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Spin-Polarized Photoelectrons with Circularly and Linearly Polarized Radiation from an Au Monolayer on Pt(111).

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Abstract. – Spin-, angle- and energy-resolved photoemission with circularly and linearly polarized synchrotron radiation from BESSY has been used to characterize the electronic structure of an Au monolayer on Pt(111). All studies were done with normal radiation incidence and normal electron emission. With σ-radiation the symmetry of the different types of surface and interface states in the Au monolayer on Pt(111) system has been determined. Using π-radiation spin polarized electrons are only found for photoemission from states with symmetry Λ_{45}^{3}. One of the states involved in the transition (either initial or final state) was always localized at the surface. In addition to earlier findings of Schmiedeskamp *et al.* and Stoppmanns *et al.* spin-polarized electrons are now also obtained for the photoemission from a state which is located only in the Au layer. The spin polarization depends strongly on the energy of the incident radiation.

Spin-polarized photoelectrons from an Au monolayer on Pt(111) can be obtained even for the highly symmetrical experimental set-up of normal light incidence and normal electron emission with both circularly and linearly polarized radiation.

Using circularly polarized radiation one obtains spin-polarized electrons usually due to optical orientation which requires spin-orbit interaction.

The spin polarization vector $\boldsymbol{P}$ is parallel or antiparallel to the direction of light propagation z and of course does not change if the crystal is rotated about its surface normal. The occurrence of spin-polarized electrons in the photoemission with circularly polarized radiation is a very general phenomenon. It has been observed for a large number of surfaces and adsorbate systems [1] and can be used for a symmetry characterization of the electronic states. It is theoretically obtained within the one- and the three-step model of photoemission [2,3] and an identical mechanism exists in the photoionization of free atoms and molecules [4].

If the incident radiation is linearly polarized, spin-polarized electrons can be expected much less generally but they can exist for surfaces of threefold rotation symmetry, if the photoemission is described in the *one-step model* and if spin-orbit interaction is again present. In this case the spin polarization vector $\boldsymbol{P}$ stands perpendicular to the electron emission direction and rotates by 3Φ, if the crystal is rotated by Φ about the surface normal. This has been predicted in [5] and experimentally high spin polarization values have indeed been found for Pt(111) [6] and for Au/Pt(111) [7]. The size and sign of the spin polarization

depend significantly on the geometric surface structure [7]. It is therefore of interest to establish how the spin polarization depends on other parameters. The dependence on photon energy, the symmetry of the states involved in the transitions and its surface location are addressed in this work. The photon energy can be varied, since synchrotron radiation is used in contrast to a gas discharge tube in the earlier measurements [7]. The symmetry properties of the states are determined using spin-polarized photoemission with circularly polarized light and information about the surface location of the states is gained by comparison of the experimental data with a calculation of Tamura and Feder [7].

The experiments were done with circularly polarized (σ-) off-plane and linearly polarized (π-) in-plane radiation from the 6.5 m normal incidence VUV monochromator [8] at BESSY. The apparatus has been described earlier [9] and an Au evaporator was additionally installed. All spin-resolved photoemission results given in this work were obtained for the highly symmetrical experimental set-up of normal light incidence and normal electron emission. Kinetic energy and emission angle are selected by an electron spectrometer [10]. The value of overall energetic resolution (electron plus photons) was smaller than 200 meV at an angular resolution of $\pm 5°$.

The Pt(111) surface normal coincided within 0.5° with the [111]-direction and within 0.3° with the direction of the incident radiation. A clean Pt(111) surface was prepared by cycles of Ar^+ and Ne^+ bombardment, heating in oxygen and flashing. It was controlled by Auger electron spectroscopy (AES) and LEED.

Au was evaporated from a resistively heated source which was placed ~ 20 cm away from the Pt surface. The Au beam was collimated by a small tube. After an initial outgassing the evaporator worked without strong influence on the UHV conditions ($< 10^{-9}$ mbar during

