Hosting of surface states in spin-orbit induced projected bulk band gaps of W(110) and Ir(111)

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Abstract. Spin-momentum locking of surface states has attracted great interest in recent years due to envisioned technological applications in the field of spintronics. Normal metal surfaces like W(110) and Ir(111) show surface states with energy dispersions and spin-polarization textures, which are reminiscent of topologically non-trivial surface states. In order to understand this phenomenon the connection of bulk and surface states has to be explored. Using time-of-flight momentum microscopy with soft X-ray excitation, we present a comprehensive analysis of the bulk bands of W and Ir. Surface states are determined by the same method with photon excitation in the vacuum ultraviolet region. The superposition of both spectral densities reveals the hosting of surface states within the gap structure of bulk bands projected on the surface Brillouin zone. Quantitative differences in the extension of experimental and theoretical local band gaps indicate an underestimation of electron correlation effects in theory.

Keywords: Soft X-ray, photoelectron spectroscopy, ARPES, momentum time-of-flight electron spectroscopy

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1. Introduction

The spin-momentum locking of electronic surface states has enormous potential for spintronic applications [1–7]. The spin-orbit induced spin momentum locking covers a broad range of phenomena including Rashba surface states [8], topological insulators [9], Weyl systems [2] and switchable systems such as ferroelectric semiconductors [10–13]. Even normal metal surfaces like W(110) and Ir(111) show surface states with energy dispersions and spin-polarization textures, which are reminiscent of topological (non-trivial) surface states within their local bulk band gaps [14–24]. It is therefore interesting to investigate the structure of local bulk band gaps of W and Ir and to combine this information with the position of surface states in reciprocal space. The full information on the electronic states is contained in the spectral density function $\rho^{\uparrow\downarrow}(E_B, k_x, k_y, k_z)$, where k_i are the Cartesian components of the electron momentum in k -space, E_B is the binding energy (referenced to E_F) and the arrows denote the electron spin projected on a relevant quantization axis.

Photoemission spectroscopy is the most common method for the determination of the spectral density ρ [25, 26]. The spin averaged spectral density function can be derived from the measured photoemission intensity $I(E_B, k_x, k_y, k_z)$, which is the discretized experimental mapping of ρ , weighted by the photoemission cross section. A high surface sensitivity for excitation in the vacuum ultraviolet regime stems from the limited mean free path of the emitted electrons at low kinetic energy. Bulk states are often hardly visible at low excitation energies. It is common belief that the small spectral density from bulk states originates from their strong k_z - dispersion in combination with a limited momentum resolution along the surface normal (k_z component). The limited k_z resolution in turn is usually attributed to the short mean free path of emitted low-energy electrons.

With increasing energy one expects that the increasing number of contributing atomic layers significantly enhances k_z -resolution. For tungsten, the inelastic mean free path increases from 0.48 nm at 20 eV to 2.5 nm at 2000 eV [27]. Similarly, the electron escape depth increases with increasing photon energy [28] giving access to the bulk electronic structure with excitation in the soft X-ray regime. Photoemission intensity from bulk states increases on the expense of intensity from surface states with increasing photon energy. Higher photon energy also strengthens the assumption of a free-electron-like final state because the high energy final states are less affected by the crystal potential. These advantages have been exploited in many soft X-ray ARPES experiments using conventional spectrometers, in particular for W(110) [29, 30], spintronic-relevant semiconductors [31, 32], and Weyl systems [33], that are relevant for the results discussed here. Hussain et al. [34] and Gray et al. [35] have shown that the concept of direct (i.e. k -conserving) transitions persists at larger photon energies in the tender X-ray regime and that band features are even visible up to $h\nu = 3000$ and 6000 eV. A sufficiently large Debye-Waller factor and hence low temperature is crucial for the observation of band dispersion [29].

However, distinguishing surface states from bulk states by photon energy is difficult because in general the photoemission probability depends not only on the photon energy. Examples have been published where surface states are still visible at soft X-ray energies for topological insulators [36] or ferroelectric semiconductors [12, 37]. In other cases surface states are indeed suppressed at soft X-ray energies [38, 39].

