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Spin- and angle-resolved photoemission spectroscopy study of the Au(1 1 1) Shockley surface state

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Abstract

The spin character of the splitting of the Shockley surface state on Au(111) is directly verified by measurements of the in-plane and out-of-plane spin polarizations in angle-resolved photoemission spectra. The two parabolic sub-bands that are momentum-shifted with respect to each other, reveal a distinct, opposite spin polarization that within the errors lies in the surface plane. The measured in-plane orientation of the spin vectors is consistent with the simple spin structure expected from a nearly-free-electron model, where the polarization axis is tangential to the Fermi surface of the surface state.

Keywords: Photoemission; Spin polarization; Gold; Surface state; Spin–orbit interaction

1. Introduction

High-resolution angle-resolved photoemission spectroscopy (ARPES) experiments by LaShell et al. [1], and more recently by Reinert et al. [2] show that the free-electron like Shockley surface state in the L-gap of Au(1 1 1) is split into two parabolic sub-bands that are shifted in momentum with respect to each other. The authors of these studies interpret this splitting as due to the spin–orbit interaction. For bulk band states in centrosymmetric crystals such splitting cannot occur due to the Kramers degeneracy [3], but at the surface inversion symmetry with respect to the surface normal is lifted. This interpretation is supported by tight-binding model calculations [3], and by a recent relativistic density functional theory study involving Au(1 1 1) slabs [4]. The direct experimental demonstration of a spin splitting in this system has not yet been presented, and it is the purpose of this paper to provide this evidence by spin-resolved high-resolution ARPES experiments.

A similar scenario has recently been described for surface states on W(1 1 0)-(1 × 1)H, where the spin–polarization of the split bands has already been confirmed experimentally in spin-resolved photoemission measurements [5]. However, while the spin splitting is of the order of 600 meV in the W(1 1 0)-(1 × 1)H system, it is only a maximum of 110 meV on Au(1 1 1) which makes the spin-resolved spectroscopy a challenging task.

A new photoelectron spectrometer has recently been designed and built by our group that proved to be up to this task. It combines a high-resolution hemispherical energy analyzer with a novel spin polarimeter that is based on two Mott detectors arranged in a geometry that provides full sensitivity to all three components of the electronic spin polarization. With the apparatus placed at the surface and interface spectroscopy (SIS) beamline of the Swiss light source (SLS), a wide range of photon energies are available for excitation [6]. The instrument permits to measure all quantum properties of the photoelectrons, and it has thus been termed the complete photoemission experiment (COPHEE) [7]. In combination with a new, versatile data acquisition system [8] and a computer-controlled sample goniometer [9], it enables us to perform various conventional modes of ARUPS experiments now in a spin-resolved fashion, such as energy distribution curves (EDC), momentum distribution curves (MDC), and Fermi surface maps, or, more generally, momentum distribution maps (MDM) [10].

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A direct measurement of the spin-character of the split Au(1 1 1) surface state is presented in this paper. The data confirm the original hypothesis by LaShell et al. [1]. A more detailed study, including selected spin-resolved MDCs and complete MDMs providing a detailed view on the actual spin structure of this interesting system, is the subject of a forthcoming publication [11].

In contrast to the usual spin-resolved photoemission from a magnetized sample two difficulties arise in the analysis of data measured with a Mott detector from a non-magnetic sample. First the axis of reference for the spin–polarization is not easily chosen. In a magnetized sample the magnetization direction is the natural axis of reference. In the case of spin–orbit split surface states the polarization vector does not align along a fixed axis for all electrons. Second the instrumental asymmetry of the Mott detector needs to be compensated for by numerical treatments. Any Mott detector will show a residual scattering asymmetry even in the case of a completely unpolarized beam and this artificial signal must be removed in the analysis of the data. In the case of a magnetic sample a reversal of the magnetization also reverses all spin-polarizations and therefore the instrumental asymmetry can be removed by forming the correct differences between measurements with opposite magnetizations. In the case of spin–orbit splitting the sign of the spin–polarization cannot be reversed because it is given by the physical situation in the sample.

