Exceptional behavior of d-like surface resonances on W(110): the one-step model in its density matrix formulation

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Abstract
Spin–orbit-induced spin splitting of surface states has attracted great interest in recent years because of the high potential for technological applications associated with this phenomenon. This Rashba physics is found in a variety of systems ranging from simple metals like Ag or Au to the so-called topological insulators which are of special interest in spintronics. A very special and unique case is found at the W(110) surface. In this metal d-like surface resonances exhibit energy dispersions and spin-polarization structures which are reminiscent of topological surface states. In our theoretical study, we present a complete analysis of the surface electronic structure of W(110) and show that the atypical linear-shaped dispersion behavior is triggered by the amount of charge transfer from the bulk into the first few vacuum layers. Furthermore, we compare our theoretical spectra with experimental photoemission data on W(110) and

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demonstrate that our state-of-the-art photoemission theory is able to deal with these peculiar surface features in a quantitative way. Our analysis is based on a generalization of the relativistic one-step model of photoemission, recently extended by us to study photoelectron spectroscopy at high photon energies. This theoretical approach was realized in the full spin-density matrix formulation for the photocurrent, which allows for an unrestricted calculation of the spin-polarization vector of the photoelectron. As an additional result we predict very peculiar behavior of these surface features showing up even at soft and hard x-ray energies. This observation is very surprising, unprecedented for ordinary surface features on simple metal surfaces.

1. Introduction

Rashba physics has aroused enormous scientific activity over the last decade [1–14]. A successful material design relevant for technological applications is intimately connected with a detailed understanding of the surface and interface electronic structure of the investigated system. Given the complexity of the problem, it is reasonable to start with relatively simple Rashba systems, such as ordinary non-magnetic metals like Ir, [15], Bi [16] or W [17–22], which show features in their surface emission profiles similar in some aspects to those of topological insulators [23–27]. Remarkably, in Ir and W, the Rashba-split surface features are d-type surface resonances in contrast to conventional Rashba systems [14, 28–39] where the spin–orbit split surface states exclusively exhibit sp-like character.

The most successful theoretical approach to deal with photoemission is the so-called one-step model as originally proposed by Pendry and co-workers [40–42]. The main idea of the one-step model is to describe the actual excitation process, the transport of the photoelectron to the crystal surface as well as the escape into the vacuum [43] as a single quantum-mechanically coherent process including all multiple-scattering events [44–46]. In our study we used a recently developed relativistic generalization of the one-step model which allows photocurrent calculations for excitation energies ranging from about 10 eV to more than 10 keV [47–52]. We predict that surface features discovered on W(110) are visible in photoemission spectra even at hard x-ray energies of 3 keV. This is very atypical behavior for surface states which was found up to now only for a few systems, such as, for example Al(001) [53] or, recently, in our calculations for topological surface states on Bi$_2$Se$_3$(0001) or Sb$_2$Te$_3$(0001) surfaces. To account properly for the different components of the spin-polarization vector, in particular for the so-called Rashba component, which is directed in the surface plane and perpendicular to the reaction plane, we have completely revised this theoretical approach by use of the spin-density matrix formulation of the photocurrent, which is introduced in section 2.

Within this model, lifetime effects, which give rise to damping in the quasi-particle spectrum, are properly included in both the initial and final states. Treating the initial and final states within the fully relativistic version of layer Korringa–Kohn–Rostoker (KKR) theory [54] in its tight-binding formulation (TB-KKR), it is relatively simple to deal with thin films, multilayers or self-consistently calculated half-space configurations. Such electronic structure calculations supply in a most convenient way the necessary potential function to be used in subsequent layer-KKR based photoemission studies. By use of these electronic structure calculations we also performed a complete analysis of the surface electronic structure of
W(110), from which we were able to demonstrate that the atypical linear-shaped dispersion behavior strongly depends on the charge transfer from the bulk into the first few vacuum layers.

Furthermore, we present a comparison of photocurrent calculations with experimental angle-resolved photoemission (ARPES) data measured at an excitation energy of $h\nu = 43\text{ eV}$ along all three symmetry directions $\Gamma-V$, $\Gamma-S$ and $\Gamma-H$ by use of both linear s- and p-polarized light. This way we were able to present a complete overview on the surface electronic structure of W(110) from the spectroscopical point of view. The power of our new formalism is documented by the agreement between the experimental data and our calculations, which is almost quantitative for all three symmetry directions.

The paper is organized as follows. In section 2 we present the spin-density matrix-based photoemission theory. In section 3 we discuss the computational details. Section 4 is devoted to our experimental and theoretical results. A summary is given in section 5.

