Induced Rashba splitting of electronic states in monolayers of Au, Cu on a W(110) substrate

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Abstract. The paper sums up a theoretical and experimental investigation of the influence of the spin–orbit coupling in W(110) on the spin structure of electronic states in deposited Au and Cu monolayers. Angle-resolved photoemission spectroscopy reveals that in the case of monolayers of Au and Cu spin–orbit split bands are formed in a surface-projected gap of W(110). Spin resolution shows that these states are spin polarized and that, therefore, the spin–orbit splitting is of Rashba type. The states evolve from hybridization of W 5d, 6p-derived states with the s, p states of the deposited metal. Interaction with Au and Cu shifts the original W 5d-derived states from the edges toward the center of the surface-projected gap. The size of the spin–orbit splitting of the formed states does not correlate with the atomic number of the deposited metal.

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and is even higher for Cu than for Au. These states can be described as W-derived surface resonances modified by hybridization with the p, d states of the adsorbed metal. Our electronic structure calculations performed in the framework of the density functional theory correlate well with the experiment and demonstrate the crucial role of the W top layer for the spin–orbit splitting. It is shown that the contributions of the spin–orbit interaction from W and Au act in opposite directions which leads to a decrease of the resulting spin–orbit splitting in the Au monolayer on W(110). For the Cu monolayer with lower spin–orbit interaction the resulting spin splitting is higher and mainly determined by the W.

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### 1. Introduction

The investigation of the spin structure of low-dimensional metal systems under spin–orbit interaction has been attracting considerable interest recently [1–19] due to the larger spin–orbit splitting as compared with that in semiconductors, and the larger spin currents which can evolve in such systems due to the spin Hall effect [20, 21]. In the bulk the spin–orbit-induced spin polarization of the valence-band states is forbidden, because the requirements of time reversal and of central inversion symmetry of the wave functions should be met simultaneously [1–6]. At the surface, however, due to the breaking of the periodic potential and the corresponding distortion of the wave function symmetry the condition of spin degeneracy is lifted, thus making the spin polarization of the corresponding surface states by spin–orbit interaction possible. A prominent experimental demonstration of this effect has been presented for a surface state of Au(111) in [1].

The most successful model describing the spin–orbit splitting of surface states is that by Rashba [6], which was developed for a two-dimensional (2D) electron gas restricted in the direction perpendicular to the plane by a potential barrier with a certain potential gradient. The presence of this potential gradient leads to a splitting of the parabolic dispersions characteristic for a free electron into two parabolas with opposite spin directions, which are shifted along the parallel component of the electron momentum \( k_{\parallel} \). The value of the energy splitting for states with oppositely oriented spins increases with increasing \( k_{\parallel} \). This behavior has been confirmed for the surface state of Au(111) by angle-resolved photoelectron spectroscopy [1–5]. In particular, the direct measurement of the spin revealed the lifting of spin degeneracy [3] which is a key indication for a Rashba-type spin–orbit splitting. An analysis of the spin–orbit splitting
measured for the Au(111) surface state revealed that the spin–orbit splitting is determined rather by the nuclear potential gradient characteristic for atoms at the surface [1–5]. The surface potential gradient is smaller and, hence, governs the magnitude of the resultant spin–orbit splitting to a much lesser extent. Therefore the spin–orbit splitting of the same surface state on Ag(111) (atomic number \(Z_{\text{Ag}} = 47\) as compared to \(Z_{\text{Au}} = 79\)) is substantially smaller [2, 4]. Measurements from other pure metal surfaces [3, 10–13] and layered metallic systems [7–9] have supported this dependence. The atomic number is, however, not sufficient to describe the large difference between the spin–orbit splitting on Ag(111) and Au(111) and in the framework of a tight-binding model it has been shown that atomic number \(Z\) and the asymmetry of the wave function are both decisive for the spin–orbit splitting, which is valid for other systems as well [5, 7–9]. Similar effects of the spin–orbit splitting of electronic states were found for other quasi-2D metal systems, i.e. quantum-well states (QWS) [15–19], e.g. in Au and Ag films on W(110) [15, 16]. It was shown that the parabolic dispersions characteristic of s, p-type QWS are also split by the spin–orbit interaction with a splitting increasing in proportion to \(k_{\parallel}\) in accordance with the Rashba model. A pronounced spin splitting was observed up to ten monoatomic layers. Spin–orbit splittings of these s, p-type QWS reached \(\sim 0.2–0.3\) eV close to the Fermi level. These values are higher than for, e.g. QWS in Pb layers on the Si(111) surface [22] at the same \(k_{\parallel}\). Incidentally, the observed spin–orbit splitting in Au and Ag films for the QWS with the same quantum number \(n\) and for equal thicknesses of Au and Ag layers was found to be comparable in magnitude, irrespective of their atomic number. This appeared surprising in view of the noticeably different values of the spin–orbit splitting characteristic for the surface states of these metals [2, 4]. It was suggested that the spin–orbit splitting of QWS in Au and Ag on W(110) is induced by the substrate and is determined by the nuclear potential gradient of the substrate atoms (\(Z_{\text{W}} = 74\)) [15, 16].

Effects originating from a large substrate-induced spin–orbit splitting of quantum-well and interface states of the deposited metal were observed also with a substantially lighter metal, Al (\(Z_{\text{Al}} = 13\), deposited on W(110)) [17–19]. A more comprehensive analysis [18] revealed that in addition to spin–orbit split Al QWS there are interface states, the spin splitting of which is also determined by the W substrate. The two types of spin polarized states hybridize and, as a result, the overall spin structure of these systems is more complex in comparison with that expected from the 2D Rashba model.

