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d-like surface-state bands on Cu(100) and Cu(111) observed in angle-resolved photoemission spectroscopy

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Surface states at the top of the bulk *d* bands of Cu(100) and Cu(111) single crystals have been observed using angle-resolved photoemission spectroscopy. The measured dispersion of the surface-state bands falls in absolute energy gaps of the projected bulk band structure near the symmetry point $\bar{M}$ of the two-dimensional Brillouin zone, for both faces. Since the parent energy gaps are not caused by the hybridization of crossed energy bands, the observed states are of the Tamm rather than the Shockley type; surface states of the latter type have been observed before in *sp* gaps of several noble metals. Tamm states require a sufficiently strong surface "perturbation." Only the self-consistent calculations of Gay, Smith, and Arlinghaus recently reported for Cu(100) contain surface states in the energy–wave-vector region studied here. The observed peaks are very narrow, due to their energy location above the bulk *d*-band continuum as well as the good angle and energy resolution of our spectrometer.

I. INTRODUCTION

The electronic structure of crystalline copper has been extensively studied by the technique of angle-resolved photoemission spectroscopy.[1-10] Within the direct model, and assuming an ideal surface, the simultaneous measurement of emission angles and energies permits the identification of $\vec{k}_{\parallel}$, the surface projection of the wave vector, for each bulk transition. The perpendicular component $k_{\perp}$ can be approximately inferred[5] from accurate energy-band calculations[11] or from assumed free-electron final bands[12] or, in the case of zone-boundary transitions, by searching a set of energy distribution curves for critical-point behavior.[4] A purely geometric method[9,13] for determining the three components of the wave vector, initially proposed by Kane,[14] uses angle-resolved data from two or more low-index faces. The use of polarized light[2-6] in conjunction with selection rules[15] is a further tool for clarifying the symmetry of observed interband transitions. Through systematic application of these techniques, a rather complete picture of the bulk energy-band structure of copper has been obtained. Close agreement between measured and calculated energy bands is obtained when a self-energy correction[11] is applied to the final- and initial-state dispersion ($m^*/m = 1.08$).

Attention has turned recently to the surface electronic structure of the noble metals, following the observation by Gartland and Slagsvold[6] of a surface peak in the angle-resolved photoemission spectra of Cu(111). The peak is observed at small polar angles of emission, in an *sp* gap of the projected bulk band structure (PBBS) near the Fermi energy E_F. The polarization dependence[6,15] of the emission confirms that the surface state is derived from bulk energy bands of Λ_1 symmetry for normal emission ($\vec{k}_{\parallel} = 0$). Surface states of this type have also been identified on Ag(111) and Au(111) for near-normal emission.[7,16] On other low-index faces of the noble metals, *sp* gaps extending below E_F exist near special points of the two-dimensional surface Brillouin zone (SBZ). In these gaps, which are also associated with the L gap of the bulk bands, surface states have been observed for Cu(110),[8] Cu(112),[17] and the (100), (110), and (112) faces of gold.[18] These findings confirm the theoretical prediction of Shockley,[19,20] that surface states tend to occur in energy gaps caused by the hybridization of "crossed bands", e.g., in *sp* gaps for which the lower band has odd symmetry at the zone boundary. This is the situation encountered for *sp* gaps at the L point in noble metals: The $L_{2'}$ level is found at the lower band edge, while the symmetric state L_1 is at the upper edge of the gap. Calculations for *d*-band metals, for example Cu(100),[21] W(100),[22] W(110), and W(111),[23] show that surface states also tend to appear in *sd* hybridization gaps of the PBBS. Tomášek and Pick[24] have emphasized that a knowledge of the PBBS and its energy gap structure is an important first step towards elucidating the existence and nature of surface states.