2. Density-matrix formulation of the fully relativistic one-step model of photoemission

We start our considerations by a discussion of Pendry’s formula for the photocurrent which defines the one-step model of photoemission (PES) [41]:

$$I_{\text{PES}} \propto \text{Im} \langle \epsilon_f, k_\parallel | G_2^+ \Delta G_1^+ \Delta^\dagger G_2^- | \epsilon_f, k_\parallel \rangle.$$  \hspace{1cm} (1)

The expression can be derived from Fermi’s golden rule for the transition probability per unit time [55]. Consequently, $I_{\text{PES}}$ denotes the elastic part of the photocurrent. Vertex renormalizations are neglected. This excludes inelastic energy losses and corresponding quantum-mechanical interference terms [41, 55, 56]. Furthermore, the interaction of the outgoing photoelectron with the rest system is not accounted for, which means that the so-called sudden approximation has been applied. This approximation is expected to be justified for not too small photon energies. We consider an energy, spin and angle-resolved photoemission (ARPES) experiment. The photoelectron state at the detector is written as $|\epsilon_f, k_\parallel \rangle$, where $k_\parallel$ is the component of the wave vector parallel to the surface and $\epsilon_f$ is the kinetic energy of the photoelectron. The spin character of the photoelectron is implicitly included in $|\epsilon_f, k_\parallel \rangle$, which is understood as a four-component Dirac spinor. The advanced Green function $G_2^-$ in equation (1) characterizes the scattering properties of the material at the final-state energy $E_2 \equiv \epsilon_f$. $|\Psi_f \rangle = G_2^- |\epsilon_f, k_\parallel \rangle$ guarantees that all multiple-scattering corrections are formally included. For an appropriate description of the photoemission process we must ensure the correct asymptotic behavior of $\Psi_f(r)$ beyond the crystal surface, i.e. a single outgoing plane wave characterized by $\epsilon_f$ and $k_\parallel$. Furthermore, lifetime effects in the final state are accounted for by the imaginary part of the inner potential $V_{0i}(E_2)$. The final state is constructed within spin-polarized low-energy electron diffraction (SLEED) as a so-called time-reversed SLEED state [45, 46]. Many-body effects are included phenomenologically in the SLEED calculation, by using a parameterized, weakly energy-dependent and complex inner potential $V_0(E_z) = V_{0r}(E_z) + iV_{0i}(E_z)$ as usual [40]. This generalized inner potential accounts for inelastic corrections to the elastic photocurrent [55] as well as the actual (real) inner potential, which serves as a reference energy inside the solid with respect to the vacuum level [57]. Due to the finite imaginary part $V_{0i}(E_z)$, the inelastic mean free path (IMFP) is simulated and thus the amplitude of the high-energy photoelectron state can be neglected beyond a certain distance from the surface.

As mentioned before, the fully relativistic one-step model, in its spin-density matrix formulation, is needed to describe properly the complete spin-polarization vector in particular
for Rashba systems. The spin-density matrix of the photocurrent is defined by the following equation [58]:

$$\rho_{{s's'}}^{\text{PES}}(k||, \epsilon_f) = \langle s', \epsilon_f, k|| | G_2^+ \Delta G_1^+ \Delta G_2^- | \epsilon_f, k||, s' \rangle. \quad (2)$$

It then follows that for the spin-density matrix $\rho$:

$$\rho_{{s's'}}^{\text{PES}}(k||, \epsilon_f) = \frac{1}{2i} (\rho^{\text{PES}}_{{s's'}}(k||, \epsilon_f) - \rho^\ast_{{s's'}}^{\text{PES}}(k||, \epsilon_f)). \quad (3)$$

The intensity of the photocurrent results in

$$I^{\text{PES}}(k||, \epsilon_f) = Sp(\rho_{{s's'}}^{\text{PES}}(k||, \epsilon_f)) \quad (4)$$

and the corresponding spin-polarization vector is given by

$$P = \frac{1}{I} Sp(\sigma \cdot \rho). \quad (5)$$

Finally, the spin-projected photocurrent is obtained from the following equation:

$$I^\pm_{\text{PES}} = \frac{1}{2} (1 \pm n \cdot P). \quad (6)$$

The spin polarization is calculated with respect to the vector $n$. This, for example, allows the complete calculation of all three components of the spin-polarization vector for each pair of $(k_x, k_y)$ values which define the coordinate system for constant energy surface plots.

