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Core level shifts in the $3d$ transition metals and tin*

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We present estimates of various contributions to the free-atom–metal binding-energy shifts, ΔE_B, for the $2s$ and $2p$ core levels of the iron series elements and, for comparison, the $3d_{5/2}$ level of Sn. Our results indicate that the sharp break in the experimental ΔE_B values occurring between Ni and Cu is due to variation in differences of d-electron count, i.e., d configuration, between atom and metal. Ley *et al.* who neglected the d-configuration differences, attributed the break in ΔE_B to a change in extra-atomic screening. Through free-atom calculations we find extra-atomic screening energies of 6–8 eV for Ti through Zn, with no break between Ni and Cu, and ~ 10 eV for Sn. In conjunction with charge-renormalization and dipole-term estimates, these results suggest that intra-atomic screening of core holes in metals is an important factor influencing free-atom–metal binding-energy shifts.

I. INTRODUCTION

The shift in the binding energy of a core electron between the free atom and solid environments has been a quantity of considerable interest since Siegbahn *et al.*'s first volume[1] on x-ray photoelectron spectroscopy. Recently, inert-gas atoms imbedded in metallic hosts have been investigated,[2] but incomplete knowledge of host-implant interactions has unfortunately hampered rigorous comparison of theory with experiment. Core level shifts of metal atoms between the free and metallic states constitute an alternate case in which the behavior in the solid is somewhat better understood, although there is a paucity of experimental free-atom binding-energy information. In this paper we consider the factors[3] contributing to the free-atom–metal shifts of $2s$ and $2p$ core levels in the transition metals Ti through Zn. The shift of the $3d_{5/2}$ level in Sn, a nontransition metal of interest[4,5] to us, will be examined for comparison.

Emphasizing extra-atomic screening, that is, the screening of the final-state hole by the medium surrounding the photoexcited atom, Ley and coworkers[6] have studied core level shifts in the $3d$ metals. The conclusions reached in the present investigation contrast with those of Ley *et al.* in three principal respects:

(i) Except for Cr and Cu, the free $3d$ atoms have $3d^n4s^2$ ground-state electronic configurations, whereas the metallic configuration is approximately $3d^{n+1}4s$; the change in d occupancy significantly affects the binding-energy shift ΔE_B. Ley *et al.* noted a break in ΔE_B between Co and Ni, having open d bands, and Cu and Zn, whose d bands are filled; this break was attributed to a change in extra-atomic screening associated with d-band filling. We find that the break derives instead from the change, from element to element, in d occupancy difference between free atom and metal.

(ii) In estimating the extra-atomic screening energy associated with allowing an additional electron to screen the final-state hole, we employ the approach of Ley *et al.* and replace the difficult question of screening in the metal by the computationally tractable *and well-defined* question of screening in the free atom. Treating that model with greater computational rigor, we find that the additional orbital penetrates the valence orbitals already present in the atom, causing them to relax and hence to "screen" the screening electron. The d screening energies we obtain are a factor of 2 to 3 smaller than Ley *et al.*'s estimates which were constrained by a model not including such relaxation effects. For the transition metals d and non-d (s-like) screening are found to be roughly equivalent. In general, however, the screening energy does depend upon the orbital character of the screening electron; s and p screening are quite different in Sn, for example.

(iii) The ability of an atom's valence electrons to screen the final-state hole should vary with chemical environment. Changes in this intra-atomic screening are computationally inconvenient and are usually ignored in the literature. Although in this work we do not calculate directly the intra-atomic contributions to the binding-energy shifts, estimates of the other components of ΔE_B afford us indirect evidence of their presence and sign.

The various contributions to ΔE_B are described in Sec. II, and the experimental situation is reviewed in Sec. III. Several terms in ΔE_B are then estimated, results for Sn are compared with those for the transition metals, and our conclusions summarized in Sec. VII.

