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PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Surfaces of Transition Metals

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(Received 18 December 1972)

We study the properties of transition-metal surfaces, with particular emphasis on Ni. Using the renormalized-atom approach, it is argued that the d-state excitations are narrowed at the surface and the d-hole count is reduced. The magnetic coupling of the surface layer to bulk is investigated in detail. Spin-dependent surface resonances of the Friedel type can exist and in the magnetic metals, can cause antiferromagnetic coupling of the surface moment to bulk. Model calculations are presented in an attempt to describe Ni.

I. INTRODUCTION

Relatively little progress has been made towards an understanding of the electronic states at the surface of a d transition metal. These states are important for a determination of many surface properties,[1] chemisorption, and catalysis. In addition, recent electron-emission and tunneling experiments[2] designed to probe bulk-metal properties have yielded results which suggest some participation of surface states. It is the purpose of this paper to discuss the electronic and magnetic properties of these states within the framework of existing theories of transition metals, with particular emphasis on Ni.

In Sec. II, the electronic properties of the paramagnetic region are studied using an extension of renormalized-atom picture[3] to the surface problem. We determine the position of the resonant d level ϵ_d with respect to the bottom of the s continuum ϵ_Γ at a surface site. The change in $\epsilon_d - \epsilon_\Gamma$ gives rise to a change in the hole count. For Ni, the d-band hole count is found to be reduced from its bulk value of 0.3 per spin to ~ 0.2 at the surface.

In these computations, it is found to be important to include screening of the bare Coulomb integrals as well as the changes caused by both d-d and s-d Coulomb repulsion. Furthermore, the surface site has a lower symmetry than its bulk counterpart, which can lift the degeneracy of the bulk e_g and t_{2g} states. This results in a modification of the surface density of states and we estimate that all of the d-band holes at a (100) surface site reside in a singlet. All of these effects are important for magnetic properties, as well, and are omitted in a recent treatment of transition-metal surfaces,[4] similarly based on the renormalized-atom picture.

The magnetic properties of the surface sites are of interest for their relation to the polarized-electron-emission and tunneling measurements in Ni. Interpreting some of these measurements in the simplest fashion seems to require majority spin density of states in bulk above the Fermi level, in contrast to the Slater–Wohlfarth picture.[5] However, these experiments are all sensitive to electronic states at the surface layer to some extent. An understanding of the surface magnetic properties can thus be important for those experiments, and are discussed in Sec. III.

There is a close analogy between the surface problem and the more familiar magnetic impurity problem. Extending models of transition-metal impurities to our surface problem, we derive and solve the self-consistent Hartree–Fock equations for a surface site. In the first model, the d electrons are treated in a tight-binding approximation, with hopping between nearest neighbors on a simple cubic or face-centered-cubic lattice. The surface is introduced by requiring that electrons may not hop beyond a particular (100) plane. This model is solved exactly, and numerical results are presented for special cases. We study, secondly, an impurity model that treats a surface site as an impurity in bulk. The latter model has the advantage of using a more realistic density of states for bulk Ni, but only approximates the surface effects.

The parameters in these models are chosen to give agreement with the results of the renormalized-atom calculations, which were limited to the paramagnetic region. In the ferromagnetic region, we find spin-dependent surface resonances can exist, similar to Friedel resonances in bulk. This leads to a local surface density of states that is dominated by the *majority* spin at the Fermi level. When these resonance states exist, the surface magnetic moment is either antiparallel to the bulk moment, or exhibits a sizeable reduction in its magnitude. It does not vanish, unless the paramagnetic surface hole count is reduced to essentially zero, an assumption incompatible with the surface of Ni.

II. HOLE COUNT AND CHARGING AT THE SURFACE OF NICKEL

Let us first consider the band properties of bulk paramagnetic Ni. These are plotted in absolute energy with respect to the vacuum zero and the atomic 4s and 3d energies appropriate to a Ni $d^9 s^1$ atom in Fig. 1. The X_3 and X_5 band levels have been used as a measure of the extrema of the d bands. ϵ_Γ, the bottom of the s-band continuum, lies well below its atomic 4s counterpart because of the Wigner–Seitz-boundary-condition allowed conduction bands in a periodic structure; i.e., ϵ_Γ is the energy at which the wave function is flat at the Wigner–Seitz radius r_{WS}, whereas the 4s function goes appropriately to zero at large r. The position of the resonant d level, on the other hand, is essentially atomic in character, depending on

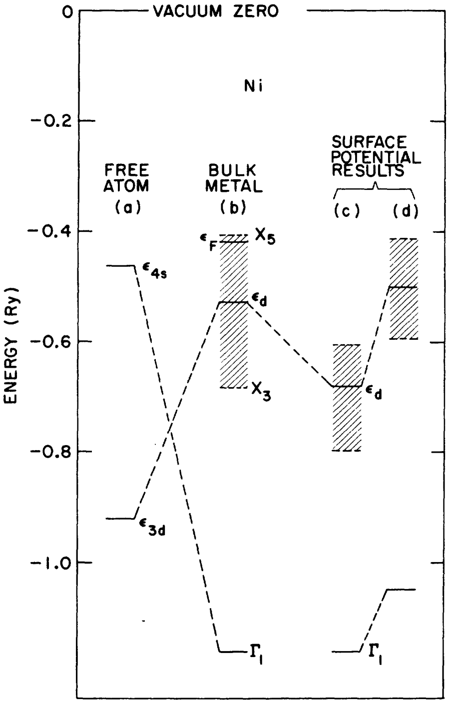

FIG. 1. Energy level diagram to illustrate changes encountered for an "averaged" surface Ni site, in the renormalized-atom picture of Sec. II. Part (a) is the free atom, part (b) shows the levels for bulk Ni, part (c) contains the changes encountered at a neutral surface site, and part (d) includes the charge transfer to the surface site.

the potential within the Wigner–Seitz cell and not on boundary conditions. ϵ_d lies considerably above its atomic counterpart because of the charge *compression* encountered in forming the metal.[3] There is a flow of charge of approximately one electron into the volume appropriate to the Wigner–Seitz cell in order to maintain charge neutrality. For atomic Ni in the $3d^9 4s^1$ configuration approximately three-fourths of this renormalization charge flow is associated with the $4s$ electron and one-fourth with the nine $3d$ electrons but, because of stronger d-d Coulomb interaction, the $3d$ Coulomb contribution is as important as the $4s$ to the shift of ϵ_d from the free-atom value. The width of the resonant level is determined by boundary conditions with the X_3 and X_5 levels corresponding to the energies (to ~0.02 Ry) at which the d functions are flat and noded at r_{WS}, respectively.

The d bands plotted in Fig. 1(b) are the result of a self-consistent band calculation employing Hartree-Fock–Wigner-Seitz potentials. The ϵ_Γ position was adjusted (downwards) so that there are 0.3 holes per spin lying between E_F and the top of the d bands. Such a hole count is commonly attributed to Ni. The resulting band structure lies, if anything, low with respect to the vacuum zero and the free-atom levels.

Given an estimate of the bulk band behavior, let us consider how it changes at the surface of the metal. Three aspects of the problem, important to the sections which follow, are considered here. First there is the shift of ϵ_d relative to ϵ_Γ assuming a neutrally charged surface atom at a "clean" surface. There is some hope of making a reasonable estimate of this shift since the motion of ϵ_d dominates, and ϵ_d is essentially a *local* atomic quantity. The shift, and the associated variation in resonant level width, affect both the d-hole count at the site and the local Fermi level. Secondly, there must be charge flow to or from the site in order to maintain the Fermi level at the bulk value. This charge flow and its effect on the band structure is the second matter to concern us. Thirdly, the fact that the potential at a surface site is of lower than cubic symmetry has a variety of implications. We consider the one of most immediate importance, namely, that d-band degeneracies are lifted, changing the character of the bands at and above the Fermi level.