Furthermore, the surface described by a barrier potential can be easily included into this formalism as an additional layer. A realistic surface barrier model which shows the correct asymptotic behavior has been introduced, for example, by Malmström and Rundgren [59]. As this surface barrier represents a $z$-dependent potential, $V_B = V_B(z)$, a surface contribution $I^\text{surf}(\epsilon_f, k||)$ as part of the total photocurrent results, which accounts explicitly for the energetics and dispersion of all surface features. Furthermore, the relative intensities of surface-related spectral distributions are quantitatively accounted for by calculating the corresponding matrix elements in the surface region. This procedure is described in detail, for example, in [35, 36]. Also, energy and momentum conservation are naturally included in the low-energy electron diffraction formalism, which is used to calculate the initial- and final-state wave functions [42, 45]. This way the effect of the photon momentum is quantitatively included in the formalism. Within a soft x-ray photoemission study on Ag(100) [60] we have shown the importance of photon momentum effects on spectral distributions measured at higher photon energies.

Our implementation of the spin-density matrix formulation within the Pendry approach to ARPES needs a more detailed explanation. Conventionally, the component of the spin-polarization vector perpendicular to the surface $P_z$ is calculated. For such a calculation, only the diagonal elements of the spin-density matrix are needed. They are available by a conventional spin-polarized calculation assuming that the time-reversed SPLEED state at the detector is determined by the corresponding basis spinors $\chi^\uparrow = (1, 0)$ or $\chi^\downarrow = (0, 1)$ and is modified by spin-dependent scattering within the different layers of the semi-infinite half-space. This means that the time-reversed SPLEED state $|\epsilon_f, k|| \rangle$ is calculated twice with the corresponding boundary conditions. In the case where full access to the spin-polarization vector is needed, one has to calculate also the off-diagonal elements of the spin-density matrix with the consequence that
the calculational scheme described above is no longer sufficient. The way out is to calculate the time-reversed SPLEED state $|\epsilon_f, k_\parallel \rangle$ in a first step, but with unpolarized boundary conditions $\chi = (1, 1)/\sqrt{2}$. Having done this, it is possible, due to the plane-wave formulation of $|\epsilon_f, k_\parallel \rangle$, to extract the spin-up $|\epsilon_f, k_\parallel, \uparrow \rangle$ and spin-down contributions $|\epsilon_f, k_\parallel, \downarrow \rangle$ of the time-reversed SPLEED state. Using the proper combinations of these quantities one is able to calculate in a second step all four elements of the spin-density matrix. This procedure, as addressed in the introduction, needs a more or less complete reformulation of Pendry’s one-step model approach. This new version of the theory has been used in our present study.

3. Computational details

Self-consistent electronic structure calculations were performed within the ab initio framework of spin-density functional theory. The Vosko et al parameterization [61] for the exchange and correlation potential was used. The electronic structure was calculated in a fully relativistic mode by solving the corresponding Dirac equation. This was achieved using the relativistic multiple-scattering or KKR formalism in the TB-KKR mode [62–64]. The resulting half-space electronic structure represented by single-site scattering matrices for the different layers and the corresponding wave functions for initial- and final-state energies were used as input quantities for the corresponding photocurrent calculations. The self-consistent half-space electronic structure calculation was performed for the W(110) surface with the inward relaxation of the first atomic layer accounted for. The relaxation value of 3% was taken from the literature [65]. For the photoemission calculations, we added three vacuum layers to the semi-infinite half-space of atomic layers and, in addition, took into account the Rundgren-type surface potential. To take care of impurity scattering, a small constant imaginary value of $V_i = 0.03 \text{ eV}$ was used for the initial state. For the final state a constant imaginary value of $V_f = 2.5 \text{ eV}$ has been chosen again in a phenomenological way for excitation energies in the ARPES regime. For higher photon energies of 0.5, 1.0 and 3.0 keV, we used values of $V_i = 4.0, 4.5$ and 6.0 eV. Finally we have renormalized the Fermi level by a rigid energy shift of 0.2 eV to account for a well-known shortcoming of the local density approximation (LDA). Using the LDA one systematically underestimates self-energy effects in the electronic structure of simple metals [66].