For the present work we have used soft X-ray photon excitation with energies $h\nu = 300 - 1300$ eV and a sample temperature of 30 K. As an example for a complex band-structure including partially filled d -states we investigate the W(110) and Ir(111) surfaces. A comprehensive mapping of bulk bands using soft X-ray photons, representing the precondition for the identification of local band gaps in k -space, has not been performed, previously. It requires an efficient parallel detection technique of the photoemitted intensity I with demanding k -range and k -resolution. These requirements are met by time-of-flight (ToF) momentum microscopy [40–43]. The spectral density function $\rho \propto I$ results from recording $I(k_x, k_y)$ via imaging of the Fourier plane of the cathode lens. The time-of-flight method determines the binding energy E_B . The momentum coordinate k_z follows from scanning the photon energy, exploiting the concept of direct transitions. The variation of dipole transition matrix elements is partly averaged out by exploiting crystal symmetry and illumination with circular left and right polarization. Constant energy cuts of I (isosurfaces) at a given binding energy E_B form a two-dimensional surface in the three-dimensional k -space. A projection of these isosurfaces along the surface normal onto the surface plane leads to the surface-projected density of states. Finally, the projections at various binding energies are concatenated to the complete projected bulk band structure. This projection reveals areas of not-allowed electronic states, i.e. local bulk band gaps. The experimental results are discussed in comparison with theory, revealing good qualitative agreement with the calculations but quantitative deviations. The combination of this bulk-sensitive spectroscopy with surface-sensitive photoemission spectroscopy in the vacuum ultraviolet range not only allows to distinguish between surface states within the projected bulk band gaps and surface resonances but also sheds light on the connections of these surface states to specific bulk bands.

2. Experimental

The W(110) single crystal surface was initially cleaned in-situ by extended heating cycles in oxygen. During measurements the crystal was flashed to 2200 K about every hour. No traces of impurities were present in the spectra. The Ir(111) crystal was cleaned by repeated cycles of sputtering, heating in oxygen at 1400 K and an annealing flash at 1600 K. The surface quality was checked by LEED prior to UHV-transfer into the microscope. The samples were mounted on a He-cooled hexapod manipulator for precise six-axis adjustment. During measurements the samples were cooled down to 30 K. The photon beam impinges at 22° with respect to the sample surface. The soft X-ray experiment was performed at beamline P04 [44] of the storage

ring PETRA III at DESY in Hamburg (Germany), characterized by a resolution of 40.000 in the spectral range between 270 and 2000 eV. For the experiments we used the 40-bunch mode providing a pulse period of 192 ns, fitting to the 5 MHz count-rate capability of the detector. The data was averaged for circularly left and right polarized light. Photoemission experiments with photon energies of 15-27 eV were performed at beamline U125-NIM at BESSY II in Berlin (Germany) with linearly p-polarized light. The lens system of the ToF momentum microscope [43] was set to record momentum discs of a diameter up to $4 \text{ \AA}^{-1}$. The smallest observed width of a spectral feature for $h\nu = 22 \text{ eV}$ in a constant energy slice along a momentum direction parallel to the surface is $0.025 \text{ \AA}^{-1}$. A low-energy drift section serves as energy-dispersive element of the instrument. Constant kinetic energy slices were binned to 36 meV energy width for each slice. Then 150 constant energy slices with different E_B are acquired simultaneously covering an energy range of approximately 5 eV, with an overall energy resolution of about 60 meV. These parameters hold both for soft X-ray excitation and measurements in the vacuum ultraviolet regime, because the electrons are decelerated by the sample bias to identical energies in the column of the microscope with little influence on the focal length of the objective in view of the large extractor voltage of ca. 11 kV. This results in identical kinetic energies of the valence electrons within the ToF section and hence to identical energy resolution. The grazing incidence of the light causes a linear dichroism in the photoemission intensity. This linear dichroism and additional variations of the photoemission yield depending on the initial state orbitals is described by the photoemission matrix elements. The observed photoemission intensity is modified by these matrix elements. Thus, a correct recovery of the spectral density from experimental photoemission data would require knowledge of the matrix elements. However, part of these effects and in particular the linear dichroism are removed by symmetrizing the data considering the crystal symmetry. Corresponding symmetrization has been performed for the data shown here in order to approximate the spectral density function.

The perpendicular momentum component k_z for emission along the surface normal results from the photon energy $h\nu$ according to:

$$k_z = \sqrt{2m^*(h\nu + V_0^* - E_B)/\hbar} - \sin \Theta k_{h\nu}, \quad (1)$$

assuming a free electron-like final state. Here m^* denotes the effective electron mass, V_0^* the inner potential with respect to the Fermi energy and $k_{h\nu}$ the photon momentum. For the inner potential we have assumed $V_0^* = 10 \text{ eV}$. The effective mass $m^* = 1.07m_e$ (free electron mass m_e) results from known values of k_z at identifiable high symmetry points in k -space, e.g. the N points of W, for consecutive repeated Brillouin zones. The deviation from the free electron mass results from the lattice-modulated potential acting on electrons even at higher energies. $k_{h\nu}$ is directed opposite to the electron momentum, thus reducing k_z . Data is acquired across the 5th repeated Brillouin zone for photon energies of 460, 472, 484, 496, 508, 521, 534, 547, 560, 574 eV in the case of W(110), providing equal spacing of ca. $0.14 \text{ \AA}^{-1}$ along k_z from Γ to N. In the case of Ir(111) we

Figure 1. Lower part: Three-dimensional representation of the measured spectral density of states of tungsten at the Fermi level $\rho(E_B = 0, k_x, k_y, k_z)$ (Fermi surface). Upper part: Projected spectral density $\rho_{110}(E_B = 0, k_x, k_y)$ for the (110) surface, illustrating the integration defined in Eq. 2 [same data as shown in Fig. 2(a)].

measured data for photon energies 369, 391, 413, 436, 460, 484, 512, 535, 561, 588, 616, 700 eV, providing equal spacing of ca. $0.3 \text{ \AA}^{-1}$ along k_z from k_z^0 to $k_z^0 + G_z$. Both data sets have been symmetrized according to $\rho(E_B, k_x, k_y, k'_z) = \rho(E_B, k_x, k_y, -k'_z)$ with k'_z measured relative to the Γ point.

