Surface states on low-Miller-index copper surfaces

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(Received 12 October 1984)

The results of an extensive high-resolution angle-resolved photoemission study of electronic surface states on the low-Miller-index copper surfaces are reported. New states located in the *s-d* hybridizational gaps Cu(001) and Cu(011) have been observed and characterized. The former is located near the $\bar{X}$ point of the surface Brillouin zone at a binding energy of 4.61 ± 0.03 eV in fair accord with recent calculations, while the latter is located near the $\bar{Y}$ point at a binding energy of 4.72 ± 0.05 eV. The current experimental situation concerning the existence of surface states on copper surfaces, their energy dispersion relations, and photon-energy-dependent intensity are reviewed and compared to the latest self-consistent calculations. Tabulations are presented of the binding energies of all occupied surface states observed so far in photoemission and of all unoccupied surface states observed so far in inverse photoemission on low-Miller-index faces of Cu.

I. INTRODUCTION

The low-Miller-index copper surfaces provide ideal model systems for comparisons between angle-resolved photoemission (ARP) experiments and first-principles or nearly-first-principles calculations of surface electronic structure. Numerous surface states have been observed,[1-11] and their energy dispersion relations are in qualitative or semiquantitative accord with calculated results.[12-20] We report here an extensive study of the surface electronic structure of copper surfaces. In the course of these studies we have observed and characterized two new surface states located in the *s-d* hybridizational gaps between bands 1 and 2 of the projected bulk band structure. The first of these is centered near the $\bar{X}$ point of the surface Brillouin zone of Cu(001) at a binding energy relative to the Fermi energy of 4.61 ± 0.03 eV, in fair accord with recent self-consistent calculations.[14,15] The latter is located near the $\bar{Y}$ point of Cu(011) at a binding energy of 4.72 ± 0.05 eV. These states are qualitatively similar to a state observed previously at $\bar{\Gamma}$ on Cu(111);[8] the reason they have not been observed before now is that their photoemission intensity is significant over only a limited range of photon energies. As has been shown elsewhere,[8,21] this observation can be used to quantify certain aspects of the surface-state wave function. Similar studies at $\bar{K}$ on Cu(111) have not yielded any new clearly resolved states despite the fact that a recent calculation predicts several to exist.[16]

A search for surface states often begins with a projection of the bulk band structure onto the appropriate surface Brillouin zone for the copper surfaces.[22] True surface states can exist in the projected band gaps of a particular symmetry.[23] The zeroth-order search for a surface state entails performing an ARP experiment at an energy and momentum parallel to the surface $\mathbf{k}_{||}$ where there exists a projected gap. Invoking specular boundary conditions, $\mathbf{k}_{||}$ is conserved in ARP to within a surface reciprocal-lattice vector $\mathbf{g}_{||}$:[23]

$$\mathbf{k}_{||,i}+\mathbf{g}_{||}=\mathbf{k}_{||,f}=0.512(E_K)^{1/2}\sin\theta\,\hat{\mathbf{k}}_{||}\ , \tag{1}$$

where $\mathbf{k}_{||,i}$ and $\mathbf{k}_{||,f}$ are the initial- and final-state momenta, E_F and θ are the emission energy and angle, and $\hat{\mathbf{k}}_{||}$ is a unit vector in the azimuth of emission.

While this procedure often meets with success, in several cases one must consider the momentum perpendicular to the surface $\mathbf{k}_\perp$ as well. Its location in a projected bulk band gap insures that the surface-state wave function decays evanescently into the bulk, and as such $\mathbf{k}_\perp$ is not a good quantum number. However, most surface-state wave functions oscillate as they decay so that their Fourier spectrum is peaked about a particular value of $\mathbf{k}_\perp$. $\mathbf{k}_\perp$ must in this sense be approximately conserved.

This can be seen more clearly in the simple treatment given by Louie.[8] We start by expanding the surface-state wave function $\Phi_S(\mathbf{k}_{||})$ in terms of the bulk functions $\Phi_B(\mathbf{k}_{||},\mathbf{k}_\perp)$. Since $\mathbf{k}_{||}$ is a good quantum number for the surface state, $\Phi_S(\mathbf{k}_{||})$ projects out those bulk states at the same $\mathbf{k}_{||}$:

$$\Phi_S(\mathbf{k}_{||})=\sum_{\mathbf{k}_{\perp,n}}\alpha_{\mathbf{k}_{\perp,n}}\Phi_B(\mathbf{k}_{||},\mathbf{k}_{\perp,n})\ . \tag{2}$$

