The surface state–surface resonance transition on Ta(011)

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Abstract. We study an unusual surface state–surface resonance transition recently identified in photoemission on Ta(011) using surface electronic structure calculations performed with the surface embedded Green function method. The transition is understood in terms of the relative movement of the bulk bands and surface potential with increasing parallel momentum, which switches the condition for a surface state below the band at the zone centre to a resonance within the band beyond 0.11 Å^{-1} along $\bar{\Delta}$. A simple two-band model is constructed to illustrate the effect. Comparison of the calculated and experimental surface bands away from the zone centre shows sizable differences, and we predict the existence of several unoccupied surface states which should be visible to inverse photoemission.

1. Introduction

Surface states, electronic states localized at surfaces, and surface resonances, states with enhanced weight in the surface region, contribute significantly to the total charge density at the solid–vacuum interface and hence play an important role in a variety of physical processes such as promoting catalytic reactions, molecular adsorption and surface reconstruction. Much work has been directed toward an understanding and characterization of these states, on a fundamental level (e.g. Davison and Levine 1970, Heine 1963), through accurate surface electronic structure calculations (Inglesfield 1982) and through the interpretation of various surface spectroscopies, primarily photoemission (Kevan 1992).

Recent high-resolution angle-resolved-photoemission (ARP) experiments by Kneedler *et al* (1990) have concerned the Ta(011) surface electronic structure. This work has identified an unusual surface feature, previously unobserved, in which a zone-centre surface state makes an apparently discontinuous transition to a surface resonance when passing into the continuum with increasing $k_{\parallel}$. On the basis of the relative energies and widths of these two features, deduced from the ARP spectra, these workers have interpreted the transition as an 'avoided crossing' between surface and bulk bands. Here we report a theoretical investigation into the origin and nature of this surface feature. In addition we report a detailed study of the surface states and resonances of the clean Ta(011) surface, finding significant differences when compared to the photoemission results.

We have determined the surface electronic structure of Ta(011) using the surface embedded Green function method (Inglesfield and Benesh 1988, Crampin *et al* 1992).

The important feature of this technique is the use of an embedding potential to constrain the surface wavefunctions to match correctly onto the bulk continuum. This is an important prerequisite to the study of surface state/surface resonance behaviour, permitting their identification even within the one-surface-layer calculation presented here. In the finite slab or supercell geometry, the spectrum of states at fixed parallel momentum $k_\parallel$ consists of a series of delta functions (Benesh and Inglesfield 1984) and *it is questionable whether such a calculation could ever yield the same information*, particularly with regard to the identification of resonance levels and their associated width.

Experimentally, a surface state is identified as a prominent feature in the photoelectron spectrum which is sensitive to the presence of adsorbates, with constant energy with respect to photon energy (eliminating direct bulk transitions) and within a band gap of the projected continuum. A surface resonance is similarly defined but overlaps with the projected continuum. From a theoretical point of view these definitions are unsatisfactory since they do not unambiguously distinguish between surface resonances and certain bulk-derived features. In the bulk, extrema of the band structure at fixed $k_\parallel$, $E_{k_\parallel}(k_z)$, give rise to singular band-edge behaviour in the density of states: $n(E) \sim \mathrm{Re}(E - E_0)^{-1/2}$. At a surface the band-edge density of states becomes $n(E) \sim \mathrm{Re}(E - E_0)^{1/2}$ but can still give rise to strong features in the surface density of states (SDOS), particularly when the band edge is associated with a nearby surface state/surface resonance. This is especially well illustrated in the results presented below. Because the bulk band structure is stationary at these energies, and the wavefunctions have considerable weight in the surface region, the *band-edge feature within the SDOS is not distinguishable from the surface resonance within the above definition*. Furthermore, as shown by Heine (1963), the decay length of a surface state as it approaches the band edge at which it terminates becomes increasingly large, and so within the finite resolution of ARP a near-band-edge surface state cannot be distinguished from the band edge itself. Within our calculations, surface states can be unambiguously identified by reference to the exact limits of the projected band structure. We identify as resonances, peaks within the the surface density of states which do not coincide with extrema of the bulk band structure, and as bulk derived features those peaks which are related to extrema. With these definitions, a consistent picture emerges with regard to surface state–surface resonance development.