We have observed a different type of surface state for Cu(100) and Cu(111), which occurs in nonhybridizational energy gaps of the PBBS.[25] The identification of these states requires good angle and energy resolution for the photocurrent owing to their proximity to the bulk band edge, as well as the utilization of several tests of the surface character of the observed peaks. The surface states are observed at or above the top of the bulk *d* bands, i.e., at about 2 eV below E_F, and are located near the $\bar{M}$ point of the SBZ for each face. The parent energy gaps are associated with the *X* point of the three-dimensional Brillouin zone, where the *d* bands have their maximum energy. Shockley's model[19] does not apply to such states in nonhybridizational gaps. Instead we interpret our observations in terms of the so-called Tamm surface state,[20,26] whose existence requires that the surface "perturbation" of the one-electron potential be sufficiently strong compared with the bandwidth. Although several calculations of the surface electronic structure of Cu(100) (Refs. 21, 27, and 28) and Cu(111) (Refs. 29 and 30) have appeared, only the self-consistent *a priori* calculations by Gay, Smith, and Arlinghaus[28] for Cu(100) contain a surface state at the top of the bulk *d* bands. The surface-state band in the latter calculation has a dispersion in reasonable agreement with our observations. A second self-consistent calculation,[30] for Cu(111), does not contain the band we observed near $\bar{M}$.

A brief discussion of the angle-resolved photoemission experiment is given in Sec. II. Our results for Cu(100) and Cu(111) are presented in Secs. III and IV, respectively, together with our theoretical interpretations. Concluding remarks are given in Sec. V.

II. EXPERIMENT

The experimental apparatus described in Ref. 31 was modified to allow rotation of the sample; a schematic drawing of the improved setup is given in Fig. 1. The instrument consists of two ultra-high-vacuum chambers, connected by a bakeable gate valve, which can be pumped separately: (a) a preparation chamber containing an argon ion gun and a low-energy electron diffraction (LEED) system and (b) the analyzer chamber to which has been added a grazing incidence electron gun for exciting Auger electron emission. The sample is fixed to a manipulator and can be transferred from the preparation chamber to the measuring position in front of the hemispherical analyzer. Sample annealing temperatures of about 800 K can be reached by the use of a heating system mounted in the sample holder. As shown in the inset of Fig. 1, the manipulator allows independent rotation of the sample about two axes; the two rotary motion feed throughs are connected to stepping motors and can be controlled by a computer system. The sample is introduced into the spectrometer without breaking the vacuum in the analyzer chamber. After baking, the samples are cleaned *in situ* by repeated cycles of argon ion bombardment and heating. Surface geometry and orientation can be checked with the LEED system, while surface cleanliness is monitored through the Auger spectrum.

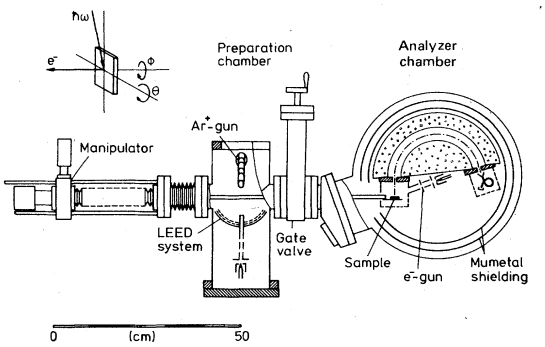

FIG. 1. Sketch of the angle-resolved photoemission apparatus, including the sample preparation chamber and the analyzer chamber. Details are given in the text.

The hemispherical analyzer is described in detail in Ref. 31 and has an energy resolution of better than 60 meV full width at half-maximum (FWHM). The angle resolution was improved to be 2° (half-angle of the acceptance cone). Since the energy resolution is an almost linear function of the kinetic energy of the photoelectrons, except near threshold, we extrapolated peak widths to zero kinetic energy in order to estimate the natural width of the surface-state peak (see below).

Radiation was obtained from rare-gas resonance lines of He (21.22 eV) and Ne (16.85 eV). This unpolarized radiation strikes the sample at nonnormal incidence, in general; the emission plane coincides with the plane of incidence of the light. In this configuration the optical electric field has nonvanishing components both parallel and perpendicular to the emission plane. Thus, while most emission data were collected in mirror planes of the crystal, the selection rules[15] do not exclude transitions from any initial states. No attempt was made to correlate intensity variations and the changing components of the optical electric field. Instead we focused on the dispersion of peaks in the angle-resolved energy distribution curves (AREDC's) with the emission angles, in order to relate the transitions to bulk and surface electronic structure.

