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Unoccupied surface states of W(001) studied by angle-resolved ultraviolet inverse photoemission

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Abstract. Isochromat inverse photoemission spectroscopy (IPES), at a photon energy of 20 eV, has been used to map an intrinsic surface state/resonance in the $\bar{\Gamma}\bar{M}$ direction of the W(001) two-dimensional Brillouin zone. The state is found just above the Fermi level approaching halfway along the $\bar{\Sigma}$ line and disperses upwards to ~2 eV above the Fermi level towards $\bar{M}$. Calculations of the surface electronic structure and the role of the surface states in the reconstruction of the W(001) surface are discussed in the light of the data presented here together with existing high-resolution angle-resolved photoemission spectroscopy data.

1. Introduction

The W(001) surface reconstruction has attracted the attention of both experimental and theoretical surface scientists for many years. The W(001) surface is found to undergo a reversible temperature-dependent reconstruction [1,2] and a hydrogen-induced reconstruction [3]. For an overview of the earlier work in this field one is referred to the review articles by King [4] and Inglesfield [5], and references therein.

The clean surface of W(001) at and above room temperature exhibits a (1×1) LEED pattern as one would expect from a simple termination of the bulk structure. On cooling below room temperature, the surface undergoes a continuous phase transition to a c(2×2)$p2mg$ structure [2], in which the surface atoms are displaced in rows along the diagonal direction, shown in figure 1(a). Adjacent rows move in opposite directions, thereby giving rise to the zigzag pattern [2].

The surface reconstruction is now commonly believed to be an order–disorder transition [6–14]. Much recent attention is focused on the nature of the disordered high-temperature (1×1) phase. It was inferred from helium atom scattering experiments [6,8] that the surface has an incommensurate periodicity with the substrate above ~280 K. However, recent x-ray scattering studies did not show this incommensurability [13], in agreement with earlier LEED studies [1,2].

Inglesfield has discussed the various theories that have been postulated to explain the origin of this W(001) reconstruction [5]. Although controversy exists as to the nature of the driving force leading to the reconstruction, it is commonly believed to be electronic in nature. One proposed mechanism for the temperture-dependent reconstruction involves the formation of surface charge-density waves (CDW) [15–20]. This model requires the existence of a surface state in the $\bar{\Gamma}\bar{M}$ direction of

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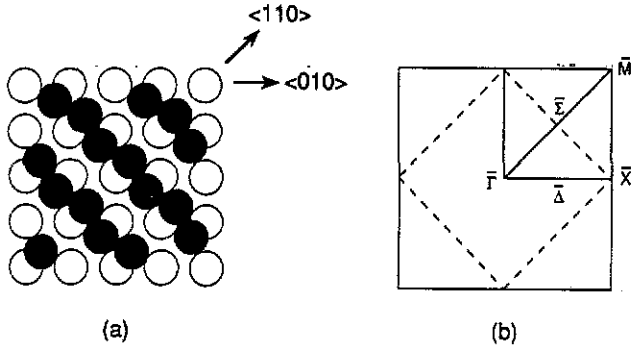

Figure 1. (*a*) The hard-sphere model of the W(001) c(2×2) $p2mg$ reconstruction. Filled (open) circles represent surface (sub-surface) atoms. (*b*) Surface Brillouin zone of (1×1) (——) and c(2×2) (- - - -) surfaces.

the surface Brillouin zone (SBZ), i.e. in the direction parallel to the [110] vector in real space, which crosses the Fermi level at halfway between $\bar{\Gamma}$ and $\bar{M}$. Upon reconstruction, the size of the unit cell is doubled [2], and the size of the SBZ thus halved, as depicted in figure 1(*b*). A surface state crossing the Fermi level will be split at the new zone boundary creating a Peierls-like gap. The occupied states close to the new zone boundary will be driven slightly downwards in energy and the unoccupied states slightly upwards resulting in a lowering of the total energy of the occupied states, favouring reconstruction. Another proposed mechanism [10,21–24] for the surface reconstruction invokes the instability of the (1×1) surface atoms to lateral displacements, based on a local bonding model. The driving force for the reconstruction is provided by the surface states favouring a displacement of the surface atoms which couples the surface states together. Since both these mechanisms involve the surface electronic structure, they can be tested using electron spectroscopies such as photoemission and inverse photoemission which are ideal techniques for studying bulk and surface electronic structures of solids [25,26].