Eq. 1 holds for normal emission. Corrections for finite parallel momentum are considered. The variation of k_z with E_B corresponds to a change of $0.06 \text{ \AA}^{-1}$ at $h\nu = 500 \text{ eV}$ for a binding energy range of 5 eV and has been neglected accordingly. The total acquisition time for the series of photon energies including both helicities was about 6 hours.

Figure 2. Projected bulk spectral density $\rho_{110}(E_B, k_x, k_y)$ for tungsten represented as constant energy slices at E_B as denoted in (a-f). The lattice constant of W, $a = 3.165 \text{ \AA}$, results in the basic momentum units $\overline{\Gamma\overline{N}} = \overline{\Gamma\overline{H}} = 1.404 \text{ \AA}^{-1}$.

Figure 3. Projected bulk spectral density $\rho_{110}(E_B, k_x, k_y)$ for tungsten represented as constant momentum cuts through $\overline{\Gamma}$ along $\overline{\Gamma\overline{N}}$ (a), $\overline{\Gamma\overline{S}}$ (b), and $\overline{\Gamma\overline{H}}$ (c) ($\overline{\Gamma\overline{S}} = 1.216 \text{ \AA}^{-1}$).

Figure 4. Projected bulk spectral density $\rho_{110}(E_B, k_x, k_y)$ for tungsten in a three-dimensional representation. Dark regions correspond to local band gaps.

3. $W(110)$

3.1. Experimental results for $W(110)$

Fig. 1 shows the Fermi surface of W. The Fermi surface of W is a fragmented object with several isolated electron and hole pockets. At each of the 12 N points of the first Brillouin zone a small ellipsoidal hole pocket appears. The 6 H points are covered by an octahedral hole pocket with high Fermi velocity. The Γ point is the center of an electron pocket of octahedral shape and at each of its corners directed along Γ -H an electron ball pocket shows up. The three-dimensional surface of constant energy has been obtained from $\rho(E_B, k_x, k_y, k_z)$ by setting $E_B = 0$. By integrating ρ along k_z , i.e. parallel to the (110) surface normal, over the full Brillouin zone (BZ):

$$\rho_{110}(E_B, k_x, k_y) = \int_{BZ} \rho(E_B, k_x, k_y, k_z) dk_z, \quad (2)$$

one obtains the projected Fermi surface shown in Fig. 1 on top of the Brillouin zone. The numerical integration performed here is in fact a summation of the corresponding data. While the center of the surface Brillouin zone is fully covered by projected bulk states, empty k -space appears in the direction of the $\bar{S}$ points. The $\bar{S}$ points being the projection of the N points of the three-dimensional Brillouin zone are occupied by the circularly shaped projections of the small hole pockets. Empty k -space also exists around the projection of the small hole pockets at the $\bar{N}$ points, the projection of the H points lies directly on top of the N points in this projection. Near the center a reminiscent empty space around the small projected hole pocket shows up in the $\bar{\Gamma}$ - $\bar{N}$ - direction. In this (110) projection surface states would show up with high intensity as they lack a k_z - dispersion. Their absence in the soft X-ray regime indicates that for

tungsten the photoemission cross section for surface states is considerably smaller than that for bulk states. In addition the increasing electron escape depth with increasing photon energy leads to a decrease of the relative contribution of the surface layer.

Similarly, we obtain the projected isosurfaces for various constant binding energies E_B as shown in Fig. 2(a-f). These projections reveal a shrinking area of empty k -space with increasing binding energy. The remaining bulk band gaps vanish nearly completely for $E_B > 1.5$ eV.

A cut through $\rho_{110}(E_B, k_x, k_y)$ along the in-plane high symmetry directions reveal the energy dispersion of the local gaps as shown in Fig. 3. The cut along $\bar{\Gamma}$ - $\bar{N}$ (Fig. 3(a)) uncovers the local band gap at about 0.2 and 0.75 $\bar{\Gamma}\bar{N}$ close to the Fermi level. At larger binding energy $E_B = 1.0$ eV an area of considerably reduced spectral density occurs around $\bar{\Gamma}$, and a further gap exists between 0.25 and 0.5 $\bar{\Gamma}\bar{N}$. Along the $\bar{\Gamma}$ - $\bar{H}$ direction (Fig. 3(c)) the k -space is almost completely covered except a small area close to the $\bar{H}$ point. The $\bar{\Gamma}$ - $\bar{S}$ direction (Fig. 3(b)) exhibits the largest local band gap extending to $E_B = 1.5$ eV. At larger binding energy $E_B > 4$ eV, the projected bulk spectral density reveals a further extended local band gap around $\bar{\Gamma}$.