The copper single crystals were spark cut along the (100), (110), and (111) faces, and were oriented within an accuracy of 1° as deduced from the Laue diffraction patterns. After mechanical and elec-

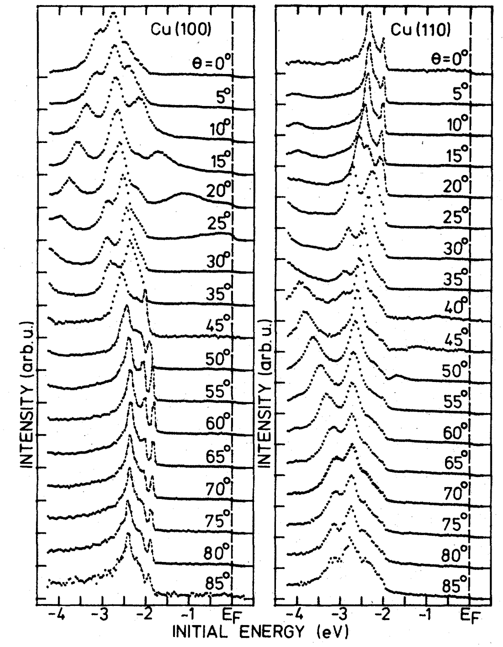

FIG. 2. AREDC's of Cu(100) and Cu (110), at the photon energy 21.22 eV. For both faces, the emission azimuth is in the (001) mirror plane containing the symmetry points Γ, *X*, *W*, and *K* of the Brillouin zone.

trolytical polishing, the samples were cleaned *in situ* as described above.

A test of the surface character of AREDC peaks on Cu(100) was performed by admitting dry air into the sample chamber through a gas-inlet system. The coverage, primarily due to oxygen, was monitored by examining the Auger spectra. Exposure to 5200 L (1 langmuir $= 10^{-6}$ Torr sec) produced a coverage of approximately half a monolayer.

III. Cu(100)

AREDC's for emission in the (001) mirror plane of Cu(100) and Cu(110) single crystals are given in Fig. 2; the photon energy is 21.22 eV. Polar angle variation within each set of curves are equivalent to variation of the magnitude of $\vec{k}_\parallel$ according to the relation (in the extended zone scheme of the SBZ)

$$|\vec{k}_\parallel| = (2m/\hbar^2)^{1/2}\,(E_i + h\nu - \Phi)^{1/2}\sin\theta\,, \qquad (1)$$

where E_i is the initial energy measured relative to E_F, $h\nu$ is the photon energy, Φ is the work function, and θ is the polar angle of emission measured with respect to the surface normal. Although $\vec{k}_\parallel$ varies within a single AREDC's because E_i does, a definite value can be assigned to the centroid of an emission peak, within an accuracy determined by the angle resolution. Mirror plane emission is associated with a planar cut through the Brillouin zone of the bulk, as shown in Fig. 3 for the (001) plane, which passes through the symmetry points Γ, *X*, *W*, and *K*. Insets in Fig. 3 identify the symmetry points of the SBZ for the (100) and (110) faces. Note that each point $\vec{k}_\parallel$ within the SBZ corresponds to a line in three-dimensional $\vec{k}$ space perpendicular to the surface plane. The (001) plane (the emission plane for the AREDC's of Fig. 2) is associated with the $\bar{\Gamma}\bar{\Sigma}\bar{M}$ symmetry line of the (100) SBZ and the $\bar{\Gamma}\bar{\Sigma}\bar{X}$ line of the (110) SBZ; normal emission occurs at $\bar{\Gamma}$ in both cases.

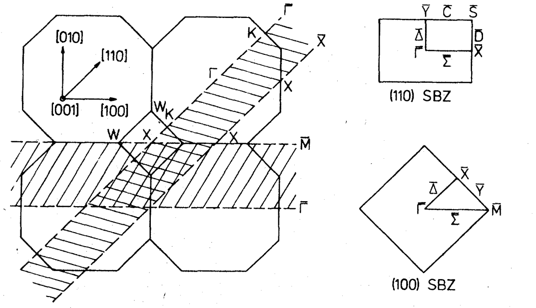

FIG. 3. Γ*XWK* plane of the bulk Brillouin zone. Emission from the shaded strips can contribute to the AREDC's shown in Fig. 2, for Cu(110) (diagonal strip) and Cu(100) (horizontal strip). The SBZ for each face is also given.

