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Observation of an unoccupied surface state on Cu(110) by inverse photoemission

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We have observed an unoccupied surface state on the Cu(110) surface using k-resolved inverse photoemission. It is located 2.5 ± 0.2 eV above the Fermi level and disperses parabolically about the $\bar{Y}$ point of the surface Brillouin zone with an effective mass of $m^*/m=1.1$. These results, when considered along with photoemission data from the $\bar{Y}$ gap, represent the first definitive observation of two crystal-induced surface states in the same bulk band gap of a metal. The origin of the two states is discussed in terms of a two-band model.

I. INTRODUCTION

Momentum-resolved inverse photoemission has proven to be a useful tool for examining the unoccupied states of solids.[1–7] Its unique strength is that it reveals the states between the Fermi level (E_F) and the vacuum level without creating a core hole. The surface sensitivity of the technique has been demonstrated by the observation of unoccupied surface states on semiconductors[1,3] and metals,[7] and of adsorbate-induced states in several systems.[1–3]

We have investigated the surface electronic structure of Cu(110) using inverse photoemission, and report here the observation of an unoccupied surface state in the $\bar{Y}$ gap of the surface Brillouin zone. As an *occupied* surface state has been seen at $\bar{Y}$ by conventional photoemission,[8] our results represent the first definitive confirmation of the existence of *two* surface states in the same bulk band gap of a metal. An unoccupied surface state very similar to the one we report here was recently seen by Reihl *et al.* on Ag(110),[7] but no correpsonding occupied surface state has been reported in the $\bar{Y}$ gap on that surface. The Cu(111) surface also has an occupied and an unoccupied surface state in one band gap.[9] However, the unoccupied state is an image-potential state that results from the long-range part of the surface potential and is tied to the vacuum level. We argue below that both states seen on Cu(110) are "crystal induced," i.e., due to the short-range part of the surface potential. This point of view is supported by a simple calculation based on a nearly-free-electron treatment of the bands which form the $\bar{Y}$ gap.

The remainder of this paper is organized as follows. Section II outlines the experimental technique. In Sec. III we present the data and discuss the results in terms of the aforementioned model. We also compare our results to predictions from a slab calculation of Cu(110). Finally, Sec. IV summarizes our conclusions.

II. EXPERIMENTAL

Inverse photoemission involves detection of ultraviolet photons emitted by a sample while it is bombarded with a collimated beam of low-energy electrons. Our data were obtained with a spectrometer which operates in the isochromat mode, i.e., it measures the intensity of emitted photons of a particular energy as a function of the incident electron energy. The electron source is a modified commercial electron gun equipped with a BaO cathode to reduce the thermal energy width of the emitted electrons. The beam spot on the sample is less than 2 mm in diameter as measured with a phosphor screen. The electron current is approximately 3 μA. The angular divergence is estimated as 5° based on the spectral variations observed. The electrons leave the gun with an energy of 50 eV and are decelerated to the desired kinetic energy range (6 to 18 eV) by applying a retarding voltage to the sample. For one set of experiments a pair of retarding grids were inserted between the sample and the electron gun to ensure a field free region near the sample. Since the addition of the grids introduced no observable shifts in peak positions and a large inelastic background was generated, these grids were omitted in the work described below. Judging from the observed symmetry of the dispersion relation, this procedure does not introduce significant angular distortions in our experimental geometry.

The photons, generated by electrons making radiative transitions, are detected by a Geiger-Müller tube similar to that first described by Denninger *et al.*[10] A bandpass of $\hbar\omega=9.7$ eV±0.4 eV is achieved by using a CaF window (to provide the high-energy cutoff) and iodine gas (to give the low-energy cutoff). The vapor pressure of I_2 is sufficiently high at room temperature that the gas can be introduced into the detector by opening a valve to a tube containing a few iodine crystals. Following Woodruff *et al.*,[11] we chose not to use a buffer gas. The energy resolution (electrons and photons) is 0.8 eV (as measured by the Fermi level width) and the count rates are of the order of 100 counts/s. The detector is centered at an angle of 57° from the electron source in the plane of incidence. The incidence angle of the electron beam is varied by rotating the sample. The Cu(110) crystal was cleaned using standard techniques.[12,13] Auger electron spectroscopy was used to monitor surface cleanliness. Low-energy electron diffraction (LEED) showed a sharp (1×1) pattern for the clean surface at room temperature.