To identify the part played by the substrate in the induced spin–orbit splitting, an earlier study compared similar noble-metal monolayers with different atomic numbers (Au, Ag) on comparable substrates with different atomic numbers [W(110), Mo(110), \(Z_{\text{Mo}} = 42\)] [14] inspired by a similar comparison of H/W(110) [23, 24] with H/Mo(110) [23]. Spin- and angle-resolved photoemission studies showed that the size of the spin–orbit splitting of the states formed in the W(110)-surface-projected energy gap is similar (\(\sim 0.4\) eV) for both deposited metals (Au, Ag), with even slightly higher value for Ag. Replacing, on the other hand, W(110) by Mo(110) brings about a substantial decrease of the spin splitting of these states [14]. A comparison with the value of spin–orbit splittings of the states formed in the Al monolayer on W(110) [17–19] reveals that the splitting has similar values for all the metals deposited (Au, Ag, Al). In other words, it appears that the value of the spin–orbit splitting of the formed states does not visibly depend on the atomic number of the deposited metal and is practically fully governed by that of the substrate.

The decisive role of the substrate as well as the Rashba-character of the spin–orbit splitting become especially evident for graphene, i.e. a material with \(Z_{\text{C}} = 6\), which shows, accordingly,
a very small intrinsic spin–orbit splitting (less than 1 meV [25]). It was revealed [26, 27] that intercalation of Au under graphene generates an induced spin–orbit splitting of the graphene \( \pi \) states of \( \sim 100 \) meV in the region where the dispersion relations near the \( \bar{K} \) point of the Brillouin zone are linear. It was found that this large spin–orbit splitting is driven by spin-dependent hybridization of the Au 5d and graphene \( \pi \) states.

The present study undertakes a more comprehensive investigation and analysis of the Au monolayer on W(110) in comparison with Cu, both experimentally and theoretically. Recently, the spin- and angle-resolved photoemission experiments of Au and Ag monolayers on W(110) [14] have been analyzed by density functional calculations [28]. In [28] the spin-dependent dispersions of the formed in-gap states and their spin–orbit splittings have been calculated resulting in good agreement with the experiment [14]. The authors connected the higher value of the experimentally observed spin–orbit splitting for the Ag monolayer in comparison with that for the Au monolayer on W(110) with a higher asymmetry of the wave functions formed at the surface (Ag and Au) atoms.

Our current work spans a wide range of spin–orbit interaction strength when comparing Au with Cu. We report a detailed investigation of the spin structure and corresponding dispersion relations of W 5d- and W 6p-derived states on W(110) in the \( \bar{\Gamma} \bar{S} \) direction of the surface Brillouin zone, including the surface-projected gap region, as well as of the variation of the electronic and spin structure due to the deposition of Au and Cu monolayers. We have analyzed separately the different contributions of d, p states of the deposited metals and the substrate caused by the hybridization between the electronic states of substrate and adsorbate. The contributions in electronic structure from atoms of the adsorbed metals and W atoms directly at the interface and those from deeper W layers down to the sixth layer underneath the surface were separated. The experimentally measured dispersion dependences and the corresponding changes in the spin structure were compared with theoretical calculations. As a result, it will be shown that in contrast to the conclusions in [28], the electronic states formed under deposition of Au, Ag and Cu monolayers on W(110) can be rather considered as modified W-derived surface resonances with significant contributions of the d, p wave functions from W and the adsorbate atoms which are distributed mainly in the two uppermost layers of the system (adsorbed layer and interface layer of W). The main factor responsible for their large spin–orbit splitting is the nuclear potential gradient of W probed by the corresponding hybrid wave function at the interface instead of the asymmetry of the adsorbate-derived wave functions distributed at the atomic sites of the monolayer (the topmost atomic layer), as was concluded in [28]. We argue instead that the spin–orbit interaction contributed from Au and W act in opposite directions. If the spin–orbit interaction is switched off separately in Au in the calculations, the spin–orbit splitting even increases which is opposite to the expected behavior for a heavy element. The dispersion relations become similar to those for the light noble metal Cu.

2. Experimental and theoretical details

The experiments were conducted at Helmholtz–Zentrum Berlin (BESSY II) at beamline U125/2-SGM with linearly p-polarized light using a ‘PHOIBOS’ energy analyzer and Mott spin detector operated at 26 keV. The angle of light incidence on the sample under normal emission was 45° relative to the surface normal. Part of the experiment was carried out at the Resource Center of St Petersburg State University ‘Physical methods of surface investigation’. The W(110) surface was cleaned by standard technique, which involved preliminary oxidation.
of the surface at 1200 °C with subsequent flashing to 2000 °C [15–20]. Monoatomic layers of Au and Cu were deposited by evaporation from pieces of Au and Cu melt-tipped on a thin W–Re wire. The Au and Cu monolayers were deposited on a W(110) substrate maintained at room temperature. The layer thickness was calibrated by the intensity maximum of the QWS corresponding to the formation of the first atomic layer [15, 29, 30]. Preliminary calibration of the evaporator flux was effected by the quartz microbalance method. The base pressure in the experimental chamber was maintained during the experiment below 1–2 × 10⁻¹⁰ mbar. The dispersion dependences for the clean W(110) surface and that with Au and Cu monolayers were measured by spin- and angle-resolved photoelectron spectroscopy in the Γ̂Ŝ direction of the surface Brillouin zone of W(110), at photon energies of 60–65 eV. To distinguish the surface states and resonances in the spectra the energies of specific features in the valence-band spectra of the W(110) surface were measured in normal-emission geometry (center of the surface Brillouin zone, Γ̂) as a function of photon energy from 40 to 110 eV.