The AREDC's of Cu(100) exhibit two peaks which can be related to bulk energy band transitions using a geometrical method.[9,13,14] In this method the two sets of AREDC's given in Fig. 2 are examined for energy-coincident pairs of emission peaks. Since the photon energy, the kinetic energy, and the emission plane are fixed, one may assume that both members of a peak pair are associated with the same direct transition in $\vec{k}$ space. Then the wave vector $\vec{k}$ may be reconstructed geometrically, from its known projections $\vec{k}_\parallel$ on the two crystal faces. Thus it is possible to obtain a direct measurement of *E* versus $\vec{k}$, without reference to the computed energy bands.[9] As an example application of the method, consider the narrow peak at −2.03 eV observed in normal emission from Cu(110); this emission must originate along the Γ*KX* line in Fig. 3 since $\vec{k}_\parallel$ vanishes. A peak at the same energy is found in the AREDC's of Cu(100) when the polar angle $\theta = 60°$, corresponding to the symmetry point $\bar{M}$ of the (100) SBZ, i.e., the *WXW* line in $\vec{k}$ space. Thus a bulk transition of energy −2.03 eV must occur at the intersection of the Γ*KX* and *WXW* lines, namely the *X* point:

this energy is in excellent agreement with previous measurements of the X_5 level.[5] This peak and its lower-energy partner have been examined in detail using the described method. Their dispersion but not their position is in excellent agreement with the computed energy bands of Burdick.[32] Measurements by Dietz and Himpsel[5] have shown that the X_5 level has a spin-orbit splitting of 0.1 eV. Most of the observed transitions do not occur on symmetry lines in $\vec{k}$ space but lie within strips shown in Fig. 3 by the shaded regions.

A narrow peak observed in the AREDC's of Cu(100) for larger polar angles does not appear in the emission data of the (110) face, as seen in Fig. 2. The absence of this peak cannot be due to the selection rules,[15] since the incident light is unpolarized. Moreover the energy of the peak is −1.8 eV at $\theta = 60°$, the $\bar{M}$ point of the (100)SBZ, clearly above the d-band maximum at −2.03 eV. In fact the E-versus-$\vec{k}_{\parallel}$ dispersion of this peak lies entirely within an absolute energy gap of the PBBS,[33] as shown in Fig. 4. This behavior is required for a true surface state. To confirm the surface character of the peak we also measured its dispersion at the photon energy 16.85 eV. Our result, that the dispersion is independent of photon energy (see Fig. 4), is expected for a surface but not a bulk excitation (the dispersion of the two bulk d-band peaks depended on the photon energy).

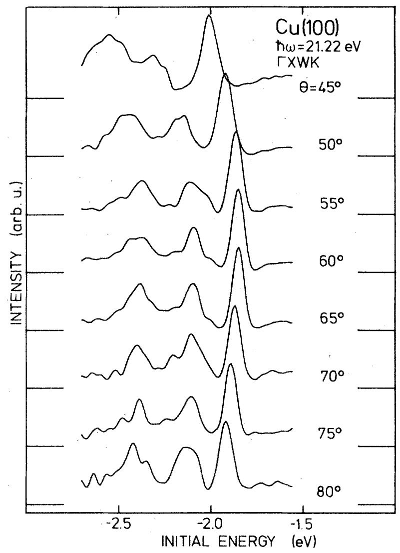

FIG. 5. Angle-resolved difference spectra [emission of the contaminated surface (2500-L air) subtracted from that of the clean surface] for Cu(100), obtained at the photon energy 21.22 eV.

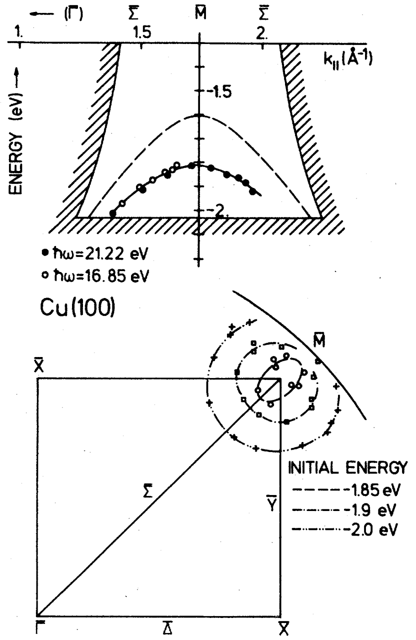

FIG. 4. Measured dispersion of the surface-state band on Cu(100), for photon energies 16.85 and 21.22 eV, along the $\bar{\Sigma}$ line of the SBZ. The sd gap of the PBBS is bounded by the shaded region, and the dashed line is a surface-state band computed in Ref. 28. The lower figure contains constant initial-energy lines of the surface state; the region of the SBZ beyond the curved solid line is not accessible at the photon energies we used.