II. COMPONENTS OF BINDING-ENERGY SHIFTS

The binding energy of an electron as measured by photoemission is simply

$$E_B = E_{\text{final}} - E_{\text{initial}} . \tag{1}$$

E_{initial} and E_{final} are the initial- and final-state total energies of the system and are eigenvalues of the N- and $(N-1)$-electron Hamiltonians, respectively. If the $N-1$ electrons were unaffected by the photoevent, Koopmans's theorem would apply

$$E_B = -\epsilon_i , \tag{2}$$

where ϵ_i is the one-electron energy of the excited electron. Here we are interested in the shift ΔE_B of the binding energy between the free atom and metallic states

$$\Delta E_B = E_B^{\text{atom}} - E_B^{\text{metal}} . \tag{3}$$

Chemical effects that modify the charge density surrounding an atom alter the potential sampled by a core electron and shift its one-electron energy, even though the spatial character of the core electron wave function remains unaffected by the change of environment. If Koopmans's theorem were valid, ΔE_B could be identified with the change $-\Delta\epsilon_i$ in the one-electron energy of the core electron, but correlation effects and the tendency of the remaining electrons to screen the final-state hole restrict the applicability of Eq. (2). Correlation effects are not expected to vary significantly with environment, while final-state screening can be drastically modified. The reference level with respect to which the binding energies of Eq. (3) are defined is another matter of concern. We consider these factors in turn below.

A. Chemical effects

If the core electron charge is entirely within the valence charge, the change in one-electron energy due to valence electron modification is

$$\Delta\epsilon_i = \Delta \sum_j (\langle e^2/r \rangle_j + \text{exchange terms}) , \tag{4}$$

where the sum is over the valence electrons. A 3d electron orbital is much more compact than a 4s orbital, and its Coulomb interactions with a core electron is roughly twice as great. The 4s → 3d conversion which usually occurs when a transition metal is formed from its constituent atoms consequently makes a positive contribution to $\Delta\epsilon_i$ and means a reduction in binding energy. For the chemistry of elements such as C and Sn, on the other hand, the interplay of s and p wave-function character is of great importance. The two electrons have the same principal quantum number, and their radial wave functions are quite similar, the s somewhat more compact than the p. As a result $s \rightleftharpoons p$ conversion effects in such elements have less impact on binding energies than $s \rightleftharpoons d$ effects in the transition metals.

In a free atom the valence charge extends well outside the core, while in a monatomic solid it is normalized to the Wigner-Seitz (WS) cell. Because each cell is electrically neutral, one need only consider the potential shift associated with the charge in the cell containing the ion core of interest. Compression of the free-atom valence charge into the cell makes a positive contribution to $\Delta\epsilon_i$, again corresponding to a reduction in binding. In an alloy or compound there may be a net charging of atomic sites and an associated Madelung-like term from the remainder of the lattice which also enter $\Delta\epsilon_i$. A simplifying feature of the free atom → monatomic solid case at hand is that such charging effects are absent.

B. Screening contributions

Screening energy contributions to ΔE_B may be both intra-atomic (that is, due to relaxation of electrons of the photoexcited atom) or extra-atomic (due to other electrons). After photoemission a free atom is in an ionized final state; there is obviously no extra-atomic screening in this instance, and the intra-atomic screening energy Δ_I is

$$\Delta_I = |\epsilon_i| - [E(\text{ion}) - E(\text{atom})] . \tag{5}$$

Here E(atom) and E(ion) are the total energies of the initial and final states, respectively. If the conditions of Koopmans's theorem were met, there would be no relaxation of the remaining electrons around the core hole, and Δ_I would be zero. In a solid the surrounding medium also acts to screen the final-state hole. The extent of this extra-atomic screening depends on the medium, but whatever its magnitude it reduces the binding energy of the photoelectron by lowering the final-state total energy; its sign is thus the same as the chemical shift due to valence charge renormalization discussed above. Extra-atomic screening was of primary concern to Ley *et al.*[6]

Since a change of environment may modify the valence electron states of an atom, the ability of the valence charge to screen the final-state hole may change as well. Such intra-atomic effects are difficult to estimate in the solid. The common procedure is to assume that they are the same as in the free atom and thus to ignore changes in them. While we will not directly calculate the intra-atomic screening component of ΔE_B, one purpose of the present paper is to estimate it indirectly.