In order to visualize the shape information contained in the projected density of states we present the three-dimensional view of ρ in Fig. 4. Dark areas correspond to the local band gaps in k -space. The restriction of this view to the central part around $\bar{\Gamma}$ emphasizes the diamond-shaped region with a central hole that hosts those surface states that have been discussed in previous work [14] as reminiscent features of topologically non-trivial surface states.

3.2. Discussion of results for W(110)

At first we discuss the spin-orbit induced gap close to the $\bar{\Gamma}$ point in comparison to theoretical results. Fig. 5 shows the magnified details in comparison with results from Ref. [16] obtained by a fully relativistic calculation. The experimentally obtained local gaps show a good general agreement with the calculated gaps, but their precise extensions in (E_B, k_x, k_y) -space deviate. The gap around $E_B = 1$ eV results from the spin-orbit-induced splitting of the Σ_1 band into a Σ_1^5 and Σ_3^5 band [16] (in relativistic double group notation). This has been verified by a non-relativistic calculation where the two bands merge at $\bar{\Gamma}$. Directly at $\bar{\Gamma}$ the spin-orbit gap is closed by the second Σ_1^5 band starting at $\bar{\Gamma}$ above E_F with negative dispersion. This bulk band forms the small hole ellipsoid of the Fermi surface at the bulk N point. The dotted lines in Fig. 5(d) indicate the corresponding region in k -space. In the projected bulk band structure this closing at $\bar{\Gamma}$ causes an effective gap only for those surface states of certain symmetry that do not hybridize with the bulk band. At larger $k_{||}$, the symmetry gap develops into a total gap as indicated by the white area in Fig. 5(d). While this gap is complete in theory, the experiment still shows a small but finite spectral density. This might be a result of the generally increased lifetime broadening close to a spin-orbit induced splitting region.

Figure 5. Comparison of the measured projected bulk spectral density $\rho_{110}(E_B, k_x, k_y)$ (a-c) for tungsten with calculations from Ref. [16] (d-f). Constant momentum cuts through $\bar{\Gamma}$ along $\bar{\Gamma}\bar{N}$ (a,d), $\bar{\Gamma}\bar{S}$ (b,e), and $\bar{\Gamma}\bar{H}$ (c,f). Arrows indicate a local band gap at the Fermi energy showing up along the three high-symmetry directions.

Along the $\bar{\Gamma}\bar{S}$ direction one finds that the gap is quite large in fact and dominates the constant momentum cut in this direction (see Fig. 5(b)). At larger $k_{\parallel}$ the gap even extends to E_F . In this case one expects that surface-related features should dominate the photoemission spectra measured with vacuum ultraviolet excitation in the corresponding binding energy range. This extended gap also shows up in the calculation (Fig. 5(e)). It appears larger in the calculation where it fully extends to the $\bar{S}$ point at E_F . In the experiment, instead, the bulk band forming the hole pocket at the N point restricts the gap.

In contrast to the gap near $E_B = 1$ eV, the gap region observed close to E_F and $k_x = 0.2 \bar{\Gamma}\bar{N}$ (see Fig. 5(a), marked by arrows) does not show up in the calculation. The same discrepancy occurs along $\bar{\Gamma}\bar{S}$ and $\bar{\Gamma}\bar{H}$. The outer rim of this gap is defined by the electron octahedral feature centered at Γ and the inner boundary is the hole ellipsoid at the N-point (both of Σ_1^5 symmetry). Within this area pure surface states are likely to occur.

In order to determine the position of surface states relative to the projected bulk

Figure 6. Bulk-related projected spectral density $\rho_{110}(E_B, k_x, k_y)$ from soft X-ray data (red) overlaid with the surface-related spectral density $\rho_{\text{surf}}(E_B, k_x, k_y)$ from vacuum ultraviolet excitation (22 eV) (green). Regions, where bulk-related projected spectral density and surface-related spectral density from low photon energy excitation occur simultaneously, appear yellow. The yellow areas thus correspond to surface resonances. Constant energy slices are shown for the Fermi level $E_B = 0$ (a) and just above the $\bar{\Gamma}$ crossing of linearly dispersing surface states at $E_B = 1.1$ eV (b). Constant momentum cuts through $\bar{\Gamma}$ are oriented along $\bar{\Gamma}\bar{N}$ (c), $\bar{\Gamma}\bar{H}$ (d), $\bar{\Gamma}\bar{S}$ (e), and the constant momentum cut parallel to $\bar{\Gamma}\bar{H}$ lies at $k_x = 0.27 \bar{\Gamma}\bar{N}$ (f). The top right panel shows the corresponding color code for $\rho_{110}(E_B, k_x, k_y)$ and $\rho_{\text{surf}}(E_B, k_x, k_y)$.

band gaps, we superimpose the projected density of bulk states determined with soft X-ray radiation with photoemission data measured for $h\nu = 22$ eV from Ref. [14] in Fig. 6. Upon low energy excitation almost exclusively electrons from surface states or surface resonances are emitted, as we verified by Ref. [14]. This fact is also verified by a data series measured with $h\nu = 15 - 26$ eV showing the absence of any k_z dispersion.