The energies and dispersions of the surface states below the Fermi level have now been well established by angle-resolved photoemission spectroscopy (ARPES) using both discrete line sources and synchrotron radiation sources [23,27–29]. Holmes and Gustafsson [28] found a surface state to disperse up towards the Fermi level crossing it at $\sim 0.43\bar{\Gamma}\bar{M}$. This led to the search for the continuation of this surface state above the Fermi level using inverse photoemission spectroscopy (IPES) [30,31]. In none of these studies reported to date has the continuation of the surface state dispersion, above the Fermi level, been observed. More recent ARPES measurements by Smith *et al* [29] found the surface state/resonance to disperse towards the Fermi level at $0.34 \pm 0.12\bar{\Gamma}\bar{M}$, but were unable to conclude whether or not it crossed the Fermi level. Furthermore, they suggested that it might remain below the Fermi level, presumably since it had not been observed above the Fermi level. Controversy therefore exists between the interpretation of the previous ARPES spectra. In our work, employing different experimental conditions to those of previous IPES workers, we do observe an unoccupied intrinsic surface state/resonance and have measured its dispersion in the $\bar{\Gamma}\bar{M}$ direction of the SBZ. Thus our results provide strong evidence for the existence of an unoccupied surface state/resonance. This can be interpreted to be the unoccupied portion of the surface state/resonance which is thought to play an important role in

the surface reconstruction.

The observation of the surface states/resonances by both ARPES and IPES on W(001) (the latter reported here) has several implications. In particular, to describe quantitatively the tunnelling process in scanning tunnelling microscopy (STM) and spectroscopy, in which the probe tip is usually tungsten, one needs to know the surface density of states [32]. Calculations which successfully simulate experimental results of the surface electronic structure for a semi-infinite system, i.e. such as that studied here, are a forward step towards accurate calculation of the surface density of states for a small cluster of tungsten atoms simulating the STM probe tip.

This paper is organized as follows: experimental details are given in section 2, followed in section 3 by presentation of the results. The discussion of the results in section 4 and their implications on previous theoretical work is followed by a brief summary in section 5.

2. Experimental details

The IPES experiments were performed in a diffusion and titanium sublimation-pumped ultra-high vacuum chamber. The experimental apparatus has been described elsewhere [33,34] and is only described briefly here. The low-energy electron beam generated from a LaB_6 cathode is focused onto the sample, which is mounted on a goniometer. The emitted photons are collected by a platinum-coated holographically-etched glass diffraction grating and are dispersed onto a single channeltron detector located behind a slit aperture. The locations of the electron gun and the grating are fixed, subtending an angle of 40° at the specimen. The 92 mm diameter grating, mounted on the Rowland circle of diameter 300 mm, thereby collects light over a solid angle of 0.024π steradians.

All the measurements were made in the isochromat mode by scanning the incident electron energy and measuring the photon flux for a fixed photon energy. For the experiments described in this paper the photon energy was fixed at 20 eV and the angle of the incident beam, with respect to the surface normal, was changed from spectrum to spectrum, thus scanning different regions of $E\,k_{\parallel}$ space. Measurements were made by rotating the crystal both towards (positive angles) and away from (negative angles) the grating, thereby collecting light emitted close to the crystal normal and more parallel to the surface respectively, for the same incident electron angle. These two experimental geometries are depicted in figure 2.

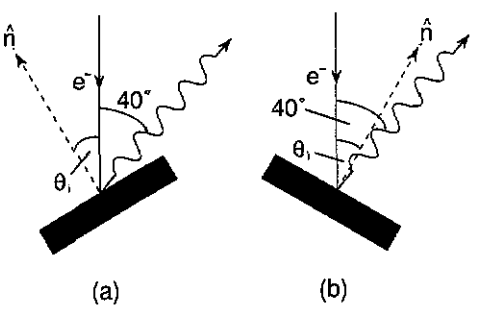

Figure 2. (*a*) Experimental geometry for negative-angle data. (*b*) Experimental geometry for positive-angle data.

The total energy resolution was determined to be 0.6 eV (FWHM) at a photon energy of 20 eV from the observed Fermi level threshold of polycrystalline gold. The momentum resolution is approximately 0.1 $Å^{-1}$. All the experiments were performed in a vacuum of better than 8×10^{-11} mbar.

