Surface-atom core-level shifts of W(111)

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The W(111) $4f$ photoemission spectrum has been further investigated to determine whether the extra width of the surface component is due to unresolved contributions from two lattice planes. Although a satisfactory fit is obtained by this ansatz, the intensities of the resulting components are incompatible with an escape-depth model. The earlier suggestion that this width is due to unresolved surface crystal-field splitting remains the most likely explanation.

Some years ago the surface-atom core-level shift of various W and Ta surfaces were examined in considerable detail.[1-3] For W(111) two surface components were resolved in the $4f$ spectrum, a subsurface component with a small negative shift and a broadened surface component with a significantly larger shift. A recent communication[4] has shown that the W(111) $4f$ photoemission spectrum could be equally well represented by replacing the single broadened surface component by two, each having the same shape as the bulk and subsurface. This has motivated an extension of our earlier analysis[3] to examine this possibility.

Our approach here is to use the better signal-to-noise ratio in the data from Ref. 3 to see whether a clear distinction can be made between the two representations. In Figs. 1–3 we show the results of fitting these data with model functions consisting of a bulk line and (1) three surface components, (2) two surface components, with extra Gaussian broadening in the outer one, and (3) two surface components with independent Gaussian width. The lifetime width, singularity index, and combined phonon and instrumental width are the same for all components in a given fit. A comparison of the residuals shown at the bottom of each figure demonstrates that qualitatively the three model functions are equally successful in representing the data. No clear choice emerges. Quantitative confirmation of this dilemma is provided by the sum of the squares of the deviations, shown in Table I, which are identical for Figs. 2 and 3 and only 5% larger for Fig. 1. Even this difference is clearly too small to discriminate among the models.

There are, however, constraints based on physical considerations that must be satisfied before we can accept the output of data analysis. A major requirement is that the intensities of the components reflect the number of atoms
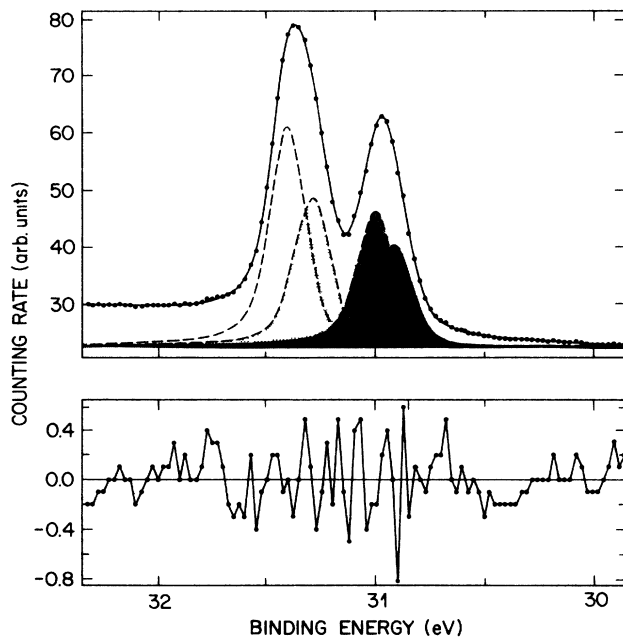

FIG. 1. Least-squares analysis of the W(111) $4f_{7/2}$ photoemission data of Ref. 3, using a model containing one bulk and three surface lines with identical shape on a quadratic background. The line shape is the result of the convolution of the Doniach-Šunjić function with a Gaussian (see, e.g., Ref. 3). The model contains 14 parameters, which are all freely adjustable. Numerical results are given in Table I.
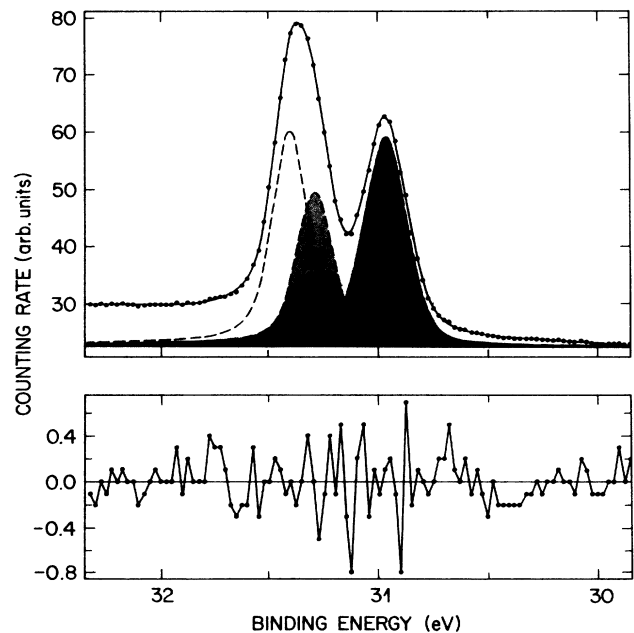

