Spin-orbit splitting of the *L*-gap surface state on Au(111) and Ag(111)

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We present high-resolution photoemission results on the *L*-gap surface state on Au(111) and Ag(111), in combination with fully relativistic density-functional calculations. In the case of Au(111), both experimental and theoretical results demonstrate that the lack of inversion symmetry at the surface leads to a considerable spin-orbit splitting of this surface state over the whole Fermi surface, whereas in the case of Ag(111) this splitting is far too small to be experimentally resolved in our data.

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Several years ago LaShell, McDougall, and Jensen[1] investigated the *L*-gap surface state on Au(111) by angular-resolved photoemission spectroscopy with a high-momentum resolution. Their data show a particular splitting of the surface state peak in the energy distribution curves (EDC's), that increases when the peak disperses toward the Fermi level. Although the authors already interpreted this splitting as due to the spin-orbit (SO) interaction of the surface *sp* state, there has been a long-standing discussion about possible other reasons for the splitting in the literature,[2–4] mostly because the observed doublet has not been reproduced in photoemission spectroscopy until recently.[5] In addition, the splitting has not been observed by tunneling spectroscopy using a scanning tunneling microscope,[2,6,7] probably because this is not possible due to principle limitations of the method, as described in Ref. 8. Another detail that complicates the understanding of the electronic properties of the Au(111) surface is the existence of a particular $(22\times\sqrt{3})$ reconstruction which forms—triggered by elastic stress in the topmost surface layer—the so-called herringbone pattern,[9] that might also influence the electronic structure of the surface.[6]

In this paper we present high-resolution photoemission data and a fully relativistic slab layer calculation for the Au(111) surface, which both show a splitting of the surface state over the complete Fermi surface. The excellent qualitative and quantitative agreement between experiment and theory gives unambiguous evidence of SO interaction being the reason for the observed spectral doublet of the Au(111) surface state. Furthermore, we explain why this SO splitting has not been observed experimentally for other noble-metal surface states, e.g., on Ag(111).

The experimental setup and the surface preparation were described elsewhere in detail (see Refs. 5 and 10); therefore, we only give a short summary here. Important for the experimental results is the high spectrometer resolution in energy and angle ($\Delta E=3.5$ meV, $\Delta\theta\approx 0.3°$), and in particular the short measuring time of approximately 15 min for one data set, that contains the complete occupied surface state band for both Ag(111) and Au(111). This is important to avoid a surface deterioration from adsorbates that influence the photoemission spectra significantly. An influence of the intense vacuum ultraviolet radiation[11] could not be observed in the spectra. In contrast to the work by LaShell, McDougall, and Jensen, our spectra were taken at low temperatures ($T\approx 30$ K) with a photon energy of $h\nu=21.23$ eV (HeI), and the complete two-dimensional Fermi surface was measured.

The presented slab calculations were performed using the full-potential linearized-augmented-plane-wave (LAPW) method as embodied in the WIEN 97 code.[12] The calculations are based on density functional theory using the local-density approximation.[13] In contrast to the theoretical investigations within a simple model approach in Ref. 8, our *ab initio* calculations contain no external parameters to describe the spin-orbit interaction and yield *quantitative* results for the SO splitting over the complete investigated **k** range. We used a well-converged basis set of about 1600 LAPW's and a *k* mesh of 12 *k* points in the two-dimensional irreducible Brillouin zone. SO coupling was included in a second variational step. We modeled the surface by a periodic slab of 23 Au layers, separated by 20 bohr of vacuum. Preliminary test calculations with fewer layers or reduced vacuum have shown that in the artificial slab geometry the two surfaces interact weakly with each other, both via the ''bulk'' as well as via the ''vacuum'' (cf. Ref. 14). This spurious interaction leads to a splitting of the two surface states, which for, e.g., a seven-layer slab is much larger than the SO splitting of the Au(111) surface state (we have two surfaces and thus two surface states, even without SO interaction). Thus we increased both the number of Au layers and the vacuum region, until the calculations without SO did show a splitting of the two surface states below 1 meV, which is negligible compared to the actual splitting due to SO interaction.

