

Ta(110) surface and subsurface core-level shifts and $4f_{7/2}$ line shapes

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(Received 21 January 1992; revised manuscript received 5 October 1992)

High-resolution $4f$ core-level spectra of the Ta(110) surface region have been obtained at 80 and 300 K with 70- and 100-eV synchrotron radiation. The data show that the subsurface core-level binding-energy shift (compared to deeper-lying atoms) for a close-packed bcc(110) surface can be substantial: 65 ± 15 meV for the first underlayer atoms of Ta(110). The surface core-level shift is 360 ± 12 meV at 80 K and decreases by 13 ± 2 meV at 300 K. Final-state screening in both the bulk and surface layers is well described by a constant singularity index of 0.133 ± 0.012 . An enhanced phonon broadening at the surface corresponds to a reduced perpendicular Debye temperature for the surface atoms of 128 ± 18 K compared to the bulk Debye temperature of 225 K.

I. INTRODUCTION

Recent advances in the resolution and intensity of synchrotron-based photoemission have led to an increased understanding of the modification in the electronic response at the surface of a solid, especially regarding the response to core-electron excitation. Especially rich has been the investigation of alkali metals which have shown differences at the surface with regard to phonon excitation during the core-level transition^{1,2} and final-state screening behavior of the core hole.³ Furthermore, the alkali-metal studies have yielded a deeper understanding of thermal and surface shifts of core-electron binding energies in metals.⁴ Somewhat more scarce has been high-resolution data on tight-binding transition metals, although spectra from the W(110) surface have demonstrated that final-state screening and the core-hole lifetime can be altered by modification of the valence band at the surface.⁵

While there have been several earlier synchrotron-based investigations of Ta-surface core levels,⁶⁻¹¹ comparatively poor resolution (150–265 meV) has hindered critical assessment of surface core-level shifts (SCS's) and line shapes. For example, from a combined theoretical and experimental study,^{10,12} it was suggested that the electronic screening in bulk Ta differs significantly from the Doniach-Šunjić (DS) form¹³ while other work^{6,11,14} indicates no deviation from the simple DS description with a constant singularity index α . For all three low-index faces the surface lines appear broader than the bulk lines. This extra width has been ascribed to various mechanisms: increased phonon broadening [Ta(100)],¹⁰ a larger singularity index [Ta(100) and Ta(110)],^{8,9} a shorter core-hole lifetime [Ta(111),⁶ Ta(100),^{7,8,9,15} Ta(110) (Refs. 8 and 9)], and crystal-field splitting of the surface peak [Ta(111) (Ref. 14) and Ta(110) (Ref. 11)] have all been put forth as the cause of the extra width.

In order to further the quantitative understanding of the differences in electronic response at the surfaces of

transition metals in general and to resolve these issues about Ta specifically, we have measured, using high-resolution synchrotron radiation, the $4f$ photoemission spectra of atoms in the Ta(110) surface region at both 80 and 300 K. As in the case of W(110),⁵ the Ta(110) surface was chosen with the expectation that the subsurface shift would be negligible due to the close-packed nature of the surface (the subsurface atoms have nearest- and next-nearest-neighbor coordinations such as those of the bulk atoms) and hence would not interfere with characterization of the bulk and surface photopeaks. Surprisingly, we find that a consistent description of the data requires the subsurface atoms to have core-level binding energies shifted significantly from atoms deeper in the bulk. The high resolution also allows a small temperature dependence of the SCS to be discerned. As for the line shapes, the bulk and surface lines overlap too much to distinguish separate lifetime widths. However, the final-state screening in both the bulk and surface are well described by constant singularity indices, which are equal to within the accuracy of the data. Additionally, the room-temperature surface feature is clearly broader than the bulk feature. As in the case of the alkali metals, this extra width can be ascribed to the excitation of relatively soft phonon modes perpendicular to the surface.^{1,2}

II. EXPERIMENTAL DETAILS

Data were obtained on the AT&T Bell Laboratories–University of Oregon 6-m toroidal-grating-monochromator (TGM) beamline on the vuv ring at the National Synchrotron Light Source. A 100-mm hemispherical electron-energy analyzer operating at 2-eV pass energy contributed 40 meV to the instrumental resolution. Photon energies of 70 and 100 eV at total system resolutions $G_{\text{res}} = 80 \pm 3$ and 100 ± 5 meV, respectively, were used in collecting the Ta core-level data. The monochromator resolutions were determined from Cu Fermi edges obtained at 80 K.¹⁶ All data were obtained

at normal emission with p -polarized light incident at an angle of 45° .

