Zeitschrift: Helvetica Physica Acta
Band: 56 (1983)
Heft: 1-3

Artikel: Theory of surface core-level shifts in metals
Autor: Johansson, Börje / Mårtensson, Nils
DOI: https://doi.org/10.5169/seals-115387

Nutzungsbedingungen
Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation
L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use
The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 28.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Helvetica Physica Acta,
Vol. 56 (1983) 405-426

0018-0238/83/010405-22$1.50+0.20/0
© Birkhäuser Verlag Basel, 1983

THEORY OF SURFACE CORE-LEVEL SHIFTS IN METALS

Börje Johansson
Institute of Physics
University of Aarhus
8000 - Århus C, Denmark
and
Nils Mårtensson
Institute of Physics
Uppsala University
S - 75121 Uppsala, Sweden

Abstract. From the complete screening picture for the core electron ionization process in a metal, a theoretical expression for the surface core-level binding energy shift is derived. By means of the equivalent core approximation this expression is evaluated for the 5d transition metal series and comparisons with experiment are made. Surface core-level shifts are shown to be related to the surface heat of segregation of a substitutional (Z+1) impurity, and are calculated to depend on the surface crystal plane. Also the possibility of valence changes at the surface of the rare-earth metals is briefly treated.

1. Introduction

Experimental determinations of core-level binding energies by means of X-ray photoelectron spectroscopy is an important technique for probing electronic structure. These energies depend on the chemical environment of the atom which is core excited (chemical shift). Since the environment for a surface atom is different than for a bulk atom, one expects a shifted core-level binding energy for a surface atom relative to a bulk atom. This will in the following be referred to as a *surface core-level shift*. Due to its surface sensitivity the photoelectron spectroscopy is well suited for studies of these shifts.

Already long ago the existence of surface core-level shifts was anticipated. However, it is only relatively recently that these shifts have been verified experimentally [1-5] and have been studied in a more systematic way [5-18]. For this development to take place the improvement of the experimental resolution has been an absolute necessity, since the magnitude of the surface

shifts are small, generally less than 0.5 eV, making their separation from the more intense bulk signal most difficult. The increased availability of tunable photonenergy sources (synchrotron radiation) has been extremely valuable for the development of the field. By variation of the photon energy, the experiments can be performed with a varying degree of surface sensitivity, which is extremely helpful in the identification of the surface signal. Presently available resolution has, however, limited the experimental studies to include only core levels with binding energies $\lesssim$ 100 eV. Due to further experimental development this is expected to change rather dramatically in the near future. For metals, this restriction on the binding energies together with the obvious requirement of narrow core-level lines have essentially limited the studies to the 5d transition series, the lanthanides and the lightest simple metals.

The fact that the surface-shifted core-level signals originate exclusively from atoms in the topmost surface layer(s), makes them very attractive in studies of problems within surface and interface physics. Thus, they might become useful in investigations of catalytic activity, corrosion resistance, surface and grain boundary segregation in alloys, just to mention a few possibilities. At the present stage of development we believe that they already now can be fruitfully applied, especially in connection with surface segregation.

In the present contribution we will present a theoretical model of the surface core-level shifts for metallic systems. The most essential ingredient in this theory is the assumption of a completely screened final state [19], i.e. in the final state the conduction electrons are assumed to have attained a fully relaxed configuration in the presence of the core hole, corresponding to the position of the symmetric part of the line profile for the core level. The core-level binding energy is then expressed as the difference between the total energy of the (electronically relaxed) final state and the initial unperturbed state. Based on this we derive an expression for the surface core-level shift, which shows the kind of information that can be obtained from the measured shift.

In Table I we have collected presently available experimental data on surface core-level shifts for pure metals. Detailed accounts of various experimental aspects are given elsewhere in this volume [21,22].

Table I: Experimental surface core-level binding energy shifts (in eV) for metallic elements. When nothing else is indicated, the data refer to polycrystalline samples.

Lanthanides			
Ce	$\lesssim 0.4$[a]	Dy	0.55(5)[b]
Pr	0.5(1)[b]	Ho	0.63(5)[b]
Nd	0.5(1)[b]	Er	0.65(5)[b]
Eu	0.60(5)[c]; 0.63(3)[b]	Tm	0.70(5)[b]
Gd	0.50(5)[b]	Yb	0.62(3)[c]; 0.60(3)[b,d]
Tb	0.55(5)[b]	Lu	0.70(5)[b]
5d transition series			
Yb	0.62(3)[c]; 0.60(3)[b,d]	Ir(111)	-0.50[e]
Lu	0.70(5)[b]	(110)-(5x1)	-0.49[e]
Hf	0.44(5)[b]	(100)-(1x1)	-0.68[e]
Ta	0.3[e]	Pt(110)	-0.35(2)[i]
(111)	0.40[f]	(111)	-0.4[j]
W (111)	-0.43[f]	Au	-0.40(2)[k]
(100)	-0.35[g]	(111)	-0.35[l]
(110)	-0.30[h]	(110)-(2x1)	-0.35[l]
		(100)-(1x1)	-0.38[l]
		(100)-(5x20)	-0.28[l]
Noble metals			
Cu	-0.24(2)[k]	Au	-0.40(2)[k]
Ag	-0.08(3)[k]		see above
Simple metals			
Na	0.22[m]	Al(100)	-0.12[m], -0.06[n]
Mg	0.14[m]	(111)	~ 0.0[m]

a) Parks et al. [16]
b) Schmidt-May et al. [10]
c) Kaindl et al. [17]
d) Alvarado et al. [18]
e) van der Veen et al. [5]
f) van der Veen et al. [6]
g) van der Veen et al. [7]
h) Tran Minh Duc et al. [3]
i) Shek et al. [11]
j) Apai et al. [12]
k) Citrin et al. [2,20]
l) Heiman et al. [13]
m) Kammerer et al. [15]
n) Chiang et al. [14]

2. Theoretical model

The energy needed to create a core hole in level X for the metal is given by the total energy difference

$$E_c^M(X) = E_{N-1}^M(X) - E_N^M \ . \tag{2.1}$$

The superscript M means that a metal is considered, while the superscript A will be used for the free atom in the following. N is the total number of electrons in the metal. For the free atom the corresponding number will be denoted by n, and the atomic core-level binding energy is given by

$$E_c^A(X) = E_{n-1}^A(X) - E_n^A \ . \tag{2.2}$$

It is useful to consider the shift in binding energy between the free atom and the metal, δE_c. This shift can be rewritten as follows,

$$\begin{aligned} \delta E_c &= E_c^A(X) - E_c^M(X) = \left[E_{n-1}^A(X) - E_n^A\right] - \left[E_{N-1}^M(X) - E_N^M\right] \\ &= \left[E_{n-1}^A(X) - E_{N-1}^M(X)\right] - \left[E_n^A - E_N^M\right] \ . \end{aligned} \tag{2.3}$$

The total number of atoms in the metal is N/n and the total metallic energy E_N^M can be expressed as

$$E_N^M = (N/n)(E_n^A - E_{coh}) \ , \tag{2.4}$$

where E_{coh} (defined positive) is the cohesive energy for the metal. The shift δE_c then takes the form

$$\begin{aligned} \delta E_c &= \left[E_{n-1}^A(X) - E_{N-1}^M(X)\right] + ((N/n)-1)(E_n^A - E_{coh}) - E_{coh} \\ &= \left[E_{n-1}^A(X) - E_{N-1}^M(X)\right] + E_{N-n}^M - E_{coh} \ , \end{aligned} \tag{2.5}$$

where E_{N-n}^M is the total energy of a metal with (N/n)-1 atoms, i.e., one less than for E_N^M. In (2.5) we have thereby isolated one contribution to the shift, E_{coh}, which in fact *precisely* describes how the *initial state* in the atom differs in energy from the *initial state* in the metal. We emphasize that the cohesive energy here enters the shift expression for δE_c in a most natural way.