FIG. 2. As in Fig. 1, but using only three lines with independent Gaussian widths for the component at smallest binding energy. There are 13 free parameters. Numerical results are given in Table I.
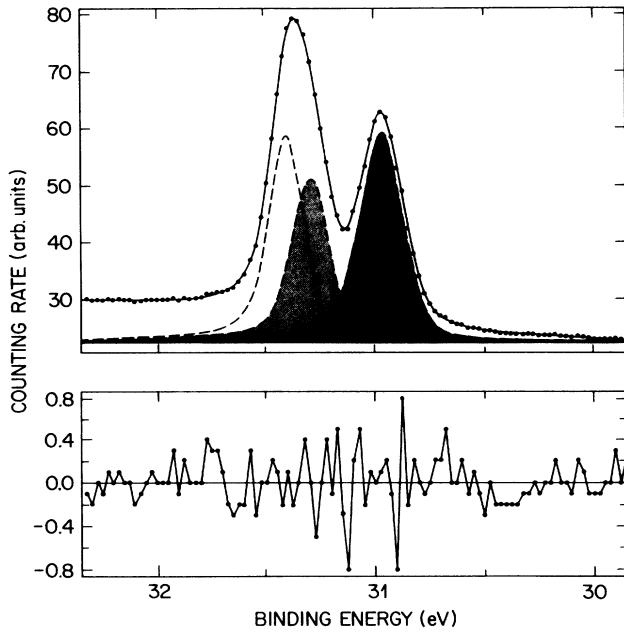
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FIG. 3. As in Fig. 2, but with independent Gaussian widths for all three lines. There are again 14 free parameters. Numerical results are given in Table I.

of each type and their distance from the surface. For the W(111) surface each layer contains the same number of atoms, see Fig. 4. The labeling of the layers is also defined in that figure. The effect of the depth of the layer below the surface has usually been found to be well represented by an exponential attenuation characterized by an escape depth λ. The data used here[2,3] were taken

with an analyzer acceptance angle of 87°, sufficient to average out diffraction effects. In the three-surface-component analysis shown in Fig. 1 the intensities of S, SS1, and SS2 normalized to that of B are found to be 0.465, 0.616, and 0.678, respectively. That is, the outermost layer is *weakest* and the innermost *strongest*. Since each layer has the same number of atoms, these intensities cannot be reconciled with the attenuation expected for electrons traveling through the crystal. The results of the other models are compatible with an exponential attenuation as noted earlier.[2] This fact provides a strong argument against the three-surface-component model, unless the signals from outermost layers are selectively attenuated by other considerations.

One possible source of attenuation is surface contamination. The detailed work of Ref. 2, in which a W(111) surface was deliberately exposed to hydrogen or oxygen, serves to clarify this issue. Hydrogen, the most likely contaminant, attenuates the surface line and results in the growth of a new one with a shift of -0.26 eV. No extra intensity was found at this energy, which falls between the two main peaks. Hydrogen contamination can therefore be ruled out. Oxygen exposure results in a gradual shift of the surface line, but with little loss of intensity in the initial stages. Broadening of the emission from the outermost layers could then conceivably have its origin in residual surface oxygen, but the reduced intensity cannot. Moreover, the ease of removing and detecting surface oxygen and the care with which the clean W(111) data were obtained make this possibility remote.

In this connection it is worth noting that the chemisorption experiments[2] gave no indication that the component at smallest binding energy is made up of signals from different atomic layers. Chemisorption would be

TABLE I. Summary of line-shape parameters determined from least-squares fits in Figs. 1, 2, and 3.