III. RESULTS AND DISCUSSION

Typical spectra, taken at several angles of incidence, are shown in Fig. 1. All spectra show a sharp onset that we associated with the Fermi level. Little structure is observed above E_F for the $\theta=0°$ (normal incidence) and $\theta=5°$ spectra. At $\theta=10°$ we begin to see intensity near 3.5 eV, which grows and disperses towards E_F as θ increases. The peak reaches a minimum energy of 2.5 eV around 30° and then disperses to higher energy with increasing angle.

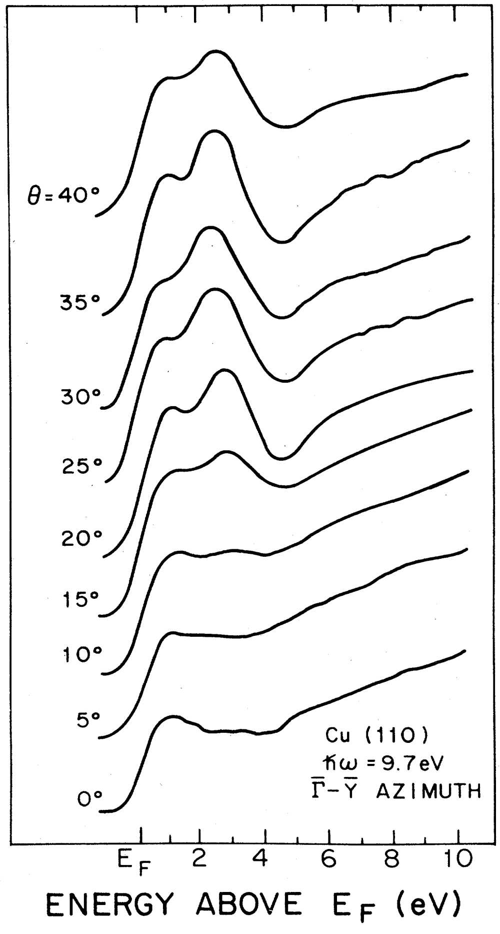

FIG. 1. Inverse photoemission spectra of Cu(110) take in the isochromat mode at $\hbar\omega=9.7$ eV. θ is the angle of the incident electron beam measured from the crystal normal, along the $\langle 100\rangle$ azimuth. The spectra have not been normalized to the incident electron current.

Before we may associate this 2.5-eV feature with emission from a surface state, it must meet several criteria. Firstly, a surface state may only exist in regions of the bulk structure where no bulk states of the same symmetry are allowed. Secondly, it may disperse with electron momentum parallel to the surface ($\mathbf{k}_{\parallel}$) as it is delocalized in the surface plane, but it should show no dispersion with momentum normal to the surface ($k_{\perp}$). Finally, a surface state is expected to show sensitivity to surface contamination.

