Line shapes in surface-atom core-level photoemission from Ta(111), W(111), and W(100)

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Photoemission data for the $4f$ levels of oriented, clean surfaces of W and Ta have been reanalyzed, using improved descriptions of the line shape and background. The results confirm the earlier values for the surface and subsurface core-level shifts and intensities, and yield new values for the lifetime widths and singularity indices which remove previously noted inconsistencies. The surface components were found to have different Gaussian broadening in the two spin-orbit lines. This indicates that the broadening can be due only in part to surface phonon excitation. The rest is tentatively attributed to unresolved surface crystal-field splitting.

INTRODUCTION

During the last few years a number of publications have elucidated the binding energy shifts of surface-atom core levels[1,2] and their dependence on surface orientation[3] and chemisorption.[4] Least-squares fitting procedures have been used[5] to good advantage to demonstrate the existence of surface core-level shifts (SCS) even in metals in which either a large core-hole lifetime width or a small SCS leaves them unresolved. Such fitting procedures have also been used[6,7] to determine SCS's for surface and subsurface atoms in Ta(111), W(111), and W(100). The SCS values of these metals are large compared with their $4f$ lifetime widths. This, combined with the open structure of these crystal surfaces and the high-energy resolution attainable at low binding energies, makes these systems ideal for the study of surface effects. Since the initial work on these surfaces[6,7] was mainly concerned with the material and structure dependence of the SCS, no attempt was made to extract detailed information on their line shapes. A recent review[8] of these studies had questioned the reliability of the SCS values because some of the line-shape parameters were not physical. Specifically, the singularity index for W was reported to be vanishingly small[9] and the relative magnitudes of the lifetime widths of the W and Ta $4f$ hole states was reversed.[10] In the present study the data from Refs. 6 and 7 are reanalyzed with better line shapes using previously developed least-squares procedures and an improved parametrization of the background of secondary electrons. This fitting procedure provides values for spectral widths and singularity indices of the Ta and W $4f_{7/2}$ and $4f_{5/2}$ core-hole states which are different from those reported earlier[4,6,7] and are now physically reasonable. However, contrary to what had been previously suggested,[8] the magnitude of the surface core-level binding energy shifts and the relative amplitudes of the surface components are found to be essentially unaffected by these modifications. The basic results and conclusions of the initial analyses therefore remain unaltered. Finally, from the improved analyses reported here, evidence is obtained for differences in line widths of the surface and bulk components. The source of these differences does not appear to be phonon excitation and, instead, is tentatively assigned to differences in the surface crystal field.

METHODOLOGY

The numerical spectra were fitted with model functions using nonlinear least-squares optimization as described in Refs. 11 and 12. In the model function each photoemission line is represented by a line with Doniach-Šunjić[13] (DS) shape. The DS line shape is the result of a convolution of a Lorentzian with a one-sided power law with singularity index α. The Lorentzian reflects the lifetime width of the core-hole state and the singularity index manifests the effects of the many-body screening response of the conduction electrons. The DS line is broadened by convolution with a Gaussian, which represents the combined effects of the instrumental resolution function, phonon excitation, and other possible sources of inhomogeneous broadening. A single line is therefore specified by five parameters: position, height, Lorentzian width, Gaussian width, and singularity index.

The background of inelastically scattered electrons generally rises with positive curvature toward the work-function cutoff. It is normally represented by a quadratic specified by three parameters, which are left free and adjustable during the fitting. The suitability of a so-called integral background, proportional to the integral of the photoemission lines taken toward higher binding energy, was also investigated. This was the form used in Refs. 6 and 7. As judged by the residuals, it invariably gave inferior results and was abandoned.