A summary of the experimental and analysis procedures is given in Section 2. Further details can be found in separate articles on “spin-resolved Fermi surface mapping” [7] (including a description of the COPHEE spectrometer), and on conventional “Fermi surface mapping by photoemission” [10].

2. Experimental

All measurements have been taken with the complete photoemission experiment (COPHEE) [7] at the surface and interface spectroscopy beam line at the Swiss synchrotron light source (SLS) [6]. Fig. 1 shows the measurement geometry. For angle-resolved measurements the two-axis goniometer can rotate the sample about an axis parallel to the surface (polar rotation), and about the surface normal $\vec{n}$ (azimuthal rotation). The angle scanning and data acquisition procedures (spectra or single-shot counts) are fully automated, and all the various devices are comfortably controlled from the same computer application software, which has been developed in the group [8]. The directions of photon incidence and electron detection are fixed in space, whereas the sample is rotated.

Two 50 keV Mott detectors [12] measure the spin polarization P of the photoelectron beam, after passing through the modified Omicron EA125 analyzer, with respect to three fixed axes x, y, and z (the z-axis is the direction of emission, thus P_z is the longitudinal spin component). In the

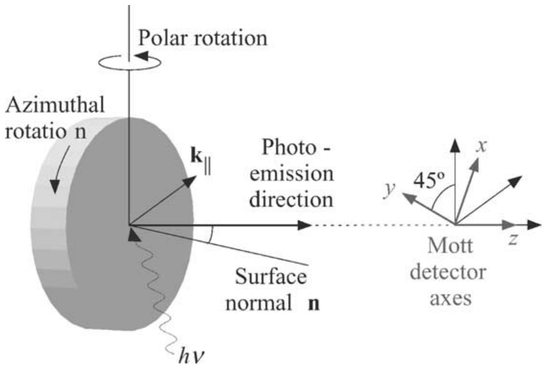

Fig. 1. Measurement geometry: the directions of light incidence and electron detection are fixed in space whereas the sample is rotated about a polar axis and the surface normal. The light is linearly polarized in the incidence-detection plane. The P_x and P_y polarization components measured in the Mott detectors form the in-plane component, P_z the out-of-plane component.

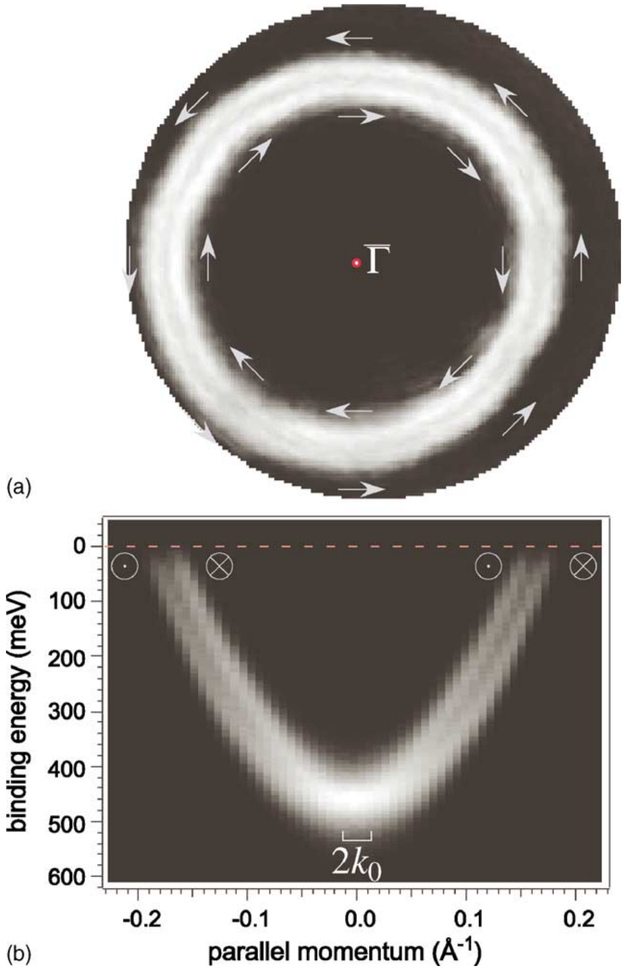

Fig. 2. Conventional (spin-integrated) high-resolution photoemission data of the Au(1 1 1) surface state excited with linearly polarized light of 21.1 eV: (a) Fermi surface map; (b) dispersion map. The measured intensities are shown in a linear gray scale where white corresponds to highest intensity. The resulting spin orientation is indicated by arrows.

