Observation of the noble-metal L-gap surface state in Cu(311)

LETTER TO THE EDITOR

Observation of the noble-metal L-gap surface state in Cu(311)

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Abstract
The surface of a Cu(311) crystal is formed by a regular distribution of narrow (111) terraces, giving rise to a well-ordered step superlattice. Angle-resolved photoemission experiments demonstrate the existence of a surface resonance related to the L-gap noble-metal surface state. The surface resonance is observed at the edge of the surface Brillouin zone, regularly repeated with the superlattice periodicity, and its wavefunction is referred to the Cu(311) mean surface. The intensity distribution of the surface state in reciprocal space has been probed using different photon energies. The results can be well understood on the basis of a simple model involving the bulk band properties.

(Some figures in this article are in colour only in the electronic version)

Stepped metal surfaces have deserved attention as model systems for the growth of one-dimensional nanostructures [1–4]. The most important example of this kind are noble-metal surfaces vicinal to the (111) orientation. By changing the lateral periodicity (miscut angle), the periodicity of the step superlattice can be easily tuned. Obviously, not all the orientations are stable [5], but in many cases a high-quality superlattice can be produced. The (111) surface of noble metals is characterized by a prominent Shockley surface state, which originates at the L-point bulk band gap [6]. This surface state behaves as a two-dimensional electron gas, as it exhibits strong vertical confinement at the (111) surface. A step superlattice may induce lateral confinement in the surface electrons [7, 8], and affects their dispersion properties. The degree of confinement can be tuned by changing the miscut angle [9]. There are two different regimes reported for surfaces vicinal to Cu(111). For miscut angles below ∼7°, the surface state propagates parallel to the (111) terraces [10]. Above this critical angle (which corresponds to a critical terrace size of ∼17 Å), the surface state wavefunction is referred to the optical surface. The switch from one regime to the other has been related with the closing of the absolute surface band gap for miscut angles larger than ∼7°, which modifies the degree of vertical confinement of the surface state. Indeed, for miscut angles above the critical value,
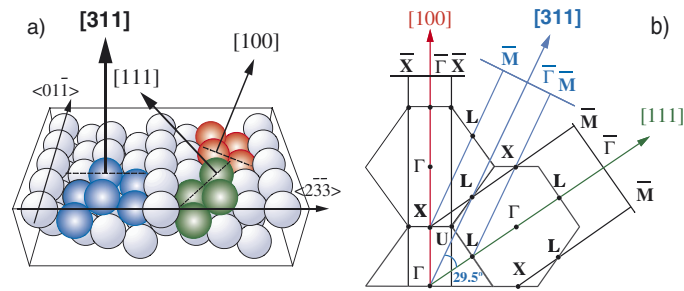
Figure 1. (a) Atomic-ball model representation of the Cu(311) surface, including the high-symmetry directions. Left grey balls (blue) highlight the (311) unit cell, while right grey at the front (green) and right grey at the rear (red) balls highlight the (111) and (100) unit cells, respectively. (b) Reciprocal space representation along the ΓLUX bulk plane, including the projection of bulk points along [311], [111] and [100] directions. Notice that surface $\overline{M}$-points are obtained by projecting bulk L high-symmetry points.

the surface state should become a surface resonance. It is an open question to what extent the surface state survives above this miscut angle, since it has been observed at least for miscut angles close to 15° [11, 12], and what would be the nature of the wavefunction of this surface resonance. Several other interesting effects have been reported. We may mention the change of the binding energy (BE) at the bottom of the surface band, which diminishes as the miscut angle increases [13, 14]; the observation of one-dimensional states [15]; the influence of the step superlattice in the Fermi surface [15, 16]; and recently the opening of surface band gaps related to the surface reconstruction of stepped Au(111) [17].

In this work, we analyse the surface electronic structure of a Cu(311) crystal using angle-resolved photoemission spectroscopy (ARPES). Photoemission spectroscopy is a powerful technique to probe the momentum dependence of electron energy bands. This analysis is combined with the use of different photon energies to provide a map of its intensity distribution in reciprocal space. We characterize first the bulk band structure of the crystal to conclude that, besides the expected bulk bands, there is a surface resonance related to the L-point bulk band gap. We demonstrate that, in spite of the small (111) terrace size in Cu(311) (only two atomic rows), there is surface localization of charge. From an analysis of its dependence with photon energy and its dispersion we conclude that this electronic state is of similar nature to the L-gap surface state, and that its wavefunction is referred to the mean (311) optical surface.

