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Photoemission from surface-atom core levels, surface densities of states, and metal-atom clusters: A unified picture

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A model is presented which relates the observed narrowing and shifting of the surface density of states, reported in the preceding paper, with the sign and magnitude of the surface-atom core-level shift (SCS). This relationship, along with the identical line shapes observed for the bulk and surface-atom core-level photoemission peaks, is shown to provide strong support for a predominantly initial-state interpretation of the SCS. Inclusion of final-state screening energy differences between surface and bulk atoms is discussed within the framework of a more quantitative description of the SCS. General consideration of the effects responsible for the modified surface band structure, i.e., reduced coordination number and the resulting redistribution of charge between and within the s,p and d bands, allows our model to be extended to the transition metals and allows apparently different theoretical explanations of the SCS to be unified within a single picture. The special case of those rare-earth metals in which narrow corelike f levels appear close to the Fermi energy is also discussed. Our previously described measurements and analytical procedures are compared with other recently reported surface-atom core-level studies, and all experimental results are compared with self-consistent and semiempirical thermodynamic calculations. Generally encouraging qualitative agreement is obtained, particularly the sign of the SCS which changes from element to element across the Periodic Table. Quantitative agreement is most lacking for the more-open single-crystal surfaces and for the metals near the ends of the transition series. Finally, the closely related photoemission experiments from small metal-atom clusters (akin to supported catalysts) have been reinterpreted. Consistency between these and the present results is obtained, provided that a proper reference level is employed.

I. INTRODUCTION

In the preceding paper[1] we reported on surface-atom core-electron binding-energy shifts and surface-atom valence-band narrowing for the noble metals, completing a study which was partially presented in 1978.[2] That first publication of an incontrovertible surface-atom core-level shift (SCS) and a narrowed surface density of states (DOS) laid to rest the question[3–11] whether surface-atom photoemission from clean metals can be experimentally distinguished from bulk photoemission. A number of other publications have since provided (i) examples of a SCS in transition,[12–14] rare-earth,[15–18] and free-electron-like[19] metals, (ii) demonstrations of surface orientation[13,14,20] and adsorbate effects[12,21–24] on the SCS, and (iii) theoretical interpretation of these shifts based on thermodynamic[25–28] and band-structure[29–31] considerations. As a result there now exists a large body of work which has transformed surface-atom effects from a hypothetical concept into a well-established experimental fact of photoemission. At the same time, however, there still exists confusion over the exact nature of the SCS: Are different mechanisms responsible for the SCS in the simple, noble, transition, and rare-earth metals? How does the SCS relate to the surface DOS in these systems? What is the role of final-state screening in the interpretation of the SCS?

In the present paper we provide a unified interpretation of the available data and of the various theoretical models and show how they are related to the modification of the band structure of the surface. We also critically compare our results and analysis procedures reported in the preceding paper[1] with earlier and subsequent surface-atom core and valence photoemission experiments (including work on semiconductors) and point out areas for future development and improvement. Finally, the closely related surface-atom photoemission experiments on supported small-atom clusters are reinterpreted and shown to be consistent within our unified picture provided the appropriate reference level corrections are made.

II. OUR MODEL FOR THE SCS: QUALITATIVE EFFECTS

A. Noble metals

We start our discussion with the expectation that initial-state electron binding energies of atoms in the surface of a metal should be intermediate between those in the bulk and those in the free atom. The effect of final-state screening of the core hole by the metal conduction electrons, which always lowers the measured bulk binding energy with respect to that of the free atom, is discussed later. Another effect associated with the photoemission measurement process, which will be discussed in Sec. IV C, is the difference in reference levels between the two systems, viz., the vacuum level for the free atom versus the Fermi level for the metal. Our focus on the initial state will be shown to be essential for an appropriate description of the SCS phenomenon. The recognition of the reference level corrections will become important when comparison between the free atom and the bulk are made.

Since we assume that surface-atom properties are intermediate between those of the free and bulk atoms, it is instructive to consider the total energy involved in going from the free-atom state to the bulk. This is the cohesive energy, which has been calculated by a variety of methods. From a heuristic point of view we consider the approach of Gelatt *et al.*[32] who partition the calculation for the 3*d* and 4*d* transition metals into five computationally expedient terms: (i) the reconfiguration energy required to excite the atom from its ground state into the configuration it will adopt in the metal, (ii) the renormalization energy required to compress the reconfigured atomic orbitals into the appropriate Wigner-Seitz radius, (iii) the conduction-band energy gained by allowing the free-electron-like *s,p* charge to broaden into a band, (iv) the *d*-band energy gained when the *d* electrons form a band, and (v) the *s*-*d* hybridization energy gained by mixing the *s* and *d* bands. For reference later on in this section we write this explicitly as

$$E_{\text{coh}} = \Delta_{\text{config}} + \Delta_{\text{norm}} + \Delta_{s\text{ band}} + \Delta_{d\text{ band}} + \Delta_{s\text{-}d\text{ hybrid}} \cdot \tag{1}$$

With this decomposition it is easy to see how the reduced coordination number for the surface atoms (relative to the bulk) leads to narrower, more atomiclike *d* bands with reduced *s*-*d* hybridization and an overall average configuration intermediate between those of the free and bulk atoms. For free atoms of the noble metals the configuration is $d^{10}s^1$, whereas in the bulk solid it is $d^{10-x}s^{1+x}$. For noble-metal surface atoms the configuration should then be $d^{10-y}s^{1+y}$, with $y < x$. The delocalized *s* and *d* bulk states, which are of bonding character, are reduced for the surface atoms and the more localized *d* states, which are of nonbonding and antibonding character, are enhanced. Thus the noble-metal surface atoms are expected to contain a greater fraction of *d* states (relative to *s* states) and are expected to be less bound than the bulk.

We can arrive at this conclusion in another way. In the hypothetical state *A* (left) of Fig. 1(a) we show a schematic noble metal DOS, solid line, and the corresponding narrowed surface DOS, dashed line. This represents an intermediate state in which we have allowed the surface-atom bands to narrow, but have not allowed charge transfer to occur between the bulk and surface layers. The core-electron binding energies remain essentially unchanged at this point because the effects of changes in the radial extent of the *d* states and of redistribution of charge between the *s* and *d* states are small. The major effect of the band narrowing is to drop the Fermi level of the surface bands below that of the bulk bands. In order to restore equilibrium and bring the Fermi levels back into coincidence, see Fig. 1(b), a small amount of charge must flow into the surface bands. The Coulomb potential of this charge raises the energy of *both* the surface-atom bands and the surface core levels by comparable amounts. The charge required to bring the Fermi levels into coincidence is only a small fraction of the empty surface density of states below E_F^b in Fig. 1(a). As a result, the deviation from layerwise charge neutrality is small. This is in agreement with conclusions based on other theoretical arguments[33] and with results of self-consistent calculations.[34] From this model we again arrive at the conclusion that the noble-metal surface atoms contain a greater fraction of *d* states, are less bound than in the bulk, and have core-level binding energies intermediate between those in the free and bulk atoms.

We can directly test the validity of our simple model[2] by comparing the *measured* difference in centers of gravity of the surface and bulk DOS with the *measured* $\Delta_{s,b}$. In previous work[1,2] we determined for polycrystalline Au that $\langle\epsilon\rangle_s - \langle\epsilon\rangle_b = -0.5\pm0.1$ eV, which should be compared with the experimental $\Delta_{s,b}$ $(\equiv E_B^s - E_B^b)$ of -0.4 eV. A self-consistent calculation[35] for surface and bulk DOS and core-level energies in Cu{111} also agrees with this trend, i.e., $\langle\epsilon\rangle_s - \langle\epsilon\rangle_b = -0.4$ eV, $\Delta_{s,b} = -0.6$ eV. The similarity in sign and magnitude is therefore taken as strong support for the dominance of initial-state effects. Further *empirical* evidence for our assertion[2] that differences in final-state screening energies are less important in deter-

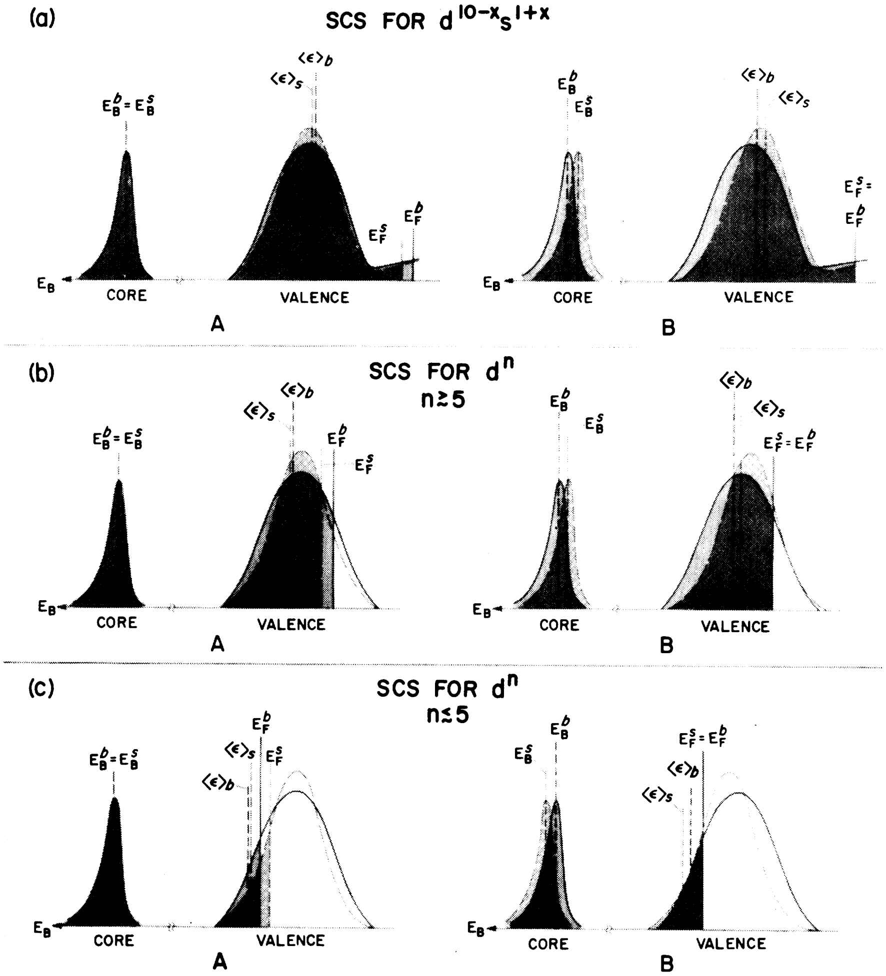

FIG. 1. Model for explaining the surface-atom core-level (SCS) for (a) noble metals and transition metals with (b) more than and (c) less than half-filled d bands. s and b denote surface and bulk. In hypothetical state A (left) the Fermi level E_F^s of narrowed surface DOS (dashed line, lightly shaded) falls below or above bulk Fermi level E_F^s due to layerwise charge neutrality. Core-level binding energies E_B for surface and bulk atoms in state A are the same. In true state B (right) Fermi levels of surface and bulk DOS are the same and core-level binding energy for surface atoms falls above or below bulk-atom binding energy. Centers of gravity $\langle \epsilon \rangle$ for surface and bulk DOS have shifts of similar magnitude and sign as corresponding core-level binding energies.

mining $\Delta_{s,b}$ is given by the experimentally indistinguishable Doniach-Šunjić line shapes[36] (containing the final-state electron-hole-pair tail) of the surface and bulk components for Au.[1,2]

In subsequent sections we will discuss theoretical calculations of $\Delta_{s,b}$ in transition metals which offer additional support for the predominance of initial-state effects. At this point, however, it is worth clarifying our view regarding the relative importance of the initial- versus final-state effects. Although we have so far focused on the former, we are by no means ruling out the possibility that there are also differences in final-state relaxation energies between surface and bulk atoms. Indeed, it could (and will) be argued that some differences *must* exist. Generally speaking, on the basis of their narrower conduction bands we would expect the relaxation energy for the surface atoms to be *smaller* than that for the bulk, not larger as calculated by Laramore and Camp.[37] A very recent calculation by Smith *et al.*[38] of the final-state relaxation energy for surface Cu{100} atoms gives results which support this view. The effect of a smaller final-state surface relaxation energy is to *increase* the measured surface-atom core-level binding energy, i.e., to make $\Delta_{s,b}$ positive, whereas experimentally the noble metals (as well as several other metals to be discussed) are found to exhibit a *decreased* surface core-level binding energy, i.e., a negative $\Delta_{s,b}$. For this reason, and the fact that the experimentally observed variation in sign of $\Delta_{s,b}$ in different metals is little effected by such final-state effects (see next section), we maintain that it is the differences in *initial-state* properties which are primarily responsible for the observed sign and magnitude of $\Delta_{s,b}$.