A surface atom on a smooth (100), (110), or (111) surface of fcc Ni has 8, 7, or 9 nearest neighbors, respectively, or, on the average, two-thirds of the 12 neighbors encountered in bulk. In first approximation, the one-third of the surface of the atomic cell that encounters no neighbors, suffers no charge compression across it. The spherical potential arising from the reduced compression results in a reduced upward shift of ϵ_d, as is indicated in Fig. 1(c). One can trivially estimate how far the surface ϵ_d lies below its bulk counterpart if the d and non-d counts of electrons, contributing to the potential, are held at their bulk metal values. With one-third the surface of the atomic cell suffering no charge compression, one would expect the upward shift of ϵ_d to be approximately one-third less than that of the bulk. This argument might seem satisfying for the d-charge renormalization, which is responsible for approximately one-half the shift, but one might prefer alternate estimates of the s-charge effect. Levin *et al.*[4] have made a Thomas–Fermi estimate of the s-band charge outside the surface plane and find it very atomiclike in character, suggesting the above renormalized-atom calculation is about right. This implies that ϵ_d at the surface lies ~0.15 Ry lower than the bulk, as is plotted in Fig. 1(c).

One expects the width of the resonant level to be narrower at the surface as well. For a disordered system in the near-neighbor tight-binding approximation, Cyrot-Lackmann has shown that the bandwidth is roughly proportional to the square root of the number of nearest neighbors.[6] It is linear in the ordered crystal and thus we expect

$$W_{\text{surface}} \cong \tfrac{2}{3} W_{\text{bulk}} \tag{2.1}$$

here. Although changes in wave-function character and potential modify this, we have taken W_{surface} equal to two-thirds the bulk value.

One also requires the position of ϵ_Γ. The Thomas–Fermi estimate of Levin *et al.*,[4] places it 0.03 Ry above the bulk value and a shift in this direction is to be expected: ϵ_Γ is relaxing back towards its free-atom counterpart. The shift is small on the scale of other uncertainties in the problem and we have set it equal to zero. Holding ϵ_Γ fixed can only lead to underestimates of the quantities of concern here.

Let us, for the moment, attribute to the surface the density of states that would be obtained by a bulk band calculation employing the spherical surface potential. Given the band data summarized in Fig. 1(c), this is readily done with an interpolation scheme such as that of Hodges *et al.*[7] Because the d bands lie lower with respect to ϵ_Γ, the local d count increases by ~0.1 electrons per spin and local d-hole count n_h drops from 0.3 to 0.2.

The results are not self-consistent, for we assumed the bulk $d^{8.9}s^{1.1}$ count when estimating the band changes and obtained $d^{8.9+0.2}s^{1.1-0.2}$. By s we, of course, mean non-d conduction bands. The simplest estimate of the effect on the bands would be

$$\Delta\epsilon_d = 2\Delta n_d\,[F^0(d,d) - F^0(d,s)] \tag{2.2a}$$

and

$$\Delta\epsilon_\Gamma = 2\Delta n_d\,[F^0(d,s) - F^0(s,s)], \tag{2.2b}$$

where

$$F^0(i,j) = \int \int P_i^2(r)\,(1/r_>)P_j^2(\rho)r^2 dr \rho^2 d\rho \,. \qquad (2.3)$$

The P's are suitably chosen wave functions, normalized either to the Wigner–Seitz radius r_{WS} or to infinity, depending on whether F^0 is being evaluated for renormalized- or free-atom charges. Inspection of the F^0 values tabulated in Appendix A indicates that Eqs. (2) predict ϵ_d moving upwards substantially and ϵ_Γ moving upwards a lesser amount, increasing the $\epsilon_d - \epsilon_\Gamma$ separation. Such predictions are wrong: When estimating the Coulomb effects associated with charge flow on or off a site or with the change of wave function character at a site, as we have here, we must replace the bare Coulomb F^0 integrals by effective Coulomb parameters U, which account for intra-atomic relaxation. Several estimates are made of $U(d,d) - U(d,s)$ and $U(d,s) - U(s,s)$ in Appendix A, alternately employing renormalized- and free-atom calculations and observed free-atom spectra. With $\Delta n_d = 0.1$ electrons per spin they yield as a body, shifts relative to $\Delta n_d = 0$, of $\Delta\epsilon_d \sim 0.02$ Ry and $\Delta\{\epsilon_d - \epsilon_\Gamma\} \sim 0.04$ Ry, i.e., the $\epsilon_\Gamma - \epsilon_d$ splitting is slightly increased and ϵ_d shifted about 10% back toward the value appropriate to the bulk metal. These estimates are crude but they are correct in their qualitative differences with Eqs. (2.2). It would therefore seem that ϵ_d, as plotted in Fig. 1(c), is slightly lower, and the $\epsilon_\Gamma - \epsilon_d$ splitting slightly reduced, such that n_h is still ~ 0.1 electrons per spin.

The local Fermi level of such an atom lies well below the bulk value, implying a flow of charge onto the surface site. The states being filled are of almost pure d character; hence the flow is crudely given by

$$2\,\Delta q = \Delta E_F / U(d,d) \,, \qquad (2.4)$$

where ΔE_F is the shift necessary to bring the local level in agreement with the bulk. Admitting no screening or relaxation, $U(d,d)$ is the bare $F^0\,(d,d)$ integral of 1.9 Ry and one obtains $\Delta q \sim 0.05$ electrons per spin. The ϵ_Γ level also moves

$$\Delta\epsilon_\Gamma \cong 2\Delta q\, U(s,d) \,. \qquad (2.5)$$

If one either assumes that U's are unscreened or equally screened, so that

$$\frac{U(s,d)}{U(d,d)} = \frac{F^0(s,d)}{F^0(d,d)} \sim 0.6 \quad , \qquad (2.6)$$

we have ϵ_Γ moving more slowly than the local E_F and we obtain the situation plotted in Fig. 1(d). Actually, intra-atomic relaxation screens $3d$-$3d$ interactions more severely than $3d$-$4s$, as is documented in Appendix A. The ratio is closer to 1.0, implying that the filling of d holes shifts ϵ_d and ϵ_Γ upwards, almost rigidly together. With a screened $U(d,d)$ of 0.9–1.0 Ry and neglecting any effects associated with bandwidth changes, Δq becomes ~ 0.1 electrons per spin and the d-hole count $n_h = 0.1$–0.15 electrons per spin. The situation is somewhat like that of Pd: the Fermi level falls higher in the d bands than it does in bulk Ni. In bulk Ni, E_F falls high in the high density of states peak of t_{2g} character at the upper edge of the d bands. At the surface, E_F falls about halfway down the slope on the high-energy side of this peak. The Fermi level in Pd lies on the same down slope and this seems to be one of the most important factors contributing to this metal's lack of ferromagnetism.

The investigation to this point has concentrated on the changes in band character associated with modifications of the *spherical* potential (e.g., the F^0 terms) at a site that has otherwise maintained its cubic symmetry. The lower symmetry of the surface introduces potential terms that partially lift the orbital degeneracies which exist at high-symmetry points, such as point Γ, for the bulk. The decompositions appropriate to d orbitals[8] are listed in Table I.

The t_{2g} decomposition is of particular importance since E_F and the hole states lie in a high-density-of-states peak of states of almost pure t_{2g} (xy, yz, and zx) character. Consider a (100) face: The yz orbital has the bulk of its charge density lying in the face, while two of the four loops of charge in the xy and zx stick out of the surface plane into, and beyond, the region of the "uncompressed" one-third of the atomic cell. Having charge lying in this region implies that these states lie lower in energy than does the yz orbital. It is plausible that the splitting is something of the order of one-half the orginal ϵ_d shift [on going from Fig. 1(b) to 1(c)]. Putting such a splitting (0.075 Ry) into the interpolation scheme yields several interesting results. First, lifting the degeneracy breaks up the t_{2g} density-of-states peak, making it less pronounced. much in the manner obtained by Haydock *et al.*[9] in their calculations. Second, and far more important, hole counts similar to the spherical-potential estimates are obtained, but the holes are effectively entirely of zy character. This situation is maintained if the $yz - zx$ and xy splitting is reduced to as little as ~ 0.05 Ry. It would seem that the one-electron states of magnetic interest at a (100) face, i.e., those associated with holes, are of a single

TABLE I. Decompositions appropriate to d orbitals at a surface.