An additional test of the surface character of the −1.8-eV peak was performed by admitting dry air into the sample chamber, as described in Sec. II. Our results, given in Fig. 2 of Ref. 10, are presented as difference spectra in Fig. 5. The curves were obtained by subtracting AREDC's of the contaminated sample from those of the clean surface, for emission near the $\bar{M}$ point. The contamination curves were normalized to the emission intensity of the lower-energy bulk peak. Two positive peaks are obtained in Fig. 5, corresponding to emission from the clean surface which is strongly suppressed by oxygen adsorption. The intense peak just above −2 eV in Fig. 5 confirms the surface character of the corresponding peak in the Cu(100) emission data of Fig. 2. The other major peak in the difference spectra, at −2.1 eV, is due to a pronounced dip in the contamination spectrum, on the low-energy side of the uppermost bulk peak. This behavior may be indicative of bulk states with enhanced surface amplitude on the clean metal. Such surface resonances were predicted by Gay, Smith, and Arlinghaus[28] over a wide region of the SBZ near the top of the bulk d bands.

The dispersion of the surface state band in the SBZ, shown in Fig. 4, is in good agreement wi the *a priori* self-consistent-field calculations[28] for a nine-layer slab simulating Cu(100). The computed dispersion rises to −1.6 eV (we shifted the computed bands[28] in order to align the *d*-band edge with the measured value at −2.03 eV) compared to the measured energy −1.8 eV at $\bar{M}$; it has the same shape as the measured dispersion, and merges into the *d*-band continuum along $\bar{\Sigma}$, well within the absolute energy gap of the PBBS.[33] Constant energy contours of the surface-state band were obtained from several sets of AREDC's with (a) fixed polar angle θ and variable azimuthal angle, or (b) fixed azimuth and variable θ angle; the results are also given in Fig. 4. The energy surface has reflection symmetry in the ΓXWK plane (the $\bar{\Sigma}$ line) and is almost isotropic about the $\bar{M}$ point.

We emphasize that the region of the SBZ where the surface state is observed is not large. As a result its contribution to the angle-integrated spectra of Cu(100) is probably small.[34] In the computed surface density of states, the surface state produces a rather weak shoulder above the *d*-band edge.[28] The observed attenuation at this edge[34] by chemisorption may be partly due to a surface resonance within the bulk bands, which extends over a wide region of the SBZ. Earlier angle-resolved studies[35] were restricted to normal emission ($\bar{\Gamma}$) and emission in the −40° azimuth relative to the (001) plane. The latter geometry corresponds to an emission plane which does not enter the region near $\bar{M}$ where we observed the surface state.

We now discuss the line shape of the surface-state peak in Fig. 2. As noted in Ref. 10, this peak is narrower than any previously observed photoemission peak in metals. The observation of a narrow peak requires good angle as well as energy resolution, since the spread of angles accepted by the analyzer corresponds to a finite region of the SBZ, while the surface-state energy depends on $\vec{k}_{\parallel}$. The natural linewidth is determined by the lifetime of the photoexcited hole, since for surface excitations a continuum of final states is available. The major decay channel for the hole is provided by the Auger excitation of electron-hole pairs. The phase space available for Auger decay increases rapidly towards the bottom of the *d* bands, and has a pronounced threshold at the upper *d*-band edge, since for initial states above this edge no *d*-band excitations are allowed by energy conservation. Then the Auger decay rate is determined by the *sp*-band density of states in the vicinity of E_F, which is much lower than the *d*-band density of states. The increase of linewidth towards the bottom of the *d* bands[5] is evident in Fig. 2.