The photoemission experiments were done in an ultra-high-vacuum chamber equipped to perform ARPES and LEED measurements. It was mounted at the SU8 undulator beam line of SuperAco storage ring at LURE (Orsay, France). Data were taken with 70° incidence angle of the light. The Cu(311) crystal was electrochemically polished and cleaned *in situ* by cycles of Ar sputtering and annealing until a sharp LEED pattern was observed [18]. The Fermi surface was measured at the COPHEE end-station of the Swiss Light Source using a standard monochromatized He source [19].

Panel (a) of figure 1 shows an atomic-ball model of the Cu(311) surface. The (311) surface can be described as the limiting case of a stepped (111) surface, or, alternatively, as a border between (100)-like and (111)-like stepped surfaces. It is formed by narrow (two atomic lines width) (111)-like terraces, separated by (100)-like steps. The distance between steps is $d = 4.23$ Å (terrace width: 3.68 Å). The [311] bulk direction lies in the ΓLUX plane (see figure 1), and it is coplanar with the [111] and the [100] directions, forming with them angles of 29.50° and 25.24°, respectively. The surface Brillouin zone is obtained by projecting
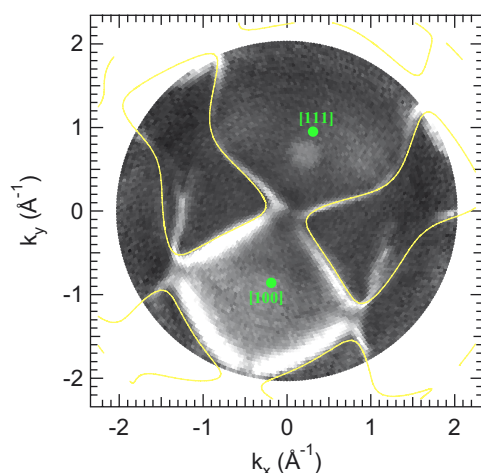
Figure 2. Fermi surface map from Cu(311) excited with He I-α, displayed on a grey scale (light colour means higher intensity). Direct transition lines represent a cut through the bulk Fermi surface. The projected theoretical cut of the Cu bulk sp band is shown as a light grey (yellow) line. The projection of the [111] and [100] directions are indicated by grey (green) points. The quasi-circular intensity close to the [111] projection lies at the surface Brillouin zone edge and it is due to the L-gap surface state.

the bulk reciprocal space along the (311) direction. The edge of the surface Brillouin zone is located at 0.740 Å^{-1} from $\overline{\Gamma}$.

Figure 2 shows a map of the Fermi surface measured with He I-α photons (21.22 eV). The high-intensity regions correspond to the crossings of the bulk Cu sp band [16]. For an easier comparison, the calculated Fermi Surface contour using a parameterized tight-binding model is over-imposed as light grey (yellow) lines[3]. The grey (green) points in the figure show the location of the [111] direction (region with 120° symmetry), and of the [100] direction (region with 90° symmetry), projected for the photon energy used. The experimental 'bone'-like shaped curves are well reproduced by the bulk Cu Fermi surface in figure 2 (note that no fitting has been made to the calculated Fermi surface). However, the intensity detected around 0.740 Å^{-1} along the [2$\overline{3}\overline{3}$] direction with approximately circular shape is not reproduced by the bulk Fermi surface contour. The band giving rise to this intensity shows a parabolic dispersion, with a binding energy bottom exactly at the edge of the Cu(311) surface Brillouin zone (which is the surface projection of a bulk L-point (see figure 1). These features agree well with the observed behaviour for a surface state in a vicinal surface.

In order to further characterize the origin of this peak, figure 3 shows energy distribution curves in the BE area closer to the Fermi energy, taken at different photon energies close to 70 eV and normalized to the photon flux. Angles are measured with respect to the [311] direction and along the [2$\overline{3}\overline{3}$] direction, which corresponds to $\overline{\Gamma M}$ and is perpendicular to the steps. The main feature is a peak near the Fermi level that has the highest intensity at 70 eV of photon energy. This peak exhibit a weak parabolic dispersion. The binding energy minimum appears at different angles as the photon energy is changed. The angular scale can be converted to parallel momentum $k_\parallel$, assuming momentum conservation parallel to the optical surface and using $k_\parallel = [(2m_e/\hbar^2)E_{kin}]^{1/2}\sin\theta$, where E_{kin} is the electron kinetic energy and θ is the