$\mathbf{k}_\perp$ runs over the first Brillouin zone and n, in principle, over all bands. In simple systems, only that bulk band n closest in energy to the surface-state energy contributes significantly so that the sum reduces to

$$\Phi_S=\sum_{\mathbf{k}_\perp}\alpha_{\mathbf{k}_\perp}\Phi_B(\mathbf{k}_\perp)\ ,$$

where now the sum is over only one band. The surface-state intensity I_S at perpendicular momentum $\mathbf{k}_f$ is given by a dipole matrix element

$$I_S\sim|\langle\Phi_S\,|\,\mathbf{A}\cdot\mathbf{P}\,|\,\Phi(\mathbf{k}_f)\rangle|^2\ . \tag{3}$$

Substituting, we obtain

$$I_S\sim\sum_{\mathbf{k}_\perp}\alpha^2_{\mathbf{k}_\perp}|\langle\Phi_B(\mathbf{k}_\perp)\,|\,\mathbf{A}\cdot\mathbf{P}\,|\,\Phi(\mathbf{k}_f)\rangle|^2\ . \tag{4}$$

If we observe that this matrix element governs a bulk direct transition and as such is a δ function,[8,23,24] we obtain

$$I_S \sim \sum_{\mathbf{k}_\perp} \alpha^2_{\mathbf{k}_\perp} I_B(\mathbf{k}_f)\delta_{\mathbf{k}_i+\mathbf{G},\mathbf{k}_f} , \quad (5)$$

where I_B is the bulk intensity at final momentum $\mathbf{k}_f$, and $\mathbf{G}$ is a bulk reciprocal-lattice vector. If umklapp processes can be neglected, one $\mathbf{G}$ vector dominates such that $\mathbf{k}_i$ is in the first Brillouin zone. We obtain

$$I_S(\mathbf{k}_f-\mathbf{G}) \sim |\alpha_{\mathbf{k}_f-\mathbf{G}}|^2 . \quad (6)$$

Under these circumstances, I_S is expected to have maxima when $|\alpha_{\mathbf{k}_f-\mathbf{G}}|^2$ is a maximum: i.e., at that value of $\mathbf{k}_f-\mathbf{G}=\mathbf{k}_i$ where the bulk band is closest in energy to the surface-state energy. At a given $\mathbf{k}_{||}$, $\mathbf{k}_{f,\perp}$ is varied in an ARP experiment by changing the photon and final-state kinetic energies:[23,25]

$$\mathbf{k}_{f,\perp}=0.512[h\nu-3.81(\mathbf{k}_{||}+\mathbf{g}_{||})^2-V_0-E_B]^{1/2}\hat{\mathbf{n}} . \quad (7)$$

V_0 is the inner potential, E_B is the observed binding energy, and $\hat{\mathbf{n}}$ is a unit vector along the surface normal. These ideas imply that some surface states will be observed to oscillate in intensity as a function of photon energy and may not be easily visible at certain energies. Simple tight-binding and nearly-free-electron models for these oscillations and the simple information concerning the surface-state wave function they yield have been given elsewhere.[8,21] Part of our intent in the present study is to determine the applicability of these simple models.

The structure of this paper is as follows. Section II outlines our experimental techniques. Section III shows the results of our recent searches for surface states, and Sec. IV summarizes available data for all known occupied surface states on low-Miller-index copper surfaces. For completeness we list in Sec. V the *unoccupied* states which have so far been observed on these surfaces using the newly emergent technique of inverse photoemission spectroscopy.

II. EXPERIMENTAL TECHNIQUES

These experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory using a 6-m torroidal grating monochromator and an ARP spectrometer which has been described elsewhere.[26,27] Photons were available between 10 and 70 eV with a resolution of ~50 meV. The copper crystals were cut from high-purity (99.999%) copper stock and polished to within $\frac{1}{2}°$ of the appropriate bulk crystalline axis. They were inserted in the vacuum system and, following several cycles of neon ion sputtering (10 μA/cm^2, 1 kV, 30 min) and annealing (5 min, 800 K), were found to be clean and ordered as determined by Auger-electron spectroscopy and low-energy electron diffraction.

III. NEW RESULTS ON COPPER SURFACE STATES

A. Cu(001)

Perhaps no other surface has been studied by ARP as thoroughly as Cu(001). Despite this, we have observed two new states at the $\bar{X}$ point of the surface zone in the past year. The observation and characterization of the first of these, situated in a narrow gap very close to the Fermi level E_F, relied on exceptional energy and momentum resolution.[11] Studies of the second, reported here, benefit from good resolution as well, but in addition require the tunability of synchrotron radiation.