Calculations of the electronic structure including spin–orbit interaction were performed for the W(110) surface separating the contributions of the W5d- and W6p-derived states from different W layers as well as the Au5d-, Au6p-, Cu3d- and Cu4p-derived states of the deposited metals in the context of the density functional theory [29–32] by the full potential augmented plane-wave method.

The crystalline structure of the systems was modeled by the supercells displayed in figure 1. Allowing for periodic boundary conditions, the calculations were performed for a set of infinite slabs consisting of (i) 14 monolayers of W (7 in equivalent positions)—for the clean W(110) surface, (ii) 12 monolayers of W (6 in equivalent positions) with one monolayer of Au (Cu) on each side. The gap between the slabs was ten empty monolayers, large enough to exclude interaction between the slabs. The calculations were conducted by using the ‘WIEN2k software’ [31], with due allowance made for local orbitals [32]. The number of k points in the Brillouin zone is 2000 (with 272 points in its irreducible part). The exchange potential was chosen in the GGA PBE form [33]. The calculation of electronic states of the inner levels (6 Ryd below the Fermi level) was in all cases fully relativistic. For valence-band electrons the calculations were performed both with (SO) and without (NSO) allowance for spin–orbit interaction, in the end separately in Au and W. The spin–orbit valence-band electron interaction was introduced as a secondary variational procedure with the use of a basis of scalar-relativistic eigenfunctions. In this case, the standard basis was extended to include p₁/₂ local orbitals [33].

The calculations involved structural relaxation of the system from the initial atomic positions derived from the bulk crystal structure to forces not in excess of 50 mRyd bohr⁻¹. Incidentally, one of the difficulties encountered in the theoretical analysis of the electronic structure of Au and Cu monolayers on W(110) was the evolvement of electron density oscillations close to the surface. Because charge oscillations die out fairly slowly (by the power law), total relaxation of the system requires using structures with a large number of inequivalent positions (not less than 10) or monolayers in a slab.

3. Experimental results

3.1. W(110) surface

Figure 2(a) displays dispersion dependences of valence-band electronic states and of the corresponding surface resonances for a clean W(110) surface, which were measured by
angle-resolved photoelectron spectroscopy (without spin resolution) at 62 eV along $\bar{\Gamma}\bar{S}$. For the sake of convenience, the dispersion relations are presented in the functional form $d^2N/dE^2$. The region of the surface-projected energy gap is marked by a yellow dotted line. This region is presented in figure 2(c) ($h\nu = 65$ eV) for more detailed elaboration. The dispersion dependences in figure 2(c) display more clearly the bending at the border of the surface-projected gap. The difference in figures 2(a)–(c) can be related to the influence of a small hydrogen adsorption from residual gases. No other differences in the measured dispersions were observed in these two cases. The spectra in figure 2(a) reveal clearly pronounced surface d-resonances (referenced as $\alpha$, $\beta$, $\gamma$) at the zone center at energies $\sim 0.8$ and $\sim 1.3$ eV, which strongly disperse with increasing $k_\parallel$. Figure 2(d) shows the corresponding angle-resolved normal emission photoelectron spectrum where just the surface d resonances at $\sim 1.3$ and $\sim 0.8$ eV are the strongest features. The spectra and the dispersions correlate well with the results presented in earlier publications, for instance, in [19, 35–37]. According to classical works [34, 36] the features noted above are interpreted as surface resonances weakly coupled to a bulk band and form in a pseudogap opened by the spin–orbit interaction. The spin–orbit pseudogap is located close to the Brillouin zone center between points $\Gamma_\gamma_+$ and $\Gamma_8+$, with binding energies $\sim 0.8$ and $\sim 1.3$ eV. Recently, studies [38–40] appeared where these states (in particular the resonance at 1.3 eV binding energy) were interpreted entirely as surface states. However, we follow here the classical assignment. In figure 2(a) these states are labeled as $\alpha$ and $\beta$ and disperse upwards with increasing $k_\parallel$. The corresponding spin-resolved spectra characteristic for these features.
Figure 2. (a) Experimental dispersion relations of electronic states measured by angle-resolved photoelectron spectroscopy in the $\bar{\Gamma}\bar{S}$ direction for a clean W(110) surface. Panel (c) shows in more detail the region of the surface-projected gap. The yellow dotted line specifies the contours of the surface-projected gap. (d) Angle-resolved photoelectron spectrum of a clean W(110) surface measured along the surface normal. The inset displays the variation of the energies of the W(110) valence-band spectral features for different photon energies. Different symbols correspond to different experiments. Panel (b) shows a series of spin-resolved photoelectron spectra measured at polar angles symmetric with respect to the surface normal for clean W(110).
measured at different value and sign of \(k\) relative to the surface normal are shown in figure 2(b). All these branches \((\alpha, \beta, \gamma)\) are antisymmetrically spin-polarized in the initial states, but in the process of photoemission the spin structure can be distorted [19]. It is pronouncedly visible at \(k = 0\) where the spin polarization in the initial state should be zero. As these surface resonances originate in the W5d\(_{3/2}\) and W5d\(_{5/2}\) orbitals, the spin–orbit splitting observed between \(\alpha\) and \(\beta\) correlates with the magnitude of the atomic spin–orbit splitting [23, 37, 42]. An analysis of similar states on the Mo(110) surface [41] showed that the width of the band gap opened by the spin–orbit interaction and the corresponding spin splitting are markedly smaller than for the W(110) surface, which again correlates with the difference between the atomic spin–orbit splittings for the 5d and 4d levels of W and Mo (0.45 and 0.12 eV, respectively) [23, 37, 42]. As seen from figure 2(c) the \(\alpha\) and \(\beta\) branches reach with increasing \(k\) the boundary of the surface-projected gap, to follow subsequently along its boundaries without entering the surface-projected gap region.