The W(001) crystal ($6\times4\times1$ mm^3 in size) was firstly mechanically polished to a mirror finish and electropolished [35] before insertion into the vacuum chamber. Crystal alignment was verified to within a few tenths of a degree using x-ray diffraction. The crystal was cleaned *in vacuo* by repeated heating in 10^{-6} mbar of oxygen at 1400 °C followed by flashing to >2000 °C [36] until cleanliness was confirmed by Auger spectroscopy. The azimuthal orientation of the crystal was verified by LEED.

All data presented here were recorded at or above room temperature after flashing the crystal to a temperature of ~2500 °C in order to restore the clean surface. Spectra were recorded for up to 1.5 h at the spectrometer base pressure before recleaning; this procedure being repeated until satisfactory statistics had been accumulated. Count rates ranged between 0.1 Hz for dark noise, (i.e. counts below the Fermi level) and 36 Hz for direct transitions into unoccupied states.

Experiments were performed on both clean and hydrogen-dosed surfaces. In all hydrogen-dosed cases, the crystal was allowed to cool to below the hydrogen desorption temperature of 500 K [3] before dosing to the saturation coverage, $\theta_H = 2$ ($\theta_H = 1$ corresponds to one hydrogen adatom per surface tungsten atom, i.e. 1×10^{15} atoms per cm^2). LEED measurements at saturation show a sharp (1×1) pattern, consistent with the observation of previous workers [3,37].

3. Results

IPES spectra for the clean surface at different angles of electron incidence in the $[1\bar{1}0]$ mirror plane, corresponding to the ΓHNP plane of the bulk Brillouin zone ($\bar{\Gamma}\bar{\Sigma}\bar{M}$ in the (1×1) SBZ of figure 1(*b*)), are shown in figure 3. The intensities of the spectra are given by normalizing the photon flux to the incident electron charge. The negative and positive angle spectra shown in figures 3(*a*) and (*b*) correspond to photon emission angles approaching parallel and normal to the surface, respectively.

The normal-incidence spectrum exhibits a prominent feature, at about 3 eV above E_F, which is insensitive to contamination and whose energy and intensity vary with photon energy [34,38]. This state has been identified as a bulk state resulting from direct interband transitions into the plateau region of the Δ_1 bulk band [38], as has been suggested by Drube *et al* [30]. Drube *et al* also observed an image potential state at 3.9 eV above E_F at normal incidence, seen most strongly in their 12.3, 14.3 and 16.3 eV constant initial state IPES spectra. Our normal incidence isochromat spectra, recorded over a range of photon energies between 15 and 30 eV [34] (i.e. over higher initial state energies than those mentioned above), however, do not clearly show such a feature, presumably due to it being masked by the prominent feature seen at ~3 eV in all our spectra combined with our slightly inferior resolution. However, the relatively broad, weak peak observed at ~4.4 eV above the Fermi level in the −5° spectrum can probably be attributed to an image-potential state which disperses in a free-electron-like manner away from $\bar{\Gamma}$.

The off-normal incidence spectra, shown in figure 3, also exhibit a prominent peak around 3 eV whose profile is dependent upon electron incidence angle. This feature is assigned to the relatively flat bands in the NP and PH directions of the bulk