The magnitude of the component of electron momentum parallel to the surface is $k_{\parallel}=(2mE_k/\hbar^2)^{1/2}\sin\theta$, where E_k is the kinetic energy of the incident electron and θ is the angle between the electron beam and the sample normal. Thus, the spectra presented in Fig. 1 explore the unoccupied bands away from $\bar{\Gamma}$. The upper panel in Fig. 2 shows the real and reciprocal space unit cells for the Cu(110) surface. The $\bar{\Gamma}$-$\bar{Y}$ direction is along the y axis of this figure and the parallel momentum vector is along the $\langle 100\rangle$ direction, i.e., perpendicular to the close-packed rows. The dispersion with $k_{\parallel}$ of the peak seen in Fig. 1 is plotted (solid circles) in the lower part of Fig. 2. The shaded portion of this figure shows the projection of the bulk bands onto the surface Brillouin zone.[14] The band edges at $\bar{Y}$ are formed by the L_2' and L_1 energy levels in the Cu band structure. The state we detect is separated from the nearest bulk band by about 1.5 eV at $\bar{Y}$, making an interpretation in terms of a surface state highly likely. The state shows only a weak dispersion in the proximity of $\bar{Y}$, but as the bulk continuum is approached, the energy changes rapidly. A parabolic dispersion with an effective mass $m^*/m=1.1$ provides a best fit to our data. This is shown as the solid curve in Fig. 2.

The sensitivity of this state to surface contamination was tested by exposure to oxygen. Figure 3 shows several spectra taken at $\theta=25°$ with increasing oxygen contamination. The shaded portion of the spectra represents emission attributed to the surface state. The figure illustrates how emission from the state diminishes with only small, submonolayer exposures of O_2. At room temperature, oxygen induces a (2×1) LEED pattern after $\approx$20-langmuir (L) exposure, corresponding to 0.5 monolayer coverage.[12] Assuming the sticking coefficient to be independent of coverage below this exposure, a significant reduction of emission intensity with only $\approx$0.05 monolayer oxygen contamination is indicated. The state is completely undetectable after a 20-L exposure. These observations are very similar to those made by Reihl *et al.*[7] in their study of Ag(110). It is interesting to note that the *occupied* surface state at $\bar{Y}$ on Cu(110) is still detectable after the (2×1) LEED pattern is established.[13]

Since our spectrometer operates in the isochromat mode, we are unable to verify that the state at $\bar{Y}$ does not disperse with $k_{\perp}$. However, based on the evidence cited above, we feel confident in assigning the feature at $\bar{Y}$ to a previously undetected, unoccupied surface state on