4. Results and discussion

4.1. The spin–orbit-induced gap on W(110)

As a first point we discuss in detail the nature of the spin–orbit-induced gap with the focus on details which are important for a complete analysis of surface-related features. In the left panel of figure 1 the band structure along the $\Gamma–N$ direction of the bulk Brillouin zone is shown. All energy scales are referred to $E_F = 0$. The fully relativistic calculation displays the electronic states dispersing around the Fermi level which are labeled in the appropriate $\Sigma_{\delta}$ double-group notation. The two bands labeled by $\Sigma^\uparrow_3$ and $\Sigma^\downarrow_1$ symbols which are dispersing around 1.5 eV binding energy define a spin–orbit-induced splitting at $\Gamma$. In the projected bulk-band structure (third panel), this causes a gap for states of certain symmetry at $\bar{\Gamma}$, indicated by orange-dotted lines in the figure. Away from $\bar{\Gamma}$, i.e. with increasing $k_\parallel$, the symmetry gap develops into a total gap.
Figure 1. (first panel) Calculated relativistic band structure normal to the W(110) surface. The spin–orbit-induced gap is located in energy between bulk bands indicated by $\Sigma_3^5$ and $\Sigma_1^5$ labels. (second panel) Non-relativistic band structure with bulk bands labeled in non-relativistic notation. The two bands labeled by $\Sigma_3^5$ and $\Sigma_1^5$ are degenerate at $\Gamma$ to $\Sigma_1$ symmetry. (third panel) The spin–orbit-induced gap is shown in the projected bulk band structure along the $\Gamma-N$ direction. The gap boundary is indicated by orange dots. (fourth panel) Projected bulk band structure along the $\Gamma-N$ direction but for the spin–orbit coupling reduced to 10% of its full strength.

The fully relativistic band structure is compared to its non-relativistic counterpart. The corresponding electronic states shown in the second panel are now degenerate at $\Gamma$ and they disperse with higher $\Sigma_1$ symmetry around this symmetry point. As a consequence the spin–orbit-induced gap disappears. To test this interpretation we can ‘increase the speed of light’ to a certain value, which means we scale the strength of the spin–orbit-interaction to zero. The projected bulk band structures which are shown in figure 1 have been calculated for 100% (third panel) and for 10% spin–orbit interaction (fourth panel) along the $\Gamma-N$ direction in the surface Brillouin zone. If 100% spin–orbit interaction is present, the spin–orbit induced gap is clearly seen for non-zero $k_{\parallel}$. The gap boundary is indicated by orange-dotted lines to show the spin–orbit induced gap, which consists of a symmetry-independent part (total gap) and a symmetry part around $\Gamma$. The gap is shifted in energy and both parts of the gap are nearly closed if only 10% spin–orbit interaction is accounted for in the calculation (fourth panel). This clearly proves that the total gap appearing in the projected bulk band structures actually is part of a gap generated by spin–orbit interaction. If one scaled the velocity of light to infinity, one could expect that the total part of the gap including the symmetry part vanishes and the bulk bands may be labeled by use of the non-relativistic single-group notation as shown in the second panel of figure 1.

Having clarified the nature of the gap, its dependence on the symmetry direction may be of interest. An overview on the changes in the gap structure as a function of $k_{\parallel}$ and energy $E$ is given in figure 2 for several high-symmetry directions on the W(110) surface. In the left panel again the projected bulk band structure along $\Gamma-N$ is shown, but now for a larger range of binding energies. One observes that no other gap structures open for binding energies less than 2.0 eV. In consequence all surface-related features around $\Gamma$, which may appear at low binding energies in the photoemission spectra, must be influenced exclusively by the presence of this spin–orbit induced gap. Furthermore, it is seen that the symmetry part which is found around $\Gamma$ accounts for about 50% of the spin–orbit-induced gap with the effect that surface resonances around $\Gamma$ are more strongly coupled to bulk electronic states. To distinguish between bulk and surface electronic structure remains complicated in this case. For $\Gamma-H$ the gap structure changes...
slightly in the sense that the total part of the gap is increased and the gap is observable nearly up to the $\bar{H}$ point. If we inspect the projected bulk band structure that was calculated along the $\bar{\Gamma}-\bar{S}$ direction (middle panel) we find a completely different situation. The total part of the gap is quite large and dominates the symmetry part. In this case it could be expected that surface-related features should dominate the photoemission spectra in the corresponding binding energy range.

The band structures shown in figures 1 and 2 reflect the bulk-like electronic structure only. To learn more about the surface electronic structure one has to apply a slab or even better a semi-infinite half-space geometry for the electronic structure calculation. Because of the two-dimensional nature of such calculations, all crystal-induced surface states and resonances should be observable in the corresponding spectral function. This way we present a quantitative explanation for the linear dispersion behavior.

