

Hybridization between the unoccupied Shockley surface state and bulk electronic states on Cu(111)

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(Received 27 May 2011; published 23 August 2011)

Multiphoton photoemission, scanning tunneling spectroscopy, and first-principles electronic structure calculations have been applied to determine the dispersion of the occupied and unoccupied Shockley surface state of Cu(111). The dispersion deviates significantly from the paradigmatic parabolic behavior of quasi-free electrons with increasing energy above the Fermi level. Based on our calculations, we ascribe this deviation to the shift of the spectral weight of the surface state into the bulk, and of bulk states toward the surface, which leads to an enhanced hybridization between the states with increasing energy.

DOI: [10.1103/PhysRevB.84.073107](https://doi.org/10.1103/PhysRevB.84.073107)

PACS number(s): 73.20.At, 71.20.-b, 79.60.Bm

Electronic states in solids are strongly modified near the surface region. There, electrons can occupy additional, surface-localized states in the band gaps of the bulk electronic structure $E(\vec{k})$. Prototypical examples¹ are Shockley surface states and image-potential (IP) states in the bulk L gap of the (111) surfaces of the noble metals Cu, Ag, and Au.^{2–9} These states serve as model systems for the study of quasi-two-dimensional electron systems, where their specific dynamical,¹⁰ collective,¹¹ and spin-dependent properties¹² are studied.

Angle-resolved photoemission^{2–5,12} and scanning tunneling spectroscopy (STS)^{8,9,13,14} have revealed that the dispersion of the occupied Shockley surface state of Cu(111) can be well described by a quasi-free-electron behavior $E(k_{\parallel}) \propto k_{\parallel}^2/m_{\text{eff}}$, with an effective mass $m_{\text{eff}} = 0.4m_e$. The significantly *smaller* effective mass as compared to the free-electron mass m_e is ascribed to an intrinsic coupling of the surface state with bulk states, and this questions the general validity of a free-electron model over a wider energy range.

The model of a quasi-free-electron behavior for the description of Shockley surface states is a severe approximation, and its deficiency becomes obvious particularly for unoccupied states above the Fermi level. This unoccupied part at increasing k_{\parallel} was previously probed by angle-resolved inverse photoemission spectroscopy^{6,7} and later by STS studies.^{15,16} The conclusions that can be drawn from the inverse photoemission experiments on the dispersion of the unoccupied states are limited by a relatively poor energy and momentum resolution, but the STS measurements indicated a nonparabolic dispersion in the unoccupied part of the Shockley surface-state band. However, to the best of our knowledge, a first-principles-based, in-depth understanding of these deviations from the parabolic dispersion has not been reached yet.

We investigate the electronic dispersion of the Cu(111) surface state in the occupied and unoccupied regime by k_{\parallel} -resolving multiphoton photoemission (mPPE) measurements with a momentum microscope¹⁷ in combination with Fourier-transform STS (FT-STS) and relativistic first-principles calculations. Our combined application of these complementary techniques advances the understanding of the hybridization between Shockley surface states and the bulk electronic structure. Our calculations identify an energy-dependent variation of the spatial extension of the corresponding states. This

finding offers a first-principles-based understanding of the energy-dependent hybridization between surface and bulk states, and it leads to a reliable, quantitative description of the experimental electron dispersion relation.

We prepared clean Cu(111) surfaces by Ar-ion sputtering (at 2 keV) and annealing (900 K). The surface quality was checked by spatial imaging in a photoelectron emission microscope (PEEM), by atomically resolved scanning tunneling microscopy (STM), and by mPPE spectra. Figure 1 illustrates the principle of our measurements. The two-dimensional photoemission intensity distribution $I(k_x, k_y)$ at fixed energy E in Fig. 1(a) is obtained by a momentum microscope,¹⁷ which directly maps the energy-resolved in-plane momentum components k_x and k_y of photoelectrons emitted into the full hemisphere. We employ multiphoton photoemission, mPPE ($m = 2, 3$), where photoelectrons are excited by the second harmonics of a Ti:sapphire femtosecond laser with a single photon energy of $h\nu = 3.1$ eV and a pulse width of ~ 20 fs. All photoemission measurements were performed at 170 K in ultrahigh vacuum ($p < 8 \times 10^{-11}$ mbar). 2PPE probes the occupied states from below the Fermi level via a virtual intermediate state, as shown by the vertical arrows in the left-hand transition sketched in Fig. 1(c). At $E_F - 50$ meV in Fig. 1(a), the occupied surface state shows up in the 2PPE momentum microscope measurement as a circle, which is surrounded by a threefold distorted ring of the well-known *sp-sp* bulk transition.¹⁸ In comparison, the 3PPE process allows to populate and probe the unoccupied Shockley surface state, as indicated in the right-hand transition of Fig. 1(c). The schematic electronic structure on the right-hand side [Fig. 1(c)] also comprises the approximate parabolic dispersion of the surface state with the $m_{\text{eff}} = 0.4m_e$ (red, dashed line) as well as the true dispersion (blue, solid line).

