however, calculations tend to focus on ultra-thin films. This presents two problems in interpretation. First, the magnetic film is very thin, so the surface and interface effects cannot be separated for comparison. Second, the substrate itself is treated as a thin film, which in some cases could pose a problem. Moreover, for the Ni on Cu system, comparison with experiment is somewhat ambiguous; Ni deposited on a Cu surface may be expected to form clumps, which would drastically alter the magnetic behavior.

We therefore chose to calculate the magnetic and electronic structure of one and two monolayers of Cu on the (100) face of a semi-infinite ferromagnetic Ni crystal. The results are of great interest for several reasons. 1) The system is realistic, since Cu does form almost ideal layers on Ni. 2) Even for a single layer of Cu, the effect of the surface on the magnetic behavior of the Ni substrate is very small. For two layers of Cu, the interface is quite ideal, i.e. isolated from the surface. 3) Because only one or two Cu layers are needed, the interface can be directly probed experimentally, e.g. by photoemission. It should therefore be possible to observe interface states, reduced local exchange splitting, etc.

We find a reduction in the Ni magnetic moment at the interface of about 0.46 μ_B, mostly in the first layer. This is in excellent agreement with the experimental results of Bergmann[3], who found that depositing a Pb-Bi alloy on a Ni film reduced the magnetic moment, apparently by ∿0.4 μ_B. This reduction is caused by changes in the shape of the projected Ni local density of states (LDOS), and by a weaker local exchange interaction resulting from reduced local d character of the states at the Fermi energy (E_F). We find that the Cu d-band does not play a crucial role. These effects are discussed in more detail below.

2. Calculation

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[28,29].

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 $\underline{m}^{th}$ 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 $I = (\varepsilon-H)G$. We handle the orbital indices implicitly in matrix notation, but write the layer indices explicitly as subscripts. For example, $\tilde{G}_{mn}(\vec{k},\varepsilon)$ is a matrix such that $[\tilde{G}_{mn}(\vec{k},\varepsilon)]_{ij} \equiv \langle \phi_{im}(\vec{k})|G(\varepsilon)|\phi_{jn}(\vec{k})\rangle$. 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

$$\begin{aligned}\tilde{I} &= (\varepsilon - \tilde{H}_{11})\,\tilde{G}_{11} - \tilde{H}_{12}\,\tilde{G}_{21}\ , \\ 0 &= (\varepsilon - \tilde{H}_{22})\,\tilde{G}_{21} - \tilde{H}_{21}\,\tilde{G}_{11} - \tilde{H}_{23}\,\tilde{G}_{31}\ , \qquad (6) \\ 0 &= (\varepsilon - \tilde{H}_{33})\,\tilde{G}_{31} - \tilde{H}_{32}\,\tilde{G}_{21} - \tilde{H}_{34}\,\tilde{G}_{41}\ , \text{etc.}\end{aligned}$$

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 $\underline{m}$ and $\underline{n}$, for $\underline{m}$ is sufficiently large. The transfer matrices for each $\vec{k}$ and ε may be calculated once and stored.

In equations (6) above, we include self-consistency only as a shift in the diagonal elements of the Hamiltonian. For example, if we treat two layers self-consistently, i.e. only H_{11} and H_{22} differ 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 (6) 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 (6) 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 $D_{md}(\varepsilon)$ in which we project out the contribution from the d orbitals in layer m,

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

where Trd denotes a partial trace, taken only over the indices corresponding to d orbitals. The d occupancy on a site in layer m is $n_d = \int_{-\infty}^{\varepsilon_F} D_{md}(\varepsilon)\, d\varepsilon$.

We sampled 15 wavevectors in the irreducible eighth of the two-dimensional (square) surface Brillouin zone. The potential was converged in each case to 0.03 eV (2 mRy).

3. Results

To test our Hamiltonian and method we first calculated the magnetic and electronic properties of the Ni bulk and ideal (100) surface. We found excellent agreement with results of Callaway and Wang[24] and Wang and Freeman[30]. In principle these fully self-consistent calculations, which use a Local-Spin-Density approximation for the potential, should be more accurate than the parameterized tight-binding approach used here. However the favorable comparison suggests that our method is fully adequate for this sort of problem. In addition, by permitting us to treat a semi-infinite crystal, the method avoids the spurious enhancement of the Friedel-like spin oscillations, which occurs in calculations for very thin films.

We then performed calculations for one and two layers of Cu on Ni (100). For the interface and adjacent layers of Ni, Table II gives the magnetization μ; the change Δn_d in the occupancy of the d orbitals at the site, relative to the bulk; and $D_d(E_F)$, the projected d component of the LDOS at E_F for the layer. The excellent agreement between the two geometries shows that even for a monolayer of Cu, the Ni properties are a good approximation to the ideal interface. This means that, with regard to the Ni magnetic behavior, the "isolated" interface is surprisingly accessible experimentally. For example, it should be possible to observe the highly localized majority-spin interface state which splits off the top of the Ni d-band at the corner ($\overline{M}$) of the surface Brillouin zone. Details of interface states will be reported elsewhere.

The Ni interface layer has its magnetic moment reduced to about half the bulk value. The loss of magnetic moment due to the interface is almost entirely confined to the first two Ni layers. Each layer is essentially charge neutral, and the localized magnetic moment in the Cu is negligible ($<0.02\ \mu_B$) even in the interface Cu layer.

There is a slight increase in the local d occupancy in the Ni interface layer, because narrowing of the Ni LDOS at the interface causes the local d band to pull below E_F and become more full. This effect is quite modest, however, due to the energy cost of transferring charge from the sp band to the d band. Charge transfer cannot explain the substantial reduction in magnetization at the interface.

Part of the explanation can be seen in Figure 2, where we show the LDOS at various layers near the interface for two-layer Cu on Ni (100). The bulk Ni is also shown for comparison. At the interface, the Ni LDOS becomes rounded, and in particular it loses the sharp upper band edge characteristic of the ideal fcc d-band. This reduces the LDOS at E_F at the interface, as seen in Fig. 2 and Table II. For a rounded band there is less tendency for the magnetization to go to saturation (one spin-band completely full) than in a band with a sharp edge. In a rigid-band model such as the Stoner model, for a square band the magnetization of a ferromagnet always proceeds to saturation at T = 0. For a band with a smooth tail, however, saturation is never achieved.

In addition, the states at E_F have reduced local d character due to hybridization with the Cu conduction band at the interface. The local effective exchange potential felt by a state is roughly proportional to its local d character, and this local d character is reduced at the interface.

Some of the most interesting experiments[3] with thin Ni films have used free-electron-like substrates, and so it is important to know whether the d orbitals in Cu play an important role here. To examine this question we repeated the calculation above, but artificially removed the Cu d orbitals from the Hamiltonian. The resulting changes were remarkably small: no more than 0.04 μ_B for μ, and 0.02 for Δn_d, at any Ni site. For our purposes, the Cu d band can practically be regarded as an inert core level. This suggests that any difference between results for Ni on Cu, and on free-electron-like substrates, is due either to the lattice mismatch for substrates other than Cu, or more probably to the different hybridization strength between Ni d-band and substrate conduction-band.

4. Conclusion

We have found that there is a significant suppression of local magnetic moment at the Ni-Cu (100) interface.