1. Surface state near E_F

We have extended our studies of the former by measuring its photon-energy-dependent intensity. The gap in which this state lies is easily visualized in the Fermi-surface data shown in Fig. 1 for the Γ–L–U–X–Γ plane.[28] The $\bar{X}$ point projects from the lines parallel to the (001) axis connecting the L symmetry points of the bulk Brillouin zone. This line does not intersect the Fermi surface; there is hence a narrow projected gap near E_F and the possibility of a surface state arises. Such a state was reported previously.[11] As the photon energy is varied while maintaining $|\mathbf{k}_{||}|$ fixed at $\bar{X}$ (1.231 Å^{-1}), $\mathbf{k}_f$ varies so that in a direct transition model,[23,25] one samples bulk states along this line according to Eq. (7). Band 6 is predicted always to be close to E_F: at L, its binding energy (measured here) is $E_B=0.8\pm0.05$ eV, while at the point along Σ labeled A in Fig. 1, one can extrapolate the Fermi-surface data[28] to yield $E_B=0.45$ eV. We expect to measure two peaks in the *sp* band: the surface state and band 6 from which it is derived. This is observed approximately to be the case in Fig. 2, where we show energy distribution curves (EDC's) of the *sp* band at photon energies between 10 and 40 eV. As expected, there are two

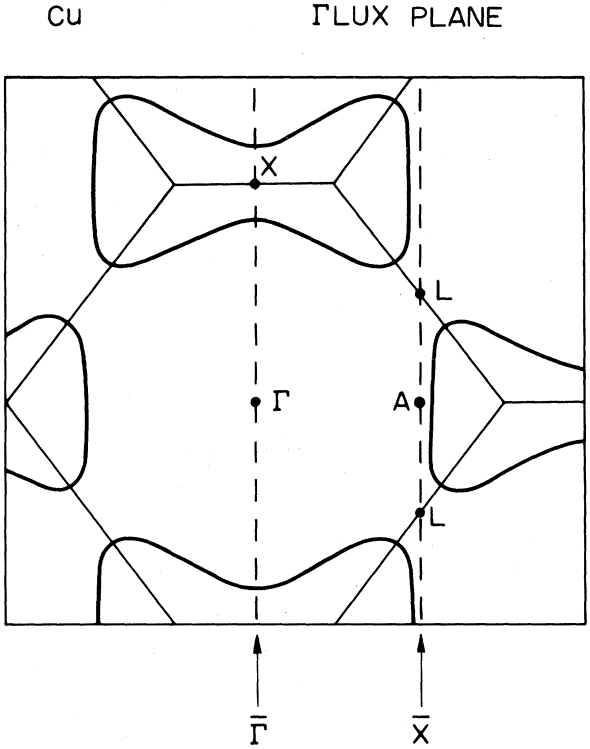

FIG. 1. Fermi surface of copper in the Γ–L–U–X–Γ plane of the Brillouin zone. The $\bar{X}$ point of Cu(001) projects from a line parallel to the (001) axis and passing through the L symmetry points.

main features: the nondispersive surface state at E_F and a feature derived from band 6 at higher binding energy. The latter of these is observed to be composed of two features at photon energies greater than $h\nu \sim 23$ eV. This energy is very close to the threshold for the onset of an umklapp process with $\mathbf{g}_{\parallel}=(2\pi/a)(-2,0,0,)$. The next-highest threshold occurs for $\mathbf{g}_{\parallel}=(2\pi/a)(-2,-2,0)$ at $h\nu \sim 43$ eV. In these two cases the intensity in the umklapp peak can be as large or larger than the direct process, explaining the unusual intensity oscillations of band 6 relative to the d bands as a function of photon energy (see Fig. 4). This fact, along with an excessive sensitivity to angular alignment, renders an accurate study of this bulk band's dispersion relation at $\bar{X}$ impossible.[25,29]

Of greater interest here is the relative intensity of the surface-state peak to that of the bulk. In particular, one wants to measure $I_S/(I_S+I_B)$ in order to normalize the fact that the spectral intensity passes back and forth between the two features as $\mathbf{k}_{\perp}$ is varied.[21,29–31] This effect is seen clearly at $h\nu \sim 11$ eV in Fig. 2, where nearly all of the intensity is transferred to the surface state. Figure 3 shows a plot of this quantity against $|\mathbf{k}_{f,\perp}|$ calculated from Eq. (7) assuming primary processes $[\mathbf{g}_{\parallel}-(0,0,0)]$ dominate. The simple treatment given in the Introduction indicates that this plot should reflect the square of the expansion coefficients $\alpha_{\mathbf{k}_{\perp}}$ of the surface-state wave function in terms of those of the bulk. Clearly, the largest $\alpha_{\mathbf{k}_{\perp}}$ occurs at $\mathbf{k}_{\perp}=(0,0,\pi/a)$, implying that this is the dominant oscillation frequency of the surface state as it decays