For the plot shown in Fig. 6 we apply as color code red for the projected bulk states from the soft X-ray data and green for surface states from 22 eV excitation. For this plot the intensity of the projected bulk states and surface states were normalized to their intensity maxima. Regions where both intensities (from projected bulk states and surface states) occur simultaneously appear in yellow. Please note the color code table given in Fig. 6. These regions correspond to surface resonances. In Fig. 6(c,d) the greenish yellow color of the surface state crossing at $\bar{\Gamma}$ and $E_B = 1.25$ eV reveals its strong overlap with bulk states and a correspondingly large mixing. This crossing is also visible in the $\bar{\Gamma}$ - $\bar{S}$ direction (Fig. 6(e)). In the $\bar{\Gamma}$ - $\bar{N}$ direction (Fig. 6(a)), however, the crossing is actually strongly elongated as has been pointed out in Ref. [18]. In contrast, the surface state crossing showing up at the off-center cut at $k_x = 0.27 \bar{\Gamma}\bar{N}$ (Fig. 6(f)) reveals a clear surface state character with linear dispersion lacking any degeneracy with bulk states. In combination with the helical spin polarization of this state as shown in Ref. [14] this state strongly resembles a topologically non-trivial surface state within the bulk band gap. This surface state connects bands forming hole and electron pockets at the Fermi surface: We see that this state splits off the projected bulk bands with electron character above the Dirac point that are related to the central octahedral Fermi surface. Below the Dirac point the surface band attaches to projected bulk bands with hole character that form the octahedral Fermi surface centered at the H point. It is remarkable that the two host bands are located at different positions in k -space, constituting an indirect local band gap.

4. Ir(111)

4.1. Experimental results for Ir(111)

Fig. 7 shows the Fermi surface of Ir. The two-dimensional surface of constant energy in k -space results from $\rho(E_B, k_x, k_y, k_z)$ by setting $E_B = 0$. The Fermi surface of Ir comprises two closed and connected isosurfaces IS1 and IS2 centered at Γ showing an almost octahedral structure. The inner isosurface IS1 is not visible in this representation as it is fully covered by the outer isosurface IS2. Both isosurfaces are electron-like with a positive dispersion curvature. Centered at each of the six K points two almost sphere-shaped hole-like isosurfaces IS3 and IS4 appear. In this case the inner sphere IS3 becomes visible because the experimental data have been cropped at the zone boundary. By integrating ρ along k_z , i.e. parallel to the (111) surface normal over the full Brillouin zone (see Eq. 2) one obtains the projected Fermi surface $\rho_{111}(E_B, k_x, k_y)$ shown in Fig. 7 on top of the bulk Brillouin zone. As in the case of $W(110)$ the center of the surface

Figure 7. Lower part: Three-dimensional representation of the measured spectral density of states of iridium at the Fermi level $\rho(E_B = 0, k_x, k_y, k_z)$ (Fermi surface) comprising the four different isosurfaces IS1 - IS4. The extended isosurface IS2 centered at Γ encloses IS1 (not visible) that is also centered at Γ . A surface resonance S2 splits off from IS1 forming a hexagonal prism along k_z . Two concentric spheres centered at the X points form IS3 and IS4. Upper part: Projected spectral density $\rho_{111}(E_B = 0, k_x, k_y)$ for the (111) surface, obtained by integration as defined in Eq. 2.

Figure 8. Constant momentum cuts for $k_y = 0$ (a) and $k_x = 0$ (b) through the spectral density of states of iridium at the Fermi level $\rho(E_B = 0, k_x, k_y, k_z)$ (Fermi surface). The surface resonance S2 is marked by the (red) arrows. The tilted appearance of B6 in (b) stems from the threefold symmetry.

Figure 9. Projected bulk spectral density $\rho_{111}(E_B, k_x, k_y)$ for iridium represented as constant-energy slices at E_B as denoted in (a-f). The lattice constant of Ir, $a = 3.839 \text{ \AA}$, results in basic momentum units $\bar{\Gamma}\bar{M} = 1.337 \text{ \AA}^{-1}$, and $\bar{\Gamma}\bar{K} = 1.544 \text{ \AA}^{-1}$.