	Fig. 1[a]	Fig. 2[b]	Fig. 3[c]
Bulk component, B			
Lorentzian width, $\Gamma_{7/2}$ (eV)	0.068(5)	0.061(5)	0.061(5)
Singularity index, α	0.048(8)	0.044(8)	0.044(8)
Gaussian width, Γ_B^G (eV)	0.150(8)	0.151(7)	0.148(11)
Surface component, S			
Binding energy relative to B (eV)	$-0.484(7)$	$-0.436(3)$	$-0.439(9)$
Intensity relative to B	0.465(39)	1.266(23)	1.291(41)
Gaussian width, Γ_S^G (eV)	0.150(8)	0.193(8)	0.191(12)
First subsurface component, SS1			
Binding energy relative to B (eV)	$-0.398(5)$	$-0.113(3)$	$-0.112(3)$
Intensity relative to B	0.616(32)	0.710(26)	0.803(21)
Gaussian width, Γ_{SS1}^G (eV)	0.150(8)	0.151(7)	0.154(12)
Second subsurface component, SS2:			
Binding energy relative to B (eV)	$-0.113(3)$		
Intensity relative to B	0.678(25)		
Gaussian width, Γ_{SS2}^G (eV)	0.150(8)		
Sum of square of deviations, χ^2	0.0153	0.0146	0.0146

[a]Four-line fit with B, S, SS1, and SS2 line shapes constrained to have the same α, $\Gamma_{7/2}$, and Γ^G.
[b]Three-line fit with B, S, and SS line shapes constrained to have the same α and $\Gamma_{7/2}$ but with $\Gamma_B^G = \Gamma_{SS}^G$ and Γ_S^G kept free, as in Ref. 3.
[c]Three-line fit as in Fig. 3 but with Γ_B^G, Γ_S^G, and Γ_{SS}^G all independently variable.

W(111)

TOP
(01̄1̄)

⌐→ (21̄1̄)
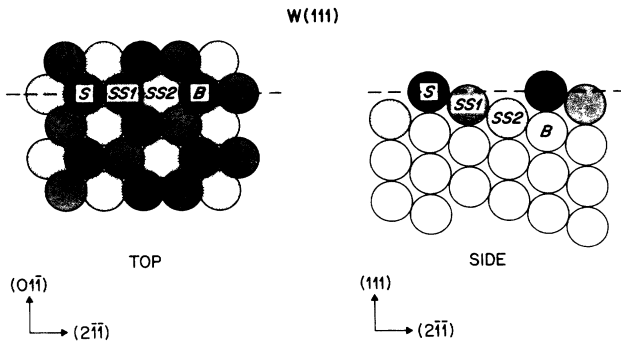
SIDE
(111)

⌐→ (21̄1̄)

FIG. 4. Hard sphere model of W(111) showing the bulk B, surface S, and subsurface layers SS1 and SS2.

expected to affect different layers at different rates or to a different degree. An adsorbate would then be expected to shift or attenuate preferentially one component relative to the other one. The data in Ref. 2 give no evidence for such an effect.

Another way to make the three-surface component results compatible with an escape depth model is to postulate that SS2 is also made up of contributions from two atomic layers. This effectively doubles the escape depth from the unusually small value of ~ 2 Å obtained in Ref. 2. We have investigated this possibility by making a four-surface-component fit to the data, but with the bulk and surface intensities constrained to be in accord with a layer-dependent exponential attenuation. The result (not shown) is significantly worse than those in the table, e.g., the sum of the squares of the deviations is $\sim 50\%$ larger. Moreover, the shifts obtained for SS2 and SS3 are identical to within a few percent. Since the SS3 atoms have bulklike nearest- and next-nearest-neighbor coordination, one would expect them to have a significantly smaller shift than the SS2 atoms which lack one nearest neighbor. The results therefore offer no support for the artifice required to make the three-component analysis compatible with an escape-depth model.