C. Reference levels

The binding energies comprising ΔE_B [see Eq. (3)] must have a common reference level in order that the shift may have a meaning independent of any such arbitrary quantity. Experimentally, the free-atom binding energy is determined with respect to the vacuum zero, while in the metallic case the reference is the Fermi level ϵ_F of the photoemission apparatus with which the sample is in contact; ϵ_F differs from the vacuum zero by the sample work function Φ. Addition of Φ to the binding energy for the metal consequently puts the measured E_B^{atom} and E_B^{metal} on the same energy scale

$$\Delta E_B(\text{expt}) = E_B^{\text{atom}}(\text{expt}) - [E_B^{\text{metal}}(\text{expt}) + \Phi]\,. \tag{6}$$

In our theoretical considerations, the reference level for free atoms is again the vacuum zero. For the bulk solid it is the natural or "crystal" zero, the potential energy of a noninteracting test charge at the boundary of a WS cell; in other words, it is the potential energy of an electron at the cell boundary when the exchange and correlation terms are set to zero. We consider the bulk metal to be composed of such neutral cells, so that the crystal zero, associated with the interior of the metal, would coincide with the vacuum zero if there were no dipole sheet at the surface. Thus to our values for $E_B^{\text{metal}}(\text{theor})$ there must be added the surface dipole energy D in order to have the vacuum zero as reference level. We then have

$$\Delta E_B(\text{theor}) = E_B^{\text{atom}}(\text{theor}) - [E_B^{\text{metal}}(\text{theor}) + D]\,. \tag{7}$$

Thus, in terms of the quantities actually measured and actually calculated, theory is directly comparable with experiment $+(\Phi - D)$. Of course, the crystal reference level need not be the zero chosen, but whatever the choice, any change in D with respect to that choice must be correctly included.

III. "EXPERIMENTAL" BINDING ENERGY SHIFTS AND THE ROLE OF CHANGE IN *d* CONFIGURATION

Unfortunately, no experimental binding energies are available for the free atom levels of interest here. Ley *et al.*[6] fell back on free-atom calculations of Siegbahn and co-workers[1] and of Gelius and Siegbahn.[7] In some instances these results are binding energies from the relation

$$E_B^{\text{atom}}(\text{theor}) = E(\text{ion}) - E(\text{atom})\,, \tag{8}$$

where E(atom) and E(ion) are the total energies for the ground-state valence electron configuration of the free atom and of the free ion with the appropriate core hole. In other cases the binding energies are optimized-Hartree-Fock-Slater (OHFS) one-electron energies reduced by a calculated relaxation energy, i.e.,

$$E_B^{\text{atom}}(\text{theor}) = -\epsilon_{\text{OHFS}} - E_R \tag{9}$$

This information, together with the available measurements for the metals, enabled Ley *et al.* to evaluate "experimental" shifts

$$\Delta E_B(\text{"expt"}) = E_B^{\text{atom}}(\text{theor}) - [E_B^{\text{metal}}(\text{expt}) + \Phi(\text{expt})]\,. \tag{10}$$

Their results for the average of the $2s$ and $2p$ level shifts appear as filled circles in Fig. 1; the $2p_{3/2}$ values are given by the closed circles of Fig. 2. In these plots there is a pronounced break between Ni and Cu, that is, at the point where the $3d$ band in the metals becomes completely occupied. Ley *et al.* argued that this break is the consequence of a change in extra-atomic screening occurring because the completely filled d band is unable to accept any of the screening charge.