Orientation of surface	Group	t_{2g}	e_g
(100)	C_{4v}	2 + 1	1 + 1
(111)	C_{3v}	2 + 1	2
(110)	C_{2v}	1+ 1 + 1	1 + 1

symmetry and thus that a *single*-band model may be adapted when treating the magnetic properties of such a surface. This is important in the section that follows.

The lower symmetry of the surface potential also leads to induced dipole and higher multipole terms in the associated one-electron densities, not present in bulk. These terms have been neglected and we expect this to be adequate for our purposes here. This should be good for the d states, which are localized, although quite inadequate for the conduction-electron states. Of primary concern, of course, are d-band position and width.

III. MAGNETIC PROPERTIES OF THE SURFACE

A. Hartree-Fock Equations at Surface

An interesting question concerns the magnetic properties of the surface layer. It is difficult to extend the considerations of Sec. II into the ferromagnetic region; hence we study here the properties of simplified models of the surface. We then choose the parameters of the models to give agreement with our previous results for the paramagnetic region. Following Moriya,[10] the Hamiltonian for bulk is taken to be

$$\mathcal{H}_B = t \sum_{i,j,m,\sigma} a^{\dagger}_{i,m,\sigma}\, a_{j,m,\sigma} + \sum_{i,m,\sigma} E^{B}_{m,\sigma} n_{i,m,\sigma} , \qquad (3.1)$$

where the $a^{\dagger}_{i,m,\sigma}$ operator creates a d electron at site i, in orbital state m, with spin σ, and $n_{i,m,\sigma} = a^{\dagger}_{i,m,\sigma}\, a_{i,m,\sigma}$. The quantity t is the hopping matrix element between sites i and j, which are assumed to be nearest neighbors, and $E^{B}_{m,\sigma}$ is the bulk Hartree-Fock energy. For fcc Ni, there are two rather completely filled e_g orbitals and three t_{2g} orbitals. For this situation the $E^{\beta}_{m,\sigma}$ are determined by

$$\begin{aligned} E^{B}_{e,\sigma} &= U(2n_{e,-\sigma} + 3n_{t,-\sigma}) + U(n_{e,\sigma} + 3n_{t,\sigma}), \\ E^{B}_{t,\sigma} &= U(2n_{e,-\sigma} + 3n_{t,e}) + U(2n_{e,\sigma} + 2n_{t,\sigma}) , \end{aligned} \qquad (3.2)$$

where the subscripts t and e label the t_{2g} and e_g orbitals. We have neglected the interelectronic intra-atomic exchange energy here, because it is small compared to the Coulomb energy U.

Several modifications arise because of the introduction of the surface. The boundary condition quite naturally changes the wave functions, but changes in the hopping matrix element and Coulomb energy may also occur. The discussion of Sec. II would also indicate the possibility of level splitting due to the lifting of bulk symmetries. Obviously, it is difficult to determine these changes quantitatively, and we content ourselves here with estimates of their consequences.

We assume that the t_{2g} orbitals are most important for determining the magnetic structure of the surface layer, since they are for bulk. At the surface, these orbitals are expected to be split into a singlet and doublet. The Hartree-Fock equations for the surface sites can be written as

$$\begin{aligned} E_{S,\sigma} &= E_1 + U_S(2n_{D,-\sigma} + n_{S,-\sigma}) + 2U_S n_{D,\sigma} - E^{B}_{t,\sigma} \\ E_{D,\sigma} &= E_2 + U_S(2n_{D,-\sigma} + n_{S,-\sigma}) \\ &\quad + U_S(n_{D,\sigma} + n_{S,\sigma}) - E^{B}_{t,\sigma} , \end{aligned} \qquad (3.3)$$

where S and D refer to singlet and doublet occupation numbers at the surface and U_S is the Coulomb energy at the surface. E_1 and E_2 are energy shifts of the singlet and doublet, which include the e_g contributions, and are determined by requiring the paramagnetic d-hole count to agree with the estimates of Sec. II. In Sec. II, both s-d mixing and charge transfer contributed to the reduction in the surface d-hole count. The models discussed here describe only the d electrons. Therefore, the charge transfer to the surface d states here must be chosen to given the correct *total* d-hole count.

It is now necessary to have equations for the occupation numbers $n_{D,\sigma}(E_{D,\sigma})$ and $n_{S,\sigma}(E_{S,\sigma})$. Given these two equations, together with Eq. (3.3), we can solve for the magnetic properties of the surface layer. For this purpose, we generalize the work of previous authors[11,12] to include the Hartree-Fock energies of Eq. (3.3) and the fcc lattice structure. It proves convenient to divide the solid into layers parallel to the surface, and write the Hamiltonian for bulk and surface as

$$\mathcal{H} = \sum_{l} \mathcal{H}^{(l)} + t \sum_{l,l'} a^{\dagger}_{l}\, a_{l'} . \qquad (3.4)$$

Here $\mathcal{H}^{(l)}$ is the Hamiltonian within one layer and the sum over sites l, l' includes hopping between nearest-neighbor sites in adjacent layers. The operators $a^{\dagger}_{l} \equiv a^{\dagger}_{l,n,m,\sigma}$ are creation operators for electrons at site n, in layer l, in quantum states m, σ. $\mathcal{H}^{(l)}$ is given by

$$\begin{aligned} \mathcal{H}^{(l)} = t &\sum_{n,n',m,\sigma} a^{\dagger}_{l,n',m,\sigma}\, a_{l,n,m,\sigma} \\ &+ \sum_{n,m,\sigma} (E^{B}_{t,\sigma} + \delta_{l,0} E_{m,\sigma}) n_{n,m,\sigma} , \end{aligned} \qquad (3.5)$$

where 0 refers to the surface layer and the hopping matrix elements are assumed to be the same as in bulk. When $l = 0$, it is necessary to distinguish between the singlet and doublet parts of the t_{2g} orbital; hence the m label. For $l \neq 0$, these orbitals are degenerate.

We now wish to compute the Green's function $G_{m,\sigma}(E, \vec{k}_{\parallel}; l, l')$, defined by

$$\begin{aligned} G_{m,\sigma}(E, \vec{k}_{\parallel}; l, l') = &\int_0^{\infty} \frac{dt}{i}\, e^{iEt} \sum_{n} e^{i\vec{k}_{\parallel}\cdot\vec{R}_n} \\ &\times \langle [a_{l,n,m,\sigma}(t),\, a^{\dagger}_{l',0,m,\sigma}]_{+} \rangle , \end{aligned} \qquad (3.6)$$

where $\vec{R}_n$ is a vector in a layer of the lattice and $\vec{k}_\parallel$ is a vector in the reciprocal lattice of the layer, and where we have made use of translational invariance within a layer and used standard notation for the Green's function. With these definitions, it is possible to solve directly for $G_{m,\sigma}(E, \vec{k}_\parallel;\, 0, 0)$, which determines the surface density of states $\rho_{m,\sigma}(E)$ through

$$\rho_{m,\sigma}(E) = \frac{-1}{\pi N_\parallel} \sum_{\vec{k}_\parallel} \operatorname{Im} G_{m,\sigma}(E, \vec{k}_\parallel;\, 0, 0) \;, \qquad (3.7)$$

where $N_\parallel$ is the number of sites in a layer. The occupation numbers at the surface are given by

$$n_{m,\sigma} = \int_{-\infty}^{E_F} dE\, \rho_{m,\sigma}(E)$$

and E_F is the bulk Fermi energy.