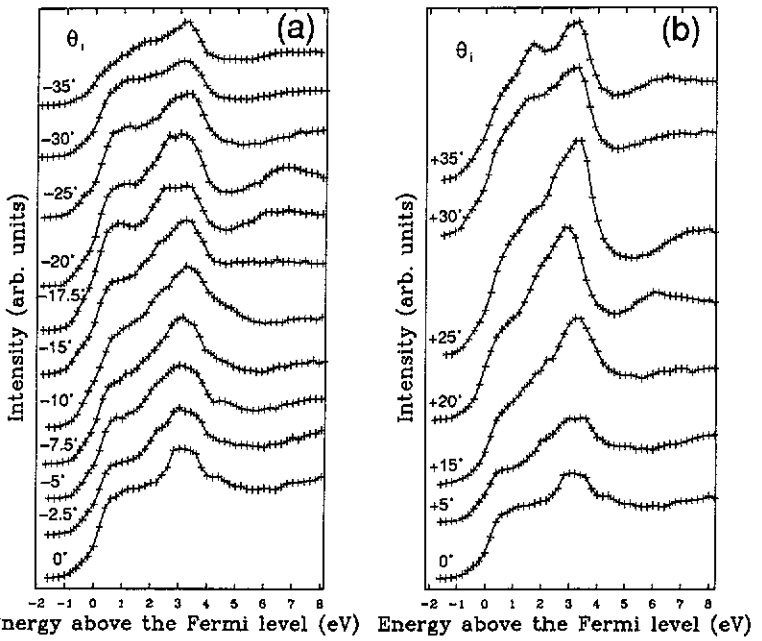

Figure 3. Isochromat inverse photoemission spectra, measured with $h\nu = 20$ eV, as a function of incident electron angle relative to the crystal surface normal, in the $\bar{\Gamma}\bar{M}$ direction for (*a*) negative-angle spectra, and (*b*) positive-angle spectra. See figure 2 for definitions of experimental geometry.

Brillouin zone, predicted by Christensen and Feuerbacher to be at around 3 eV above the Fermi level [39]. The bottom of these bands, at 2 eV above the Fermi level, is in good agreement with the feature identified at ~2 eV in the spectra. Also, a strongly dispersing broad feature is observed for final-state energies greater than 6 eV in the high-angle data. By comparison with the above-mentioned bandstructure calculation [39], this feature is assigned to the rapidly dispersing band predicted between 6 and 9 eV above the Fermi level in the NP and PH directions. A fuller analysis of this bulk-related features will be published elsewhere [40].

It is the features lying close to E_F that are of concern here. These features are assigned to surface states or surface resonances, since they exhibit considerable sensitivity to hydrogen contamination. In addition, they reside within either a projected symmetry or an absolute bandgap of the bulk bandstructure [41], as shown later in this section.

In the positive-angle spectra of figure 3(*b*), these surface-related features are observed as weak shoulders on the lower binding energy side of the 3 eV feature, with the exception of the peak at 1.7 eV in the +35° spectrum. However, in the negative-angle spectra of figure 3(*a*) these features, appearing as shoulders in the low-angle data, become prominent peaks for $\theta > 15°$.

In figure 4, pairs of IPE spectra for the clean and hydrogen-dosed surfaces at different negative angles of electron incidence are shown. The intensities of the spectra are simply given by normalizing the photon flux to the incident electron charge. The effect of dosing the surface with hydrogen can be to introduce new

states (extrinsic states) or to quench existing states (intrinsic states) at the surface. An unoccupied hydrogen-induced state exists on this surface at ~0.8 eV above the Fermi level, observable only in the spectra for $\theta < 10°$, i.e. existing close to $\bar{\Gamma}$ [34, 40]. For $\theta > 15°$, the hydrogen-dosed spectra exhibit a reduction in intensity just above the Fermi level indicating the quenching of a state associated with the clean surface, namely an intrinsic surface state/resonance, which disperses away from the Fermi level with increasing polar angle. The dispersion of these surface-related features may be deduced from the raw data of figure 3(*a*) by identifying the peak positions of the surface-sensitive features. However, this procedure has been demonstrated to be inaccurate due to the finite experimental resolution and its effect on peak positions in close proximity to the Fermi level [42, 43]. It is therefore instructive to examine the difference spectra generated from the clean and hydrogen-dosed surfaces. Difference spectra were produced for each of the angles of incidence and treated in the following way. A model spectrum that of a Gaussian truncated at the the Fermi level, was convoluted with a Gaussian representing the instrumental broadening, σ = 0.27 eV. The model parameters—centre of the ideal Gaussian E_f, its linewidth, Σ, and its amplitude—were varied in order to minimize the χ^2 [44]. The errors were taken to be purely statistical. The resulting fits were added to the hydrogen-dosed spectra and are shown as solid lines in figure 4. Taking a work function of 4.63 eV [45], the results of the fitting together with the data point derived from the +35° spectrum [46] are reduced in the usual way to a diagram of final-state energy (E_f) against $k_\parallel$ (figure 5), along with the most recent high-resolution ARPES data [29]. Also shown in these figures are the projections onto the SBZ of the odd- and even symmetry W(001) bulk bands [41].