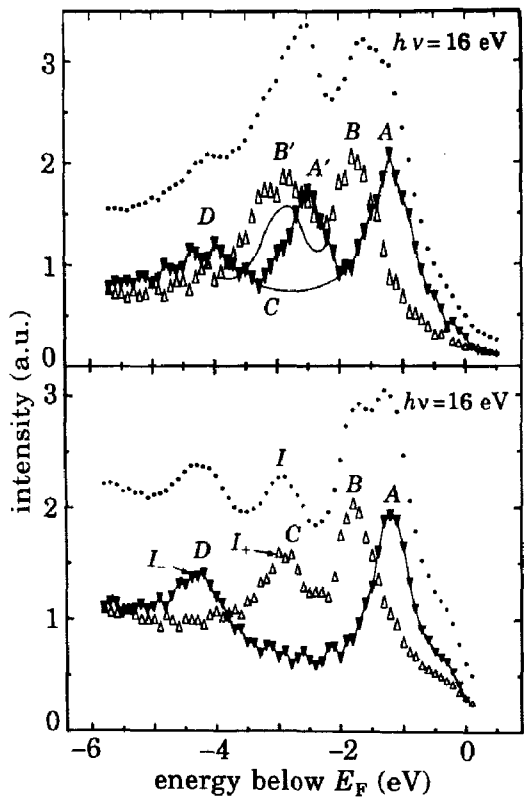

Fig. 1. – Photoelectron intensities obtained with normally incident σ-radiation in the normal photoemission from Pt(111) (bottom) and a gold monolayer on Pt(111) (top). Areas above the solid lines in the $I_+ - (I_-)$-spectra are the additional features A' and B' after Au absorption. The size of the symbols for I_+ (△) and I_- (▼) includes the total error also due to the uncertainty of the light polarization and the detector asymmetry function, $h\nu = 16$ eV.

evaporation, base pressure $< 3 \cdot 10^{-10}$ mbar). The evaporator was used for short periods, and in between the surface was controlled by LEED and AES. As shown earlier [7,11] Au grows epitaxially and two-dimensionally on Pt(111). The thickness calibration procedure is described in [7,11].

Figure 1 displays results obtained with σ-radiation and a photon energy of 16 eV for the clean Pt(111) surface and an Au monolayer on Pt(111). Curve I is the non–spin-resolved intensity. By means of the measured spin polarization component P_z it is separated into the partial intensities $I_+ = (I/2)(1 + P_z)$ and $I_- = (I/2)(1 - P_z)$ with P_z the spin polarization component parallel to the photon spin (the other perpendicular component has been measured to be zero within the experimental uncertainty). For the Pt(111) surface (fig. 1, bottom) four peaks A, B, C and D are resolved with the spin polarization sign sequence minus-plus-plus-minus. As shown earlier [9,12], these peaks are due to transitions from two spin-orbit-split valence band pairs of Pt into a free-electron–like final band. Corresponding photoemission spectra for an Au monolayer on Pt(111) (upper part of fig. 1) show additional contributions to both the I_+- and the I_--part of the spectra, which is illustrated by the areas above the solid lines in the spectra. The additional contribution to the I_--part is a sharp peak A' at 2.5 eV below E_F with high intensity, while the additional contribution B' to the I_+-part (located at about 3 eV below E_F) is considerably broader and weaker.