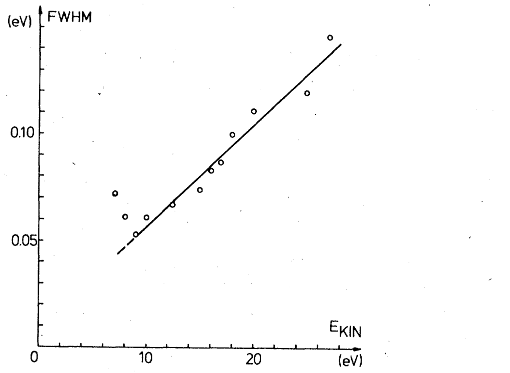

FIG. 6. FWHM of the $\bar{M}$ surface-state peak on Cu(100), extrapolated as a function of the kinetic energy of the (retarded or accelerated) photoelectrons.

To estimate the natural linewidth of the surface-state peak we analyzed data taken near the $\bar{M}$ point (where the dispersion is flat). Since the energy resolution of the spectrometer increases essentially linearly with the kinetic energy of the photoelectrons, we studied the emission for a succession of retarding and accelerating potentials and extrapolated the linewidth to zero kinetic energy, as indicated in Fig. 6. We fit a straight line to the data above 9 eV; below this energy the data deviate appreciably from the straight-line behavior due to the influence of stray fields in the analyzer region. From the zero kinetic energy intercept we obtained an estimate of the natural linewidth of 6 meV. As mentioned above, the bulk peaks are somewhat broader because they lie below the *d*-band Auger threshold.

Some insight into the physical nature of the surface state can be gained by considering the bulk energy bands of copper[30] as shown in Fig. 7. The PBBS of Cu(100) was computed by Bertoni *et al*[33]

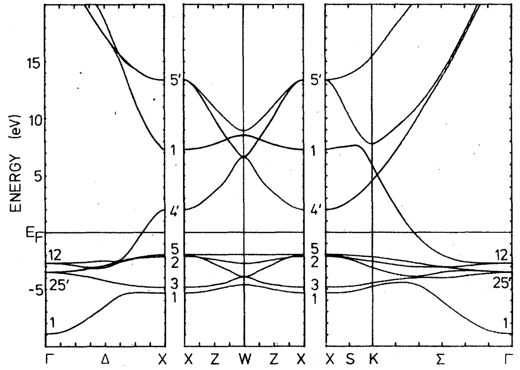

FIG. 7. Energy bands of bulk copper along selected symmetry lines, as computed in Ref. 32.

by fitting the results shown in Fig. 7 to a tight-binding interpolation scheme.[36] The absolute gap near $\overline{M}$ in Fig. 4 can be traced to the large gap between the d bands and the sp band, which rises to several eV above E_F along the entire Brillouin zone boundary (with the important exception of the region around the L points where the Fermi surface has necks which contact the (111) planes). In particular, the $\overline{M}$ point is associated with the Z line WXW as shown in Fig. 3. Along this line the uppermost d band Z_2 is extremely flat (see Fig. 7), implying that its Bloch function consists of highly localized layer orbitals parallel to the (100) plane, with virtually no interaction between adjacent layers. In fact, among the d-like orbitals only the d_{yz} function has Z_2 symmetry, and this is strongly confined to the y-z plane. A Tamm surface state can arise from the Z_2 band if the atomic potential in the surface plane is not as deep as that in the bulk. Then the d_{yz} orbitals of the surface atomic layer are simply pushed into the bulk gap, creating a highly localized surface state.

The dispersion and eventual disappearance of the surface-state band can be traced to the behavior of the bulk bands away from the Z line. The Z_2 band itself acquires a larger width, which increases as $\vec{k}_\parallel$ is varied away from $\overline{M}$. In the Tamm model,[20,26] when this width becomes too large compared with the surface perturbation, the surface state merges into the continuum. Our physical picture of the surface state is consistent with the earlier calculations, although the symmetry of this state was not discussed in Ref. 28. To confirm these ideas it would be useful to obtain AREDC's in polarized light. Since the uppermost d band has odd reflection symmetry in the ΓXWK mirror plane (i.e., the $\overline{\Sigma}$ line), the surface-state emission should vanish for optical polarization parallel to the mirror plane.[15]