To identify the surface d-resonances on W(110), photoelectron valence-band spectra were measured under variation of the photon energy \((h\nu)\). The inset to figure 2(d) displays graphically the variation in energy of the main features in the photoemission spectra in normal emission (center of the surface Brillouin zone) for 40–150 eV. For comparison, the solid lines in figure 2(d) plot theoretical dispersions for bulk W along the \(\Gamma N\) direction along with the photon energy variation. On the one hand, the data shows that the photon energy range \(h\nu = 60–65\) eV used in the present study corresponds to the region close to the \(N\) point of the Brillouin zone. On the other hand, we can distinguish in the spectra both the bulk states (i.e. the dispersing branches in the binding energy regions 1.5–3.5 and 1.7–2.2 eV, as well as 6–9 eV) and the surface resonances at constant binding energies \(\sim 0.8\) and \(\sim 1.3\) eV belonging to the \(\alpha, \beta\) branches. It is also seen that the \(\gamma\) branch contributes at the \(\bar{\Gamma}\) point to the surface resonance [19].

At photon energies corresponding to the \(N\) point, a significant contribution comes from W6p-type states [42], whose branch starts above the Fermi level dispersing toward higher binding energies as \(k_{\parallel}\) increases and evolve along the boundary of the surface-projected gap. It was shown in [43] that the W6p-derived states play a significant role in the avoided crossing with QWS of metal films on W(110). Due to the hybridization with the W6p-derived states the \(\beta\) and \(\alpha\) branches do for clean W(110) not enter to the region of the surface-projected gap and evolve along the edge of the W6p-derived state zone and the boundary of the surface-projected energy gap with increase of \(k_{\parallel}\).

The effect of the hybridization between the branches of the W5d and W6p states was also noted in a recent experiment [38]. However, in [38] only branch \(\beta\) but not branch \(\alpha\) was analyzed and it was assumed that the branch near the Fermi level in the region \(k_{\parallel} \sim 0.4\)Å\(^{-1}\) is a continuation of branch \(\beta\). We see from figure 2(c) that this is not the case. In a recent calculations of the W(110) electronic structure in \(\bar{\Gamma}H\) and \(\bar{\Gamma}S\) directions, branch \(\alpha\) can be seen but has not been discussed [40]. The experimental dispersions for W(110) in figure 2(a) and also those published previously [14, 17–19, 37] including those for H/W(110) [37] and Al/W(110) [19] testify to the pronounced relation of the states near the Fermi level to the branch \(\alpha\). The branch \(\beta\) sweeps off at the border of the surface-projected gap (see figure 2(c)) and follows the lower edge of this gap. In this region the intensity of this branch is reduced significantly.

Figure 3 displays calculated dispersions of the W(110) surface and the corresponding contributions provided by different atomic layers from the surface into the bulk of the crystal. For the surface atomic layer, the contributions that derive from different orbitals (W5d and W6p)
Figure 3. Dispersions of electronic states calculated for a clean W(110) surface with allowance for spin–orbit interaction. Panel (a) shows the total contribution from the topmost atomic layer. Panels (b) and (c) identify the contributions to the topmost atomic layer of the W5d- and W6p-derived states, accordingly. The size of the circles reflects the contribution of the corresponding states. A large contribution corresponds to a large diameter of the circles. Plotted in panels (d)–(f) are the contributions to the total electronic structure of the second, third and seventh atomic layer, respectively, as one moves from the surface into the bulk.

are also presented. In total, the presented dispersions agree with those calculated in [28] but provide detailed orbital and layer decompositions. On the one hand, these relations reveal clearly the location of the surface-projected energy gap in the electronic structure of W(110). It is important to note that the electronic W5d-derived states corresponding to surface W atoms are located along the edges of the surface-projected gap in W(110) (see the black arrows in figures 3(a)–(c). As follows from the calculations, the formation of these features is supported
also by contributions coming from the W6p-derived states. The largest contribution of the W6p-derived states is observed along the edge of the surface-projected gap and near the Fermi level. A comparison of the calculated contributions to states located along the boundary of the surface-projected gap from W atoms residing at different depths suggests that it is the surface layer of W atoms that provides the largest contribution to these states. The contributions coming from deeper atoms weaken as one moves into the bulk of the W(110) single crystal. This means that these states are indeed W5d-derived surface resonances hybridized with W6p-derived states, and that their dispersion relations for the W(110) surface do indeed evolve along the surface-projected gap. Here we note that as opposed to the analysis of the hybridization in [38] the theoretical dispersions in figure 3 show that the branch of states near the Fermi level presented in [38] as a continuation of the branch β (S1 and S1′ in the work [38]) is rather a continuation of the branch α. Additionally, both branches α and β reach the branch of the W6p states where they are hybridized and the formed branches of the W d, p hybridized states run along the border of the surface-projected gap.

The location of the W-derived surface resonances along the border of the surface-projected gap is also shown in [28]. In relation to this point the results of our work agree with those in [28]. Significantly, we do not observe a noticeable spin–orbit splitting of the W-derived states in the present dispersions. (See discussion below.)

According to the calculations, the states on the W(110) surface split at points Γ7+ and Γ8+ [36] into bands, which in figure 3 are specified by different colors. The region of the spin–orbit pseudo-gap in which the main surface W5d resonance is located is enclosed in a black circle. The presence of surface resonances located along the edges of the surface-projected gap and associated with the α, β and γ branches was discussed also in [19]. It was pointed out that the β and γ branches are opposite-spin counterparts and form at the crossing Γ a Dirac-like cone of spin states [19, 38, 39]. The calculations in [40] support this idea. While the results reported in our study are, in the first approximation, not at odds with this suggestion, its detailed analysis falls outside the scope of our paper. Our study analyzes the local contributions of states of different symmetries produced by atoms of the substrate and of the deposited metal to the formed spin-polarized states, and probes the origin of the spin–orbit splitting. As follows from our analysis of calculated dispersion relations, for clean W(110) the branches of the W surface d-resonances denoted in figure 2(a) by α and β, extend in the region of the surface-projected energy gap along its edge as a result of hybridization with the W6p states. Significantly, it is the W5d- and W6p-derived states of the surface atomic layer that provide the maximum contribution to these states.