4. Discussion

The energies and dispersions of the occupied surface states of W(001) in the $\bar{\Gamma}\bar{M}$ direction have been determined across the whole of the SBZ employing high-resolution synchrotron-radiation-excited ARPES by Holmes and Gustafsson [28] and, more recently, by Smith *et al* [29]; the results of the latter study are reproduced in figure 5. Overall, the results of the two groups are in good agreement. However, whereas Holmes and Gustafsson observed the surface state/resonance at $\bar{\Gamma}$ located at 0.3 eV below E_F (the well-known 'Swanson hump state' [47]) to disperse towards the Fermi level and cross it at $k_\parallel$ = 0.6 Å^{-1} (0.43$\bar{\Gamma}\bar{M}$), Smith *et al* observed the surface state/resonance 0.35 eV below E_F at $\bar{\Gamma}$ to disperse slowly towards E_F, reaching a binding energy of 0.25 eV at $k_\parallel$ = 0.31 Å^{-1}. The state then showed no dispersion as $k_\parallel$ increased from 0.31 to 0.64 Å^{-1} (0.34 ± 0.12$\bar{\Gamma}\bar{M}$), as can be seen in figure 5. Smith *et al* did not, however, rule out the possibility that this state might in fact cross the Fermi level somewhere over this range of $k_\parallel$. If the effects of finite resolution on states in close proximity to the Fermi level were to be considered [28, 42, 43], the surface state/resonance could perhaps be shown to cross the Fermi level. The state at $\bar{\Gamma}$ is a surface resonance, since it hybridizes with the bulk bands. At $k_\parallel$ = 0.2 Å^{-1}, this resonance crosses into an odd-symmetry bandgap of the bulk bandstructure [41], shown projected onto the SBZ in figure 5(*a*). This state has previously been assigned to be of even symmetry with respect to reflection in the [1$\bar{1}$0] mirror plane [28] and therefore probably remains a surface resonance. However, the concept of symmetry of a surface state is perhaps dubious in this case since spin–orbit effects, which

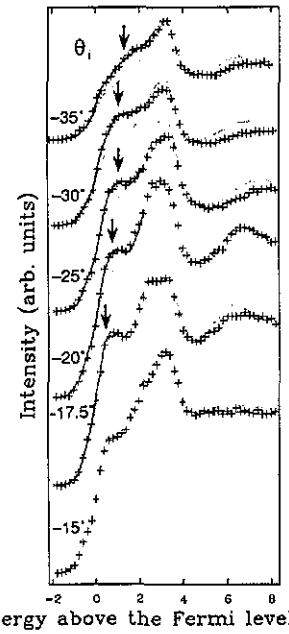

Figure 4. Isochromat inverse photoemission spectra *showing the dispersion of the surface state. Crosses* (dotted lines) denote clean (hydrogen-dosed) surfaces. Full lines show the fits to difference spectra added to the hydrogen-dosed spectra. Arrows indicate the position of the underlying fitted peak.

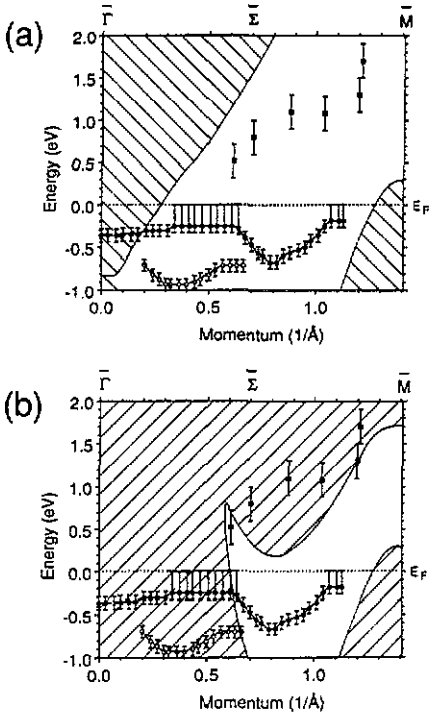

Figure 5. Dispersion plot of the surface states on W(001) *in the* $\bar{\Gamma}\bar{M}$ *direction:* ●○ARPES, $h\nu$ = 20 eV [29]; ■IPE, $h\nu$ = 20 eV [this work]. Shown in these figures are the projections onto the SBZ of (*a*) the odd and (*b*) the even symmetry W(001) relativistic bulk bands [41]. Error bars in the IPE data indicate the uncertainty in determining the Fermi level position.

become important for relatively heavy metals like tungsten, cause considerable band hybridization, as has been suggested by Inglesfield [5] and Smith *et al* [29].