In the most general terms for any metal, then, our model predicts that for an SCS to be experimentally observable *there must be a center-of-gravity shift between the bulk and surface DOS.* Metals in which this criterion should be most readily met are those undergoing a redistribution of surface valence charge at the Fermi level which can be felt by the core levels. In metals with only free-electron-like (s,p) bands, e.g., alkali and alkaline earth metals, Al, Sn, Pb, etc., the narrowing of the conduction band would not be expected to be very large due to the large number of unfilled and highly delocalized states available for rehybridization. Consequently, only a small SCS would be predicted for these metals.[2] (This expectation has been very recently confirmed for Na, Mg, and Al.[19]) In a tight-binding metal, however, the unfilled states are considerably reduced in number and are more localized. Note that for $\Delta_{s,b}$ to be sizable the Fermi level should ideally lie within some portion of the tight-binding valence band. Metals in which the tight-binding bands do not participate in the bonding, e.g., Zn, Cd, and Hg, are thus predicted to have a small $\Delta_{s,b}$.[2] A naive application of this criterion to the nominally filled d bands in the noble metals might suggest that they, too, should have $\Delta_{s,b}=0$. However, the noble-metal d bands are not completely filled by virtue of their s-d hybridization, i.e., they do indeed participate in the bonding. On this basis it is easy to see why the absolute magnitudes of $\Delta_{s,b}$ in the noble metals follow the trend $\mathrm{Au} \gtrsim \mathrm{Cu} \gg \mathrm{Ag}$ (from Ref. 1, -0.40, -0.24, and -0.08 eV, respectively): The s-d hybridization is significantly smaller in Ag relative to Cu and Au because of its more tightly bound d bands.

From the measured $\Delta_{s,b}$ values of Cu, Ag, and Au, two important conclusions can be established. First, trends in the *initial-state* bonding are seen to be responsible for the trends in $\Delta_{s,b}$. Second, it is not *solely* the redistribution of delocalized to localized d states which accompanies the SCS but it is *also* the redistribution of s (and p) states into d states which ultimately occurs. Thus, with respect to the bulk, *all* the terms in Eq. (1) are modified for surface atoms. We will see below that these conclusions bear weight in the interpretation of the SCS in transition metals and of the core-level shifts observed in small metal-atom clusters.

B. Transition metals

Using the qualitative principles of our model in the preceding section it is straightforward to extend it to the transition metals. The only difference now is that because the average number of d electrons per atom is no longer fixed (~ 10) as in the noble metals, the center-of-gravity shifts between bulk and surface DOS need not be of the same sign. For less than half-filled d bands $\langle \epsilon \rangle_s - \langle \epsilon \rangle_b$ is *positive*, whereas for more than half-filled d bands $\langle \epsilon \rangle_s - \langle \epsilon \rangle_b$ is *negative* (as in the case of the noble metals). The core levels of the surface atoms feel this change in potential and are accordingly pulled either up or down in binding energy with respect to the bulk. This is schematically illustrated in Figs. 1(b) and 1(c) and is in all respects analogous to the arguments presented above and in Fig. 1(a). The extension of our model for the noble metals[2] to the transition-metal series in explaining their SCS trend in terms of a center-of-gravity shift has been made explicitly by Feibelman and co-workers[29,30] and later by Desjonquères *et al.*[31]

Still another way of describing the trend in $\Delta_{s,b}$ is in terms of the differences between Hartree-Fock core-level eigenenergies of free and bulk atoms.[2,29,30] Denoting the free atom, the surface atom, and the bulk atom by a, s, and b, and the one-electron Hartree-Fock core-level eigenenergies by ϵ_c, we have

$$\Delta_{s,b} \propto \Delta_{\text{eigen}} \;, \tag{2}$$

where

$$\Delta_{\text{eigen}} \equiv \epsilon_c^a - \epsilon_c^b \;. \tag{3}$$

Depending on whether the d band is less or more than half-filled the *surface*-atom eigenvalue ϵ_c^s is either greater or smaller than the corresponding bulk atom value ϵ_c^b. Comparison with the free-atom eigenvalues ϵ_c^a follows the trend bulk→ surface →atom, i.e., $\epsilon_c^b > \epsilon_c^s > \epsilon_c^a$ or $\epsilon_c^b < \epsilon_c^s < \epsilon_c^a$. The qualitative success of one-electron eigenvalues[29,30,35] in predicting the trend of binding-energy differences $\Delta_{s,b}$ across a transition-metal series again confirms the greater importance of initial-state effects.[2]

The physical explanation underlying the trend in $\Delta_{s,b}$ for transition metals is actually *identical* to that given for the noble metals, although casual inspection of the two might make it appear otherwise. In both cases the surface atoms have fewer neighbors than the bulk so, invoking layerwise charge neutrality, the charge density per bond is greater for the surface atoms. The increased localization of charge results in either an increase or decrease in overall bonding for the surface atoms with respect to the bulk depending upon whether the previously bulk-like delocalized charge is of bonding or (non-) antibonding character. For d^n transition metals with $n \gtrsim 5$ the additionally localized charge in the surface bonds is antibonding so the surface atoms are less bound; for $n \lesssim 5$ the reverse is true. The noble-metal surface atoms are also less bound because of their greater localization of (non-) antibonding charge. The difference between transition and noble metals is that for transition metals the increased localization of d charge appears to be accomplished *solely* by a reduction of d banding in the surface layer—corresponding to $\Delta_{d\text{ band}}$ in Eq. (1)—while for noble metals the increased localization of d charge appears to be accomplished by a reduction of d banding and by an electronic reconfiguration and reduction of s-d hybridization in the surface-layer terms $\Delta_{d\text{ band}}$, Δ_{config}, and $\Delta_{s\text{-}d\text{ hybrid}}$ in Eq. (1). Since the effects of electronic reconfiguration and reduced s-d hybridization at the surface seem unnecessary to explain the trend in $\Delta_{s,b}$ for the transition-metal atoms it might be inferred[31] that this effect does not also occur for those atoms and that, because of this, the mechanism responsible for the SCS in the noble metals is therefore different. It should be obvious, however, that it is the *sum total* of all the terms in Eq. (1) which is modified for surface atoms regardless of whether the atoms are from noble or transition metals. It is only because the noble-metal d shell is nominally filled that the additional effects of reduced s-d hybridization [redistribution of delocalized (s,d) charge to localized (s,d) charge] and modified electronic configurations seem more apparent (renormalization and s-band modifications, of course, also occur). Arguments for electronic reconfiguration of transition-metal surface atoms are clear. The atomic configuration of Ti, for example, is $3d^2s^2$, whereas in the bulk it is $3d^{2+x}s^{2-x}$. The surface-atom configuration must be intermediate, i.e., $3d^{2+y}s^{2-y}$, where $x > y$. Similarly, evidence for the occurrence of s-d hybridization modifications in transition-metal surface atoms can be seen by comparing the results of a model DOS calculation for bulk Ti with and without s-d hybridization, cf. Figs. 3(e) and 3(f) of Ref. 32, with the results of a self-consistently calculated surface and bulk DOS for Ti, cf. Fig. 1 of Ref. 29. The striking similarity between the calculated *surface* DOS with s-d hybridization[29] and the *bulk* DOS without s-d hybridization[32] demonstrates that the s-d hybridization at the surface is, as expected, actually reduced. We thus see that the principal driving mechanism responsible for the SCS, i.e., localization of surface-atom electron density, as well as the other effects which necessarily accompany this, i.e., electronic renormalization and reconfiguration, s-band and s-d hybridization modifications, occur for *both* noble and transition metals.

III. OTHER MODELS AND CALCULATIONS OF THE SCS: QUANTITATIVE RESULTS

A. General models

In the preceding section we focused on the initial-state factors which determine $\Delta_{s,b}$ and their qualitative magnitudes in going across the Periodic Table. While these factors have been discussed in terms of changes in d banding, s banding, s-d hybridization, and electronic redistribution, they can also be conveniently grouped in terms of chemical and configurational origin. This is just the language used by Williams and Lang[39] in their calculation of free-atom—bulk-atom core-level binding-energy shifts, $\Delta_{a,b}$. Since our goal in this section is to discuss $\Delta_{s,b}$ in more quantitative terms it is tempting to describe it using their theory. These authors express the total core-electron binding-energy shift between a free atom and that atom in the bulk by

$$\begin{aligned}\Delta_{a,b} &\equiv E_B^a - E_B^b \\ &= [E^a(n_c-1) - E^a(n_c)] \\ &\quad - [E^b(n_c-1) - E^b(n_c)] \\ &= \Delta'_{\text{config}} + \Delta_{\text{chem}} + \Delta_{\text{relax}} ,\end{aligned} \tag{4}$$

where

$$\Delta'_{\text{config}} = E_B^a - E_B^{a'} \tag{5}$$

and

$$\Delta_{\text{chem}} = \epsilon_c^b - \epsilon_c^{a'} . \tag{6}$$

Here a, a', and b denote the free atom, the electronically reconfigured free atom as it would be in the bulk, and the bulk solid, respectively, E_B is the core-level binding energy, ϵ_c is the core-level eigenenergy, and $E(n_c)$ is the total energy as a function of the number of electrons in that core level. The term Δ_{relax} accounts for the readjustment of valence charge in the solid upon production of a core hole in the final state. It is important to note that Δ'_{config} in Eq. (4) is not the same as Δ_{config} of Eq. (1) because the former looks at differences in total energy between two differently configured free atoms with and without a core hole (i.e., differences in free-atom binding energies), whereas the latter looks at differences in total energy between two differently configured atoms in their initial state only, i.e.,

$$\Delta_{\text{config}} = E^a(n_c) - E^{a'}(n_c) . \tag{7}$$

The SCS value, $\Delta_{s,b}$, which we have argued in the preceding section is accompanied by configurational changes between surface and bulk atoms in their initial state, is therefore *not* represented by Δ'_{config}. By the same token, because Δ_{chem} in Eq. (6) is not the same as Δ_{eigen} in Eq. (3), but is, rather, defined as a consequence of Eqs. (4) and (5), $\Delta_{s,b}$ is also *not* represented by Δ_{chem}.[40] We thus see that the terms used in the theory of Williams and Lang,[39] while useful for describing core-level binding-energy differences between bulk and free atoms, are of little value in describing binding-energy differences between bulk and surface atoms. The principal reason for this is that the effects of the core hole in the final state have been implicitly included in both Δ'_{config} and Δ_{chem}, whereas $\Delta_{s,b}$ is due to effects that are predominantly initial state in origin.

An entirely different approach which captures the essence of the effects responsible for $\Delta_{s,b}$ has been given by Johansson and Mårtensson (JM).[25] These authors begin with a description of the free-atom—bulk-atom binding-energy difference, as did Williams and Lang, but use empirical rather than calculated quantities. They construct a Born-Haber cycle from the following energies: (1) the cohesive energy E^{Z}_{coh} required to remove an atom of atomic number Z from the bulk metal, (2) the binding energy E^{a}_{B} required to remove a core electron from that atom, (3) the screening energy I^{Z^*} gained by neutralizing that atom with a core hole (denoted by an asterisk), (4) the cohesive energy $E^{Z^*}_{\text{coh}}$ gained by reassembling such atoms to form a metal, and (5) the energy $E^{\text{imp}}_{Z^*}(Z)$ gained by dissolving one of these impurity metallic sites into the original host metal Z. The sum of these terms is just the energy $E^{b}_{B}(F)$ required to move a core electron from an atom in a bulk Z metal to the Fermi level, and thus the free-atom—bulk-atom binding-energy difference is

$$\begin{aligned}\Delta_{a,b} &= E^{a}_{B} - E^{b}_{B}(F) - \phi_B \\ &= I^{Z^*} + E^{Z^*}_{\text{coh}} - E^{Z}_{\text{coh}} - E^{\text{imp}}_{Z^*}(Z) - \phi_B \ , \end{aligned} \tag{8a}$$

where ϕ_B is the work function of the bulk metal. By assuming that an unscreened Z^* atom with a core hole can be replaced by a $Z+1$ atom with an outermost valence hole (the equivalent-cores approximation) and by assuming that the screening electron occupies the lowest unoccupied valence state (the excited-atom approximation), it is possible to approximate the fully screened core-ionized Z^* atom by the neutral $Z+1$ atom. The term I^{Z^*} then becomes the first ionization potential $I^{Z+1}_{(Z)}$ and the term $E^{Z^*}_{\text{coh}}$ becomes the cohesive energy E^{Z+1}_{coh}, leading to

$$\Delta_{a,b} \simeq I^{Z+1}_{(Z)} + E^{Z+1}_{\text{coh}} - E^{Z}_{\text{coh}} - E^{\text{imp}}_{Z+1}(Z) - \phi_B \ . \tag{8b}$$

Except for the impurity term which is more poorly established but is also comparatively small in magnitude,[25] all the terms in Eq. (8b) involve purely empirical energies. A similar expression for the free-atom—surface-atom binding-energy shift can now be derived, giving

$$\begin{aligned}\Delta_{a,s} &= E^{a}_{B} - E^{s}_{B}(F) - \phi_B \\ &= I^{Z+1}_{(Z)} + E^{Z+1}_{\text{coh,surf}} - E^{Z}_{\text{coh,surf}} - E^{\text{imp,surf}}_{Z+1}(Z) - \phi_B \ , \end{aligned} \tag{9}$$

where $E^{Z}_{\text{coh,surf}}$ is the surface cohesive energy of the Z metal and the impurity term is the solution energy of the $Z+1$ impurity at the surface of the Z metal. Finally, JM use the empirical observation from liquid-surface tension data that the surface and bulk cohesive energies are related by

$$E_{\text{coh,surf}} \approx 0.8 E_{\text{coh}} \tag{10}$$

to obtain [along with the assumption of a similar relationship for the impurity terms in Eqs. (8) and (9)]

$$\begin{aligned}\Delta_{s,b} &\equiv E^{s}_{B} - E^{b}_{B} = E^{s}_{B}(F) - E^{b}_{B}(F) = \Delta_{a,b} - \Delta_{a,s} \\ &\approx 0.2[E^{Z+1}_{\text{coh}} - E^{Z}_{\text{coh}} - E^{\text{imp}}_{Z+1}(Z)] \ . \end{aligned} \tag{11}$$

Ignoring the last term in brackets (it has been shown to be negligible),[25] Eq. (11) simply states that $\Delta_{s,b}$ is about 20% of the difference between two thermodynamical quantities.