As we observed above, band theoretical results[8] indicate that the metals Ti through Ni are well described as having $3d^{n+1}4s$ electronic configurations, whereas most of these elements have $3d^n4s^2$ configurations as free atoms. These d and non-d electron counts are obtained from population analyses of the occupied "d" bands in which the s-d hybridization of the bands has been included. Assigning pure d character to the total occupation count in these so-called d bands would lead to d counts in excess of $n+1$. A change in configuration on going from free atom to solid is not sur-

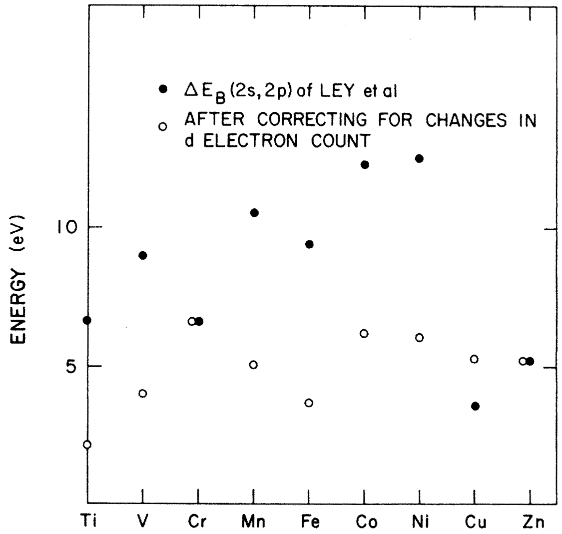

FIG. 1. Filled circles are the "experimental" free-atom–metal binding-energy shifts for the average of $2s$ and $2p$ levels of the $3d$ transition elements, as obtained by Ley *et al.* [the ΔE_B("expt") of Eq. (10)]. The open circles are the shifts $\Delta\bar{E}_B$[Eq. (11)] *after* the effect of differing free-atom-metal d count is *subtracted* from ΔE_B("expt").

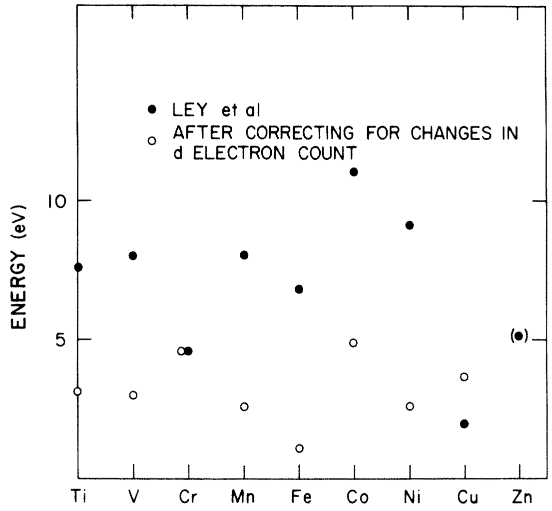

FIG. 2. Filled circles show the "experimental" free-atom–metal binding-energy shifts of the $2p_{3/2}$ level for the transition elements according to Ley *et al.* [ΔE_B ("expt") of Eq. (10)]. Open circles are the shifts, $\Delta\bar{E}_B$[Eq. (11)], *after* the effect of changing free-atom–metal *d* count is subtracted from ΔE_B("expt"). The Zn value is estimated, due to lack of experimental data.

prising because the two free-atom configurations lie quite close in energy. In order to eliminate the effects of free-atom–versus–metal electron configuration differences which contribute varyingly to the ΔE_B(expt) values, we compare each metal with its free atom in a valence configuration corresponding to that of the metal. Using one-electron energies from free-atom relativistic-Hartree-Fock (RHF) calculations for the $2p_{3/2}$ level in both the $3d^n4s^2$ and $3d^{n+1}4s$ configurations, we obtain

$$\Delta\bar{E}_B \equiv \Delta E_B(\text{"expt"}) + [\epsilon_{2p_{3/2}}(d^{n+1}s) - \epsilon_{2p_{3/2}}(d^ns^2)] . \tag{11}$$