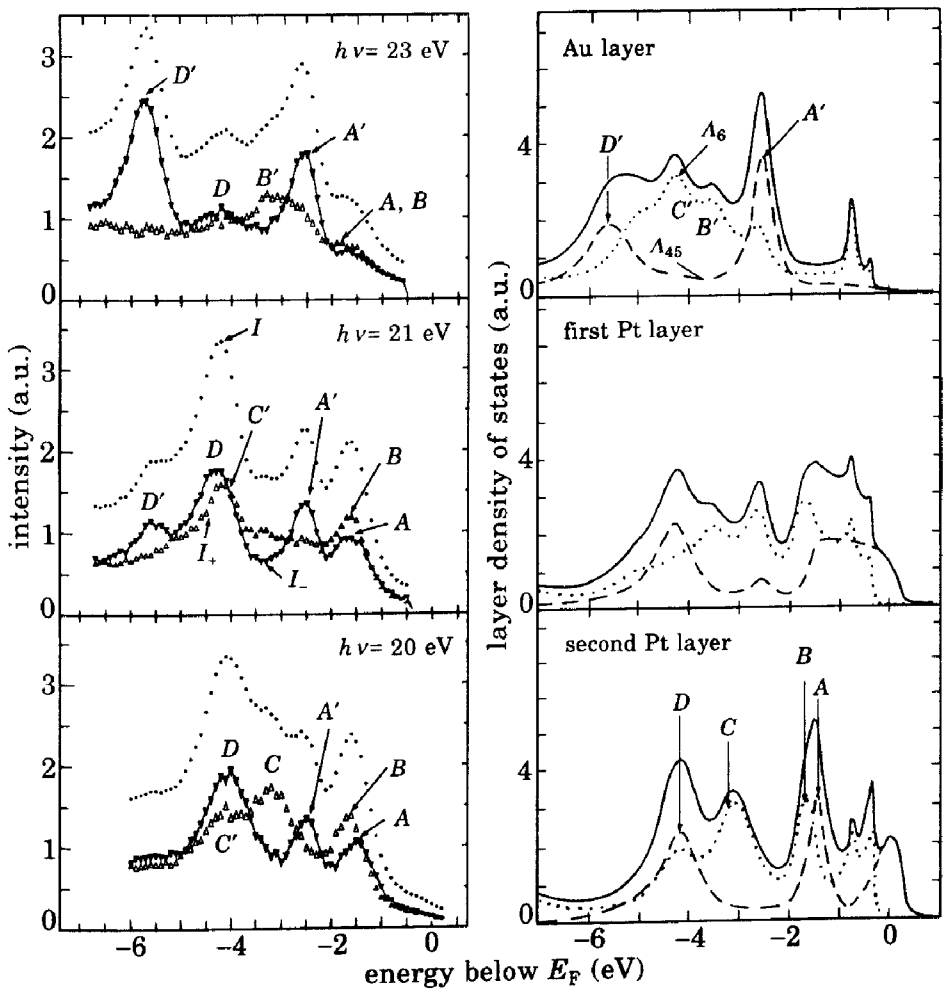

Fig. 2. – Left: photoelectron intensities obtained with normally incident σ-radiation in the normal photoemission from an Au monolayer on Pt(111). Key to the symbols and experimental errors as in fig. 1. A, B, C, D denote peaks, which are due to photoemission from Pt states. A', B', C', D' are due to emission from states mainly located in the Au layer. Right: relativistic densities of states for the three topmost layers of a regular stacking of one monolayer of Au on Pt(111): symmetry types $\Lambda_{4,5}$ (– – –) and Λ_6 (···), and their sum (——) (from Tamura and Feder, ref. [7]).

Corresponding measurements were also performed for photon energies between 20 and 23 eV and are displayed in the left part of fig. 2. In all spectra we again observe the sharp peak A' in I_- at 2.5 eV below E_F, but the separation of the spectra into its Au- and Pt-parts is more complicated for the other features in the spectra. We therefore compare the spectra with a layer- and symmetry-resolved density-of-states calculation for an Au monolayer on Pt(111) (fig. 2, right, from Tamura and Feder [7]). The upper part shows the density of states for the Au layer (solid line). It is separated into its parts with symmetry Λ_6^3 (dotted) and Λ_{45}^3 (dashed). The middle and lower right part of fig. 2 shows the density of states for the first and second Pt layer. Comparing the experiments in the left part of fig. 2 with this calculation we find peaks A' and D' in I_- at 2.5 eV and 5.7 eV below E_F which are not present in the spectra of the clean Pt(111) surface [9, 12] and peaks in the Λ_{45}^3-Au layer density of states at the same energies in the calculation. These peaks are therefore also denoted as A' and D'. While peak D' at 5.7 eV below E_F is only located in the Au layer, the calculation reveals an Au-layer–induced density-of-states contribution to peak A' in the first Pt layer at 2.5 eV below E_F (denoted as «Au-induced surface state on Pt(111)»). The Λ_6^3-part in the Au-layer density of states is a broad structure (B', C') with maximum at 4.2 eV below E_F. It is also qualitatively reproduced in the experimental spectra. The other contributions in the photoemission spectra of fig. 2 left are due to photoemission from the Pt substrate. At 4.3 eV due to emission from a bulk state with symmetry Λ_{45}^3 (peak D), at 3 eV due to emission from a Pt bulk state with symmetry Λ_6^3 (peak C, only visible for $h\nu = 20$ eV) and at 1.5 eV below E_F due to surface emission from two Pt states with symmetry Λ_6^3 and Λ_{45}^3 (peaks B and A) which are almost degenerate. The peak intensities vary strongly with photon energy between 20 and 23 eV; this is a property which has been studied in detail earlier for a number of clean d-metal surfaces [11, 13] and turns out to be valid also for the photoemission from an Au monolayer.

