

Intensity oscillations in the inverse photoemission cross section of an unoccupied surface state on Cu(001)

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It is shown that inverse photoemission cross sections of unoccupied surface states are subject to the same intensity oscillations as are observed in ordinary photoemission studies of occupied surface states. In particular, we compare observations of the unoccupied surface-state intensity as a function of k_{\perp} with a calculation of the bulk band structure obtained using a combined interpolation scheme. We are able to show that the surface state peaks in intensity at the value of k_{\perp} for which it lies closest to the bulk band from which it is derived.

Electronic surface states have been the subject of numerous investigations using both photoemission¹ and inverse photoemission spectroscopies.² Most of these studies have concentrated on measurements of the binding energies and the dispersions of these states. In particular, the recent observation of a new class of surface state derived from the long-range image potential has led to renewed interest in the factors that determine the binding energies of these states.³

A different class of photoemission experiment has been concerned with measuring the cross section of emission from surface states as a function of photon energy. These experiments have been interpreted in terms of simple models which consider the surface state as derived from close-lying bulk bands.^{4,5} It has been observed in these experiments that, as the photon energy is swept, the surface-state intensity goes through a maximum at that value of k_{\perp} (the component of momentum perpendicular to the surface) for which the surface state lies closest in energy to the band from which it is mainly derived.

Such observations represent a transfer of spectral intensity back and forth between the bulk transition and the surface-state peak. It has been shown that these experiments may be used to furnish information regarding the decay lengths of surface states and hence their wave functions.⁵

In this study we show for the first time that similar intensity oscillations may also be observed in inverse photoemission studies of unoccupied surface states. In particular, we present inverse photoemission spectra at the \bar{X} point of the Cu(001) surface Brillouin zone (SBZ). Such a study is of interest because there exists an earlier photoemission study by Kevan, Stoffel, and Smith⁶ of the intensity of the occupied surface state in the same band gap. As we show later, these two surface states are derived from different bands and this is reflected in their respective cross sections as a function of photon energy.

The spectra presented in this paper were obtained with a new ultraviolet spectrometer designed specifically for inverse photoemission. This spectrometer, described in detail elsewhere,⁷ uses the focused spot from an electron source as an entrance slit and achieves a resolving power of approximately 75 in the range 10–30 eV. Conventional low-energy electron diffraction and Auger techniques were used

to determine the azimuthal orientation of the sample and to verify surface cleanliness.

Figure 1 shows our measured spectra for the \bar{X} point of Cu(001). The seven spectra were taken at fixed electron energies E_{e1} ranging from 20.5 to 26.5 eV above E_F , the angle of electron incidence being selected so as to maintain constant $k_{\parallel} = \pi/a(1, 1, 0)$ corresponding to the \bar{X} point of the SBZ. These spectra are dominated by a surface state (labeled S_2 in Fig. 1) at 3.97 eV above E_F . The surface character of this state is demonstrated by its lack of disper-

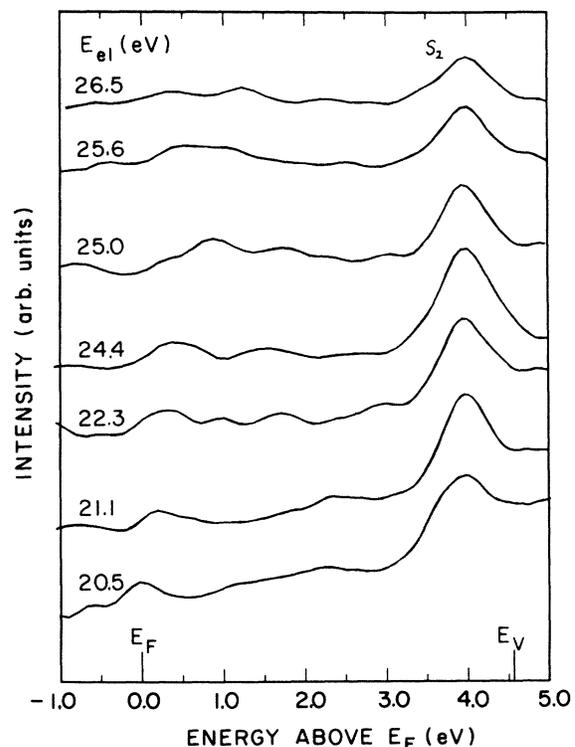


FIG. 1. Inverse photoemission data for Cu(001) at $k_{\parallel} = \bar{X}$ taken as a function of initial-state electron energy E_{e1} relative to the Fermi energy E_F .