The term $E_{N-1}^M(X)$ in (2.5) can be decomposed into one term, $E_N^M(X)$, where the core electron corresponding to X has been brought up to the Fermi level and one term, where an electron from the Fermi level has been brought to the vacuum level. The energy for the last process is given by the work function ϕ. Thus, (2.5) can be written as

$$\delta E_c = \left[E_{n-1}^A(X) - E_N^M(X) - \phi\right] + E_{N-n}^M - E_{coh} \ . \tag{2.6}$$

The fact that the work function ϕ enters in the expression for the shift, δE_c,

is most favourable from a practical point of view, since ϕ can be taken care of by simply relating the measured solid-phase binding energy, not to the vacuum level but to the Fermi level. This is also the most natural and the most accurately determined reference level for a solid phase measurement.

In the same way, the atomic contribution $E^A_{n-1}(X)$ in (2.6) can be decomposed into one term, $E^A_n(X)$, where the core electron from X has been brought into the lowest unoccupied valence orbital in the atom (in the presence of the core hole X) and one term, $I^*(X)$, where this extra valence electron is ionized away. The equation (2.6) can now be expressed as

$$\delta E_c = \left[E^A_n(X)+I^*(X) - E^M_N(X)-\phi\right] + E^M_{N-n} - E_{coh} \ . \qquad (2.7)$$

The total energy $E^M_N(X)$ stands for a metallic system with (N/n)-1 atoms without a core hole and one atom with a core hole (X), but where the missing core electron has been brought to the Fermi level so that $E^M_N(X)$ still refers to a neutral system. This total energy can be decomposed into three terms: one describing the total energy for (N/n)-1 metallic (non-excited) atoms, i.e. E^M_{N-n}, one describing the total energy for a (condensed) metal atom with a core hole but with an extra valence electron, $E^M_n(X)$, and, finally, a contribution describing the mutual influence between this core-hole metal atom and the surrounding metal, $E_{cross-term}$, i.e.,

$$E^M_N(X) = E^M_{N-n} + E^M_n(X) + E_{cross-term} \ . \qquad (2.8)$$

This expression together with (2.7) give

$$\delta E_c = I^*(X) - \phi + E^A_n(X) - E^M_n(X) - E_{cross-term} - E_{coh} \ . \qquad (2.9)$$

However, the difference $E^A_n(X) - E^M_n(X)$ describes how an atom with a core hole in X, but with an extra electron in the lowest valence orbital, changes its energy when it condenses to a corresponding metallic state. This defines a generalized cohesive energy, $E_{coh}(X)$. Thus, (2.9) now becomes

$$\delta E_c = I^*(X) - \phi + E_{coh}(X) - E_{coh} - E_{cross-term} \qquad (2.10)$$

or

$$\Delta E_c = \delta E_c + \phi = I^*(X) + E_{coh}(X) - E_{coh} - E_{cross-term} \ . \qquad (2.11)$$

This last expression is exactly of the form derived in Ref.19 for the Fermi level related core-hole shift between the free atom and the metal. The $I^*(X)$ term accounts for the charge neutralization of the final state (screening) and $(E_{coh}(X) - E_{cross-term})$ describes how this screening charge is modified within the metallic host. Thus, while E_{coh} describes the energy change

of the initial state between the free atom and the metal, the rest of the terms in (2.11) describe the corresponding change of the final state.

This decomposition of the metallic core-level binding energy (measured relative to the Fermi level), $E^M_{c,F}$, is illustrated in Figure 1. From this follows immediately that

$$E^M_{c,F} = E^A_c + E^Z_{coh} - E^{Z*}_{coh} - I^{Z*}_1 + E^{imp}_{Z*}(Z) \ . \qquad (2.12)$$

Here we have used a slightly different notation than in (2.11) in that Z is used to denote the atomic number of the metal and Z* stands for a core-ionized Z-atom. $E^{imp}_{Z*}(Z)$ is the substitutional heat of solution of a metallic Z*-atom into the Z metal.

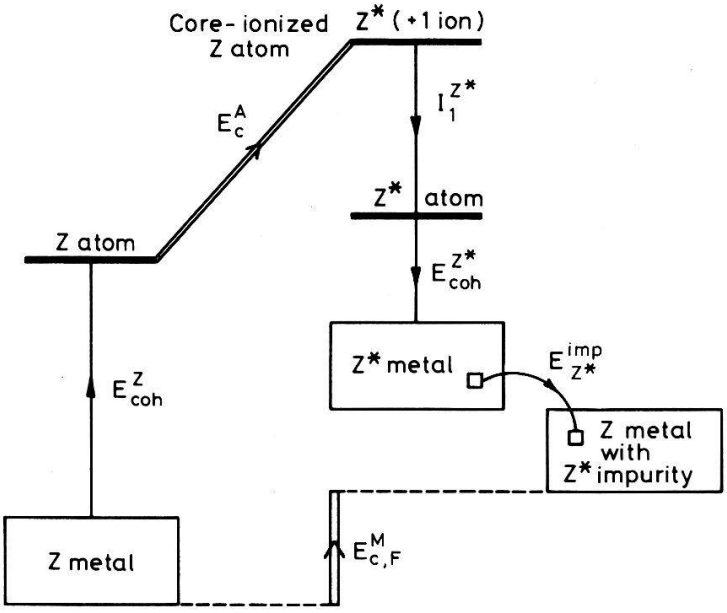

Fig. 1: Diagram showing the connection between the atomic core ionization energy, E^A_c, and the metallic core level binding energy, $E^M_{c,F}$.