That is $\Delta\bar{E}_B$ gives the binding-energy shift which remains after configuration changes are accounted for. These values are plotted as open circles in Figs. 1 and 2 for Ti, V, and Mn through Ni. The point for Cr is unshifted since the ground free-atom configuration is d^5s. In Cu hybridization with conduction electron states above ϵ_F depletes the amount of *d* electron character in the occupied bands, even though the *d* bands are filled. Band calculations[8] indicate that this depletion leads to an approximate $d^{9.75}s^{1.25}$ assignment. Interpolating between RHF results for the $d^{10}s$ and d^9s^2 free atoms yields the open circles for Cu in Figs. 1 and 2. The points lie above their filled-circle counterparts because the free-atom *d* count is higher than that of the metal, the reverse of the case for the other elements. It is quite apparent from Figs. 1 and 2 that $\Delta\bar{E}_B$ exhibits considerably less variation across the series than ΔE_B("expt"); in particular, there is no abrupt decrease from Ni to Cu. In principle it would be better to replace the one-electron energies of Eq. (11) by atom-ion total energy differences. Calculations for all but two of the elements involved indicate that this replacement has no effect on ΔE_B which is significant in relation to experiment.

Since the work of Ley *et al.* was done, somewhat more carefully calibrated core level data have been obtained[9] for some of the metals. In conjuction with RHF total energies for the $d^{n+1}s$ atoms and for ions with $2p_{3/2}$ core holes, these yield another set of $\Delta\bar{E}_B$ values which on the average agree with the open circles of Fig. 2, though disagreeing by as much as 1.5 eV in some cases. These results substantiate the magnitudes, but not the detailed structure, of the shifts given by the open circles of Figs. 1 and 2.

Similar estimates may be made for the $3d_{5/2}$ level of tin. Photoelectron data[5] and chemical considerations[10] suggest that the electronic configuration of white (metallic) β-Sn is approximately $5s^{1.6}5p^{2.4}$. Again employing RHF total energy differences, we calculate $3d_{5/2}$ free-atom binding energies of 494.2 and 492.6 eV for the sp^3 and s^2p^2 configurations, respectively. Interpolation leads to a binding energy of 493.3 eV for the $s^{1.6}p^{2.4}$ free atom. With a metal binding energy[11] of 484.9 eV and a work function of 4.4 eV, we obtain a binding energy shift, $\Delta\bar{E}_B$ of 4.0 eV; this is comparable to the $d^{n+1}s$ shifts of Fig. 2.

The principal shortcoming of the "experimental" shifts inferred in this section is, of course, the reliance upon calculation for the free-atom binding energies. Comparison of theory and experiment for those free-atom levels whose binding energies have been measured displays no consistent relation, even in sign, between E_B^{atom}(expt) and E_B^{atom}(theor). Results (cf. Watson *et al.*[2]) for the $2p_{3/2}$ levels of Ne and Ar, however, suggest that the shifts of Fig. 2 may be as much as 2 eV too small.

As actual free-atom experimental data become available, we expect experimental atom to metal core level shifts indeed to resemble the filled circles ΔE_B("expt") of Figs. 1 and 2. These ΔE_B values, presented by Ley *et al.* on the basis of Eq. (10) as representing screening effects, in fact represent the effects not only of screening but also of differences between electron configurations of the free atom and those of the metals. This configuration difference ranges from that characteristic of most of the 3*d* transition elements, d^ns^2(atom) → $d^{n+1}s$(metal), to no difference for Cr, $d^{n+1}s$ in both forms, and to $d^{10}s$(atom) → $d^{9.75}s^{1.25}$ (metal) for Cu. It is in particular the shift in this difference, and not a shift in the screening description, that is responsible for the sharp break between Ni and Cu in the trend of the Ley *et al.* ΔE_B values. The core level shifts, which remain to be accounted for after dealing with the configuration changes, i.e., the $\Delta\bar{E}_B$ of Figs. 1 and 2, are $+3$ to $+5$ eV with no marked structure from Ti to Zn.