In Figs. 2–4 we have plotted, with small circles connected by a solid line, the calculated $\Delta_{s,b}$ values[41] using Eq. (11) (ignoring the impurity term) for the $3d$ and $4d$ series, as well as for the $5d$ series already reported by JM. The dashed lines at the beginning and end of each series indicate the inapplicability of Eqs. (10) and (11) because the cohesive energy is no longer represented primarily by d electron interactions (see discussion below). For the $5d$ series we see that with d bandfilling the sign of $\Delta_{s,b}$ changes at about $d=5$ as discussed in the preceding section (the sign change actually occurs at less than $d=5$ because the real d bands are not symmetric). The trends of $\Delta_{s,b}$ across the $3d$ and $4d$ series are not monotonic because the approximated surface tensions [introduced by Eq. (10)] do not follow a parabolic dependence with Z.[42] This results from the Coulomb correlation energies, which are largest for the $3d$ metals and are essentially absent for the $5d$ metals.

The obvious advantages of using a simple expression containing empirical values [thereby automatically incorporating several competing effects, viz., Eq. (1)] is counterbalanced by the possible ambiguity in interpreting the reasons for its success. JM have maintained that it is the bonding versus (non-) antibonding character of the *screening charge in the final state* which determines the trend in $\Delta_{s,b}$ across the transition series, whereas we have argued that it is predominantly the bonding versus (non-) antibonding character of the *initial-state charge in the narrowed surface density of states* which is responsible. To shed light on this question let us consider in somewhat greater detail the physical meaning of the terms in Eqs. (8)–(11). Explicitly, we expand Eq. (11) (again ignoring the impurity terms), to get

$$\Delta_{s,b} \simeq [E^{Z+1}_{\mathrm{coh,surf}} - E^{Z+1}_{\mathrm{coh}}] - [E^{Z}_{\mathrm{coh,surf}} - E^{Z}_{\mathrm{coh}}] \tag{12a}$$

$$\simeq [E^{Z+1}_{\mathrm{coh,surf}} - E^{Z}_{\mathrm{coh,surf}}] - [E^{Z+1}_{\mathrm{coh}} - E^{Z}_{\mathrm{coh}}] \; . \tag{12b}$$

Because the cohesive energy differences in Eq. (12) involve the $Z+1$ atom, which is obtained (approximately) by creation of a core hole in the photoemission final state, JM argue that it is this state which determines the overall trend of $\Delta_{s,b}$. The analysis given below leads to a different conclusion.

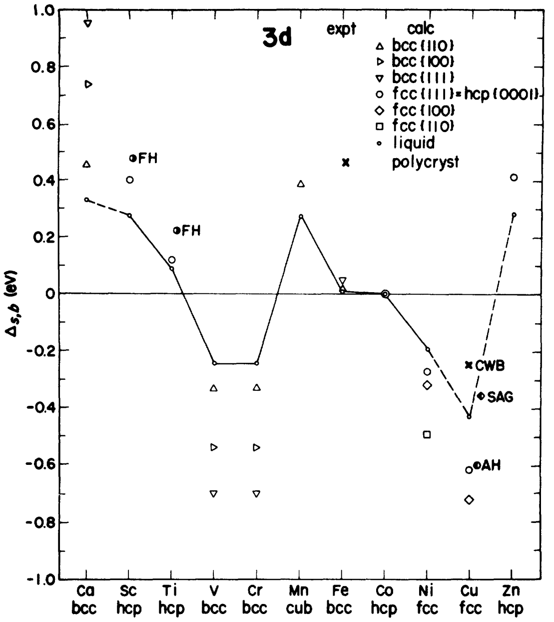

FIG. 2. Calculated and experimental values of surface-atom core-level shift, $\Delta_{s,b}$, for 3*d* transition-metal series. Small circles connected by solid line are from Eq. (11), Ref. 25. Open geometrical shapes are from Ref. 28. Neither of these calculations are applicable in dashed region of series. Other calculations indicated by half-filled symbols: AH: Ref. 35; FH: Ref. 30, SAG: Ref. 38. Experimental results: CWB: Ref. 1.

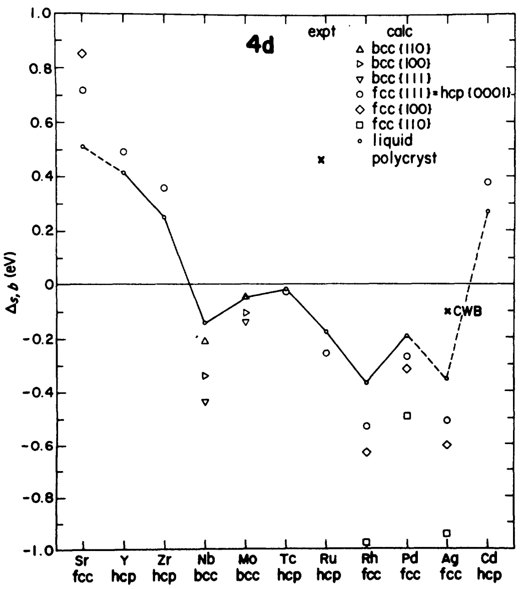

FIG. 3. Calculated and experimental values of surface-atom core-level shift, $\Delta_{s,b}$, for 4*d* transition-metal series. Small circles connected by solid line are from Eq. (11), Ref. 25. Open geometrical shapes are from Ref. 28. Neither of these calculations are applicable in dashed region of series. Experimental results: CWB: Ref. 1.

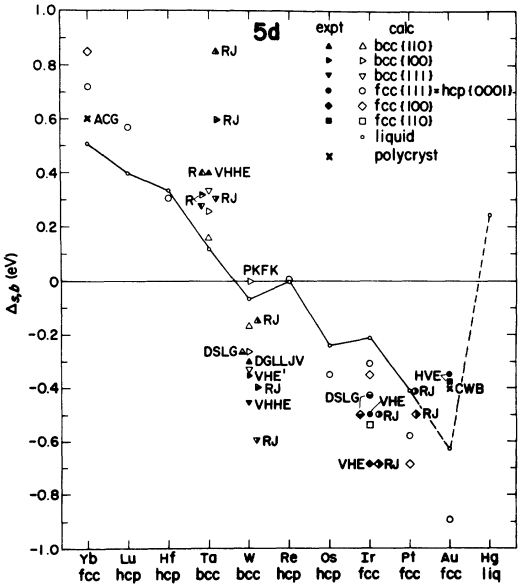

FIG. 4. Calculated and experimental values of surface-atom core-level shift, $\Delta_{s,b}$, for 5*d* transition-metal series. Small circles connected by solid line are from Eq. (11), Ref. 25. Open geometrical shapes are from Ref. 28. Neither of these calculations are applicable in dashed region of series. Other calculations indicated by half-filled symbols: RJ: Ref. 26; DSLG: Ref. 31; PKFK: Ref. 50; R: Ref. 27. Experimental results: CWB: Ref. 1; DGLLJV: Ref. 12; VHE: Ref. 13; ACG: Ref. 15; HVE: Ref. 14; VHHE: Ref. 20; VHE′: Ref. 23.

The cohesive energy differences in Eq. (12) represent differences in total energy between two states, much the same as core-electron binding energies represent differences in total energy between two states. However, the fact that one of those states contains a core hole does not imply that it alone is responsible for the trend in E_B. To see this, recall that the one-electron core eigenenergy ϵ_c (i.e., the "frozen-orbital" or Koopmans's theorem energy) also represents differences in total energy between two (frozen) states, which can be related to the actual E_B by inclusion of a correction term, E_R, the orbital relaxation energy, i.e.,

$$\begin{aligned} E_B &= E(n_c-1)-E(n_c) \\ &= E'(n_c-1)-E(n_c)-E_R \\ &= \epsilon_c - E_R \; . \end{aligned} \tag{13}$$

Here, we are using the notation of Williams and Lang in Eq. (4) and use the prime to denote that the orbitals have been kept frozen in the presence of the core hole. If we write Eq. (13) in the notation of JM, we obtain

$$E_B = E'(Z^*)-E(Z)-E_R \; . \tag{14a}$$

With the use of the equivalent-cores approximation and, for metals, the excited-atom approximation, this is simply

$$\begin{aligned} E_B &\simeq E(Z+1)^{+1}-E(Z) \quad \text{(atom)} \\ &\simeq E(Z+1)-E(Z) \quad \text{(metal)} \; . \end{aligned} \tag{14b}$$

Depending on Z and the core level involved, E_R can range between ~5% and ~0.5% of E_B for free atoms; for bulk metals E_R is larger due to the additional relaxation (screening) of the conduction electrons.[43] The point here is that the final-state relaxation energy is typically only a small fraction of E_B for core electrons; it is actually the *initial-state* one-electron eigenvalue containing the total (frozen-orbital) energy of the Z^* state which primarily accounts for E_B.

Now the fact that Eq. (12) uses cohesive energies to approximate core-level binding energies or that differences of differences are being used does not weaken the above arguments. From Eqs. (13) and (14) we have

$$\begin{aligned} \Delta_{s,b} &= E_{\mathrm{B}}^s - E_{\mathrm{B}}^b \\ &= [\epsilon_c^s - \epsilon_c^b] - [E_R^s - E_R^b] && (15) \\ &= [E'^s(Z^*)-E^s(Z)]-[E'^b(Z^*)-E^b(Z)] \\ &\quad -[E_R^s - E_R^b] && (16) \\ &\simeq [E^s(Z+1)-E^s(Z)] \\ &\quad -[E^b(Z+1)-E^b(Z)] \; . && (17) \end{aligned}$$

The first term in brackets in Eq. (15) represents differences in the initial state, the second term differences in the final state. As we have argued in Sec. II A and in our initial work[2] on the basis of (i) measured surface and bulk photoemission line shapes (they are similar), (ii) measured values of $\Delta_{s,b}$ (they are often negative), (iii) measured surface and bulk DOS center-of-gravity shifts and $\Delta_{s,b}$ (they are of comparable sign and magnitude), and (iv) a purely initial-state model relating these latter two quantities, the second term in brackets in Eq. (15) is small relative to the first. This then implies that the first two terms in brackets in Eq. (16) are approximately equal to the respective terms in Eq. (17), which in turn means a corresponding near-equivalence with the terms in brackets in Eq. (12b). [Note that the terms within the brackets are clearly different, e.g., $E_{\mathrm{coh,surf}}^{Z} \neq E^s(Z)$, etc.] By neglecting the small final-state relaxation energy differences between surface and bulk atoms, we see that the success of using cohesive energy differences (which are approximately equal to frozen-orbital eigenvalue differences[44]) rests on the fact that the SCS is primarily an initial-state effect.

Several additional points are worth noting here. Inspection of Eq. (16) shows why Eq. (2) is valid: Differences between surface and bulk one-electron eigenvalues, which are intermediate between differences of atomic and bulk eigenvalues, clearly dominate the sign of $\Delta_{s,b}$. The qualitative signs and magnitudes of $\Delta_{s,b}$ will be seen in Sec. IV A to be correctly predicted for various metals using Eq. (15) with the assumption that $E_R^s = E_R^b$. For a quantitative description of $\Delta_{s,b}$, however, Eqs. (16) and (17) show that the many-electron final-state differences between surface and bulk atoms must be included. Use of empirical cohesive energies in Eq. (11) automatically incorporates these final-state differences, explaining why it is so successful despite the crude approximation of Eq. (10).

Although this section deals with general models rather than specific calculations (see next section), the above discussion of final-state relaxation energies makes our reference to a recent calculation by Smith *et al.*[38] more appropriate here. These authors considered the effect of final-state relaxation energy differences in Cu{100} by calculating not only the bulk and surface core-electron eigenvalues but also the total energy of the bulk- and surface-atom transition states E_{TS}^b and E_{TS}^s, which were assumed to approximate experimentally measured binding energies E_B^b and E_B^s. Specifically,

$$\Delta_{s,b} \approx E_{\mathrm{TS}}^s - E_{\mathrm{TS}}^b \tag{18}$$

$$= (\epsilon_c^s - \epsilon_c^b) - (E_R^s - E_R^b) \; . \tag{15}$$

Smith *et al.*[38] subtracted $(\epsilon_c^s - \epsilon_c^b)$ from $(E_{\mathrm{TS}}^s - E_{\mathrm{TS}}^b)$ to get $(E_R^s - E_R^b)$; for Cu{100} these values are, respectively, -0.66, -0.36, and $+0.30$ eV. Their calculations thus directly support our arguments above that the relaxation energies for surface atoms should be smaller than for the bulk and that the dominant effect in determining the nature of the SCS is found in the initial state.