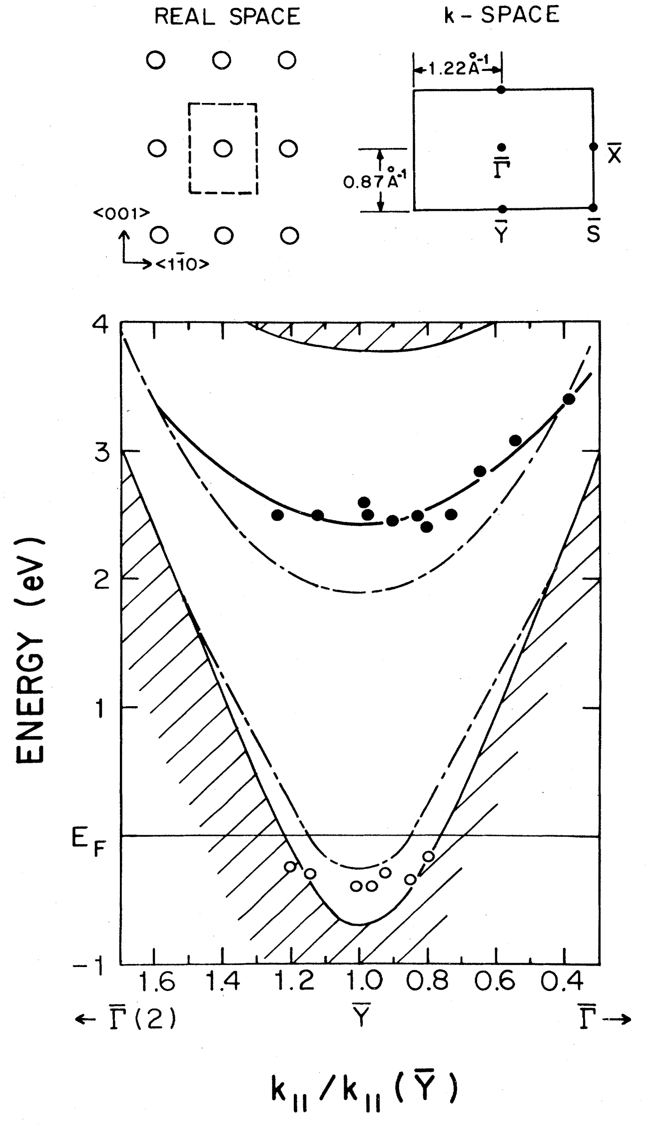

FIG. 2. Surface electronic structure of Cu(110) near the $\bar{Y}$ point. The solid circles are the unoccupied state measured here. The shaded regions are the projected bulk bands and the dot-dashed lines are the two surface states as calculated in Ref. 14. The open circles are the data for the occupied surface state observed in Ref. 8. $\bar{\Gamma}(2)$ is the center of the second surface Brillouin zone. The top panel shows the geometry of the Cu(110) surface in real and reciprocal space.

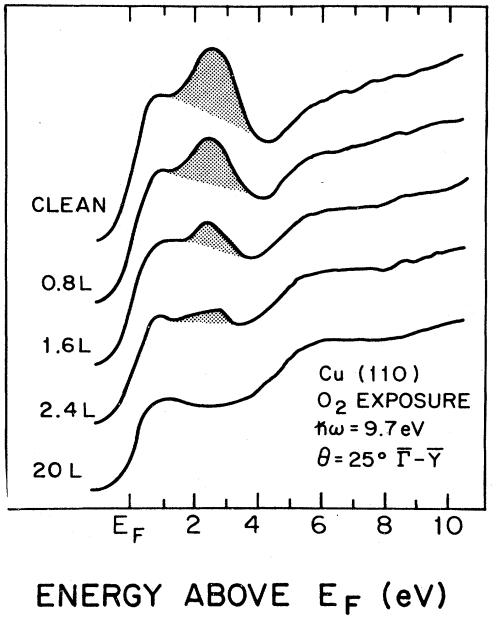

FIG. 3. Inverse photoemission spectra from Cu(110) at $\theta=25°$ along $\bar{\Gamma}\rightarrow\bar{Y}$, as a function of oxygen exposure. The shaded area illustrates the diminishing surface-state intensity as the exposure is increased. An oxygen-induced feature is seen near 5.8 eV.

Cu(110). The state is not caused by the image potential[9] as is evident from its energy and dispersion. Image-potential states are generated by the long-range part of the surface potential and thus lie close to the vacuum level. Since the work function of Cu(110) is 4.48 eV,[15] we would expect an image-potential state to lie higher than the state we observe.[9] In addition, the free-electron nature of an image-potential state implies that its energy should be an increasing function of $k_{\|}$. The state in Fig. 2, however, clearly disperses toward lower energy as $k_{\|}$ approaches $\bar{Y}$. Such a behavior indicates that the state senses the two-dimensional periodicity of the surface and obeys the symmetry of the surface Brillouin zone. To our knowledge, this is the first time it has been clearly established that two crystal-induced surface states may exist in the same bulk band gap on a metal.[16]

The question of the number of surface states that can exist on a given surface at a given $k_{\|}$ has been considered by Forstmann[17] and by Pendry and Gurman.[18] Using a simple model similar to the one discussed below, Forstmann concluded that one and only one surface state will exist in the model band structure in which the relevant band gaps are interior to the Brillouin zone.[17] Using a more general argument Pendry and Gurman concluded that either one or two surface states can exist.[18] We have carried out an analysis within a nearly-free-electron (NFE) approximation to the bulk band structure relevant to the $\bar{Y}$ point in the surface Brillouin zone and have reached conclusions similar to those of Pendry and Gurman.[18] We believe that the disagreement with Forstmann is associated with the choice of crystal plane at which the matching with the exterior solution is performed.