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[3] The Fermi surface contour is calculated using the freeware core *Flan1.0* implemented by V Joco, which uses a parameterized tight-binding bulk Fermi surface to calculate the Fermi contour measured with photoemission for a particular photon energy.
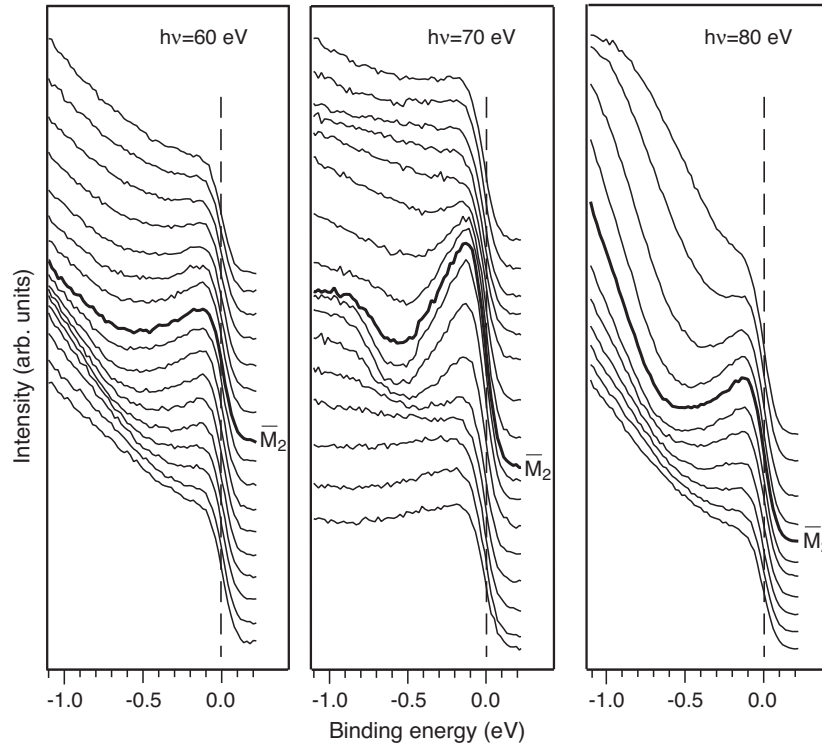
Figure 3. Energy distribution curves along the surface $\overline{\Gamma M}$ direction (perpendicular to steps) of Cu(311) taken with three different photon energies. In each panel the spectrum corresponding to second surface $\overline{M}$-point ($\overline{M}_2$) is highlighted. The surface state has maximum intensity at this high-symmetry point.

emission angle. The BE minimum appears at a constant value of parallel momentum equal to 2.225 Å^{-1}, which corresponds to the second surface $\overline{M}$ symmetry point (see also figure 4). We may compare this value with the one obtained from figure 2. We find that the two $k_{\parallel}$ values where the surface state is observed are split in reciprocal space by $\Delta k_{\parallel} = 1.49$ Å^{-1}, in agreement with the step lattice vector $2\pi/d = 1.485$ Å^{-1} of the Cu(311) surface. The appearance of a second parabola at $k_{\parallel} = 3\pi/d$ (as observed with higher photon energies) is due to the interaction of the surface state electrons with the step superlattice, which produces a new periodicity along the surface plane. These findings remind of similar effects observed in high-quality stepped Cu and Au surfaces, for lower miscut angles [9, 20, 21], but this is, to the best of our knowledge, the first observation of superlattice splitting in a stepped Cu surface with such a large miscut. The surface state band minimum is located at ~0.15 meV. This value agrees well with previous findings for other vicinal Cu(111) surfaces with 9° miscut (0.3 eV [10]), 11.5° miscut (0.26 eV [20]) and 15.8° miscut (0.17 eV [16]).