Because the occupied part of the surface state is far away from the surface Brillouin-zone boundary, its dispersion can be regarded as identical for all in-plane directions. Therefore, we restrict most of our following discussion to the dispersion along $\overline{\Gamma}\overline{M}$, denoted as the *x* direction with the in-plane wave vector defined as $\mathbf{k}_{\parallel}=k_x\cdot\hat{e}_x+k_y\cdot\hat{e}_y$. Figure 1 shows the results of this band-structure calculation along the $\overline{\Gamma}\overline{M}$ direction. The surface state, represented by solid lines, appears inside the *L* gap of the projected bulk band states (shaded area). Obviously, the surface state is split for all points k_x

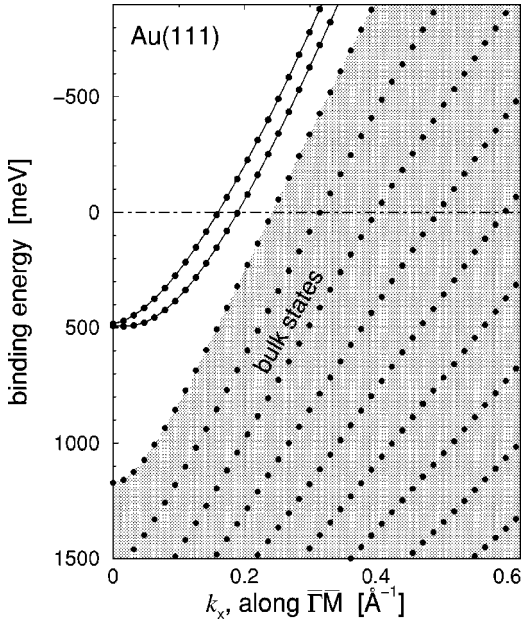

FIG. 1. Results of the band-structure calculation along the $\bar{\Gamma}\bar{M}$ direction for a 23-layer slab of Au(111). The shaded area represents the projected bulk states, and the solid lines give the surface state dispersion. The Fermi level has been adjusted to the experimental position.

$\neq 0$, forming two parabolas with the same maximum binding energy, but shifted horizontally in the positive and negative k_x directions, respectively. This splitting disappears when the calculation is performed without SO interaction. Note that the maximum binding energy of the lowered band appears not at $k_x=0$. For the comparison with the experimental results the Fermi level of the calculations has been adjusted to the experimental value, i.e., the states were shifted by ≈ 100 meV to higher binding energies.

The experimental photoemission results on the Au(111) surface state are summarized in Fig. 2. The upper panel gives a Fermi surface map (FSM) of the surface state, which technically speaking is the spectral intensity at E_F for different emission angles or wave vectors $k_\parallel$. The two concentric circles represent the twofold Fermi surface of the Au(111) surface state, surrounded by a dark ring that is due to the low spectral intensity in the projected band gap of the bulk states. The small deviations ($<0.5°$) from perfect circles are caused by electrostatic or magnetic fringe fields in the experimental setup; an azimuthal rotation of the sample does not change the experimental distortion of the Fermi surface. In the picture proposed by LaShell *et al.*, the electron spin lies in the surface plane and is oriented perpendicular to $\mathbf{k}_\parallel$. The spins of the two Fermi surfaces point in opposite directions, as indicated by the white arrows in Fig. 2. The difference between the radii of the two Fermi surfaces directly gives the SO splitting Δk of the surface state in k space. Within the experimental errors we cannot observe any azimuthal dependence of Δk.

The lower panel shows a gray scale plot of the dispersion $E(k_x)$, that was measured with an angular step width of $\approx 0.07°$ in one single experiment. Clearly visible are the two