Figure 10. Projected bulk spectral density $\rho_{111}(E_B, k_x, k_y)$ for iridium represented as constant-momentum cuts through $\bar{\Gamma}$ along $\bar{\Gamma}\bar{K}$ (a), $\bar{\Gamma}\bar{M}$ (b), and along $\bar{K}\bar{M}\bar{K}$ (c) ($\bar{M}\bar{K} = 0.772 \text{ \AA}^{-1}$).

Brillouin zone is covered by projected bulk states. In contrast to the case of W(110) the projected Fermi surface extends over a large part of the surface Brillouin zone. Similarly, we obtain the projected bulk states of constant binding energy E_B as shown exemplarily in Fig. 9(a-f). Band gaps in the projected Fermi surface only appear near $0.7 \bar{\Gamma}\bar{K}$ (labelled G1) and at $\bar{K}$ (G2 in panel(c)) as circularly-shaped dark areas. The local band gaps at E_F vanish with increasing binding energy. A ring-shaped band gap G3 appears near $E_B = 1$ eV (Fig. 9(d)). A bulk band gap centered at $\bar{\Gamma}$ opens for energies $E_B > 1.5$ eV (G4 in Fig. 9(e)). Finally, a band gap with sixfold symmetry appears at $E_B > 3$ eV (G5 in Fig. 9(f)).

Constant-momentum cuts through $\rho_{111}(E_B, k_x, k_y)$ along the in-plane high symmetry directions reveal the energy dispersion of the local band gaps as shown in Fig. 10. The cut along $\bar{\Gamma}\text{--}\bar{K}$ (Fig. 10(a)) shows the dispersion of the local band gaps G1 and G2 at E_F extending only up to $E_B = 0.2$ eV and $E_B = 1$ eV, respectively. Both have a circular shape in the constant energy map at E_F shown in Fig. 9(a). The constant-momentum cuts along $\bar{\Gamma}\text{--}\bar{K}$ and $\bar{\Gamma}\text{--}\bar{M}$ (Fig. 10(a,b)) reveal the small off-center band gaps near $E_B = 1$ eV (G3) and the central larger band gap G4 extending from $E_B = 1.5$ eV to $E_B = 2.7$ eV. Further band gaps open at $E_B = 3$ eV at the $\bar{K}$ points (G5) and below $E_B = 4.5$ eV at the $\bar{\Gamma}$ point (G6). The constant momentum cut along $\bar{K}\text{--}\bar{M}$ (Fig. 10(c)) also reveals the local band gaps G2 and G5 near the $\bar{K}$ point at E_F and below $E_B = 3$ eV, respectively, corresponding to the gaps G2 and G5 labeled in (Fig. 10(a)).

The pronounced parabolic band S2 starting at $\bar{\Gamma}$ and $E_B = 0.9$ eV shows up for all constant k_z cuts and changes only very little with varying k_z (see Fig. 8). This band forms a hexagonal prism as Fermi surface and its long prism axis with six-fold rotational symmetry coincides with the line through the Γ and L points along k_z (Fig. 7). The feature S2 represents a surface resonance because it depends only on k_x and k_y and not on k_z . Furthermore, it appears in regions where no bulk Fermi surface is expected. The prismatic surface resonance S2 crosses the bulk Fermi surface sheets IS1 (bulk band B6) and IS2 (bulk band B5) of Ir. A second surface resonance S3 appears in the k_x cut, and coincides with the Fermi surfaces IS2 (bulk band B5) in the k_y cut. The observation of surface resonances stays in contrast to the case of W(110) where the soft X-ray excitation revealed only bulk states. The appearance of the surface resonance in the case of Ir(111) hints to its deep extension into the bulk.

4.2. Discussion of results for Ir(111)

Fig. 11 shows magnified details of the local band gaps in comparison with theoretical results from Ref. [45] obtained by a fully relativistic calculation. The experimentally observed local band gap G1 very close to the Fermi level at $k_x = 0.7 \bar{\Gamma}\bar{K}$ has no corresponding gap in the theoretical calculation. The second local band gap at the Fermi level G2 opens at the $\bar{K}$ point. It corresponds to the calculated gap near the $\bar{K}$ point but it has a considerably larger energy width in the calculation. In the experiment

Figure 11. Comparison of the measured projected spectral density $\rho_{111}(E_B, k_x, k_y)$ for iridium (a-c) with calculations from Ref. [45] (d-f). Constant momentum cuts through $\bar{\Gamma}$ along $\bar{\Gamma}$ - $\bar{K}$ (a,d), $\bar{\Gamma}$ - $\bar{M}$ (b,e), and $\bar{K}$ - $\bar{M}$ (c,f).

the local band gap covers an interval of $E_B = 0 - 1$ eV while it extends to $E_B = 1.6$ eV in the calculated data.