Photon-energy dependent photoemission experiments enable a three-dimensional wavevector analysis of the surface state wavefunction [9, 20, 21]. The bottom of the surface band θ_m and the measured E_{kin} are converted into $k_{\parallel}$ and $k_{\perp}$ (perpendicular momentum) values via $k_{\parallel} = [(2m_e/\hbar^2)E_{kin}]^{1/2} \sin \theta_m$ and $k_{\perp} = [(2m_e/\hbar^2)(E_{kin} + V_0) - k_{\parallel}^2]^{1/2}$ [10, 20, 21]. $k_{\perp}$ represents the wavevector perpendicular to the surface inside the crystal. It can be approximately obtained assuming a free-electron-like final state band in a constant inner
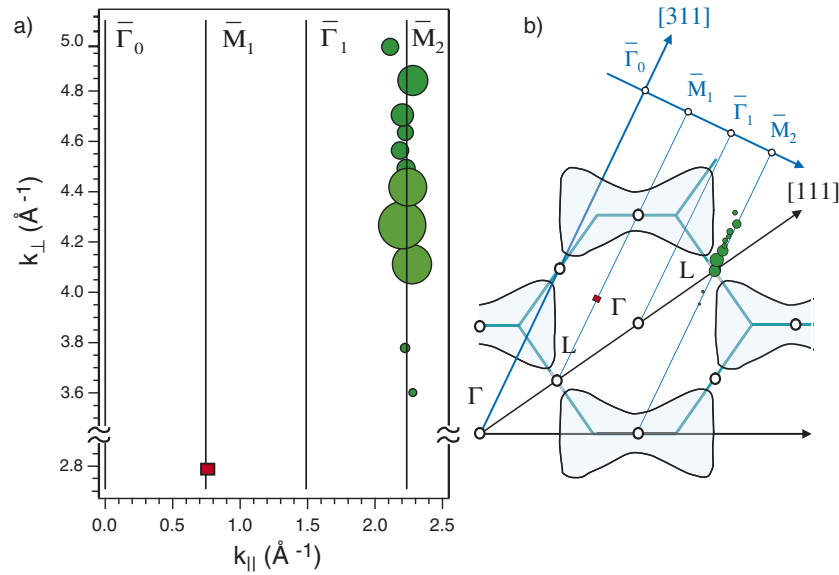
Figure 4. Reciprocal-space representation of the bottom of the surface resonance taken at 21.21 eV (red square) and at photon energies centred at 70 eV (green circles). The size of the circles is proportional to the intensity of the surface state, in logarithmic scale. Panel (a) shows a wavevector plot of the surface band bottom as a function of $k_\parallel$ and $k_\perp$ while in panel (b) the same data are represented in the ΓLUX bulk plane (see text for details).

potential $V_0 = -13.5$ eV [10]. Figure 4 shows the $k_\parallel$ and $k_\perp$ values for the data of figure 3, and also for several other photon energies. By covering a broad photon energy range, the distribution in $k_\perp$ of the surface state intensity is probed. Data points in figure 4 line up at π/d and $3\pi/d$ along the (311) direction, as expected for p_z-like surface states of Cu(111) vicinals [21] with a miscut angle larger than 7°, because in this case the surface state wavefunction propagates along the average surface.

The size of the green circle data points in figure 4 is proportional (in logarithmic scale) to the photoemission intensity normalized to the photon flux[4]. The photoemission intensity is maximum for transitions close to the L-point of the bulk band structure. The spectral map in figure 4 qualitatively reflects the Fourier distribution of the surface state wavefunction in the vicinal surface. In the direction parallel to the surface and perpendicular to the steps, the surface state is a Bloch wave of the step lattice with $k_\parallel = G/2 = \pi/d$. In the direction perpendicular to the surface, the $k_\perp$ broadening corresponds to an evanescent wave with the fundamental frequency $k_\perp = k_L$. The relative intensity of the surface state depends on the spectral weight of the component of the wavevector perpendicular to the surface. Thus, the intensity distribution observed in figure 3 can be understood in view of figure 4. As in LEED [22], the intensity peaks for in-phase interference, but at variance with LEED, the maxima in photoemission appear at the projection of L bulk points.

While $k_\parallel$ is a good quantum number for the description of the surface state bands in a vicinal surface, $k_\perp$ is strongly broadened due to the electron confinement at the surface region. The distribution of experimental points in figure 4 directly describes a surface-state wavefunction delocalized along the mean Cu surface and modulated by the step superlattice

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[4] Note that the surface state intensity measured with the He I line cannot be easily related with the intensities measured with synchrotron light, due to the different polarizations of the light.

periodicity. The state should be described more properly as a surface resonance, because it appears outside the bulk band gap. Interestingly, in spite of the high density of steps and the large distance to the [111] direction, spectral intensity with surface resonance features is still detected for the (311) surface.

In summary, the surface electronic states of a Cu(311) crystal have been probed using photoemission spectroscopy. The L-gap Cu surface state found reproduces the step-induced superlattice periodicity. When probed along the surface normal, the photoemission intensity is maximum in the vicinity of bulk L-points. The periodicity and intensities observed are rationalized in a simple model involving the step superlattice properties and bulk band parameters.

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