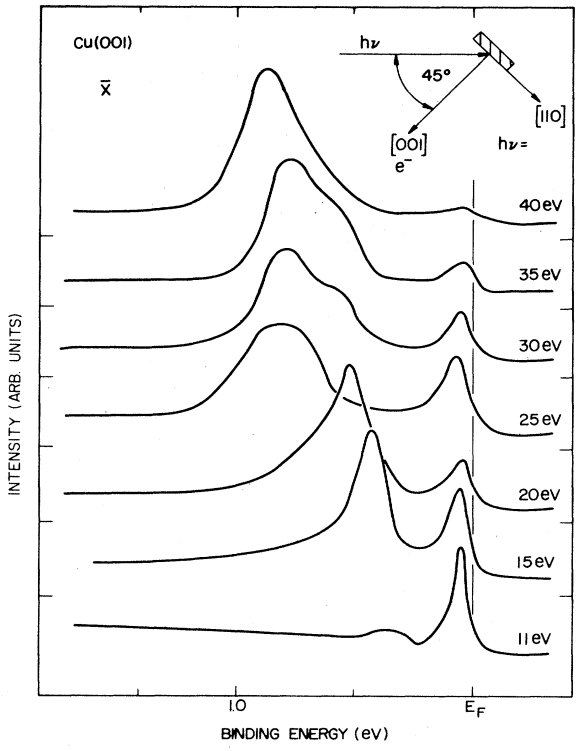

FIG. 2. EDC's of the *sp* band region near E_F at $\bar{X}$ of Cu(001) for photon energies between 10 and 40 eV. The lower-energy peak is due to direct transitions from band 6, while the peak at E_F is the surface state.

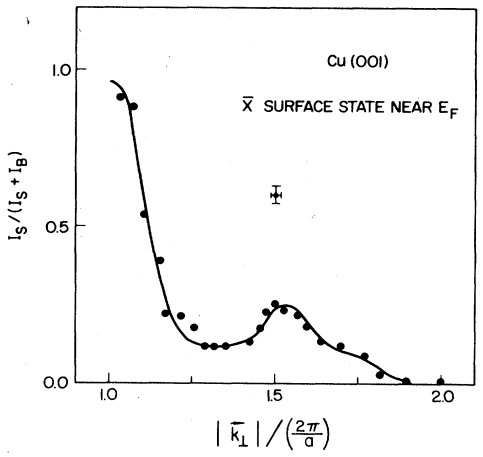

FIG. 3. Plot of $I_S/(I_B+I_S)$ from Fig. 3 against $|\mathbf{k}_{\perp,f}|$, as explained in the text.

into the bulk. The fact that the bulk feature vanishes near this $\mathbf{k}_{\perp}$ has been explained in the analogous case on Cu(111) as the nonpenetration of the surface region by those bulk states which contribute most to the surface state.[30] This value of $\mathbf{k}_{\perp}$ is reasonable considering that the bulk band energy approaches most closely the energy of the surface state. It is interesting that the point $\mathbf{k}_{\perp}=(0,0,2\pi/a)$ does not yield a maximum even though this bulk-surface energy separation is the same as at $\mathbf{k}_{\perp}=(0,0,\pi/a)$. Apparently, the surface state is exactly out of phase with the final state at $\mathbf{k}_{\perp}=(0,0,2\pi/a)$. The surface state should reappear near $\mathbf{k}_{\perp}=(0,0,3\pi/a)$, or $h\nu \approx 100$ eV. Unfortunately, to do the experiment at this energy with sufficient signal and resolution becomes prohibitively difficult.

These observations indicate a qualitative difference between this surface state and those near E_F at $\bar{\Gamma}$ on Cu(111) and at $\bar{Y}$ on Cu(011). All three of these states in some sense exist in gaps opened by hybridization of the sixth bulk band near the L point. On Cu(111) and Cu(011) (see Sec. IV) the surface state derives predominantly from the lower of these bands near L, while on Cu(001) the state derives mainly from a different point altogether. The secondary maximum near $\mathbf{k}_{\perp}=(0,0,3\pi/2a)$ could indicate smaller contributions to the Cu(001) state from bulk eigenstates near an L point. The energy separation between the bulk and surface bands at L is a maximum. An alternative and more likely explanation assigns this secondary intensity maximum to an interference effect at or near the threshold for emission of band 6 via the umklapp process explained earlier. A similar effect has been observed on Al(001).[31] The splitting observed in Fig. 2 of band 6 near this threshold lends credence to this explanation. In any case, the accurate and complete interpretation of the curve in Fig. 3 using a simple model as has been done elsewhere[8,21] is not possible.

2. *Low-lying surface state at* $\bar{X}$

A final result on Cu(001) concerns the existence of a low-lying surface state at $\bar{X}$. Such a state was predicted in two different self-consistent calculations,[14,15] but the pre-

vious experiment using resonance radiation[11] failed to observe it. A qualitatively similar state has been observed in the s-d gap at $\bar{\Gamma}$ on Cu(111) but is visible over a limited range of photon energies for the reasons outlined in the Introduction.[8,29,30] We initiated a careful, frequency-dependent search for the Cu(001) state.