It is straightforward to derive the equation for the Green's function of Eq. (3.6), for the Hamiltonian of Eq. (3.4), and (3.5). The result is

$$\begin{aligned} G_{m,\sigma}(E, \vec{k}_\parallel;\, l, l') = {} & G_{m,\sigma}(E, \vec{k}_\parallel)\delta_{l,l'} + t G_{m,\sigma}(E, \vec{k}_\parallel) \\ & \times \sum_{l''} G_{m,\sigma}(E, \vec{k}_\parallel;\, l'', l') \\ & + \delta_{l,0} E_{m,\sigma} G_{m,\sigma}(E, \vec{k}_\parallel) G_{m,\sigma}(E, \vec{k}_\parallel;\, 0, l') \;, \qquad (3.8) \end{aligned}$$

where $G_{m,\sigma}(E, \vec{k}_\parallel)$ is the Green's function within a bulk layer, $(E - \epsilon_{\vec{k}_\parallel} - E^B_{t,\sigma})^{-1}$ for an electron at energy $\epsilon_{\vec{k}_\parallel}$ propagating in that layer. The sum l'' runs over nearest-neighbor layers to l, terminating with but including the surface layer $l'' = 0$. Setting $l' = 0$, we can solve for $G_{m,\sigma}(E, \vec{k}_\parallel;\, 0, 0)$ using the method of Mills *et al.*,[12] or simply by Fourier transforming and using the function

$$N_l^{-1} \sum_{l \geq 0} e^{ik_z l} G_{m,\sigma}(E, \vec{k}_\parallel;\, l, 0),$$

where N_l is the number of layers, the l sum runs over all bulk layers including the surface, and we take the lattice constant equal to unity. Both methods give the result

$$G_{m,\sigma}(E, \vec{k}_\parallel;\, 0, 0) = \frac{g_{m,\sigma}(E, \vec{k}_\parallel)}{1 + t h_{m,\sigma}(E, \vec{k}_\parallel) - E_{m,\sigma} g_{m,\sigma}(E, \vec{k}_\parallel)} \;, \qquad (3.9)$$

where

$$\begin{aligned} g_{m,\sigma}(E, \vec{k}_\parallel) &= N_l^{-1} \sum_{k_z} (E - \epsilon_{\vec{k}_\parallel} - 2t \cos k_z - E^B_{t,\sigma})^{-1} \\ &= (2t)^{-1} (\xi^2 - 1)^{-1/2} \\ h_{m,\sigma}(E, \vec{k}_\parallel) &= N_l^{-1} \sum_{k_z} (E - \epsilon_{\vec{k}_\parallel} - 2t \cos k_z - E^B_{t,\sigma})^{-1} \cos k_z \\ &= (2t)^{-1} [\xi (\xi^2 - 1)^{-1/2} - 1] \;, \end{aligned}$$

with $2t\xi = E - E^B_{t,\sigma} - 2t(\cos k_x + \cos k_y)$. In these calculations, we have taken k_z perpendicular to the (100) surface of the sc lattice, k_x and k_y in the other (100) directions, and defined $\epsilon_{\vec{k}_\parallel} = 2t(\cos k_x + \cos k_y)$. Using Eq. (3.7) we find

$$\begin{aligned} \rho_{m,\sigma}(E) = {} & \frac{\operatorname{Im}}{\pi t} \int_{-\pi}^{\pi} \frac{dk_x}{2\pi} \int_{-\pi}^{\pi} \frac{dk_y}{2\pi} \\ & \times [(A^2 - B^2)^{1/2} + A - t^{-1} E_{m,\sigma}]^{-1} \;, \qquad (3.10) \end{aligned}$$

where $A = (E - E^B_{t,\sigma})(2t)^{-1} - \cos k_x - \cos k_y$, and $B = 1$ for the sc lattice. The reason for writing Eq. (3.10) in terms of A and B, is that the result for the (100) surface of the fcc lattice can also be written in this form. Repeating the steps of Eqs. (3.8)–(3.10) for this lattice, we find $A = (E - E^B_{t,\sigma}) \times (2t)^{-1} - \cos k_x \cos k_y$, and $B = 2(\cos k_x + \cos k_y)$. In both cases, we require $\operatorname{Im}(A^2 - B^2)^{1/2} < 0$ for $A^2 < B^2$, which specifies our convention for the branch cut.

It is worth comparing Eq. (3.10) with the expression for the bulk density of states $\rho^B_{t,\sigma}(E)$ written as the same integral,

$$\rho^B_{t,\sigma}(E) = \frac{\operatorname{Im}}{\pi t} \int_{-\pi}^{\pi} \frac{dk_x}{2\pi} \int_{-\pi}^{\pi} \frac{dk_y}{2\pi} (A^2 - B^2)^{-1/2} \,. \qquad (3.11)$$

Comparing with Eq. (3.10) shows the modifications due to the change in the Hartree–Fock energy at the surface, the $t^{-1}E_{m,\sigma}$ term, and the boundary condition, which introduces the extra A in the bracket of (3.10). When $E_{m,\sigma} = 0$, it is easy to verify that both $\rho_{m,\sigma}(E)$ and $\rho^B_{t,\sigma}(E)$ are nonzero only in the same interval. Thus the continuum of states at the surface overlaps the bulk density of states. However, for sufficiently large $|E_{m,\sigma}|$, it is possible for the bracket in Eq. (3.10) to vanish outside the bulk continuum. Such solutions are analogous to Tamm states, but here they would be broadened by *s-d* hybridization as well as by the integration over k_x and k_y. These states are surface resonances, by analogy to Friedel resonances, which are familiar in the impurity problem. For the sc lattice, the threshold for the appearance of these states is $|E_{m,\sigma}| = t$, which is only $\frac{1}{12}$ of the bulk bandwidth $12t$.

It is also worth realizing that the surface problem is truly a one-dimensional scattering problem, with $\vec{k}_\parallel$ a conserved quantity. Thus the surface resonance appears as a bound state of that problem, with freely propagating solutions parallel to the surface. Eventually these states decay through the *s-d* hybridization—however, the two-dimensional propagation parallel to the surface introduces the two-dimensional density of states into the $\rho_{m,\sigma}(E)$ calculation, which we estimate to be much broader than the hybridization width. Hence we neglect the latter in subsequent calculations.

This completes the derivation of the equations for $n_{m,\sigma}$, which together with Eq. (3.3), permit explicit solution for all occupation numbers at the surface and the surface density of states. We now proceed to study them for the special case of Ni.

B. Solution of Surface Model

Before evaluating the integrals in Eq. (3.10) and solving the Hartree–Fock equations, it is necessary to discuss the approximations involved in applying this model to Ni. Although Eq. (3.10) is valid for both sc and fcc lattices, it will not reproduce the real Ni density of states. The sc lattice with nearest-neighbor hopping has no density-of-states peak, while the fcc result has a logarithmic singularity at the band edge. Furthermore, it is difficult to introduce a surface into a model that does reproduce the bulk density of states, because $\epsilon_{\vec{k}_\parallel}$ and k_z appear explicitly in the one-dimensional scattering equation. It is necessary to have them both, as well as the correct boundary condition, and an expression much more complicated than Eq. (3.10) is the result.

Because of this difficulty, we give here two separate calculations to illustrate separately the roles of the surface and the Ni density of states. The first of these is a solution of Eq. (3.10) for the sc lattice, to indicate how the surface density of states and magnetization behave for this model. The second treats the surface atom as an impurity in bulk, permitting us to use a better model for the bulk density of states. We argue that the latter approach should lead to an understanding of the occupation numbers at the surface, but is probably not accurate for determining the shape of the surface density of states.

We now proceed to solve the Hartree–Fock equations (3.3) together with (3.10) for the occupation numbers. For the sake of continuity the actual computation of $n_{m,\sigma}$ is given in Appendix B. The results are presented in Fig. 2. If this model is applied to Ni, it is appropriate for the bulk density of states to represent one of the three degenerate t_{2g} electron bands, since the e_g states are nearly filled. From the discussion of Sec. II, we take bulk Ni to have 0.6 holes. The bulk Stoner criterion for this situation is $U \cong 1.3$, where our energy unit is the bandwidth $12t$. Strong ferromagnetism $(n_{t,\uparrow} - n_{t,\downarrow} = 0.2)$ occurs when $U \gtrsim 1.5$, the majority spin band is completely filled and the minority spin band is filled to an energy of 0.7, corresponding to 0.2 holes in each band, as indicated in Fig. 4. It is now necessary to make assumptions about the paramagnetic properties of the surface atom. We discuss several cases, based on the treatment of Sec. II.