sion with k_{\perp} and by its sensitive dependence on surface contamination.⁸ We note that this state has previously been observed at points away from the \bar{X} point ($k_{\parallel} < \pi/a$) by Dose, Kolac, Borstel, and Thorner⁹ in a fixed photon energy (isochromat mode) inverse photoemission experiment.

In Fig. 2 we plot the intensity of photon emission from the surface state as a function of k_{\perp} , where

$$k_{\perp} = 0.5123[E_{ei} - 3.81(k_{\parallel} + g_{\parallel})^2 - V_0]^{1/2}. \quad (1)$$

Here g_{\parallel} can be any reciprocal-lattice vector parallel to the surface, but in the evaluation of Eq. (1) it is generally set equal to zero; V_0 is the inner potential, for which the nearly-free-electron value is -6.65 eV, and E_{ei} is the incident electron energy with respect to the Fermi level.

The observed variation in strength of the surface state as a function of k_{\perp} is explained in terms of the bulk band structure of Cu for k_{\parallel} equal to the \bar{X} point of the Cu(001) SBZ. This point is a projection of the line in the bulk Brillouin zone that passes through the A [$\pi/a(1,1,0)$, on the Σ line] and L symmetry points. Shown in Fig. 3, bands 6, 7, 8, and 9 of the bulk band structure from A to L in the reduced zone scheme are obtained using a combined interpolation scheme¹⁰ for Cu with input parameters from Ref. 11 optimized to fit the bulk L gap.¹² These parameters are appropriate because, as noted above, the \bar{X} point of the Cu(001) SBZ lies within the (001) projection of the bulk L gap.

The intensity of the surface state, which peaks at $E_{ei} = 24.4$ eV in Fig. 1, corresponds to $k_{\perp} = 3\pi/a$ from Eq.

(1) and coincides with the bulk L point in the reduced-zone scheme. Band 7, from which this surface state (S_2 in Fig. 3) is mainly derived, comes closest to S_2 at the L symmetry point, and its intensity is transferred into the surface state at this value of k_{\perp} . Similar behavior has been observed previously for the occupied surface state (S_1 in Fig. 3) in the equivalent photoemission experiment.⁶ We note that there are no bulk transitions observed in Fig. 1, even though the G_{002} plane-wave component of the initial-state band-8 wave function (to which the incoming electron wave function will couple most strongly^{13,14}) is peaked at the L point, as determined by the combined interpolation scheme eigenvectors.

The \bar{X} gap on the Cu(001) surface is capable of supporting two crystal-derived or Shockley-type surface states,¹⁵ and for comparison we show in Fig. 2 the cross-section effects previously observed in angle-resolved photoemission data for the occupied Cu(001) \bar{X} surface state S_1 .⁶ The measured intensity of that state was found to be largest at a photon energy $\hbar\omega = 10.6$ eV corresponding to a value of $k_{\perp} = 2\pi/a$. This perpendicular momentum coincides with the bulk A point (see Fig. 3), where the surface-bulk state energy difference (S_1 -band-6) is smallest.