In the crossover regime between the realms of 2PPE and 3PPE, from E_F to $E_F + 0.4$ eV, the mPPE experiments cannot reliably probe the dispersion, due to vastly different intensities of 2PPE (high-intensity) and 3PPE (low-intensity) processes. Here, STS bridges this energy gap and provides additional data to complement mPPE data of the occupied and unoccupied regime. The STS experiments were performed at 7 K in the vicinity of a step edge on clean Cu(111). Scattering of surface-state electrons at the selected step edge leads to the formation of standing-wave patterns in the local electron density.^{8,13–15}

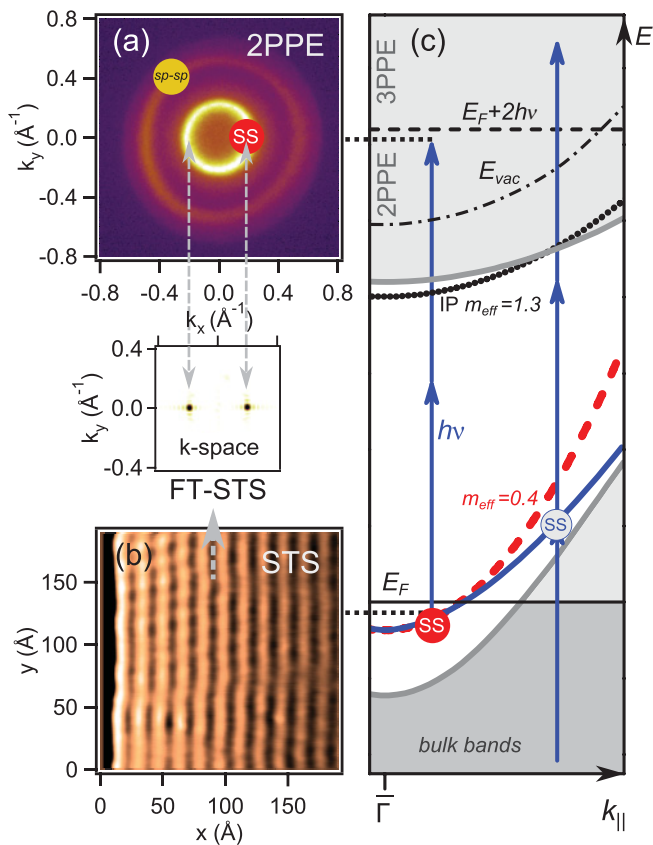


FIG. 1. (Color) Experimental mapping of the dispersion relation $E(\vec{k}_{\parallel})$ of surface states on Cu(111). (a) In multiphoton photoemission (2PPE and 3PPE), intensities $I(\vec{k}_{\parallel}, E)$ at fixed E (bright = high intensity) give access to the dispersion. (b) In scanning tunneling spectroscopy (STS), the standing-wave pattern at a step edge is Fourier transformed to \vec{k} space (FT-SPTS). (c) Schematic energy level system with Shockley state (SS), the image potential state (IP), and bulk-band regions (gray background). The experimental dispersion of the SS (blue solid line) deviates from a parabolic dispersion (red dashed line).

This spatial oscillation is observed in maps of the differential conductance dI/dV , which are referred to as STS images, shown in Fig. 1(b). A Fourier transformation (FT) of the STS image reveals the k vectors, which describe the standing-wave pattern. The dispersion of the surface-state bands is extracted by performing these measurements as a function of the gap voltage between sample and tip of the STM. The inset of Fig. 1 (left center, k space) displays the Fourier transformation of such a STS image at $E_F - 50$ meV, which yields \vec{k}_{\parallel} values for direct comparison with the data obtained by 2PPE. We find that both techniques lead to the same electron dispersion relation, as outlined below.