Photoemission with *linearly* polarized radiation results in the spectra displayed in fig. 3. The total intensities I are almost identical to those in fig. 2 (which were detected for σ-radiation). As described above, photoemission with π-radiation can yield a spin polarization component $P_\perp$ perpendicular to the direction of light propagation. The intensities I are separated into partial intensities $I_+^\perp$ and $I_-^\perp$ by means of $I_+^\perp = (I/2)(1 + P_\perp)$ and $I_-^\perp = (I/2)(1 - P_\perp)$. For $h\nu = 21$ eV we obtain strong spin polarization for 3 of the 4 peaks: peak A at 1.5 eV below E_F is due to surface emission from the Pt substrate. Though the initial state is a Pt bulk state the process is surface-sensitive, because the transition occurs in a gap region of the Pt band structure [6]. Peak A' at 2.5 eV below E_F corresponds to a state which is mainly localized in the Au layer with some additional contribution in the first Pt layers (Au-induced surface state on Pt(111) [7]).

While the states contributing to these first two peaks extend over at least, two layers which guarantees a threefold symmetry, the third peak at 5.7 eV below E_F is due to transitions from a state which is located only in the Au layer, as can be seen from the calculation in fig. 2. Spin polarization for photoemission from this state was thus not necessarily expected, since the Au monolayer itself most probably has a sixfold rotation symmetry. All peaks, for which spin-polarized electrons are found, are thus due to photoemission from states with symmetry Λ_{45}^3 (as predicted in [5]) and in all cases states are involved which are localized at the surface. While the spin polarization is only slightly changed when going from $h\nu = 21$ eV to $h\nu = 20$ eV (fig. 3, bottom), far more dramatic changes of the spin polarization occur for a photon energy of 23 eV (fig. 3, top). The spin polarization for peak A at 1.5 eV below E_F remains almost identical, the spin polarization for emission from the Au-induced surface state at 2.5 eV below E_F (peak A') vanishes and the spin polarization for emission from the Au state at 5.7 eV below E_F (D') shows even a sign change. The sign change indicates that final-state effects must play a significant role in this

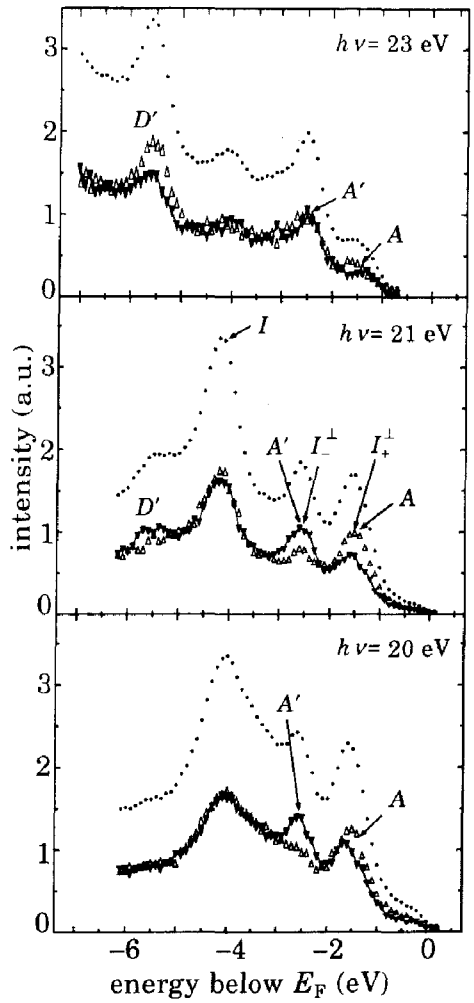

Fig. 3. – Photoelectron intensities obtained with normally incident π-radiation in the normal photoemission from an Au monolayer on Pt(111). Experimental errors as in fig. 1. $I_+^\perp$ and $I_-^\perp$ are the intensities of electrons with spin polarization vector parallel and antiparallel to a direction perpendicular to the propagation direction of the incident radiation.

case, in contrast to the earlier examples [6, 7] where the spin polarization was mainly due to spin-orbit interaction in the initial states [7, 5].

In summary, the electronic structure of an Au monolayer on Pt(111) has been studied by means of spin-polarized photoemission with circularly and linearly polarized radiation. Photoemission with σ-radiation yields the symmetries of the different types of states at the surface. Photoemission with π-light results only in spin-polarized electrons for emission from states with Λ_{45}^3-symmetry and if, in addition, one of the states involved in the transition is localized at the surface. Spin polarization is even found for the photoemission from a state which is located only in the Au layer. Either this Au surface state or the corresponding final state has thus threefold rotation symmetry. Strong variations of the spin polarization are observed when the photon energy of the π-radiation is varied. This shows that properties of the final states contribute considerably to the mechanism that produces the spin polarization.

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