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Surface-core-level shifts for low-index surfaces of W and Ta

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With the assumption of a fully screened final state and within the $(Z+1)$ approximation a simple semiempirical model is presented for calculating surface-core-level shifts. Numerical results are given for shifts for first, second, and third surface-layer atoms of low-index surfaces of W and Ta.

Surface-core-level binding-energy shifts are currently an active field of research. Such shifts have been measured for the $4f$ core level in photoemission from gold,[1] tungsten,[2–4] iridium,[5] and tantalum.[3] The shifts are dependent on surface crystallography,[2–5] and therefore the surface-core-level shifts (SCS) could become a most useful tool to study transition metal surfaces.[5] In a recent paper[6] we gave a theoretical treatment of these shifts, and presented numerical calculations for the SCS for low-index surfaces of the elements of the $5d$ series. Underlying the theory was the assumption of a fully screened final state and the $(Z+1)$ approximation for the screening valence-charge distribution around the core-ionized site. We then showed that the SCS could be related to the difference in surface energy between elements $Z+1$ and Z, and for these surface energies we used tight-binding calculations.[7] The theory accounted in a simple way for the shift in sign of the shift through the $5d$ series, and also the quantitative agreement with experiment was satisfactory for the less open surfaces. From recent experiments[3,4] it is clear that the theoretical predictions for more open surfaces overestimated the SCS. One reason for this could be that surface-layer contraction is important in these metals for the more open surfaces,[3] another reason could be that the tight-binding method (including surface contraction or not) used to calculate the surface energy is somewhat too crude a method to obtain SCS with high enough an accuracy for open surfaces.

Here we present a method which enables us to calculate core-level shifts for second and third surface-layer atoms and which has the advantage over the tight-binding method that it is so simple that it may readily be extended to more complicated surface systems. To calculate the SCS's we use a pair-bonding model, including pairs of nearest, next-nearest, and next-next-nearest neighbors, and including surface bond relaxation. For tungsten the SCS for the low-index surfaces (110), (100), and (111) are known,[2–4] and we have used these shifts to determine the parameters entering the model. We then calculate the core-level shifts originating from core-ionized atoms in the first three surface layers of tungsten and tantalum and compare with experimental data.

As was mentioned above, the assumption of a fully screened final state is essential to the theory. This means that, if we have a metal of atoms with atomic number Z, we can treat a core-ionized site as a charge-neutral Z^* *impurity* ($*$ means core-ionized atom). The $(Z+1)$ approximation, i.e., the final-state screening valence-electron distribution resulting from the photoemission of a deep core electron of a Z atom can be described by the valence-electron distribution of a $(Z+1)$ substitutional atomic site, enables us to substitute this Z^* impurity by a $(Z+1)$ impurity. Thus we have for the bulk excitation process the following picture: The initial state is a perfect metal of Z atoms and the final state is the same metal with one of the bulk Z atoms substituted by a $(Z+1)$ atom. For the surface excitation process the final state is trivially the perfect metal with a Z atom in one of the surface layers substituted by a $(Z+1)$ atom. The surface-core-level shift is given as the difference between the surface and bulk excitation energies. The initial and final states mentioned above are easy to describe within a pair-bonding model. If we, for brevity, call the Z metal A and the $Z+1$ metal B, we get the following expression for the surface-core-level shift $\Delta_c(A)$:

$$\Delta_c(A)=\sum_i \frac{Z_b^{(i)}-Z_r^{(i)}\delta^{(i)}}{Z^{(i)}}[E_{\text{coh}}^{(i)}(B)-E_{\text{coh}}^{(i)}(A)-E_B^{(i)}(A)] , \quad (1)$$

where Z_b denotes the number of broken bonds for the core-ionized atom in a surface plane, and Z_r denotes the number of renormalized surface bonds for this atom. Only lateral and vertical bonds including atoms in the first (topmost) layer are assumed to be renormalized. Bond renormalization at the surface is conventionally in pair-bonding models expressed by a parameter δ defined by