The geometry of the surface is shown in the top panel of Fig. 2. The free-electron band structure corresponding to the $\bar{Y}$ point in the surface Brillouin zone is shown in Fig. 4 (dashed lines), where the bands are labeled by their three-dimensional wave vectors. In an NFE model, the lattice potential produces gaps centered at the points marked L and L'. The bulk states at these points are L_2' and L_1 mapped into the three-dimensional Brillouin zone constructed from the surface Brillouin zone appropriate to the (110) surface. Thus, there are two possible regions of $k_{\perp}$ where the bands may become complex and support a gap state.

Following Heine,[19] we study the "real lines" corresponding to Bloch states with energy in the gap at real $\mathbf{k}_{\|}$ but complex $k_\perp$. One may show that in the NFE model, the Bloch function which complex wave vector for the gap state at L may be written as

$$\Psi_L = e^{\kappa r_\perp}/(2^{1/2})\{(a_1+i\,|a_2|)\exp[i(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|}+k_0 r_\perp)] \\ -(a_1-i\,|a_2|)\exp[-i(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|}+k_0 r_\perp)]\}.$$

Here, $\mathbf{k}_{\|}=\overline{Y}=(0,0,1)\pi/a$, the parallel wave vector of interest; $k_0=\sqrt{2}\pi/a$, the perpendicular wave vector for the L point; $r_\perp$ and $\mathbf{r}_{\|}$ are coordinates in the perpendicular and parallel directions, respectively, and κ is the magnitude of the complex part of $k_\perp$. The quantities a_2 and a_1 are the amplitudes of the upper (s-like) and lower (p-like) Bloch functions at the band edges, which are mixed to form the gap states. At the bottom of the gap $|a_1|=1$, $a_2=0$; at the top of the gap $|a_2|=1$, $a_1=0$; they are monotonic functions in between.

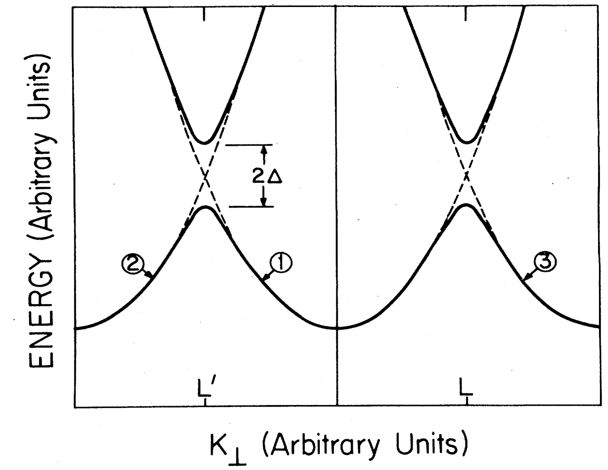

FIG. 4. The nearly-free-electron-like band structure as a function of $k_\perp$ at the $\overline{Y}$ point in the surface Brillouin zone. The three plane-wave branches denoted 1, 2, and 3 are formed by the physical wave vectors $\mathbf{k}$, $\mathbf{k}-(-1,-1,1)2\pi/a$, and $\mathbf{k}-(1,1,1)2\pi/a$, respectively.

The state at L' has the same functional form as that at L, but with the replacements $k_0\rightarrow -k_0$ and $|a_2|\rightarrow -|a_2|$. The algebra is more transparent if one exploits the symmetry $\mathbf{k}_{\|}\rightarrow -\mathbf{k}_{\|}$ appropriate to the $\overline{Y}$ point. We form even and odd solutions:

$$\Psi_e=\exp(\kappa r_\perp)\cos(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|})[(a_1+i\,|a_2|)\exp(ik_0r_\perp)-(a_1-i\,|a_2|)\exp(-ik_0r_\perp)]$$

and

$$\Psi_o=\exp(\kappa r_\perp)\sin(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|})[(a_1+i\,|a_2|)\exp(ik_0r_\perp)+(a_1-i\,|a_2|)\exp(-ik_0r_\perp)]\ .$$