The single-crystal Ta(110) sample had been previously cleaned of bulk contaminants by repeated sputter and anneal cycles.¹⁷ After insertion into the present vacuum chamber but before any experiments, the surface oxide was removed by flashing to ~ 2900 K in a H_2 -dominated vacuum of 1×10^{-10} Torr. As judged by the Ta $4f$ core-level spectra, which show large shifts upon oxidation, this was sufficient to yield a clean surface. Before each experimental run, the sample was again flashed to ~ 2900 K to remove any new contamination and then cooled to the measurement temperature of either 80 or 300 K in ~ 5 min. An individual spectrum was collected in 4.2 min; up to eight spectra were collected and coadded between flashes. During a maximum 35-min data-acquisition time, the surface peak shifted by no more than 2.5 meV (1.3 meV) at 300 (80) K, indicating that average H contamination was less than 0.025 (0.013) monolayers during any run.⁹

III. RESULTS AND ANALYSIS

Figure 1 displays 80-K spectra encompassing the whole $4f$ photoemission region obtained at both 70- and 100-eV photon energies. The signal from the first layer at higher binding energy (BE) is clearly resolved from the signal from deeper layers. Somewhat unexpected and in contrast to spectra from other Ta surfaces,^{6,8} as well as from a wide range of simple-metal^{1,2,18} and other transition-metal^{5,6} surfaces where the surface lines are al-

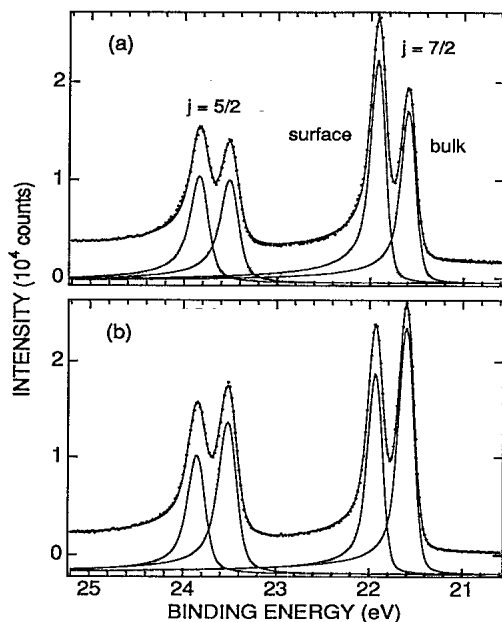


FIG. 1. Ta(110) $4f$ photoemission spectra including the $j = \frac{5}{2}$ (higher BE) and $j = \frac{7}{2}$ (lower BE) spin-orbit components taken at 80 K with two photon energies [70 eV (a) and 100 eV (b)]. Shown as solid lines are four DS line shapes convolved with Gaussians peaks (see text for further explanation of fitted curves).

ways distinctly broader than those from the deeper layers, the surface and bulk lines appear to have almost identical widths.

Quantitative assessment of the data is obtained by a nonlinear least-squares analysis. In fitting this, as well as later spectra, the line shape of each photopeak is described by a Doniach-Šunjić function,¹³ which combines a Lorentzian width Γ to describe the lifetime width of the excitation with the Anderson singularity index α to describe the many-body asymmetry caused by final-state screening of the core hole. The Gaussian width G_{total} , which includes instrumental (G_{res}) and vibrational broadening (G_{ph}), is introduced by convolution. Secondary electrons make a remarkably small contribution in the $4f$ region for the photon energies used, so that the background is adequately characterized by a constant over most of the energy range. A power-law function is used to describe high kinetic-energy tails of plasmons (in spectra of the total $4f$ region) or higher BE lines (in $4f_{7/2}$ spectra).

Because the available resolution and inherent widths of the surface and bulk lines result in significant overlap between the two components, constraints on the line shapes are required in order to obtain physically meaningful results. In particular, we find it necessary to constrain the bulk and surface Lorentzian widths to a common value. A similar constraint on α was also imposed in all of the fits shown. In analyses where bulk and surface α 's were left free, there was no decided propensity for any difference in their values beyond the scatter in fits to different data sets. Hence, α was also constrained to have the same value for all lines in any given spectrum.

Figure 1 also includes (as a solid line) such a least-square fit to the data encompassing the whole $4f$ region. The individual components clearly show the asymmetry produced by the many-body screening. From the fits we deduce a spin-orbit splitting of 1.915 ± 0.003 eV and a surface core-level shift of ~ 0.33 eV.

The $4f$ data as well as detailed data encompassing only the $4f_{7/2}$ electrons, taken to investigate the particulars of the line shapes, exhibit a seemingly unphysical feature. The apparent SCS is *not* the same for the two photon energies. This can clearly be seen from 80-K $4f_{7/2}$ raw data displayed in Fig. 2. In the figure the data obtained at both 100- and 70-eV photon energies have been rigidly shifted in kinetic energy and scaled in intensity so that the surface features from all four data sets overlap. Clearly, the bulk feature from the 70-eV data has a smaller shift relative to the surface than does the 100-eV data. A purely visual determination of the difference in SCS suggests a discrepancy in SCS of approximately 11 meV as indicated by the vertical lines in the figure.