Let us repeat the above decomposition of the bulk metal core-hole binding energy, but for a surface atom. Thereby we arrive at the following expression for the surface core-level binding energy

$$E^{surf}_{c,F} = E^A_c + E^Z_{coh,surf} - E^{Z*}_{coh,surf} - I^{Z*}_1 + E^{imp,surf}_{Z*}(Z) \ . \qquad (2.13)$$

We have introduced the surface cohesive energy, $E_{coh,surf}$, both for the original metal (Z) and for the hypothetical one core-hole metal (Z*). (With the surface cohesive energy is meant the energy gained when a free atom is brought to the metal surface, while enlarging the surface area correspondingly.) A corresponding surface impurity solution energy, $E^{imp,surf}_{Z*}(Z)$, also enters the expression. This is the solution energy for bringing a surface atom of the (hypothetical) Z*-metal into the Z-metal surface.

The shift of the core-level binding energy between the surface and the bulk, Δ_c, is found by combining (2.13) with (2.12)

$$\Delta_c = E^{surf}_{c,F} - E^M_{c,F} = E^{Z*}_{coh} - E^{Z*}_{coh,surf} - (E^Z_{coh} - E^Z_{coh,surf}) - (E^{imp}_{Z*}(Z) - E^{imp,surf}_{Z*}(Z)) \qquad (2.14)$$

This expression for the surface core-level shift can be interpreted as the energy difference between having a Z*-atom impurity in a substantial surface position or in a substitutional bulk position. This is illustrated in Figure 2, which, in fact, could have been used directly to give the above expression for the surface shift. From this it becomes immediately clear that Δ_c is nothing but the *surface segregation energy* of such an impurity [19]. With a (Z+1) equivalent core replacement (see below) the surface shift would then give important information about the segregation potential for a (Z+1) substitutional impurity in the Z metal host.

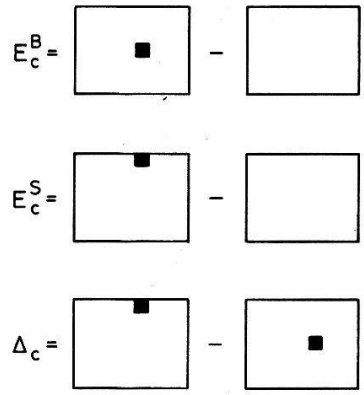

Fig. 2: Illustration of the correspondence between the surface core-level shift Δ_c and the surface heat of segregation of the Z* impurity.

It should perhaps be remarked upon that the expression in (2.14) is of a general form and can be applied to any metal. Since the difference between E_{coh} and $E_{coh,surf}$ is just the surface energy, the surface core-level shift can be expressed as

$$\Delta_c = E_S^{Z*} - E_S^Z - (E_{Z*}^{imp}(Z) - E_{Z*}^{imp,surf}(Z)) \ . \qquad (2.15)$$

In this form we note that there is a direct connection between the surface core-level shift and surface energies, modified only by the difference in heat of solution for a bulk and a surface substitutional impurity.

3. Calculated shifts

The calculation of the core-level shift between the free atom and the metal can be performed very simply by means of the equivalent core approximation. In Fig. 1 we note that for all the processes on the right-hand side only the valence electrons are actively involved. Since the valence charge distribution will be very similar for an atom with a core hole and for an atom with an additional nuclear charge, the (Z+1) atom, an accurate approximation is obtained by replacing Z* by (Z+1) in the shift expression, (2.15). As a well-known example we mention trivalent ytterbium, which has one core hole in the f shell and behaves almost identically to its (Z+1) element lutetium (i.e., as far as bonding is concerned). By means of this approximation the atom-metal core-level energy shift has been calculated for all the elemental metals and a very good agreement with experiment was obtained [19]. This first

of all shows the appropriateness of the complete screening picture, but also the accuracy of the (Z+1) replacement for the core-ionized atom.

Introducing the equivalent core approximation, the surface shift takes the relatively simple form

$$\Delta_c = E_S^{Z+1} - E_S^{Z} - (E_{Z+1}^{imp}(Z) - E_{Z+1}^{imp,surf}(Z)) \ . \qquad (3.1)$$

This relation will form the basis for most of our following discussions.

With the (Z+1) approximation, the surface core-level shift can be interpreted as the heat of surface segregation of a (Z+1) substitutional impurity in the Z metal. Due to severe experimental difficulties, this technologically most important quantity has not been measured thermochemically. It follows that experimentally determined surface core-level shifts indirectly can provide us with segregation data not available otherwise. The obvious limitation is that it can only give information about the segregation potential for the (Z+1) element in the Z metal. Still it is true that many technologically important alloy systems (e.g. in catalysis) are of the type $Z_x(Z+1)_{1-x}$, where studies of surface core-level shifts would be of high interest and importance. This aspect has been discussed in more detail in Ref. 23.

In order to calculate the surface core-level shift, we will introduce some further approximations. From experimental surface tension measurements it has been found that *empirically* the surface energy is approximately related to the cohesive energy as [24]

$$E_S \approx 0.2 \ E_{coh} \ . \qquad (3.2)$$

This type of relation can also be derived from considerations of the number of broken bonds for a surface atom as compared to a bulk atom. Furthermore, it seems plausible that, at least approximately, the impurity term would obey a similar type of relation.

$$E_{Z+1}^{imp,surf}(Z) \simeq 0.8 \ E_{Z+1}^{imp}(Z) \ . \qquad (3.3)$$

It should be emphasized that the relation (3.2) is derived from surface tension data for the metallic liquid phase, *extrapolated* to low temperatures (and crystalline structure). However, the coordination number for an atom at the surface of the liquid might be quite different from the crystalline phase. At best, the liquid surface coordination number may correspond to the average of the different types of surfaces possible for the crystalline phase. These limitations have to be born in mind when the simple relations in

(3.2) and (3.3) are applied to specific cases.

These additional approximations give the following expression for the surface core-level shift

$$\Delta_c \approx 0.2\left[E_{coh}^{Z+1} - E_{coh}^{Z} - E_{Z+1}^{imp}(Z)\right] . \qquad (3.4)$$

Since normally the heat of solution of a (Z+1) impurity in a Z metal is quite small, we can to first order neglect the impurity contribution to the shift. Thus we finally obtain a very simple relation for the surface shift [19]

$$\Delta_c \simeq 0.2\left[E_{coh}^{Z+1} - E_{coh}^{Z}\right] . \qquad (3.5)$$

In Figure 3 we have plotted the calculated shifts for the 5d elements (where experimental values for the cohesive energies have been used).