3.2. Au and Cu monolayers on W(110)

Figures 4(a) and (b) visualize the variations in the valence-band spectra measured by angle-resolved photoelectron spectroscopy along the surface normal under deposition of Au and Cu on the W(110) surface. We readily see that under the Au and Cu deposition the feature which is related to the W5d-derived surface resonance lying at about ∼1.3 eV falls off in intensity, with peaks of QWS corresponding to one Au and Cu monolayer appearing in the spectra. For Au, these are peaks at ∼3.1 and ∼3.7 eV (d-character QWS) and ∼4.9 eV (s, p-character QWS). A detailed analysis of the quantum-well spectra of s, p- and d-character formed in thin layers of Au and Ag on W(110) beginning from submonolayer coverages and up to 15 monolayers can be found in [29, 30]. In the current work we used the quantum-well spectra for
Figure 4. Series of angle-resolved photoelectron spectra measured along the surface normal which show appearance and growth of peaks of d- and s, p-derived quantum states in the course of formation of monolayers of Au (a) and Cu (b) on the W(110) surface.

precise determination of the completion of the formed monolayers of Au and Cu. For Cu, the corresponding peaks of QWS lie at energies 2.5 and 3.1 eV (d-character QWS) and ∼5.1 eV (s, p-character QWS). As deposition of Au and Cu on W(110) continues, the features in the photoelectron spectra corresponding to these QWS grow in intensity. After these features have reached their maxima, deposition of Au and Cu on W(110) is interrupted before the quantum states signaling the onset of growth of the second monolayer [29, 30] emerge in the spectra. The coatings formed in this way have one monolayer thickness.

After the Au and Cu monolayers have been formed, the W-derived features located at about 0.8 and 1.3 eV (identifying the α and β/γ states for a clean W(110) surface) remain in the spectra, with weaker intensity and partially modified in shape. Incidentally, deposition of Au and Cu monolayers affects noticeably the dispersion relations of these states.

Figures 5(a) and 6(a) display experimental dispersion relations of the electronic states that evolved after deposition of Au and Cu monolayers on W(110). As seen from the dispersions, the spectra reveal now, besides the features originating from the corresponding QWS, other peaks as well, which derive from the α, β, γ states described above. After deposition of the Au and Cu monolayers, however, these states, rather than extending along the edge of the surface-projected energy gap, form at the gap center two distinct split branches of electronic states instead. Interestingly, the value of the splitting between the branches of these states in the region with smaller $k_\parallel$ is similar for the Au and Cu monolayers, and even somewhat higher for the system Cu/W(110), despite the notable difference between the atomic numbers of these metals.
Figure 5. Experimental dispersion relations of electronic states for the monolayer of Au on W(110) derived from angle-resolved photoelectron spectra measured along $\bar{\Gamma}S$ of the Brillouin zone by scanning under different polar angles to the surface normal (a) and series of corresponding spin-resolved photoelectron spectra measured at different polar angles symmetric with respect to the surface normal (b).

As the states approach the Fermi level (i.e. as $k_\parallel$ increases), the value of the splitting for the Au monolayer on W(110) decreases, these branches practically merge, whereas for the Cu monolayer the value of the splitting remains virtually unchanged up to the Fermi level. Analogous observations were noted in theoretical [28] and experimental [14] works where similar differences in the dispersion dependences for monolayers of Au and Ag on W(110) were analyzed.

Figure 7 analyzes the contributions to the overall electronic structure of the Au monolayer on W(110) provided by states with different (d and p) orbital character of the W atomic layer at the interface (top row) and the Au monolayer (bottom row). As follows from the calculations, the split states inside the surface-projected gap of Au/W(110) originate from the states which for a clean W(110) surface are located along the edge of the surface-projected gap. Deposition of the Au monolayer is followed by hybridization of the W d,p substrate states with the Au d,p states which leads to a displacement from the edges toward the center of the surface-projected gap (see the black arrows in figure 7). A comparison of the contributions coming from states of different atoms reveals that the evolving bands receive contributions from the Au5d- and Au6p-derived states; this all comes to the statement that the formation of these states evolves from hybridization of the W-derived d,p states with those of the deposited metal. One can consider these states as W-derived d-resonances modified by interaction with the states of the adsorbed metals. Therefore, the value of the spin–orbit splitting of the states (as we will show below) is determined mainly by the atomic number of the substrate. For the Au monolayer
Figure 6. Experimental dispersion relations of electronic states for the monolayer of Cu on W(110) derived from angle-resolved photoelectron spectra measured along $\bar{\Gamma}\bar{S}$ of the Brillouin zone by scanning under different polar angles to the surface normal (a) and series of corresponding spin-resolved photoelectron spectra measured at polar angles symmetric with respect to the surface normal (b).

On Mo(110) the value of the observed splitting is significantly lower (see [14]). Because the hybridized states thus formed are initially derived from the atomic W5d$^{3/2}$ and W5d$^{5/2}$ levels, their resulting spin splitting should be likewise assigned to the high atomic spin–orbit splitting characteristic of the atomic states. The calculations show that dominant contribution in the formed resonances noted above is made by atoms from the topmost atomic layer of the substrate. The contributions of deeper W atoms decrease significantly.