There is no appreciable penetration of the magnetization into the Cu. Rather, the Ni magnetization is reduced by 0.46 μ_B, most of this in the interface layer. We attribute this reduction to the change in the shape of the Ni LDOS at the interface, and the consequent reduction in the LDOS at E_F; and to hybridization with the Cu conduction band, which reduces the d character of the states at E_F. For the Cu-film on Ni geometry, a single layer of Cu gives a good interface, so the Ni interface behavior is surprisingly accessible to experiments such as photoemission. Since the Cu d-band plays almost no role here, our results should apply equally to free-electron-like metals, except that the degree of hybridization between the Ni d band and sp-metal conduction band should very from metal to metal.

C. Presence and Absence of Magnetism in Thin Ni films

The magnetic behavior of thin nickel films has been a subject of great interest since Liebermann *et al*[2] reported the observation of magnetically "dead" layers in such films. Despite extensive experiments on Ni films[2-5,31] and surfaces[32-34], as well as numerous theoretical calculations[27,30,35-37], a coherent picture of the important effects has not yet emerged.

We have already seen that the Ni magnetization is suppressed at a Ni-Cu interface. On the other hand a calculation[36] for an isolated monolayer Ni film suggests that a thin film with vacuum on both sides has a substantially enhanced magnetization. Thus for a supported thin film we expect a complicated behavior, with competing effects due respectively to the interaction of the film with the substrate, and to the surface and intrinsic thinness of the film.

It has been established, both experimentally[32-34] and theoretically[30,35,37], that there are not magnetically "dead" layers at the surface of a Ni crystal, as had been suggested[2] by Liebermann et al. For thin Ni films, however, a degree of confusion remains. Some experiments find[2,3,5] that Ni films of less than three atomic layers are paramagnetic, and these reports have sparked great interest. However, other experiments[4,31] indicate that even a film of 1-2 atomic layers of Ni is ferromagnetic.

Only one theoretical calculation for a supported Ni film has been reported. Wang et al[27] find that a single atomic layer of Ni on Cu (100) is ferromagnetic, though with a magnetic moment reduced from the bulk Ni value. Here we report results of an extensive theoretical investigation of the magnetization of Ni films on the (100) and (111) surfaces of Cu, and of the respective ideal Ni surfaces. We find that a single atomic layer of Ni on Cu (100) is ferromagnetic, in quantitative agreement with Wang et al[27]. However, for a monolayer of Ni on Cu (111), we find only a minute magnetic moment ($\lesssim 0.1\mu_B$), consistent with the possible observation of a magnetically "dead" layer. In addition, we find that the magnetization of a thin Ni film is very sensitive to the degree of coupling of the Ni *d* band to the substrate conduction band. Thus for substrates other than Cu, one might expect very different behavior. This explains the fact that experiments[3,5] which use normal-metal substrates generally find 2 or 3 "dead" layers, while experiments performed with noble-metal substrates set an upper bound of one dead layer[4,31], except for the original report by Liebermann *et al*[2] of two dead layers, based on an extrapolation from relatively thick films ($\gtrsim$5 atomic layers). Our results are thus consistent with all experiments reported to date except perhaps that of Liebermann *et al*[2]. Moreover, by demonstrating the crucial importance of substrate composition and orientation, we resolve most of the apparent discrepancies among experimental results.

It is difficult within the tight-binding approximation to treat charge transfer accurately at the surface. In the next chapter we confront this problem, and we see that our method exaggerates the transfer of electrons from the *s* and *p* orbitals into the *d* orbitals at the surface. To avoid this problem and still treat charge transfer and potential shifts at the surface in a simple way, we impose upon our potential the constraint

$$\Delta n_{sp} = \Delta n_d = 0 \quad . \tag{7}$$

That is, the average on-site potential of the d orbitals, and of the s and p orbitals, are fixed by the requirement that the total occupancies of the sp and d complexes at any site not differ from the bulk values. More fully self-consistent calculations[36,38] suggest a transfer of about 0.1 electrons per atom from the sp band to the d band at the surface. By neglecting this, we may expect to exaggerate the surface magnetization by roughly $0.1\mu_B$ per atom, an acceptable level of error.

In Figure 3 we display our results for the magnetic moment of the surface and interface layers of Ni films on Cu (100). The results of refs. 27 and 37 are also shown. The agreement is excellent. The films exhibit reduced magnetization at the interface and enhanced magnetization at the surface [perhaps somewhat exaggerated by approximation (7)].

Results for Ni films on Cu (111) are displayed in Figure 4. The (111) films show no significant surface enhancement of the moments, and also less substrate-induced suppression of interface magnetization than (100) films, consistent with the smaller change in Ni coordination at the (111) surface and interface. However for the monolayer Ni film on Cu (111) we find a moment smaller than $0.1\mu_B$ per atom, which is consistent with a "dead" layer if approximation (7) is taken into account. Finite temperatures should kill the small magnetization, if any.

For an itinerant ferromagnet such as Ni, low coordination causes band narrowing, and may reduce sp-d hybridization; both these effects favor stronger magnetization. The isolated Ni atom is more strongly spin-polarized than an atom in the bulk. Calculations[36] for an unsupported Ni monolayer find a spin polarization intermediate between the atomic and bulk values. It is the interaction of the Ni film with the substrate conduction band which suppresses the film magnetic moment here, just as the sp-d interaction suppresses the moment of a magnetic impurity in the Anderson model[7]. We attribute the stronger magnetization of the (100) surface and monolayer film largely to the symmetry-induced "decoupling" of adjacent layers, which occurs [at certain wavevectors] for the (100) surface.

Most experimental investigations of thin Ni films have been carried out with polycrystalline fcc substrates, which form microfacets mostly of (111) orientation, so comparison with theoretical results for the (100) surface may be misleading.

Finally, to illustrate the crucial role of the coupling between the Ni d band and the substrate conduction band, we report results of a numerical "experiment" in which we vary this coupling. Specifically, we consider the monolayer Ni film on Cu (100). We multiply all matrix elements in the Hamiltonian which couple Ni d orbitals to Cu s and p orbitals, by a factor t. Thus $t = 1$ corresponds to the realistic case already discussed, while *t* > 1 corresponds to enhanced coupling. For various values of *t*, we calculate the Ni film magnetization self-consistently. The results are shown in Figure 5. The magnetization of the Ni film is strikingly sensitive to the degree of coupling to the substrate conduction band. For sufficiently small coupling we find magnetization greater than that in bulk Ni, in agreement with the enhanced magnetization reported[36] for the hypothetical isolated monolayer Ni film. On the other hand, when the coupling is doubled relative to the Ni-Cu (100) value, the Ni is found to be paramagnetic. Since the *sp-d* coupling may vary among substrates, our results suggest that generalizations about film magnetization which ignore substrate composition are risky at best.

In conclusion we find that the Ni monolayer film on Cu (100) is substantially magnetic, while on Cu (111) it may be magnetically "dead". Similarly the Ni (100) surface has a magnetization which is significantly enhanced relative to the bulk, while the Ni (111) surface does not. We attribute these differences largely to the partial uncoupling of neighboring layers due to symmetry for the (100) surface. It should be noted that the results of Figures 1 and 2 exhibit a strong non-linear behavior with layer thickness, and cast serious doubts on extrapolated conclusions from thick film measurements[2,31]. Finally, we find that the

Ni film magnetization is very sensitive to the degree of coupling between the Ni d band and substrate conduction band. Thus the magnetic behavior of Ni films depends crucially on both substrate composition and orientation. These results serve to explain the origin of the apparent discrepancies among experiments. Since the substrate plays a direct role in modifying Ni film magnetization, it is essential to consider the substrate composition and orientation in making comparisons between results of various experiments and calculations.