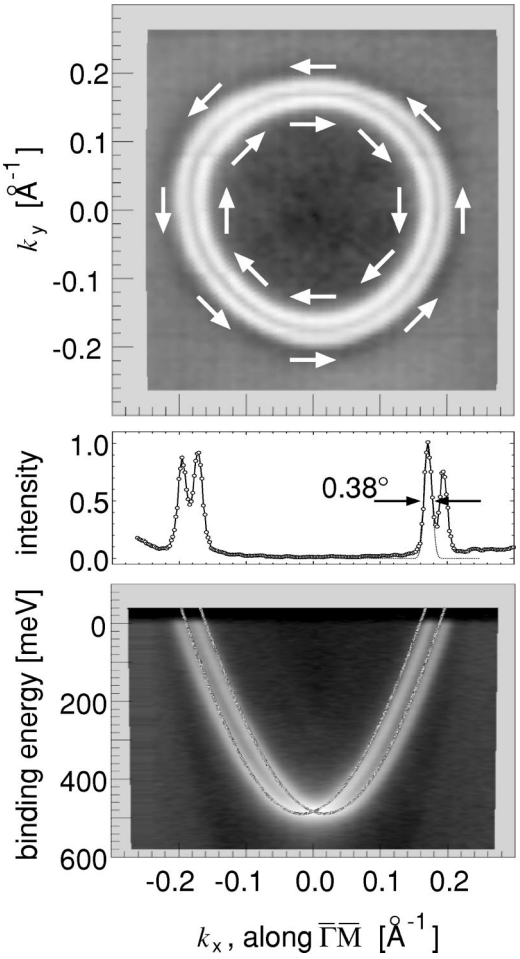

FIG. 2. Experimental results of the Au(111) L-gap surface state, from HeI photoemission data at $T=30$ K (see Ref. 5 for more information). Upper panel: FSM with spin orientation indicated by the white arrows; middle panel: MDC at $k_y=0$; lower panel: gray scale plot of the dispersion, including the calculated band structure as thin solid lines. Clearly visible in all three plots is the splitting of the surface state.

bright parabolas of the surface state, embedded in the band gap of the projected bulk states that appear as a slightly increased intensity toward both sides of the plot. The splitting of the surface state is constant in k, corresponding to a linear increase of the splitting in energy: $E_\pm(k_x)=-\hbar^2(k_x \pm \Delta k/2)^2/2m^*+E_0$. A least-squares fit of the experimental dispersion gives a value of $\Delta k=0.025$ Å^{-1}, a maximum binding energy of $E_0=487$ meV, and an effective mass $m^*=0.255m_e$. Note that not only the binding energy but also this SO splitting can be modified by a coverage of the surface, e.g., by a Xe monolayer that causes a shift of approximately 140 meV toward E_F and a $\approx 20\%$ increase of the splitting.[15] For the two surface-state Fermi vectors we obtain $k_F=\pm 0.172$ Å^{-1} and $k_F=\pm 0.197$ Å^{-1}. For a comparison with the theoretical results, we included into this figure the calculated surface state bands from Fig. 1 as solid lines. The agreement is striking: theory and experiment describe exactly the same dispersions, including the size of the SO splitting. In comparison, the free-electron model by Petersen *et al.*[8]—that qualitatively describes the splitting and

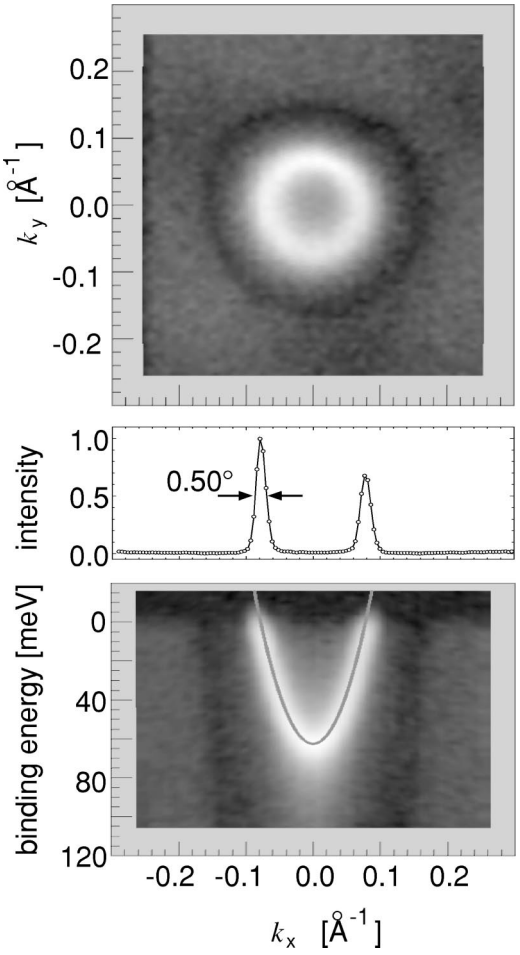

FIG. 3. Photoemission results on the L-gap surface state on Ag(111), analogous to Fig. 2. From the experimental data we obtain the parameters of the parabolic dispersion: $E_0=62$ meV, $m^*/m_e=0.40$, and $k_F=\pm 0.080$ Å^{-1}. The theoretical surface state dispersion (cf. Fig. 4) is given as a solid line in the lower panel (shifted by ≈ 70 meV toward E_F).