Least-squares analysis of the data better quantifies this apparent difference in SCS. Figure 3 illustrates a two-line fit to 80-K $4f_{7/2}$ data using the model function described above. From this and other data the resulting difference in SCS is determined to be 9.3 ± 0.9 meV, consistent with the visual estimation of 11 meV. The least-squares analysis also reveals that with the two-line fit the 80-K surface Gaussian width is approximately 10 meV narrower than the bulk. The narrower surface line is puz-

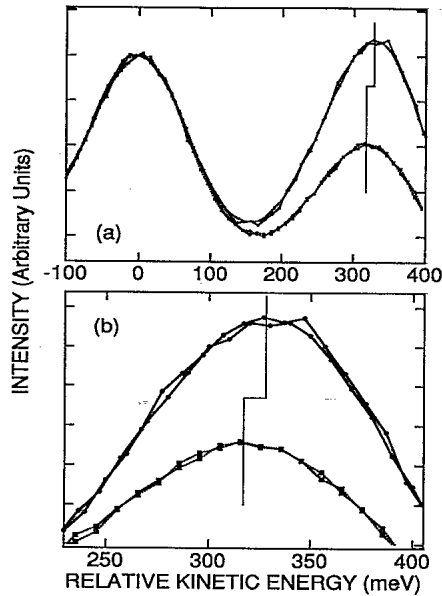


FIG. 2. Visual comparison of 100-eV (solid lines) and 70-eV (dotted lines) 80-K data showing the apparent discrepancy of the surface core-level shift of ~ 11 meV. (b) is an enlargement of the right-hand side of (a).

zling in light of previous results for alkali¹ and transition metals^{5-11,14,15} which all show larger surface widths.

A photon-energy-dependent SCS is a clearly unphysical result in need of rectification. Since core-level shifts of subsurface atoms have been observed on more loosely packed surfaces of Ta, the natural ansatz is that the second layer (first underlayer) of the Ta(110) surface has a

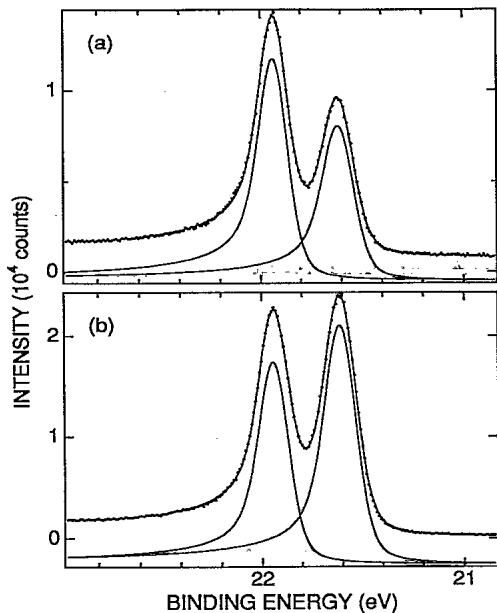


FIG. 3. Ta $4f_{7/2}$ spectra at 80 K taken at (a) 70- and (b) 100-eV photon energies. The solid lines are from a fit with two identical DS line shapes convolved with separate Gaussian widths for the bulk and surface.

significant core-level shift relative to the atoms deeper in the bulk. One must consequently abandon the two-line description of the data in favor of a three-line representation.

In order to test this ansatz, a model function consisting of three components, one for the surface layer, one for the second layer, and one for the rest of the atoms in the bulk, was used to analyze the data. Because second-layer vibrational properties are essentially identical to deeper layers,¹⁹ the Gaussian width of this layer was constrained to be the same as for the bulk. As in the two-line fit, the Lorentzian width and singularity index were held to be the same for all lines. Since the first underlayer peak position is so close to the bulk, a constraint on the relative heights of the bulk and second layer was also required for convergent analysis. From the areas of the bulk and surface lines in the two-line fits an effective escape depth was determined; this effective escape depth was then used in the three-line model function to constrain the relative heights of the second-layer and bulk lines to a fixed value.

Using this escape-depth assumption, the subsurface core-level shift Δ_{ss} (core-level binding-energy shift of subsurface relative to bulk binding energy) was varied between zero (essentially just the original two-line fit) and 90 meV. Figure 4 plots the resulting SCS's for the data obtained at both 80 and 300 K. For the 80-K data the SCS's at the two photon energies become equal for $\Delta_{ss} = 60$ meV. For room-temperature data the crossing point comes at a slightly higher value of 75 meV. As shown below, due to the inherently broader data at 300 K, this value is less well defined than that obtained at 80 K. Clearly though, the same qualitative behavior is observed in the data taken at both temperatures. Note that the surface shift is temperature dependent.