$$\epsilon_{jk}^{S}=\epsilon_{jk}(1+\delta_{jk}) , \tag{2}$$

where ϵ_{jk}^{S} and ϵ_{jk} are surface and bulk bond enthalpies, respectively, for a jk bond ($j=A,B$ and $k=A,B$). [As pointed out in Ref. 8, bond renormalization can physically be thought to account for changes in bond enthalpies due to changes in bond lengths at the surface (surface contraction) and for the fact that the cohesive energy does not properly represent the surface bond enthalpies.] Further, in Eq. (1), Z denotes the number of neighbors of a bulk atom, and the superscript (i) denotes nearest neighbors ($i=1$), next-nearest neighbors ($i=2$), and so on. The entity $E_{\text{coh}}^{(i)}(j)$ is that part of the cohesive energy of element j that is attributed to neighbor (i), and correspondingly $E_B^{(i)}(A)$ is the difference between the surface and bulk heats of solution (for the infinitely dilute case) of B metal in A metal. In the derivation of Eq. (1) the assumption $\delta_{AB}^{(i)}=\delta_{AA}^{(i)}=\delta^{(i)}$ was made.

In order to include next-next-nearest neighbors in the model we have used effective coordination number,[9] $Z_{\text{eff}}^{(2)}=Z^{(2)}+\beta Z^{(3)}$, where we have chosen $\beta=\frac{1}{4}$. This corresponds to that $\frac{1}{3}$ of the total contribution to the cohesive energy from next-nearest and next-next-nearest neighbors originates from the latter ones. Furthermore, we introduce variables α_j by

$$E_{\text{coh}}^{(1)}(j)=E_{\text{coh}}(j)(1-\alpha_j)E_{\text{coh}}^{(1)}(j)=E_{\text{coh}}(j)(1-\alpha_j) \tag{3a}$$

and

$$E_B^{(1)}(A)=E_B(A)(1-\alpha_C)E_B^{(1)}=E_B(A)(1-\alpha_c) . \tag{3b}$$

For brevity $E_{\text{coh}}(A)$, $E_{\text{coh}}(B)$, and $E_B(A)$ is denoted A, B, and C, respectively, in the following.

The SCS's for the topmost layer of the (111), (100), and (110) surfaces can now be written, respectively, as

$$\left[\frac{15-21\delta_{111}^{(2)}}{36}-\frac{1-\delta_{111}^{(1)}}{2}\right](\alpha_B B-\alpha_A A-\alpha_C C)+\frac{1-\delta_{111}^{(1)}}{2}(B-A-C)=\Delta_c^{(111)}(A) , \tag{4a}$$

$$\left[\frac{2-7\delta_{100}^{(2)}}{9}-\frac{1-\delta_{100}^{(1)}}{2}\right](\alpha_B B-\alpha_A A-\alpha_C C)+\frac{1-\delta_{100}^{(1)}}{2}(B-A-C)=\Delta_c^{(100)}(A) , \tag{4b}$$

$$\left[\frac{13-23\delta_{110}^{(2)}}{36}-\frac{1-3\delta_{110}^{(1)}}{4}\right](\alpha_B B-\alpha_A A-\alpha_C C)+\frac{1-3\delta_{110}^{(1)}}{4}(B-A-C)=\Delta_c^{(110)}(A) . \tag{4c}$$

In order to calculate the SCS's, we further have to specify the δ's appearing in Eq. (4) above. The simplest assumption to be made would be proportionality between δ and Z_b, but we have here also included a quadratic term, so the expressions for the δ's are

$$\delta^{(1)}=Z_b^{(1)}k+(Z_b^{(1)})^2t \tag{5a}$$

and

$$\delta^{(2)}=s\left[Z_b^{(2)}k+(Z_b^{(2)})^2t\right] . \tag{5b}$$

We have in the expression for $\delta^{(2)}$ included a factor s, to take care of the fact that the next-nearest-neighbor bond renormalization is expected to be weaker than the nearest-neighbor bond renormalization. In the calculations to be performed we have chosen $s=\frac{1}{2}$. (We have varied s from zero to one and found the variation of the calculated values ±0.01 eV.) The surface shifts for the topmost layer of the (111), (100), and (110) surfaces of W are known experimentally[2–4] and these are now used to determine the parameters entering the model. Equations (4) and (5) give us a system of three equations with five unknowns: α_A, α_B, α_C, k, and t. If we first consider the α's we see that Eq. (4) describes the set of three parallel planes and in order to find a solution these planes must coincide. This gives us two coupled equations for k and t, and k and t so determined give us together with one of Eqs. (4) the entity $\alpha_B B-\alpha_A A-\alpha_C C$. The α's only enter the equations for core-level shifts in this combination, so the remaining shifts we are interested in can now all be calculated from a knowledge of this entity and of k and t. For the values of the cohesive energies we have used for W, Re, and Ta, 205.2, 185.2, and 186.8 kcal/mol, respectively.[10] Since it is known that the heat of solution between neighboring transition metals is small,[11,12] the term C in Eq. (4) has been neglected in the calculations.[6]