The structure of this article is as follows. We briefly describe our calculation method, before examining in detail the surface state–surface resonance transition. We describe a simple model system which displays identical behaviour. We then present our calculated surface bands over the full surface Brillouin zone, before closing.

2. Calculation details

The real and reciprocal space structure of the Ta(011) surface is shown in figure 1. The surface electronic structure was obtained within the full-potential linear augmented plane-wave (LAPW) basis implementation of the surface embedded Green function method. Calculation details follow those in Inglesfield and Benesh (1988). The surface potential was iterated to self-consistency within the volume of the top surface layer, using 103 LAPWs, and the surface barrier. The substrate

was incorporated via an embedding potential, expanded in 29 surface plane waves, calculated from a self-consistent muffin-tin potential. Working within the local density approximation, we use the Ceperley–Alder exchange–correlation functional, and we treat relativistic effects within the conduction bands in the semi-relativistic limit of Koelling and Harmon (1977), neglecting spin-orbit coupling but incorporating the mass–velocity, Darwin and higher-order terms.


surface layer

second layer
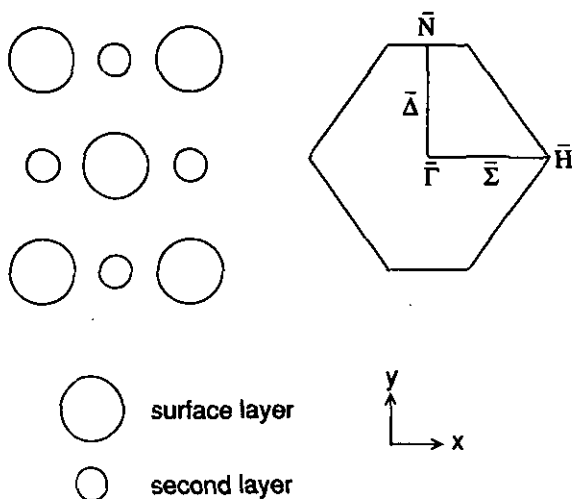
Figure 1. The real space structure of the ideal BCC (011) surface and the associated Brillouin zone. The z-direction is the surface normal (into the paper). We have not included relaxation of the interlayer spacing in the calculations reported.

Analysis of the surface electronic structure was performed via surface density of states (SDOS) calculations. These give the number of electrons within the total calculation volume or muffin-tin volume as a function of energy, E, and the parallel momentum, $k_{\parallel}$. In order to locate sharp surface features, the SDOS was scanned at fixed $k_{\parallel}$ over an energy range from 9 eV below the Fermi energy to 3 eV above, and initially broadened by working with a relatively large imaginary energy component. This was subsequently reduced to ~ 0.0001 eV when resolving the detail. Examples are displayed in the following section. In addition, the relevant bulk states were identified via band-structure calculations. We present our results along the high-symmetry directions in the surface Brillouin zone, and project into even and odd components with respect to the relevant mirror plane.

3. The surface state–surface resonance transition

The surface state–surface resonance transition was identified by Kneedler *et al* (1990) within the spectrum of electron states of even symmetry near the zone centre along the $\bar{\Delta}$ direction of the surface Brillouin zone, just below the Fermi energy. In figure 2 we display our calculated even surface bands in this range, along with the bands deduced from the photoemission. We notice immediately that the features identified within the calculation include a surface state–surface resonance transition. At $\bar{\Gamma}$ an even surface state with a binding energy of 0.5 eV lies just below the bulk continuum, the state exhibiting essentially no dispersion. Along $\bar{\Delta}$ the nearby