Simultaneous fitting of data taken with 100- and 70-eV photon energies allows a more precise determination of the subsurface and surface shifts. In simultaneously

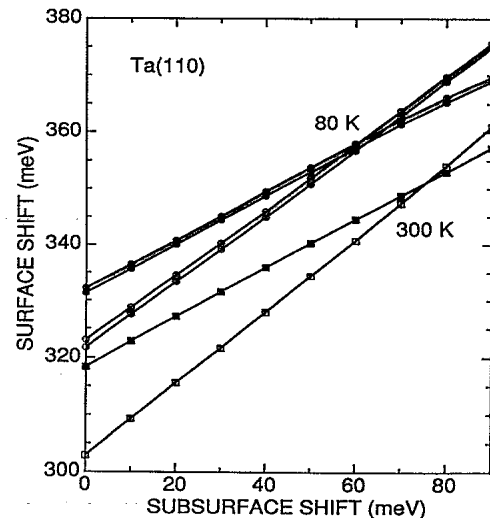


FIG. 4. The surface shift obtained when subsurface shift is held at a constant value from 0 to 90 meV using three-line model function and escape-depth assumption for line intensities. Closed circles: 80-K sample temperature and 100-eV photon energy. Open circles: 80 K and 70 eV. Closed squares: 300 K and 100 eV. Open squares: 300 K and 70 eV.

fitting two data sets the same model function described above was used with the additional physical constraints that Δ_{ss} and Δ_s are the same for both data sets. Figure 5(a) plots χ^2 (normalized by the minimum χ^2) as a function of Δ_{ss} . Here the underlayer-bulk intensity ratios were also held to the escape depth values determined from the two-line fits. Both the 80- and 300-K data exhibit a clear minimum in the vicinity of the crossings shown in Fig. 4, with the uncertainty in the room-temperature (RT) data larger than the 80-K data due to its larger Gaussian broadening. A value of Δ_{ss} consistent with the data at both temperatures would clearly fall in the vicinity of 70 meV. Shown also in Fig. 5(b) is the resultant Δ_s as Δ_{ss} is varied. The RT data exhibit a SCS ~ 13 meV smaller than the 80-K data.

Since photoelectron diffraction can skew core-level line intensities away from a simple escape-depth description, the effects of different underlayer-bulk intensity ratios R were explored to determine possible influences on the results for Δ_{ss} and Δ_s . Previous photoelectron diffraction work on Ta(100) suggests that surface-bulk intensity ratios vary by approximately $\pm 20\%$ from a simple escape-depth description.²⁰ With this in mind, we simultaneously analyzed 80-K, 70-, and 100-eV photon-energy data with underlayer-bulk intensity ratios varying by a slightly larger amount, up to $\Delta R = \pm 30\%$ from the escape-depth ratios of $R_{100} = 0.78$ and $R_{70} = 1.36$ for the 100- and 70-eV data, respectively. The results are displayed in Fig. 6. Figure 6(a) displays contours of reduced χ^2 in this $\pm 30\% - \pm 30\%$ region. Taking a reduced χ^2 of 2 as a generous upper limit on reasonably good agreement between the data and the model function shows that Δ_{ss} [Fig. 6(b)] varies between 45 and 70 meV. Within the same χ^2 region Δ_s [Fig. 6(c)] is seen to vary from 347 to 363 meV.

Physical parameters obtained from an assessment of all the data are presented in Table I. Note that both the life-

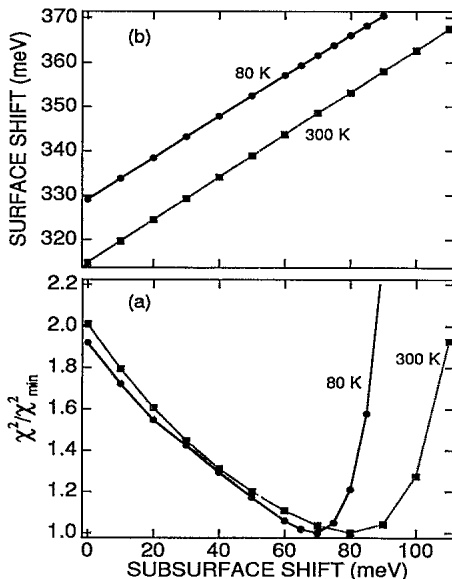


FIG. 5. Results of simultaneously fitting 70- and 100-eV data with the three-line model function and escape-depth assumption for each set of data. The goodness of the fit (χ^2) and surface shift (Δ_s) are shown as functions of the subsurface shift (Δ_{ss}).

TABLE I. Summary of Ta(110) $4f_{7/2}$ core-level parameters obtained from the three-line model function described in the text.

Parameter	80 K	300 K
Δ_s (meV)	360 ± 12	347 ± 12
Δ_{ss} (meV)		65 ± 15
Γ (meV) ^a		52 ± 7
α^a		0.133 ± 0.012
$G_{ph,bulk}$ (meV)	88 ± 20	146 ± 12
$G_{ph,surf}$ (meV)	110 ± 10	189 ± 10

^aParameter constrained to the same value for bulk and surface.