Following other authors,^{4,5} we anticipate that the widths of the intensity peaks in Fig. 2 are related to the decay lengths of the surface states. Kevan, Stoffel, and Smith⁵ applied a simple two-plane-wave model in an attempt to derive the surface-state decay length from a photoemission experiment that measured the intensity variation of the surface state at the center of the surface Brillouin zone on Al(111). That model does not easily transfer to the present

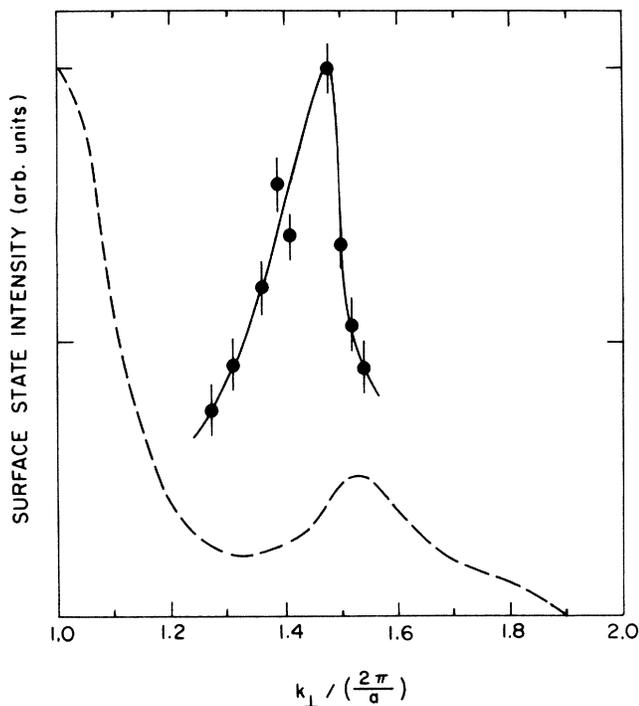


FIG. 2. Intensity of emission for the unoccupied surface state S_2 (solid line) observed in the present experiment and the occupied surface state S_1 (dashed line) from Ref. 6 as a function of k_{\perp} , the component of electron momentum perpendicular to the Cu(001) surface.

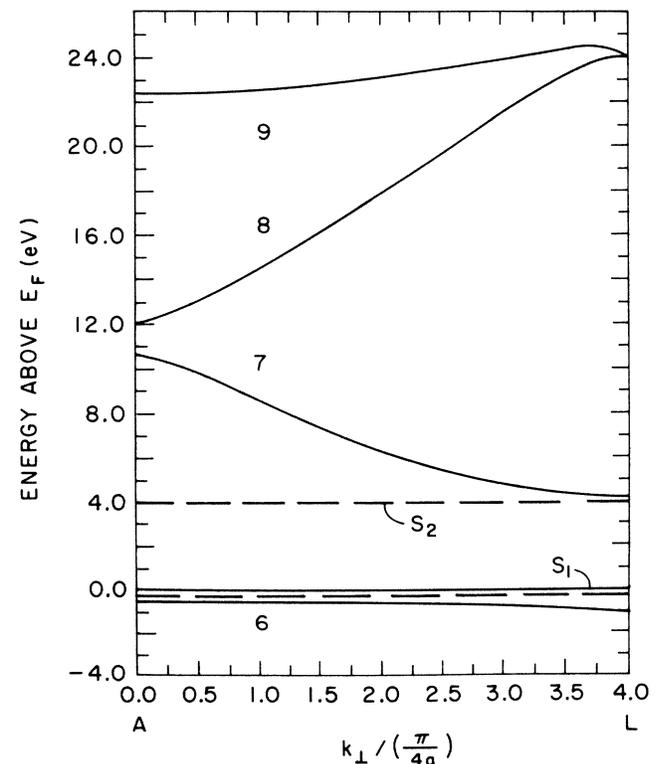


FIG. 3. Bulk band structure calculated as a function of k_{\perp} from A to L for $k_{\parallel} = \bar{X}$ of the Cu(001) surface Brillouin zone from the combined interpolation scheme (Refs. 10–12).