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TABLE I

Electronic and magnetic properties of Ni in ordered Ni-Cu alloys(a)

Alloy	z_{Ni-Ni}	$\mu(\mu_B)$	Δn_d	$D_d(E_F)(eV^{-1})$	α
Ni	12	0.62	0	1.77	0.97
Ni_3Cu	8	0.47	0.07	0.93	0.88
NiCu	4	0.09	0.15	1.20	0.79
$NiCu_3$	0	0.00	0.22	0.58	0.35

(a) All quantities defined in the text

TABLE II

Properties of Ni layers at Ni-Cu (100) interface -- magnetic moment, d-band filling and d LDOS at E_F.

	$\mu(\mu_B)$	Δn_d	$D_d(E_F)(eV^{-1})$
Cu 1-Ni			
I	0.30	0.09	1.33
I-1	0.50	0.00	1.61
I-2	0.60	0.00	1.63
Cu 2-Ni			
I	0.28	0.08	1.29
I-1	0.49	0.00	1.62
I-2	0.60	0.00	1.62
Ni bulk	0.62	0	1.60

The Ni interface layer is denoted by I.

FIGURE CAPTIONS - CHAPTER II

Figure 1 The d-orbital component of the local DOS per Ni atom, projected by spin at the Ni site. a) Pure Ni. b) Ni_3Cu. c) NiCu. d) $NiCu_3$. See text for alloy geometries. Solid line--Minority spin, dashed line--majority spin.

Figure 2 Projected d component of LDOS at interface (I) and neighboring (I-1) layers of Ni-Cu (100) interface, from calculation for two layers Cu on Ni (100). The Ni bulk is shown for comparison. Solid line--minority spin; dashed line--majority spin.

Figure 3 Spin polarization of surface (triangles) and interface (circles) layers of Ni films on Cu (100), for films of from one to four atomic layers. The point for "infinite" film thickness refers to the ideal Ni surface. The bulk value (dashed line) is shown for comparison, as are results of refs. 27 and 37 (squares) for the monolayer (100) film and the Ni (100) surface.

Figure 4 Spin polarization of Ni films on Cu (111); symbols as in Figure 1.

Figure 5 Spin polarization of a monolayer Ni film on Cu (100), for various values of the (artificially altered) coupling *t* between Ni *d* and Cu *s* and *p* orbitals. The value *t*=1 corresponds to the realistic case.