normal emission geometry, the z component coincides with the out-of-plane component of the electron spin in the surface state, while the x and y components reflect the in-plane components. For off-normal geometries the in-plane and out-of-plane components mix in their contributions to the x, y and z polarization components. Each component is thereby evaluated from the angular asymmetry in the intensities of two Mott scattered electron beams, and two constant instrumental parameters: the effective Sherman function $S_{\text{eff}} \approx 0.1$–$0.15$, and a relative gain factor $\eta \approx 0.97$–1.03 to compensate for the instrumental asymmetry.

$$P = \frac{1}{S_{\text{eff}}} \frac{I_{\text{L}} - \eta I_{\text{R}}}{I_{\text{L}} + \eta I_{\text{R}}}. \tag{1}$$

In order to separate the oppositely polarized bands, spin-resolved intensities $I^{\uparrow}$ for spin-up (parallel to the reference axis), and $I^{\downarrow}$ for spin-down (antiparallel), are calculated from the respective polarization component P and the total intensity I_0:

$$I^{\uparrow,\downarrow} = I_0(1 \pm P). \tag{2}$$

For the Au(1 1 1) surface state, which is measured close to normal emission ($\theta < 7°$), P_z approximately corresponds to the out-of-plane polarization. The in-plane component must be calculated from P_x and P_y with respect to an appropriately chosen reference axis. For the EDC shown in Figs. 3 and 4 we refer the in-plane polarization for all data points to the polar rotation axis. It is actually calculated from P_x multiplied by $\sqrt{2}$ (the inverse projection factor). Separate P_y measurements fully support this interpretation.

The sample is prepared in situ from a mechanically polished gold single crystal (1 1 1) surface by many repeated