4.2. Origin of the linear dispersion behavior

In figure 3 we present the Bloch spectral function which displays the occupied electronic states of a W(110) half-space calculated along the $\bar{\Gamma}-\bar{S}$ direction. Light colors indicate high spectral intensities. The color map shown in the right panel is based on a standard TB (TB-SPRKKR) setup where the electronic structure results from a fully relativistic self-consistent calculation for a semi-infinite stack of atomic layers. The quality of the surface potential close to the first few atomic layers is improved accounting for charge multipoles up to the dipole level. This approximation goes well beyond the standard spherical atomic sphere approximation potential construction. The total gap is visualized by dark colors and the bulk bands dispersing along $\bar{\Gamma}-\bar{S}$ appear for binding energies higher than 1.3 eV in grey. The bulk continuum which is indicated by light colors is mainly located around $\bar{\Gamma}$ but also shows up at the zone boundary. Besides this bulk-like feature of the electronic structure, two d-like surface resonances are clearly observable by their dispersion behavior. The first one disperses close to the upper gap boundary of the symmetry gap and with a zigzag course disperses upwards in energy when entering the total part of the gap. The second one reveals quite unexpected dispersion behavior. The left branch...
Figure 3. Bloch spectral functions for the $\Gamma - \bar{\Sigma}$ direction, (left panel) calculated without dipole correction terms, (right panel) calculated with dipole correction terms in the surface potential.

disperses downwards in energy, passes the symmetry part of the spin–orbit-induced gap with linear dispersion and again enters the direct part of the gap at positive $k_\parallel$ values. The right branch of this surface feature is mirrored in its dispersion and crosses the left branch at $\Gamma$ for a binding energy of about $1.25 \, \text{eV}$. This dispersion behavior is exceptional for surface states dispersing on simple metal surfaces and it reveals similarities to the dispersion of topological surface states. Nevertheless, this surface resonance cannot belong to the same topology class because of the missing total gap which does not exist around the crossing point. Also the symmetry character is d-like, whereas topological surface states typically have sp-like symmetry. A further significant difference is found in the fact that this surface feature is sensitive in its dispersion behavior to residual gas contamination of the surface. Our ARPES measurements on a W(110) surface exposed to residual gas show an increase of the binding energy, which pushes the state toward the bulk region. With this, the formerly clear linear dispersion behavior is observed similar to the situation shown in figure 3(a). This finding indicates that the surface state, although it does not vanish, is sensitive to impurities and/or disorder.

The reason why this surface resonance exhibits such an unconventional dispersion is surprisingly found in the dipole correction terms. Inspecting the left panel of figure 3 again, the Bloch spectral function for W(110) is shown, but here without using dipole correction terms. The surface state dispersion is no longer linear and the crossing point touches the lower bulk region at $\Gamma$ at a binding energy of about $1.5 \, \text{eV}$. Therefore, the linear dispersion behavior is triggered by the dipole correction terms. This is easily explainable due to the enhanced charge transfer that these correction terms induce in the first few vacuum layers. By use of monopole terms only, the charge transfer in the empty spheres is strongly reduced and in consequence the split-off from the bulk states is made much more difficult for the surface state. Furthermore, the split-off in energy of the surface resonance is supported by the inward relaxation of the topmost atomic layer [65] which forces a change in the shape of the surface potential.

As a last point concerning the electronic structure of the occupied states, we want to discuss the spin polarization of bulk and surface-related features. This can be done via the use of the
relativistic spin-projection operator that allows calculation of the spin polarization in a certain direction [67]. Of major interest is the so-called Rashba component, which is directed parallel to the corresponding surface and points perpendicular to the reaction plane. This quantity is shown in the right panel of figure 4 together with the Bloch spectral function (left panel), which was presented first in figure 3. Focusing on the $k_\parallel$ region around $\Gamma_1$ and the energy region where the crossing point is located, the spin polarization of the surface resonance changes sign from negative to positive for negative $k_\parallel$ values and vice versa for positive $k_\parallel$ values. This again is a result that is typically found in a similar way for topological surface states [68, 69]. The crossing point itself remains unpolarized.

4.3. One-step calculations of photoemission spectra in the angle-resolved photoemission regime

The previous subsection was devoted to the electronic structure of the initial state. An ARPES experiment, on the other hand, measures the outgoing electrons with energy and angular resolution. This means ARPES measures the so-called final state defined by the photoelectron and not the initial state in a direct way. In consequence, matrix-element effects, final-state effects and the influence of the surface, as discussed in the introduction, must to be considered in a quantitative theoretical analysis. To give a first impression of typical $E$ versus $k_\parallel$ intensity maps we present in figure 5 contour plots obtained along different symmetry directions and discuss the dependence of the intensity distributions on the polarization of the incoming light. The spectra shown in the top row display the intensity variations as a function of $E$ and $k_\parallel$ calculated for a photon energy of $h\nu = 22.5$ eV with linear p-polarized light [24, 25]. According to the experimental geometry which was used in [24, 25] the angle between the incident light and the outgoing electrons was chosen constant with a value of $50^\circ$. The contour plots belonging to the $\Gamma-\bar{N}$ (left panel) and $\Gamma-H$ directions (right panel) deviate strongly in their intensity behavior, although the bulk-related properties for both directions on this surface are similar in the vicinity of $\Gamma$. The reason for the intensity behavior is found in different transition probabilities for these two symmetry directions which strongly depend on the direction of the incoming light. It should be mentioned here that the ‘bulk’ part of the surface potential has been identified,
Figure 5. Calculated photoemission intensities for different symmetry directions at a photon energy of $h\nu = 22.5$ eV with linear p-polarized light (top row) and s-polarized light (bottom row). (Left panel) $\Gamma$–$N$ direction, (middle panel) $\Gamma$–$S$ direction, (right panel) $\Gamma$–$H$ direction.