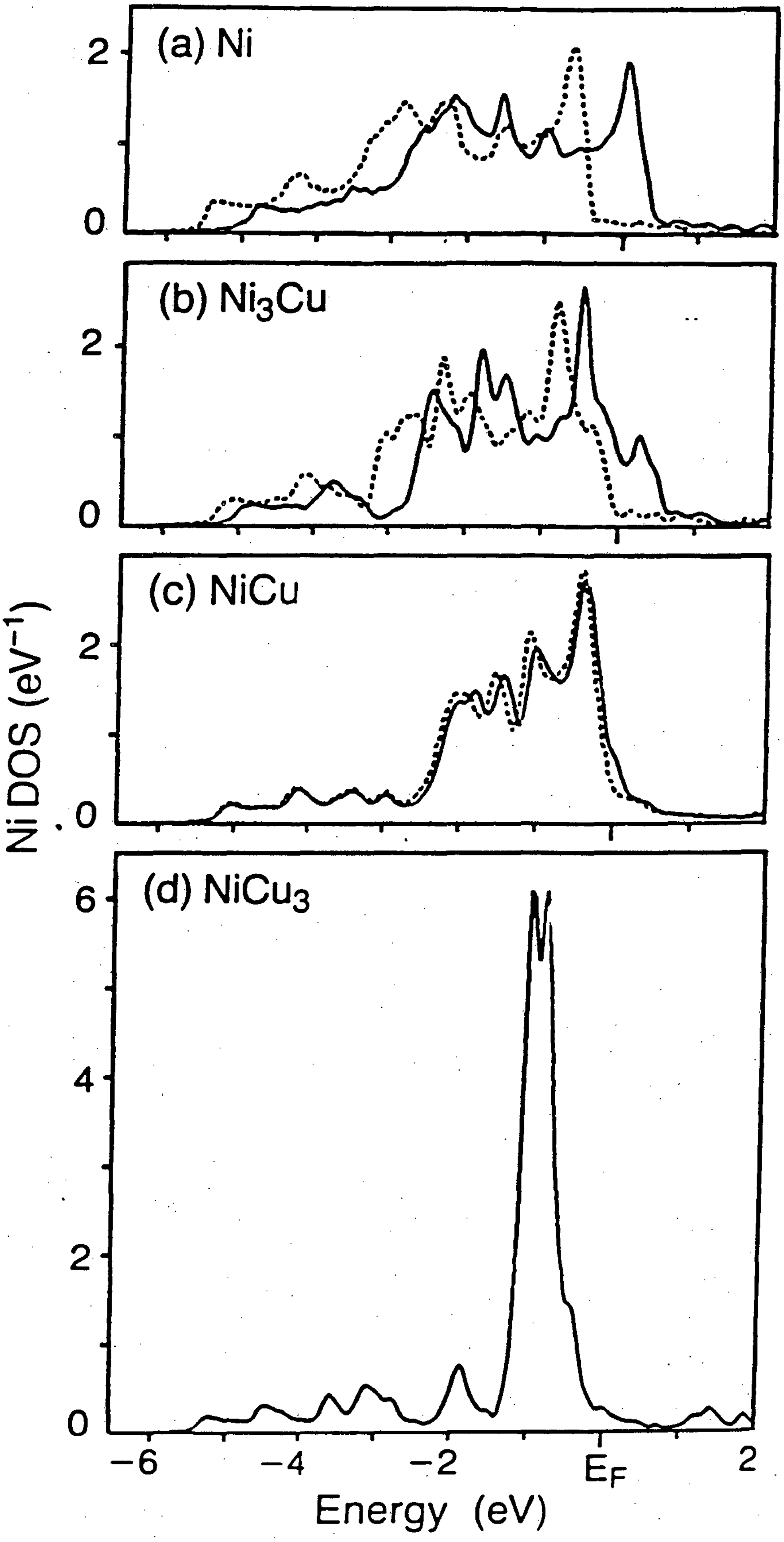

Figure 1

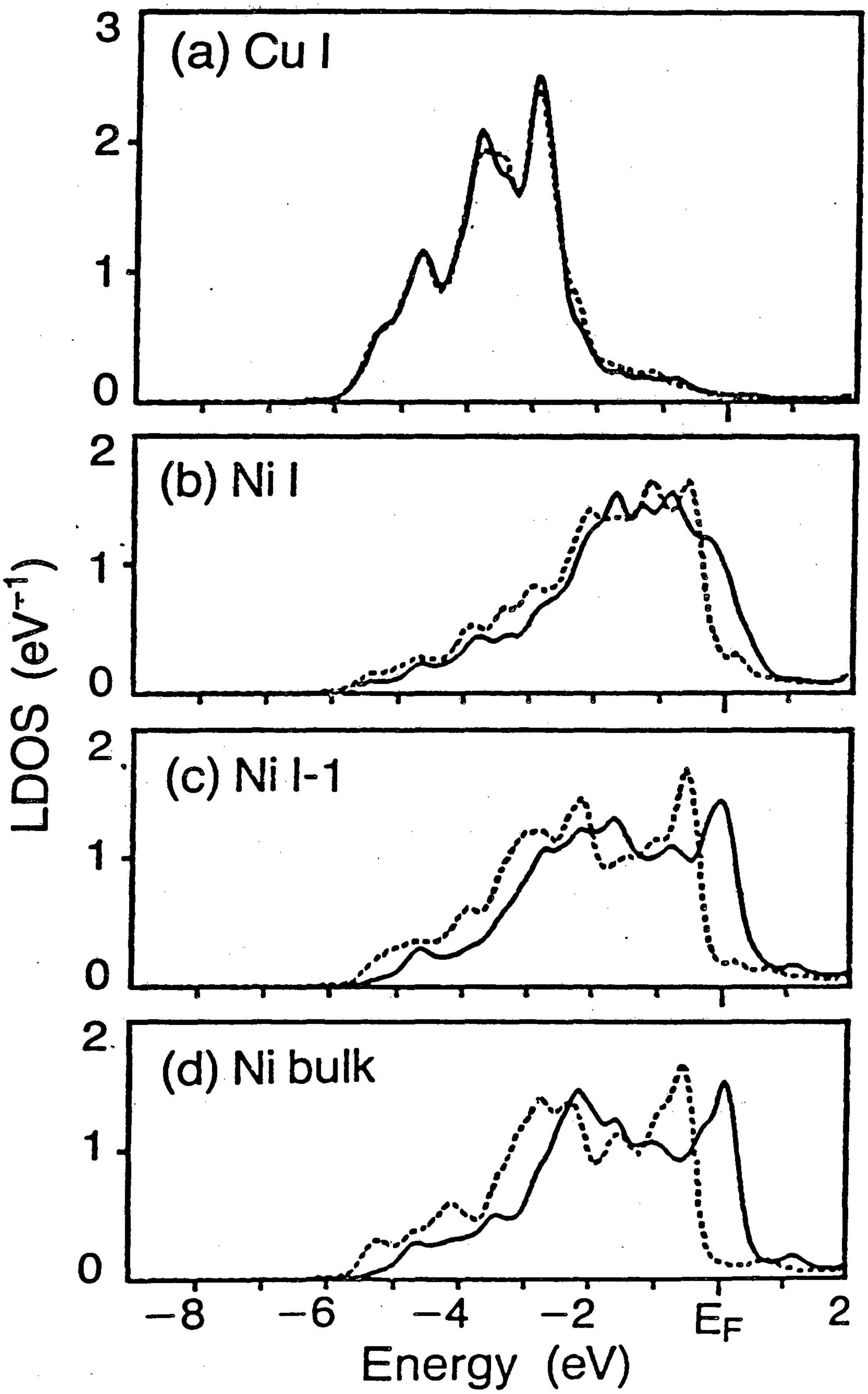

Figure 2

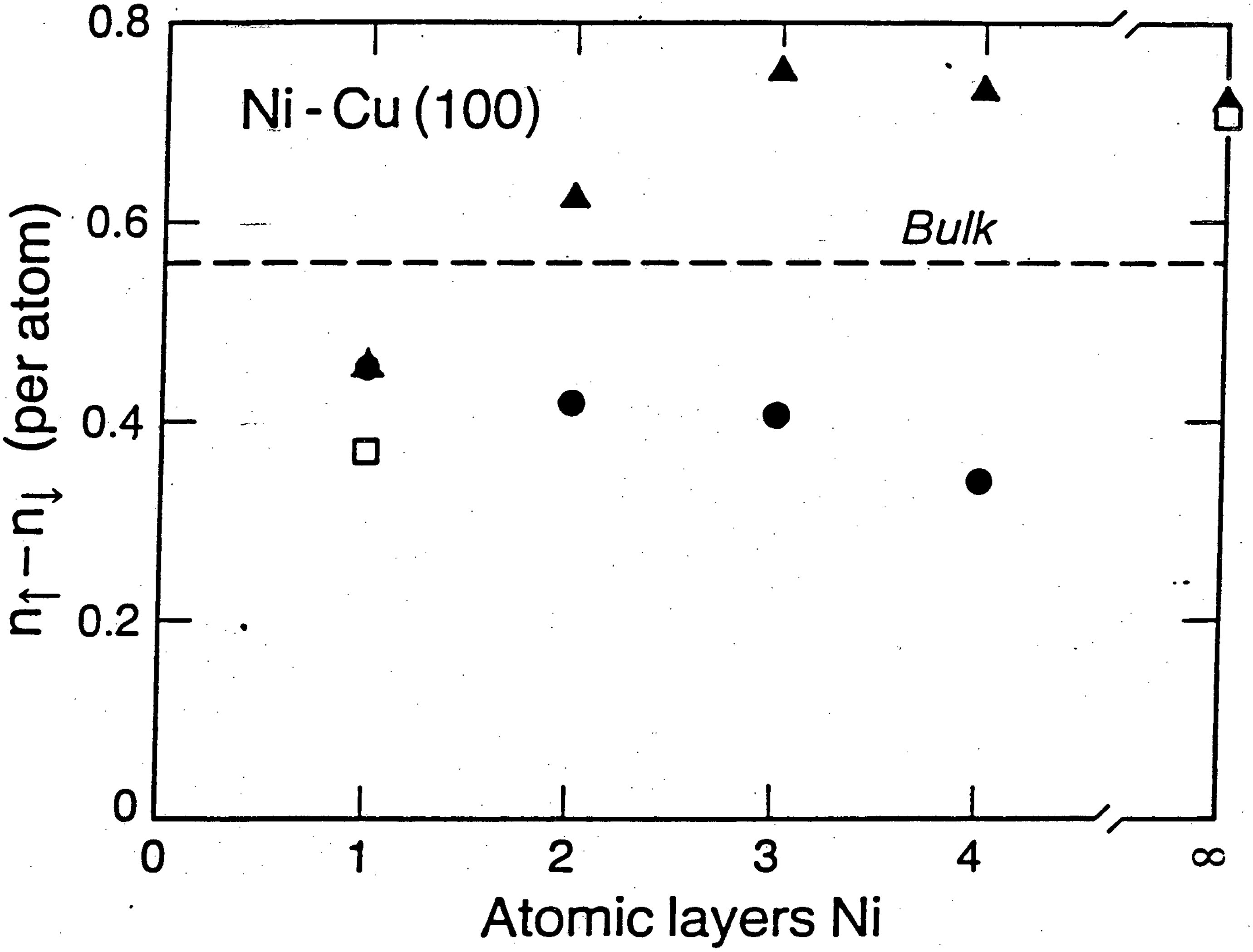
Ni - Cu (100)
Bulk
$n_\uparrow - n_\downarrow$ (per atom)
0.8
0.6
0.4
0.2
0
0
1
2
3
4
∞
Atomic layers Ni