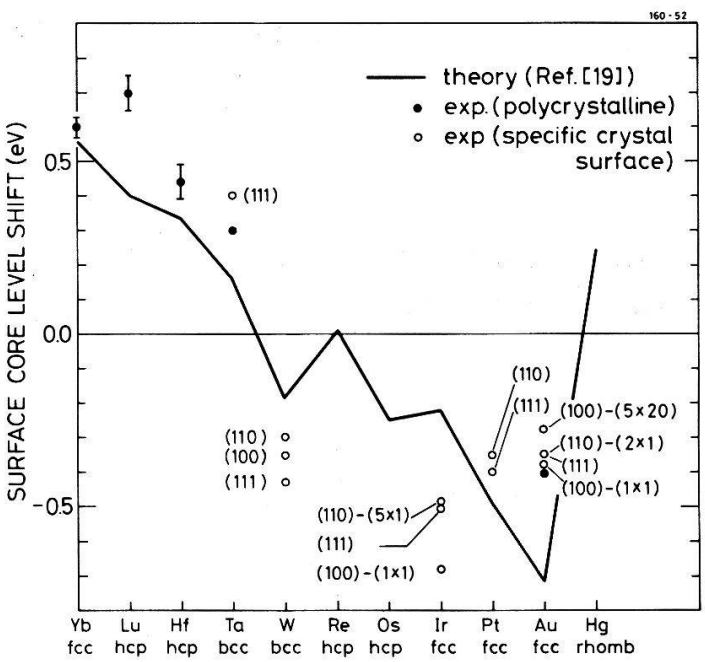

Fig. 3: Comparison between calculated surface core-level shifts, (3.5), and experimental data (Table I).

The most salient feature is the change of sign of the surface shift near the middle of the series. Thus, for the earlier transition elements the core electron is more bound at the surface than in the bulk, while in the latter part of the series the reverse holds. This can be understood as follows: The final-state valence-charge distribution around the core hole is essentially that of the (Z+1) element. For elements in the beginning of the series this means that the bonding due to the conduction electrons is stronger in the final state than in the initial state. (*Note*: We compare the *initial* state with the *final* state.) This is so, since, for the earlier d elements the (Z+1) screening takes place in the *bonding* part of the d band. Therefore, the gain in bonding in the final state relative to the initial state is *larger* for a bulk atom than for a surface atom, due to the higher coordination number in the bulk. This immediately explains the increased core-level binding energy for the surface atom in the earlier transition metals. For the heavier elements with a half-filled or more than a half-filled d band the situation is opposite, since here the (Z+1) screening utilizes the antibonding part of the d band,

and relative to the initial state some bonding is thereby lost in the final state.

Since it has been repeatedly stated in the literature that only final state effects enter into the present treatment, we want to emphasize that this is a misunderstanding. This should be clear from our verbal description above or from the shift expression, (3.1), where both the indices Z and (Z+1) enter.

In Fig. 3 we have also included all the presently available data for surface shifts of the elemental 5d transition metals. It is interesting to note that also experimentally the surface core-level shift has been found to change sign through the series. Even though the quantitative agreement between theory and experiment is far from perfect, it is still gratifying that the simple expression in (3.5), by and large, reproduces the essential features of the data.

4. Single-crystal surfaces

As already hinted at in the previous section, different crystallographic surfaces are expected to show different surface core-level shifts. If we limit ourselves to the approximate expression

$$\Delta_c = E_S^{Z+1} - E_S^Z \quad , \tag{4.1}$$

the problem is reduced to a calculation of surface energies for various crystal surfaces. This is a very difficult and delicate theoretical problem. The bonding in transition metals is dominated by the d electrons, and therefore the surface energies should also be mainly determined by the d electrons. Since the s-electron contribution to the surface energy should be relatively similar for a Z and a (Z+1) metal, the fortunate circumstance that (4.1) involves a difference between surface energies leads to a large cancellation of the s contribution. The d contribution to the variation of the anisotropy of the surface tension as a function of the band filling was calculated within a tight-binding scheme for fcc and bcc structures by Desjonquères and Cyrot-Lackmann [25]. These results were used to derive theoretical values for the surface core-level shift for different crystal surfaces [26]. The results obtained are summarized in Figure 4. Here we note a strong dependence of the surface core-level shift on the plane of cleavage, especially for the bcc structure. Thus the core-level energy is quite sensitive to the geometric arrangement of neighbouring atoms. In the same figure experimental values have

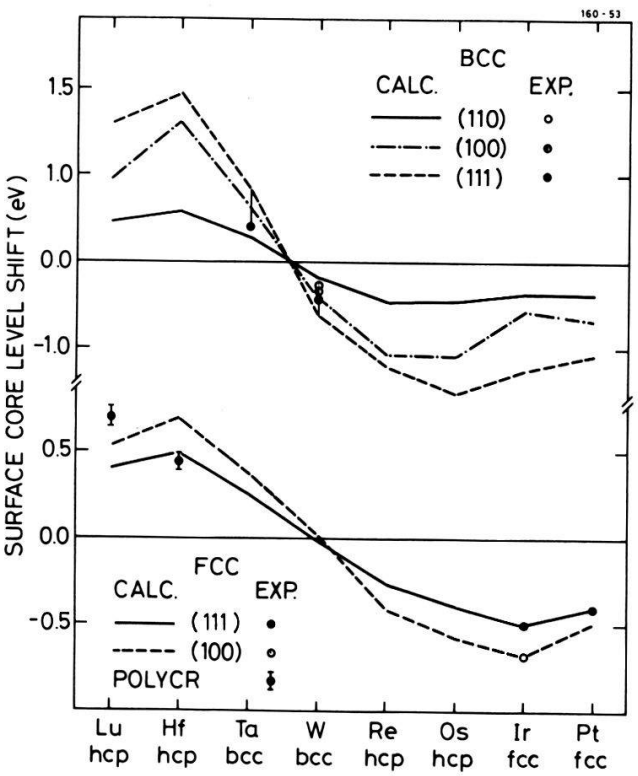

Fig. 4: Calculated [26] and experimental shifts (Table I), Δ_c, for different crystal surfaces of the 5d transition metals.

also been included for comparison. The single-crystal data for Ir and Pt agree extremely well with the calculated shifts. The polycrystalline data for lutetium and hafnium are not directly comparable with the calculations, since they are hcp metals. However, since the hcp and fcc phases both have the same coordination number, it is still meaningful to compare data for the hcp phase with theory for the fcc phase, and a reasonable agreement is found. For the bcc phase the agreement between theory and experiment is considerably less convincing. The more open a surface, the larger the deviations. It seems likely that the main reason for these deviations is due to surface atom bond length relaxation, a phenomenon not accounted for in the surface tension calculations, and which should be most pronounced for the most open surfaces.

These deviations together with the experimentally reported *second* layer core-level shifts led Rosengren [27] to apply a pair-bonding model, including nearest, next-nearest, and next-next-nearest neighbour interaction and also including surface bond relaxation. Fitting the parameters so that the theory reproduced the experimental data for the topmost surface layer core-level shifts for tungsten, he calculated the second layer shifts and the shifts for tantalum. Also Tománek et al. [28] made a similar type of investigation, based essentially on (3.1) and the pair-bonding approximation. In Table II we compare these two calculations with data, and we note a reasonable agreement but also some obvious deviations. Tománek et al. also considered the core-level shifts for stepped and reconstructed surfaces. In this connection it should be remarked upon that the analysis of the experimental data is far from straight-forward when trying to identify a second layer shift. This has been discussed by Citrin and Wertheim [31].