The only question that emerges from the fits in Figs. 2 and 3 concerns the origin of the extra broadening of the surface line. The 0.15-eV Gaussian width of the bulk component is readily accounted for by the 0.11-eV theoretical phonon width[5] and a 0.10-eV resolution function. The 0.19-eV width of the surface component then corresponds to a phonon width of 0.16 eV, which has generally been considered excessive.[3,4] One likely source of surface core-level broadening is unresolved crystal-field splitting due to the lower symmetry of the surface-atom site. This is not a new suggestion, having been proposed in Ref. 3 to account for the finding that the difference in line shape between the $4f_{7/2}$ and $4f_{5/2}$ spin-orbit components is not due to a difference in Lorentzian lifetime width. The crystal-field splitting of $4d$ core levels of β-Sn has recently been determined.[6] There is unfortunately little prospect of resolving this splitting experimentally, because it is no greater than the phonon width and splits the $j = \frac{7}{2}$ line into a number of components.

Finally, it seems appropriate to consider the comparison between the results of the various fits and the theoretical calculations of layer-dependent surface-atom core-level shifts. These theories are quite simple in concept, relying largely on the different numbers of nearest and next-nearest neighbors in the surface layers,[7] a so-called pair-bonding model. The model predicts shifts for the three outermost layers that are in a ratio of 1.00:0.56:0.16. The shifts obtained from the three-surface-component analysis do not conform to this ratio, yielding a subsurface shift for SS1 that is too *large* (1.00:0.84:0.26). The two-surface-component analysis is no more successful, showing the subsurface component SS1 shifted by an amount much *smaller* (1.00:0.26) than the prediction of the pair-bonding model.

In view of the lack of success of the pair-bonding model, we return to an earlier model,[8] in which the surface core-level shift Δ^S is simply proportional to the narrowing of the band structure at the surface. We use the tight-binding approximation in which the bandwidth is proportional to the square root of Z_s, the coordination number of the surface atom. The fractional band narrowing normalized to the bulk coordination number Z_b is then[8] $1 - (Z_s/Z_b)^{1/2}$. Applying this relationship to the W(111) surface and subsurface layers, with $Z_s^S = 4$, $Z_s^{SS1} = 7$, and $Z_b = 8$, we obtain

$$\Delta^{SS1} \approx \Delta^S(1 - \sqrt{0.875})/(1 - \sqrt{0.5}) .$$

The measured value of $\Delta^S = 0.44$ eV then leads to $\Delta^{SS1} \approx 0.10$ eV, which is close to the value of 0.11 eV from the fit in Fig. 2 and in much better agreement than the theoretical prediction of 0.24 eV from the pair-bonding model. The limitation of this approach emerges when it is pushed to predict the core-level shift for the SS2 layer, which has the same nearest-neighbor coordination number as SS1 but a shift that is much smaller. Some improvement is obtained by taking account of the fact that the interaction with the six next-nearest neighbors must also contribute to the bandwidth. Alternately one can attempt to account for the difference between the second and third layer by recognizing that only one of the seven nearest neighbors for atoms in layer SS1 are bulklike, compared to four in SS2. However, it is clearly too much to expect significant agreement with experiment from these parametrizations which cannot do justice to the full complexity of the physical problem. A calculation of the layer-dependent band structure is required.

In summary, we have confirmed that the surface-atom photoemission spectrum of W(111) can be fitted with three surface components, but find that the resulting line intensities are in conflict with the attenuation of signals originating from deeper layers. A credible analysis resolves only two surface layers, with significant broadening of the signal from the outermost layer. The signals from other near-surface layers merge with the bulk signal. The broadening of the surface signal is too large to be due solely to excitation of phonons, and is tentatively ascribed to surface crystal-field splitting.