Figure 4 shows EDC's collected at the $\bar{X}$ point of the copper valence band for $25 \leq h\nu \leq 70$ eV. Most of the features observed are due to direct transitions in the bulk band structure and can be understood completely using standard models.[23,25,29] For $40 \leq h\nu \leq 65$ eV, a weak nondispersive feature at $E_B = 4.61 \pm 0.03$ eV is observed. It is located in the measured projected s-d gap between bands 1 and 2. As evidenced in the top EDC which shows a contaminated surface [500 L (1 L = 10^{-6} Torr sec) oxygen] at $h\nu = 50$ eV, the state is sensitive to surface contamination. We assign this feature to the predicted low-lying surface state. Its observed energy at $\bar{X}$ is in fair accord with the calculated binding energy of $E_B \sim 4.1$ eV.[14,15] This 0.5-eV discrepancy can be attributed in part to systematic errors in using the Kohn-Sham approximation for exchange and correlation: the calculation sets the top of the d bands ~ 0.2 eV too high as well.[15]

Perhaps a better comparison with theory involves examining the position of the surface state in the projected gap. Both calculations locate the state just below the center of a 1.20-eV gap. At $h\nu = 50$ eV, our EDC's sample the surface state as well as bands 1 and 2 near their extrema which determine the magnitude of the gap at $\bar{X}$. The measured gap is 1.25 eV, and the surface state is located 0.50 ± 0.03 eV above the lower band. This can be seen more clearly by determining the state's dispersion relation near $\bar{X}$. Figure 5 shows the appropriate EDC's at $h\nu = 50$ eV at 1° intervals in $\bar{\Gamma}\bar{X}\bar{\Gamma}$ azimuth near $\bar{X}$. A small upward dispersion of the surface state away from $\bar{X}$ is visible. Figure 6 shows these results graphically. We plot our measured dispersion relation and bulk continuum along with the calculated dispersion relations shifted arbitrarily upward so that the bottom edges of the bulk continuum match. Seen in this way the calculation yields a rather good fit to our data.

Of further interest is this state's intensity as a function of photon energy. Its inherent low intensity combined with the close proximity of the neighboring bulk features renders extraction of results similar to those shown in Fig. 3 impossible. It is clear, however, that the state is observable over a limited range of photon energies near $h\nu = 50$ eV. From Eq. (2), this corresponds to $\mathbf{k}_f = (0,0,2\pi/a)$, indicating a qualitative difference from the state near E_F, which was intense at $\mathbf{k}_f = (0,0,\pi/a)$ and invisible at $\mathbf{K}_f = (0,0,2\pi/a)$. Another qualitative difference between this state and the other is the failure in this case of the bulk band at lower energy to disappear at the photon energy where the surface state is most intense. This is undoubtedly because the state derives from two (and possibly more) bulk bands, leading to deviations from the simple models explained in the Introduction.

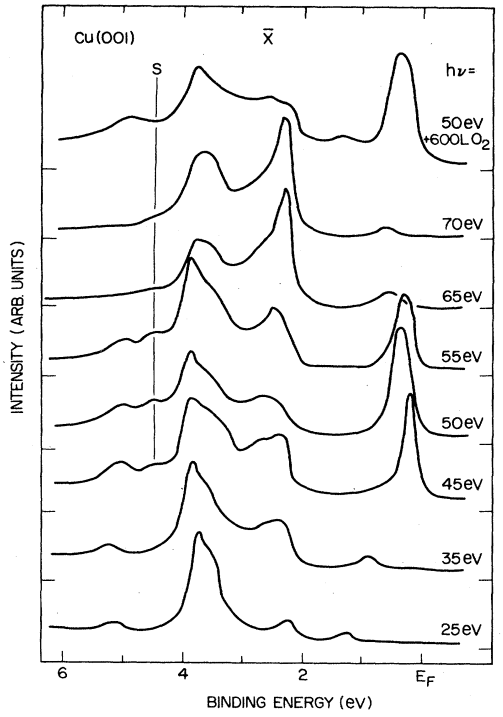

FIG. 4. EDC's of the Cu(001) valence band for various photon energies between 25 and 70 eV. At a binding energy of ~ 5 eV, $\mathbf{k}_{||}$ is at the $\bar{X}$ point. A weak feature at $E_B = 4.61 \pm 0.03$ eV exists in the projected s-d band gap and is sensitive to contamination (see top curve). It is assigned to emission from a surface state.

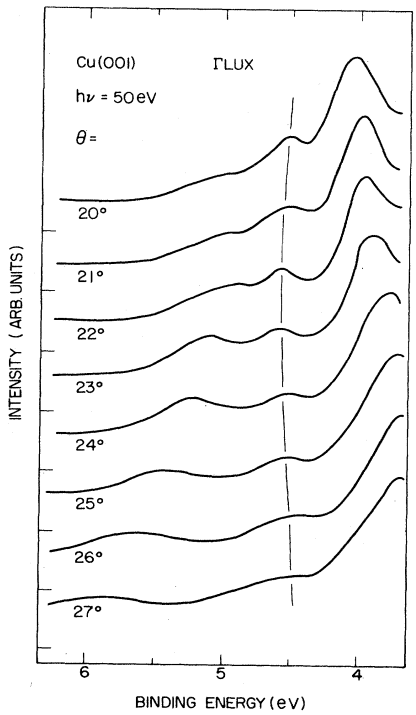

FIG. 5. Expanded EDC's of the low-lying $\bar{X}$ surface state on Cu(001) for various angles of emission near $\bar{X}$ in the $\bar{\Gamma}\bar{X}\bar{\Gamma}$ azimuth.