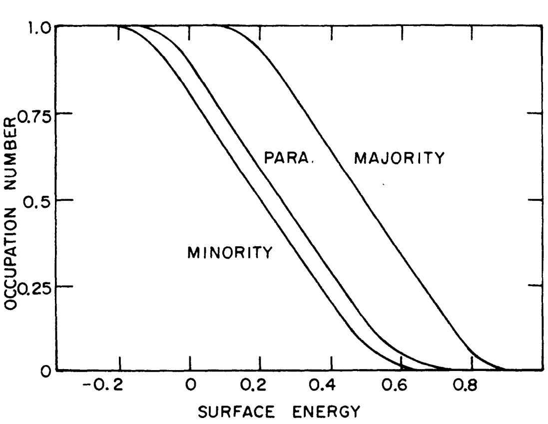

FIG. 2. Surface site occupation number $\eta_{m,\sigma}$ as a function of the Hartree–Fock surface energy $E_{m,\sigma}$ (in units of the bandwidth), appearing in Eq. (3.3) and discussed in Appendix B.

The simplest situation neglects the splitting of the three t_{2g} orbitals at the surface, and takes $U_S = U = 1.5$. Although we consider this situation to be unlikely, it is nonetheless useful for comparison with the results of Ref. 4. Solving Eq. (3.3) and using $E_1 = E_2$ and $n_{S,\sigma} = n_{D,\sigma}$, together with Fig. (2), leads to

$$\begin{aligned} n_{S,\uparrow} &= 1\,, & \Delta Q &> -0.25 \\ n_{S,\downarrow} &= 0.80 + 2.2\Delta Q\,, & \Delta Q &< 0.091 \\ &= 1\,, & \Delta Q &> 0.091\,, \end{aligned} \tag{3.12}$$

where $3\Delta Q$ is the total charge transfer to the surface in the paramagnetic region. Taking $3\Delta Q \cong 0.15-0.2$ electrons per spin, from Sec. II, leads to a ferromagnetic surface moment of $0.27 - 0.15\mu_B$. For very large charge transfer, $3\Delta Q > 0.27$, the moment is entirely quenched. For very large charge repulsion from the surface, $\Delta Q < -0.25$, we find additional solutions of the Hartree–Fock equations (3.3). These solutions correspond to antiferromagnetic coupling. However, they occur at such large values of $|\Delta Q|$ that they are not of interest here.

Solving Eq. (3.3) in the paramagnetic region, we find the Wolff criterion to be given by $U_S = \frac{2}{3}$. Thus the present case corresponds to a magnetic surface atom. However, even if the surface atom does not satisfy the Wolff criterion, we expect the strong exchange field of the bulk to induce a magnetic moment at the surface. That can be seen by subtracting from Eq. (3.3) the same equation, but evaluated in the paramagnetic regime, to find:

$$E_{S,\sigma} - E_S^p = 3U_S(n_{S,-\sigma} - n_S^p) + 2U_S(n_{S,\sigma} - n_S^p) + 0.1\,U_\sigma\,, \tag{3.13}$$

where the superscript p indicates paramagnetic values, and we have used $n_{t,\uparrow} - n_t^p = -(n_{t,\downarrow} - n_t^p) = 0.1$ for the bulk occupation numbers. The bulk term, in the far right-hand side of Eq. (3.13) gives an antiferromagnetic coupling, in opposition to the intrinsically ferromagnetic terms containing the U_S. The authors of Ref. 4 do not solve the Hartree–Fock equations, but argue that the surface moment vanishes because it does not satisfy the

Wolff criterion. This ignores the exchange coupling to bulk which will induce a moment. Only if the charge transfer is made improbably large can the surface moment vanish.

Proceeding with our discussion, we next include the possible splitting between the singlet and doublet. As discussed in Sec. II, the doublet is expected to be lower, corresponding to an attractive E_2. We assume that it is completely filled, implying that $|E_2|$ is large, which requires that the charge transfer to or from the surface resides in the singlet. The estimated surface hole count thus requires a repulsion of 0.15 electrons per spin from the singlet.

We solve Eq. (3.3) for three different situations, ($U_S = 1.5$; $U = 1.5$), ($U_S = 2$; $U = 2$), and ($U_S = 0.75$; $U = 1.5$), as a function of charge transfer ΔQ to the singlet, keeping the doublet filled. The results for the magnetization are shown in Fig. 3. The interesting new feature is the appearance of multiple solutions, which pose a problem in the determination of the ground state. The estimated value of $\Delta Q \cong -0.15 \pm 0.05$ can lie in this region, depending on the assumptions made about the Coulomb parameters.

It is interesting to consider the surface density of states corresponding to the antiferromagnetic solution at ($U_S = 0.75$, $U = 1.5$) and $\Delta Q = -0.1$. For this case, we find $E_{S,\uparrow} = 0.35$ and $E_{S,\downarrow} = -0.15$, which provide an expression for $\rho_{S,\sigma}(E)$ when substituted into Eq. (3.10). The results are shown in Fig. 4 along with the bulk density of states in this model. A surface resonance has formed at the majority-spin Fermi level, indicated by the arrow in Fig. 4, which produces a large majority-spin density of states. It is this resonance that is responsible for the magnetization reversal and provides a source of majority-spin electrons at the surface.

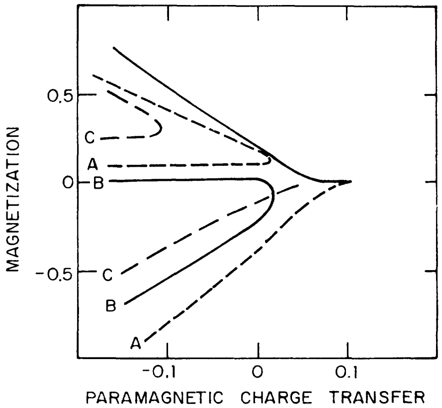

FIG. 3. Allowed solutions to the Hartree–Fock equations for the surface magnetization as a function of the paramagnetic charge transfer. Curve *A* assumes $U = U_S = 2$, in units of the bandwidth, curve *B* is for $U = U_S = \frac{3}{2}$, and curve *C* takes $U = \frac{3}{2}$ and $U_S = \frac{3}{4}$. The strong ferromagnetism condition is $U = \frac{3}{2}$.

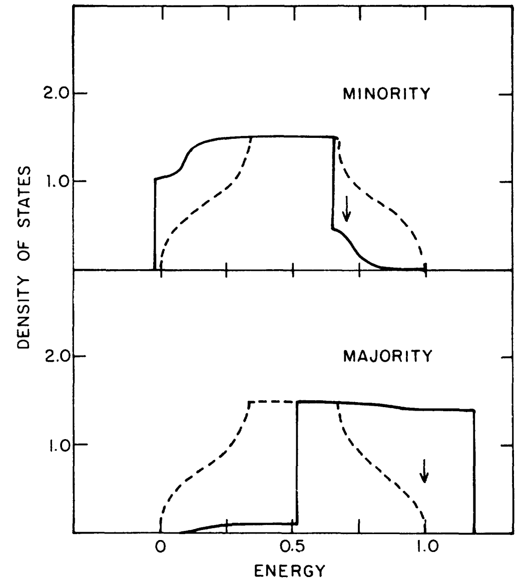

FIG. 4. Local surface density of states for paramagnetic charge transfer of -0.1, $U = \frac{3}{2}$, and $U_S = \frac{3}{4}$. The zero of energy is the bottom of the corresponding bulk band, and the Fermi level is indicated by the arrow. Dashed line indicates bulk density of states. The energy is measured in units of the bandwidth and the density of states in terms of its reciprocal.

This result could have been anticipated directly from Eq. (3.13). If we set $U_S = 0$, there remains only an antiferromagnetic coupling to bulk. Decreasing U_S thus tends to favor the single antiferromagnetic solution, if the other parameters are held constant.

