

Spin polarization of the L-gap surface states on Au(1 1 1): a first-principles investigation

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Abstract

Spin polarization and dispersion of the L-gap surface states on Au(1 1 1) are investigated theoretically by means of first-principles electronic-structure and photoemission calculations. In analogy to a two-dimensional electron gas, spin-orbit coupling results in a large in-plane spin polarization. A small component normal to the surface is reported for the first time. The photoelectron spin can differ considerably from that of the initial surface states, e.g., depending on light polarization and detection azimuth.

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1. Introduction

One important manifestation of spin-orbit coupling (SOC) is the removal of degeneracies in the electronic structure. A prominent example shows up in a two-dimensional electron gas (2DEG), typically formed in semiconductor heterojunctions. The structural asymmetry normal to an interface produces the Rashba–Bychkov spin-orbit interaction [1,2] which leads to a splitting of the electronic states, $E_{\pm} = \frac{1}{2}k_{\parallel}^2 \pm \gamma_{\text{so}}|\vec{k}_{\parallel}|$ (in atomic units, $e = \hbar = m = 1$). Here, γ_{so} represents the SOC strength and $\vec{k}_{\parallel} = (k_x, k_y)$ is the wavevector parallel to the interface (for a review, see [3]). This splitting is accompanied by a complete electron

spin polarization (ESP) \vec{P} which is perpendicular to \vec{k}_{\parallel} , $\vec{P}_{\pm} = (\pm k_y, \mp k_x, 0)/|\vec{k}_{\parallel}|$. Since time-reversal symmetry implies $\vec{P}_{\pm}(\vec{k}_{\parallel}) = -\vec{P}_{\pm}(-\vec{k}_{\parallel})$, the system remains nonmagnetic.

Because the potential at a surface induces a structural asymmetry, too, electronic states confined to a metal surface can also be subject to the Rashba–Bychkov effect. Indeed, a splitting was observed experimentally by means of photoelectron spectroscopy for the free-electron-like L-gap surface states on Au(1 1 1) [4], later being corroborated theoretically [5]. Lesser splittings were found in Cu and Ag [6]. In analogy to a 2DEG, the ESP was *believed* to be complete and perpendicular to \vec{k}_{\parallel} [7].

For a 2DEG, one usually assumes a system which is invariant under rotations about the interface normal. The geometrical arrangement of the atoms, however, reduces this symmetry and, hence, leads to nonequivalent directions in

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reciprocal space. For the Au(111) surface with its threefold rotational symmetry, one could therefore expect deviations from the 2DEG behavior. Further, the corrugation of the surface potential could considerably influence the ESP of the surface states, in particular, as it can produce an ESP component along the surface normal (z axis).

Up to now, ESP and photoemission of the L-gap surface states on Au(111) were not investigated theoretically on a first-principles level. Issues to be addressed comprise the effect of the surface symmetry and a comparison of the SOC strength compared to that in a 2DEG. Another question concerns the ESP being probed by photoelectron spectroscopy. Since in general SOC results in spin-polarized photoelectrons from nonmagnetic surfaces (see [8] and references therein), the ESP of an initial surface state can be obscured by the photoemission process. A question arises whether one can nonetheless find set-ups that allow to conclude from the photoelectron ESP on the initial-state ESP. To give answers we performed both first-principles electronic-structure and photoemission calculations, some results of which are presented in this paper.

2. Computational

The electronic structure of the Au(111) surface was computed within the local spin-density approximation to density-functional theory,

applying the spin-polarized screened Korringa–Kohn–Rostoker (KKR) method (for details, see [9,10]). The potentials of the six outermost Au layers and of three vacuum layers of the semi-infinite system were relaxed in the self-consistency loop. To obtain better agreement with the experimentally obtained surface-state dispersion [11], an outward relaxation of the vacuum layers by 4% of the bulk-interlayer distance was assumed.

Spin- and angle-resolved photoelectron spectra were calculated within the relativistic one-step model of photoemission, as formulated in layer-KKR [12,13]. The used computer program proved to be very successful in describing the spin-orbit induced photoelectron ESP [14].

3. Results and discussion

The dispersion of the L-gap surface states is obtained from the maxima in the \vec{k}_{\parallel} - and layer-resolved spectral density. In accordance with the Rashba–Bychkov picture, one finds parabolae that are shifted with respect to \vec{k}_{\parallel} , therefore suggesting the nomenclature of an ‘inner’ and an ‘outer’ surface state (Fig. 1a). The minimum energy of -0.51 eV agrees well with the experimental value of -0.49 eV [6]. The spin-orbit splitting in terms of the Fermi wavenumbers, $\Delta k_F = k_F^{\text{out}} - k_F^{\text{in}}$, compares also well with the experimental data (0.012/Bohr vs. 0.013/Bohr), although the dispersion in theory is slightly too large ($k_F^{\text{in}} = 0.079/\text{Bohr}$ and