continuum edge disperses downward and, at a parallel momentum $k_{\parallel} = 0.11$ Å^{-1}, merges with the surface state. The remarkable behaviour of this transition is that the surface state does not enter the continuum and continue dispersing across the Brillouin zone as a surface resonance, as might be expected. Instead a surface resonance appears *within the centre* of the projected continuum, fully 0.6 eV above the energy of the surface state and at a parallel momentum $k_{\parallel} = 0.22$ Å^{-1}. Given the flat dispersion of the surface state, this represents a discontinuous transition.
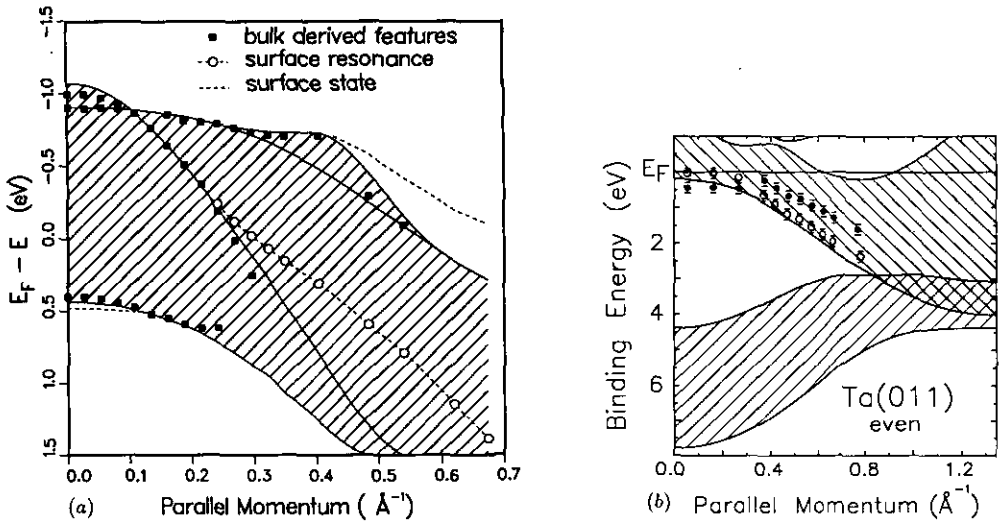
Figure 2. (*a*) Calculated even surface bands of Ta(011) along $\bar{\Delta}$ showing the surface state–surface resonance transition. Surface states: dashed lines. Surface resonances: dashed lines with o. Solid lines indicate the extrema of the projected bulk bands. Of these, the line falling most rapidly corresponds to a maximum at the end point of the k_z Brillouin zone. The shaded region is the bulk continuum. (*b*) Experimental even surface bands along $\bar{\Delta}$ obtained from photoemission (Kneedler *et al* (1990)).

The behaviour of our calculated surface bands is consistent with the photoemission results, although a quantitative comparison shows the calculated transition occurs at smaller $k_{\parallel}$. This discrepancy can probably be accounted for by the presence of bulk-derived features in the SDOS, indicated in figure 2, and which can be seen in the sequence of SDOS plots of figure 3 which cross the surface state–surface resonance transition. In figure 3(*c*), the surface state has entered the continuum, but the band edge still represents a significant surface density of states. The bulk-derived surface feature associated with the lower continuum edge when merging with the surface state extends 0.25 Å^{-1} along $\bar{\Delta}$, which is the range over which the surface state has been followed in the photoemission. Note that we have only determined the SDOS in the top surface layer. On sub-surface layers the bulk derived features will be even more prominent as the band-edge density of states approaches the bulk profile.

In the photoemission results, a bulk-like feature was identified near the Fermi level at small $k_{\parallel}$ which was interpreted as participating in the 'avoided crossing'. Although
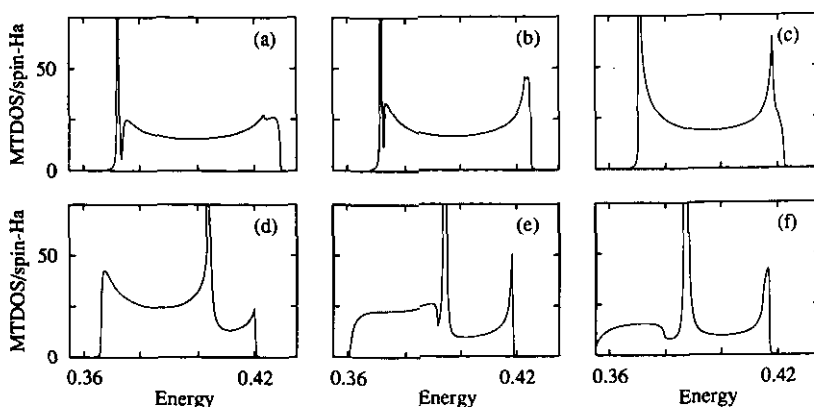
Figure 3. Even density of states within the surface atom muffin-tin spheres for varying momentum along $\hat{\Delta}$, illustrating the transition from surface state to surface resonance, and the interaction with the bulk band. (*a*) $\hat{\Gamma}$. (*b*) 0.06 $\hat{\Gamma}\hat{N}$ (*c*) 0.10 $\hat{\Gamma}\hat{N}$ (*d*) 0.16 $\hat{\Gamma}\hat{N}$ (*e*) 0.20 $\hat{\Gamma}\hat{N}$ (*f*) 0.24 $\hat{\Gamma}\hat{N}$. All were calculated with an imaginary energy 5×10^{-5}H.