Assuming that the potential jumps discontinuously to the vacuum level, the exterior wave function is either $\cos(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|})$ (for the even solution) or $\sin(\mathbf{k}_{\|}\cdot\mathbf{r}_{\|})$ (for the odd solution) times $e^{-\sqrt{|E|}z}$, where E is the perpendicular energy with respect to the vacuum level. A surface state will exist if the wave function and its derivative are continuous at the interface. To satisfy this condition, the logarithmic derivative $(1/\Psi)(\delta\Psi/\delta z)$, of the internal and external wave functions must be equal at the solid-vacuum interface. This is illustrated graphically in Fig. 5, for which we have performed the matching halfway between atomic planes at $r_\perp=a/4\sqrt{2}$. The vertical axis is $\gamma=(1/\Psi)(\delta\Psi/\delta z)$ and the horizontal axis is energy with the gap ranging from $-\Delta<E<+\Delta$. The curves labeled γ_e (γ_o) illustrate the logarithmic derivative of the even (odd) complex Bloch state. For the external function, γ_{ext} is a negative, monotonically increasing function of energy. From this figure we see that for the assumed symmetry of the band edges there may be either one or two surface states in the gap.

The situation on Cu(110) presumably corresponds to the case where γ_{ext} crosses both γ_e and γ_o, as shown in Fig. 5. The simple exterior wave function mentioned above has a logarithmic derivative equal to k_0 for Cu at an energy of 5.8 eV below the vacuum level. Thus, it is plausible that minor modifications of the model will produce the situation illustrated in the figure. The analysis shows that the occupied surface state is odd under reflec-

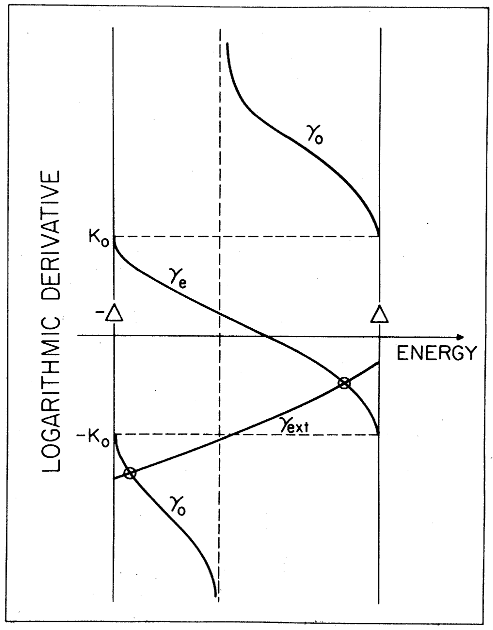

FIG. 5. Qualitative plot of the logarithmic derivatives for the even (γ_e) an odd (γ_o) interior solutions and for the external solution (γ_{ext}) corresponding to the model discussed in the text.

tion in the mirror plane while the unoccupied state is even. Unfortunately, this symmetry is hard to exploit in photoemission or inverse photoemission since the electron detector (or the electron beam) does not lie in the mirror plane.

It is not useful to pursue this discussion in more quantitative detail. It is well known that the Cu L gap is not described quantitatively by a nearly-free-electron model. This is due to the presence of the d bands, which make the gap much larger than an NFE model would predict. This increase in gap size is not symmetric, since L_1 does and L_2' does not interact with the d states.

A realistic slab calculation for Cu(110) has been performed by Dempsey and Kleinman.[14] They predict two surface states at $\overline{Y}$ and correctly find that one is occupied and one unoccupied. In addition, their partial density of states (PDS) for the first layer has a contribution from the unoccupied state. No structure is seen in the PDS of the surface region due to the occupied state. This is expected, based on elementary considerations, since the decay length for a surface state is shortest in the center of the gap. The occupied state is so close to the band edge that it penetrates well into the bulk, thus spreading its charge over several layers. This is consistent with the oxygen contamination results mentioned above.