C. Impurity Model of Surface

As mentioned previously, Eq. (3.10) has the disadvantage of giving an unrealistic bulk density of states for Ni. If we consider the surface atom to be an impurity in bulk, it is possible to solve the Hartree–Fock equations using a more realistic model for bulk Ni. Although this procedure cannot be expected to give good results for the surface density of states, it can be a good approximation for the occupation number which is an integral over that function. This single-impurity problem has been studied in detail by Moriya.[10]

Concentrating on the singlet part of the t_{2g} states at the surface, we have the following equations to solve:

$$n_{S,\sigma} = \int_{-\infty}^{E_F} d\epsilon\, \rho_\sigma(\epsilon) \{[1 - E_{S,\sigma} F_\sigma(\epsilon)]^2 + [\pi E_{S,\sigma} \rho_\sigma(\epsilon)]^2\}^{-1}, \tag{3.14}$$

with $E_{S,\sigma}$ given by Eq. (3.3) and

$$F_\sigma(\epsilon) = P \int_{-\infty}^{\infty} d\omega\, \rho_\sigma(\omega) (\epsilon - \omega)^{-1}.$$

$\rho_\sigma(\omega)$ is taken as the steeple model density of states:

$$\begin{aligned} \rho_\sigma(\omega) &= 1.64(\omega - E^B_{b,\sigma}), & 0 < \omega - E^B_{t,\sigma} < 0.90 \\ &= 1.48 + 89.0(\omega - E^B_{t\sigma}), & 0.90 < \omega - E^B_{t,\sigma} < 0.95 \\ &= 5.93 - 118.6(\omega - E^B_{t\sigma}), & 0.95 < \omega - E^B_{t,\sigma} < 1.00 \end{aligned} \tag{3.15}$$

As in the previous model, we take 0.3 holes per spin for bulk Ni. The Stoner criterion is $U \cong 0.2$ and strong ferromagnetism occurs for $U = 0.3$, in units of the bandwidth.

The first case of interest assumes there to be no charge transfer in the paramagnetic region, leaving 0.3 holes per spin in the singlet, and takes $U = U_S = 0.3$. The doublet is assumed to be filled. Numerical solution of Eq. (3.3) and Eq. (3.14) leads to three possible values for the surface occupation numbers: $(n_{S,\uparrow};\ n_{S,\downarrow}) = (1.00;\ 0.47)$, $(0.46;\ 0.92)$, and $(0.65;\ 0.78)$. The Wolff criterion for this impurity is given by $U_S = 0.6$. We assume[10] that the solution with the smallest impurity moment corresponds to the nonmagnetic solution in paramagnetic Ni. Since the impurity is intrinsically nonmagnetic, this solution is expected to have the lowest energy, and is seen to be antiferromagnetically coupled to bulk.

The sign of the surface-bulk coupling does depend on U. For example, with $U = U_S = 0.5$, the numerical solutions are $(n_{S,\uparrow};\ n_{S,\downarrow}) = (1;\ 0.40)$, $(0.28;\ 0.98)$, and $(0.77;\ 0.69)$. As above, the assumptions of Ref. 10 indicate the last solution to be the ground state that is weakly ferromagnetic. In both of these cases, however, the majority-spin occupation number is less than unity. This can only occur if some density of states has been pushed above the top of the Fermi level. But the Fermi level is above the bulk majority-spin continuum, therefore this depletion implies the existence of a majority-spin surface resonance above the Fermi level, as found in the previous model.

Introducing the charge transfer of somewhat less than 0.1 electron per spin to the surface, estimated in Sec. II, modifies the above solution. We believe that this situation most closely corresponds to Ni, and for completeness we consider both singlet and doublet parts of the t_{2g} triplet. From the arguments of Sec. II, the singlet is higher, and the doublet filled, requiring 0.2 holes per spin in the singlet. The surface atoms are intrinsically magnetic for all values of $U = U_S > 0.3$. For $U = 0.3$, there is only one solution: $n_{S,\uparrow} = 1$, $n_{S,\downarrow} = 0.59$. Larger U leads to three solutions, as before. For $U = 0.5$, the three solutions are $(n_{S,\uparrow};\ n_{S,\downarrow}) = (1,\ 0.54)$, (0.43), (0.99), and $(0.83,\ 0.82)$. Since the surface atoms are intrinsically magnetic, the previous argument favoring the minimum moment does not apply, although this solution is closest to the paramagnetic value of the charge transfer.

The computation of the ground-state energy is somewhat more sensitive to the detailed shape of the density of states than is the occupation number. It is thus uncertain whether the impurity model can be trusted to predict the proper ground state when the solutions lie close in energy, which is the case here.

If the doublet is higher in energy at the surface, we assume that the singlet is filled, and $\Delta Q = +0.1$. The number of holes in the doublet is then the same as in bulk Ni. This holds true for the ferromagnetic as well as the paramagnetic state of bulk Ni.

IV. DISCUSSION AND CONCLUSIONS

One purpose of this paper has been to make reasonable estimates of the electronic properties at transition-metal surfaces, based on the renormalized-atom picture. The many assumptions that were necessary are indicative of the infancy of this field. Important experimental and theoretical questions remain unresolved. It is quite clear, however, that Coulomb screening must be included, as attempted here. Our reasoning makes the charge transfer of approximately 0.1 electrons per spin to a Ni surface site plausible, indicates a d-hole count less than 0.2 per spin, and suggests that the splitting of the t_{2g} electrons at the surface is significant. However, we know of no experiment which unambiguously confirms or contradicts these results.

We also proposed and solved an extension of the magnetic impurity model to surfaces. Here, the results depend on the assumptions made about the surface site, such as the paramagnetic charge transfer, splitting of the t_{2g} states, and Coulomb parameters. For appropriate choices of the model parameters, a spin-dependent surface resonance exists in the ferromagnetic region. The local surface density of states then differs drastically from bulk, and the surface magnetic moment can be coupled antiferromagnetically to bulk. Nonmagnetic surface resonance states have been considered previously[13] and evidence found for their existence in tungsten.[14] To our knowledge, however, this is the first time the importance of spin-dependent surface resonances for magnetic properties has been discussed.

The possibility of magnetic surface resonances leads to a tempting interpretation of the spin polarization measured in recent tunneling and photoemission experiments in Ni. It is plausible that both are sensitive, to some degree, to the surface wave function. The escape depth of photoelectrons in these experiments[15] is 5–10 Å, while the tunneling wave function is determined by the boundary condition at the surface. A surface resonance of majority spins at the Fermi level would provide a source of majority spin electrons capable of influencing the emitted electron polarization. One requires better evaluation of the model and a better understanding of the photoemission process for any quantitative comparison of theory and experiment.

There are, of course, other proposals for interpreting these experiments. In addition, field-emission experiments, which also should be sensitive to surface properties, complicate this interpretation. They yield the opposite sense of polarization to that found in the other experiments, e.g., on the (100) surface. No description concentrating solely on the surface or on bulk has to date led to a satisfactory explanation of all these measurements.[16]

Regardless of the resolution of this experimental contradiction in Ni, our model does suggest a variety of new magnetic phenomena associated with a surface. In general, the rules for obtaining antiferromagnetic impurities in bulk can be expected to hold here. An analysis of other transition-metal surfaces could provide other situations favorable to spin-dependent surface resonance states and antiferromagnetic coupling.

Note added in proof. In a recent letter, Houston *et al.*[17] compare experimental electron-excited and phonon-excited appearance potential results and from these conclude that the core $2p$ levels of Ni (and Ti and Cr) lie higher at the surface than in bulk, consistent with our d-level results of Sec. II. Houston *et al.* rationalize their results in terms of a set of (uncharged site) calculations which place the free-atom levels higher than those in bulk. This is opposite to what we predict[3] [see Figs. 1(a) and 1(b)]. Experimental evidence, which supports our view of the relative positions of such levels, will be reviewed in a future publication. The requirement that the local Fermi level at the surface matches that of the bulk implies that the center of gravity of the (narrower) d levels lies higher at the surface. The core $2p$ level suffers quantitatively similar Coulomb shifts to that of $3d$ and hence is expected to also lie higher at the surface than in bulk by about $\frac{1}{2}$ eV, in semiquantitative agreement with experiment. The pinning of the Fermi level taken with the narrowing of the d bands generally implies shallower levels at the surface of the heavy high $\rho(E_F)$ transition metals, no matter where the free-atom level lies relative to bulk.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge many discussions with H. Ehrenreich and with L. Hirst and H. Fukuyama. One of the authors (P. F.) is grateful for support from the National Science Foundation while visiting Harvard University during the formative stages of this work.

APPENDIX A: EFFECTIVE COULOMB PARAMETERS

This appendix is concerned with estimating the various effective Coulomb parameters $U(i,j)$ appropriate to the charging question considered in Sec. II. Of particular interest will be how much the U differ from bare Coulomb (F^0) integrals.