While a fit to an n-component involves $5n+3$ adjustable parameters, there are physical considerations which reduce this number. For example, the lifetime widths due to intra-atomic Auger processes should be essentially the same for the bulk, surface, and subsurface components of a given spin-orbit line, leaving $4n+4$ free parameters. For these components there are thus 16 free parameters in

the model. Fits in which all of these are left unconstrained tend to give results with large statistical uncertainties because of strong parameter correlations. Therefore, fits were made with additional constraints which were subsequently relaxed. Initially all Gaussian widths and singularity indices were constrained to be the same, leaving 12 free parameters. This gave generally satisfactory fits, but there was some nonrandom behavior in the residuals. Moreover, the Gaussian width was considerably larger than the width of the resolution function. By relaxing the constraint on the Gaussian widths, significantly better results were obtained, i.e., the rms deviations between the data and the fitted line were reduced by a third. More important, however, was the finding that in W the Gaussian widths of the bulk and subsurface components closely approached the width of the resolution function, and only that of the surface was larger. In subsequent fits to W the Gaussian widths of the bulk and subsurface component were then constrained to have the same value, but that of the surface was left free. Relaxing the constraint on the singularity index of the surface component did not significantly improve the fits, so in subse-

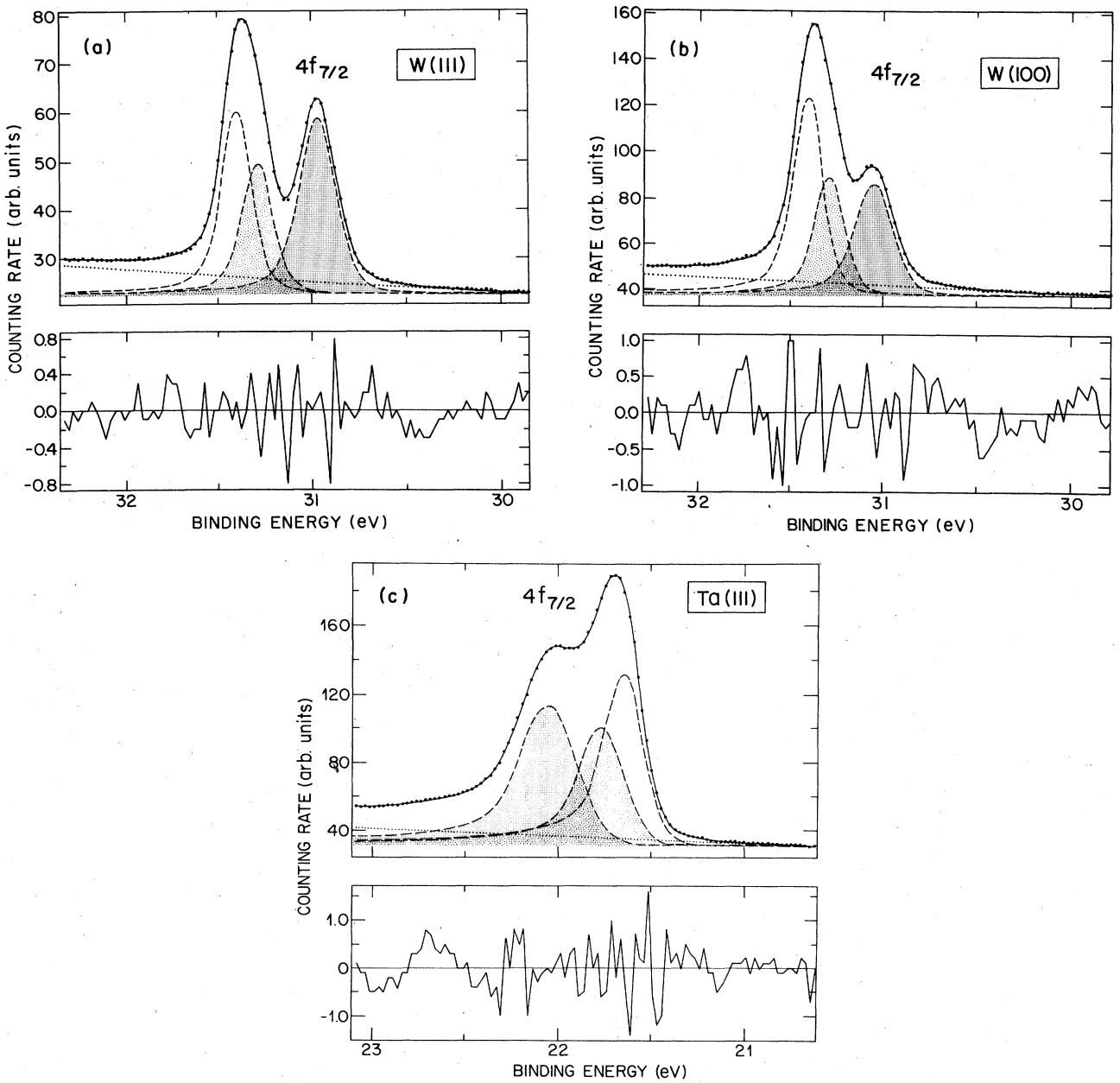

FIG. 1. Least-squares fits to the $4f_{7/2}$ spectra of the clean W(111), W(100), and Ta(111) surfaces. Each spin-orbit component is decomposed into a bulk, surface (dark shading), and subsurface line (light shading). The background, shown as a dashed line, has a general parabolic shape. The singularity index was constrained to have the same value for all components. An independent Gaussian width was used for the surface component. Residuals, i.e., differences between the data and the fitted lines, are shown in the same units as the original data.

quent fits all singularity indices were constrained to be the same.

RESULTS AND DISCUSSION