Table II: Comparison between experimental and theoretical values for the first and second layer core-level shifts, Δ_{S_1} and Δ_{S_2}, respectively.

Element		Exp.	Theory[d]	Theory[e]	Theory[f]	Theory
Ta(111)	Δ_{S_1}	0.40(1)[a]	0.85	0.40	0.35	
	Δ_{S_2}	0.19(2)[a]		0.22	0.17	
W(111)	Δ_{S_1}	-0.43(1)[a]	-0.60	(-0.43)	-0.39	
	Δ_{S_2}	-0.10(2)[a]		-0.24	-0.18	
W(100)	Δ_{S_1}	-0.35[b]	-0.40	(-0.35)	-0.30 (-0.28)	0.0[g]
	Δ_{S_2}	-0.13[b]		-0.11	-0.04 (-0.07)	
W(110)	Δ_{S_1}	-0.30[c]	-0.17	(-0.30)		-0.27[h]
	Δ_{S_2}			-0.02		

a) van der Veen et al. [6]
b) van der Veen et al. [7]
c) Tran Minh Duc et al. [3]
d) Rosengren et al. [26]
e) Rosengren [27]
f) Tománek et al. [28]
g) Posternak et al. [29]
h) Desjonquères et al. [30]

5. Lanthanide metals

The surface core-level shifts of the 4f level for the lanthanides have been thoroughly studied by Schmidt-May et al. [10], so that experimental shifts are now available for practically all the elements in the series. Of special interest is also the work by Kaindl et al. [17], where the surface shift of both the 4f and 5p levels in Yb were determined. This is up to now the only case where for the same element more than one core-level has been investigated with respect to surface shifts. Within the experimental uncertainties, identical shifts were found for the two levels.

In the absence of reliable data for the lanthanide surface energies, we use (3.5) for the calculation of the surface shifts. Due to the practically constant cohesive properties throughout the series, the shift values for Yb and Lu should be appropriate for the whole series, at least to a first-order approximation. A comparison between the theoretical values and the experimental data is made in Figure 5. As can be seen, the agreement is fairly good, but there are clear systematic deviations for the heavier elements.

From the data in Fig. 5 we note that the surface shift is about

0.5 eV for the earlier elements, but reaches values of the order of 0.7 eV for the heavier elements. The shift for the divalent metals, Eu and Yb, appears to be more constant throughout the series, and agrees quite well with theory.

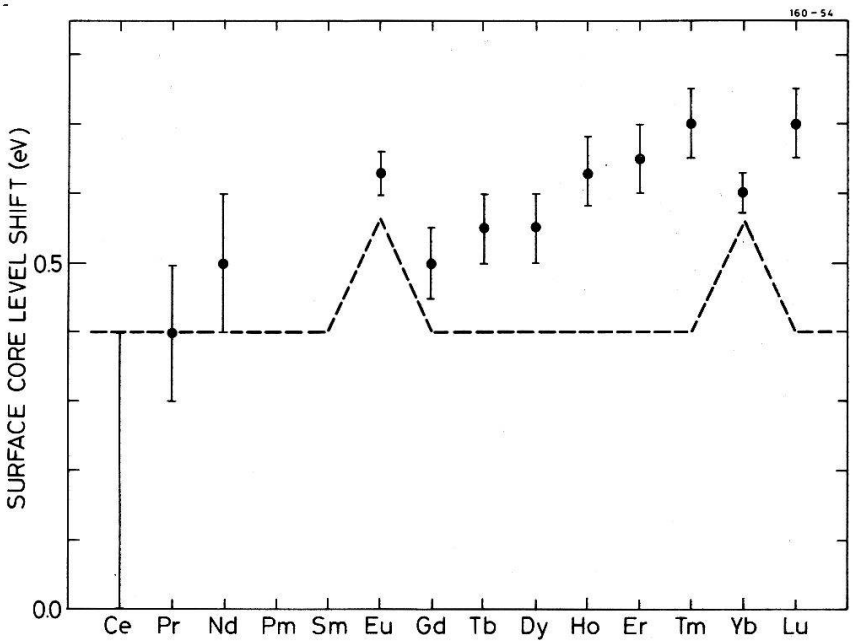

Fig. 5: Calculated, eq. (3.5), and experimental shifts (Table I), Δ_c, for the lanthanide metals.

The main difference in the electronic structure of the light and the heavy lanthanide elements is the number of 5d electrons. Energy band calculations give for lanthanum $n_d = 2.0$ and for lutetium $n_d = 1.4$ [32]. For hafnium the number of d-electrons is 2.3, i.e. about one more than in lutetium. Thus, as regards the number of d-electrons, lanthanum is intermediate between lutetium and hafnium. Assuming that the d-electrons are mainly responsible for the surface energies, one obtains, according to (4.1), that the lanthanum surface shift should be somewhere between that of lutetium and hafnium. Since experimentally the surface shift is 0.70(5) eV for lutetium and 0.44(5) for hafnium [10], this gives a reasonable explanation for the smaller surface shift for the lighter lanthanides as compared with the heavier ones. For the divalent elements the number of d-electrons relative to the number of s-electrons is probably too low for the assumption about a dominating d-contribution to the surface energy to be valid. Therefore there will not necessarily be a corresponding variation with Z.

6. Surface valence state

Photoelectron spectra of the 3d and 4d core levels from metallic samarium showed that there are contributions both from a trivalent and a divalent component [33]. This focused the interest towards investigations of the samarium surface, and by improvements of the experimental technique, it could be shown that the divalent signal originated from the surface layer [1]. This work actually preceded the work on the surface core-level shift in gold [2].

This valence change at the samarium surface can be set into relation to the above treatment of surface shifts in the following way: From Bremsstrahlung Isochromate Spectroscopy (BIS) it is known that the bulk $f^5(+3) \rightarrow f^6(+2)$ transition is about 0.5 eV above the Fermi level [34]. From the same type of argument as in the previous section, one would expect that also this transition should undergo a surface shift; indeed of about the same size as for the core-level shift of the divalent rare-earths (i.e. ∿0.6 eV). This means that the surface BIS energy should be lower than the bulk value and become -0.1 eV. The minus sign implies that the surface is unstable, i.e. a divalent surface atom has a lower energy than a trivalent surface atom, and there will be a valence change. Originally it was thought that the surface might be in a homogeneously mixed valence state. Photoemission studies showed, however, that the f-level for the divalent component was situated at about 0.7 eV below the Fermi energy [34,35], which ruled out this possibility. This value together with the BIS value then implies a surface shift of 0.7 + 0.5 = 1.2 eV, i.e. a factor of 2 larger than what we have seen to be normal for surface shifts. This "abnormal" surface shift has been explained from a consideration of the environment of the core-excited atom, in the bulk and at the surface [36], which showed that the combined BIS and XPS shift for samarium cannot be directly compared with a normal surface shift.