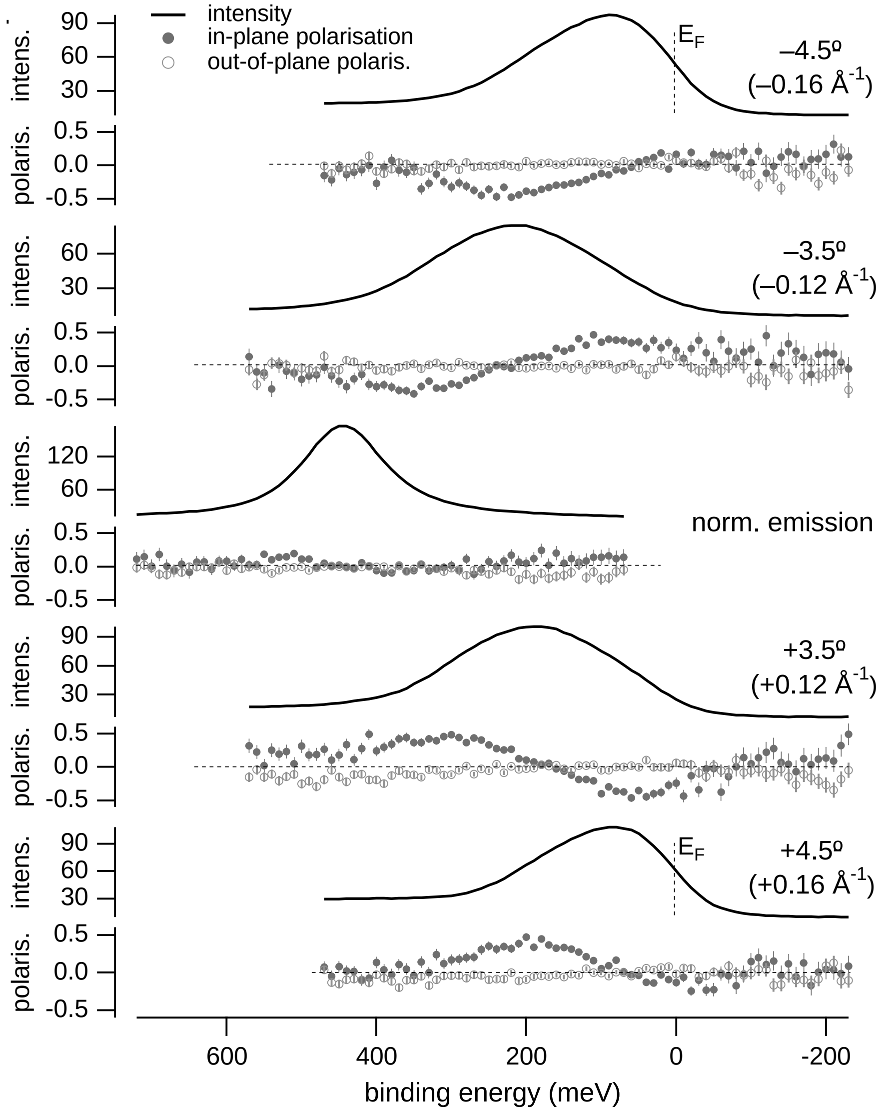

Fig. 3. Spin-resolved photoemission measurements of the Shockley surface state on Au(1 1 1) at various emission angles. The top curves of each data set show the intensity measured by all channels of the Mott detector. The lower curves show the measured polarization components determined according to Eq. (1) for the in-plane and the out-of-plane components of the polarization vector. The spectrometer resolution was set to 120 meV and 1.2° FWHM, respectively. The analysis of these data is discussed in the text.

cycles of 1 keV Ar^+ ion sputtering and annealing at 800 K. For the measurements the sample is cooled to 150 K after preparation. Its cleanliness and crystalline order is inferred from the surface state line width (<80 meV at normal emission). The surface remains clean for at least 18 h under 2×10^{-10} mbar base pressure of the vacuum system. All measurements use undulator-generated linearly p-polarized light of $h\nu = 21.1$ eV.

3. Results and discussion

Fig. 2 illustrates the performance of the spectrometer and the quality of the Au(1 1 1) sample. A high-resolution Fermi surface map of the surface state is shown, as well as a dispersion map, both measured with the conventional electron multiplier of the analyzer. The instrumental resolutions in these measurements are 20 meV in energy, 0.5° in angle (FWHM). Like in the earlier measurements at the same photon energy by the Hüfner group [2] the band appears clearly split, and the two free-electron-like parabolae are shifted in momentum by $2k_0 = 0.026\,\text{Å}^{-1}$. The slight irregularities in the Fermi surface map (a) are due to small non-uniformities in the sample surface which are probed as the sample is rotated.

A series of five spin-resolved EDCs has been measured, covering the full dispersion of the surface state. The data were acquired in an arbitrarily chosen azimuth, which is centered between the azimuths of the $\bar{\text{M}}$ and $\bar{\text{K}}$ points in the surface Brillouin zone. The raw data are shown in Fig. 3, where the intensities summed over the Mott channels are given as well as the in-plane and out-of-plane polarization components as obtained using Eq. (1) and the conventions described earlier. In order to obtain higher count rates in the inefficient Mott scattering signals, the resolutions in energy and angle have been relaxed (120 meV and 1.8° FWHM, respectively), as can be seen by comparing Figs. 2 and 3. The lower angular resolution in particular is responsible for the strong and asymmetric broadening of the photoemission peak as it disperses towards the Fermi energy. The splitting of the band is no longer observed in these data. However, in the ±3.5° off-normal directions where the band is split, the in-plane polarization shows a strong signal around the energy of the peak. The polarization reaches values of 44% and the sign changes at the center of the peak. The out-of-plane component shows no significant polarization.