The best fits obtained for the $j=\frac{7}{2}$ lines of the W(111), W(100), and Ta(111) data over a 2.5-eV interval are shown in Fig. 1. In these fits the background had the general quadratic form, the lifetime widths and singularity index had common values for all three components, but the Gaussian widths had two independent values for W and three for Ta. The residuals show only random fluctuations of the expected magnitude, indicating that the model function offers an adequate representation of the information content of the data.

Analysis of the $j=\frac{5}{2}$ line is complicated by the fact that it is superimposed on the many-body and energy-loss tails of the $j=\frac{7}{2}$ line. The quadratic background function may not, therefore, be sufficiently flexible to represent all these contributions. Nevertheless, analysis of the $j=\frac{5}{2}$ lines gave generally similar results, but with small discrepancies between the line positions, intensities, and Gaussian widths and those obtained in the analysis of the $\frac{7}{2}$ line.

In order to investigate these discrepancies, fits were made over a 5-eV interval containing both spin-orbit lines. In the fits to W it was necessary to include the tail of the W $5p_{3/2}$ line, which is broad and lies just to the high-energy side of the $4f$ spectrum. Initially it was thought that the only difference between the $\frac{5}{2}$ and $\frac{7}{2}$ lines would lie in the lifetime widths, so surface and subsurface shifts, fractional intensities, and Gaussian widths were all assumed to be the same. However, results obtained with these constraints were unsatisfactory and showed large misfits in the $\frac{5}{2}$ lines. The fact that the shape of the $\frac{5}{2}$ line could not be reproduced by a simple Lorentzian broadening of the $\frac{7}{2}$ line was verified by a stripping technique which simply subtracts the broadened $\frac{7}{2}$ spectrum from the $\frac{5}{2}$ spectrum. A cancellation could not be obtained, see Fig. 2. Note that this result is *independent* of the mathematical representation of the data.

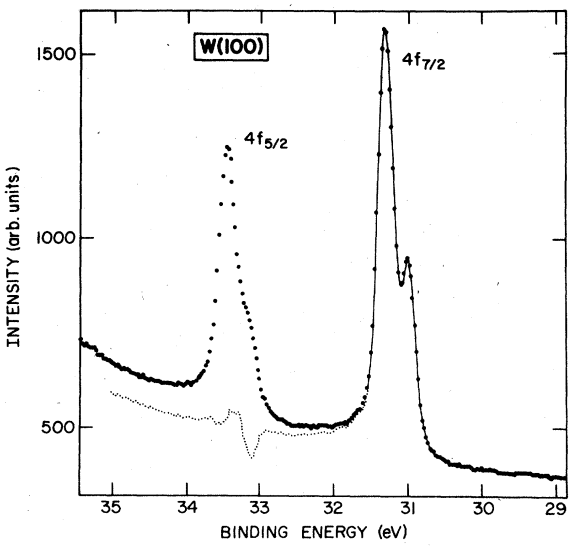

FIG. 2. Stripping procedure applied to the entire spin-orbit spectrum of W(100). The result, shown as dotted line, indicates that the shape of the $\frac{5}{2}$ component is not reproduced by a Lorentzian broadening of the $\frac{7}{2}$ line.