The average surface tension of a liquid can only provide an approximate value for the configuration of surface atoms in a single crystal, so the model of JM using Eq. (10) must be modified to make it more quantitatively applicable to single-crystal data. Rosengren and Johansson[26] have taken calculated surface tensions for a variety of crystal orientations and, using calculated bandwidths and bandfillings, related these to the surface energies E_S, where $E_S = E_{\mathrm{coh}} - E_{\mathrm{coh,surf}}$. From Eq. (12) of the JM model (again ignoring the impurity term), this gives simply

$$\Delta_{s,b} = E_S^{Z+1} - E_S^Z \ . \tag{19}$$

Despite the possible inaccuracies in each of the absolute E_S values for the Z and $Z+1$ atoms, their difference is expected to be more reliable because of cancellation of similar errors. In Fig. 4 we show (with the symbol RJ) the calculated $\Delta_{s,b}$ results using Eq. (19). Only part of the 5*d* series is shown because the surface tensions of the metals at the beginning and end of the series are, as calculated, zero. Also, no calculations of the {110} fcc or any of the hcp orientations were reported. The most striking feature to be noted in Fig. 4 is the sensitive dependence of the calculated $\Delta_{s,b}$ on crystal face and crystal structure. The largest calculated $\Delta_{s,b}$ values are predicted for the {111} surfaces of bcc metals which have the fewest surface atoms per unit area. Comparison of these results with experiment is deferred to Sec. IV A.

The work of Rosengren and Johansson[26] relied on tight-binding calculations of E_S. The limitations of such calculations and their likely breakdown for more open surfaces led Rosengren[27] to consider a more reliable way of calculating E_S. Semiempirically accounting for the number of broken bonds on a particular surface, he calculated $\Delta_{s,b}$ for the first, second, and third layers of the {111}, {100}, and {110} surfaces of W and Ta. His results for the first layer are shown in Fig. 4 with the symbol R. A similar semiempirical approach has also been recently reported by Tománek *et al.*[28] Using heats of vaporization and assumptions closely related to those made by JM, these authors considerably simplified and extended the bond-breaking model to include $\Delta_{s,b}$ for almost all of the 3*d*, 4*d*, and 5*d* metals and their different surfaces. Their results are shown in Figs. 2–4 as open geometrical shapes for the various crystal orientations. As with the JM model, the calculations are not expected to be valid at the beginning and end of the series. Tománek *et al.* have also calculated $\Delta_{s,b}$ for the first and second layers of clean and H-covered Ta{111} and W{111} surfaces as well as stepped Ir{332} surfaces. The trends of $\Delta_{s,b}$ seen in Figs. 2–4 are, not surprisingly, very similar to those found using the approach of JM because of the close relationship between metal cohesive energies and heats of vaporization, but the results now take into account different crystal surfaces. These calculations are also compared with experiment in Sec. IV A.

Desjonquères *et al.*[31] have reported on the $\Delta_{s,b}$ for the transition-metal series. The basic physics underlying their model, viz., the preservation of layerwise charge neutrality of the narrowed surface density of states by alignment of the surface and bulk layer's Fermi levels, is just that given by us in our initial work[2] and in the preceding section. These authors, however, emphasized the importance of the mechanism by which the surface-atom core levels actually experience a change in electrostatic potential $\Delta n e^2/R$, where Δn is the very small but finite transfer of charge from the surface to subsurface (bulk) atom layer and R is the effective radius of the *d* states. Because this charge transfer is so small (typically $\lesssim 0.1e$) the concept of layerwise charge neutrality (more rigorously, quasineutrality) is still valid, but it is this small deviation from strict neutrality which actually brings about the surface-atom core-level shift. With the assumption of strict layerwise neutrality, earlier tight-binding surface-potential calculations[45] for selected crystal structures and surface orientations of the 5*d* metals were reexpressed in terms of *d*-level bandfilling and used to demonstrate the trend in $\Delta_{s,b}$. The strong similarity between purely initial-state calculations, see Fig. 4, and the results[25] calculated from surface energies using Eq. (14) is again clear supporting evidence that $\Delta_{s,b}$ is predominantly of initial-state origin[2] [Desjonquères *et al.*[31] also showed a connection between their model and that of JM (Ref. 25)].

B. Specific calculations

In this section we very briefly summarize the most recent results of DOS and core-level eigenvalue calculations for a variety of transition- and noble-metal surfaces. Only those results which are self-consistent (SC) and which allow for comparison with experimentally determined surface DOS and surface-atom core-level shifts are mentioned. A more complete description of various SC as well as non-self-consistent (NSC) surface electronic calculations has been recently given by Arlinghaus *et al.*[46]

SC calculations of transition- and noble-metal surfaces have been reported for the {100} surfaces of Nb,[47] Mo,[48] Cu,[38,49] W,[50] Ni[51] and Pd,[52] the {111} surfaces of Pd (Ref. 34) and Cu,[35] and the {0001} surfaces of Ti (Refs. 29 and 30) and Sc.[30] Rather than discuss the individual calculations and their findings (see Sec. IV A for comparison with experiment), we make the following observation. Despite the many differences between the particular metal surfaces and the methods used to calculate the surface band structures (pseudopotential, Gaussian expansion local orbital, numerical basis set), the results all exhibit three common features.

(1) The band structure of the surface layer is found to be substantially narrowed and different from that of all other layers, with the second and third layers being similar to the bulk.

(2) Through orbital population analysis the narrowing of the surface layer is seen to be accomplished by a redistribution of the bonding d charge at the lower portion of the d band into the (non-) antibonding states at the upper portion of the d band. This enhanced density of states near or at the Fermi level (which also comprises the surface state and resonance *structures* measured in angle-resolved photoemission work because they are resolvable only at symmetry points and lines along the Brillouin zone) is thus made up from states previously involved in bonding to bulk nearest-neighbor atoms and is primarily of d-like character.

(3) The total amount of charge transferred [both from delocalized d to localized d states and from localized (sp,d) to localized d states] is found to occur almost completely within the surface layer, thereby accounting for the essentially overall neutrality of that layer and each successive layer.

All of these features were present in the model for $\Delta_{s,b}$ in our initial study of Au (Ref. 2) and in Sec. II A above.

Surface-atom core-level shifts $\Delta_{s,b}$ have been calculated self-consistently only for the surfaces of Cu{111},[35] Cu{100},[37] Ti{0001},[29,30] Sc{0001},[30] and W{001}.[46] These values are, respectively, -0.6, -0.36, $+0.22$, $+0.48$, and 0 eV, and are included in Figs. 2–4. The model presented in Ref. 2 and the preceding section argued that for a SCS to be observed there must also be a corresponding center-of-gravity shift in the surface DOS. Only for the Cu{111} surface has this quantity been calculated,[35] -0.4 eV, which is close to the calculated $\Delta_{s,b}$ of -0.6 eV.

To calculate the center-of-gravity shift the *total* density of states, i.e., the filled and unfilled portion of the band, must be known for the surface and bulk layers. In metals of $d \lesssim 5$, the unfilled portion lies too high in energy above E_F to make such calculations reliable as a means for further testing the validity of this correlation. Although the center-of-gravity shift the Pd{111} surface had not been reported,[34] its width was calculated and so it should also be possible to determine the center-of-gravity shift (i.e., the first moment). This would be particularly useful in predicting $\Delta_{s,b}$ for the surface since a core-level eigenvalue cannot be readily obtained from the pseudopotential method used in that calculation.

IV. OTHER PHOTOEMISSION WORK FROM CLEAN METAL-SURFACE ATOMS

A. Surface-atom core-level shift

As mentioned in the Introduction of the preceding paper,[1] the expectation that metal atoms in the surface should be distinguishable from those in the bulk prompted numerous attempts to detect core-electron binding-energy shifts in a variety of metals. The systems chosen included the pure metals Ti, Cr, and Ni,[3] Cu,[5], Au,[10] W,[7,8] Ru,[7] and Al, Ni, and In,[11] as well as small-atom clusters (treated separately in Sec. IV C). The pure-metal studies gave generally negative results. The identification of a SCS for Au and the model advanced to explain its origin[2] have helped to define the criteria for observing a sizable SCS in other metals and clarify the reasons for these earlier negative findings.

(a) High resolution is essential because the magnitude of $\Delta_{s,b}$ is typically no larger than ~ 0.5 eV.

(b) Long-lived core levels should be used to facilitate the resolution of the surface and bulk photopeaks.

(c) The small magnitude of $\Delta_{s,b}$ dictates that the surface and bulk components be measured from the same sample under the same experimental conditions to avoid spurious energy shifts.

(d) Surface sensitivity should be enhanced to help distinguish the surface signal from the bulk photoemission.

(e) The metal under study should ideally have a narrowed and shifted surface DOS (with respect to the bulk DOS) containing orbitals of tight-binding character.

In the remainder of this section we summarize the work on clean metals in which a SCS has been observed and compare the results with the theoretical models and calculations presented in Sec. III B.

Although the $4f$ levels of W had been studied almost as extensively as those of Au, the existence of a SCS for W had gone unnoticed until Duc *et al.*,[12] resolved the surface and bulk W $4f$ components from W{110}. Using synchrotron radiation and very high energy and angular resolution at surface normal detection, $\Delta_{s,b}$ was measured to be -0.30 eV. With p polarization, the surface-component intensity was actually greater than that of the bulk. The surface intensity decreased when using s-polarized radiation and decreased upon exposure to H_2 and O_2, results typically associated with valence-band surface states. Interestingly, the surface-to-bulk intensity ratio varied periodically with changing photoelectron kinetic energy, suggesting a diffraction phenomenon similar to that seen for adsorbate core photoelectrons. Finally, a slight broadening of the surface photopeak line shape was noted (0.22 versus 0.19 eV), consistent with the broadening reported for the noble metals.[1] Such broadening could be of lifetime origin, as has been suggested by Hertel and Pfuff[53] for free-electron metals, or alternatively of phonon origin as tentatively suggested in Ref. 1. Very high energy resolution and temperature-dependent studies are required to resolve this question.

The observation of a SCS in the Ir $4f$ levels from Ir{111}, Ir{100}-(1×1), and Ir{100}-(5×1) was used to test the correlation between surface-atom structures and surface-atom binding energies and intensities. van der Veen *et al.*[13] fitted their measured spectra assuming identical surface and bulk line shapes[2] and found $\Delta_{s,b}$ values of -0.68 eV for the metastable {100}-(1×1) surface and -0.49 and -0.50 eV for the {100}-(5×1) and {111} surfaces, respectively. These values are internally consistent with the strictly tight-binding s-band prediction[54,55] that the bandwidth is simply proportional to $\sqrt{z}$, where z is the coordination number (this concept is further discussed in Sec. IV B). Since in a tight-binding metal the core levels experience the same electrostatic potential as does the valence band, the narrowing of the surface DOS for different surfaces should simply be $\Delta'_{\{100\}}/\Delta'_{\{111\}}=[1-\sqrt{z_{\{100\}}/z_b}]/[1-\sqrt{z_{\{111\}}/z_b}]$, where $z_b=12$ for the bulk and $z_{\{100\}}=8$ and $z_{\{111\}}=9$ for the surfaces. The good agreement between the calculated and measured ratios suggested that the SCS could be used for structural analyses of surface layers. Additional support for this possibility was obtained from the agreement between measured surface-to-bulk intensity ratios and empirically determined λ values. Heimann *et al.*[14] also measured various surfaces of Au and these show a much weaker correlation between $\Delta_{s,b}$ and surface structure. Specifically, the quoted $\Delta_{s,b}$ values are -0.35, -0.35, -0.38, and -0.28 eV for the Au {111}, {110}-(2×1), {100}-(1×1), and {100}-(5×20) surfaces, respectively. The authors report[14] that they attempted to fit Doniach-Šunjić (DS) line shapes[36] to their background-subtracted Au data but that a simple Lorentzian proved sufficient. Our own analyses[1] consistently give better fits to unmodified data using DS functions, and give smaller $\Delta_{s,b}$ values for fits using pure (unphysical) Lorentzians. Our somewhat larger value of -0.40 eV for polycrystalline Au was attributed by Heimann *et al.*[14] to be due to the sampling of "edge" atoms. However, this suggestion is incompatible with the fact that the surface-atom binding energies were found to be insensitive to takeoff angle (see Table I in Ref. 1).

van der Veen *et al.*[20] have also measured $\Delta_{s,b}$ in Ta and W and quote values of -0.43 eV for W{111}, -0.35 eV for W{100}, and $+0.40$ eV for Ta{111}. Furthermore, they report to have separated first- and second-atom layer components from the bulk. The quoted $\Delta_{s,b}$ values for the second layers of W{111}, W{100}, and Ta{111} are -0.10, -0.13, and $+0.19$ eV, respectively. The analyses of the W and Ta data require critical examination. From the fits it is apparent that the model function used in these analyses is unable to represent the complete range of data, particularly for Ta, because of non-negligible deviations in the low- and high-binding-energy regions of the photopeaks. These deviations indicate that inappropriate values are being used for the lifetime width Γ and the asymmetry parameter α, e.g., for W α was found to be zero,[20] which is unphysical. The choice of these values can be traced[1,56] in part to the assignment, via background subtraction, of most of the high-energy tail to extrinsic inelastic losses (their contribution should be negligible within 1—2 eV from the main peak[1,56]). If the unmodified data were fitted with smaller Γ and larger α values the intensities and positions of the surface components would undoubtedly be altered. As discussed in the Introduction in Ref. 1, attempts to extract unresolved components, e.g., second-atom layer surface peaks, are reliable only if the fits are compatible with the data to within their statistical uncertainty. This is not to say that there is reason to doubt the presence of a second-layer surface components in the data, especially for the open {111} surfaces of bcc metals. The H adsorption experiments (most notably for Ta) provide good evidence that more than one surface peak is present.[20,24] The issue raised here is the reliability of the physical parameters for unresolved subsurface components in the data for *clean* surfaces. The values obtained may depend sensitively on the fitting procedures and on the quality of agreement between the fitted line and the data over their entire range. Thus, while the magnitudes of the first-atom layer shifts reported by van der Veen *et al.*[20] appear to be sound, the quantitative values for the second-layer components are less compelling in view of the details of the analyses.