The question arises whether there will be other rare-earth metals with a divalent surface. As free atoms, most of the lanthanides are divalent, i.e. have a configuration $f^{n+1}s^2$. In the bulk, with a high coordination number, the trivalent state (f^n) is much favoured and most of the lanthanides, except Eu and Yb, become trivalent. The energy difference between the divalent and trivalent states, $\Delta H_{II,III}$, has been calculated [37] and is plotted in Figure 6. At the surface, due to the reduced coordination number, the energy balance between the two valence states will be changed, in fact by an amount corresponding to the surface shift calculated from (4.1) [38]. This is illustrated by the horizontal line denoted 'surface' in Fig. 6. From this follows that among the lanthanides only samarium will have a divalent surface. This also agrees with experimental evidence [39].

For an edge atom or a corner atom the energy balance will be changed even more, and in Fig. 6 we have indicated tentative values for these changes. As can be seen, in these situations quite a few of the lanthanides may become divalent.

It should be emphasized that for a deep core level (3d or 2p) in samarium, the surface core level shift is utterly extreme, namely of about 7 eV [1]. The reason for this is the radical change of the spatial charge distribution between a bulk f^5 and a surface f^6 samarium atom [19]. Except possibly for californium, there is no other element that will show such a dramatic surface shift.

The divalent surface layer explains the lack of data in Fig. 5 for the surface shift in samarium. Indeed, the explicit demonstration of the absence of a surface-shifted trivalent peak in the samarium valence band spectrum showed that there can be at most 10% trivalent atoms at the surface [40].

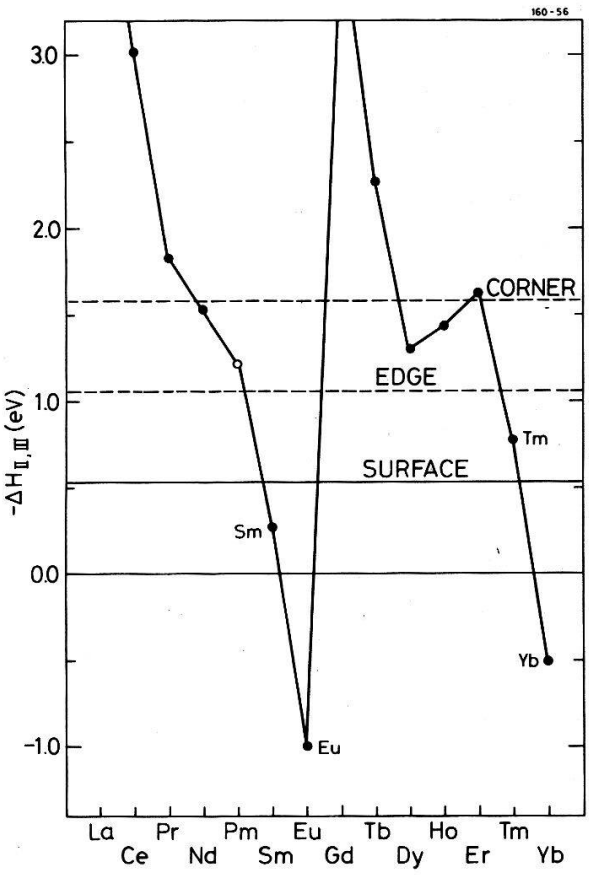

Fig. 6: Energy difference, $\Delta H_{II,III}$, between the divalent and trivalent state of the rare-earth metals. For the elements where $-\Delta H_{II,III}$ falls below the critical line labelled 'surface', the surface will be divalent. Similarly for the case of an edge or a corner.

7. Adsorbate-induced substrate shifts

The first unambiguous observation of an adsorbate-induced substrate core-level shift was made by Flodström et al. [41], who found that the Al 2p level is shifted towards 1.3 eV higher binding energy at low oxygen coverage of an aluminium film. In the present connection such studies of adsorbate-induced shifts of the surface core-level binding energy are of particular interest. Investigations have been made for several W-surfaces and Ta(111), where the influence of chemisorbed hydrogen and oxygen on the surface core levels was recorded [6,42,43]. Also the W(110)-O system [44] and the Ir(332)-H system [45] have been studied experimentally from this point of view. Theoretical calculations connected to these data are presented in Refs. 44 and 28.

The most recent experimental results for Pt(110)-CO [11] and Pt(111)-CO [12] are especially informative and will be discussed below. Since the results for the (110) and (111) surfaces are very similar, we will only

consider the (110) case.

The experiments showed that for the clean Pt(110) surface, the surface core level is shifted by -0.35(2) eV. However, upon CO chemisorption, the surface level is shifted by +0.71(4) eV. Thus, the position of the surface level relative to the bulk level has changed side upon CO exposure! Since Fig. 2 applies equally well to the case where the surface is covered by an adsorbate, the data can be interpreted as follows: With the (Z+1) replacement and the surface segregation interpretation, the clean (110) surface shift implies that for low concentrations of Au on Pt, Au will segregate to the surface, the heat of surface segregation being quite substantial, -0.35 eV. However, for a CO covered surface the situation is completely reversed, i.e. in a Pt-Au alloy covered by CO, Pt will segregate to the surface. Thus, the presence of an adsorbate can change the direction of the segregation. The physical reason for this is that Pt forms considerably stronger bonds with CO than does Au. Studies of the surface core level can therefore be very informative concerning the energetics of the segregation phenomena and should be helpful in finding suitable procedures for controlling the degree of segregation. Certain aspects of catalyst poisoning could be clarified by this type of investigations. Furthermore, the recording of the intensities of the surface and bulk peaks of the components in an alloy system, directly monitors the degree of segregation. The first investigation of this kind has already been performed for Eu-Au and Yb-Au systems [8].

Adsorbate-induced substrate shifts were used by Egelhoff [46] to indirectly determine the surface core-level shift of the 2p level for Ni(100) (-0.46 eV). By depositing Co on the nickel surface and subtracting the measured Ni 2p core-level spectrum from the corresponding 2p spectrum of the clean surface, a feature remained which was displaced by -0.46 eV relative to the Ni 2p peak position in presence of the adsorbate. The consistency obtained in this procedure was taken as evidence for that the deposited Co overlayer shifts the surface Ni core-level peak to its bulk position. Similar results were obtained from depositions of Cr, Mn, and Fe. It is interesting to note that Egelhoff found that when the Ni(100) surface is saturated with CO molecules, the surface peak is shifted even more, appearing on the high binding-energy side of the bulk peak. This is exactly the same situation as discussed above for Pt, and has the same implications.

Adsorbate shift measurements for Au deposited on Ni and for Ni de-

posited on Au were done by Steiner and Hüfner [47]. By means of the (Z+1) approximation they related their results to heats of surface segregation.

8. Other models

Here we want briefly to make contact with some other theoretical treatments of the surface core-level shifts. The origin of the shift has been much discussed in the literature, and the majority of workers in the field seems to take the view-point that it is almost exclusively due to initial state effects (see e.g. [48,13,30]). This view is particularly strongly expressed in a recent work by Citrin and Wertheim [31].

