Electronic structure of thin ytterbium layers on W(110)

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Abstract. In the present contribution we report on the results of the angle-resolved photoemission (PE) studies of thin layers of Yb (1-3 ML-thick) on W(110) surface. The clear splitting of the Yb 4f7/2 state was observed in the PE spectra measured around Γ point for 1 ML-thick Yb film. The measured PE spectra were analyzed by means of the simplified periodic Anderson model.

Among the lanthanides, Yb and Ce are of fundamental interest, because of strong interaction between 4f and valence-band (VB) states leading to mixed-valence and Kondo phenomena in a number of compounds [1,2]. This analogy between Yb and Ce systems has been explained on the basis of the electron-hole symmetry of the quasiatom 4f shell. While the correspondence has been established for a number of compounds, no evidence for such symmetry has been reported up to now for the pure metals. Motivated by the recent work [3], in the present contribution we report on the results of the photoemission (PE) studies of thin layers of Yb (1-3 ML-thick) on W(110) surface.

PE experiments were performed at U49/2-PGM-1 beamline at BESSY (Berlin). PE spectra were acquired with a hemispherical electron-energy analyzer. The overall-system energy resolution accounting for the thermal broadening was set to 150 meV (FWHM) and an angular resolution better than 1° was used. A structurally ordered layers of Yb metal was grown on a W(110) substrate kept at room temperature. Prior to the deposition of Yb, the W(110) substrate was carefully cleaned by repeated cycles of heating up to 1300°C in oxygen ambient pressure of 5×10^-6 mbar for 15 min each and subsequent flashing up to 2300°C. The samples prepared in this way exhibit a high crystalline quality as monitored by low-energy electron diffraction (LEED). The thickness of the deposited Yb was monitored with a calibrated quartz oscillator. All PE spectra were taken at hν = 110 eV in order to increase the photoelectron emission from Yb 4f states considerably and suppress that from 5d states of tungsten that are close to a Cooper minimum of the photoionization cross section at this photon energy. The base pressure in the experimental chamber was below than 5×10^-11 mbar rising to 1×10^-10 mbar during metal evaporation as monitored by the absence of any oxygen trace in the spectra.

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Series of photoelectron spectra (taken at 5° off-normal emission in order to eliminate effects around the Γ point which are discussed later) of thin Yb layers on top of W(110) surface is shown in Fig. 1. The initial spectrum of pure W(110) surface shows valence band emission from 5\textit{d} states between Fermi level (\(E_F\)) and 2.5 eV of binding energy (BE) as well as from 6\textit{s} states at about 7 eV. Deposition of the Yb metal on top of W(110) surface leads to the development of Yb 4\textit{f} emission in the spectra: divalent component in the region between Fermi level and 3.5 eV of binding energy and trivalent component in the range of 4-12 eV of BE. We would like to note that trivalent Yb 4\textit{f} component is visible in the spectra only for thicknesses of Yb less than one ML due to possible emission of electrons from Yb atoms which are located at the steps of W(110) crystal or at the edges of Yb islands, where there are more tungsten atoms in the surrounding. In this case due to a large number of neighboring W atoms and their large electronegativity, tungsten atoms attract more electron density from ytterbium atoms compared to the inner part of Yb islands on flat W surface.

By following the change of the data with deposition time an unambiguous assignment of the different peaks in the spectra can be done. The spectral features of the tungsten substrate are quickly disappear and practically not visible already at the thickness of Yb layer of approximately 0.75 ML. At the thickness of Yb layer of exactly 1 ML, BE of the 4\textit{f} spin-orbit doublet is 0.91 and 2.18 eV for 4\textit{f}_{7/2} and 4\textit{f}_{5/2} components, respectively. Continuous deposition of Yb leads to further modification of the spectra and respective 4\textit{f} emission lines have BEs which are listed in Table 1 for 1, 2, and 3 ML thick Yb thin films on W(110) surface. The corresponding energy diagram (thick vertical lines) is shown as an inset of Fig. 1 together with scheme shown the positions of Yb atom in the layer.

In order to interpret the measured BE of Yb 4\textit{f} states for different positions of Yb atoms we have performed the calculations of the electronic structure of the Yb/W(110) system. The atomic structure was simulated by slabs consisting of three atomic layers of tungsten covered by one, two or three Yb layers. The atomic structure of Yb layers were chosen hexagonal, in agreement with LEED data and corresponding to the bulk Yb(111) plane. Note that, due to a lattice mismatch between incommensurate Yb(111) and W(110) surfaces it is impossible to create a suitable for calculations...
periodic structure of the slab without further simplifying assumptions. Here we have changed the rectangular structure of the W(110) layers to the hexagonal one matching them with the Yb(111) overlayer. In spite of choosing the interlayer distances that give correct W-W spacing between adjacent layers, the tungsten atomic structure in the layer retains to be stretched with increased W-W spacing.