Let us first consider how the position of the d resonance ϵ_d is affected by the addition of Δn electron's worth of d charge to an atomic site. In this appendix, it is convenient to work with units of total charge ΔN. Setting U equal to the bare integral, we obtain

$$\Delta\,\epsilon_d/\Delta N = U(d,\,d) \to F^0(d,\,d) = 1.8\text{–}1.9\ \text{Ry}, \quad \text{(A1)}$$

using the renormalized atom integrals of Table II. Now the addition of the d charge causes the d shell to relax outwards thus reducing the average d-d interaction. The effect of this on the d-d Coulomb contribution to ϵ_d can be estimated:

$$U(d,d)\,(d^n \to d^{n+\Delta N}) = \frac{[(n+\Delta N-1)\,F^0(d,\,d)]_{n+\Delta N} - [(n-1)\,F^0(d,\,d)]_n}{\Delta N}\,, \quad \text{(A2)}$$

where the F^0 integrals in the brackets are evaluated in the $d^{n+\Delta N}$ and d^n configurations, respectively. Each bracket represents the d-d Coulomb interaction of one d electron with all the others. Using Table II, we can evaluate this for $\Delta N=1$, obtaining

$$\begin{aligned} U(d,\,d)\,(d^9 \to d^{10}) &= 0.92\ \text{Ry}, \\ U(d,\,d)\,(d^8 \to d^9) &= 1.07\ \text{Ry}. \end{aligned} \quad \text{(A3)}$$

Thus relaxation effects yield a shift in ϵ_d which is approximately one-half that predicted with bare Coulomb integrals. These values were obtained with the integrals of Table II, which assume atomic charge distributions that are renormalized to the Ni Wigner–Seitz cell and the renormalization impedes the relaxation process. Free-atom estimates place U between 0.4 and 0.8 Ry.

The U considered above is important in the determination of the charge necessary to bring the local Fermi level into agreement with that of the bulk. Prior to this, however, one must consider the effect of changing s and d count on going from the bulk [Fig. 1(b)] to the uncharged surface [Fig.

TABLE II. Slater F^0 integrals obtained from Hartree–Fock calculations for configurations of Ni, where the resulting $3d$ and $4s$ functions were renormalized to the Wigner–Seitz cell of metallic Ni (all integrals in Ry).

		$F^0(d,d)$	$F^0(s,d)$	$F^0(s,s)$
Ni	d^{10}	1.77		
	d^9s	1.87	1.05	
	d^8s^2	1.97	1.07	0.90
Ni^+	d^9	1.88		
Ni^{2+}	d^8	1.99		

1(c)] density of states. The simple shifted-band estimates of Sec. II showed ϵ_d lying closer to ϵ_Γ, causing an increase in d and decrease in s count of about 0.2e. This implies additional shifts in ϵ_d and ϵ_Γ of

$$\Delta\epsilon_d = 0.2[U(d, d) - U(d, s)] \tag{A4}$$

and

$$\Delta\epsilon_\Gamma = 0.2[U(d, s) - U(s, s)] \,.$$

Using bare renormalized-atom integrals, we find

$$[U(d,d) - U(d, s)] = F^0(d, d) - F^0(d, s) = 0.8 - 0.9 \text{ Ry} \tag{A5}$$

and

$$[U(d, s) - U(s, s)] = F^0(d, s) - F^0(s, s) \sim 0.2 \text{ Ry}. \tag{A6}$$

If correct, such values would imply that ϵ_d, and hence the local surface Fermi level move back close to the bulk-metal levels. Relaxation effects may be estimated in the manner of Eq. (A2) by taking d-d (and s) Coulomb energy differences between $d^n s^x$ and $d^{n+1} s^{x-1}$ states. For the term important to $\Delta\epsilon_d$ we have

$$\begin{aligned}[U(d, d) - U(d, s)]_{d^9 s \to d^{10}} &= [9 F^0(d, d)]_{d^{10}} \\ &\quad - [F^0(s, d) + 8 F^0(d, d)]_{d^9 s} \\ &= -0.09(-0.16) \text{ Ry},\end{aligned} \tag{A7}$$

$$\begin{aligned}[U(d, d) - U(d, s)]_{d^8 s^2 \to d^9 s} &= [F^0(s, d) + 8 F^0(d, d)]_{d^9 s} \\ &\quad - [2 F^0(s, d) + 7 F^0(d, d)]_{d^8 s^2} \\ &= 0.11(0.075) \text{ Ry},\end{aligned} \tag{A8}$$

and

$$\begin{aligned}[U(s, d) - U(s, s)]_{d^8 s^2 \to d^9 s} &= [9 F^0(s, d)]_{d^9 s} \\ &\quad - [F^0(s, s) + 8 F^0(s, d)]_{d^8 s^2} \\ &= -0.05(-0.54) \text{ Ry},\end{aligned} \tag{A9}$$

where the number preceding the parentheses is the renormalized-atom estimate and that inside is obtained with free-atom integrals. The negative signs seen in Eqs. (A7) and (A9) imply that the Coulomb effects are *weaker* in the configuration having more d electrons, contrary to what is suggested by bare integral considerations [Eqs. (A5) and (A6)].

An independent estimate can be made for the free-ion case employing experimental free-atom spectra. A *difference* in ionization energies I provides a measure of the difference in effective Coulomb terms, e.g.,

$$[U(d, d) - U(d, s)]_{d^9 s \to d^{10}} = -I(d^{10} \to d^9) + I(d^9 s \to d^8 s). \tag{A10}$$

Such a quantity measures any effect due to the spatial change of the d orbital in question, i.e., changes in kinetic, nuclear, and core potential energy, in addition to the change in d-d and s-d terms. [The apparent reversal in signs of the term of Eq. (A10) as compared with Eq. (A 7) is due to taking the ionization energies I as positive quantities.] Employing the average of the experimental multiplet energies[18] of any give $d^n s^x$ configuration, Eq. (A10) yields 0.3 Ry and similarly one has

$$\begin{aligned}[U(d, s) - U(s, s)]_{d^8 s^2 \to d^9 s} &= -I(d^9 s \to d^9) + I(d^8 s^2 \to d^8 s) \\ &= 0.1 \text{ Ry}.\end{aligned} \tag{A11}$$

It is quite clear that considerable uncertainty must be attached to any estimate of these quantities but it would appear that

$$U(d, d) - U(d, s) = 0.1 \pm 0.2 \text{ Ry} \tag{A12}$$

is an appropriate estimate for use in Sec. II. In any case it is substantially smaller than estimates omitting screening [i.e., Eq. (A5)]. Of equal concern is the shift of ϵ_Γ relative to ϵ_d, which is governed by

$$[U(s, d) - U(s, s)] - [U(d, d) - U(d, s)] \sim -0.2 \text{ Ry}. \tag{A13}$$

These values are employed in Sec. II.

The small values of the above parameters implies that the local Fermi level of an uncharged surface atom would lie well below that of the bulk in the manner pictured in Figs. 1(b) and 1(c). The charge flow, necessary to raise the surface level, will be into the d holes at the surface sites. To estimate the effect of the flow on ϵ_d and ϵ_Γ, we require $U(d, d)$ and $U(d, s)$, respectively. $U(d, d)$ was estimated with Eq. (A2) at the beginning of this appendix. Unfortunately, lacking a set of $\text{Ni}^+ d^8 s$ wave functions, we cannot make a similar estimate for $U(d, s)$. Using the $d^8 s^2$ atom integrals, we can make the crude estimate

$$U(s, d) = [9 F^0(s, d)]_{d^9 s} - [8 F^0(s, d)]_{d^8 s} = 0.84 \text{ Ry}, \tag{A14}$$

a value that is probably too large because of the integral employed in the second term. This estimate is to be compared with bare $F^0(s, d)$ of ~ 1.05 Ry and with the $U(d, d)$ of 0.9–1.0 Ry.