In Fig. 2 we have plotted the dispersions of the two surface states as predicted by Dempsey ad Kleinman (dot-dashed lines). We also include the measured dispersion of the occupied surface state[10] (open circles). The agreement between experiment and theory is satisfying, but quantitative differences exist. The unoccupied (occupied) surface state is about 0.5 eV higher (0.2 eV lower) than predicted theoretically. Also, the measured effective masses for both states are larger than the calculation would indicate.

These discrepancies may have their origin in one of several effects. Firstly, Dempsey and Kleinman based their (non-self-consistent) surface calculation on a fit to the bulk band structure of Cu as calculated (non-self-consistently) by Burdick,[20] who finds the L_2' and L_1 symmetry points at -0.61 and $+3.95$ eV, respectively. A more recent (self-consistent) calculation obtains $L_2' = -0.9$ eV and $L_1 = +4.26$ eV.[21] Photoemission data by Lindau and Walldén[22] put L_2' at -0.75 eV and L_1 at $+4.05$ eV, while Knapp *et al.*[23] place the L_2' point at -0.9 ± 0.2 eV. This shows that the gap at L is underestimated by the calculation to which Dempsey and Kleinman fit. A larger gap indicates a stronger interaction potential between states near the zone boundary, so the predicted surface-state bands would be expected to split further apart.

Secondly, the calculation by Dempsey and Kleinman used the geometry of the ideally truncated Cu(110) structure. It is known from high-energy ion scattering[24,25] and LEED[24,26,27] that the Cu(110) interlayer spacing shows an oscillatory relaxation: The outermost interlayer spacing is reduced, while the following one is increased from the bulk value. As the surface states have different weight on different layers, incorporating this differential relaxation in a surface-state calculation could well cause the predicted surface-state bands to shift in opposite directions, again improving numerical agreement with the data.

As mentioned earlier, the unoccupied surface state on Cu(110) shows many similarities to the one on Ag(110). Comparison of the bulk band structures and results from previous angle-resolved photoemission experiments indicates strong similarities for the occupied states as well. This leads one to expect that there may be an occupied surface state at $\overline{Y}$ on Ag(110). In electroreflectance experiments on Ag(110), a strong signal was observed at $\hbar\omega = 1.77$ eV,[28] well below the onset of bulk interband transitions. This was interpreted as originating in transitions from bulk bands around L_2' to an unoccupied surface state,[29] the state eventually observed directly by Reihl *et al.*[7] However, no theoretical evidence was given for an occupied surface state at $\overline{Y}$. Our results suggest that the region just below E_F at the $\overline{Y}$ point on Ag(110) should be reinvestigated, both theoretically and experimentally. It may well be the case that the signal observed in electroreflectance measurements is not exclusively due to bulk band to surface-state transitions, but may have a very substantial component from surface-state to surface-state transitions. Photoemission experiments addressing this question would require good energy and angular resolution as the L_2' point in Ag is located only 0.31 eV below E_F.[30]

IV. CONCLUSIONS

In summary we have observed a previously undetected, unoccupied surface state in the $\overline{Y}$ gap of the Cu(110) surface. It has an energy of 2.5 ± 0.2 eV above E_F at $\overline{Y}$ and disperses parabolically with an effective mass of $m^*/m = 1.1$. These results, when considered along with published data on the occupied surface state[8] at $\overline{Y}$, represent the first observation of two crystal-induced surface states in a single band gap on a metal surface. We have presented a plausibility argument that explains why two surface states may exist in this gap. The surface states calculated by Dempsey and Kleinman[14] agree quantitatively with those observed experimentally, but the exact energy positions and dispersions differ somewhat for both the occupied and the unoccupied states.

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