for $k_{\parallel} < 0.25$ Å^{-1} there exists a bulk-derived surface feature whose dispersion can be continued on to that of the surface resonance, this is too high in energy, being above the Fermi level and hence inaccessible to photoemission which probes the occupied spectra. Thus the bulk state observed by Kneedler *et al* (1990) prior to the transition is presumably an artifact of the Fermi cut off, which would account for it lying (constant with $k_{\parallel}$) at the Fermi energy. Following the transition, the experimentally deduced bulk band would correspond to the lower continuum edge, which shows up increasingly strongly on sub-surface atoms.

We now consider the nature of the surface state–surface resonance transition. It is evident from figure 2, and from the sequence of $k_{\parallel}$-resolved SDOS plots in figure 3, that the weight of the surface state is taken up by the lower band edge, and that the surface resonance takes weight from the extremum-edge associated with a local maximum in the bulk band structure. At no point is a resonance seen to pass between these two points, and given the discontinuous dispersion one would conclude that the two surface features are not related. By projecting the Green function into symmetrized orbitals we are further able to establish the character of the two features (table 1). The surface state is d$_{z^2}$, i.e. out-of-surface, which accounts for the lack of dispersion. The surface resonance, however, has large p$_z$, d$_{yz}$ contributions. The orbital composition changes discontinuously across the surface state–surface resonance transition, and this disallows the possibility of the feature being an avoided crossing in the sense proposed by Kneedler *et al* (1990).

However, the surface state and surface resonance are related via the complex band structure. In figure 4 we show schematically the topology of the bulk bands in the relevant energy region. The real band exhibits three extrema: maxima at the end points of the k_z Brillouin zone, and a minimum in between. For $0.2 < k_{\parallel} < 0.3$ the maximum at $k_z = 0$ in the true Ta(011) k_z band structure moves to finite k_z and the band has a minimum at $k_z = 0$ but this does not participate in the surface state–surface resonance transition and we omit it.

Associated with each extremum are bands of complex k_z. In the bulk these states are forbidden due to their exponential growth but at a surface such growth is

Table 1. Orbital character of the even surface state/surface resonance along $\tilde{\Delta}$. The contributions, expressed in percentages, were obtained by integrating through a small energy range encompassing the feature at the specified parallel momentum, and thus include a small background contribution in the resonance data (last two columns).

Orbital	Distance along $\tilde{\Gamma}\tilde{N}$				
	0	2%	8%	18%	24%
s	3.1	3.1	3.4	0.1	1.6
p_y	0.0	0.0	0.0	0.2	0.2
p_x	3.4	3.4	3.0	47.5	33.8
d_{yx}	0.0	0.0	0.4	31.5	41.6
$d_{x^2-y^2}$	0.2	0.3	0.5	4.2	0.8
d_{z^2}	93.3	93.2	92.7	16.4	22.0

terminated and they can be used to match with wavefunctions integrated through the surface potential (Heine 1963). Below the real band in figure 4 extends a complex band (labelled (a)) originating from the minimum within the $E_{k_\parallel}(k_z)$ band structure. The surface state is associated with this branch of the complex band structure. Consequently, when the minimum of the real band structure moves below the energy of the surface state, the weight of this state is absorbed into the bulk-derived feature arising from the band edge. Distinct from this is the case when the complex band associated with the surface state does not terminate at the band edge. In this case the surface state would become a resonance. With reference to figure 4, such a situation would occur with a surface state associated with the complex branch labelled (b), if it dispersed down (relative to this band) from energies above the projected continuum. As the energy of the surface state crossed into those spanned by the continuum the surface state would become a resonance, hybridizing with the bulk states. Further reduction in the resonance energy would bring it close to the energy of the extremum, and when the two coincided the weight of the resonance would be taken up by the bulk-derived feature of the extremum edge. In fact, the resonance *is* associated with this branch, as may be seen in figure 3 where it takes all the weight from the extremum edge, but its dispersion is such that it never escapes from the continuum energies and hence never exists as a true surface state.