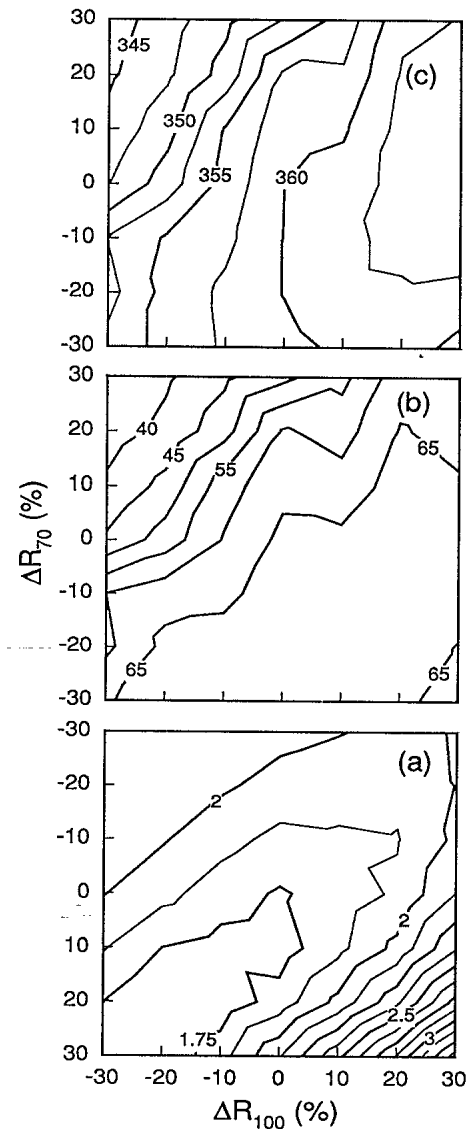


FIG. 6. Results of varying the underlayer-bulk intensity ratios R_{100} and R_{70} away from an escape-depth assumption in simultaneous fitting of 80-K data taken at 70- and 100-eV photon energy. Variation in each ratio R_{100} and R_{70} is over a $\pm 30\%$ range about the escape-depth-assumption values. Contours of χ^2 , Δ_{ss} , and Δ_s are shown in (a), (b), and (c), respectively.

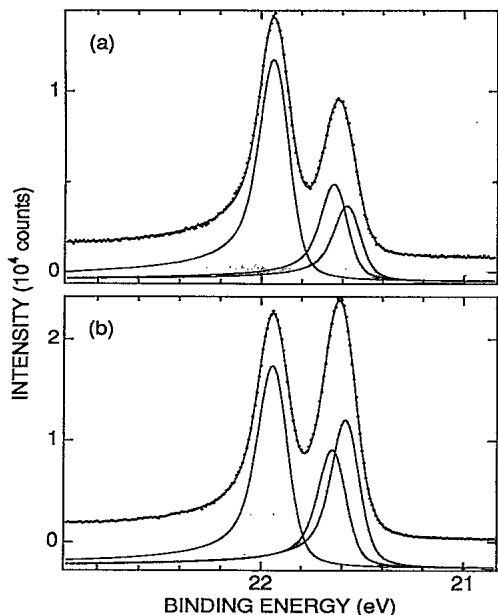


FIG. 7. Three-line model-function fits to 80-K data taken with (a) 70- and (b) 100-eV photon energies. Δ_{ss} is held to 65 meV and Δ_s at 360 meV. The highest BE line is the surface line, the middle line is from subsurface layer, and the lowest BE line is from second underlayer and deeper (bulk).

time width and the singularity index are insensitive to the use of either the two-line or three-line analysis. Values for and uncertainties in Δ_{ss} and the SCS Δ_s are based on an analysis of all the data in a manner similar to that shown in Figs. 5 and 6. The difference in SCS between 80 and 300 K is determined to be 13 ± 2 meV. The uncertainty here is much smaller than the uncertainty in either

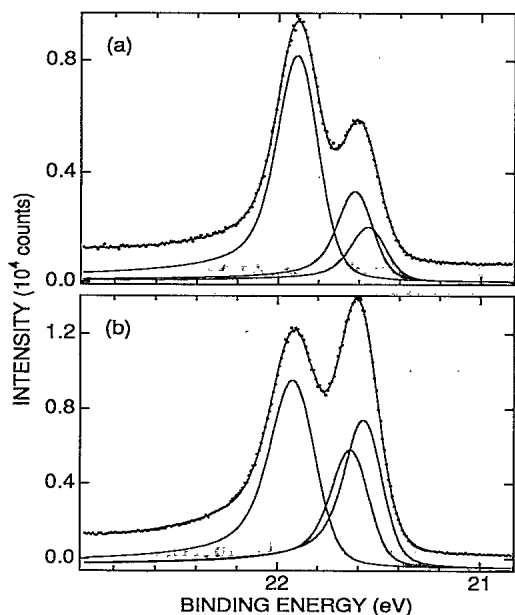


FIG. 8. Same as Fig. 7 for 300-K data except Δ_s held to 347 meV.

SCS since changes in the RT and 80-K SCS's with varying parameters are highly correlated. The errors in the surface and bulk phonon contributions to the Gaussian widths, $G_{ph,surf}$ and $G_{ph,bulk}$, respectively, also include uncertainties in G_{res} . The larger uncertainty in the bulk phonon widths is due to the strong correlation of the bulk Gaussian width with Δ_{ss} .