In the treatment given in Section 2, leading to the shift expression (2.15), both the initial and final state effects are included. Indeed, the relation for the surface shift Δ_c is almost symmetric in Z and Z*.

The work by Desjonquères et al. [30] expressed the surface core-level shift in terms of a surface potential U(Z), which is closely related to the shift of the centre of gravity of the surface d-band relative to the centre of gravity of the bulk d-band. (This latter picture is in its turn close to the picture of a shifted centre of gravity of surface and bulk density of states, used by Citrin et al. [2] to explain the core-level shift in Au.) Taking the simplified form for the surface shift, (4.1),

$$\Delta_c(Z) = E_S(Z+1) - E_S(Z) \ , \tag{8.1}$$

Desjonquères et al. expanded $E_S(Z+1)$ in a Taylor series around Z and obtained

$$\Delta_c(Z) \simeq \frac{\partial E_S(Z)}{\partial Z} + \ldots\ldots \ . \tag{8.2}$$

This first-order term can be shown to correspond to -U(Z). Indeed for a model where the surface band is rigidly displaced by U(Z), in order to maintain surface neutrality, $\partial E_S(Z)/\partial Z$ is strictly equal to -U(Z). Thus, from this point of view the surface shift appears to be mainly an initial state effect.

However, (8.1) can equally well be expanded around (Z+1). Thus we obtain

$$\Delta_c(Z) = \frac{\partial E_S(Z+1)}{\partial Z} + \ldots \ , \tag{8.3}$$

which is directly related to -U(Z+1). This then suggests that the surface shift is mainly a final state effect.

Naturally, the most appropriate expansion of (8.1) is given by

$$\Delta_c(Z) \approx \frac{\partial E_S(Z+\frac{1}{2})}{\partial Z} \ , \tag{8.4}$$

which is connected to $-U(Z+\frac{1}{2})$. This explains the similarity between the results obtained by Desjonquères et al. and those obtained from (8.1), since they should essentially only be displaced from each other by 'half an element'. When using the scheme by Desjonquères et al., one should consider a hypothetical $(Z+\frac{1}{2})$ element in order to get the most appropriate value for the surface shift of the Z element.

Feibelman and Hamann [49] calculated the core orbital energy difference between a surface atom and a bulk atom and identified this with the surface core-level shift. For Cu(111) Appelbaum and Hamann showed [50] that this eigenvalue energy shift is quite similar to the centre of gravity shift of the density of states, which then gives a connection to the treatment by Desjonquères et al. [30].

The discussion above in (8.1) - (8.4) suggests that when orbital energy surface shifts are used in the calculation of the surface core-level shift for an element Z, this calculation should actually be performed for the $(Z+\frac{1}{2})$ 'element'. This is essentially Slater's transition state. It is then interesting to reconsider the calculations by Posternak et al. [29] for the W(100) surface, where a zero surface shift was obtained (i.e. zero shift of the orbital energy). The argument above shows, however, that this calculation should be interpreted as being more appropriate for the (hypothetical) $(Z-\frac{1}{2})$ metal, i.e. a fictive element midway between tungsten and tantalum. For Ta(111) the surface shift is 0.40 eV and for W(111) it is -0.43 eV (Table I), so that the average value is close to zero. Accordingly, also for the other crystal planes for Ta and W one can expect very similar magnitudes of the shifts but of opposite sign [27], so that the average value is close to zero. Thus, with this reinterpretation of the calculations by Posternak et al., there seems to be a good agreement with experiment.

The transition state concept for surface core-level shift calculations has been applied by Smith et al. [51] for Cu(100). In fact, instead of making the $(Z+\frac{1}{2})$ replacement for the whole crystal as implied above, they went one step further and introduced only a plane of $(Z+\frac{1}{2})$ atoms. This plane is first placed in the bulk and then it is moved to the surface. This should be a better approximation to (2.15) than just a uniform $(Z+\frac{1}{2})$ transition state atom replacement. Smith et al. found that both initial and final state effects are important and calculated a shift of -0.36 eV. This should be compared with the experimental value of -0.24 eV for a polycrystalline sample [20] .

9. Summary

Improved experimental techniques have recently made it possible to separate surface core-level signals from bulk signals. Thereby new types of very surface-sensitive investigations become possible, and above we have briefly indicated some of the most obvious applications. Already at the present stage of development it seems clear that, for example, surface segregation can be fruitfully studied by means of the surface core levels. Naturally, the main difficulty will be the somewhat unfortunate fact that the surface core-level shifts are relatively small. In many cases this will require accurate data-fitting procedures, before the relevant information can be extracted. This calls for theoretical work on the modifications of the line widths and line profiles for surface atoms relative to bulk atoms.

In this review we have exclusively considered surface core-level shifts for elemental metals, although corresponding shifts have for example also been recorded for semiconductors [52,53]. The present general interest in rare-earth systems has led to the observation of surface shifts in quite a few rare-earth intermetallic systems [54-56] and compounds [57-59]. For mixed-valence systems it has been noted that the surface layer(s) tends to attain the lower valence state, in conformance with simple bonding arguments. Theoretical calculations for these more complicated systems have also been performed [60].

On the theoretical side, several different approaches have been applied, leading to rather similar results. The reason for these similarities was briefly indicated in Section 8. The main principle obstacle in the theoretical treatment is the difficulty encountered when dealing with an impurity problem.

In the same way as for core levels, also Auger electrons are expected to undergo surface energy shifts [61]. However, experimentally the separation into bulk and surface contributions will be more difficult than for core levels.

Acknowledgment

We would like to thank A. Flodström and collaborators at DESY, Hamburg, for their permission to quote their data prior to publication.

References

[1] G.K. Wertheim and G. Creselius, Phys.Rev.Lett. 40, 813 (1978).

[2] P.H. Citrin, G.K. Wertheim and Y. Baer, Phys.Rev.Lett. 41, 1425 (1978).

[3] Tran Minh Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet and J.C. Vedrine, Phys.Rev.Lett. 43, 789 (1979).

[4] J.W. Allen, L.I. Johansson, R.S. Bauer, I. Landau and S.B.M. Hagström, Phys.Rev.Lett. 41, 1499 (1978).

[5] J.F. van der Veen, F.J. Himpsel and D.E. Eastman, Phys.Rev.Lett. 44, 189 (1980), Errata: Phys.Rev.Lett. 44, 553 (1980), idem, Sol.St.Commun. 40, 57 (1981).

[6] J.F. van der Veen, P. Heiman, F.J. Himpsel and D.E. Eastman, Sol.St. Commun. 37, 555 (1981).

[7] J.F. van der Veen, P. Heiman, F.J. Himpsel and D.E. Eastman. Sol.St. Commun. 38, 595 (1981).

[8] L.I. Johansson, S.A. Flodström, S.-E. Hörnström, B. Johansson, J. Barth and F. Gerken, Sol.St.Commun. 41, 427 (1982).