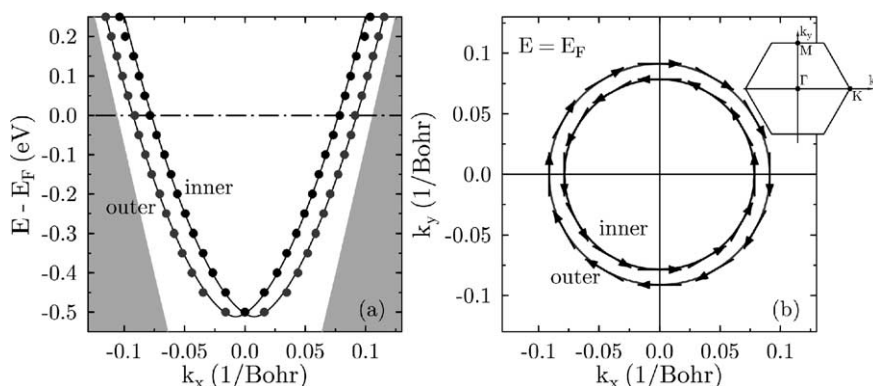


Fig. 1. L-gap surface states on Au(111). (a) Dispersion along $\bar{K}-\bar{\Gamma}-\bar{K}$ [$\vec{k}_{\parallel} = (k_x, 0)$]. Black and grey circles indicate the inner and the outer surface state, respectively. The grey areas depict the region of bulk bands. (b) Momentum distribution at the Fermi energy E_F in the vicinity of the Brillouin-zone center (see inset). Arrows indicate the in-plane directions of the surface-state spin polarizations.

$k_F^{\text{out}} = 0.091/\text{Bohr}$ vs. $0.091/\text{Bohr}$ and $0.104/\text{Bohr}$, respectively).

The momentum distribution of the surface states (i.e., \vec{k}_{\parallel} at fixed energy) consists of two concentric circles (Fig. 1b), which suggests to expand the spin polarization \vec{P} in terms of circular functions. Considering the symmetry of the (111) surface as well as time-reversal symmetry, one finds $\vec{P}(\varphi_e) = (\alpha \sin \varphi_e, -\alpha \cos \varphi_e, \beta \cos 3\varphi_e)$, with $\vec{k}_{\parallel} = |\vec{k}_{\parallel}|(\cos \varphi_e, \sin \varphi_e)$. For a 2DEG, one has $\alpha = \pm 100\%$ and $\beta = 0\%$ since the structural asymmetry is completely along the z axis (pointing towards the bulk). However, the corrugation of the Au(111) surface potential induces an additional in-plane asymmetry component. Therefore, P_z becomes nonzero but small ($\beta^{\text{in}} = -1.4\%$ and $\beta^{\text{out}} = 1.3\%$). Because the z -derivative of the surface potential still dominates, α is much larger than β : $\alpha^{\text{in}} = -96.7\%$ and $\alpha^{\text{out}} = 92.6\%$.

The Rashba–Bychkov effect in Au(111) surpasses that in semiconductor heterostructures. For example, the SOC strength γ_{so} in a 2DEG is about 0.8×10^{-9} eV cm (cf., e.g., [15,16]) whereas for Au(111) we obtain 4.4×10^{-9} eV cm. Further, the relative \vec{k}_{\parallel} -splitting at E_F is about 3.5 times larger (4% vs. 14%).

In order to investigate whether the initial-state ESP can be reliably probed by photoemission, we calculated spin-resolved spectra from the Fermi energy E_F . Since the initial-state ESP is mainly perpendicular to \vec{k}_{\parallel} (Fig. 1b), a suitable set-up comprises p-polarized light incident within the scattering plane (azimuth $\varphi_{\text{ph}} = \varphi_e$) which results mainly in a photoelectron ESP perpendicular to

the scattering plane. However, depending on φ_e , the other ESP components can become nonzero. In the following, we concentrate on the azimuthal dependence of the photoelectron ESP at the Fermi wavenumbers k_F^{in} and k_F^{out} , which correspond to polar angles $\vartheta_e^{\text{in}} = 4.1^\circ$ and $\vartheta_e^{\text{out}} = 4.9^\circ$ (for photon energy 21.22 eV; polar angle $\vartheta_{\text{ph}} = \vartheta_e - 45^\circ$).

The tangential ESP component $P_{\text{tan}}^{\text{in}}$ (in-plane, perpendicular to \vec{k}_{\parallel} ; cf. Fig. 2b) of the inner surface state is almost constant (-98.4%), with a tiny 120° -oscillation amplitude superposed (Fig. 2a). The radial component $P_{\text{rad}}^{\text{in}}$ is comparably small (in-plane, parallel to \vec{k}_{\parallel} ; less than 2% in absolute value), hence establishing a nice agreement with the ESP of the respective initial state ($\alpha^{\text{in}} = -96.7\%$). P_z displays threefold rotational symmetry, too, but its amplitude of 4.5% is too high compared to β^{in} (-1.4%) and shows opposite sign.