To understand the relative behaviour of the surface state/surface resonance and the bulk bands, consider the standard Tamm surface state model. Within this model, a sufficiently large shift v in the potential at the surface pulls a surface state off the top or bottom of the bulk band. A one-state semi-infinite linear-chain tight-binding realisation of this model with site energies $E = 0$, nearest-neighbour hopping term h (> 0) and with the shift restricted to the end-terminating ('surface') atom has band limits $-2h < E < 2h$ and a surface state when $|v/h| > 1$. Viewed as a continuously varying parameter, with $v < -h$ a surface state lies below the band; increasing v, the surface state approaches the lower band edge and at $v = -h$ it merges. Increasing v further, it must reach $v = h$ before the condition for the surface state is satisfied again, and for $v > h$ a surface state exists above the band, moving higher with greater v.

For the Ta(011) surface state–surface resonance transition, $k_\parallel$ is the continuously varying parameter, with the bulk band structure moving with $k_\parallel$ relative to the surface potential (viewed within a frame fixed to the centre of the bulk band the surface

potential varies with $k_\parallel$, more like the standard discussion of Tamm states above). For small $k_\parallel$ the criterion for a surface state below the band is satisfied. With increasing $k_\parallel$, the condition approaches the critical point at which the surface state merges with the band, and then after a further variation in $k_\parallel$ the criterion for a surface state to appear above the band is satisfied. In the case of Ta(011), however, the band topology is distorted by hybridization, and it is possible for a surface resonance to appear within the band. To model this, we have generalized the chain model to a two-band semi-infinite linear-chain tight-binding system (Appendix A). The essential ingredients are two bulk on-site energies and three bulk nearest-neighbour hopping terms. These are parametrized in terms of a variable $k_\parallel$ so that the topology of the upper band develops in the same manner as the Ta(011) band. The end-terminating atom is given different site-energies, chosen to generate a surface state at $k_\parallel = 0$ and then fixed independent of $k_\parallel$. The resulting 'surface band structure' is displayed in figure 5. As $k_\parallel$ increases the continuum edge disperses downwards, the surface state enters the band, and a surface resonance appears within the continuum, rising off the extremum associated with the local maximum within the bulk band. This is exactly comparable with the true Ta(011) surface, a direct consequence of the model including the correct bulk band topology. In figure 5 a second surface state is seen to appear above the continuum. On Ta(011) the bulk bands are further distorted by additional inter-band hybridization, and the bulk band rises slightly from a local minimum at $k_z = 0$ to a global maximum before following the form in figure 4. However, we do in fact observe a surface state rising off the top of this band, also shown in figure 2.
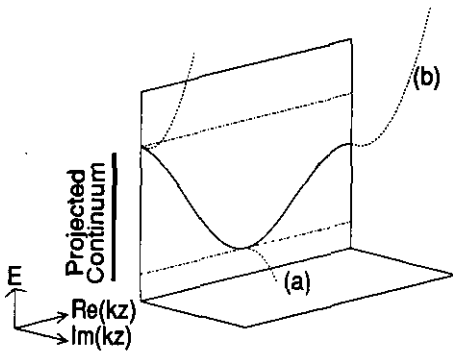

Figure 4. The characteristic topology of the complex bands participating in the surface state–surface resonance transition. Solid line: real band. Dotted line: complex bands. The band limits are marked and the projected continuum shown.
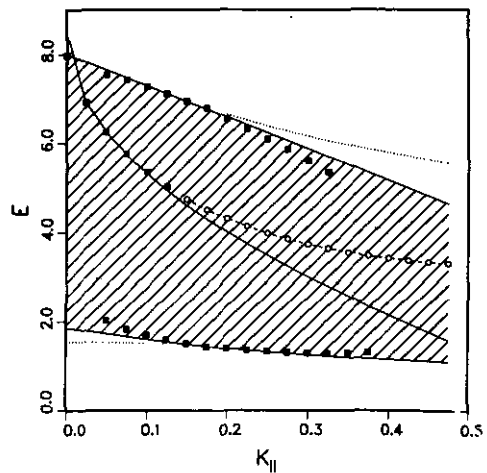
Figure 5. Surface bands of the semi-infinite two-state linear-chain tight binding model as discussed in the text. Surface states: dotted lines. Surface resonances: dashed lines with o. Solid lines indicate the extrema of the projected bulk bands. The shaded region is the bulk continuum.