Figure 3

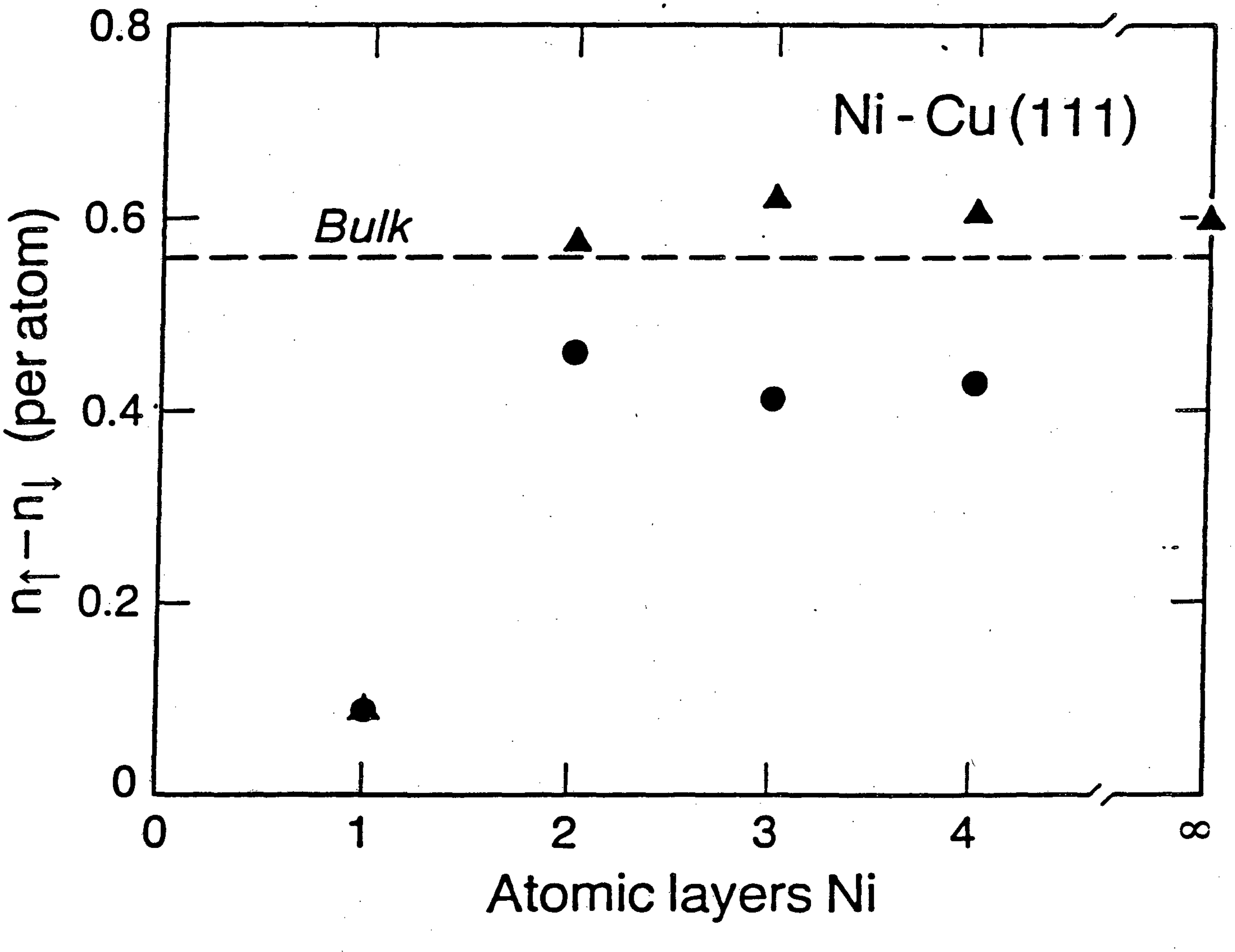
0.8
0.6
0.4
0.2
0
Ni - Cu (111)
Bulk
$n_{\uparrow} - n_{\downarrow}$ (per atom)
0
1
2
3
4
∞
Atomic layers Ni

Figure 4

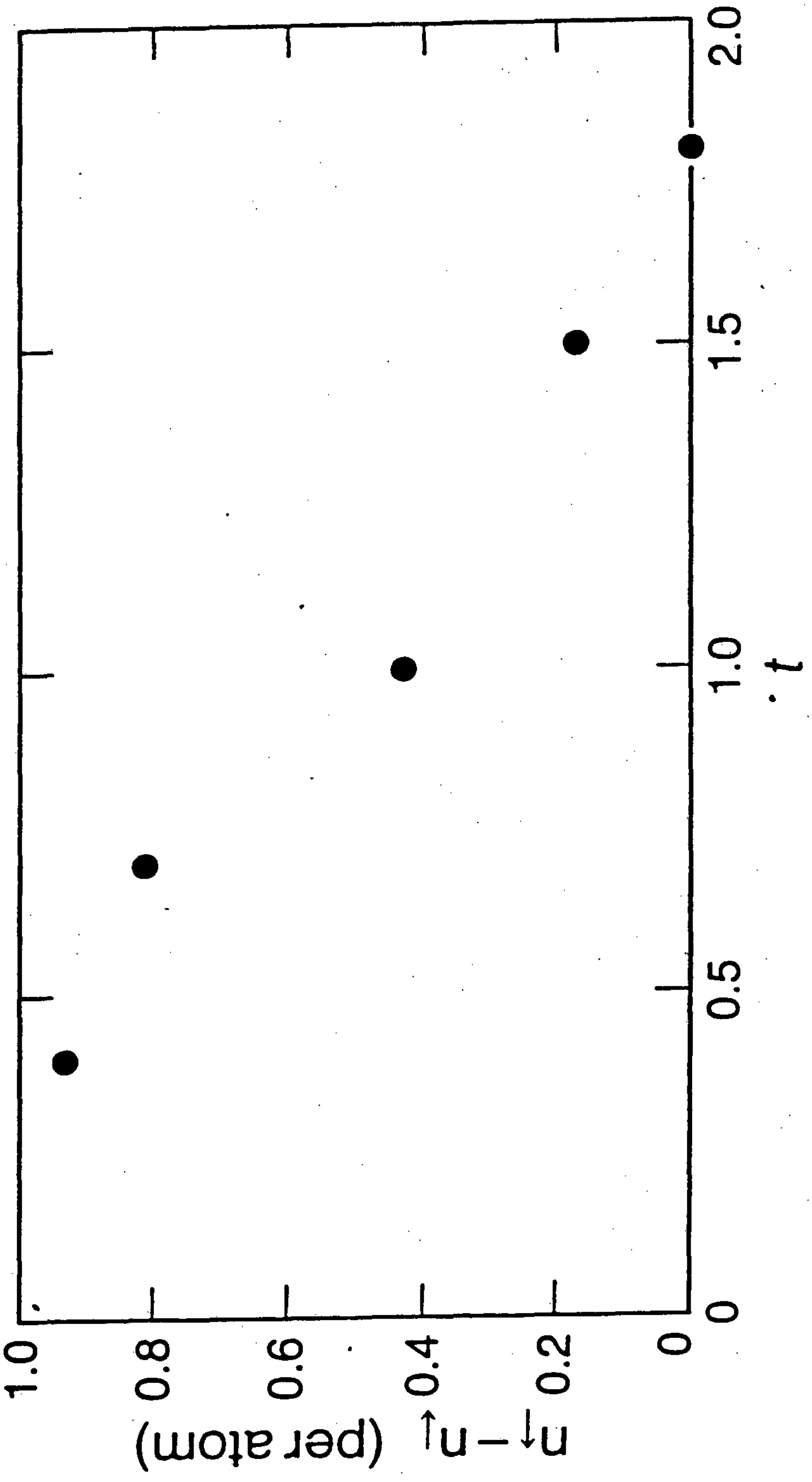

Figure 5

III. ELECTRONIC STRUCTURE AND SURFACE CHEMICAL ACTIVITY

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.