from our spectral function calculations, as the dominant contribution to the surface electronic structure. The influence of the Rundgren–Malmström correction on the surface potential is of minor importance for features dispersing around $\Gamma$. Furthermore, the intensity pattern obtained for the $\Gamma$–$N$ direction reveals various surface-related features not present in the contour plot for the $\Gamma$–$H$ direction because of the different surface electronic structure. This argument may also serve as an explanation for the invisibility of the highly anisotropic surface resonance that is clearly visible in the contour plots for the other two directions. A situation close to linear dispersion is certainly found along the $\Gamma$–$S$ direction (middle panel) where no other surface features lead to a modified or even distorted dispersion of this surface resonance. The lower row shows corresponding contour plots, but calculated for linear s-polarized light. The bulk-related intensities appearing for binding energies greater than 1.5 eV deviate strongly from their counterparts presented in the upper row. This again is explainable in terms of different transition probabilities existing for s- and p-polarized light. Also, the surface-related features seem to be modified in their intensities. This is due to the extreme sensitivity of surface features to the different components of the vector potential, which enters the dipole matrix elements via the dipole operator $[55, 70]$. The deviation is most pronounced for the $\Gamma$–$N$ direction which shows up with a much simpler intensity pattern concerning surface-related intensities. For the $\Gamma$–$S$ direction, which is not a high symmetry line, the whole intensity pattern is only slightly affected by the different light polarizations and the interesting surface resonance disperses linearly. In the following we compare our calculations to spectroscopical data from ARPES measurements with linear polarized light at $h\nu = 43.0$ eV.
Figure 6. (top row) Experimental photoemission intensities for different symmetry directions at a photon energy of $h\nu = 43.0$ eV with linear p-polarized light; (left panel) $\Gamma - N$ direction, (middle panel) $\Gamma - S$ direction; (right panel) $\Gamma - H$ direction. (bottom row) Corresponding theoretical spectra.

The top panels of figures 6 and 7 show the experimental photoemission intensities obtained for the $\Gamma - N$ (left), $\Gamma - S$ (middle) and $\Gamma - H$ directions (right) by excitation with linear p- and s-polarized light for a photon energy of $h\nu = 43.0$ eV. The corresponding theoretical results are shown in the bottom panels. The experimental details have been described elsewhere [24, 25].

Using p-polarized light in the experiment, a Dirac-cone-like dispersion is clearly observable along the $\Gamma - S$ and $\Gamma - H$ lines. For the $\Gamma - N$ direction, on the other hand, the corresponding surface state is found with a substantially weaker intensity and other more or less complex features appear instead. By excitation with s-polarized light, the measured intensity of the Dirac-cone-like feature is lower. However, this feature is somewhat more intense along the $\Gamma - N$ direction but with a flattened energy dispersion. This behavior was also discussed previously [25]. A surface resonance that traces the upper edge of the bulk-part of the symmetry gap is commonly recognized at about 0.8 eV binding energy at the $\Gamma$ point for all three symmetry directions. For s-polarized light, the corresponding intensity distribution is enhanced along the $\Gamma - N$ direction, whereas it almost disappears along the $\Gamma - H$ direction. Another surface-derived feature that crosses the Fermi energy at $k_\parallel = \pm 0.2$ Å is observed along the $\Gamma - S$ and $\Gamma - H$ lines for excitation with p-polarized light, while it shows up weaker in intensity along the $\Gamma - N$
Figure 7. (top row) Experimental photoemission intensities for different symmetry directions at a photon energy of $h\nu = 43.0$ eV with linear s-polarized light; (left panel) $\Gamma$–$N$ direction, (middle panel) $\Gamma$–$S$ direction; (right panel) $\Gamma$–$H$ direction. (bottom row) Corresponding theoretical spectra.