For $k_{\|} \geqslant 0.64$ Å^{-1}, the peak observed by Smith *et al* [29], at a binding energy of 0.25 eV in their spectra, followed the dispersion depicted in figure 5. This state, now lying in an absolute bandgap, eventually dispersed towards the Fermi level at $k_{\|} = 1.19$ Å^{-1}. Here again, Smith *et al* were unable to conclude whether or not this surface state crossed the Fermi level [29]. The weak shoulder at ~0.8 eV above E_F, tentatively identified in our +35° and −35° spectra, can perhaps be assigned to this surface state. The significantly larger peak width for the fitted −35° spectrum perhaps indicates the presence of an additional unresolved structure. Unfortunately, technical difficulties did not allow spectra to be recorded for angles >35°.

Previous IPES workers [30] observed a surface resonance near $\bar{\Gamma}$ and assigned it to the tail of the surface state/resonance 0.3 eV below E_F, arguing that this state extended above E_F due to its hybridization with the bulk bands. Since, in ARPES, this state was observed to disperse towards the Fermi level with an associated decrease in intensity and also no continuation of this state was observed by Drube *et al*, they argued that the intensity decrease away from $\bar{\Gamma}$ of their non-dispersing state

was characteristic of increased hybridization with bulk bands. They also observed a surface-related structure 1.4 eV above E_F at $0.87\bar{\Gamma}\bar{M}$ and tentatively associated it with the high-density states at the $\bar{M}$ point, resulting from the $\bar{\Sigma}_2$ surface state, calculated to be at 2 eV above the Fermi level [19]. This surface-related feature corresponds well with the position of our dispersing state near $\bar{M}$ and can therefore probably be associated with this surface state/resonance. A possible explanation for the failure of Drube *et al* to observe the dispersion of this state may lie in the different experimental conditions employed. Drube *et al* performed experiments in the fluorescence mode (i.e. fixing the incident electron energies and scanning the photon energies), using a constant incident electron energy of 14.3 eV. However, our experiments were performed in the isochromat mode, (i.e. with fixed photon energies and scanning incident electron energies), and are therefore more analogous to conventional ARPES employing fixed photon energies. In addition, by using a photon energy of 20 eV, we have exploited similar experimental conditions to those used by Holmes and Gustafsson [28] and Smith *et al* [29]; the energies of the initial states in an IPES experiment using $h\nu = 20$ eV to probe final states just above E_F correspond closely to the final states used in an ARPES experiment using $h\nu = 18$, 20 and 22 eV to probe states just below E_F. We suggest that initial-state effects are perhaps responsible for the non-observation of the dispersion of the unoccupied surface state/resonance in the data of Drube *et al*. Similar arguments could perhaps also explain the prominent appearance of the surface resonance located just above the Fermi level which they observed close to $\bar{\Gamma}$; this is barely resolved in our data. In fact, the intensity of this surface resonance observed by Drube *et al* was seen to vary strongly as a function of initial-state energy [30]. Initial-state effects have previously been shown to be important in comparing IPES data taken in the two different modes [48]. Our slightly inferior resolution would, in addition, tend to smear out the already broad surface resonance (~1 eV FWHM) thereby rendering it less observable.

A number of surface states and resonances have been predicted to occur in the $\bar{\Gamma}\bar{M}$ direction of the SBZ [16–20, 49, 50]. Most of these were calculated using the self-consistent slab linearized augmented plane wave (LAPW) approach, the exception being that of Bullett and Stephenson [50] who used a self-consistent atomic orbital approach. These calculations for states close to the Fermi level give similar results. On the whole they predict a state of d_{z^2} character close to $\bar{\Gamma}$ and a doublet state, comprising of even-($\bar{\Sigma}_1$) and odd-($\bar{\Sigma}_2$) symmetry components, which disperse from ~0.5 eV below the Fermi level close to $\bar{\Gamma}$, cross the Fermi level around halfway along the $\bar{\Sigma}$ line and meet the zone boundary, $\bar{M}$, at about 2 eV above the Fermi level. It is this doublet state that is thought to play an important role in the clean-surface reconstruction, either via a CDW mechanism because it crosses the Fermi level halfway along the $\bar{\Sigma}$ line or in a local bonding model since the $\bar{\Sigma}_2$ component is primarily of d_{xy} character. It should be noted that all these calculations, with the exception of those performed by Mattheiss and Hamann [49], were performed within the non-relativistic limit, i.e. do not include the spin–orbit interaction. Mattheiss and Hamann [49] demonstrated that inclusion of spin–orbit coupling into their fully relativistic self-consistent tight-binding 19-layer slab LAPW calculation produces significant changes in the surface-state dispersions. Moreover, they showed that the predicted surface states contain a mixture of even and odd components, i.e. the bands hybridize.

