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Spin structure of the Shockley surface state on Au(111)

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The free-electron like surface state on the (111) surface of gold shows a splitting into two parabolic subbands induced by the spin orbit interaction. Spin-resolved high-resolution photoemission experiments performed with a full three-dimensional spin polarimeter provide a detailed image of the resulting spin structure. In particular, spin-resolved momentum distribution maps show that the spin vector lies in the surface plane and is perpendicular to the momentum of the electrons as expected in a free-electron model. This method of measuring the spin structure of a two-dimensional electron gas allows the observation of the direction of electric fields as probed by the electrons. Although the energy splitting can only be understood as a consequence of strong atomic electric fields, no modulation of the spin direction due to these fields is detected.

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The rapidly growing field of spintronics[1] introduces functionalities in electronic devices that are based on the electron spin. Doing so requires knowledge and control of spin structures in real space and/or in reciprocal space. The requirement for both is best illustrated by the seminal concept of a spin field effect transistor by Datta and Das:[2] ferromagnetic source and drain electrodes represent simple real space spin structures, whereas the momentum dependence of the spin in the active channel is necessary for the control of the spin precession by the electric field of the gate electrode. This momentum dependence is due to the spin-orbit effect that can arise for a two-dimensional electron gas (2DEG) in an asymmetric confining potential and is called the *Rashba effect*.[3] This Communication presents a detailed measurement of the resulting spin structure in momentum space for a system where the effect is large: the Shockley surface state on Au(111).[4] For this purpose, a high-resolution photoemission spectrometer with a full vectorial spin polarimeter has been built.[5]

The *sp*-derived surface states on the (111) faces of noble metals (Cu, Ag, Au) form a quasi-free electron gas which is well confined in directions perpendicular to the surface to a region around the first few atomic layers.[6] A splitting into two parabolic subbands of equal effective mass and maximum binding energy but shifted in momentum space was found in the case of Au(111),[4,7] and was interpreted as due to the spin-orbit interaction. No such splitting is allowed in the bulk of gold due to the combined restrictions of the time-reversal symmetry, $E^{\uparrow}(\mathbf{k})=E^{\downarrow}(-\mathbf{k})$ and the inversion symmetry, $E^{\uparrow}(\mathbf{k})=E^{\uparrow}(-\mathbf{k})$ leading to the Kramers degeneracy $E^{\uparrow}(\mathbf{k})=E^{\downarrow}(\mathbf{k})$.[4] The surface breaks the inversion symmetry and opens the possibility for a lifting of the spin degeneracy. The appropriate spin-orbit coupling Hamiltonian operator for electrons moving with a well-defined $\mathbf{k}$ parallel to the surface is written as[8]

$$H_{\mathrm{SOC}}=\frac{\mu_B}{2c^2}(\mathbf{v}\times\boldsymbol{\mathcal{E}})\cdot\boldsymbol{\sigma}, \tag{1}$$

where $\mathbf{v}$ is the velocity of the electron, $\boldsymbol{\mathcal{E}}$ is the electric field vector, and $\boldsymbol{\sigma}$ is the vectorial spin operator. For a quasi-free-electron gas this Hamiltonian imposes a splitting on the electronic bands, which is proportional to v and therefore to the electron wave number k. The dispersion is found as

$$E^{\uparrow,\downarrow}(k)=E_0+\frac{\hbar^2k^2}{2m^*}\pm\alpha k=E_0'+\frac{\hbar^2(k\pm k_0)^2}{2m^*}, \tag{2}$$

with $\hbar^2k_0=m^*\alpha$ and $E_0'=E_0-\hbar^2k_0^2/(2m^*)$.

The spin-quantization axis of this Hamiltonian is perpendicular to both, the electron velocity $\mathbf{v}$ and the average electric field vector $\boldsymbol{\mathcal{E}}$. The latter is perpendicular to the surface and an in-plane polarization of the ground state is expected. The former implies that the polarization vector must always be transverse with respect to the electron motion. This predicted spin structure for a two-dimensional free-electron gas is indicated by the arrows in Fig. 1. No fixed quantization for all $\mathbf{k}$ exists in this case and no macroscopic magnetic moment can be derived from the spin-orbit split quasi-free electron states due to the time reversal symmetry.