In Table I one we present the calculated shifts for W for the second and third topmost surface layer and compare with experimental data when available. We have in the table also included Ta. The calculations for this element were performed under two assumptions, namely that the bond renormalizations obtained for W are representative also for Ta and that $\alpha_{\text{Ta}}=\alpha_{\text{W}}=\alpha_{\text{Re}}$.

First of all we note that the calculations reproduce the change in the sign of the shift taking place between Ta and W. From Eq. (1) it is evident that an increased (decreased) surface atom core-level binding energy is predicted for elements in the beginning (end) of a transition-metal series, since the cohesive energy is known to vary parabolically through such a series. Actually it is the parabolical variation of *surface* energies through a series that is physically important,[6] but since a broken-bond model expresses surface energies as fractions of cohesive energies, the surface energies in such a model will also vary parabolically. However, it should be born in mind that one reason for our introduction of the δ's was that the surface bond enthalpies are not properly represented by the cohesive energies.[8] This means that a simple broken-bond model introduces an error growing rapidly going from the 5*d*, via the 4*d*, to the 3*d* transition-metal series.[13] From Table I we further note the overall good agreement between calculated values and experiment, even for second surface-layer core shifts, with one exception, the shift from second-layer atoms of the (111) surface of tungsten. The experimental value assigned to this shift, −0.10 eV,[3] resembles more closely the shift calculated for the third-layer atoms instead. We do not know the reason for this, but one possible explanation might be that the absolute value calculated for the second-layer shift is too low and that the surface-peak experimentally ascribed to the first-layer peak actually consists of both first- and second-layer peaks, and that the peak experimentally ascribed to the second layer actually is a third-layer peak. This would explain from a bond-breaking model point of view the peculiar facts that, in absolute numbers, the second-layer shift for W is almost half that for Ta, and that the second-layer shift for W is greater for the (100) surface than for the more open (111) surface. Some support for such a conjecture may be given from the intensities for the surface peaks fitted to the experimental curve.[3] For the Ta(111) surface the ratio of the intensity for the surface peak ascribed to the first layer and the intensity of the bulk peak is 0.7, while the corresponding ratio for W is 0.9. This could of course be explained, as was implicitly done in Ref. 3, by different mean free paths for the photoelectrons for Ta and W. On the other hand, if it is assumed that the mean free path of W equals that of Ta, the difference in the intensity ratios could be explained by a surface peak in W built up by both first- and second-level surface peaks. Another explanation is of course that the disagreement is due to deficiencies in the pair-bonding model used.

To summarize, we have presented a simple pair-bonding model to calculate surface core-level binding energy shifts. The model used is based on the assumption of a fully screened final state for the excitation process and on the $(Z+1)$ approximation. This assumption and this approximation has been successfully used for calculating core-level binding energy shifts between free and condensed metallic atoms.[14] With bond renormalization at

TABLE I. Surface core-level shifts for W and Ta low-index surfaces. Δ_c^1, Δ_c^2, and Δ_c^3 denote the shifts from first-, second-, and third-layer atoms, respectively.

	Shift (eV)	Δ_c^1		Δ_c^2		Δ_c^3	
Element	Surface	Theory	Expt.	Theory	Expt.	Theory	Expt.
W	(111)	(−0.43)	−0.43	−0.24	−0.10	−0.07	
	(100)	(−0.35)	−0.35	−0.11	−0.13	−0.00	
	(110)	(−0.30)	−0.30	−0.02		−0.00	
Ta	(111)	0.40	0.40	0.22	0.19	0.06	
	(100)	0.32		0.10		0.00	
	(110)	0.28		0.01		0.00	

the surface taken into account, the model gives quite good agreement between calculation and experiment. The advantage of the model is its simplicity, which makes it easily extended to more complicated surfaces.

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