Because catalysis is such a complex process, it is difficult to make useful generalizations. Different reactions demand different catalysts, and the role of surface structure varies depending on the adsorbate and substrate[1].

Nevertheless it seems safe to say that 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.

For simplicity we have confined ourselves to Ni and Cu in our calculations. However, since we wish to be able to generalize our results to other metals such as Pt, in this chapter we treat Ni as paramagnetic.

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.) Erly 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 quasi-atomic configurations[3]. 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 bulk-like 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.

There is one subtle and fascinating aspect of the role of local coordination which we have not considered explicitly here. Anderson and Haldane[4] have suggested that hybridization between the _sp_ and _d_ bands plays a crucial role in catalysis, by reducing the energy difference between different valence states of the substrate atom. The results of the previous chapter show that such hybridization is reduced at sites of lower coordination. At a step, a site of low coordination would therefore have <u>reduced</u> catalytic activity. The most active site would be that in the hollow of the step, which has high coordination. We see that several related lines of reasoning lead to the same conclusion regarding the roles of various sites at a step.

In order to define and quantify local valence fluctuations, we first consider the usual probability density matrix

$$\tilde{P} = \int_{-\infty}^{\varepsilon_F} d\varepsilon \sum_{\nu} |\psi_\nu\rangle\langle\psi_\nu| \ \delta(\varepsilon-\varepsilon_\nu)$$

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

$$\tilde{P} = -\frac{1}{2\pi} \sum_{k} \int_{-\infty}^{\varepsilon_F} d\varepsilon \ \mathrm{Im}[\tilde{G}(k,\varepsilon) - \tilde{G}^{\dagger}(k,\varepsilon)] \quad .$$

The diagonal elements of $\tilde{P}$, $[\tilde{P}_{mm}]_{ii}$, give the probability that the orbital <u>i</u> on a site in layer <u>m</u> is occupied. Off-diagonal elements represent coherence effects. We neglect coherence between layers, and between the <u>sp</u> and <u>d</u> bands, and focus on the (5x5) submatrix of $\tilde{P}$ corresponding to the <u>d</u> 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.

A. Surface and Steps

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 sparce 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[5].

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. In the notation of Lang et al[6], 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 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 in 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 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 numerical 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.

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.

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 Wertheim[7]. The same effect occurs at step sites, more or less dramatically depending on the coordination of the site.

This transfer of electrons from the _sp_ band to the _d_ band is unfortunately exaggerated by our use of orthogonalized bases orbitals. The _s_ and _p_ orbitals have a large orthogonalization (kinetic) energy, leading to an artificially enhanced sp deficit at the surface. Comparison with fully self-consistent calculations[8,9] indicates that the correct surface d filling is somewhat smaller than reported here, but trends in d-orbital occupancy with coordination should be unaffected.

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.

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 examined 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 anti-bonding 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.

B. Overlayer Systems

Sachtler *et al*[10] 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.

Having a clear physical picture of how local geometry affects chemical activity, we would like to test it on this system. 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 or overlayers, as do Ni and Cu. We have therefore calculated the electronic structure for a monolayer of Ni on Cu (111) and of Cu on Ni (111), in the same manner as for the ideal and stepped surfaces. The results are given in Tables III and IV. 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.

These results 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.

Thus far we have considered only the close-packed (111) surface, whereas the results of Sachtler et al were for Au and Pt (100).

The (100) surface is quite open, and crude bond-length estimates suggest that a hydrogen 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 al_[10]. 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. Recently, Wang _et al_[11] have reported results of a calculation for a monolayer of Au on Pt (100), which appear to confirm our conclusions.

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TABLE I

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

Site	z	Δn_{total}	Δn_{sp}	Δn_d	$\Delta \varepsilon_{sp}$	$\Delta \varepsilon_d$
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

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

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

$\Delta \varepsilon_d$ = 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 *a*	.148	.117	.108	.055	.044
atom *b*	.155	.117	.102	.060	.037
atom *c*	.194	.161	.119	.067	.060
atom *d*	.179	.137	.131	.068	.054
Cu Bulk	.041	.041	.041	.013	.013
Cu Surface	.031	.028	.028	.008	.008
Cu Steps					
atom *a*	.026	.021	.021	.006	.004
atom *b*	.024	.019	.012	.008	.008
atom *c*	.047	.043	.025	.016	.008
atom *d*	.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	$\Delta\varepsilon_{sp}$	$\Delta\varepsilon_d$
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.