The three parameters of Eq. (1), namely the effective Sherman function S_{eff} and two gain factors η for the x and z components of the Mott scattering were adjusted simultaneously during the analysis of all the spectra until a well balanced result for the whole data set was obtained. The Sherman function $S_{\text{eff}} = 0.15$ determined in this way is consistent with independent calibration measurements on this type of Mott detectors.

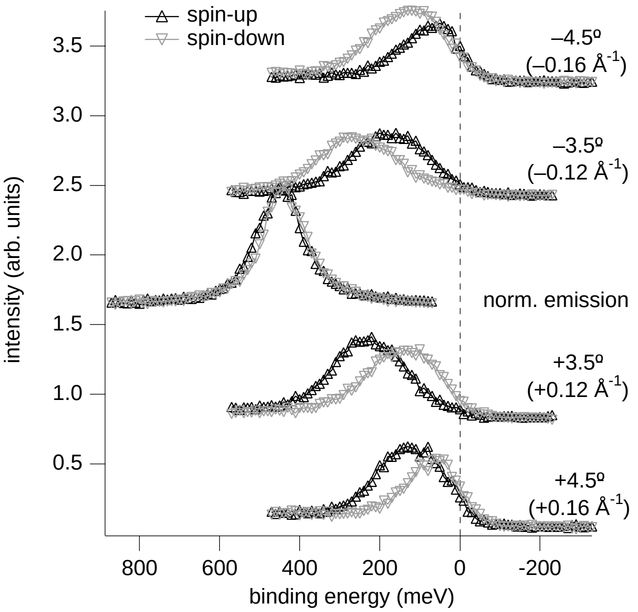

Fig. 4. Spin-resolved photoemission spectra of the Au(1 1 1) surface state at various polar emission angles as derived from the data shown in Fig. 3. The spin is determined from the in-plane component of the polarization vector with respect to the polar rotation axis.

Fig. 4 presents the spin-resolved EDCs as obtained by applying Eq. (2) to the data of Fig. 3. At normal emission both spin directions exhibit identical spectra, resulting from the zero net polarization. At $\theta = \pm 3.5°$ two peaks are produced with a splitting of 85 meV, fully consistent with the data in Fig. 2. At $\theta = \pm 4.5°$ the Fermi-level crossing of the upper band changes the weight and the shape of this component, and thus also the apparent spin splitting. These data fully confirm the spin character of the splitting, and thus the spin–orbit origin of this phenomenon, as had already been recognized by LaShell et al. [1]. The polarization values do not approach 100% as in the study on $W(1\,1\,0)$-$(1 \times 1)H$ by Hochstrasser et al. [5] due to the large overlap of the two spin–split peaks in the measured spectra, mostly a result of the relaxed resolution. Nevertheless, the results demonstrate how spin-resolution effectively enhances the energy resolution of the spectrometer in separating spin–split features.

An interesting issue of the spin–orbit induced surface state splitting is that it produces non-trivial spin structures at the Fermi level that might potentially be relevant for questions regarding magnetic anisotropies at surfaces and interfaces, or, for that matter, for the spin-dependent transport properties along and through the surface. Based on a nearly-free-electron model and a spin–orbit operator, LaShell et al. [1] have provided a picture for the spin structure where the spins are entirely in plane and tangential to the Fermi surface. The outer state has the spins rotating in a counterclockwise fashion around the Fermi surface, the inner state in the opposite way, as is sketched in Fig. 2. The sign of the spin polarization that we measure as the band disperses towards the Fermi level on either side of the surface normal is fully consistent with this model, as is the absence of any significant out-of-plane polarization. In a forthcoming publication we address the question of the detailed spin structure in more detail by presenting full spin-polarized MDM data sets [11].

4. Conclusions

Direct spin-resolved ARPES measurements show that the split bands of the Au(1 1 1) surface state are highly spin-polarized in opposite directions. The polarization vector lies in the surface plane and is perpendicular to the momentum vector of the probed state, in full agreement with the model proposed by LaShell et al. [1].

The combination of angle- and spin-resolved photoelectron spectroscopies allows to investigate in detail the spin structure of the surface state.

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