IV. ROLE OF VOLUME EFFECTS IN FREE-ATOM-TO-METAL CHEMICAL SHIFTS

A simple estimate of the chemical shift associated with the compression of the valence charge on formation of the metal may be made by truncating the free-atom valence electron wave functions at the WS radius, normalizing them to the WS sphere, and calculating the shift in the core one-electron energy associated with this modification [see Eq. (4)]. The renormalized atom charge density provides a good first-order estimate of the change in charge density between metal and free atom, and it furnishes an estimate of the potential sampled by the core electron in the metal. [Total energies of renormalized atoms and ions are not good variational quantities and cannot be employed in expressions such as Eq. (7).] With the use of RHF wave functions computed for the $d^{n+1}s$ free-atom configurations, we find that the $2p_{3/2}$ shift $|\Delta\epsilon_{2p_{3/2}}|$ is 9 eV for Ti, increasing to 11 eV for Fe and Co, decreasing to 9 eV for Cu. Shifts of 5 and 6 eV are calculated for the $2p_{3/2}$ level of Zn and the $3d_{5/2}$ level of Sn, respectively.

The $|\Delta\epsilon_i|$ values thus obtained are overestimates of the effect because simple renormalization of free-atom wave functions does not adequately describe the buildup of bonding charge in states at the bottom of the bands. Such states have more charge in the outer regions of the WS cell than simple renormalization predicts; hence, the reduction in binding energy is smaller than $|\Delta\epsilon_i|$ indicates. A band calculation for Ni which has been taken almost to self-consistency yields a $2p_{3/2}$ binding energy decrease of 6 eV as opposed to the 10.5 eV calculated by simple renormalization. Self-consistent band calculations[12] have been done for other $3d$ metals in which, unfortunately, the $2p$ level shifts were not monitored, but which nevertheless indicate similar effects in the d band positions. In the light of the band calculations an actual charge renormalization shift of ~6 eV appears appropriate for the $3d$ metals. Although we have no equivalent information for Zn and Sn, we expect a charge renormalization shift of $+3$ to $+5$ eV for them.

V. EXTRA-ATOMIC SCREENING

We use free-atom calculations to approximate the extra-atomic screening energy in the metallic case. Specifically, we ask what energy change would occur if a screening electron were supplied to the final-state free atom, i.e., the free ion with a core hole. Ley *et al.*[6] adopted the "equivalent-core" approach to calculate the Coulomb and exchange interactions of the screening electron with the core orbital of interest. In this scheme one ignores the relaxation of the valence electrons already present on the ion when the screening electron is introduced. We calculate instead the effect of replacing the $(N-1)$-electron final-state energy of Eq. (1) by the N-electron energy of the system comprised of the core hole plus screening electron. That is, we compute

$$\Delta_S \equiv E(\text{ion}) - E(\text{ion} + \text{screening electron}) \; ; \qquad (12)$$

we emphasize that a complete RHF calculation is performed for each configuration. Results for this extra-atomic screening contribution to the binding-energy shifts are displayed in Fig. 3 for both $3d$ and $4s$ ($4p$ for Zn) screening orbitals. The one-electron eigenvalues of the screening electrons are also shown. Comparison of the two quantities provides an indication[13] of the extent to which the valence orbitals adjust to the extra electron and reduce the effect of its screening. From Fig. 3 we see that this accommodation is substantial for $3d$ screening but slight for $4s$ and $4p$; the Δ_S values, however, are almost identical for d and non-d screening.

In Fig. 4 our results are compared with those of Ref. 6. Ley *et al.* assumed $3d$ screening for

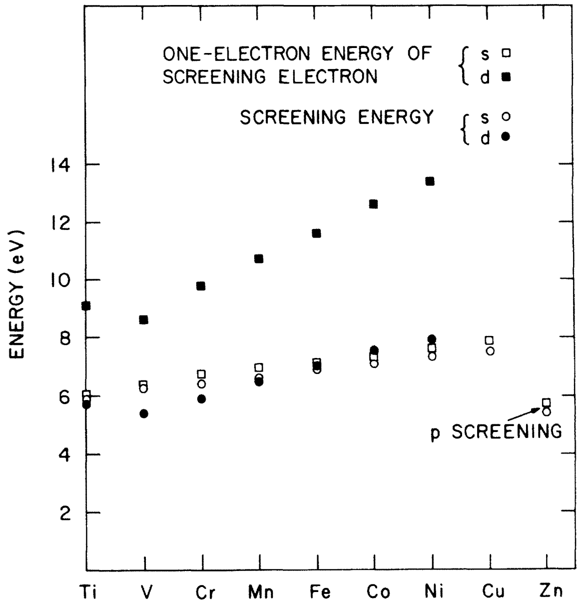

FIG. 3. Free-atom estimates of extra-atomic screening energies for the transition metals ($2p_{3/2}$ core holes). Shown are absolute values of the one-electron energies for the screeening electrons, and the screening energy Δ_S defined by Eq. (12).