4. The surface electronic structure of Ta(011)

We now briefly describe the surface bands over the rest of the Ta(011) surface Brillouin zone, considering energies within 3 eV of the Fermi level and below. In figure 6 and 8 these are shown against the bulk continuum, determined from the extrema in the bulk band structure $E_{k_\parallel}(k_z)$. The even continuum agrees well with that of Kneedler *et al* (1991), reproduced in figure 7, which was evaluated with the tight-binding code of Papaconstantopoulos (1986), although differences within the unoccupied states presumably reflect limitations in our muffin-tin substrate potential or the restricted range of validity of the fitted tight-binding parameters.
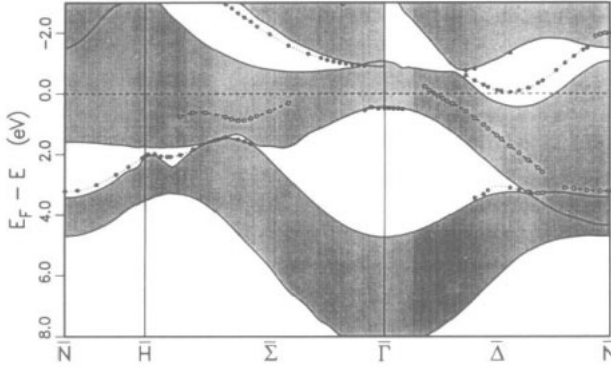

Figure 6. Calculated even surface features of the electronic structure of Ta(011).
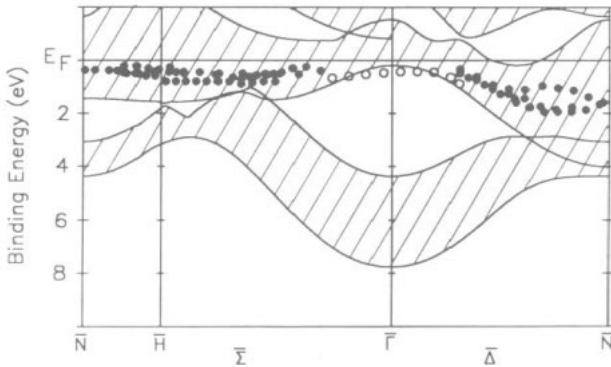

Figure 7. Experimentally derived surface features of the electronic structure of Ta(011) (Kneedler *et al* (1991)).

The surface resonance discussed in the previous section continues dispersing downward along $\bar{\Delta}$, parallel to the lower edge of the continuum band. In doing so, the level width steadily increases (e.g. 0.5, 0.9 and 1.1 eV FWHM at 0.36, 0.44, and $0.52\bar{\Gamma}\bar{N}$ respectively). Beyond $k_\parallel = 0.7\bar{\Gamma}\bar{N}$ the two occupied continuum bands overlap, and the resonance is no longer discernible in the SDOS, which exhibits unusual
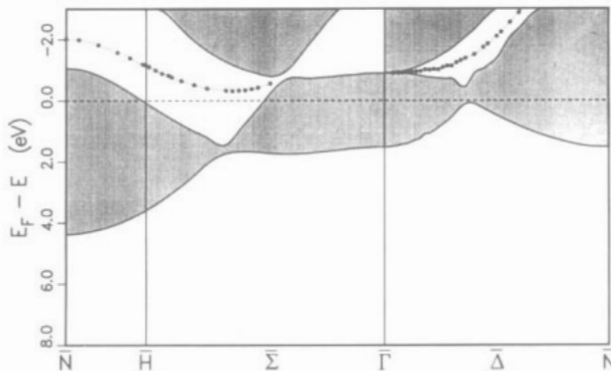
Figure 8. Calculated odd surface features of the electronic structure of Ta(011).

structure due to the distorted bulk bands. Just prior to the closure of the gap, a surface state (spd character) appears above the lower continuum band, becoming a rapidly decaying resonance after the gap has closed. A final feature along $\bar{\Delta}$ is a surface resonance, at a binding energy of 3.2 eV, which broadens as $k_{\|}$ moves away from $\bar{N}$ along $\bar{\Delta}$.