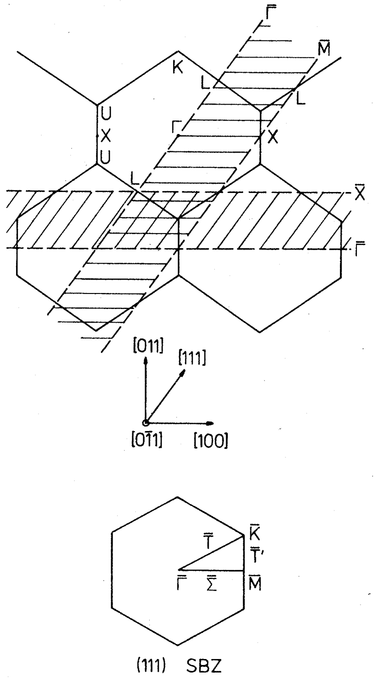

FIG. 8. ΓLUX plane of the Brillouin zone; bulk emission from the shaded strips can contribute to the AREDC's shown in Fig. 9, for Cu(111) (diagonal strip) and Cu(100((horizontal strip). The (111) SBZ is also given.

IV. Cu(111)

A surface-state band was also observed at the top of the bulk d bands of Cu(111). This state was identified by comparing AREDC's of Cu(111) and Cu(100), for emission in the (0$\overline{1}$1) mirror plane. As shown in Fig. 8, the emission plane contains the symmetry points Γ, L, U, and X of the three-dimensional Brillouin zone. The SBZ symmetry points $\overline{\Gamma}$ and $\overline{M}$ for Cu(111), as well as $\overline{\Gamma}$ and $\overline{X}$ for Cu(100), are associated with lines in the ΓLUX plane.

AREDC's for Cu(111) and Cu(100) are presented in Fig. 9. The photon energy is 21.22 eV, the azimuth is defined by the (0$\overline{1}$1) plane, and the polar angle variations correspond to variations of $\vec{k}_\parallel$ along the $\overline{\Gamma}\overline{\Sigma}\overline{M}$ line for Cu(111), and the $\overline{\Gamma}\overline{\Delta}\overline{X}$ line

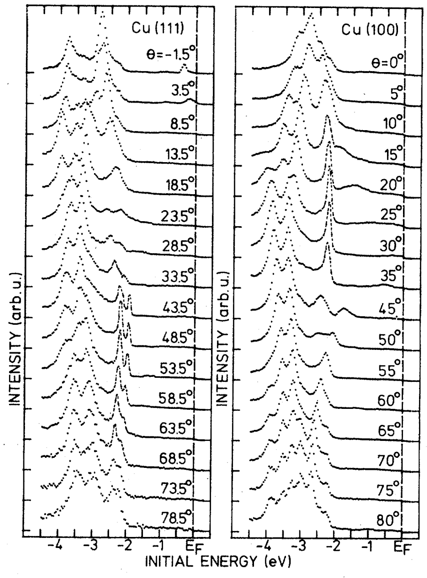

FIG. 9. AREDC's for Cu(111) and Cu(100), at the photon energy 21.22 eV. For both faces, the emission azimuth was in the (0$\overline{1}$1) mirror plane containing the symmetry points Γ, L, U, and X of the Brillouin zone.

for Cu(100). Notice that the emission data of the (100) face do not contain the surface-state band discussed in Sec. III, since the $\overline{\Gamma}\overline{\Delta}\overline{X}$ line does not pass through the region around $\overline{M}$ where we observed the surface state (see Fig. 4).

The AREDC's of Cu(111) contain two narrow peaks near −2 eV, for polar angles of emission near 50°. While the lower energy peak is also observed in the (100) data, near $\theta = 20°$, the higher-energy peak ($E_i \geq -2.0$ eV) appears only for emission from the (111) face. Since no bulk initial states are forbidden by the selection rules in our geometry, the higher-energy peak is attributed to a surface state. The lower-energy peak ($E_i \leq -2.2$ eV) is due to the bulk transitions near the LX line of the Brillouin zone, corresponding to the $\overline{M}$ point of the (111) SBZ, as determined by the geometrical method.[9,13,14]

To confirm the surface interpretation of the upper peak in the (111) data of Fig. 9, we measured its E-versus-$\vec{k}_{\parallel}$ dispersion for two photon energies, 16.85 and 21.22 eV. As seen in Fig. 10, the dispersion is independent of the photon energy and falls in an absolute energy gap of the PBBS. As in the (100) case, the gap is not caused by hybridization, since the free-electron sp band is several eV above E_F in a wide region of the SBZ near the $\overline{M}$ point. We interpret the uppermost peak of the (111) data as emission from a d-like surface-state band. Though the dispersion falls below the X_5 level at −2.03 eV it does not enter the bulk continuum. The long lifetime of the photoexcited hole is again attributed to the small phase space available for Auger excitations of the d electrons.