Our calculations, which we performed for the $\Gamma$–$N$ and $\Gamma$–$H$ directions, have been found in very good agreement with previous theoretical results from Henk and co-workers [27]. Going beyond this work, we show photoemission spectra calculated along $\Gamma$–$S$ and this in direct comparison to corresponding experimental data. In addition, we analyze in detail the momentum-resolved intensity distributions which appear asymmetric with respect to $\overline{\Gamma}$, and discuss this behavior in context with the polarization of the incoming light. Our polarization-dependent calculations reveal that the origin of this left–right asymmetry in $k_\parallel$ can be identified as a typical matrix-element effect. If the photoelectrons are excited by p-polarized light the vector potential $A_0$ varies strongly with $k_\parallel$ because the angle between the incident light and the outgoing electrons was chosen constant. In other words, $A_0$ is a function of $k_\parallel$ in this case. Since the dipole selection rules are sensitive to variations in $A_0$, one expects strong intensity variations generated by the corresponding matrix elements. For s-polarized light the spectra appear symmetric in their emission profiles because in this case the $z$-component $A_0z$ of the vector potential $A_0$ is zero. A similar explanation can be given for the intensity variations which are found as a function of the emission direction. For example, the spectra excited with s-polarized light strongly differ in their relative intensities for $\Gamma$–$N$ and $\Gamma$–$H$, although the...
intensity pattern remains symmetric with respect to $k_\parallel$. The reason for this is found on the one hand in the initial states located around the Fermi level, which have mainly d-character with relatively low symmetry. On the other hand, the excitation probabilities are strongly orbital-dependent quantities, and they could be very different for $A_0x$ and $A_0y$ in the presence of strong spin–orbit coupling. The $\Gamma–N$ and $\Gamma–H$ lines are orthogonal to each other. Therefore, the excitation is sensitive, for example, to $A_0x$ along $\Gamma–N$ and vice versa to $A_0y$ along $\Gamma–H$.

The reason why we do not compare with spin-resolved data is simply found in the experimental setup. The measurements were done in the spin-integrated mode, spin-resolved data obtained with linear polarized light are not yet available. Besides this fact we have compared our spin-resolved calculations with that shown in [27], and again found quantitative agreement. In particular, the observation that the spin polarization of the surface resonance changes sign as a function of the light polarization was confirmed in our calculations.

Furthermore, we found that most of the experimental findings have been reproduced in the spectroscopic calculations. Inspecting first figure 6 we observe altogether a good agreement in the dispersion behavior as well as in the corresponding intensity distributions for all three symmetry directions; only minor deviations are visible. In detail, the relative intensities of the d-like surface resonances seem to be overestimated by the calculations, especially for higher $k_\parallel$ values where these features disperse in the total part of the spin–orbit-induced gap. Also the strong asymmetric behavior in the measured intensity distributions is less pronounced in the calculations. The reason is found in terms of matrix-element effects. Due to the experimental geometry the intensity distributions behave very sensitive to the relative magnitude of the different vector potential components. This is not fully reproduced by theory because direct transitions induced by the $z$-component of the vector potential may predominate with their relative weights the corresponding intensity pattern. Figure 7 shows a similar scenario. The energetics and dispersion of different features is more or less in quantitative agreement concerning experiment and theory whereas in the relative intensities minor deviations are visible. Noteworthy here is that the calculated photoemission cross-section appears enhanced for higher binding energies when compared to the experimental data. Also, the surface resonance which disperses at about 0.8 eV binding energy around $\Gamma$ is not well reproduced in intensity for excitation along the $\Gamma–S$ and $\Gamma–H$ directions. Again, these deviations between experiment and theory can be assigned to the radial parts of the dipole matrix elements which determine the relative weights of the different transitions.

4.4. One-step calculations of photoemission spectra for x-ray energies

It is known from ARPES and inverse photoemission [71–73] that the intensity distributions of surface states strongly decrease with increasing photon energy. The reason is found in the strong dependence of the cross-section of the surface state photoemission on the photon energy [71]. In fact, two general types of mechanisms exist which are responsible for the cross-section variations. The first one is of atomic nature and is based on the spatial extent of the wave functions. The wave functions of real Shockely as well as Tamm states are mainly located in front of the first atomic layer. The second one is a solid state effect and is due to a release of momentum selection rules for the momentum perpendicular to the surface [71]. If the photon energy is increased to the soft or even hard x-ray regime the enhanced bulk sensitivity [37], which is due to the increase in the IMFP [37, 47–49, 51], has to be considered too. Real surface states contribute to the layer-resolved photocurrent with an intensity distribution only non-zero
Figure 8. (top row) Photoemission intensities calculated for different photon energies with linear p-polarized light along the \( \Gamma - S \) direction. (left panel) Intensity map calculated at \( h\nu = 0.5 \) keV. (middle panel) Intensity map calculated at \( h\nu = 1.0 \) keV and (right panel) intensity map calculated at \( h\nu = 3.0 \) keV. (bottom row) Corresponding spin polarizations in the Rashba configuration: in-plane, perpendicular to the reaction plane.

for the first atomic layer. In consequence the contribution to the total spectral weight decreases with increasing number of layers contributing to the photocurrent. The combined effect of energy-dependent cross-sections and greater IMFP causes then a strong decrease of surface state photoemission as the photon energy increases.