Satisfactory fits to both $\frac{7}{2}$ and $\frac{5}{2}$ lines could be obtained for W(111) and Ta(111) by allowing the surface contributions in each of the two spin-orbit lines to have independent Gaussian widths, while constraining the surface and subsurface shifts and subsurface intensity ratios to be identical in both; see Fig. 3. Fits in which the Gaussian was constrained to be the same for all lines, but the shift and intensities were left free, gave different subsurface shifts in the two spin-orbit components, a result considered unphysical. It shows that the properties de-

TABLE I. Summary of line-shape parameters.

	Ta(111)		W(111)		W(100)	
	Ref. 4	Present[a]	Ref. 4	Present[a]	Ref. 4	Present[a]
Δ_{surf} (eV)	0.40(1)	0.39(1)[b]	−0.43(1)	−0.43(1)	−0.35(1)	−0.36(1)
$\Delta_{subsurf}$ (eV)	0.19(2)	0.11(2)	−0.10(2)	−0.11(1)		
$\Delta_{reconst}$ (eV)					−0.13(1)[c]	−0.14(1)
$\Gamma_{7/2}$ (eV)	0.15(2)[d] 0.19(3)[e]	0.04(1)	0.11(2)	0.555(5)	0.11(2)	0.051(5)
$\Gamma_{5/2}$ (eV)	0.19(2)[d] 0.23(3)[e]	0.07(1)	0.16(2)	0.09(1)	0.16(2)	0.09(1)
α	0.06(3)	0.15(1)	0.00(3)	0.05(1)	0.00(3)	0.06(1)
Γ^G_{bulk} (eV)	0.15	0.22(1)	0.15	0.155(5)	0.15	0.152(5)
Γ^G_{surf} (eV)	0.15	0.32(1)	0.15	0.195(5)	0.15	0.205(5)
s.o. split (eV)	1.90(1)	1.90(1)	2.16(1)	2.16(1)	2.16(1)	2.16(1)
s.o. ratio		0.65		0.65		0.63

[a]Averages of the numerical values of the fits shown in Figs. 1 and 3.
[b]Numbers in parentheses indicate probable error in last significant figure.
[c]See Ref. 7.
[d]Bulk linewidth.
[e]Surface linewidth.