$k_{\parallel} \neq 0$ experiments where the surface state should be represented by a wave function derived from four plane waves rather than two. Thus the wave function of this state (S_2) has the form

$$u = e^{-qz} \cos(k_{\parallel} r_{\parallel}) \cos(pz + \delta) \quad (2)$$

where q , the complex component of the wave vector, describes the decay of the surface state into the bulk and relates to the decay length λ by $q = 1/\lambda$. The cosine terms simply describe the characteristics of the wave function parallel and perpendicular to the surface. However, further complications arise from the involvement of the d bands in determining the band-gap characteristics at the \bar{X} point in Cu(001). In fact, we determine from the combined interpolation scheme that at the A point band-6 has 50% d character, and at the L point band-7 has 25% d character. We anticipate that extraction of quantitative decay lengths for these surface states at points away from the center of the zone will prove difficult. However, by comparison with the photoemission measurements of the observed intensity of the occupied Cu(111) surface state at the center of the zone⁴ we are able to make qualitative comments on the observations in the present study of the unoccupied surface state. Any width of the intensity maxima in Fig. 2 due to the localization of the surface state will be increased by the momentum broadening of the electron in the final state in photoemission or initial state in inverse photoemission. Using the experimentally measured mean free paths appropri-

ate to the different final state/initial state energies measured with respect to the Fermi level and allowing for the fact that the experiments are made at different values of k_{\parallel} we estimate that the momentum broadening in the earlier Cu(111) study is of the order of $\Delta k \sim 0.2 \text{ \AA}^{-1}$ and in the present Cu(001) \bar{X} study $\Delta k \sim 0.1 \text{ \AA}^{-1}$. The full width at half-maximum of the intensity maxima for the two experiments are 0.626 \AA^{-1} for the Cu(111) study and approximately 0.35 \AA^{-1} in the present case. Thus by deconvolving Lorentzians of the appropriate width due to the momentum broadening we are left with intensity maxima which indicate that the decay length of the $\bar{\Gamma}$ surface state on Cu(111) is shorter than that for the state in the \bar{X} gap on Cu(001). This is consistent with the fact that in the Cu(111) case the surface state binding energy is displaced further from the closest-lying continuum edge.

In summary, we have demonstrated that unoccupied surface states show the same cross-section variations previously observed for occupied surface states. Thus these states may be expected to peak at values of k_{\perp} at which their overlap with their "parent" bulk band is largest. We make the further observation that in the present case these intensity variations show a periodicity determined by the perpendicular component of the reciprocal-lattice vector that generates the band gap (G_{111}) rather than the reciprocal-lattice vectors that run perpendicular to the surface of the type G_{002} .

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¹E. W. Plummer and W. Eberhardt, *Advances in Chemical Physics* (Wiley, New York, 1982), Vol. 49.

²N. V. Smith, *Appl. Surf. Sci.* **22/23**, 349 (1985).

³S. L. Hulbert, P. D. Johnson, N. G. Stoffel, W. A. Royer, and N. V. Smith, *Phys. Rev. B* **31**, 6815, (1985).

⁴S. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesis, and J. Lecante, *Phys. Rev. Lett.* **44**, 549 (1980).

⁵S. D. Kevan, N. G. Stoffel, and N. V. Smith, *Phys. Rev. B* **31**, 1788 (1985).

⁶S. D. Kevan, N. G. Stoffel, and N. V. Smith, *Phys. Rev. B* **31**, 3348 (1985).

⁷P. D. Johnson, S. L. Hulbert, R. F. Garrett, and M. R. Howells (unpublished).

⁸S. L. Hulbert, P. D. Johnson, M. Weinert, and R. F. Garrett, *Phys. Rev. B* **33**, 760 (1986).

⁹V. Dose, V. Kolac, G. Borstel, and G. Thorner, *Phys. Rev. B* **29**, 7030 (1984).

¹⁰N. V. Smith, *Phys. Rev. B* **19**, 5019 (1979).

¹¹R. Lasser, N. V. Smith, and R. L. Benbow, *Phys. Rev. B* **24**, 1895 (1981).

¹²The parameters that differ from the set given for Cu in Ref. 10 are $V_{111} = 0.087$ and $S = 0.75$.

¹³D. P. Woodruff, N. V. Smith, P. D. Johnson, and W. A. Royer, *Phys. Rev. B* **26**, 2943 (1982).

¹⁴S. L. Hulbert, P. D. Johnson, N. G. Stoffel, and N. V. Smith, *Phys. Rev. B* **32**, 3451 (1985).

¹⁵N. V. Smith, *Phys. Rev. B* **32**, 3549 (1985).