**Table 1.** Experimental binding energies in eV of Yb 4f emission lines for Yb films on W(110) surface.

| Yb layer | 1 ML | 2 ML | 3 ML |
|----------|------|------|------|
| 4f/2     |      |      |      |
| surface  | A: 0.91 | A: 2.18 | B: 1.66 | B: 2.89 | D: 1.73 | D: 2.89 |
| bulk     | – | – | – | – | E: 1.19 | E: 2.45 |
| interface | – | – | C: 0.54 | C: 1.86 | – | – |

The calculations were performed by linear-muffin-tin-orbital (LMTO) method [4]. The fully occupied Yb 4f states were treated as localized core levels, and their BEs were estimated by means of the Slater's transition state concept [5] that is shown to be a good approximation for description of electron transitions within local-density approximation (LDA) approach. The theoretically calculated positions of 4f/2 emission lines are also shown in the inset of Fig. 1 by thin lines. For better comparison with the experiment all presented data are shifted from originally calculated values by 0.6 eV to lower BE. This adjustment is necessary because of shortcomings of the theoretical model: (i) In the calculations the excited electron was removed from each equivalent site of the respective Yb monolayer instead from only one site. In this case the screening charge of the final-state hole is strongly reduced; (ii) Due to increased in-layer W-W spacing the potential produced by the tungsten valence-electron density at the Yb overlayer atoms is weaker. Both these effects lead to an overestimation of the BE of Yb localized states in the calculations. Nevertheless, the calculated values give a correct qualitative insight and support experimentally observed tendency of changes of Yb 4f line positions in the spectra from layer to layer.

In order to study the electronic structure of the Yb monolayer on the W(110) substrate the angle-resolved PE measurements were performed. Fig. 2 (left panel) shows a series of PE spectra of this system measured along the $\Gamma - \Sigma$ direction of the surface Brillouin zone (SBZ) of W(110) (see inset). Clear splitting of the Yb 4f/2 state is visible in the PE spectra measured around the $\Gamma$ point. Additional spectral features which are visible in the spectra at approximately 1.3 eV BE and in the vicinity of the Fermi level can be ascribed to the emission from the tungsten VB (see plot in the inset of Fig. 2, right panel). It should be noted, that the energy bands measured by means of the angle-resolved PE for a pure W(110) surface agree well with the calculated energy bands for the $\Gamma - \Sigma$ direction (also shown in the inset of Fig. 2, right panel).

The measured PE spectra were analyzed by means of the simplified periodic Anderson model (PAM) that has been recently successfully applied for interpretation of angle-resolved PE data of 1 ML Ce/W(110) and YbIr$_2$Si$_2$ [3,6]. However, in the case of Yb/W(110) system a determination of the valence states that could be hybridized with Yb 4f electrons is not straightforward. For Ce/W(110) system [3] the strong hybridization effects observed in PE spectra were caused by interaction of 4f states with Ce 5d electrons in the monolayer. This scenario, however, can not be realized for monolayer of divalent Yb atoms due to negligible contribution of the electron states with d symmetry in Yb-derived valence bands. A contribution of the W 5d electron states to the 4f-VB hybridization matrix elements can not be reliably estimated from the band-structure calculations due to incommensurate Yb and W surfaces. In this case, taking into account that escaping electrons are
analyzed for the emission direction close to the surface normal ($\bar{S}$ point is reached at the polar angle $\approx 13^\circ$), we may expect that the PE intensities $I(E,\mathbf{k})$ measured for a pure W(110) surface are determined mainly by W 5$d$ orbitals directed out-of-surface. Then, it could be assumed that namely these orbitals are responsible for $4f$-VB hybridization, and the respective PE intensities could be chosen as a measure for the VB contribution to the hybridization matrix element: 

$$V_k(E) = \Delta \sqrt{I(E,\mathbf{k})}. $$

For calculations, we have taken the hybridization parameter $\Delta = 0.22$ eV, the value used for other Yb compounds [6], whereas all $\sqrt{I(E,\mathbf{k})}$ values were scaled under the condition that the splitting of the Yb 4$f_{7/2}$ component around the $\Gamma$ point is reproduced in the PAM approach. The corresponding scaling factor can be considered as an adjustable parameter of the model (only one for the whole set of PE spectra). Other, fixed parameters were $\varepsilon_{5/2} = 2.18$ eV and $\varepsilon_{7/2} = 0.91$ eV, these values are equal to the energy positions of the Yb 4$f$ PE peaks for emission angles where we may expect hybridization to be negligible (see Table 1).

The calculated results are presented in Fig. 2 (right panel). It can be seen that the form of measured spectra as well as the changes in the PE spectra with increasing polar angle are well described by the calculations. Because the calculated results show only Yb 4$f$ PE intensities, we can conclude that the hybridization effects lead not only to the splitting of the Yb 4$f_{7/2}$ component around the $\Gamma$ point, but also to the intensity variations between both spin-orbit split peaks and near the Fermi energy up to the polar angle of $5^\circ$. These effects are caused by W 5$d$ bands, one of them goes to the Fermi level and two others go to higher BE if the polar angle increases. In the experimental spectra these effects are enhanced due to direct VB emission from the W 5$d$ bands. The W 5$d$ bands cross also the position of the Yb 4$f_{5/2}$ component, and in the calculated spectra a small dispersion of this component can be seen at about $6^\circ$. The corresponding effect is not observed in the experimental spectra.

In summary, the electronic structure of thin Yb layers on the W(110) surface was studied by PE spectroscopy. The angle-resolved PE data demonstrates the clear splitting of the Yb 4$f_{7/2}$ component around the $\bar{S}$ point. This effect is successfully explained in the framework of the PAM model as due to hybridization between the 4$f$ and valence band states.
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