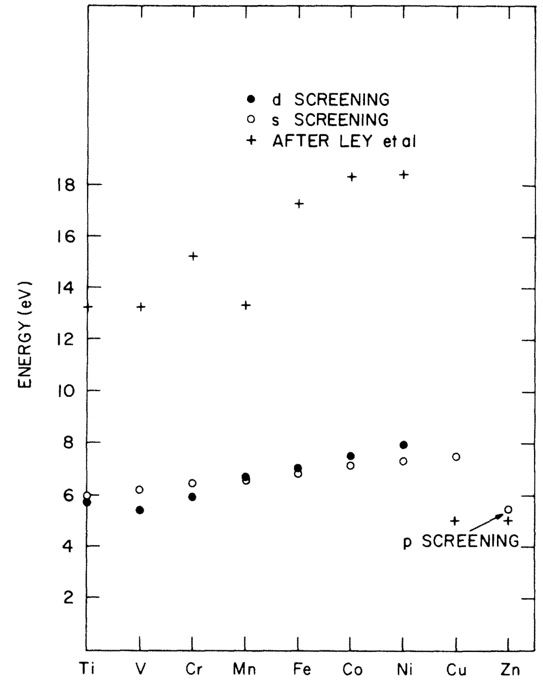

FIG. 4. Comparison of our extra-atomic screening-energy contributions to the $2p_{3/2}$ core level shifts in the transition metals with those of Ley *et al.* The filled (*d*-screening) and open (*s*-screening) circles represent our Δ_S results based on Eq. (12), also shown in Fig. 3. The crosses are the results of calculations by Ley *et al.* based on their screening description, outlined in the text and given in Ref. 6.

Ti through Ni, and 4*s* and 4*p* screening for Cu and Zn, respectively. The break between their Ni and Cu values is associated with the fact that the 3*d* electron penetrates more deeply into the core than the 4*s* and 4*p* and hence has a greater Coulomb interaction with it (compare the one-electron energies of Fig. 3). In contrast, our Δ_S results [based on Eq. (12)] indicate that the increased penetration induces increased response from the valence electrons already present; consequently, screening from *d* electrons is no more effective than that from non-*d*.

Δ_S decreases slightly between Cu (*s* screening) and Zn (*p* screening). Our results for *s* and *p* screening of the $3d_{5/2}$ hole in Sn are given in Table I and show qualitatively similar behavior. The 5*s* charge density is more compact than the 5*p*, and its screening is a factor of two more effective; the magnitude of the difference is in significant contrast to the transition metal results. From these calculations we conclude that extra-atomic screening of mixed *s*-*p* character is to be expected in Sn metal and that the associated energy Δ_S is 10 ± 2 eV.

VI. SURFACE DIPOLE TERM

The work functions Φ have been incorporated into the "experimental" shifts of Sec. III [cf. Eq. (10)], but the metal reference level for the calculations of the preceding two sections is the crystal zero discussed in Sec. II. Therefore, we require the surface dipole energy D defined with respect to that level. This can be found either by direct calculation of D or by calculating $\epsilon_F - E_{\text{crystal zero}} = \Phi - D$.

Following the work[14] of Lang and Kohn we can apply either method to Sn; for the transition metals no reliable computational scheme exists, and we must resort to a surmise based on experience with simpler metals.