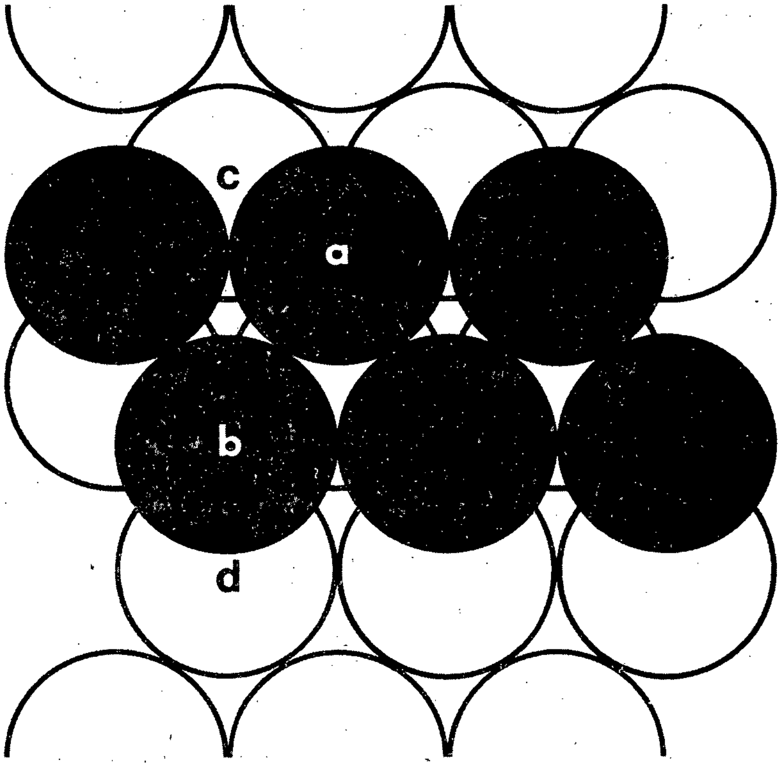

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Figure 1

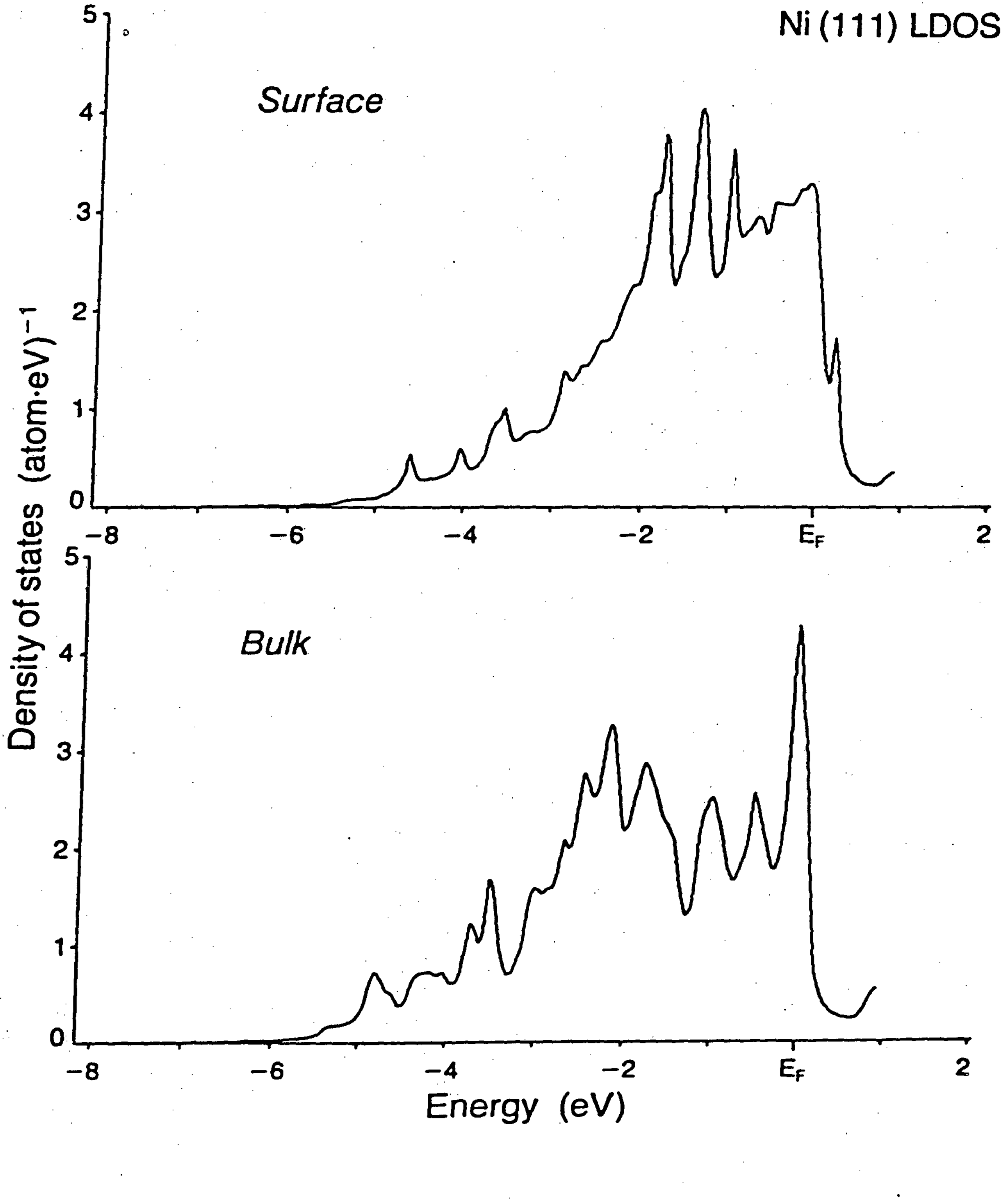
Ni (111) LDOS
Surface
Bulk
Density of states (atom·eV)$^{-1}$
0
1
2
3
4
5
−8
−6
−4
−2
E$_F$
2
Energy (eV)

Figure 2

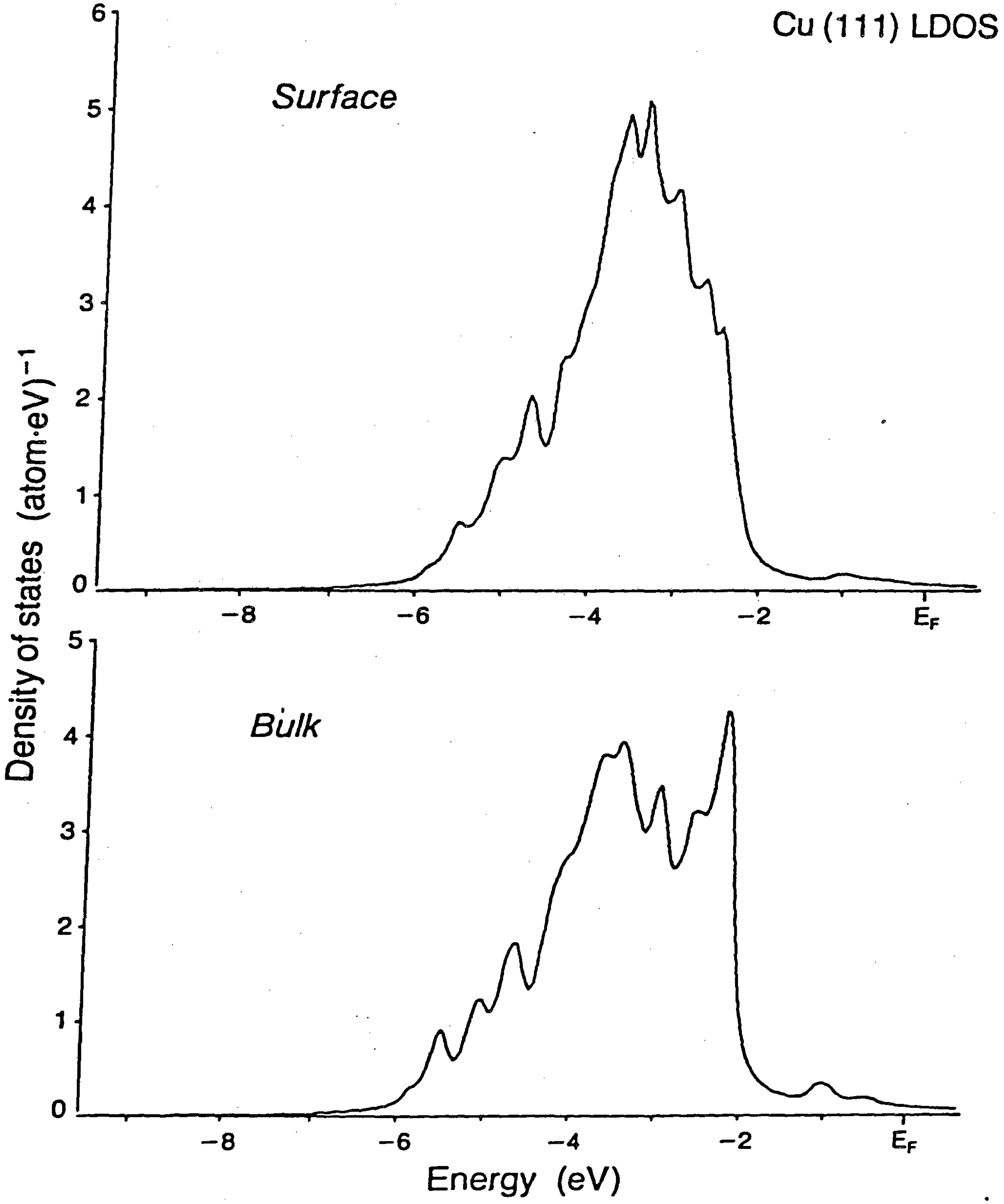
Cu (111) LDOS
Surface
Bulk
Density of states (atom·eV)$^{-1}$
Energy (eV)
0
1
2
3
4
5
6
−8
−6
−4
−2
E_F