For surface resonances the situation can be very different if the coupling to the bulk continuum is relatively strong. This is because the cross-section dependence of surface-resonance emission on the momentum selection rules is significantly reduced due to their bulk-like behavior. Furthermore, a typical surface resonance shows up with a valuable spectral weight within the first three or even four atomic layers. In particular, on W(110) the surface emission has a considerable bulk contribution [27] triggered by the symmetry gap around \( \Gamma \). As a consequence the spectral weight of the resonance could be much larger than that of a real surface state with the result that a surface resonance can be observable at soft x-ray or even hard x-ray energies. In this sense one can use soft x-ray ARPES (SARPES) and hard x-ray ARPES (HARPES) measurements or calculations to estimate the fraction of bulk-like photoemission as part of surface-related intensity distributions. This is somewhat opposed to the so-called determinant criterion [74] that serves as a test for the surface sensitivity of a given intensity distribution.

We performed HARPES calculations shown in figure 8 to reveal the bulk-like part of the highly anisotropic surface resonance. In the upper row (left panel) we show an intensity plot...
calculated for p-polarized light along the $\Gamma - S$ direction at $h\nu = 0.5$ keV, which is a typical soft x-ray energy. The surface resonance is clearly observable but with maximum intensity around $\Gamma$, i.e. within the symmetry part of the spin–orbit-induced gap. However, the intensity decreases when the surface resonance enters the total part of the gap. All other surface-related features have more or less vanished in intensity. This trend continues when one inspects the middle panel where we present the corresponding calculation for a photon energy of 1.0 keV, which defines an excitation energy on the border between the SARPES and HARPES region. The real HARPES case is presented in the right panel. For a photon energy of 3.0 keV the surface emission is completely suppressed and only bulk-like emission survives. Surprisingly, the surface resonance is still observable at $h\nu = 3.0$ keV. This tells us that this surface-related feature is different from conventional surface states [75]. Although no dependence on the photon energy is visible, we have a clear cut argument against a pure bulk state. This result is new and it is very uncommon for simple metals [53], but it was recently discovered in our calculations for the surface emission of topological insulators like Bi$_2$Se$_3$(0001) or Sb$_2$Te$_3$(0001).

The bottom row shows the corresponding spin-polarization pattern of the Rashba component for all three excitation energies. The polarization calculated under HARPES conditions appears the most symmetric. For lower excitation energies the polarization pattern appears to be less symmetric if one moves from negative to positive $k_\parallel$ values. This observation reflects the fact that the symmetry of the $\Gamma - S$ direction is lower than the symmetry of the $\Gamma - N$ and $\Gamma - H$ directions. In other words, the spectra at lower photon energies reflect more the surface than the bulk symmetry due to the combined effect of energy-dependent cross-sections and reduced IMFP [37, 47–49, 51].

5. Summary

Rashba physics has aroused enormous scientific interest during the last decade because of the high potential for technological applications. As a bridge between conventional Rashba systems and topological insulators the W(110) surface turned out to be a unique system showing highly anisotropic surface features which exhibit peculiar energy dispersions and spin-polarization structures. This has been documented already in the literature by experimental and first theoretical photoemission investigations.

Using in our spectroscopical study a recently developed spin-density formulation of the photoemission process, which is applicable to a wide range of photon energies, we discuss in detail the origin of the linear dispersion behavior. The reason is found in a very sensitive interplay between spin–orbit interaction, relaxation of the first atomic layer and enhanced charge transfer in the first few vacuum layers. Furthermore, we demonstrated the applicability of our new formalism by a direct comparison to experimental photoemission data. We found our spectroscopical calculations to be almost in quantitative agreement with the measured spectra. Also, our HARPES calculations reveal considerable bulk-like behavior of this surface emission since it is visible in the spectra even at hard x-ray energies of 30 keV. This is remarkable behavior, which we recently discovered in our calculations for the surface emission of topological insulators like Bi$_2$Se$_3$(0001) or Sb$_2$Te$_3$(0001).

Finally, it would be of interest to answer the question whether or not W is the only element in the periodic table that exhibits such peculiar surface-state behavior.
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