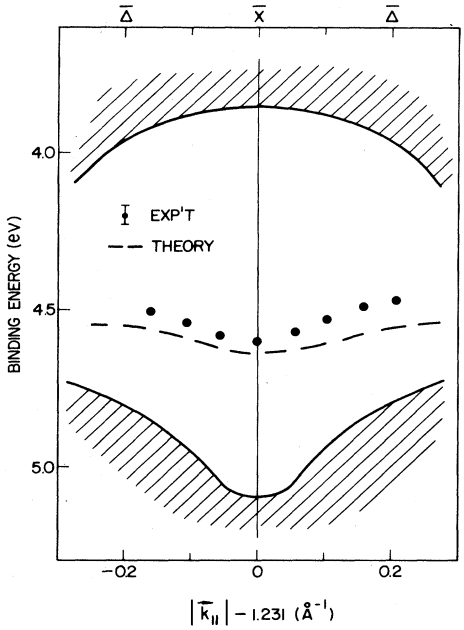

FIG. 6. Experimental dispersion relation of the s-d surface state located near $\bar{X}$ on Cu(001) in the $\bar{\Gamma}\bar{X}\bar{\Gamma}$ azimuth. The shaded region and curve are the projected bulk continuum and calculated dispersion relation shifted as described in the text.

B. Cu(011)

As indicated in the Introduction, we have also observed a new surface state in the s-d gap at $\bar{Y}$ on Cu(011). The state is qualitatively similar to though weaker in intensity than that described previously on Cu(001). Figure 7 shows expanded EDC's taken at $\bar{Y}$ at various photon energies. The dispersionless peak observed at $E_B = 4.72 \pm 0.5$ eV for $40 \leq h\nu \leq 65$ eV exists in the projected s-d gap at $\bar{Y}$ and was found to be sensitive to surface contaminants. As such we assign the peak to emission from a surface state. Its maximum intensity relative to neighboring d bands occurs near $h\nu = 50$ eV, implying dominant contributions from bulk bands at $\mathbf{k} = (2\pi/a)(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$. The state's low intensity precludes further accurate study. There has not been a self-consistent calculation of this surface; an older non-self-consistent calculation[22] predicts a low-lying surface state approximately midgap at $\bar{Y}$, in rough accord with our results.

C. Unfilled projected band gaps

At this point it may seem that there is a one-to-one correspondence between projected gaps and surface states. This clearly is not the case; numerous gaps are observed in Ref. 22 in which no surface states are predicted or observed. Good examples occur at $\bar{X}$ and $\bar{S}$ on Cu(011) just above the d-band continuum. The bulk band contours at both points are qualitatively similar to those observed at $\bar{M}$ of Cu(111) and Cu(001) where well-defined and well-characterized d-like states exist.[4-6] A limited search for similar states on Cu(011) was not successful. A clue to the explanation of this observation lines in the experimentally observed splittings of the surface states on Cu(001) (0.2 eV) and Cu(111) (0.1 eV) from the d-band continuum. The existence of these states relies heavily on symmetry to decouple atoms in neighboring layers.[14,15] The highest symmetry surface [Cu(001)] yields the largest splitting, while that with the lowest symmetry yields no splitting at all (or least one which is unobservably small). Clearly such considerations defy a one-to-one correspondence between surface states and projected gaps. The results of the next section summarize those gaps located near symmetry points which are filled by surface states.

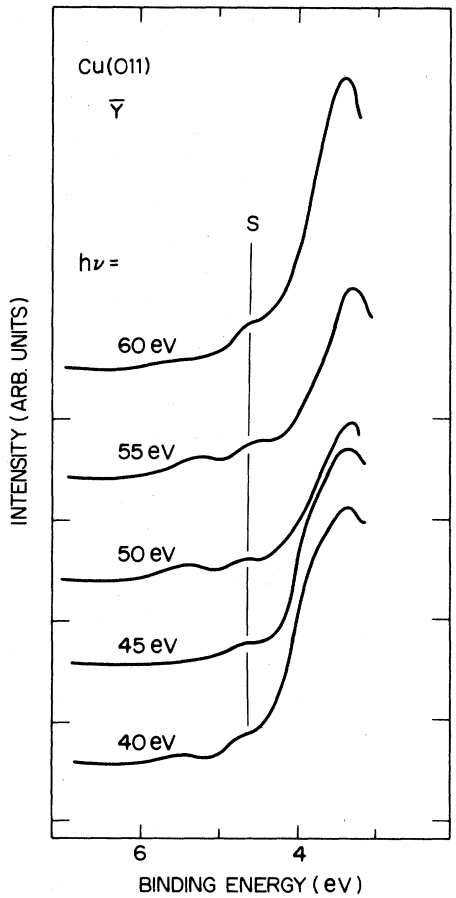

FIG. 7. Expanded EDC's of the Cu(001) valence band at $\bar{Y}$ of Cu(011) for $40 \leq h\nu \leq 65$ eV. The dispersionless shoulder at $E_B \sim 4.72$ eV is assigned to emission from a surface state.