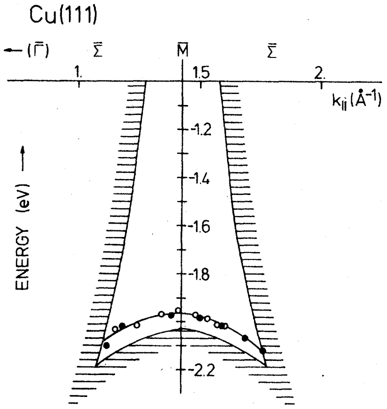

FIG. 10. Measured dispersion of the surface-state band on Cu(111), for photon energies 16.85 and 21.22 eV, along the $\overline{\Sigma}$ line of the SBZ. The sd gap of the PBBS is bounded by the shaded region.

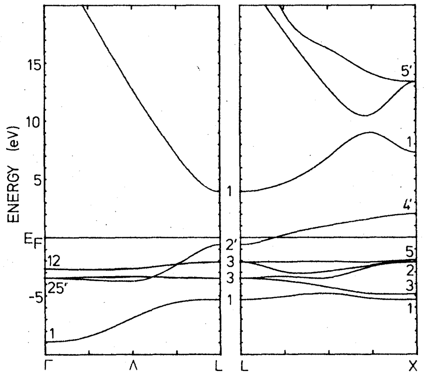

FIG. 11. Energy bands of bulk copper along the ΓL and XL lines, as computed in Ref. 32.

The bulk energy bands along the XLX line associated with the $\overline{M}$ point of Cu(111) are given in Fig. 11. The uppermost d band, which has odd symmetry in the (0$\overline{1}$1) reflection plane, is very flat along the XLX line, but becomes broader away from this line. The observed surface state may be roughly described as a Tamm state. Previous self-consistent calculations[30] for the (111) surface of Cu do not contain a surface state in this energy–wave-vector region. As noted above, the energy and existence of Tamm states are very sensitive to the surface potential. Our interpretation could be tested using polarized light: The surface-state emission should vanish when the optical electric field lies in the (0$\overline{1}$1) emission plane.[15]

V. SUMMARY

Using the technique of angle-resolved photoemission spectroscopy, we have observed a new type of surface state on the (100) and (111) faces of copper, which may be described as a Tamm state. This state is found in nonhybridizational energy gaps of the PBBS, between the d-band complex and the sp band above E_F. For both faces, the uppermost d band is very flat along the line in $\vec{k}$ space associated with the $\overline{M}$ point of the SBZ: these lines pass through the X point, where the band has its maximum energy. The surface-state bands exist in a small region of the SBZ near $\overline{M}$ on each face, and lie within a few tenths of an eV of the d-band maximum. The observed AREDC peaks are very narrow, due to our good energy and angle resolution as well as the long lifetime of the hole. A contamination test, performed for the Cu(100) face, showed that the peaks were strongly attenuated compared with the bulk peaks. For both faces, we conjecture that the surface states have odd symmetry in their respective mirror planes. This conjecture could be tested using polarized light.

We did not observe a surface-state band on Cu(110) in the absolute energy gap of the PBBS at the top of the *d* bands near $\bar{X}$ (Ref. 37) [see Fig. 2 for emission in the (001) mirror plane passing through $\bar{X}$]. Note that the $\vec{k}$-space line corresponding to $\bar{X}$ passes through the X point of the bulk zone (see Fig. 3), but the uppermost *d* band is not as flat as in the two cases discussed above. Presumably the surface perturbation is not strong enough to produce a surface state out of the wider band. Other nonhybridizational energy gaps above the *d* bands are located near $\bar{X}$ of the (100) SBZ, $\bar{S}$ of the (110) SBZ, and $\bar{K}$ of the (111) SBZ; we did not explore these gaps for surface states. A hybridization gap surface state[21] at the bottom of the *d* bands of Cu(100) was not observed.

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