For the outer surface state, the deviation of the photoelectron ESP from the initial-state ESP is considerably larger. While $P_{\text{tan}}^{\text{out}}$ is almost constant (88% compared to $\alpha^{\text{out}} = 92.6\%$, with a superposed oscillation of 2% amplitude), $P_{\text{rad}}^{\text{out}}$ oscillates with a sizable amplitude of about 7.5%. Further, the P_z^{out} -amplitude of -14% is significantly larger (in absolute value) than β^{out} (1.3%) and has opposite sign.

4. Concluding remarks

Summarizing, the ESP of the inner surface state can be probed well with the photoemission set-up considered here, in particular the tangential in-

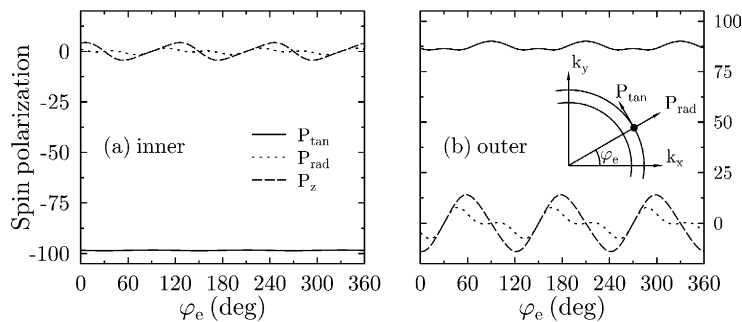


Fig. 2. Spin-resolved momentum distribution in photoemission from the Fermi energy E_F for the inner (a, left) and the outer (b, right) surface state. The ESP components are distinguished by line styles, as indicated. An azimuth of $\varphi_e = 0^\circ$ corresponds to the $\bar{\Gamma}$ – \bar{K} direction.

plane component. Using s- or circularly polarized light instead, it is difficult to conclude from the photoelectron ESP on that of the initial surface state [10].

The different behavior of the inner and the outer surface state shows also up in the photoemission intensities (not shown here): the oscillation amplitude (relative to the mean value) of the outer surface state is about twice as large than that of the inner (33% vs. 15%). These differences can be traced back to SOC in the initial states since they increase with SOC strength [10]. We hope that these findings will stimulate further experiments.

References

- [1] E.I. Rashba, *Sov. Phys. Solid State* 2 (1960) 1109.
- [2] Y.A. Bychkov, E.I. Rashba, *Sov. Phys. JETP Lett.* 39 (1984) 78.
- [3] S.D. Ganichev, W. Prettl, *J. Phys.: Condens. Matter* 15 (2003) R935.
- [4] S. LaShell, B.A. McDougall, E. Jensen, *Phys. Rev. Lett.* 77 (1996) 3419.
- [5] L. Petersen, P. Hedegård, *Surf. Sci.* 459 (2000) 49.
- [6] F. Reinert, G. Nicolay, S. Schmidt, D. Ehm, S. Hüfner, *Phys. Rev. B* 63 (2001) 115415.
- [7] F. Reinert, *J. Phys.: Condens. Matter* 15 (2003) S693.
- [8] R. Feder, J. Henk, in: H. Ebert, G. Schütz (Eds.), *Spin–Orbit Influenced Spectroscopies of Magnetic Solids*, *Lecture Notes in Physics*, vol. 85, Springer, Berlin, 1996, p. 466.
- [9] A. Ernst, M. Lüders, W.M. Temmerman, Z. Szotek, G. van der Laan, *J. Phys.: Condens. Matter* 12 (2000) 5599.
- [10] J. Henk, A. Ernst, P. Bruno, *cond-mat/0305530*, 2003.
- [11] G. Nicolay, F. Reinert, S. Hüfner, P. Blaha, *Phys. Rev. B* 65 (2002) 033407.
- [12] J. Braun, *Rep. Prog. Phys.* 59 (1996) 1267.
- [13] J. Henk, in: H.S. Nalwa (Ed.), *Handbook of Thin Film Materials*, vol. 2, Academic Press, San Diego, 2001, p. 479 (Chapter 10).
- [14] J. Henk, T. Scheunemann, S.V. Halilov, E. Tamura, R. Feder, *omni2k—fully relativistic electron spectroscopy calculations*, 2000.
- [15] J. Luo, H. Munekata, F.F. Fang, P.J. Stiles, *Phys. Rev. B* 41 (1990) 7685.
- [16] G. Engels, J. Lange, T. Schäpers, H. Lüth, *Phys. Rev. B* 55 (1997) R1958.