A more rigorous test would involve a one-to-one correspondence between states predicted to fill certain gaps and corresponding experimental observations of such states. A good test occurs on Cu(111) at $\bar{K}$. The lack of symmetry at this point largely precludes the bulk bands from crossing. All five d bands are nearly dispersionless and band 6 lies above E_F so that there exist five projected gaps below E_F. A recent calculation predicts many surface states to occur, filling every gap.[16] There are, however, no clearly resolved surface states observed experimentally between $15 \leq h\nu \leq 60$ eV. Some of the spectral features show sensitivity to contamination, implying significant amplitude on the surface layers. It may be that well-defined surface states exist at $\bar{K}$ or Cu(111), but that

their emission intensity is low or that their splitting from nearby bulk features is small so that clear experimental assignment is precluded.

IV. SUMMARY OF PHOTOEMISSION RESULTS

It is useful to tabulate the experimental observations of copper surface states and the corresponding theoretical results (see Table I). The observables which we compare here are those which are not very model dependent. In particular, the analyses used in Refs. 8 and 21, which extract decay lengths, etc. of the surface-state wave function, are difficult to apply in general (see Sec. III and Fig. 3) and will not be used here. The dominant bulk frequency contribution to the surface state is easier to extract directly from experiment. While theoretical results often are not cast in this framework, we include these results in our summary in hope of provoking further theoretical work. The parameters we summarize are as follows.

(1) Existence and symmetry of a particular band.

(2) Binding energy E_B with respect to E_F and dispersion relation. We tabulate the effective mass m^* in terms of the free-electron mass m_e as a convenient way to parametrize the dispersion relation near a symmetry point:

$$E_B(\mathbf{k}_{||})=E_0+\frac{\hbar^2}{2m^*}(\mathbf{k}_{||}-\mathbf{k}_0)^2 .$$

$\mathbf{k}_0$ is the symmetry point parallel momentum and E_0 is the binding energy at the symmetry point. These masses are tabulated for the direction toward $\bar{\Gamma}$ for states located away from the zone center and toward the next-highest symmetry point for zone center states. This parametrization in terms of m^* is perhaps of less fundamental significance in some cases than in others.

(3) Dominant bulk frequency, reduced to the first Brillouin zone.

(4) Estimated natural peak width at the symmetry point, a quantity which reflects the inverse lifetime of the final-state hole.[2,6–9]

We have not included calculations which exclude self-consistency, since these have yielded results in significant variance with experiment in the past. In addition, where more than one calculation exists we have arbitrarily chosen to show those values which yield the best match to experiment. Different experiments have not yielded contradictory results on these surfaces. In any case, the references are intended to be complete.

A few general comments concerning this collection of results are in order. First, the most recent calculations yield generally excellent accord for the existence, symmetry, and dispersion of the high-lying *sp* surface states. This observation was emphasized elsewhere for Cu(001),[11] but is true as well for the well-known surface state at $\bar{\Gamma}$ near E_F on Cu(111). Since experiments in the region near E_F are less subject to systematic errors due to final-state relaxation shifts, this accord is an indication that calculations are approaching the degree of sophistication required to match experiment where the comparison is most meaningful.

The existence and energy of the states located further down in the *d* bands are less well predicted by calculation. Essentially all *d*-like surface states are predicted to be at too high an energy relative to experiment. Note that relaxation shifts in the photoemission final state will shift the experimental value up relative to theory and hence cannot explain the observed discrepancy. As explained earlier for the low-lying surface state at $\bar{X}$ on Cu(001), most of this shift can be understood in terms of systematic errors in using a local approximation for exchange and correlation resulting in an upward shift of both the bulk and surface states.[16] Of greater concern is that a well-defined low-lying surface state observed[8,29] at $\bar{\Gamma}$ on Cu(111) is not observed in the calculation.[16] This is curious considering that the gap at L which produces this state helps to produce the gaps at $\bar{X}$ on Cu(001) and $\bar{Y}$ on Cu(011) where we have observed low-energy surface states. The original interpretation of the peak on Cu(111) as a surface state has been questioned by an alternative assignment as a density-of-states feature from the nearby L_1 point.[33] A value for the energy of the L_1 point can be

TABLE I. Binding energies (relative to E_F) and other properties of occupied surface states on copper (a denotes this study; nm denotes not measured.)