In Figs. 2—4 we have entered the currently available first-atom layer $\Delta_{s,b}$ data from this work and those reported for polycrystalline and single-crystal metals of the 3*d*, 4*d*, and 5*d* series. These experimental values are compared with the self-consistently calculated $\Delta_{s,b}$ values, with the semi-empirical thermodynamics values, and with each other.

The most reliable calculations should be the self-consistent ones. Unfortunately, of the five that are available for comparison, experimental data exist for only one. The W{111},[20] W{110},[12] and W{100} (Ref. 20) experimental results show negative $\Delta_{s,b}$ values, whereas the calculated value for W{100} (Ref. 50) is 0 eV. Our experimental value for polycrystalline Cu (Ref. 1) is less than half that calculated for Cu{111}.[35] Only for the case of Cu{100} (Ref. 38) is there reasonably good agreement with our measurement (polycrystalline Cu should consist primarily of {111} and {100} surfaces). Since the initial-state eigenvalue difference between surface and bulk atoms for Cu{100} is -0.66 eV, which is close to the corresponding calculated value of -0.6 eV for Cu{111},[35] the improved agreement with experiment is most likely due to the inclusion of the $+0.30$-eV final-state relaxation energy difference. If we generalize this result to conclude that all metals have a similarly small but uniformly positive contribution to their initial-state calculated eigenvalues, then the disagreement for W{100} between theory[50] and experiment[20] is worsened and the calculated $\Delta_{s,b}$ values for Sc and Ti are increased even more positively. Without knowledge of experimental $\Delta_{s,b}$ values for Sc and Ti and without calculations analogous to those of Ref. 38 for these systems it is not possible to assess the generality (which we believe is reasonable) of a small and positive final-state screening correction to all metals. From Eq. (15), however, we can conclude that while initial-state effects determine the qualitative sign and magnitude of $\Delta_{s,b}$, the small size of their absolute values requires that the still smaller (but comparatively non-negligible) final-state screening effects must be included for a more complete quantitative description.

The next most reliable calculations should be those of Rosengren and Johansson,[26] of Rosengren,[27] and of Tománek *et al.*,[28] which are derived from calculated surface energies. Here there are corresponding data for comparison, with the agreement ranging from fair to excellent depending on the metal, the surface, and the calculation. Since these calculations are extensions of the JM model, which already includes final-state screening effects (see preceding section), no uniformly positive *ad hoc* corrections should be applied as above. Generally speaking, all of the calculations[26–28] appear to overestimate the magnitude of $\Delta_{s,b}$ for the transition metals, particularly for the open crystal faces. The only exceptions lie in the excellent agreement between theory and experiment for Ta (Refs. 20 and 26) and Ir (Refs. 13 and 27).

The calculations of JM (Ref. 25) might have been thought to be on weakest ground because they are derived from empirical bulk cohesive energies and liquid-surface tension data [Eqs. (10) and (11)]. However, the agreement with the existing data, though not quantitative, is not that much worse than that seen for the other calculations. In fact, considering the simplicity of Eq. (11), the use of purely empirical values, and the qualitatively correct predictions in both sign and magnitude of $\Delta_{s,b}$ in going across the transition-metal series [particularly near the ends of the series where Eqs. (10) and (11) do not apply] the agreement with the experimental results can be regarded as wholly satisfactory.

In addition to the work on the transition metals, experimental efforts to observe a SCS in free-electron-like metals have also been made. Eberhardt *et al.*[57] looked at evaporated films and single crystals of Al (and Au) and reported a 0.1—0.2-eV symmetric broadening for the Al $2p$ photopeaks with increasing surface sensitivity. A similar broadening for the Al $L_{2,3}$ absorption edges taken by partial yield was also observed, suggesting that the broadening is not an artifact. The authors have considered a number of possible explanations for this broadening, and propose that a crystal-field splitting of 0.065 eV for the $2p_{3/2}$ component may be responsible. Whatever the explanation, they claim that this effect is a general one based on a similar symmetric broadening observed in their Au $4f$ data. We point out, however, that while these authors' observations for the Al $2p$ data are qualitatively consistent with ours[1] (we observed a somewhat smaller broadening), their symmetrically broadened Au $4f$ results are at odds with the asymmetric broadening observed by us[1,2] and by Heimann *et al.*[14] The Au $4f$ linewidths measured by Eberhardt *et al.*[57] are actually broader than those obtained by us with poorer resolution, which leads us to conclude that their Au $4f$ data contain some extraneous broadening. Recent partial yield measurements of Chiang and Eastman[58] for Al{100} reported a much smaller symmetric broadening (not determined) and a $\Delta_{s,b}$ value of -0.057 ± 0.007 eV. The $\Delta_{s,b}$ value in this latter work[58] is of the same sign but is smaller than that calculated by Lang[59] and by Wimmer *et al.*,[60]

-0.120 eV. Independent surface-sensitive photoemission data from Al{100} (Ref. 19) were very recently reported to be compatible with either a surface component shifted -0.12 eV from the bulk or a single symmetrically broadened bulk component. Using Eq. (19),[26] $\Delta_{s,b}$ values of -0.120 and 0.003 eV were also calculated[19] for Al{100} and Al{111}, respectively. The agreement between this semiempirically calculated Al{100} value[26] and the other independent calculations[59,60] is striking. Also remarkable is the fact that essentially no SCS for Al{111} is predicted by Eq. (19) and no broadening of the Al $2p$ data with increasing surface sensitivity was observed.[19] This, along with the results of Wimmer *et al.*[60] in which a second-atom layer $\Delta_{s,b}$ value of -0.050 eV is calculated, suggests to us that the observed symmetric broadening of the Al{100} photoemission data[19,57] is likely due to a combination of first- and second-layer shifts. The small magnitude of these shifts (which may be somewhat smaller than calculated due to small differences between surface and bulk final-state relaxation energies) precludes quantitative evaluation of possible crystal splitting (Wimmer *et al.*[60] calculated this to be 0.038 eV). In addition to Al $2p$ data, surface-sensitive Na and Mg $2p$ photoemission data were obtained[19] from which $\Delta_{s,b}$ values of 0.22 and 0.14 eV were reported.

Changes in the electronic structure at the surface and the concomitant core-level shifts have also been observed in rare-earth metals and intermetallics. Attention typically focuses on the $4f$ electrons, which are corelike in radial extent but valencelike in binding energy. The $4f$ energy levels are less than 0.1 eV in width, with successive levels separated by a Coulomb correlation energy of 6—7 eV. If the $4f$ level is well removed from the Fermi level, there is no opportunity for charge redistribution among the orbitals of surface atoms. The major phenomenon at the surface is a narrowing of the $5d\,6s$ conduction band which contains two or three electrons in the elemental metals.

Looking back through the literature it is interesting to note that shifted surface contributions were observed before they could be confidently identified as such. Perhaps the clearest example of this is found in Yb. The $4f$ electrons of this metal were studied with synchrotron radiation by Alvarado *et al.*[15] From evaporated or scraped samples prepared in ultrahigh vacuum, two well-resolved components split by 0.6 eV were observed, with the intensity of the higher binding-energy line varying with surface sensitivity. The authors originally attributed the higher-lying $4f$ component to contamination, presumably in the form of an oxide. Johansson and Mårtensson[25] subsequently argued against such an assignment: (1) For a given energy the intensity ratio of the components was the same for different samples, (2) the ratio remained constant for several hours in the ultrahigh vacuum, and (3) the impurity component, which would most likely be Yb_2O_3, was ruled out because no trivalent Yb was observed. An alternative explanation, consistent with the above observations, is that the extra component represents an inherent property of the clean Yb surface, i.e., a SCS. This assignment was strengthened by the prediction of $\Delta_{s,b}$ for Yb from Eq. (11) (Ref. 25) whose sign and magnitude are in very good agreement (see Fig. 4) with the observed splitting between bulk and surface species. The identification of a SCS in Yb has recently been made.[16]

Kammerer *et al.*[17] have recently reported shifts of the $4f$ level in two other rare-earth metals with stable valence, e.g., Eu and Gd. Both have the $4f^7$ configuration, with $4f$ binding energies of ~ 2 and ~ 8 eV. The final-state multiplet structure is spread over only ~ 0.5 eV, making it easy to detect split-off surface components. In Eu, the surface $4f$ level is resolved from the bulk in the ultraviolet photoelectron spectroscopy (UPS) spectra. In Gd only a broadening relative to less surface-sensitive x-ray photoelectron spectroscopy (XPS) spectra is observed. There is no charge flow into the $4f$ state. In fact, the SCS is readily understood in terms of the narrowing of the conduction band which raises the Fermi level relative to the core levels. Since the Fermi level of the surface is pinned to that of the bulk, the net result is a depression of the core-electron levels, increasing the initial-state binding energy. This is exactly the mechanism described above for the noble and transition metals. The shifts reported for evaporated Eu and Gd metals are 0.63 and 0.48 eV, respectively.

Gerken *et al.*[18] have made similar studies of all the rare-earth metals. Data for evaporated Dy in the 40 to 100 eV photon energy range show a superposition of two similar but shifted multiplet spectra with relative intensities which identify the one with greater binding energy as a surface signal. For evaporated Tb and Dy the quoted $\Delta_{s,b}$ values are 0.51 and 0.53 eV, respectively. The available data suggest that $\Delta_{s,b}$ will be ~ 0.5 eV for the trivalent rare earths, and ~ 0.6 eV for the divalent metals. The experimental results for the trivalent metals are consistently larger than the theoretical estimates of Johansson[61] who obtained values in the 0.3 to 0.4 eV range.

If the $4f$ level lies just above E_F in the bulk, then the changes at the surface can have more dramatic effects. These were first observed in Sm (Refs. 62 and 63) and $YbAu_2$,[64] and may be described as a valence transition in which the surface atoms gain one *f* electron. The initial indications of this phenomenon came from the observation of both divalent and trivalent components in the Sm 3*d* and 4*d* spectra,[62] but it was the later study of angle-dependent core-level data which showed that the divalent component resides only in the surface layer.[63] Because of surface roughness effects at the larger takeoff angles, it had not been established whether the surface is fully divalent or mixed valent. Further work using lower-energy synchrotron radiation[65,66] and higher-energy resolution[67] showed that the lowest energy $^6\mathrm{H}_{5/2}$ multiplet lies well below the Fermi energy ($\sim$0.8 eV), thereby ruling out homogeneous mixed-valence behavior. At this point it seems likely that the surface of Sm is fully divalent.

The explanation for the unusual surface phase transition[63,68] in Sm is found in its unique electronic structure. Like most rare-earth metals, Sm is divalent as a free atom ($4f^6 6s^2$) and trivalent in the metal ($4f^5 5d\, 6s^2$), but unlike all the other rare earths the empty 4*f* level of bulk Sm lies only 0.46 eV above E_F (Ref. 67) in the unoccupied part of the 5*d* conduction band. Any perturbation which raises E_F by this amount will therefore cause electrons to flow into the 4*f* level. Such a perturbation is provided by the reduced coordination number of the atoms which narrows the *d* band. The population of the previously unfilled $4f^6$ state at the surface produces a localized lattice expansion, which in turn leads to further narrowing of the 5*d* band. This valence instability of the surface results in a complete conversion to the divalent state, whose core-electron binding energy is 7.6 eV lower than that of the trivalent state. This value corresponds to a unit change in valence and should not be compared with the $\Delta_{s,b}$ values of the metals discussed above. However, only the existence of a nearby unfilled discrete state distinguishes the surface atoms of Sm from those of the other metals. We thus reemphasize that it is the initial-state narrowing of the density of states at the surface which is primarily responsible for the difference between surface and bulk core-level binding energies.

Another manifestation of the surface phase transition in Sm was found in a recent valence-band study[69] of small particles of Sm supported on amorphous carbon. The data show a clear increase in the $\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}$ ratio with coverage which was ascribed to mixed-valence behavior. We note, however, that the data show that the divalent multiplets lie well below E_F at all coverages, thereby ruling out the existence of homogeneous mixed valency. A more likely explanation is that the particles consist of a divalent surface layer surrounding a trivalent core. Homogeneous mixed-valence behavior in Sm, if it exists at all, must be restricted to particles consisting of only a few atoms.