Figure 2(a) shows the 3PPE momentum map for a final state energy of 7.4 eV. Here, the unoccupied Shockley surface state appears as the outer circle, and the inner circle corresponds to the $n = 1$ IP state. The dispersion relation of these states is extracted from a cut of the combined 2PPE and 3PPE momentum maps at $k_y = 0$, which is shown in Fig. 2(b) and corresponds to the $\overline{M}-\overline{\Gamma}-\overline{M}$ direction. Neither in experiment nor in theory we found significant deviations from circular

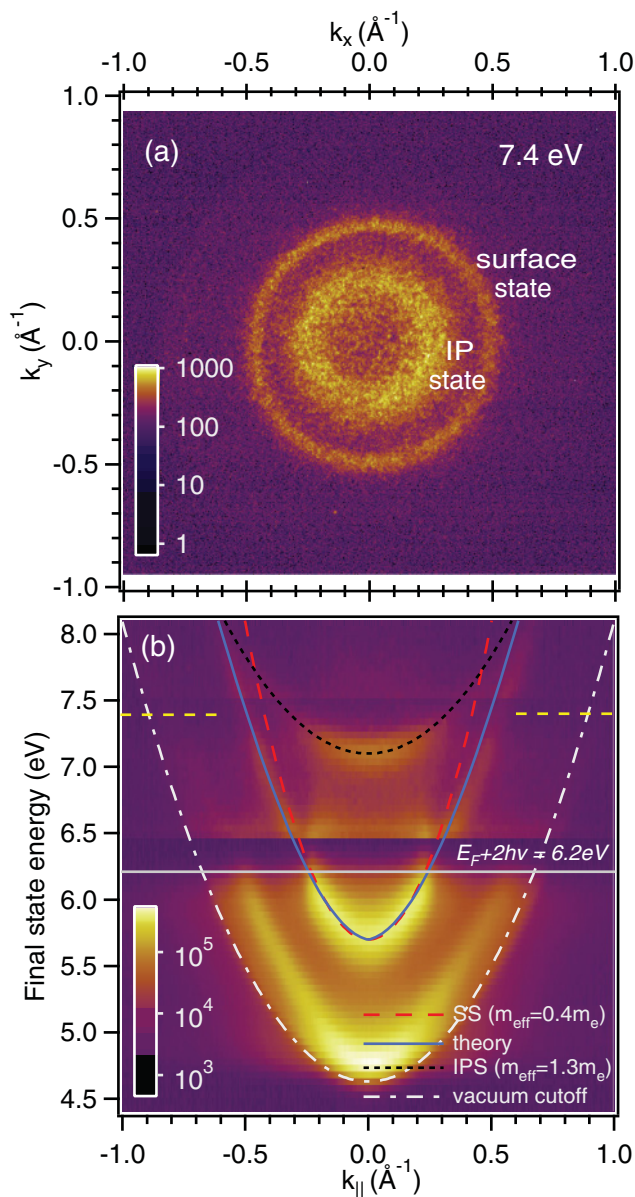


FIG. 2. (Color) Experimental 2PPE and 3PPE intensities from Cu(111) accessed by 3.1-eV photon energy. (a) Momentum map $I(k_x, k_y, E = 7.4$ eV) showing the unoccupied Shockley state (outer circle) and image-potential state (IP state, inner circle) in a logarithmic color scale. (b) Dispersion $I(\vec{k}_{\parallel}, E)$ along $\overline{M}-\overline{\Gamma}-\overline{M}$ of occupied and unoccupied Cu(111) bands showing $sp-sp$ bulk transitions, the Shockley state (broken line), and the image potential states (dotted line). The dashed-dotted line indicates the electrons with maximum parallel momentum for the respective energy, moving in the surface plane. Horizontal yellow lines at $E = 7.4$ eV indicate the energy of the momentum map of (a).

constant-energy contours for the surface states. The effective mass of the IP state was determined as $(1.35 \pm 0.1)m_e$, and it agrees well with previous work.¹⁹ There is no apparent deviation from the parabolic dispersion of the IP state for k_{\parallel} up to 0.5 \AA^{-1} .