Figure 3

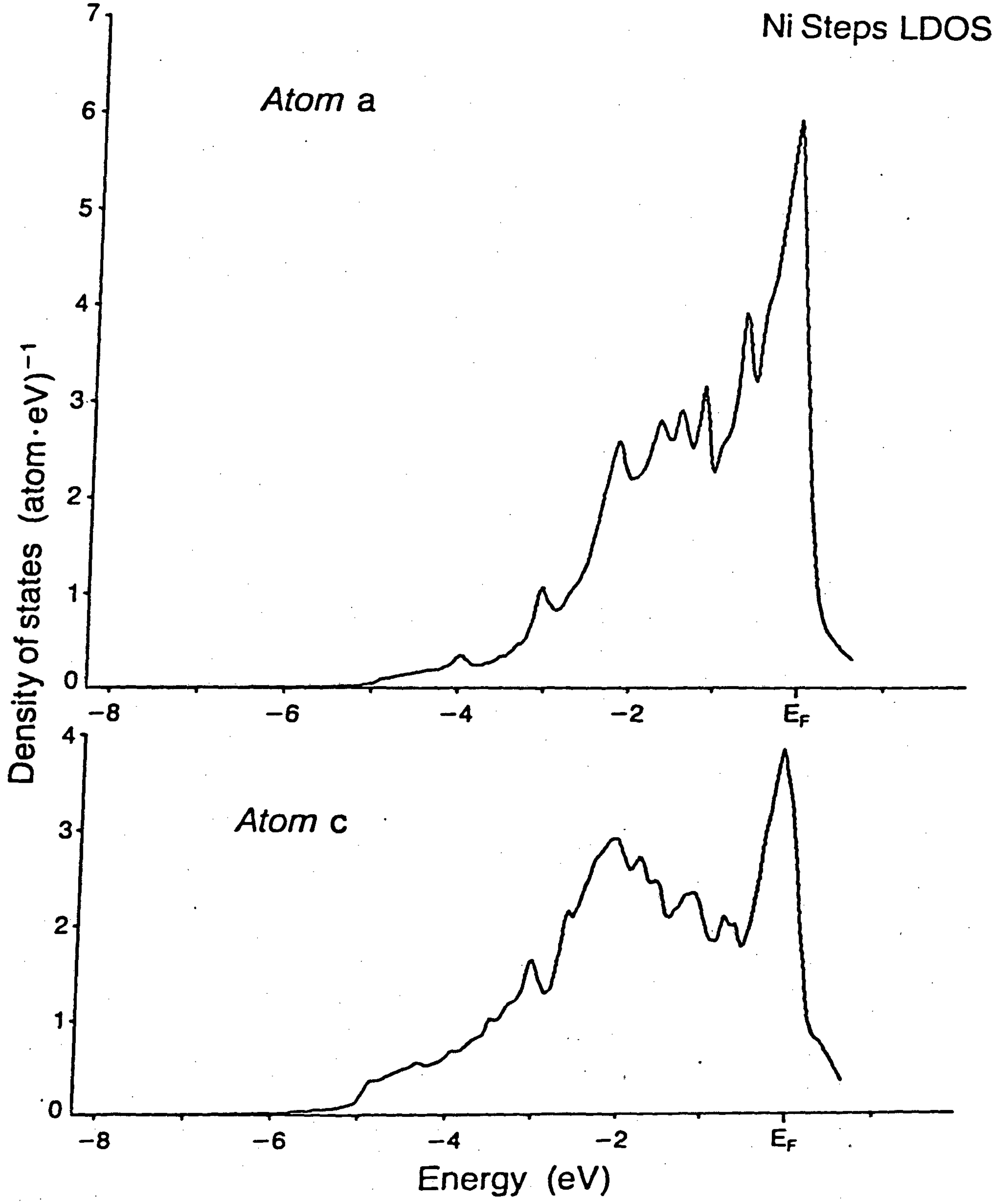
Ni Steps LDOS
Atom a
Atom c
Density of states (atom·eV)$^{-1}$
7
6
5
4
3
2
1
0
−8
−6
−4
−2
E_F
4
3
2
1
0
−8
−6
−4
−2
E_F
Energy (eV)

Figure 4

IV. CONCLUSION

Because of their rich and fascinating behavior, inhomogeneous transition metal systems have generated considerable controversy. In the case of alloy magnetism, the rigid-band approximation cannot be trusted, yet no theory of comparable simplicity and predictive value has taken its place. For thin film magnetism, the variety of apparently contradictory experimental results has led to confusion, largely due to neglect of the role of the substrate. Moreover, conflicting theoretical results for Ni (100) surface magnetism suggest that even the most sophisticated calculations may not be uncritically trusted.

The chemical and catalytic behavior of inhomogeneous transition metal systems is far less well understood than the magnetic properties. No theory, either microscopic or phenomenological, has succeeded in isolating one or two key factors which can explain observed trends in the role of catalyst composition and structure.

Nevertheless, by treating a variety of structures within a simple consistent framework, we have made progress towards a unified understanding of the properties of inhomogeneous transition-metal systems. The low-temperature magnetic properties of these systems can be understood in terms of a Stoner type rigid-band model, once the electronic properties (such as the DOS) have been found self-consistently at least for the paramagnetic case. While a realistic calculation is required for a quantitative understanding, the trends in magnetic behavior are well understood in terms of two simple factors: the arrangement of Ni neighbors about a Ni site, which determines the d-band behavior; and the arrangement of normal-metal versus missing neighbors in any remaining sites, which determines the degree of hybridization and electron transfer between the sp and d bands.

There is one very interesting factor which we have neglected by confining ourselves to Ni and Cu systems. For a less full d band, as in Fe or Mn, the Fermi level does not fall near the band edge. Since the effect of sp-d hybridization is seen most strongly just at the edge of the d band, we expect that hybridization, while crucial for Ni, is far less important for Fe and Mn.

In the area of surface chemistry we cannot draw straightforward conclusions. Nevertheless, the results presented are interesting and very suggestive. While it has been widely assumed that the enhanced catalytic activity of stepped surfaces is attributable to the exposed (corner) step site, arguments presented here suggest that the high-coordination "hollow" site may be the crucial one. We have also presented evidence against any chemical activity on the part of the Au atom in the Au-on-Pt film system.

Much research remains to be done in establishing a quantitative understanding of the heterogeneous systems discussed in this thesis. We believe that the results presented here are a useful step in identifying the important physical principles underlying the electronic, magnetic and chemical properties of transition-metal surfaces, films and alloys.

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