Finally, there is a third class of rare-earth materials, one in which the 4*f* level is pinned at E_F which results in a fluctuating homogeneous mixed-valence system. Narrowing of the 5*d* band at the surface raises E_F, causing an electron to flow into the 4*f* level. Generally, the effect is strong enough to push the surface into the stable lower valence state. This phenomenon has been seen in a number of materials including YbAu_2,[64] SmB_6,[65] YbAl_2,[70] YbAl_3,[71] and TmSe.[72] It is probably present in all mixed-valence materials, and poses a significant problem in surface-sensitive studies. It seems safe to generalize the results on rare-earth metals and their compounds with the prediction that they will all have a positive $\Delta_{s,b}$ of $\sim$0.5 eV, and that intermediate valence systems will have divalent surface layers.

B. Surface density of states

The intuitive expectation that core-electron binding energies of surface atoms should be energetically different from those of the bulk goes hand in hand with the expectation that the surface DOS should be narrower than that of the bulk. Using a strictly tight-binding *s*-band model, Cyrot-Lackmann[54,55] predicted that the root-mean-square width of the surface DOS will be narrower than the bulk by $1-\sqrt{z_s/z_b}$, where z_s is the coordination number of the surface atom. The DOS for the $\{111\}$, $\{100\}$, and $\{110\}$ surfaces of an fcc metal, for example, are predicted by this model to be narrowed by about 13%, 18%, and 24%, respectively. Such large effects should be readily observable in surface-sensitive photoemission spectra. Following the work of Cyrot-Lackmann numerous theoretical treatments of surface DOS and their narrowing have appeared,[73] but as of this writing relatively little experimental work in this area has been reported and the extant work leads to a number of unresolved questions. In this section we briefly summarize these experimental studies and compare their findings with the work reported in the preceding paper[1] and with relevant surface DOS calculations. (Experimental surface DOS from evaporated small-atom clusters are discussed in Sec. IV C.)

The metal most thoroughly studied with the intent of demonstrating surface versus bulk DOS behavior is copper. Various NSC calculations of the $\{111\}$, $\{100\}$, and $\{110\}$ surfaces have been reported,[33,74] followed by SC calculations for the $\{100\}$ (Ref. 49) and $\{111\}$ (Ref. 35) surfaces. Experimentally, the DOS of Cu has been measured by angle-resolved photoemission from polycrystalline and single-crystal surfaces using He*I*,[75] Al*K*α,[5] and synchrotron radiation sources.[76] There are notable differences between the various calculations, between experimental results, and between theory and experiment. The NSC calculations of Kleinman and co-workers[33,74] for many-layer (≥ 30) films of $\{111\}$, $\{100\}$, and $\{110\}$ surfaces do not show a concentration of surface-state bands at the top of the d band. In fact, they show a decrease of surface DOS near the top of the d band relative to the bulk. This should be contrasted with the nine-layer $\{111\}$-film SC calculation of Appelbaum and Hamann[35] and the 11-layer $\{100\}$-film SC calculation of Gay *et al.*[49] which both show a significant surface DOS enhancement in this energy region. Except for the earlier three-layer $\{100\}$-film calculation of Gay *et al.*,[49] all the NSC and SC calculations have shown a narrowed surface DOS, with the narrowing resulting from the transfer of varying amounts of states density from the lower part of the d band to portions of the upper part of the d band. In view of the fact that the *distribution* of surface-state structure varies between the different calculations it is clearly not meaningful to discuss a d-band width in terms of a full width at half maximum (FWHM). A better measure is the square root of the second moment,[54,55] which should be used for making comparisons between different calculations or between experiment and theory. Another difference between NSC and SC calculations is the position of the top of the d band with respect to E_F. The largest difference is seen for the $\{100\}$ surface, where the NSC calculations of Abbati *et al.*[77] show the d-band edge of the surface DOS to be further from E_F than that of the bulk, whereas the SC calculations of Gay *et al.*[49] show the d-band edge of the surface and bulk DOS to be essentially the same.

On the experimental side, the azimuthal- and polar-angle-resolved photoemission study by Stöhr *et al.*[76] of the Cu $\{100\}$ and $\{111\}$ surfaces reported d-band narrowing for both surfaces as the polar-emission angle was reduced from 0° to 55°. The data were taken with synchrotron radiation at 90 eV, an energy region in which spectra still show the effects of the unoccupied band structure. Furthermore, because the data were angle resolved and were measured from single crystals, only a limited region of k space was sampled in the initial and final states. These facts considerably complicate the interpretation of the observed narrowing in terms of an initial-state effect as discussed in the preceding sections. The approximate agreement between the 35°-$\{100\}$ data and the surface DOS calculations of Gay *et al.*[49] may thus be fortuitous, particularly in view of the lack of similar agreement between the 35°-$\{111\}$ data and the surface DOS calculations of Appelbaum and Hamann.[35]

Comparison of azimuthal-angle-resolved data with angle-integrated calculations requires averaging over many azimuthal angles. This can be accomplished either by accepting data within a large solid angle or by studying samples randomly oriented, i.e., polycrystalline samples. Kowalczyk[75] has looked at azimuthal- and polar-angle-resolved photoemission from evaporated Cu films using He*I* radiation. A narrowing of the DOS was observed which was consistent with both SC calculations of the $\{100\}$ and $\{111\}$ surfaces.[35,49] Nevertheless, the significance of the unoccupied band structure in the final state and the importance of refraction at grazing emission angles (particularly at low photon energies) again make quantitative comparison with theory difficult.

The most ambitious attempt to observe surface DOS narrowing and compare it with theory was reported by Mehta and Fadley[5] (MF) in a polar-angle-resolved XPS study of polycrystalline Cu films. Their approach differed from our work for Au (Refs. 1 and 2) in several ways. The resolution of the analyzer used by MF was between 3–4 times lower and was angle dependent. To compensate for the latter problem the raw data were broadened to uniform effective instrumental resolution. A theoretically calculated escape depth was used to weigh the surface DOS calculations of Kleinman and co-workers[33,74] in the comparison between theory and experiment. Finally, to minimize the contribution of the bulk DOS, polar angles close to 90° were used. No attempt was made to separate the surface and bulk DOS. There are a number of additional observations regarding the results of MF. The corrected calculations of Kleinman *et al.* appear to agree best in qualitative shape with the data of MF for the $\{110\}$ and $\{100\}$ surfaces and least well for $\{111\}$ surface, although the $\{111\}$ surface should predominate in the polycrystalline films of fcc Cu. This result is apparently due to the use of NSC calculations; the SC calculations of Appelbaum and Hamann[35] for the $\{111\}$ surface are in better agreement with the observed low-angle data. The narrowing of the experimental DOS was discussed in terms of its FWHM, and a variety of reasons were suggested for the smaller reduction in FWHM than those calculated for the different surfaces. However, better agreement was obtained when MF compared the second moment of their data with that calculated by Kleinman *et al.*[33,74] Good agreement is also obtained if the square root of the second moment is used to compare the narrowing of the data, 10%, with that calculated by Appelbaum and Hamann, 9%.[35] Perhaps the most puzzling feature of this study is the fact that the experimental DOS show essentially no narrowing for polar angles $\lesssim 80°$; almost all the narrowing occurs between ~80°–85°. Even taking into account the fact that the sum of the bulk and surface DOS is measured (thereby requiring grazing angles to observe the surface DOS more clearly), the narrowing of the DOS should nevertheless become apparent at smaller angles. Moreover, because the effects of surface roughness are known to be most severe at grazing angles, the effective sampling of the surface-atom intensity may actually be reduced,[1,2] not enhanced as the angle approaches 90°. There does not appear to be a satisfactory explanation for this observed angular dependence, raising questions about the resolution correction and background subtraction procedures that have been applied to the data.

There have also been attempts to observe valence-band narrowing in Ni,[5] Ag,[9] and Au.[6] The work on Ni was performed by MF using procedures similar to those described above. Fuggle and Menzel[9] used polar-angle-resolved XPS to study single-crystal Ag{110} surfaces and reported a ~0.2-eV narrowing between data taken at $\theta \sim 45^\circ$ and $\theta \sim 86^\circ$. In view of matrix element effects due to the lack of k-space averaging, it is again difficult to assess such data. In a synchrotron radiation study of polycrystalline Au by Chye *et al.*[6] the photon energy was varied to enhance the photoemission surface sensitivity. No valence-band narrowing was found, due in part to insufficient instrumental resolution (0.8 eV) and to the fact that the sum of bulk and surface DOS Au is actually broader than either DOS alone (see below).

The isolation of the surface DOS for Au reported in Refs. 1 and 2 represents an approach that should be more generally explored. Polycrystalline Au was used to average out azimuthal angular modifications in the transition probabilities, but this poses difficulties in comparing the data with surface DOS calculations for specific surfaces. Since no surface DOS calculations exist for Au, we can only examine them in the light of surface DOS calculations for other systems. SC surface DOS calculations of Cu{111} (Ref. 35) and Cu{100} (Refs. 37 and 49) seem most appropriate for comparison since these orientations should predominate on the polycrystalline Au surface and because Cu metal has electronic properties similar to those of Au. Inspection of Fig. 3 in Ref. 2 (or Fig. 4 in Ref. 1) shows that, as predicted for Cu, the center of gravity shift $\langle \epsilon \rangle_s - \langle \epsilon \rangle_b$ and the overall narrowing of the surface DOS is accomplished by a redistribution of states from the bottom to the top of the d band. There is, however, an important difference in the surface DOS of Au; namely, the redistributed charge density does not reside solely near the top of the d band but is, rather, more evenly distributed. Furthermore, the very top of the surface DOS d band does not coincide with that of the bulk DOS d band, as is the case for the calculated Cu{111} and Cu{100} surface DOS. The possibility that both of these observations are an artifact of data analysis cannot be entirely ruled out, but at present this appears to be unlikely in view of the essential absence of angular-dependent instrumental effects demonstrated for the Al $2p$ levels.[1] Further experimental and theoretical work on the Au surface DOS seems necessary in order to understand these observations.

C. Small-atom clusters

One of the direct means for probing differences between surface and bulk metal-atom properties is to study metallic clusters supported by noninteracting substrates. By varying the size of the cluster, the transition from an atomic (finite) to metallic (infinite) system can in principle be observed. Such clusters also represent a close facsimile of the important small-metal particle catalysts. The metals studied to date include Cu,[78,79] Ag,[80,81] Au,[10,82–86] Ni,[78,79] Pd,[78,86,87] and Pt.[87] The substrates used include C,[78,80,81] Al,[10] Gd,[85] Zn,[77] Cd,[86] In,[86] Sn,[86] Sb,[86], Te,[86] Al_2O_3,[10] Gd_2O_3,[85] SiO_2,[86] NaCl,[82] and polymer films.[79]

With the exception of Au on Te,[86] every study has reported an *increased* core-level binding energy, relative to that of the bulk metal, with *decreasing* cluster size. The magnitude of this increase is typically larger than reported $\Delta_{s,b}$ values, ranging between 0.5 1.5 eV. The trend of this increase in binding energy correlates with a decreased valence-band width and with a similar increase in valence-band "threshold" energy, defined[87] as the point of inflection at the top of the band. These results are schematically illustrated in the upper and center panels in Fig. 5, where $E_B(F)$ and $E_T(F)$ are the binding energy and threshold energy *referenced to the Fermi level of the substrate* and the superscripts c and b denote small clustered atoms and bulk metal atoms, respectively. The observation of valence-band narrowing with decreasing particle size is clearly consistent with intuitive expectations, but the corresponding increase in core-level binding energy is, we maintain, certainly not. Mason and co-workers[87] have proposed, on the basis of comparison between calculated atomic configurations and experimental valence bands, that the core-level binding-energy shift is due to changes in the electronic configuration of the atoms in the small clusters. They conclude that the number of d electrons in the small-atom clusters is, in general, *smaller* than that in the bulk. Ag, which is not expected to change its electronic configuration in this way, does indeed exhibit only a small core-level shift.[80] This conclusion suggested[87] a correlation between the density of empty d-electron states and the observed variation in catalytic activity with cluster size.

There are, however, a number of difficulties created by the explanation of Mason *et al.* and, more generally, by the observation of *higher* core-level binding energies for small-atom clusters. All the metals studied thus far have more than half-filled d bands. For these metals $\Delta_{s,b}$ is predicted and observed to be negative, i.e., the surface-atom component has a *lower* core-level binding energy than the bulk. This is opposite to what has been reported for the small-atom clusters. We have argued above that atoms *within* a surface plane would have properties intermediate between those in the bulk and in the free state. We therefore expect the properties of atoms *on* a surface to obey the hierarchy

$$\text{free atom}\rightarrow\text{atom } \textit{on} \text{ surface}\rightarrow\text{atom } \textit{within} \text{ surface}\rightarrow\text{atom in bulk}\ . \tag{20}$$

Moreover, it is clear that the sign and magnitude of binding-energy changes between bulk and surface atoms are determined by the sum of *all* the terms in Eq. (1) and not simply the electronic reconfiguration alone (see Secs. II A and II B). In particular, we have seen that for the noble metals the surface atoms contain *more* d electrons (relative to s electrons) than the bulk atoms while for transition metals the surface atoms contain fewer d electrons (relative to s). Mason *et al.*,[87] however, propose that small-atom clusters contain *fewer* d electrons (relative to s) for both transition and noble metals.