Along $\bar{\Sigma}$, a similar surface state to surface resonance transition is observed, the zone centre surface state entering the continuum at $k_{\|} = 0.11$ Å^{-1} and a surface resonance appearing at $k_{\|} \simeq 0.5$ Å^{-1}. The resonance is already quite broad when it leaves the extremum edge (FWHM=0.12 eV), which make the exact $k_{\|}$ difficult to establish. The emergence is clearly later than along $\bar{\Delta}$, due to the less rapid downward dispersion of the bulk band *and* the greater band width. The resonance initially disperses downwards, following the lower edge of the continuum, but strong interaction between the bulk states in the region $k_{\|} = 0.9$ to $k_{\|} = 1.3$ Å^{-1} leads to peculiar dispersion with increasing $k_{\|}$. Beyond $0.85\bar{\Gamma}\bar{H}$ the resonance is no longer discernible, the level width having sharpened and broadened (e.g. 0.3, 0.05 and 0.2 eV FWHM at 0.50, 0.66 and $0.80\bar{\Gamma}\bar{H}$ respectively). A surface state lies within the gap formed by the occupied continuum bands, just above the upper edge of the lower band, and may be followed from midway along $\bar{\Gamma}\bar{H}$ to $\bar{N}$, where it corresponds to the resonance feature identified along $\bar{\Delta}$ at a binding energy of 3.2 eV. This state is over 80% $d_{x^2-y^2}$ in character along $\bar{\Gamma}\bar{H}\bar{N}$.

The agreement with the ARP results of Kneedler *et al* (1991), which indicate a single surface band across the whole Brillouin zone (figure 7), is mixed. The dispersion of the two main resonances along $\bar{\Delta}$ and $\bar{\Sigma}$ broadly agree, but we find both exist only over a part of the Brillouin zone, and if we were to broaden our results with the experimental resolution their range would be further restricted from that shown in figure 6. We find no feature along $\bar{H}\bar{N}$ which could explain the band of states found in the photoemission, nor the upper band along $\bar{\Delta}$. The two lower surface states were not identified in the ARP. If we broaden the SDOS in the vicinity of the two lower surface states, we find it is impossible to distinguish them from the band edge.

In the unoccupied energies we find two distinct surface states. Along $\bar{\Delta}$ a state appears within the band gap at $k_{\|} = 0.5$ Å^{-1} which follows the dispersion of the lower continuum edge before entering the upper continuum band just before $\bar{N}$, and

along $\bar{\Sigma}$, a surface state appears when a gap opens up near the zone centre and which disperses upwards with increasing $k_{\parallel}$.

Turning to the odd states, in figure 8, we find no occupied surface states or resonances, in agreement with the ARP experiments. However, two unoccupied states lying within the centre of band gaps should be clearly observable to inverse photoemission. Along $\bar{\Delta}$ a state at 1.0 eV above the Fermi energy near $\bar{\Gamma}$ disperses upwards with increasing $k_{\parallel}$, and along $\bar{\Sigma}$ a state with initially flat dispersion appears half way along $\bar{\Gamma}\bar{H}$ before rising to 2.0 eV above the Fermi energy at $\bar{N}$. This state probably corresponds to the surface state identified by Kneedler *et al* (1991) at the Fermi energy for the Ta(011)+H surface.

5. Summary

We have performed self-consistent full-potential surface electronic structure calculations on the Ta(011) surface with the embedded Green function method, and investigated the surface state–surface resonance transition recently observed in photoemission. We find an analogy with the Tamm surface state model, with the relative position of the bulk bands and surface potential at the zone centre giving rise to a surface state. The downward dispersion of the bulk bands with increasing parallel momentum alters this condition to give a resonance within the continuum beyond a critical momentum.

Comparing our calculated surface bands with photoemission results we find a number of significant differences. We have identified several unoccupied surface states whose observation by inverse photoemission would provide welcome support for our results. Finally, we note that the simplicity of the projected continuum can disguise complex bulk band hybridization which can significantly affect the dispersion of resonant levels, and that certain bulk-derived features within the surface density of states can complicate the identification of surface states and resonances.

Note added in proof. Following completion of this work, a discussion with Ian Collins raised a question regarding the position of the Ta Fermi energy used within the calculation, and the effect on the calculated results. The Fermi energy, taken from a separate bulk calculation used to generate the substrate potential, is high in comparison to the placement in other bulk calculations. We have examined the consequences of a lower Fermi energy by reconverging the potential with the Fermi energy reduced slightly ($\simeq 0.2$ eV) towards the upper continuum minimum at $\bar{\Gamma}$. *The effect is to improve agreement with experiment.* The zone-centre surface state lowers slightly in energy, and the bulk-derived surface feature associated with the lower continuum edge moves higher—and is apparently the experimentally observed bulk-like feature near the Fermi level for small $k_{\parallel}$. The surface state also merges with the continuum at greater $k_{\parallel}$ than previously determined. The nature of the surface state–surface resonance transition is unaffected.