Lang and Kohn employed electron gas techniques to estimate the work function and its dipole component. Their results for Φ are in semiquantitative agreement with experiment for the simple and polyvalent metals. The average internal potential is their energy reference for the dipole term; in a later paper[15] they pointed out how this may be shifted to the crystal zero by employing Ashcroft and Langreth's pseudopotentials.[16] In this way we find $D = +2.5$ eV for β-Sn ($r_s = 2.2$ a.u.) with respect to the crystal zero. The plus sign means that the dipole layer increases the stabilization of the electrons in the metal. The calculated work function for tin is 3.8 eV, which is to be compared with an experimental value[17] of 4.4 ± 0.2 eV. Taking into account the fact that the electron density in the outer regions of the WS cell is somewhat greater than that assumed in the Lang and Kohn model would produce a modest increase in Φ, but it would not bring Φ into accord with experiment.

Similar considerations cannot be applied to the transition metals. The calculated position of ϵ_F relative to the crystal zero may vary by as much as 5 eV depending on the band potential employed, and direct calculation of D is equally uncertain. From experience with simpler metals a D term of $+2 \pm 1$ eV is plausible.

TABLE I. Free-atom estimates of extra-atomic screening energies in Sn. Δ_S is defined by Eq. (12), the ionic configuration is the that before addition of the screening electron, and ϵ(screening electron) is the one-electron energy of the extra electron. (No *s* screening results are given for the $5s^2 5p^2$ case since the 5*s* shell is already filled.)

Screening electron	Ionic configuration	Δ_S (eV)	$\lvert\epsilon$(screening electron)$\rvert$ (eV)
5*p*	($3d_{5/2}$ hole) $5s5p^3$	7.4	7.9
5*p*	($3d_{5/2}$ hole) $5s^2 5p^2$	7.5	7.9
5*s*	($3d_{5/2}$ hole) $5s5p^3$	15.9	16.8

TABLE II. Summary of results for $2p_{3/2}$ binding-energy shifts in Ti through Zn. The shifts correspond to the free-atom configurations most closely approximating the metal.

"Experimental" shift with effects of free-atom–metal *d*-count changes subtracted out (Sec. III)	$\Delta\tilde{E}_B = +3$ to -5 eV
Theoretical estimates of other shift components:	
charge renormalization (Sev. IV band-theory based)	~6 eV
extra-atomic screening (Sec. V)	~6 to 8 eV
intra-atomic screening	not estimated
dipole contribution [$-D$; Eq. (7) and Sec. VI]	-2 ± 1 eV

VII. DISCUSSION

The results of the preceding sections for Ti through Zn are summarized in Table II. The sum of the extra-atomic screening, dipole term, and band theory based charge renormalization we have estimated is obviously too large in comparison with experiment. We believe the discrepancy indicates the sign, though not the magnitude, of the intra-atomic screening contribution. Comparison of free-atom one-electron energies with atom-ion total energy differences indicates that intra-atomic screening associated with the formation of a $2p$ hole in a free transition-metal atom is about 18–25 eV. The discrepancy seen in Table II suggests that compression of the valence charge, on formation of the metal, *inhibits* its ability to screen the core hole. This implies a modest reduction in the intra-atomic screening energy, hence a component of negative sign in the sense of Table II. Analogous considerations apply to Sn. The break in the "experimental" data between Ni and Cu will undoubtedly be demonstrated when real data for the free atoms become available, but the break would appear to be due primarily to *d* count changes rather than to changes in extra-atomic screening.

This investigation raises some questions. One would, for example, like to know how well the free-atom estimate of extra-atomic screening describes the situation in a metal, a medium which presumably can deliver the screening charge to the atomic site. Ley *et al.*'s idea, which we have employed, of replacing the problem in the metal by a well defined, computationally tractable atomic calculation, should prove of great use—provided that errors which it introduces can be understood. It would appear unlikely that the screening energy in the metal would exceed the 6–8 eV we here estimate, even if the renormalization term in Table II were somehow zero. A next approximation may well involve calculations of total energies associated with the initial and final states of an atomic site in a metal; some crude calculations of this type, made for rare earths[18] and actinides,[19] indicate that this approach is practicable and has promise.

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