		Experiment			Theory			
Surface	Symmetry point	E_B (eV)	$\frac{m^*}{m_e}$	$\frac{\mathbf{k}_B}{2\pi/a}$	ΔE (eV)	E_B (eV)	$\frac{m^*}{m_e}$	References
(001)	Γ_1	5.15(5)	0.45(5)	(001)	nm	4.81	0.48	14, 13, 29
	$\bar{X}_1$	0.06(1)	0.16(2)	$(\frac{1}{2},\frac{1}{2},1)$	0.03(1)	0.07	0.20	a, 11, 14, 15
	$\bar{X}_3$	4.62(3)	0.70(2)	$(\frac{1}{2},\frac{1}{2},0)$	0.35(1)	4.10	0.63	a, 14, 15
	$\bar{M}_2$	1.80(2)	−0.42(5)	(1,0,1)	0.04(1)	1.60	−0.58	4–7, 16, 32
(011)	$\bar{Y}_1$	0.39(1)	0.27(1)	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	0.09(2)			3,10
	$\bar{Y}_1$	4.72(5)	nm	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	0.40(5)			a
(111)	$\bar{\Gamma}_1$	0.39(1)	0.46(1)	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	0.06(1)	0.58	0.37	1–3, 8, 9, 13, 16
	$\bar{\Gamma}_1$	5.25(5)	nm	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	0.56(6)			16, 29
	$\bar{M}_2$	1.96(2)	−0.39(3)	(1,0,0)	0.07(2)	1.45	−0.40	a, 5, 32

extracted accurately without interference from a nearby surface state from the data shown in Fig. 4: $E_B = 5.32 \pm 0.03$ eV. The energy of the surface state is 5.25 ± 0.3 eV, implying that the state is located in the gap and is probably a true surface state. This very small separation from the bulk continuum is similar to that observed on Al(111) and would allow a long decay length into the bulk crystal. The resulting peaked frequency spectrum results in significant photoemission intensity over a narrow range of photon energy. In addition, a slab calculation would have trouble distinguishing such a slowly decaying state. In Ref. 16 there appears to be a state narrowly split from the bulk continuum above band 1 at $\bar{\Gamma}$; perhaps this is the missing state which was not assigned due to a long decay length.

Another discrepancy between experiment and calculation arises in the Tamm states split off from the top of the d bands at $\bar{M}$ on Cu(001) and Cu(111). These states are highly localized to the outermost layers and are thus particularly sensitive to small errors in the self-consistent potential. The observed and calculated[15,16] splittings are 0.20 and 0.66 eV for Cu(001) and 0.10 and 0.35 eV for Cu(111). The calculation also predicts a much larger $2p$ core-level shift on Cu(001) than has been observed[34] (1.59 versus 0.24 eV). The source of these discrepancies is not presently clear. The possibility of differential final-state relaxation between surface and bulk states has been discussed elsewhere.[16] It seems unlikely to us that this could lead to a 0.4-eV shift out of a 2-eV binding energy on Cu(001), particularly in consideration of the core-level-shift results.[34] Another possibility is that geometric relaxation of the interplanar spacing of the surface layers might alter the energy of these localized states significantly. A final way to decrease the bulk-surface state splitting is to endow the bulk continuum with additional width. This might be important in the present case since these $\bar{M}$ points project from lines runing through the X points of the bulk bands where the effect of the spin-orbit splitting is significant.[32] Further calculations will be required to investigate these possibilities.

TABLE II. Binding energies (relative to E_V) of unoccupied surface states on copper.

Surface	Symmetry point	$E_V - E$ (eV)	Reference
(001)	$\bar{\Gamma}$	0.64	38, 40
	$\bar{X}$	0.70[a]	39
(111)	$\bar{\Gamma}$	0.94(15)	40

[a]Extrapolated.

V. EMPTY SURFACE STATES

The newly emergent technique of **k**-resolved inverse photoemission spectroscopy[35] (KRIPES) has revealed a number of *unoccupied* surface states on low-Miller-index faces of Cu.[36–40] For completeness, we list the observed binding energies (relative to the vacuum level E_V) in Table II. [The work functions of Cu(111) and Cu(001) are taken to be[41] 4.94 and 4.59 eV.

Surface states within, say 1 eV of E_V, are perhaps best described as "image-potential-induced" since they sense the long-range nature of the image potential.[42] The reader is referred to the phase analysis by Hulbert *et al.*[40] for an explanation of the relation between these image-potential-induced states and the crystal-induced surface states which have been the topic of the bulk of this paper.

ACKNOWLEDGMENTS

This work was done at the National Synchrotron Light Source at Brookhaven National Laboratory under the auspices of the U.S. Department of Energy (Contract No. DE-AC02-76CH00016). We are thankful to D. Hamann, S. L. Hulbert, and P. D. Johnson for stimulating discussions.

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