The *magnitude* of the spin-orbit splitting can only be understood from atomic fields, not from a free-electron model in the electric field produced by the surface potential step.[8] A quantitative description of the energy splitting was found by *ab initio* calculations based on relativistic density functional theory (DFT).[9] The strength of the splitting was furthermore found to be influenced by the presence of adsorbates on the surface.[10] Since the atomic fields are very nonuniform, a modulation of the direction of the spin polarization vector along the two circular Fermi surfaces might be suspected. A recent DFT study[11] predicts indeed slight deviations of the ground state spin structure from the simple free-electron image. In particular a small out-of-plane component of the spin-polarization is predicted. This component reveals itself as a modulation of the spin-orientation compatible with the threefold symmetry of the crystal. The out-of-plane component modulates in leading order as $P_z=\beta\sin 3\varphi$. For electrons moving along the mirror planes ($\bar{\Gamma}-\bar{M}$ azimuth) P_z must be zero due to the symmetry. In the mirror plane of the

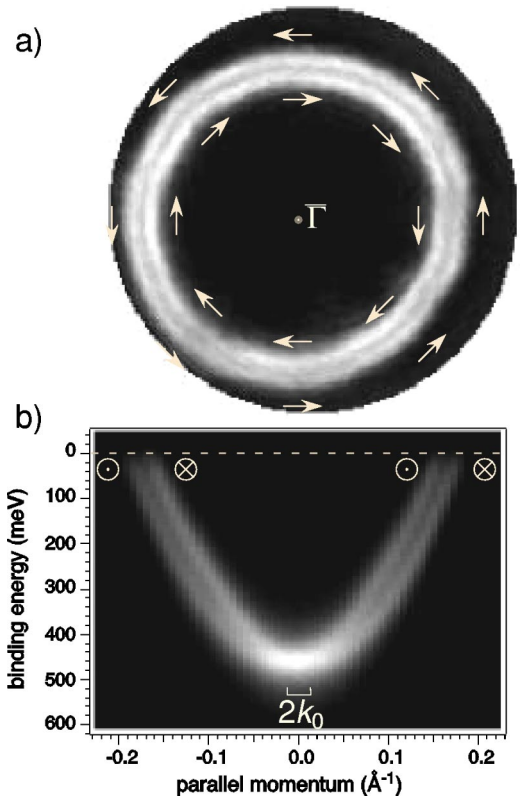

FIG. 1. High resolution photoemission data from Au(111) measured with the channeltron detector of the COPHEE spectrometer using linearly polarized light at $\hbar\omega = 21.1$ eV. (a) Fermi surface map, (b) dispersion map. The measured intensities are shown in a linear grey scale where white is the highest intensity. The spin structure predicted from a nearly free-electron model is indicated by arrows.

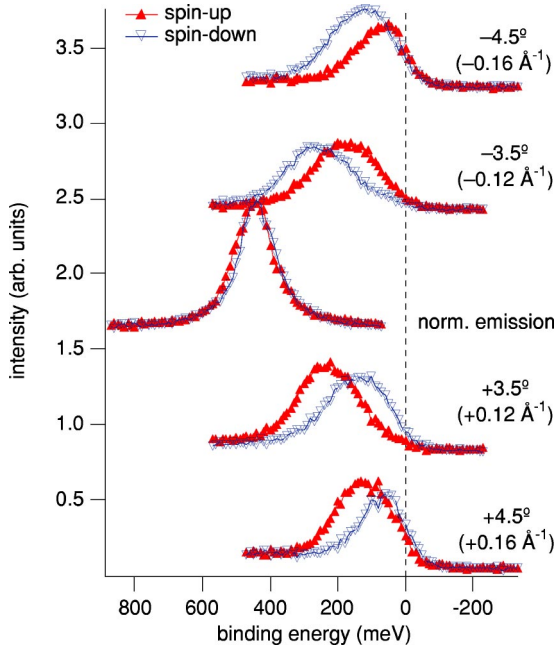

FIG. 2. (Color online) Spin-resolved photoemission spectra from the Au(111) surface state at various polar emission angles. The photon energy was $\hbar\omega = 21.1$ eV. Details of the analysis are given. The spin assignment was determined from the transverse in-plane component of the polarization vector. Spin-up and spin-down intensities are marked with filled and open triangles, respectively.

crystal the in-plane components of the electrical fields vanish and therefore the spin-polarization cannot have an out-of-plane component. The study predicts a tiny modulation amplitude of $\beta^{\text{in}} \approx -1.4\%$ for the inner and $\beta^{\text{out}} \approx 1.3\%$ for the outer Fermi surface. Earlier theoretical investigations[8,9] treated the spin as a purely energetic parameter and did not discuss the spin orientation.