On the whole, the comparison evidences a fairly good correlation between the experiment and theoretical calculations; indeed, the theoretical calculations presented match satisfactorily enough the experimentally observed dispersion relations. The presented calculated dispersions correlate well with those published in [28] for the Au monolayer on W(110). In our work we present in addition the calculations of the local contributions for d and p states for different atomic layers of W and the adsorbed metals. The results of the calculations show well the decrease of the splitting between the formed hybridized states for the Au/W(110) system when approaching the Fermi level with increasing $k_\parallel$.

Interestingly, the calculations predict the appearance of features in the spectra of spin-polarized states in the occupied band near the Fermi level in the region $k_\parallel \sim 0.2$–0.4 Å$^{-1}$ (i.e. the region near $\bar{\Gamma}$ in figure 7). In full agreement with the calculations, these states are predominantly...
Figure 7. Dispersion relations of electronic states calculated with allowance for spin–orbit interaction for a Au monolayer on the W(110) surface. The dispersion relations were calculated for the $\bar{\Gamma}\bar{S}$ direction of the Brillouin zone. Panels (a)–(c) display the total contribution to the electronic structure coming directly from the top atomic layer of W at the interface (a) and selectively the contributions of W5d-derived (b) and W6p-derived (c) states. Panels (d)–(f) specify the total contribution to the electronic structure from Au atoms (d) and specifically the contributions due to Au5d-derived (e) and Au6p-derived (f) states. The size of the circles reflects the contributions of the corresponding states.

Au 6p-type. The experimental dispersion relations (see figure 5(a)) likewise demonstrate the presence of this feature in the vicinity of the Fermi level. As will be shown later on, this feature is indeed spin polarized.

Displayed in figure 8 are the results of similar calculations including spin–orbit interaction for the Cu monolayer on W(110). A similar decomposition has been made as in figure 7.
Figure 8. Dispersion relations of electronic states calculated with allowance for spin–orbit interaction for a Cu monolayer on top of the W(110) surface, the contributions to the total electronic structure and specifically from the W5d- and W6p-derived states for the W atomic layer at the interface with the Cu ((a)–(c)), and of the contributions of the Cu 3d- and Cu 4p-derived states ((d)–(f)). The contributions of states of different types are proportional to the size of the circles in the graph.

The calculations show also in this system that the dominant contribution of the states in the gap is from the upper (interface) atomic layer of the W(110).

An analysis of the dispersion relations presented suggests that in the Cu/W(110) system the split bands in the region of the surface-projected gap form through hybridization of W5d- and W6p-derived states of surface W atoms with Cu states. The largest contribution comes from the modified W5d surface resonances which, when hybridized with the Cu states, split off the edges of the surface-projected gap. Here, however, the contribution of the Cu 3d and Cu 4p...
states to the formed bands is also large, which evidences a considerable hybridization between the electronic states of the W substrate and the deposited Cu. This interpretation is supported by the good agreement of the calculated and measured dispersions.

As already mentioned, a comparison of the dispersion relations of the hybridized states of Au and Cu monolayers on W(110) indicates certain differences between the two systems, particularly when the Fermi level is crossed (figures 5(a), 6(a), 7, 8). For Cu/W(110) the splitting of the bands at the Fermi level is much larger than for Au/W(110). This observation is analogous to that published in [28] for Au and Ag monolayers. We will discuss the reasons for this experimental observation further below.

Additionally, considering the region \( k_\parallel \sim 0.2\)–0.4 \( \text{Å}^{-1} \) (i.e. the region near \( \Gamma' \) in figure 8) for energies above the Fermi level we can also see a significant contribution of the p-type states to the hybridized bands which is even larger for Cu/W(110) than for Au/W(110). Incidentally, occupied states in this region at the Fermi level do not form for Cu/W(110) because the corresponding states lie higher in energy than those for the Au monolayer. Therefore, they are not visible in the photoemission spectra.

3.3. Spin polarization of the new electronic states

Figures 2(b), 5(b) and 6(b) display series of angle- and spin-resolved photoelectron spectra for the clean W(110) surface and for Au and Cu monolayers deposited on the W(110) surface, respectively, measured in the \( \Gamma\tilde{S} \) direction. The spectra were measured for positive and negative polar angles relative to the surface normal (i.e. for positive and negative \( k_\parallel \)). As seen from the spectra obtained for the clean W(110) surface, the clearly pronounced branches of the \( \alpha, \beta, \gamma \) surface resonances (located at energies \( \sim 0.8 \) and \( \sim 1.3 \text{eV} \) near the \( \Gamma' \) point) have oppositely oriented spin and turn out to be strongly spin polarized for positive and negative polar angles. States with oppositely oriented spins are specified by differently directed red and blue triangles, and the main spectral features are identified by the corresponding arrows. A characteristic feature of the spin-resolved photoelectron spectra displayed in figure 2(b) for W(110) is the pronounced, nearly complete, antisymmetric spin polarization of the branches of electronic states, which is opposite to that of the neighboring branches of states (\( \alpha \) and \( \beta, \beta' \) and \( \gamma' \)). In other words, the measured spin polarization obeys time-reversal symmetry. For better visualization of the spin structure, different spin states are specified by corresponding red and blue lines. The branches \( \beta \) and \( \gamma' \) form a spin structure similar to that characteristic of the Dirac cone states in topological insulators. The formation of such spin structure for the W(110) surface was noted in [19, 38–40].

As we can see, none of the branches \( \alpha, \beta \) and \( \gamma' \) splits like in the simple 2D Rashba model. One observes, instead, a pronounced antisymmetric spin polarization of the states and the formation of such spin structure is well described by the model of surface resonances for semi-infinite crystals developed in [13, 19, 44] on the basis of the Rashba effect. This model was successfully applied for the analysis of the spin structure of the surface resonances at Bi(111) [13] and for the W d resonances for W(110) and Al/W(110) [19]. The spin structure observed in our work for the W(110) surface is also well described by the model of the surface resonances.