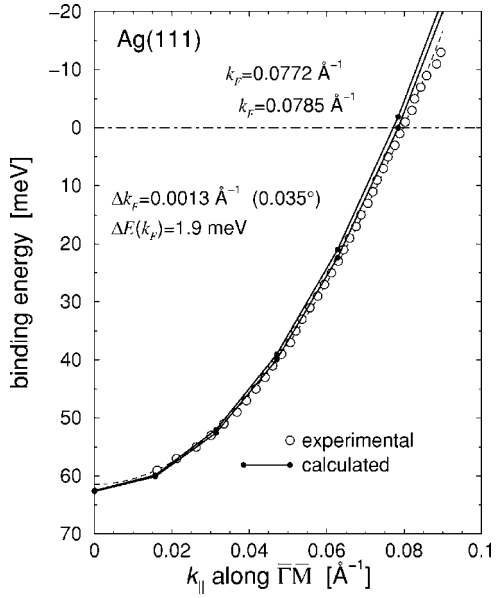

FIG. 4. Comparison of experimental (open circles) and calculated results (filled circles) of the L-gap surface state of Ag(111). The SO splitting in momentum is only $\Delta k=0.0013$ Å^{-1}, equivalent to an angle of 0.035° at Heı. At the Fermi level the corresponding splitting in the EDC's is $\Delta E=1.9$ meV.

its **k** dependence correctly—gives a SO splitting several orders of magnitude smaller than experimentally observed.

The middle panel of Fig. 2 shows the momentum distribution curve (MDC) at $E=E_F$, equivalent to a cut of the FSM at $k_y=0$. This presentation shows again the separation Δk, and allows one to determine accurately the linewidth $\Gamma(E_F)=0.014$ Å$^{-1}\equiv 0.38°$ (full width at half maximum) of the individual peaks in the MDC, which is mainly determined by the finite angular resolution $\Delta\theta$ of the spectrometer.

In the photoemission data on other noble-metal surfaces, an equivalent SO splitting of the surface state could not be observed, although an estimate from the atomic parameters[16] would give an SO splitting for Ag only about four times smaller than for Au. Such a splitting should be experimentally observable with the present resolution. Figure 3 shows the photoemission results of the L-gap surface state on Ag(111). The FSM in the upper panel consists of only one single circle, again surrounded by the dark ring of the band gap. Both the MDC in the middle panel and the gray scale plot of the dispersion $E(k_x)$ also show no indication of a splitting of the surface state. The lack of the splitting in the photoemission data on Ag(111) can be examined again by the comparison with local-density-approximation band-structure calculations. Figure 4 shows the results of the calculation together with the experimental dispersion extracted from the maxima in the MDC at different binding energies. In the case of Ag(111) the artificial surface-surface splitting of ≈ 1 meV (see above) is no longer negligible, and was therefore subtracted. Again there is an excellent agreement between experiment and theory. From the theory one would expect a splitting of about $\Delta k=0.0013$ Å^{-1} which is equivalent to an angular splitting of 0.035° at the used photon energy of $h\nu=21.23$ eV, one order of magnitude below our angular resolution of $\Delta\theta\approx 0.3°$. However, the SO splitting might be the reason for the slightly enhanced linewidth $\Gamma(E_F)=0.018$ Å$^{-1}\equiv 0.50°$ in comparison to the values of Au(111) and Cu(111) where under the same experimental conditions we obtain $\Gamma(E_F)=0.014$ Å$^{-1}\equiv 0.38°$.

Obviously there is a considerable quantitative difference between the energy splitting of the surface states and the spin-orbit splittings of the p states of a free atom, which amount to 470 and 110 meV, for Au $6p$ and Ag $5p$,[16] respectively. In the free atom the size of the splitting is determined by the gradient of the spherical Coulomb potential, that is significantly modified in the range of typical valence state energies in the solid. Compared to the atomic potential, the mean potential in the solid becomes more flat at higher energies, and the gradient decreases. Because the binding energy of the Ag(111) surface state is much smaller than for Au(111), the deviation of the surface state splitting from the atomic values is even larger. In other words, the shape of the radial wave function in the solid deviates from the atomic

wave function and reflects the delocalization of the valence states; the localized atomic character is reduced. Furthermore, one should note that the wave function of the surface state is not only of pure *p* character, but has a significant admixture from *s* states, which alone show no SO splitting.

We present a direct comparison of high-resolution photoemission data and a fully relativistic band-structure calculation of the *L*-gap surface state on Au(111) and Ag(111). The excellent quantitative agreement between experimental data and the results of the 23-layer slab calculation gives clear evidence that the splitting observed in the photoemission data on Au(111) is caused by spin-orbit interaction in the *sp* states at the surface, as it was first suggested by LaShell, McDougall, and Jensen. Experimentally, we could neither observe any influence of the herringbone reconstruction on the topology of the Fermi surface of the Au(111) surface state, nor a broadening of the spectral features. From the calculation for the Ag(111) state one can infer that in principle the splitting exists also in other noble-metal surfaces, but that it is in general too small to be experimentally observable in photoemission data.

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