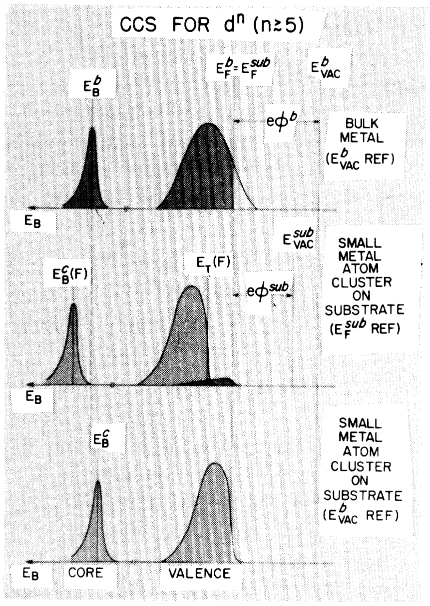

FIG. 5. Model for explaining the clustered-atom core-level shift (CCS) for transition metals with more than half-filled d bands. c denotes small clustered metal atoms evaporated on a substrate (in the limit, single atoms), b denotes evaporated bulk metal on same substrate. Work function $e\phi$ is the difference between Fermi and vacuum levels, E_F and $E_{\rm vac}$. The substrate is assumed to be a conductor and the total-atom cluster coverage (and thus the change in $e\phi^{\rm sub}$) is assumed to be negligible. Substrate conduction electrons, shown in center panel shaded above and below "threshold" energy $E_T(F)$ of metal atom d states, define $E_F^{\rm sub}$. With this reference level the core-level binding energy $E_B^c(F)$ of the cluster is measured at higher binding energy relative to that in the bulk metal. Using the physically meaningful and common reference level $E_{\rm vac}^b$, the core-level binding energy in the cluster E_b^c is actually lower than that in the bulk.

How can these differences be reconciled? In our analysis of the binding-energy difference between core electrons in *bulk* and *surface* atoms we were able to ignore two effects; one was the difference in final-state screening energy and the other was the difference in reference levels. This was justified because differences in final-state screening energy (as inferred from measured line shapes, from measured trends in $\Delta_{s,b}$, and from direct calculations) were shown to be small, and because the reference levels for these two systems are, by definition, identical. These statements do *not* apply to differences between bulk atoms and small-atom clusters evaporated on a foreign substrate. Even if the substrate is a conductor, the final-state screening energy for an adsorbed cluster would be expected to be weaker than in the bulk metal for two reasons. First, the screening within the small-atom cluster must be less effective than in the bulk metal because it is far from the many-body limit, and second, the screening by the substrate is less effective because the average distance of the screening charge is greater than in the bulk metal. For clusters evaporated on insulating substrates the screening should be even weaker. As discussed in the preceding section for bulk and surface atoms, the final-state screening differences between bulk and clustered atoms need not be large on an absolute level, e.g., only several tenths of an eV. However, because the small clustered atoms are more atomiclike than the surface atoms, see Eq. (20), the magnitude of such differences should in general be *larger* than the corresponding surface-bulk final-state screening energy differences, i.e., using the notation of Eqs. (15) and (16), $(E_R^c - E_R^b) > (E_R{}^s - E_R^b)$.

The second effect that must considered, which is independent of substrate conductivity, is the reference level used for core-level binding energies in the bulk metals and surface-atom clusters. For a bulk-metal overlayer the reference level can be either the Fermi level E_F^b, which is pinned to that of the substrate provided the two are in electrical contact, or the vacuum level of the bulk metal E_{vac}^b, which is just the work function of the bulk metal $e\phi^b$ added to E_F^b, see Fig. 5. For very *small* metal-atom clusters, on the other hand, the highest occupied level of the cluster is well defined only with respect to the Fermi level of the substrate E_F^{sub} or its vacuum level $E_{\text{vac}}^{\text{sub}}$. To see this point most clearly consider the case of a single metal atom adsorbed on the surface of a different metal substrate (our discussion also applies to the case of an atom implanted within the substrate). In this dilute limit the localized valence electrons of the impurity atom interact only weakly with the extended conduction electrons of the substrate, and the unoccupied nonbonding and antibonding levels of the atom remain well isolated from its filled valence levels. The substrate Fermi level lies between these filled and unfilled states, i.e., within the impurity "gap" of the atom. As the number of impurity atoms increases the filled and unfilled levels form bands which become raised and lowered, respectively, relative to E_F^{sub}. Eventually enough states are formed to fill the impurity gap and the isolated metal atoms can be thought of as metallic. For the purposes of this discussion we shall define a "small" metal-atom cluster as a group of atoms sufficiently large in number to form "bands" (multiple degenerate levels) but still sufficiently small to be regarded as impurity states containing a gap. This situation is schematically illustrated in the center panel of Fig. 5 where only the filled *d* levels of the cluster are shown. The conduction electrons of the substrate, accented by dark shading and shown much weaker in intensity than the metal overlayer *d* electrons, define E_F^{sub}. (These substrate electrons are usually not shown in the reported data of clustered atoms because they either have been removed by background subtraction or are too weak to observe.)

Now the average internal electrostatic potentials of the impurity atom cluster and of the substrate are the same, but those of the impurity atom cluster and of a single free impurity atom are clearly different. If one were comparing electron binding energies between the free atom and those of the atom cluster, a reference level common to both would be required, in this case the vacuum level. The procedure would simply involve adding the work function of the substrate $e\phi^{\text{sub}}$ to the energies measured from the cluster ($e\phi^{\text{sub}}$ is little affected in the dilute limit of "small" concentrations of adsorbed impurity atoms). If one were comparing free metal-atom and bulk metal-atom binding energies, the analogous procedure would apply, namely add $e\phi^b$ to the measured bulk values. In comparing small-atom cluster binding energies with those of the bulk, however, the choice of the vacuum level reference is no longer obvious. Experimentally it is convenient to reference binding energies to the Fermi level of the sample because the sample's work function is generally unknown or too difficult to measure accurately. These considerations are immaterial, however, if referencing the binding energies to the Fermi level of the sample obscures the physical interpretation of the measurements. As an example, core-level binding energies of small-atom clusters *should* provide information about the electronic configuration of its constituent valence electrons through comparison with corresponding energies of the bulk system. Assuming for the moment that such electronic configuration differences between metal atoms in the bulk and metal atoms in the small clusters were *zero,* then the physics of this situation *should* be reflected by the measured core level binding energies in these two systems being *identical.* However, if the measured binding energies were referenced relative to E_F^{sub} they would in fact be *different* as a result of the difference in work functions (i.e., vacuum levels) between the bulk metal and the substrate.[88] Referring to Fig. 5, this is given simply by

$$E_B^c(F)-E_B^b(F)=e\phi^b-e\phi^{\text{sub}} \; . \tag{21}$$

Inspection of such work-function differences in almost all of the metal-substrate systems studied shows that $e\phi^b > e\phi^{\text{sub}}$. From these results we conclude that the reported observations of $E_B^c(F) > E_B^b(F)$ are largely due to the combined effect of two terms: the *final-state relaxation energy differences and the zero-energy reference level differences between the small metal-atom cluster and the bulk metal systems.*

Let us consider the implications of our conclusion. First, the inconsistency between the small-atom cluster results and those reported in this and other work on surface-atom electron binding energies is essentially removed. Including the previously neglected differences between bulk and surface-atom binding energies as was done in Eq. (21), we define the clustered-atom core-level shift (CCS) by

$$\Delta_{c,b} \equiv E_B^c - E_b^b \; , \tag{22}$$

where E_B implicitly denotes the vacuum level reference. [Note that Eq. (22) is consistent with our definition of the SCS, $\Delta_{s,b} \equiv E_B^s - E_B^b$, even though binding energies referenced relative to E_F have been used throughout in Refs. 1 and 2, because $E_B^s - E_B^b = E_B^s(F) - E_B^b(F)$.] Based on the magnitudes of $\Delta_{s,b}$ reported for a variety of metals and our discussions of them above we know that the sign of $\Delta_{c,b}$ depends primarily upon details of the initial-state properties in the cluster and the metal. In particular, following Eqs. (8)—(11) we have

$$\Delta_{c,b} \approx \chi[E_{\text{coh}}^{Z+1} - E_{\text{coh}}^{Z} - E_{Z+1}^{\text{imp}}(Z)] \ , \tag{23}$$

where, from Eq. (10) and our previous discussion, χ should be $\gtrsim 0.2$. We have shown above that for overlayer metals with $d \gtrsim 5$ the expression in brackets in Eq. (23) is negative, meaning that $E_{\text{coh}}^{Z} > E_{\text{coh}}^{Z+1}$ (the impurity term is negligible). Mason *et al.*[87] considered only the Δ_{config} term in Eq. (1) for describing E_{coh}, i.e., Eq. (7), which in turn was directly correlated with $E_B^c(F) - E_B^b(F)$. It is, however, the sum of *all* the terms in Eq. (1) which describes E_{coh}, and it is not E_{coh}^{Z} but $(E_{\text{coh}}^{Z} - E_{\text{coh}}^{Z+1})$ which should be correlated with $E_B^c - E_B^b$. Note that this latter correlation is simply our restatement of the need to include the differences between bulk and clustered atom *total* energies which necessarily include final-state relaxation energies.[89] Note also that by considering these final-state effects (as well as the appropriate reference levels) we are clearly not ignoring the importance of initial-state differences in general or electronic configuration changes in particular (see Sec. II A). Rather, we are saying that this configurational change is only one of several electronic modifications and that it is a difference between sums of such modifications which ultimately determines the sign and magnitude of $\Delta_{c,b}$. This fact casts doubt on the inference[87] that in all the metals studied the *d*-electron density (relative to the *s*-electron density) in atom clusters is smaller than that in the bulk. The *d*-electron density in the cluster is, in fact, usually smaller for transition metals (and larger for noble metals) but the spatial distribution of this charge is also very different. Thus the proposed correlation between *d*-electron vacancies in small clusters and catalytic activity, while of potential significance, cannot be regarded as the only or most important factor.

The fact that the expression in brackets in Eq. (23) is negative for the metals studied means that E_B^c should be smaller than E_B^b, opposite to the reported trend of $E_B^c(F) > E_B^b(F)$. A reversal in binding-energy trend between two systems due almost solely to differences in their work functions (vacuum levels) has been previously observed for implanted rare-gas atoms[90] where, for example, $E_B^{\text{impl}}(F)$ for Xe implanted in Ag is found to be ~0.7 eV smaller than $E_B^{\text{impl}}(F)$ for Xe in Au, but because $e\phi^{\text{Au}} - e\phi^{\text{Ag}} \approx 1.1$ eV, E_B^{impl} for Xe in Ag is actually ~0.4 eV greater than E_B^{impl} for Xe in Au. Similarly, core-level binding energies of physisorbed rare gases that have been referenced to the substrate Fermi level were observed to change with coverage,[91] whereas when the binding energies are referenced to the vacuum level such changes are markedly reduced. Assuming there is negligible charge transfer between the adsorbed small-atom clusters and the bulk-metal substrate (as in the case of the rare-gas atoms), the effect of the substrate Fermi-level reference can be corrected by adding the quantity $(e\phi^{\text{sub}} - e\phi^b)$ to the difference $[E_B^c - E_B^b(F)]$. With the intent of performing this correction reliably we make the following comments. Only $E_B^b(F)$ of metals evaporated on amorphous carbon or polymer films are considered because (i) carbon is essentially nonreactive with the overlayers under the conditions studied (there is undoubtedly some small degree of charge transfer), (ii) it is a good electrical conductor and thus avoids sample charging and minimizes (but not avoids) final-state screening effects, and (iii) it is the only substrate upon which all metals have been evaporated. Only studies in which the metals were evaporated and analyzed *in situ* are used; the work of Pd and Pt clusters[87] in which the samples were briefly exposed to atmosphere is now believed[86] to be unreliable. The uncertainties in $E_B^c(F)$ have been assigned to be ±0.3 eV [consistent with the most recent measurements[86]; the uncertainty in $E_B^b(F)$ is assumed to be negligible]. Work functions were taken from what we judged to be the most reliable sources, i.e., data taken under high-ultrahigh vacuum conditions from clean polycrystalline samples.[92–94] The quoted work-function uncertainties were weighted with those of $E_B(F)$ to determine the error bars for E_B.

The results of our corrections are shown in Fig. 6, where we have plotted both $E_B^c(F) - E_B^b(F)$ and $E_B^c - E_B^b$ for the various metal overlayers. The overall reversals of sign for these two binding-energy differences is now more consistent with the prediction of Eq. (23). Comparison of the mean absolute magnitudes of $\Delta_{c,b}$ with the $\Delta_{s,b}$ values reported in Ref. 1 for Cu, Ag, and Au shows that $\Delta_{c,b}$ are uniformly ~0.2—0.3 eV smaller. Assuming $\chi > 0.2$ in Eq. (23), these shifts should be somewhat larger. The most obvious explanation for this discrepancy is that some of the atom clusters in these experiments are not sufficiently "small" according to our definition above. An additional likely explanation is that the final-state relaxation energy differences are actually greater than that accounted for in Eq. (23).[95] Taking into account the larger uncertainties in the $\Delta_{c,b}$ values relative to those of the $\Delta_{s,b}$ values, the results shown in Fig. 6 can be viewed as quite acceptable.