Turning to the spin-resolved photoelectron spectra observed for the d-type QWS in the Au monolayer on W(110), see figure 5(b), we can also distinguish the experimentally observed antisymmetric spin polarization of Au 5d-derived states at least for states with binding energies
of 3–4 eV. For positive and negative polar angles from the surface normal, the spin polarization, where observable, inverts its sign. This means that the spin structure of these states is also described in the framework of the model of surface resonances [44].

Here we have to note that, as shown in [19], the initial antisymmetric spin polarization of the W–Au surface resonances noted above can be affected by photoemission final state effects [45, 46]. Such effect is observed in figure 2(d) for W(110) where the sign of the spin polarization is not fully inverted and at $k_\parallel = 0$ the spin polarization is nonzero.

An antisymmetric spin polarization for positive and negative polar angles with respect to the surface normal is observed explicitly also for the bands in the surface-projected gap with Au and Cu monolayers on the W(110) surface, whose energies are $\sim 0.8$ and $\sim 1.3$ eV at $k_\parallel = 0$. Spin-resolved spectra (figures 5(b) and 6(b)) reveal a practically complete spin polarization of the above mentioned states. As it was shown above, these states are W-derived related to the branches $\alpha$ and $\beta$, and form in the surface-projected gap due to hybridization between the W d,p states and the d- and p-derived states of the deposited metals (see the split branches of electronic states in the theoretically calculated dispersion relations in figures 7 and 8).

As it was noted before, analogous comparative theoretical calculations for monolayers of Au and Ag on W(110) were carried out recently [28]. The resulting dispersion dependences calculated in that work for Au/W(110) correlate well with those calculated in this work. Hortamani and Wiesendanger [28] noted the difference in the measured spin–orbit splitting which is higher for the Ag monolayer than for the Au monolayer on W(110). They explained the observed differences in the spin splitting as related to different extension of the wave functions at the surface (Au and Ag) atoms into vacuum and their asymmetry which is formed due to hybridization with the substrate. The asymmetry in the region of the top layers of the systems (Au and Ag layers) into vacuum was assumed as the main factor responsible for the observed spin–orbit splitting [28]. Moreover, it was not discussed whether that effect would outweigh the difference in atomic number and the resulting nuclear potential gradient between Ag and Au.

In our work we compare monolayers of Au and Cu on W(110), i.e. systems with even larger difference in atomic number. Also in the present case the spin–orbit splitting of the formed hybrid states tends to increase with decreasing atomic number of the deposited metal. However, we explain the observed changes of the spin structure as caused by a modification of the W-derived surface resonances under interaction with the adsorbed monolayers of Au and Cu with the wave functions and corresponding asymmetry distributed among the two upper layers of the systems. These states originate from the W d resonances; therefore, the contribution of W (i.e. the asymmetry of the hybrid wave functions in the region of the nucleus of the W atomic layer at the interface) plays the dominant role for the value of the formed spin–orbit splitting. This agrees with the situation found for Al/W(110) in [19] (figure 4(h)), where the calculations show that the expansion of the hybrid wave functions formed in the monolayer system of Al on W(110) which contribute to the spin structure formation is of about two monolayer (Al monolayer plus upper W atomic layer).

We noted above the difference in interpretation between the recent publication [28] and ours and the advantage of a larger difference in atomic numbers (Au and Cu) to resolve this issue. To separate the contributions in the spin–orbit splitting induced by substrate and adsorbed metal we have carried out the calculations ‘disregarding’ the spin–orbit interaction alternatively in W and Au. The results are presented in figure 9. Figures 9(a) and (e) display, for comparison, the total electronic structure (the dispersion relations) calculated for the Au
Figure 9. The calculated contributions in the total electronic structure related to Au atoms in the Au monolayer and W atoms in the top layer of W located directly under the Au monolayer with and without allowance for spin–orbit interaction alternatively in W and Au. Panels (a) and (e) display corresponding contributions with spin–orbit interaction both in W and Au, panels (b) and (f) show the contributions without spin–orbit interaction both in W and Au. Panels (c) and (g) represent the results of calculations disregarding spin–orbit interaction in Au with inclusion of the spin–orbit coupling in W. Insets (d) and (h) show the results of calculations for the spin–orbit interaction ‘switched off’ in W and ‘switched on’ in Au.

monolayer on W(110) taking into account the spin–orbit interaction both in W and Au (the same as in figure 7). Figures 9(b) and (f) show results for the same system but without spin–orbit interaction. In figures 9(c), (d) and 9(g), (h) the corresponding calculations are presented where the spin–orbit interaction is alternatively switched off in Au and W, respectively. A comparison with the calculations plotted in figures 9(b), (f) and 9(a), (e) shows immediately that the branches of electronic states in the region of the surface-projected gap (α and β) merge into one branch after turning off the spin–orbit interaction. This supports our earlier conclusion that the splitting of these branches is indeed triggered by the spin–orbit interaction. Interestingly, these branches do not change position in the region of the surface-projected gap, which implies that it is hybridization of W p, d-derived states with the p, d states of the deposited metals (Au, Cu) that accounts for the splitting (shift) of these branches from the edge of the surface-projected gap.
For the following we note that blue and red colors in figure 9 identify the contributions of the d_{3/2} and d_{5/2} states, correspondingly, which are characterized by different spin orientation. This identification was carried out on the basis of calculations of density of states with partial d_{3/2} and d_{5/2} contributions: spin-up for d_{3/2} states (blue) and spin-down for d_{5/2} states (red).