The local band gap G3 around $E_B = 1.0$ eV appearing as a dark ring in the constant energy cut [Fig. 9(d)] again has no correspondence in the calculation. The fourth band gap G4 near the $\bar{\Gamma}$ point and at $E_B = 1.5 - 2.7$ eV has a circular shape in the constant energy cut and is the most pronounced gap area in the projected bulk band maps. It is related to a calculated spin-orbit induced gap showing up both along $\bar{\Gamma}$ - $\bar{K}$ and $\bar{\Gamma}$ - $\bar{M}$. However, in the calculation it does not extend to the $\bar{\Gamma}$ point in contrast to the experimental result. The fifth local band gap G5, the largest in the calculation, appears much smaller in the experimental data. In general the experimental band gaps are smaller compared to theory but new off-center gaps G1 and G3 appear in the experimental projected density of states for iridium.

In order to discuss the position of surface states and surface resonances relative to the energy gap of the projected bulk states Fig. 12 shows the projected density of bulk states overlaid with photoemission data measured for $h\nu = 17$ eV. For the plot shown in Fig. 12 we apply the same color code as in the case of W(110). The circularly shaped outer rim of the low-energy data marks the k -space boundary of the acquired data due

Figure 12. Bulk-related projected spectral density $\rho_{111}(E_B, k_x, k_y)$ for iridium from soft X-ray data (red) overlaid with the surface-related spectral density $\rho_{\text{surf}}(E_B, k_x, k_y)$ from vacuum ultraviolet excitation (17 eV) (green). Regions, where both occur simultaneously, appear yellow. Constant energy slices are shown for the Fermi level $E_B = 0$ (a), and at $E_B = 0.38$ eV (b) with a larger magnification of the center region (c). Constant momentum cuts are shown along $\bar{\Gamma}\text{-}\bar{K}$ (d,f), and $\bar{\Gamma}\text{-}\bar{M}$ (e). The corresponding color code for $\rho_{111}(E_B, k_x, k_y)$ and $\rho_{\text{surf}}(E_B, k_x, k_y)$ is the same as in Fig. 6.

to the limited detector area. The boundary does not represent a fundamental limit but the magnification in this measurement was optimized for high k -resolution.

For low-energy photon excitation the electron escape depth is small and the emitted electrons originate from states with sufficient local density near the surface. This condition is fulfilled for surface states and surface resonances. However, the feature with the highest intensity labeled B6 in Fig. 12(a) is in fact a bulk state corresponding to the Fermi surface IS1. That B6 is indeed a bulk state manifests in its three-fold symmetry in the constant k_z cut. Similar measurements with photon energies in the range from 15 eV to 27 eV give further evidence for state B6 being a bulk state because it shows a strong k_z dispersion even visible in this low energy range. The threefold symmetry is related to the fundamental three-fold symmetry of the (111)-axis of the fcc lattice. It can be seen for all k_z values except for the high symmetry points L and Γ . Using the free-electron final state model (Eq. 1) an excitation with $h\nu = 17$ eV would result in $k_z = 2.7 \text{ \AA}^{-1}$ corresponding to 1.9 Γ L. However, the effective inner potential or in an

alternative picture the final state energy is subject to electron correlation effects [46] as quantified by the self energy. An understanding of the real part of the self-energy for realistic systems is still a topic of current research. Our experimental results for $h\nu = 17$ eV indicate a smaller final state momentum of $k_z = 1.5$ Γ L. The threefold feature is then related to the inner Fermi surface pocket IS1 centered at Γ . A second bulk band B5 (see Fig. 12(e)) connected to the outer central Fermi surface pocket IS2 appears at higher binding energies $E_B > 0.4$ eV.

The central surface resonance S1 is spin split by the Rashba effect as has been discussed by Ref. [19]. The splitting is shown in more detail in the magnified images Fig. 12(c,f). The experimental data reveals a comparatively large Rashba splitting of 0.05 $\overline{\Gamma\text{K}} = 0.08$ $\text{\AA}^{-1}$ at $E_B = 0.5$ eV. A constant energy cut through this state (Fig. 12(c)) reveals a small deviation from the circular shape due to the interaction with the surface atomic potential exhibiting a six-fold symmetry in the topmost layer. S1 appears in a region where the projected bulk band states show a high intensity and it merges with this bulk band intensity below $E_B = 1.5$ eV.