However, in clear contrast to the IP state, the Shockley surface state shows a distinct change in the dispersion for larger wave vectors, as seen in Fig. 2(b). The (red) dotted line

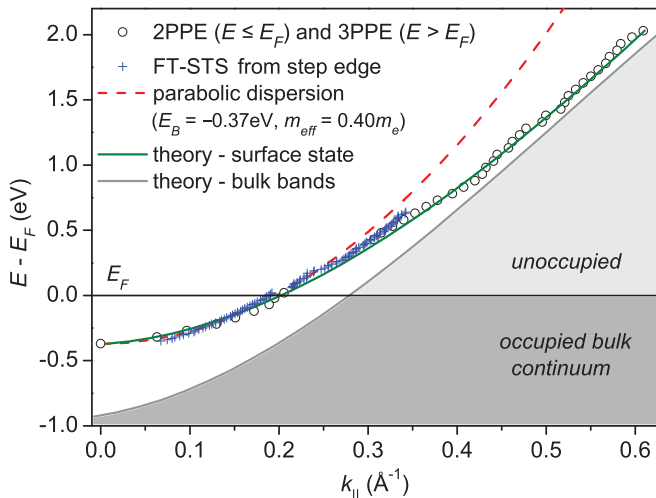


FIG. 3. (Color online) Dispersion of the surface state of Cu(111) in the bulk-band gap obtained by mPPE, FT-STs, and theory along the ΓM direction. The solid lines display the calculated dispersion of the surface state and the bulk-band edge. The experimental results are fitted by a quasi-free-electron-like parabolic dispersion (dashed red curve).

represents a parabolic dispersion, which is obtained from a fit of the experimental data in the occupied part of the Shockley state with $m_{\text{eff}} = 0.4m_e$.⁵ With increasing k_{\parallel} , the experimental Shockley-state dispersion data increasingly deviate from this parabola.

Figure 3 presents a summary of the experimental results by mPPE (open symbol) and STS (cross), which are complemented by first-principles calculations (solid line). We note that the calculation leads to a good description of the experimental dispersion relation over the complete energy range, whereas the parabolic dispersion leads to a reliable description only for the occupied states.

The first-principles surface electronic structure calculations have been performed within a relativistic multiple-scattering approach (layer Korringa-Kohn-Rostoker method), including spin-orbit coupling by the Dirac equation and relying on the Perdew-Wang exchange-correlation functional.²⁰ The electronic structure is analyzed by means of the layer-resolved spectral density $N_l(E, k_{\parallel})$ (l layer index) of the semi-infinite solid. To account for many-body effects beyond the local density approximation, the Kohn-Sham potentials have been rigidly shifted for sp and d states by $\Delta\Sigma_{sp} = +0.3$ eV and $\Delta\Sigma_d = -0.8$ eV, respectively. These self-energies have been deduced from experiments by Strocov *et al.*²¹ We note that while this is a simplified approach, it improves not only energy levels but also wave functions. It leads to an improved quantitative agreement of experimental and theoretical dispersion relations for surface and bulk states.

Figure 3 reveals that experimental data, first-principles calculations and parabolic dispersions are in very good agreement only up to E_F . Moreover, we see that the FT-STs experiments fit very well to the mPPE dispersion when we account for temperature effects between STS and mPPE,²² by referencing all measurements to the same binding energy of -0.37 eV, which is obtained in the calculation. More

importantly, with increasing k_{\parallel} after crossing the Fermi level, the Shockley-state dispersion significantly deviates from the effective-mass parabola in both theory and experiment. This behavior was interpreted previously as the influence of the surface periodic lattice potential in a tight-binding picture, where the hopping between neighbors leads to an expansion of the dispersion relation into cosine terms.¹⁵ While such a model can be used to fit the experimental results to some extent,^{15,16} it does not fully account for the k -dependent hybridization of the Shockley state with the bulk continuum. Instead, from our calculation shown in Fig. 3, which treats both the relevant bulk continuum and the surface states on the same footing, we can relate the nonparabolic dispersion to an approach of the surface state to the bulk-continuum edge and a concomitant hybridization between these two types of states.

To prove that the hybridization of the Shockley state with bulk states results in the deviation from the parabolic dispersion, we computed the layer-resolved spectral density $N_l(E, k_{\parallel})$ for selected energies shown in Fig. 4. The wave vector was chosen at the maximum of the surface state and the bulk-band edge maximum at the respective energies. For clearly separating the surface state and the bulk-band