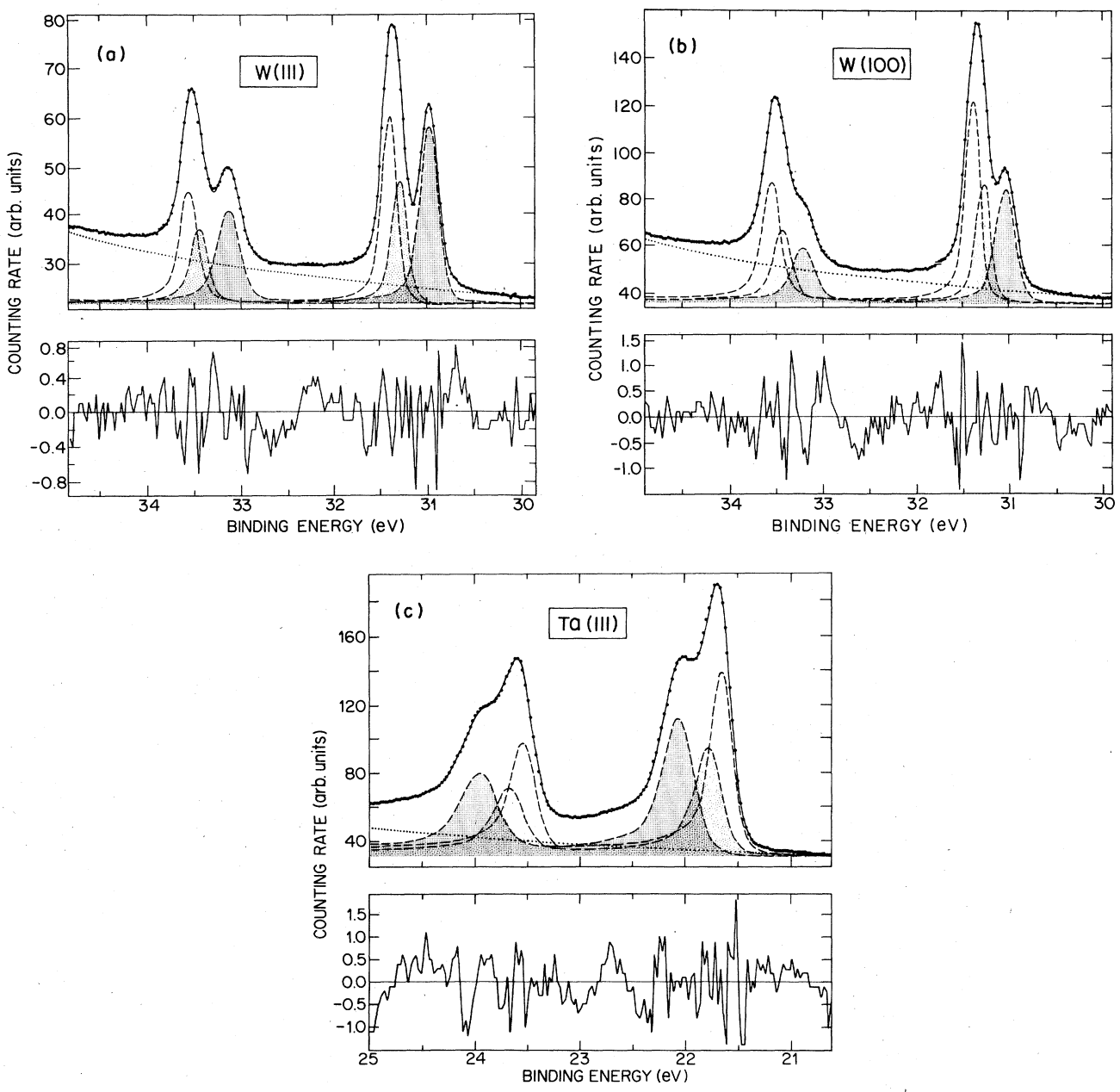

FIG. 3. Least-squares fits to the entire spin-orbit spectrum W(111), W(100), and Ta(111). Components are identified as in Fig. 1.

duced for unresolved components may be very sensitive to the line shape used in the analysis. The fact that this model was inadequate could also be seen in systematic deviations in the residuals.

The numerical results in Table I show uniformly good agreement with the original analyses[6,7] of all three cases with regard to the surface-atom core-level shift. This is hardly surprising since the surface-atom component is so well resolved. The shift of the unresolved subsurface components are also in good agreement for W(111) but not for Ta(111). For the Ta spectrum the position and intensity of the subsurface component was very sensitive to the details of the line shape used in the fitting.

The lifetime widths differ significantly from the earlier values, being in every case much smaller. The cause of this discrepancy lies in the fact that in the original analysis the Gaussian width was held fixed at the instrumental resolution function of 0.15 eV, forcing the extra width into the Lorentzian. In the present analysis both width parameters are left free. The phonon broadening then contributes to the Gaussian width, as it should. Gratifyingly, the bulk and subsurface components of W(111) have Gaussian widths close to the instrumental resolution function. The width of the surface component, however, is significantly greater. The origin of this extra width is discussed below. The Ta spectrum requires three distinct Gaussian widths, all larger than the instrumental resolution function. The new value for the Lorentzian width of

Ta is smaller than that of W, as expected on the basis of the available Auger deexcitation channels.