In order to detect deviations from the free-electron-like spin structure we have measured a number of spin-resolved momentum distribution curves (MDCs) and a spin-resolved two-dimensional momentum distribution map (MDM) on Au(111). In particular the MDM is suitable to study the azimuthal variations of the spin-polarization components and therefore the modulation of the orientation of the spin vector. The small energy and angular splitting of the Au(111) surface state make the spin-resolved data acquisition very demanding.

In a similar experiment, Hochstrasser *et al.*[12] have recently studied the spin-orbit split surface states on W(110)-(1×1)H, where the splitting is of the order of 600 meV. Values of 100% spin polarization were found for a few representative points on the Fermi surface. The electron spins are predicted to rotate in a similar fashion around large oval-shaped hole pockets that are centered at the boundary of the surface Brillouin zone. The measurements were done only for points in the mirror plane of the crystal and no out-of-plane components was found indeed as imposed by the symmetry considerations.

The experiment was performed at the Surface and Interface Spectroscopy beamline at the Swiss Synchrotron Light Source. The photon energy was set to $\hbar\omega = 21.1$ eV and linearly *p*-polarized light was used. The data were acquired using the COPHEE spectrometer,[5] which consists of a high resolution electrostatic hemispherical electron energy analyzer equipped with a pair of 50 kV classical Mott detectors.[13] The polarimeter is sensitive to all three components of the polarization vector. The sample was prepared by many repeated cycles of Ar^+ ion sputtering at 1 kV and annealing to 800 K of the mechanically polished (111) surface. For the measurements the sample was cooled to 150 K within 2 h after the preparation. In an ultrahigh vacuum of 2×10^{-10} mbar pressure the surface remained clean for at least 18 h as judged from the photoemission linewidth of the surface state at normal emission ($\delta E = 80$ meV FWHM). The sample was mounted on an in-vacuum sample goniometer for the free rotation about an axis in the surface plane and around the surface normal, which allows the measurement of spectra for any emission angle above the surface.

Figure 1 shows the measured Fermi surface map and a dispersion map of the Au(111) surface state measured by the channeltron (non-spin-resolved) detector of the COPHEE spectrometer. The two concentric Fermi surface sheets are clearly seen. The slight irregularities in the Fermi surface map (a) are due to nonuniformities in the sample surface which are probed as the sample is rotated. The analysis of

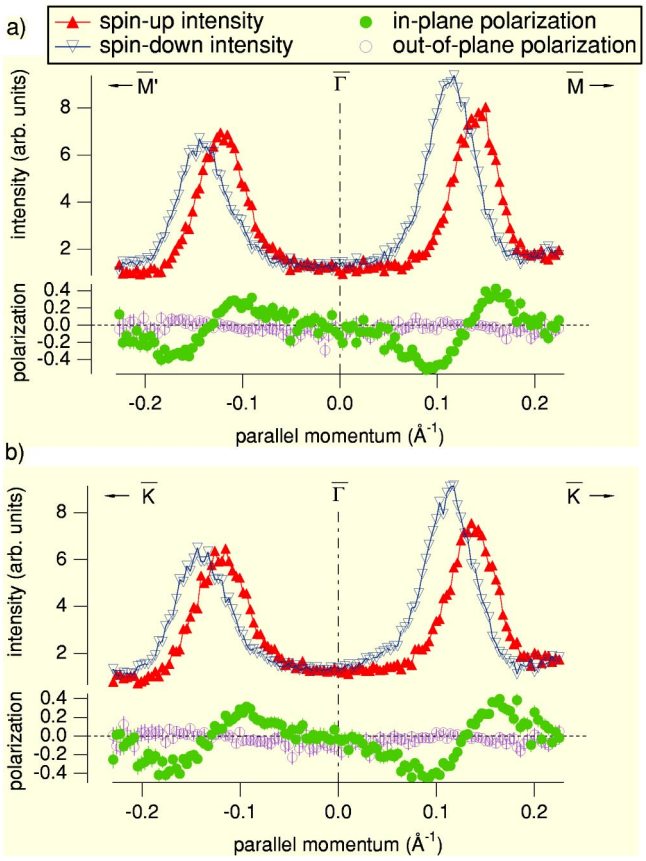

FIG. 3. (Color online) Measured spin-resolved momentum distribution curves at $E_B=170$ meV using UV-light of $\hbar\omega=21.1$ eV (a) in the $\bar{\Gamma}-\bar{M}$ and (b) $\bar{\Gamma}-\bar{K}$ azimuth. The lower part of each panel shows the measured polarization components for in-plane (transverse) and out-of-plane polarization, respectively.