The existence of the subsurface component shifted to +65-meV binding energy (compared to the bulk) brings the Gaussian widths into line with expectation. For the low-temperature data the surface Gaussian width is now larger than the bulk value. Fits to the data at 80 and 300 K, with Δ_{ss} and Δ_s fixed at the values in Table I, are displayed in Figs. 7 and 8, respectively.

IV. DISCUSSION

A. Core-level shifts

The simple two-line fits displayed in Fig. 2 show that the splitting between the surface line and average of the bulk and underlayer is approximately 0.33 eV. This is decidedly larger than the values of 0.28 eV (Ref. 8) and 0.29 eV (Ref. 11) obtained from less well-resolved data and highlights the need for sufficient resolution in determining accurate peak separations.

With the three line fits, Δ_s is determined, from the highest resolution (80-K) (LT) data, to be 360 ± 12 meV. This value for the SCS of Ta(110) combined with the recent value of 321 ± 3 meV for the SCS of W(110) (Ref. 5) brings experiment and theory into better alignment for the SCS's of Ta and W. There have been several calculations for the surface shifts of W and Ta. The two which come the closest to our experimentally derived value for Ta(110) are based on tight-binding calculations of the 5d-electron local density of states. In the first calculation the SCS is extracted from calculated surface energies E_s of the Z and (Z+1) metal via $\Delta_s(Z) = E_s(Z+1) - E_s(Z)$.²¹ In the second calculation the centroid (ϵ_d) of the 5d-electron density of states is calculated for the bulk ($\epsilon_{d,b}$) and surface ($\epsilon_{d,s}$) and related to the SCS via $\Delta_s = -1.1(\epsilon_{d,s} - \epsilon_{d,b})$.⁸ For Ta(110) the two calculations predict shifts of 310 and 400 meV, respectively. These two theoretical methods, when applied to the W(110) surface, predict values of -180 meV (Ref. 21) and -280 meV (Ref. 8) which, like the values in the experimental domain, are smaller in magnitude than the corresponding values for Ta(110).

Comparison of our subsurface shift of 65 ± 15 meV for Ta(110) with theory is rather more sparse than for the surface shift. While there have been several calculations of subsurface shifts for Ta and W low-index surfaces,^{8,22,23} only one semiempirical calculation,²² based on the idea of near-surface atoms having broken bonds which reduce their cohesive energy compared to the bulk atoms, has included the (110) subsurface atoms; it predicts a shift of 10 meV for the first Ta(110) underlayer, much smaller than our experimental value.

Part of the error in the calculation may be due to the fact that only the first three neighbor shells were considered. For the bcc(110) subsurface atoms, the first- and

second-shell coordinations are equal to those of atoms deeper in the bulk. For the third-shell atoms, at a distance of $1.41a$ (compared to $0.87a$ and $1.00a$ for the first and second shells; a is the lattice constant), only 1 of 12 bonds is broken. However, the fourth and fifth shells (at $1.66a$ and $1.73a$) are not substantially farther than the third shell. Respectively, 4 of 24 and 2 of 8 bonds are broken. Since these are much higher fractions than for the third shell, their inclusion in such a calculation may result in a significantly larger shift for the subsurface atoms.

We note that there exists prior experimental evidence that the shift of the subsurface atoms of a bcc(110) surface may be substantial. From the analysis of stepped W surfaces [(610), (310), and (320)] it has been suggested that W(110) subsurface atoms have a core-level binding-energy shift possibly greater than -50 meV.²⁴ This is approximately the same magnitude as that of Ta(110) deduced here. It is also larger in magnitude than the same semiempirical bond-breaking estimate²² of -20 meV for the W(110) subsurface atoms.

A temperature dependence of the SCS of Ta(110) emerges from our analysis; between 80 and 300 K the SCS is seen to decrease by 13 ± 2 meV. This temperature variation in SCS can be understood in light of recent results on the thermal shifts of core-level BE's in alkali metals which show shifts as large as 63 meV between 80 and 300 K.⁴ In the work on the alkali metals, it has been shown that the thermal shifts come from changes in the potential at the core and changes in the Fermi level in the initial state as well as changes in the relaxation energy associated with the screening of the core hole in the final state as the lattice expands. In the alkali metals, no difference in the thermal shifts of the surface and bulk were observed. This is the result of the valence-electron bandwidth in the bulk and surface being very similar.⁴ However, in the transition metals the more atomiclike nature of the surface atoms leads to a smaller d -electron bandwidth at the surface. This smaller bandwidth results in a dipole layer between the bulk and surface layers which gives rise to the SCS in the transition metals. For these metals as the lattice expands the bulk atoms necessarily approach the atomic state faster than the surface atoms which are already much more atomiclike. This then results in a lessening of the transition-metal SCS at higher temperatures, as observed here. In fact, very recent results on Ta(100) indeed show that the bulk BE changes more rapidly with temperature than that of the surface.²⁵