Atomic spectra can also be used to estimate the U by comparison of successive ionization energies, namely

$$\begin{aligned}U(d, d) &= I(\text{Ni}^+ d^9 \to \text{Ni}^{++} d^8) \\ &\quad - I(\text{Ni}\, d^{10} \to \text{Ni}^+ d^9) \sim 1.0 \text{ Ry}, \\ U(d, d) &= I(\text{Ni}^+ d^8 s \to \text{Ni}^{++} d^7 s) \\ &\quad - I(\text{Ni}\, d^9 s \to \text{Ni}^+ d^8 s) \sim 1.0 \text{ Ry},\end{aligned} \tag{A15}$$

and

$$U(s, d) = I(\text{Ni}^+ d^8 s \to \text{Ni}^{++} d^8)$$

$$-I(\mathrm{Ni}\,d^9 s \to \mathrm{Ni}^+ d^9) \sim 0.7\ \mathrm{Ry}, \qquad \text{(A16)}$$

where we have again employed the average energy of a $d^n s^x$ configuration.[19] These, taken with the earlier estimates, suggest that

$$U(d,\ d) = 0.9 - 1.0\ \mathrm{Ry} \qquad \text{(A17)}$$

is appropriate to the calculations of Sec. II (note that we are primarily interested in the shift of a d orbital that lies largely *within* the surface of the metal). Secondly, we require

$$U(s,\ d)/U(d,\ d) = 0.7 - 0.8\ . \qquad \text{(A18)}$$

APPENDIX B: COMPUTATION OF SURFACE OCCUPATION NUMBER

We give here the details of the computation of the surface occupation number $n_{m,\sigma}$ as a function of $E_{m,\sigma}$, appearing in Eq. (3.3). This occupation number is determined by

$$n_{m,\sigma} = \int_{-\infty}^{E_F} d\omega\, \rho_{m,\sigma}(\omega),$$

where, for the sc lattice,

$$\rho_{m,\sigma}(\omega) = \frac{-\,\mathrm{Im}}{\pi t} \int_{-\pi}^{\pi} \frac{dk_x}{2\pi} \int_{-\pi}^{\pi} \frac{dk_y}{2\pi} \times [(\xi_\sigma^2 - 1)^{1/2} + \xi_\sigma - t^{-1} E_{m,\sigma}]^{-1}\ , \qquad \text{(B1)}$$

$$2t\,\xi_\sigma = \omega - E^B_{t,\sigma} - \epsilon_{\vec{k}_\parallel}\ ,$$

and

$$\epsilon_{\vec{k}_\parallel} = 2\,t(\cos k_x + \cos k_y)$$

in the approximation of nearest-neighbor hopping parallel to the (100) surface. The integral over k_x and k_y, can be converted into an integral over the two-dimensional density of states $\rho_2(E)$. However, this density of states has a logarithmic singularity at zero energy, a property of nearest-neighbor hopping. A more realistic approximation for our purposes is the choice of an energy-independent two-dimensional density of states of the same width $8t$. We still have a maximum of one electron per spin in each orbital, which determines $\rho_2(E) = (8t)^{-1}$, $-4t < E < 4t$, and $\rho_2(E) = 0$ elsewhere. Equation (B1) can then be written

$$n_{m,\sigma}(E_{m,\sigma}) = -\int_{-\alpha}^{E_F} \frac{d\omega}{\pi t}\ \mathrm{Im} \int_{-4t}^{4t} \frac{dE}{8t} \times [(\xi_\sigma^2 - 1)^{1/2} + \xi_\sigma - t^{-1} E_{m,\sigma}]^{-1}. \qquad \text{(B2)}$$

The integrals in Eq. (B2) are straightforward to evaluate, and have a simple physical interpretation. The term in parenthesis has resulted from solving a one-dimensional scattering problem. Its imaginary part exists within the one-dimensional continuum of states $-1 < \xi_\sigma < +1$, and at discrete points outside their continuum, given by $\omega - E = (t^2 + E^2_{m,\sigma})/(E_{m,\sigma})$, whenever $|E_\sigma| > t$. The latter correspond to "bound" states, that is, states trapped at the surface. These states can propagate parallel to the surface, so that the integration over E smears out their contribution to the total density of states.

The curves plotted in Fig. 2 result from choosing E_F to give a bulk hole count of 0.1 per spin per orbital, corresponding to Ni. We choose the two-dimensional density of states in bulk to be the same as at the surface. Using Eq. (3.11) then gives the bulk density of states of Fig. (4), thereby determining $E_F = 0.78$, in units of the total bandwidth $12t$.

We need also $n_{m,\sigma}(E_{m,\sigma})$ with the bulk in the strong ferromagnetic region. This requires the majority-spin band to be completely filled, and the minority-spin band to be higher in energy by $0.2U$, when $U > 1.5\ (12t)$. For convenience, we have shifted the minority-spin band by this amount when plotting Fig. (4). E_F lies $0.7\ (12t)$ above the bottom of the minority-spin band.

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[*] Work supported in part by the National Science Foundation.

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[19] Ni^{2+} data are required here in addition to Ni and Ni^+. The tabulated (see Ref. 16) spectra for Ni^{2+} d^8 and d^7s is incomplete. Slater–Condon theory, taken with the observed levels, was used to place the centers of gravity of these configurations.

PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Electronic Structure of Vanadium Carbide

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(Received 2 January 1973)

The electronic structure of stoichiometric vanadium carbide has been computed using the augmented-plane-wave (APW) method and the energy bands for nonstoichiometric phases have been determined with the APW–virtual-crystal approximation. The energy bands exhibit a very strong dependence on the relative sizes of the assumed APW-sphere radii for vanadium and carbon. Bands for the nonstoichiometric phases show a marked deviation from a rigid-band behavior as the composition is varied. The results of x-ray-emission, heat-capacity, magnetic-susceptibility, and Hall-effect measurements are discussed in terms of the computed bands.

I. INTRODUCTION

Transition-metal carbides such as VC_{1-x} possess seemingly contradictory properties. These phases have several properties which indicate strong covalent bonds between carbon and the transition atom: for example, high melting points ranging to 3983 °C for TaC,[1] hardness values which lie between those of alumina and diamond,[2] and values of Young's modulus that are double those of the pure transition metals.[1] The electrical, magnetic, and optical properties of these phases, however, are often typically metallic and not much different from those of the parent transition metal.[1] In addition, nearly stoichiometric NbC, TaC, MoC, and WC are superconducting, with transition temperatures ranging from 10 to 14 K.[1]

Previous theories of the electronic structure and discussions of the relative importance of covalent and metallic bonding in carbides have been reviewed by Toth *et al.*[3] and Lye.[4] Several workers emphasized the importance of metal-metal bonding,[5–7] while others have declared that metal-nonmetal interactions are more important.[8,9] The latest band-structure calculations[10–14] and electron spectroscopy[15] and x-ray emission and absorption measurements[16] indicate that there is a mixture of metal-metal, metal-nonmetal, and possibly even ionic bonding.

In this paper, the electronic structures of stoichiometric and nonstoichiometric phases in the vanadium-carbon system are studied with the aid of augmented-plane-wave (APW) band-structure calculations. The calculations for the stoichiometric composition were performed using the perfect-crystal APW method due to Slater.[17] The band structures of several nonstoichiometric phases were computed using the augmented-plane-wave–virtual-crystal approximation (APW-VCA) method of Schoen.[18,19]

II. COMPUTATIONAL RESULTS AND DISCUSSIONS

A. APW Calculations for Stoichiometric VC

As a first step in the investigation of the energy bands of the vanadium-carbide system we calculated the band structure for stoichiometric VC with the NaCl crystal structure. VC phases can be prepared in the composition range from $VC_{0.88}$ to $VC_{0.65}$.[1,2] Even though stoichiometric VC does not exist, these calculations will be used as a starting point for the calculations on the nonstoichiometric phases.

In the APW scheme,[20–22] the one-electron crystal potential has a muffin-tin form; that is, the potential is spherically symmetric within spheres centered on the various atomic positions and constant in the interstitial volume. In each region, the potential is assumed to be the sum of two terms, one term which is purely electrostatic due to the nuclei and the charge density of all the electrons, and an exchange term. The Slater approximation was used for the exchange potential[23]:

$$V_x(r) = -6[(3/8\pi)\rho(r)]^{1/3},$$