The state S2 does not show a k_z dispersion in the low photon energy data as in the case of the soft X-ray experiment, clarifying that it is a surface resonance. Near $k_z = 0$ S2 attaches to bulk band B6 that forms the inner electron pocket IS1 at the Fermi surface. Because the bulk band B6 exhibits only a small k_z variation near $k_z = 0$ it leads to a high intensity in the projected bulk band maps exactly at the position of S2. For photon excitation at $h\nu = 17$ eV the k_z value is more close to the L point of the bulk BZ and hence B6 and S2 are separated. Similarly, the surface resonance S3 strongly overlaps with bulk bands B5 and B4 that form the second central electron pocket at the Fermi surface and the hole pocket at the X points, respectively, as concluded from the Fermi surface structure. In contrast to S2, S3 shows a strong warping with varying k_z in the low photon energy region. For the data shown in Fig. 12(a) S3 reveals a clear threefold symmetry, which is not expected for a surface state, but is due to the mixing with bulk band B4 for this particular photon energy of 17 eV leading to the threefold symmetry. On the other hand the experimental value for k_z excludes the occurrence of a bulk band at the Fermi surface at the observed $k_{\parallel}$ values for S3, again suggesting it to be a surface resonance.

A surface state S4 appears within the gap G1. The surface spectral density of this state shows a distributed intensity extending only very little to larger binding energies. This feature has been observed previously [47] using He I light. According to calculations [47] it has been attributed to the lower valleys of a mostly unoccupied surface state.

5. Summary

A comprehensive analysis of the bulk bands of tungsten and iridium using time-of-flight momentum microscopy with soft X-ray photon excitation has been performed. The projection of the spectral density of states onto certain surface planes (here (110) for

W and (111) for iridium) reveals the structure of local band gaps. The comparison of experimental data with theoretical spectra confirms that the local band gaps are partly caused by spin-orbit induced band splitting. Quantitative differences in the extension of experimental and theoretical local bulk band gaps indicate an underestimation of electron correlation effects in theory. For example, the experiment indicates that the N point hole pockets of W close the projected band gap at the $\bar{S}$ points of the W(110) surface completely. The corresponding bulk band exceeds the Fermi energy by at least 0.1 eV, while this bulk band misses the Fermi surface by 0.1 eV in the theoretical calculation. For the case of Ir(111), a band gap opens at the $\bar{K}$ at the Fermi level and extends to 1.0 eV binding energy. The theory agrees on the existence of this gap but it is closed at the Fermi level and extends to 1.5 eV, indicating an increased binding energy by 0.5 eV. The differences of experiment and theory are in general more pronounced in the case of iridium compared to tungsten.

In the cases of W(110) and Ir(111) soft X-ray photons excite almost exclusively bulk states or surfaces resonances with a local density extending deep into the bulk. Photoemission intensity stemming from surface states is strongly suppressed due to a smaller surface fraction of the total probed volume and in addition due to matrix element effects. On the other hand, the photoemission intensity excited with low-energy photons of 15-26 eV is dominated by states with a high local density near the surface. In the case of W(110) the low kinetic energy of emitted electrons causes an almost complete suppression of bulk states and the photoemission intensity stems from surface states. In contrast, photoemission from Ir(111) also reveals prominent bulk states for low photon energy excitation. The electron escape depth differs less than a factor of two for noble and transition metals [28] and even a smaller difference is expected comparing the two transition metals tungsten and iridium. Therefore, the apparently different surface sensitivity requires additional explanation. Decisive for the photoemission intensity is the spatial overlap of initial and final state within the electron escape depth and therefore the spatial distribution of the local density of initial states has to be considered. The total local density of occupied surface and bulk states in the valence band must not change too much between bulk and surface in order to keep charge neutrality. In the case of W(110) the presence of many occupied surface states binds a considerable amount of charge near the surface, thus suppressing the local density of bulk states within this area. This explains the predominance of surface states and missing bulk spectral density in the vacuum ultraviolet photoemission spectra of W(110). Our results for tungsten indicate that the topmost layer comprises exclusively surface states. There are six at least half-filled surface states in a 1 eV energy interval near the Fermi level within the surface Brillouin zone. Within the bulk there are the same number of states in this energy interval as can also be seen from the one-to-one correspondence of bulk and surface states in Fig. 6(a,b), indicating a complete exchange of bulk and surface states in the topmost layer. The same holds for Mo(110), where vacuum ultraviolet photoemission [42] revealed surface states that are quite similar to those of tungsten, but no bulk bands.

In the case of Ir(111) one observes a smaller number of surface resonances and one surface state is hardly occupied because only the valley bottom of this band crosses the Fermi level [47]. One true surface state exists replacing mainly bulk band B5 near the Fermi level. Surface resonances are distributed over at least five atomic layers thus counting only 20 % in the topmost layer. Consequently, bulk states possess a larger local density in the surface region, thus leading to an increased photoemission intensity stemming from bulk states.

Furthermore, the combination of bulk and surface related spectral densities allows a distinction of surface resonances from surface states also taking into account the complete spectral density function. Surface resonances are marked by an overlap in k -space of bulk states with states that are caused by the broken translational symmetry at the surface and hence show no or only weak dispersion with the perpendicular momentum component. In contrast surface states are positioned in bulk band gaps. The overlay of surface and bulk states within the four-dimensional space spanned by the three momentum components and the binding energy reveals the connection of surface states to certain bulk states thus uncovering their local symmetry and structure.

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