B. Line shapes

Analysis of previous measurements of the Ta $4f$ core levels has led to diverse descriptions of the bulk and surface line shapes, especially regarding the screening of the excited core hole. It has been suggested that the large peaks in the filled (~ -1.6 eV) and unfilled (~ 2.8 eV) $5d$ -band bulk density of states leads to a broad peak in the many-body screening tail,¹² so that a simple description by a constant α is not valid. Furthermore, such a bulk-derived peak, sitting under the surface features of

Ta(100), has been postulated¹⁰ to lead to an anomalously large surface $\alpha=0.18$ (compared to a bulk α of 0.08) (Ref. 7) when not taken into account. A similarly large value of $\alpha=0.20$ for the Ta(110) surface atoms has also been deduced.⁹ In contrast, Ta(111) data have been successfully fit with identical bulk and surface values of $\alpha=0.15 \pm 0.01$.¹⁴ Recent lower resolution (265-meV) data of Ta(110) have also been fit with a slightly smaller single value of $\alpha=0.12$.¹¹

Our analysis of the $4f$ region with lines consisting of simple DS line shapes (see Fig. 1) shows only minor deviations from this simple theoretical description for the Ta bulk and (110) surface atoms. There is no evidence for anomalous peaks in the screening response as far away as 3.6 eV from the bulk $4f_{7/2}$ photopeak. More specifically, there is no broad feature at 0.74 eV higher BE from the bulk peak where the surface feature on Ta(100) is located. This implies that for the Ta(100) surface some other mechanism besides a bulk-derived peak must be causing the anomalous line shape associated with the surface atoms.⁷ The high quality of the fits in Figs. 3, 7, and 8 demonstrates that the DS function is an excellent description in the region up to ~ 1 eV from the peaks.

In fits where the bulk and surface α 's were left free, the average value of the surface α was 10% larger than the bulk value. However, this difference is approximately the same as the statistical fluctuations in α between data sets. From fits where the bulk and surface α are constrained to be equal we deduce $\alpha=0.133 \pm 0.012$. A recent Ta(110) analysis¹¹ is in good agreement with this result. The larger value of 0.15 ± 0.01 deduced for Ta(111) (Ref. 14) suggests that the Ta(111) surface α is somewhat larger than the bulk α . This is expected. For most transition metals (including Ta and W), the surface atoms have a higher s -electron to d -electron ratio than the bulk atoms. This larger ratio, in general, leads to a larger singularity index.³ Just such an increase has been observed for the W(110) surface.⁵ The large SCS of 740 meV associated with the Ta(100) surface atoms⁸ implies that those atoms are the most atomiclike and hence have the highest s - to d -electron ratio of all low-index Ta-surface atoms. This suggests that the significantly larger value of $\alpha=0.18$, which has been deduced for these atoms,⁷ is at least qualitatively correct and contributes to their anomalously large linewidth.

The increased Gaussian width at the surface can be understood within the same framework recently used to explain the larger Gaussian width of surface-atom core levels in Na(110),¹ another bcc(110) metal, and can be used to determine the Debye temperature associated with perpendicular motion of the surface atoms. As shown for Na(110), the increased width at a bcc(110) surface comes from the softer phonon modes associated with motion of the core-excited atom perpendicular to the surface plane. In quantitative terms, the bulk phonon width $G_{\text{ph,bulk}}$ can be expressed as

$$G_{\text{ph,bulk}}^2 = \frac{C}{\Theta_D} \left[1 + \left[\frac{8}{3} \frac{T}{\Theta_D} \right]^2 \right]^{1/2}, \quad (1)$$

where Θ_D is the bulk Debye temperature and C is a pa-

parameter which depends upon the valence-band structure and mass density of the solid.²⁶ For temperatures such that $T/\Theta_D > 1$, Eq. (1) is well approximated by

$$G_{\text{ph,bulk}}^2 \approx \frac{8CT}{3\Theta_D^2} \quad (2)$$

For atoms at a low-index surface, there can be up to three independent Debye temperatures related to orthogonal vibrational motions perpendicular (Θ_{\perp}) and parallel ($\Theta_{\parallel,1}, \Theta_{\parallel,2}$) to the surface.¹⁹ Extended to the surface, Eq. (2) becomes¹

$$G_{\text{ph,surf}}^2 \approx \frac{8CT}{9} \left[\frac{1}{\Theta_{\perp}^2} + \frac{1}{\Theta_{\parallel,1}^2} + \frac{1}{\Theta_{\parallel,2}^2} \right] \quad (3)$$

For a bcc(110) surface, Θ_{\perp} is generally much lower than either $\Theta_{\parallel,1}$ or $\Theta_{\parallel,2}$ which are quite close to Θ_D .¹⁹ By approximating $\Theta_{\parallel,1}$ and $\Theta_{\parallel,2}$ by Θ_D , Eqs. (2) and (3) can be solved for Θ_{\perp}/Θ_D in terms of the experimentally determined Gaussian phonon widths as

$$\left[\frac{\Theta_{\perp}}{\Theta_D} \right]^2 \approx \frac{1}{3(G_{\text{ph,surf}}/G_{\text{ph,bulk}})^2 - 2} \quad (4)$$