We can see in figure 9 that under ‘switching-off’ the spin–orbit coupling in Au the value of the spin–orbit splitting for Au on W(110) even increases and the dispersions become similar to those observed for Cu on W(110), i.e. the large spin–orbit splitting is mainly contributed from W. On the other hand, the opposite ‘switching-off’ of spin–orbit interaction in W is not followed by a total disappearance of the spin–orbit splitting. Instead, the spin orientation for this system is reversed relative to the previous case. It means that the spin–orbit interaction contributions derived from W and Au act in opposite directions and are subtracted when both contributions are ‘switched on’. Therefore, the low spin–orbit interaction in Cu (and in Ag as well) leads to a higher value of spin–orbit splitting in the Cu/W(110) (and in the Ag/W(110)) system in comparison with that in the Au/W(110) system.

We can conclude that for a correct description of the behavior of the spin–orbit splitting an analysis of only the asymmetry of the wave functions between surface atoms and vacuum is not sufficient. For the systems with monolayers of Au and Cu (Ag) the resulting spin structure is determined by two upper W–noble-metal layers and corresponding hybrid states formed in this expanded region. For a correct analysis of the formed spin–orbit interaction it is necessary to take into account the asymmetry of the formed wave functions in the vicinity of the W atoms and an influence of the corresponding nuclear potential gradient in W. The spin–orbit interactions in W and Au act in opposite directions, i.e. they are characterized by Rashba coefficients of opposite sign.

Rashba coefficients of opposite signs have been studied in [47] for the Bi/Cu(111) system. It was shown that for a positive Rashba coefficient the wave functions expand into vacuum. For a negative Rashba coefficient the corresponding wave functions should be expanded toward the crystal. In our case for the Au/W(110) system the formed hybrid W–Au wave functions are expanded or located both in the region between the W and Au atoms (in the vicinity of W atoms) where the contribution to the Rashba coefficient should be negative and in vacuum in the vicinity of the Au atoms where the contribution to the Rashba coefficient is positive.

In the end we would like to note that besides the above mentioned states, the experimental spin-resolved photoelectron spectra of the Au monolayer on W(110) (figure 5(b)) reveal also clearly the spin polarization of the sharp peaks of states lying close to the Fermi level at \( k_1 \sim 0.2–0.4 \, \text{Å}^{-1} \), i.e. at polar angles \(+3.5^\circ\) and \(-3.5^\circ\) relative to the surface normal. In figure 5(b) these states are enclosed in dotted circles. As already mentioned, the calculations suggest that these states have a noticeable contribution of Au p-derived states (see figure 7). Incidentally, similar to the \( \alpha \) and \( \beta \) branches, these states are also characterized, while not so clearly pronounced, by antisymmetric spin polarization. Because these states are located close to the Fermi level and are antisymmetrically spin polarized, they may play an important role in the formation of the spin transport characteristics of these systems and enable dissipation-free spin transport.

4. Conclusion

Experimental and theoretical studies of the electronic and spin structure have been carried out for monolayers of Au and Cu on the W(110) surface, and directly of a clean W(110) surface in

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the \( \bar{\Gamma} \bar{S} \) direction of the surface Brillouin zone. The results of these studies can be summed up as follows:

1. Deposition of Au and Cu monolayers on W(110) gives rise to formation of spin–orbit split bands in the region of the W(110) surface-projected gap. The value of the spin splitting is mainly determined by the W substrate and only weakly depends on the atomic number of the deposited metal. For Cu/W(110) the splitting is even larger than that observed for the Au/W(110) system. As the bands move toward the Fermi level with increasing parallel component of the electron momentum, the spin–orbit splitting falls off practically to zero for Au/W(110). In contrast, for the Cu/W(110) system the spin–orbit splitting shows almost no variation.

2. These branches are W-derived surface resonances modified due to hybridization of the W d,p states with d,p states of the deposited metal. For the clean W(110) surface the branches of these resonances are located along the edge of the surface-projected gap. Interaction with the d- and p-derived states of the deposited metal splits them off the band edge into the center of the surface-projected gap. The density functional theory calculations performed in this work correlate well with experiment and demonstrate the different dependence of the spin splitting on the spin–orbit interaction in the substrate and the adsorbed metal showing that the main contribution stems from the surface layer of W(110). The wave functions of the formed hybrid states are distributed mainly in two upper layers of the system (adsorbed layer plus surface atomic layer of W). The main factors responsible for the resulting spin–orbit coupling are the nuclear potential gradient in W and an asymmetry of the formed wave functions across the two surface layers.

3. The measured spin structure of the formed states is characterized by a pronounced antisymmetric spin polarization of each band relative to \( k_\parallel = 0 \). The spin–orbit split bands are also polarized oppositely to one another. ‘Turning-off’ the spin–orbit interaction in the calculations brings about a merging of the two split branches. Disregarding the spin–orbit interaction alternatively only in W or Au allows to conclude that spin–orbit interactions in Au and W act in opposite directions and as a result the spin–orbit splitting decreases. Under ‘switching-off’ of the spin–orbit interaction in Au the resulting value of the spin–orbit splitting even increases. The dispersion dependences become similar to those for Cu/W(110) where the Cu overlayer serves as control sample with low spin–orbit interaction. This confirms that the low spin–orbit interaction in Cu leads to the higher value of the spin–orbit splitting in the Cu monolayer on W(110) as compared with that for the Au monolayer on W(110).

4. Besides the spin-split W-noble-metal resonances with d, p character located in the middle of the surface-projected gap one can also distinguish in the electronic structure hybridized states with a predominant contribution of Au p-states which are located in the region of the Fermi level. They are also characterized by a reversal of the spin polarization with \( k_\parallel \), which may be employed for efficient transport of spin currents.

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