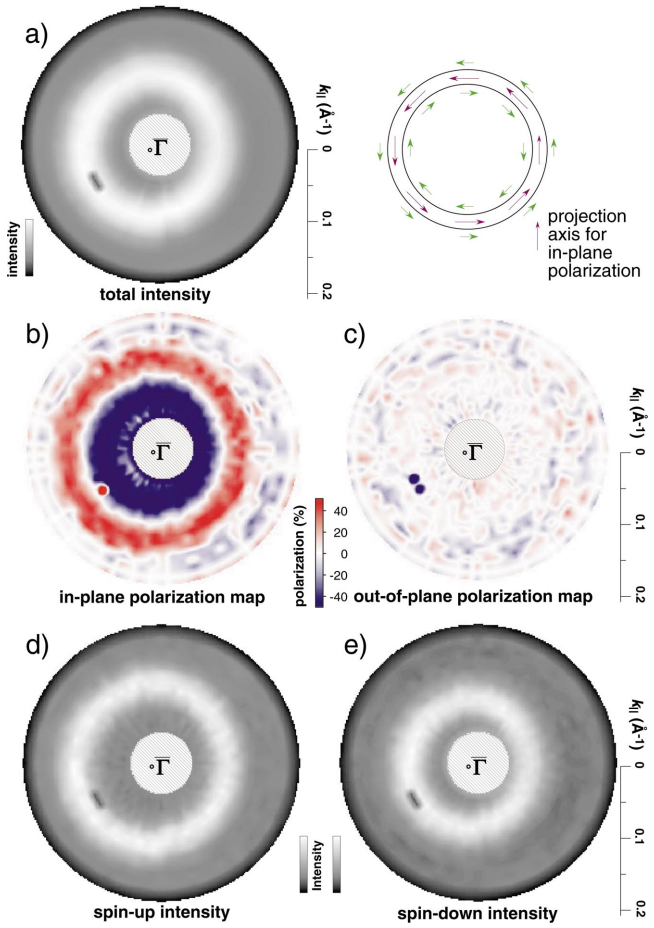

FIG. 4. (Color) Measured spin-resolved momentum distribution maps for $E_B=170$ meV using UV-light of $\hbar\omega=21.1$ eV. The top panel (a) shows the total intensity map and a sketch of the Fermi surface and the predicted spin structure. Purple arrows indicate the projection axes for in-plane polarization. The center panels (b) and (c) show the polarization maps in a color-scale representation (b) for the in-plane component and (c) for the out-of-plane component of the polarization vector. The in-plane polarization (b) is a projection on the tangents to the circular Fermi surface. Red (blue) indicates a counterclockwise (clockwise) spin orientation. The bottom panels show the individual spin-up and-spin down intensity maps derived from (a) and (b). Note the different radii of the two Fermi surfaces of the individual bands. These data consisting of 1080 angular settings were measured in 7 h including a 1 h break as the beam in the electron storage ring was lost (black blot in the intensity maps). The shift of $\bar{\Gamma}$ with respect to the center of the graphs is due to a 0.5° misalignment of the sample rotation axis. No symmetrization techniques have been used in the representation of these maps.

these data gives $m^*=0.25m_e$ and a splitting $2k_0=0.026$ Å^{-1} in agreement with earlier experiments.[7] The energy and angular resolutions were better than 20 meV and 0.5° FWHM, respectively.

The two Mott detectors in the COPHEE instrument are mounted such that the out-of-plane component of the polarization can be measured directly within the small angular range of ±7° covered in the experiment. The in-plane component is accessible by both polarimeters, with a 45° inclination of the sensitive axes with respect to the in-plane transverse direction of the spin polarization. Our data were measured using one polarimeter and the in-plane component was determined by correcting for the reduction of the measured polarization due to the geometrical projection after cross-checking with the second polarimeter. Any variation in direction of the spin polarization will be seen as a modulation of the polarization components.