Having removed the apparent inconsistencies of some of the evaporated small-atom cluster results on amorphous carbon we briefly mention two related works on other substrates. Abbati *et al.*[77] have evaporated approximately one monolayer of Cu on Zn{0001} and measured the surface DOS with angle-integrated photoemission. A band narrowing was observed along with a ∼1-eV center-of-gravity shift to higher binding energy relative to E_F. This shift compared favorably with their surface DOS calculations which showed a comparable shift in the same direction. Although the authors correctly concluded that their experimental and theoretical results are consistent with the monolayer of Cu having an atomic configuration intermediate between that in the free- and bulk-atom systems, we point out that both experimental and theoretical results are in the opposite direction to those reported here and to SC calculations.[49,96] The most likely explanation for the sign reversal in the calculated surface DOS is that the calculations of Abbati *et al.* are not fully self-consistent, while part of the cause for the reversed sign in the experimental results is due to the choice of the substrate Fermi level as the reference level. Had the vacuum level for Zn been used the shift would be reduced to ∼0.4 eV. The remaining discrepancy is due to unavoidable alloying of the Cu and Zn and additional corrections to the quoted Zn{0001} work function.[92]

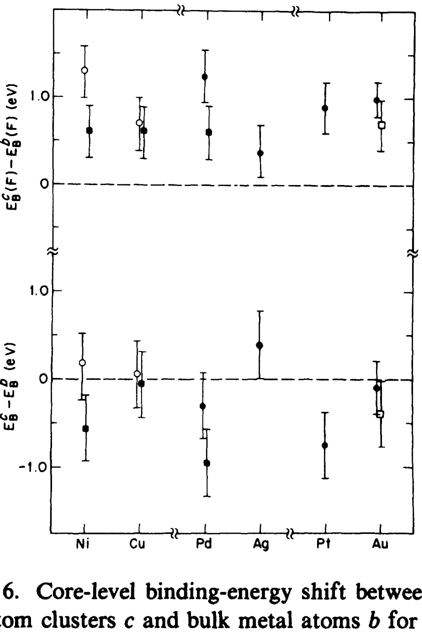

FIG. 6. Core-level binding-energy shift between small metal-atom clusters *c* and bulk metal atoms *b* for various 3*d*, 4*d*, and 5*d* metals evaporated on amorphous carbon. With binding energies referenced to the Fermi level, $E_B(F)$, the sign of the shift is reported positive, see upper half. Correcting this shift by appropriately referencing to common bulk-metal vacuum level, see text and Fig. 5, the sign of the shift is generally negative, see lower half. Open circles: Ref. 79; closed circles: Ref. 86; open squares: Ref. 83; closed squares: Ref. 78.

The second work we wish to comment on is that of Mason.[86] He has recently evaporated small clusters of Au onto Cd, In, Sn, Sb, and Te and measured $E_B^c(F)-E_B^b(F)$ values of 0.7, 1.0, 1.1, 0.2, and −0.5 eV, respectively. The smoothly varying trend of quoted values was correlated with the degree of *d*-band modification due to rehybridization. Without considering the degree to which this process occurs relative to the other effects we have argued should also be considered, we simply note that referencing to the vacuum rather than the Fermi level modifies the above values to −0.2, 0, +0.4, −0.3, and −0.6 eV, respectively. The magnitudes of the $\Delta_{c,b}$ values are now generally smaller and their trend is no longer smoothly varying . In fact, with the exception of In and Sn, the values are comparable to $\Delta_{s,b}$ for pure Au.[2,14]

V. OTHER PHOTOEMISSION FROM CLEAN SEMICONDUCTORS

Although the main subject of this work deals with surface-atom photoemission from clean metals, there have been related studies from clean semiconductors whose results deserve comment here. Eastman *et al.*[97] have identified surface-atom photoemission from cleaved GaAs{110} and GaSb{110} crystals using synchrotron radiation. Additional structures were observed on opposite sides of the anion and cation outermost *d*-level photopeaks, viz., $\Delta_{s,b}=0.28$ eV and −0.37 eV for Ga and As, respectively, and $\Delta_{s,b}=0.30$ eV and −0.36 eV for Ga and Sb. Both $d_{5/2}$ and $d_{3/2}$ components were fitted using pure Lorentzians of equal width for the bulk component and a single surface component.[1,2] The fits are quite good considering the simplicity of the analysis (Gaussian broadening from instrumental resolution and from phonons[98] was assumed to be negligible while Lorentzians, which are appropriate for semiconductors, were used). The origin of the $\Delta_{s,b}$ values was argued by these authors to arise from charge transfer from Ga to As or Sb atoms. Recently, however, Watson *et al.*[99] have questioned the uniqueness of this interpretation, suggesting instead that the observed surface shifts are due to differences between surface and bulk Madelung energies.

Two independent studies of various Si surfaces have been reported.[100,101] Himpsel *et al.*[100] observed shoulders on the $2p_{3/2}$ and $2p_{1/2}$ photopeaks from Si{111}-(2×1), Si{111}-(7×7), and Si{100}-(2×1) surfaces and analyzed the data in several steps. First, the data of Si{111}-(1×1)H were fitted with three Lorentzians of equal width, corresponding to bulk, surface, and subsurface components. Second, these latter two peaks were subtracted from the total line shape to give the bulk position in Si{111}-(1×1)H, which was then assumed to be unchanged in the other three systems. Third, the $2p_{1/2}$ components in the clean surface data were subtracted from the data to isolate the $2p_{3/2}$ components. Finally, the bulk component of Si{111}-(1×1)H was used to fit the $2p_{3/2}$ data of the other surfaces along with three additional surface components of equal shape. The surface and subsurface components in the Si{111}-(1×1)H data were found to be separated by only 0.10 eV and the subsurface component was found to be inexplicably more intense than the surface peak. The quality of the fits was high as expected from the large number of degrees of freedom in the four-line fits. The resulting three surface-peak positions and intensities for each of the three surfaces studied were discussed by Himpsel *et al.* in terms of the most widely accepted models for their reconstruction and were found to be consistent with them. The uniqueness of this analysis was not demonstrated.

Brennan *et al.*[101] also measured additional $2p$ photoemission structure from freshly cleaved Si{111}-(2×1) surfaces. They analyzed both $2p_{3/2}$ and $2p_{1/2}$ components using a three-line fit with 50% Gaussian and 50% Lorentzian line shape, corresponding to one bulk and two surface components. The bulk position was variable as were the total widths of components. The use of line shapes with different Lorentzian width for the various components is, however, at variance with the common lifetime width. The fit to the raw data was good, but as in the study of Himpsel *et al.*,[100] the number of degrees of freedom was quite large. A quantitative comparison between the two sets of results is not meaningful because of the very different data analysis procedures used. Qualitatively, both studies show a higher binding-energy component and both suggest the possibility of a lower one. Interestingly, both data sets were interpreted as being consistent with the widely accepted buckled surface model,[102] a model which has very recently been called into question by Pandey.[103]

The three studies of semiconductor surfaces[93,96,97] have clearly established the existence of distinct surface-atom photoemission, an accomplishment which itself is quite significant. The analyses could, however, be improved by use of more realistic fitting procedures.

VI. SUMMARY

The experimental work which has appeared since the report of a surface-atom core-level shift (SCS) in polycrystalline Au has firmly established this phenomenon as a universal aspect of photoemission spectroscopy. It had remained elusive for so long because the shifts are typically no larger than the width of the response functions of the best instruments that were available. It is ironic that the first two reports of a SCS dealt with Au (Ref. 2) and W,[12] metals which had been widely studied previously. (Because the Au $4f$ lines are so narrow and because of the chemical inertness of Au, it had, in fact, been generally used as a test of instrumental performance.) It is noteworthy that enhancing the surface sensitivity of the photoemission measurements alone did not reveal the surface components (the still narrower W $4f$ lines were extensively studied in this manner); only surface sensitivity with improved instrumental resolution proved successful. There are, however, many cases in which even improved instrumentation is insufficient to observe a SCS because the linewidths are limited by the lifetime of the core hole states. The best examples include the $3d$ group transition elements. It is, nevertheless, possible to obtain information about the SCS using more sophisticated data analysis procedures[1] even when the surface component is not resolved by inspection.

A fundamental question about the SCS, whether it is primarily an initial- or a final-state phenomenon, has been largely resolved in favor of an initial-state interpretation. The best *experimental* input resides in a comparison of the line shapes of the bulk and surface signals. Unfortunately this has not been adequately exploited in the majority of studies of the SCS. Only in the case of Au has an effort been made to establish the shape of the surface signal.[1,2] The conclusion that the shapes are identical within experimental uncertainty implies that the final-state screening is the same. It would clearly be of interest to check this in cases where the bulk and surface signals are better resolved (some differences would not be at all surprising, see below). Further input for an essentially initial-state interpretation lies in the surface density of states, which is the source of the SCS. Only in the case of Au has this fundamental information been obtained and found to be consistent with the core-level shift.[1,2] Again it would be of great interest to investigate other metals in which calculations for n-layer films have made available layer-by-layer densities of states. These show band narrowing in the first atomic layer and much smaller changes for even the second layer. The remaining layers are largely indistinguishable from the bulk, in agreement with photoemission data which, with few exceptions, find that only the first atomic layer is measurably modified. The fact that the change in the band structure at the surface is expected and observed to account for the surface-atom core-level shift is compelling evidence for its predominantly initial-state nature.

A major goal of this work was to provide a clear and unified understanding of the origin of the surface-atom core-level shift. Although the SCS has been explained in a number of ways,[2,25,26,29,31] its origin ultimately lies in the modification of the surface band structure. The reduced coordination at the surface of a metal, in general, causes the *s*, *p*, and *d* conduction bands to narrow and the hybridization between them to decrease, i.e., the bands become more atomiclike. The distributions of *s*-, *p*-, and *d*-derived charge between the bands is thus somewhat different for the surface atoms. The average *total* charge per surface atom, however, remains essentially the same as in the bulk, so (in atomiclike terms) the electron density per surface bond is increased. In metals with only one band at or near the Fermi level the distribution of charge at the surface is not significantly altered. If that single band is less than half-filled, meaning the charge is of bonding character, the increase in surface-atom charge density results in an increase in core-electron binding energy. If the band is more than half-filled, the increased localization of (non-) antibonding charge results in a decrease in surface-atom core-electron binding energy. The magnitude of the core-level shift is clearly greater when the band is of tight-binding character, e.g., in transition and rare-earth metals, than when it is delocalized, e.g., in free-electron-like metals. For the noble metals in which there is more than one band at or near the Fermi level, the effect of charge redistribution between the surface *s* and *d* bands must also be considered, but it is still the band narrowing (charge localization) at the surface which is the dominant source of the core-level shift. The qualitative validity of these descriptions based solely on initial-state properties has been confirmed by experimental results from transition, rare-earth, noble, and free-electron-like metals.

While the qualitative nature of the SCS is now well understood, a quantitative description for all metals remains elusive. Particularly in need of development is a more accurate theoretical account of these shifts for metals near the beginning and end of the transition-metal series and for the more open surfaces of almost all the metals. Also required is a more complete theoretical study of final-state relaxation energy differences. Only for the case Cu{100} have such differences been explicitly considered.[38] The contribution of these differences to calculated SCS values should be to make them somewhat more positive because of the less efficient screening expected from the narrowed surface conduction bands. The magnitude and sign of this contribution should be uniformly small and positive (thus explaining why the qualitative nature of the SCS is predominantly initial-state related), but additional calculations are needed to confirm these expectations. Furthermore, while these effects may be small on an absolute level they should be non-negligible on the scale of measured SCS values.

The changes in the electronic structure at the surface manifest themselves not only in the core-level binding energy, but also in the surface tension and the surface cohesive energy. This realization[25–28] has made it possible to relate core-electron binding-energy shifts to these thermodynamic quantities through a Born-Haber cycle. On the one hand, this means that we have methods of predicting core-level shifts and testing experimental results, and on the other it means that these shifts provide a new and sensitive method for measuring thermodynamic surface properties, applicable even to systems with overlayers.

The understanding of the SCS has also led to a reexamination and ultimately a reinterpretation of experiments on supported small particles. Initially these seemed at variance with the theoretical and experimental understanding that had emerged from the surface-atom studies. Through the use of a consistent reference level the data on small-metal-atom clusters were brought into better agreement with our description of surface phenomena.

The understanding of the physics of metal surface atoms has taken a significant step forward through the study of core-level shifts. The general behavior of the various types of metals is now clear, but there is a need to confirm our expectations with further study. For example, the change in sign of the SCS is predicted to occur between Ti and V, Zr and Nb, and Ta and W. Only the latter has been verified. An additional sign reversal is predicted for Mn (multiplet splittings of the $2p$ photopeaks in the $3d$ transition metals, along with comparatively short core hole lifetimes, should make the data analysis challenging). Measurements on oriented and reconstructed surfaces of metals and semiconductors and on the effects of adsorbates point to applications in surface chemistry and catalysis. The extensions to insulators introduces a new set of considerations, e.g., the surface Madelung shift, which may be more important than band-structure changes (sample charging will also be a concern). Additional measurements of surface-atom densities of states are eagerly anticipated. We are clearly at a stage where surface-atom photoemission will make important contributions to surface science.

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