Since $\Theta_D = 225$ K for Ta, the room-temperature data must be used to determine Θ_{\perp} . Substituting the values from Table I into Eq. (4) yields $\Theta_{\perp}/\Theta_D = 0.57 \pm 0.08$. Using $\Theta_D = 225$ K implies $\Theta_{\perp} = 128 \pm 18$ K. The value of $\Theta_{\perp}/\Theta_D = 0.57 \pm 0.08$ is in good agreement with an average theoretical value of 0.60 ± 0.04 for the similar transition metals Mo, W, Cr, and V.¹⁹ Compared to the alkali metals the perpendicular vibrations are relatively stiffer in the transition metals: experimental¹¹ and theoretical¹⁹ values for Na are $\Theta_{\perp}/\Theta_D = 0.41 \pm 0.03$ and $\Theta_{\perp}/\Theta_D = 0.32$, respectively. This difference in Θ_{\perp}/Θ_D between the transition and alkali metals is likely due to the directional nature of the d -electron bonding in the transition metals which produces much higher bond-bending force constants relative to the bond-stretching forces. Additionally, we note that it has been shown,¹ using the model presented here, that the increased Gaussian width at the surface of Ta(111) is also in agreement with calculations¹⁹ for the three surface-Debye temperatures of bcc(111) transition-metal surfaces.

Finally, we discuss the Lorentzian width of the $4f_{7/2}$ line which is dominated by the lifetime associated with the $N_7O_{4,5}O_{4,5}$ Auger transition.²⁷ Our value of 52 ± 7 is in agreement with earlier experimental determinations of 40 ± 10 meV (Ref. 14) and 50 meV (Ref. 11) for Ta. All of the values are quite close to a theoretical value²⁷ of 53 meV for atomic Ta; however, this is somewhat accidental since in the solid state the $5d$ -electron spatial distribution and occupancy (and hence the $5d$ - $4f$ overlap) is different from that of the free atom.⁵ As shown for W(110) the $4f_{7/2}$ lifetime width is not necessarily the same at the surface as in the bulk due to these differences in the $5d$ electrons.⁵ Unfortunately, the surface and bulk lines are inherently too wide compared to their separation to determine individual lifetime widths for Ta(110). However, based on the results for W(110), the lifetime width of 52 meV is surely an average of the bulk and surface. It is more likely that the surface width is slightly larger than

the bulk width due to a reduced delocalization of the $5d$ electrons in the more atomiclike surface as in the case of W(110).⁵ Consistent with a smaller number of $5d$ electrons compared to W, the average lifetime width of 52 meV is smaller than the average lifetime width of W bulk and (110) surface atoms (72 meV) which is also quite close to the theoretical atomic value (70 meV) for W.²⁷ Another process may increase the width at the surface. It has been suggested, on the basis of Auger-photoemission coincidence experiments, that the Ta(100) surface lifetime is shortened by an interatomic Coster-Kronig process.¹⁵ If this is the case, extrapolation of the results from that surface indicates an additional 10 -meV increase in the Ta(110) surface Lorentzian width from this separate process.

V. CONCLUSIONS

Clearly, the most interesting result to emerge from the data is a significant shift in the BE of the first underlayer atoms of a close-packed bcc(110) surface. While the high quality of the fits from least-squares analysis of data from W(110) gives no hint of such shift, the possibility certainly cannot be ruled out, especially considering the evidence from the stepped W surfaces²⁴ and the larger magnitude subsurface shift calculated for W(110) compared to the Ta(110) surface.²³ Data on W(110) for two different escape depths, as here for Ta(110), should clarify this issue.

The temperature dependence to the SCS was also unexpected. The 13 -meV decrease between 80 and 300 K can be qualitatively understood in terms of the quantities which give rise to thermal shifts of core-level binding energies in simple metals.⁴ Investigation of other transition-metal surfaces are underway in order to further delineate these BE changes in the tight-binding metals.²⁵

The line-shape information is rather more canonical compared to data on other metals. Both the bulk and surface screening properties follow the DS description of constant singularity indices. Unfortunately, the overlap of the bulk many-body tail with the surface line has thwarted any attempt to extract separate α 's and Γ 's for the bulk and surface. Ultimately, combined analysis of data from Ta(100) and Ta(110) may provide the solution to this problem since the large SCS of 740 meV for Ta(100) (Ref. 8) should allow precise determination of the bulk values of α and Γ which can then be fixed when fitting data from the (110) surface. A description of the phonon broadening in the bulk and surface is more settled. The increased Gaussian width at the surface is quantitatively described by the same mechanism responsible for the enhanced phonon broadening at the surface of the alkali metals,¹ i.e., by soft modes normal to the surface.

ACKNOWLEDGMENTS

We would like to thank S. D. Kevan for the loan of the Ta(110) crystal. The photoemission data were collected at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, which is supported by the Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

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