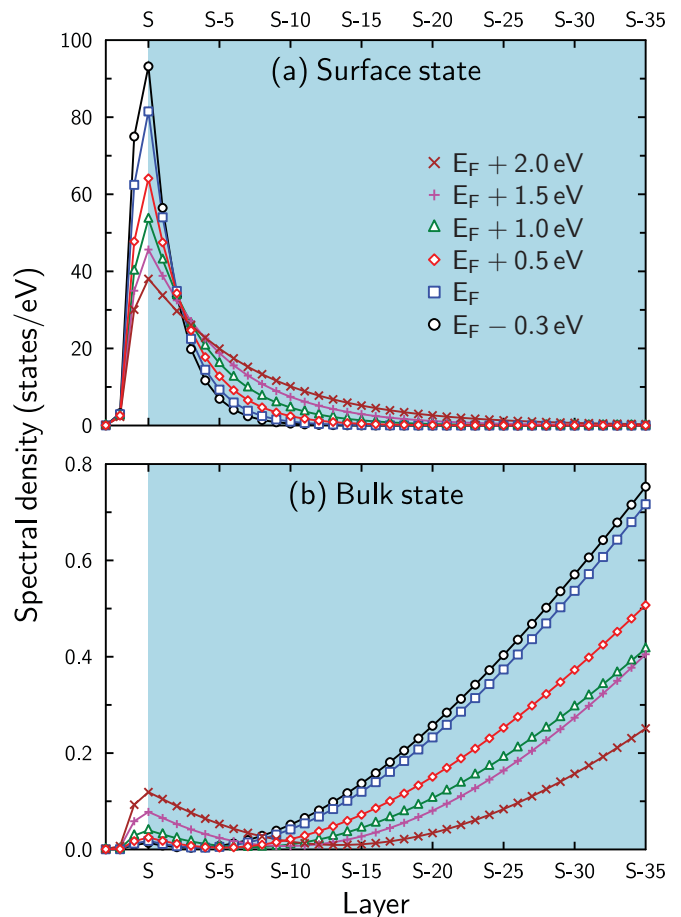


FIG. 4. (Color) Calculated localization of the L -gap surface state (a) and bulk state (b) at selected energies, as indicated in (a). The layer-resolved spectral density $N_l(E, k_{\parallel})$ is plotted as a function of the layer index l , with the surface layer at S. The spatial extension of the Cu bulk is indicated by the blue background.

contributions, especially at the higher energies, we artificially chose a very small lifetime broadening inherent to our Green's function approach. This results in very large layer-resolved weights for the surface state, as compared to that of the bulk-band edge. This weight mismatch is severely reduced for broadenings compatible with the experimental observations; however, then the surface and bulk contributions cannot be meaningfully separated in the theory at all energies.

As we see in Fig. 4, the convergence between the surface state and the bulk-band edge with increasing energy is connected with a profound change of the localization of the associated electronic states near the surface. At a small energy, e.g., at $E_F - 0.3$ eV, the surface state is localized within the first two surface layers, with a sizable spillout into the vacuum region. With increasing energy, the peak height at the surface layer **S** is strongly reduced, and simultaneously the penetration of the surface state into the bulk increases. The opposite trend is observed for the electronic states at the bulk-band edge, where it is found that the spectral weight of the bulk states *increases* at the surface **S**, whereas it decreases away from the surface and for larger wave vectors. This layer-resolved analysis offers an explanation on the electronic level for the enhanced hybridization between the Shockley state and the bulk states with increasing k_{\parallel} by identifying reciprocal trends in their spatial localization.

In summary, we investigated the surface electronic structure of Cu(111) by nonlinear mPPE and by FT-STs experiments, providing comprehensive information on the Shockley-state dispersion. We find a significant deviation from the quasi-free-electron dispersion in the occupied part. The extended mapping of the L -gap Shockley surface state on Cu(111), in combination with self-consistent electronic-structure calculations, clearly identifies the limits of simplified nearly-free-electron and tight-binding models. Our findings provide a fresh insight into the significant hybridization of the Shockley surface state and bulk states on Cu(111) with increasing wave vector and energy. Our calculations identify an increasing penetration of the surface state into the bulk near the bulk-band edge. A reciprocal behavior is found for the bulk electronic states, which become more pronounced near the surface. The lifetime broadening of the electronic states introduces a natural energy scale on which hybridization effects tend to smear out the distinction between surface and bulk states as a function of energy. Since the hybridization strength is increasing with decreasing separation of the surface band from the bulk edge, our results have implications for the calculation of k_{\parallel} -dependent electron lifetimes in both image potential and Shockley states.¹⁰ The interaction between surface states and bulk states is expected to cause reduced lifetimes, and this effect needs to be included to obtain an improved quantitative descriptions of systems influenced by such interactions.

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