[9] R. Kammerer, J. Barth, F. Gerken, S.A. Flodström and L.I. Johansson, Sol.St.Commun 41, 435 (1982).

[10] J. Schmidt-May, F. Gerken, J. Barth, R. Nyholm, L.I. Johansson, S.A. Flodström, R. Kammerer and C. Kunz, (to be published).

[11] M.L. Shek, P.M. Stefan, C. Binns, I. Lindau and W.E. Spicer, Surf.Sci. 115, L81 (1982).

[12] G. Apai, R.C. Baetzold, E. Shustorovich and R. Jaeger, Surf.Sci. 116, L191 (1982).

[13] P. Heiman, J.F. van der Veen and D.E. Eastman, Sol.St.Commun. 38, 595 (1981).

[14] T.-C. Chiang and D.E. Eastman, Phys.Rev. B 23, 6836 (1981).

[15] R. Kammerer, J. Barth, F. Gerken, C. Kunz, S.A. Flodström and L.I. Johansson, Phys.Rev. B 26, 3491 (1982).

[16] R.D. Parks, N. Mårtensson and B. Reihl, *Valence Instabilities*, ed.: P. Wachter and H. Boppart (North-Holland, 1982), p. 239.

[17] G. Kaindl, W.D. Schneider, C. Laubschat, B. Reihl and N. Mårtensson, Surf.Sci. (to be published).

[18] S.F. Alvarado, M. Campagna and W. Gudat, J.Electron Spectr. and Rel. Phenom. 18, 43 (1980).

[19] B. Johansson and N. Mårtensson, Phys.Rev. B 21, 4427 (1980).

[20] P.H. Citrin, G.K. Wertheim and Y. Baer, Phys.Rev. B (to be published).
[21] J. Lecante (this volume).
[22] Y. Baer (this volume).
[23] A. Rosengren and B. Johansson, Phys.Rev. B 23, 3852 (1981).
[24] B.C. Allen, in *Liquid Metals, Chemistry and Physics*, ed. S.Z. Beer (Dekker, New York, 1972), p. 161.
[25] M.C. Desjonquères and F. Cyrot-Lackman, Surf.Sci. 50, 257 (1975).
[26] A. Rosengren and B. Johansson, Phys.Rev. B 22, 3706 (1980).
[27] A. Rosengren, Phys.Rev. B 24, 7393 (1981).
[28] D. Tománek, V. Kumar, S. Holloway and K.H. Benneman, Sol.St.Commun. 41, 273 (1982).
[29] M. Posternak, H. Krakauer, A.J. Freeman and D.D. Koelling, Phys.Rev. B 21, 5601 (1980).
[30] M.C. Desjonquères, D. Spanjaard, Y. Lassailly and C. Guillot, Sol.St. Commun. 34, 807 (1980).
[31] P.H. Citrin and G.K. Wertheim, Phys.Rev. B (to be published).
[32] H.L. Skriver (private communication).
[33] G.K. Wertheim and M. Campagna, Chem.Phys.Lett. 47, 182 (1977).
[34] J.K. Lang and Y. Baer, Sol.St.Commun. 31, 945 (1979).
[35] J.W. Allen, L.I. Johansson, I. Lindau and S.B.M. Hagström, Phys.Rev. B 21, 1335 (1980).
[36] A. Rosengren and B. Johansson, Phys.Rev. B 26, 3068 (1982).
[37] B. Johansson, Phys.Rev. B 20, 1315 (1979).
[38] B. Johansson, Phys.Rev. B 19, 6615 (1979).
[39] L.I. Johansson, J.W. Allen and I. Lindau, Phys.Lett. 86 A, 442 (1981).
[40] F. Gerken, J. Barth, R. Kammerer, L.I. Johansson and A. Flodström, Surf.Sci. 117, 468 (1982).
[41] S.A. Flodström, R.Z. Bachrach, R.S. Bauer and S.B.M. Hagström, Phys. Rev.Lett. 37, 1282 (1976).
[42] J.F. van der Veen, F.J. Himpsel and D.E. Eastman, Phys.Rev. B 25, 7388 (1982).
[43] J.F. van der Veen, F.J. Himpsel and D.E. Eastman, Sol.St.Commun. 40, 57 (1981).
[44] G. Tréglia, M.C. Desjonquères, D. Spanjaard, Y.Lassailly, C. Guillot, Y. Jugnet, Tran Minh Duc and J. Lecante, J.Phys. C 14, 3463 (1981).
[45] J.F. van der Veen, D.E. Eastman, A.M. Bradshaw and S. Holloway, Sol.St.

Commun. 39, 1301 (1981).

[46] W.F. Egelhoff, Jr., Phys.Rev.Lett. 50, 587 (1983).

[47] P. Steiner and S. Hüfner, Sol.St.Commun. 37, 279 (1981).

[48] P.F. Feibelman, J.A. Appelbaum and D.R. Hamann, Phys.Rev. B 20, 1433 (1979).

[49] P.F. Feibelman and D.R. Hamann, Sol.St.Commun. 31, 413 (1979).

[50] J.A. Appelbaum and D.R. Hamann, Sol.St.Commun. 27, 881 (1978).

[51] J.R. Smith, F.J. Arlinghaus and J.G. Gay, Phys.Rev. B 26, 1071 (1982).

[52] F.J. Himpsel, P. Heinemann, T.-C. Chiang and D.E. Eastman, Phys.Rev. Lett. 45, 1112 (1980).

[53] S. Brennan, J. Stöhr, R. Jaeger and J.E. Rowe, Phys.Rev.Lett. 45, 1414 (1980).

[54] G.K. Wertheim, J.H. Wernick and G. Crecelius, Phys.Rev. B 18, 875 (1978).

[55] N. Mårtensson, B. Reihl, W.D. Schneider, V. Murgay, L.G. Gupta and R.D. Parks, Phys.Rev. B 25, 1446 (1982).

[56] G. Kaindl, B. Reihl, D.E. Eastman, R.A. Pollack, N. Mårtensson, B. Barbara, T. Penney and T.S. Plaskett, Sol.St.Commun. 41, 157 (1982).

[57] W. Gudat, M. Campagna, R. Rosei, J.H. Weaver, W. Eberhardt, F. Hulliger and E. Kaldis, J.Appl.Phys. 52, 2123 (1981).

[58] N. Mårtensson, B. Reihl, R.A. Pollack, F. Holzberg and G. Kaindl, Phys.Rev. B 25, 6522 (1982).

[59] G. Kaindl, C. Laubschat, B. Reihl, R.A. Pollack, N. Mårtensson, F. Holtzberg and D.E. Eastman, Phys.Rev. B 26, 1713 (1982).

[60] H.-J. Brocksch, D. Tománek and K.H. Benneman, Phys.Rev. B 25, 7102 (1982).

[61] N. Mårtensson, P. Hedegård and B. Johansson, (to be published).