Secondly, Professor S D Kevan has informed us that the surface states which we locate (a) along $\bar{\Delta}$ where the gap closes and (b) along $\bar{\Sigma}$ between $\bar{N}$ and $\bar{H}$, were seen in his experiments, but not sufficiently clearly to be identified unambiguously as surface states and be included in the experimental dispersion curves.

Appendix

We outline the solution of the two-band semi-infinite linear-chain tight-binding model. Consider a semi-infinite chain of two-level atoms, with bare-site energies E_σ, $\sigma = 1,2$ and no on-site interaction. Hopping is restricted to nearest-neighbour:

$$\langle n\sigma|H|n'\sigma'\rangle = E_\sigma \delta_{\sigma,\sigma'}\delta_{n,n'} + h_{\sigma\sigma}\delta_{\sigma,\sigma'}\delta_{n',n\pm1} \pm h_{\sigma\sigma'}(1-\delta_{\sigma,\sigma'})\delta_{n',n\pm1} \quad (A1)$$

with site label $n = 1,2,\ldots,\infty$, and where we take $h_{12} = -h_{21}$, which corresponds to state 1 even, state 2 odd. To this we couple the surface atom, site 0, which has site energies E_σ^s:

$$\langle 0\sigma|H|0\sigma'\rangle = E_\sigma^s \delta_{\sigma,\sigma'}. \quad (A2)$$

We assume the same inter-site interaction between this surface site and the neighbouring atom as between bulk neighbours.

We solve this system via the Green function. The projection of the full Green function for the chain of sites $n, n + 1, \ldots \infty$ on site n, denoted $\mathbf{G}^n(E)$, is related to $\mathbf{G}^{n+1}(E)$ by

$$\mathbf{G}^n(E) = (1 \quad 0)([\mathbf{G}_0(E) \oplus \mathbf{G}^{n+1}(E)]^{-1} + \mathcal{H})^{-1}\begin{pmatrix}1\\0\end{pmatrix} \quad (A3)$$

where

$$\mathcal{H} = \begin{pmatrix} 0 & h \\ h^T & 0 \end{pmatrix} \quad (A4)$$

and

$$[\mathbf{G}_0(E)]^{-1} = \begin{cases} [E_\sigma - E]\delta_{\sigma,\sigma'} & n > 0 \\ [E_\sigma^s - E]\delta_{\sigma,\sigma'} & n = 0. \end{cases} \quad (A5)$$

The Green function for the substrate, atoms $1, 2, \ldots \infty$ is obtained first, found by solving equation (A3) with $\mathbf{G}^n(E) = \mathbf{G}^{n+1}(E)$. This is found iteratively. The final step is the addition of the surface atom, again using (A3), and the calculation of the surface density of states:

$$\rho_s(E) = (1/\pi)\mathrm{Im\,Tr}[\mathbf{G}^0(E)]. \quad (A6)$$

The corresponding band structure for this model is given by

$$E(k) = (E_1 + E_2)/2 + (h_{11} + h_{22})\cos(k)$$
$$\pm [[(E_1 - E_2)/2 + (h_{11} - h_{22})\cos(k)]^2 + 4h_{12}^2\sin^2(k)]^{1/2} \quad (A7)$$

from which it is possible to establish combinations of the bulk parameters, the two site energies and three inter-site interactions, which mimic the Ta(011) bulk k_z-band structure, and in particular to model the topology near the zone centre along $\bar{\Gamma}\bar{N}$. The parametrization we have used is:

$$E_1 = -8.0k_\| \quad E_2 = 0.5 \quad h_{11} = 4.0 \quad h_{12} = 0.8 \quad h_{22} = -4.0 + 1.25\sqrt{k_\|}. \quad (A8)$$

The surface atom levels were used to generate a surface state at the particular choice of bulk parameters corresponding to the zone centre. The parametrization is:

$$E_1^s = 2.8 \quad E_2^s = 3.3. \quad (A9)$$

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