Figure 2 shows spin-resolved spectra of the Au(111) surface state for various polar emission angles in the $\bar{\Gamma}-\bar{M}$ azimuth. To compensate for the low detection efficiency of the Mott detectors and to be able to acquire sufficient statistics for an accurate polarization analysis, both the energy and the angular resolution had to be relaxed in the spin-resolved measurements to values of 120 meV and 1.8° FWHM, respectively. The individual spin-up and spin-down spectra were derived from the in-plane polarization component assuming an effective Sherman function of $S_{\text{eff}}=0.15$. The sign convention (spin-up vs spin-down) is defined in a spin coordinate axis that is the counterclockwise tangent to the Fermi surface contour for positive polar angles θ (see Fig. 1). The sign has been determined by considering the sign of the Mott scattering asymmetry and has been verified in a separate experiment with a magnetized sample. The instrumental asym-

metry was corrected for by numerically adjusting the gain of one of the detector channels. This analysis was performed simultaneously for the complete data set until a well balanced result was found. The same procedure for the removal of the instrumental asymmetries was performed in all data sets and always lead to the same gain factors within the error bars. The data in Fig. 2 directly confirm the prediction that the splitting is due to the spin-orbit interaction.

Spin-resolved MDCs for two different high symmetry directions above the Au(111) surface are shown in Fig. 3. A binding energy $E_B = 170$ meV was chosen to profit from the higher intensity of completely occupied states as compared to emission from the Fermi level. The polarization shown in the lower part of each panel corresponds to projections on fixed axes for each MDC, with the sign of the spins defined analogous to those in Fig. 2. The polarization values do not reach 100% as in the experiment of Hochstrasser *et al.*[12] due to the large spectral overlap between the two spin components. The momentum offset $2k_0$ for opposite spins according to Eq. (2) is directly seen in these data. A comparison of measurements in the $\bar{\Gamma}-\bar{M}$ [Fig. 3(a)] and $\bar{\Gamma}-\bar{K}$ [Fig. 3(b)] azimuths of the surface Brillouin zone shows no significant difference neither for the position and shape of the peaks nor for the measured polarization components. In both azimuths the out-of-plane component of the spin-polarization is always zero within the error bars ($\Delta P_z \approx 5\%$), although the symmetry of the crystal would allow for a nonzero value in the $\bar{\Gamma}-\bar{K}$ azimuth.

A systematic search for deviations of the predicted spin structure can be done by measuring spin-resolved MDMs covering the entire momentum region of the surface state, which is possible with our new apparatus.[5] Figure 4(a) presents the spin-integrated MDM for the electron binding energy of 170 eV, as measured from the sum of all Mott detector channels. Due to the reduced energy and momentum resolution the splitting is no longer visible. The polarization maps in the center part of Fig. 4 show the distribution of the in-plane (transverse) and out-of-plane spin polarization components. In (b) the red (blue) regions correspond to a positive (negative) spin component with respect to the quantization axis as defined earlier, which is always counterclockwise tangential to the circular Fermi surface contours. This represents the natural spin reference frame for this type of measurement where the sample is rotated about the surface normal. The arrangement of the regions of constant spin-polarization in concentric rings about $\bar{\Gamma}$ is in agreement with the free-electron like spin-structure sketched in Fig. 1(a) including the sense of the spin rotation.

Any systematic rotation of the spin polarization vector away from the transversal direction as a consequence of the nonuniform atomic electric fields should reveal itself as a three- or sixfold modulation of the the spin components. We have therefore analyzed the polarization maps for azimuthal modulations. These modulations must have their zero-point in the $\bar{\Gamma}-\bar{M}$-azimuth and they must show a sign reversal for the inner and the outer surface state.[14] No such modulations compatible with the crystal symmetries were found within the error limit of ±2% of polarization, in agreement with the theoretical work of Henk *et al.*[11] Since this theory predicts a maximum polarization value of less than 1.5%, the experiments set a tight upper limit and confirms the validity of the calculations.

In conclusion, we have demonstrated spin-resolved momentum mapping by photoemission, using a three-dimensional spin polarimeter. The spin structure of the spin-orbit split surface state on Au(111) is established to be nearly-free-electron like with no deviations within our error bars (±2%). From Eq. (1) it thus follows that the electrons move in an environment where the average electric field vector points out of the surface, away from the bulk of the solid. The small k vectors associated with the surface state on Au(111) correspond to large wavelengths, and the propagating wave functions average thus over large regions in real space. Despite the fact that the electrons receive the spin orbit energy from the strong and nonuniform atomic fields, the average electrical field experienced is thus highly homogeneous and isotropic. It would be interesting to do this same kind of study on the W(110)−(1×1)H system,[12] where surface state wave vectors near the zone boundary are involved, and where the shape of the Fermi surface deviates strongly from the circle. Moreover, by using vicinal Au(111) surfaces it should be possible to see how the spin structure is affected by the in-plane components of the electric fields in the vicinity of the surface steps.

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