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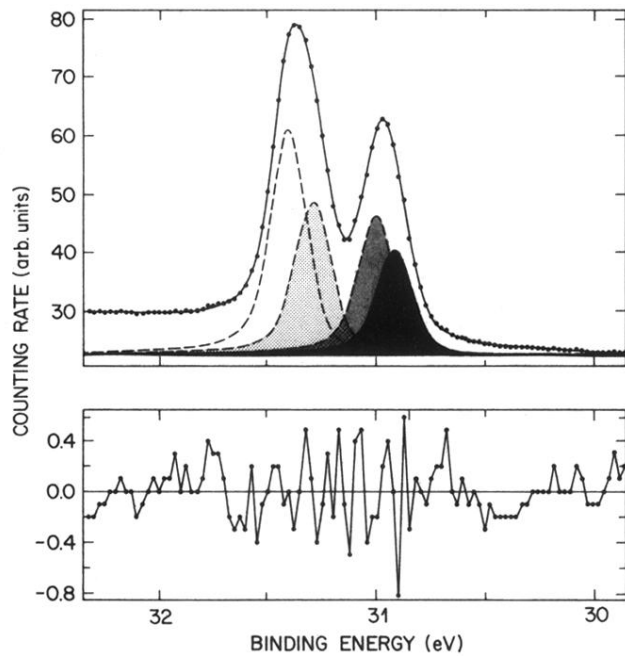
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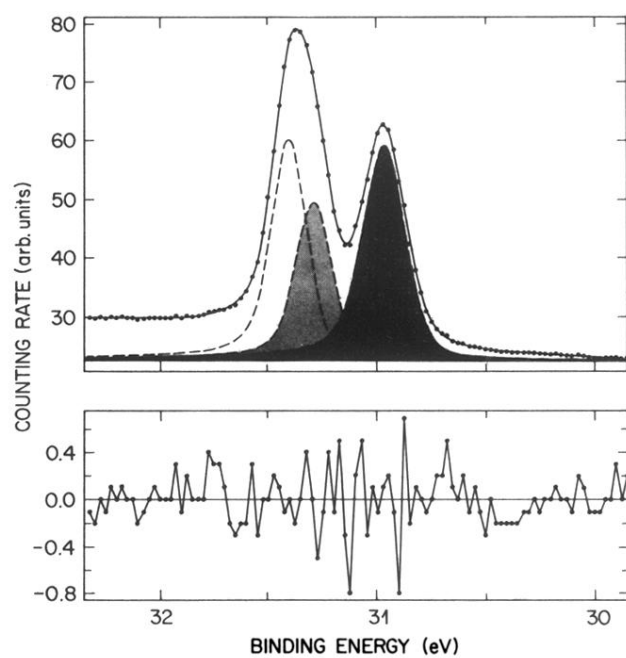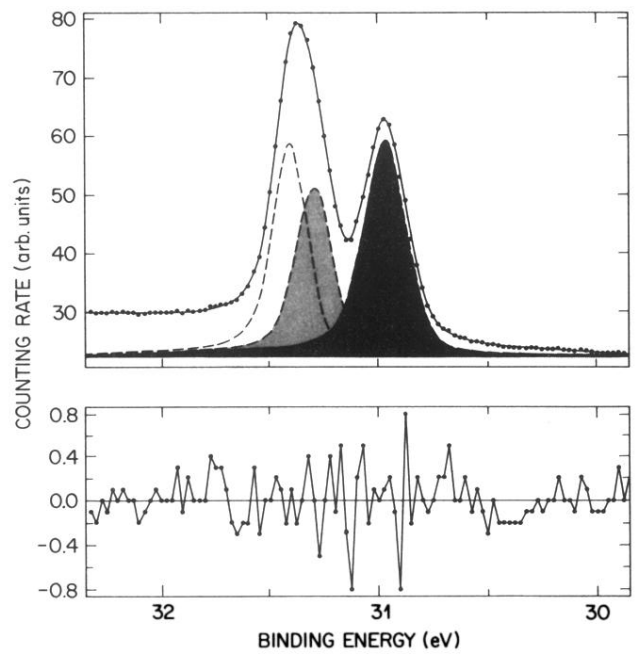
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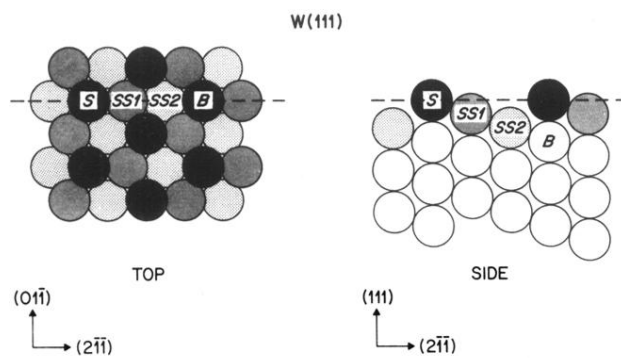
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