The singularity index for W is in the range 0.04—0.06, consistent with screening by electrons with s, p, d, and f character. In the original analysis, the increased Lorentzian width and the sloping background jointly compensated for the singularity index, which had been set equal to zero. For Ta, the singularity index of 0.15 is again greater than the value originally assigned. In the fit shown in Fig. 1(c) a large part of the signal originally assigned to background now appears in the many-body tail. The fact that the singularity index of Ta is so much larger than that of W can be understood in terms of the difference in the density of states near E_F.

A good consistency check on the analyses reported here is provided by the escape depth, which can be separately calculated from the intensities of the surface and subsurface components. A simple layerwise attenuation model with equal layer atom densities in the surface and bulk predicts[6]

$$I_{S_1}/I_B = e^{2d/\lambda} - e^{d/\lambda} ,$$

and

$$I_{S_2}/I_B = e^{d/\lambda} - 1 ,$$

where I_{S_1}, I_{S_2}, and I_B are the intensities of the surface, subsurface, and bulk components, d is the interlayer spacing, $\lambda = 1/n\sigma$ is the inelastic electron escape depth, n is the bulk atom density, and σ is the inelastic cross section. The earlier analyses[6] indicated consistency between the surface and subsurface intensities, quoting $\lambda \sim 2$ and 2.5 Å for W(111) and Ta(111) $4f$ electrons, respectively, at 35—40 eV kinetic energy. The results of the present work are summarized in Table II. There is good agreement between the surface- and subsurface-derived escape depths for Ta(111) and for W(111) and between the results here and those reported earlier.[6] For Ta(111), where three distinct Gaussian widths were required, the agreement is somewhat less good. However, an analysis in which the subsurface component was constrained to have the same width as the bulk gave incompatible values, confirming that separate widths are required.

The analysis of the complete spin-orbit (s.o.) spectra gave entirely consistent numerical results, provided the Gaussian width of the $j = \frac{5}{2}$ surface component was given an independent value. This serves to bring the question of the extra width of the surface component into focus. If it were strictly of phonon or other possible inhomogeneous origin, it should be the same in both s.o. components. Furthermore, the magnitude of the broadening, deduced by subtraction of the resolution function in quadrature, is much greater than can be readily explained in terms of surface-phonon excitation. It seems likely that the extra broadening is due to unresolved surface crystal-field splitting, which should have different effects on the two s.o. spectra. In the case of W(111), a slightly smaller surface-atom core-level shift is required for the $\frac{5}{2}$ spectrum to obtain a reasonable fit.

TABLE II. Summary of inelastic cross sections σ (escape depths λ) determined from surface/bulk and subsurface/bulk intensities.

	σ^a	(λ^b)	σ^a	(λ^b)
	surface		subsurface	
Ta(111)	9.1	(2.0)	10.7	(1.7)
W(111)	8.8	(1.8)	8.8	(1.8)
W(100)[c]	8.3	(1.9)		

[a]In units of Å^2/atom.
[b]In units of Å.
[c]Calculated on the assumption that the two signals split off from the bulk line are both due to surface atoms, see Ref. 7.

The ratios of the intensities (areas) of the two spin-orbit components, $4f_{5/2}/4f_{7/2}$, in the Ta(111), W(111), and W(100) data are 0.65, 0.65, and 0.63, compared with the statistical value of 0.75. The difference presumably arises from a difference in the cross section.

In summary, we have shown that the background in photoemission spectra can have a significant effect on the determination of the lifetime width and singularity index. The new line-shape parameters determined for Ta and W are in good agreement with theoretical expectations: W has a small but finite singularity index, Ta a much larger one; the $4f$ hole state lifetime width of Ta is smaller than that of W. We have also demonstrated that the surface-atom core-level shifts in these systems are not sensitive to the details of the background shape or to the line-shape parameters themselves. Finally, differences in the widths of the surface components in the two spin-orbit lines have been identified and tentatively attributed to surface crystal-field splitting.

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