We have seen that an intrinsic surface state/resonance is observed to disperse from just above the Fermi level approaching halfway along $\bar{\Sigma}$ towards ~2 eV above the Fermi level at $\bar{M}$. Since our spectra show no evidence for the existence of

the surface state/resonance across the whole SBZ, and on the contrary, the spectra indicate the sudden appearance of the state above the Fermi level towards the centre of the zone, then this leads us to the suggestion that the surface state/resonance is partially occupied, (i.e. has dispersed up through the Fermi level). This interpretation is consistent with the ARPES results for the occupied surface state, which disperses from $\bar{\Gamma}$ at 0.35 eV below E_F towards the Fermi level at $0.34 \pm 0.12\bar{\Gamma}\bar{M}$ [29]. In addition, we have seen a surface state, previously observed to disperse towards the Fermi level at $0.84\bar{\Gamma}\bar{M}$ in ARPES, now tentatively identified above the Fermi level in our spectra. Here, it should be pointed out that the interpretation of the states crossing the Fermi level is not totally unambiguous since the determination of the dispersion of a state, probed by either IPES or ARPES, is difficult when band or Fermi level crossing occurs, even using high-resolution measurements [29].

At this point attention must be drawn to the symmetry of the observed surface states/resonances. Unfortunately, we are unable to determine any symmetry information from our data due to the experimental arrangement employed. However, in the earlier ARPES study by Holmes and Gustafsson [28] certain symmetries, with respect to the real-space mirror plane, were assigned to the observed states. Smith *et al* [29] in a later study were unable to assign specific symmetries to these states, arguing that the observed intensity variations for different detector and sample orientations were inconsistent with any simple orbital-character picture; such a picture being dubious in the presence of strong orbital coupling. A possible explanation for the ability of Holmes and Gustafsson to assign symmetries to the states may lie in the fact that the states perhaps exhibit some symmetry character, similar to that which one would expect if the effects of relativity were not present.

The observation of surface state/resonances has implications as to the driving force for the W(001) reconstruction. Since neither of these states can be interpreted as crossing the Fermi level particularly close to the centre of the $\bar{\Sigma}$ line, the CDW mechanism would, therefore, be the less favoured of the two mechanisms for the reconstruction. On the other hand, since the surface state/resonance, which disperses up towards the Fermi level from 0.35 eV below E_F at $\bar{\Gamma}$, was assigned previously from the ARPES data to be of mainly even symmetry [28] (a specific symmetry assignment is perhaps dubious due to band hybridization caused by spin–orbit coupling), then the local bonding model would then be the less favoured. In fact, Smith *et al* [29] concluded that some combination of both models is the most likely physical reality.

5. Summary

An intrinsic surface state/resonance in the $\bar{\Gamma}\bar{M}$ direction of the W(001) SBZ has been found just above the Fermi level, approaching halfway along $\bar{\Sigma}$ and dispersing towards ~2 eV above the Fermi level at $\bar{M}$. These observations are consistent with previous ARPES and IPES experiments. The theoretically predicted surface states are in fair agreement with those observed experimentally. However, given the variation between different calculations, a direct comparison is difficult. Inclusion of spin–orbit coupling in the calculations have been demonstrated previously to be important for interpreting experimental photoemission results, since it causes signficant perturbations to the surface-state dispersions, in addition to introducing band hybridizations.

The experimental data, due to the observation of surface states/resonances close to the Fermi level, support the view that the surface electronic structure plays an important role in the reconstruction.

Further experimental work with improved energy and momentum resolutions, especially for IPES studies, is now required to determine more accurately the surface electronic structure of W(001). In addition, further theoretical work (i.e. surface electronic structure calculations which include spin–orbit coupling) is now required, following these recent experimental results.

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