

## Surface state and surface resonance at the center of the surface Brillouin zone $\bar{\Gamma}$ of Cu{001}

S. C. Wu

*Department of Physics, Peking University, Beijing 100 871, People's Republic of China*

C. K. C. Lok, J. Sokolov,\* J. Quinn, Y. S. Li, D. Tian, and F. Jona

*College of Engineering and Applied Science, State University of New York, Stony Brook, New York 11794-2275*

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Angle-resolved photoemission experiments on Cu{001} reveal a peak at 5 eV and another at 2.2 eV below the Fermi level which are, respectively, a surface state and a surface resonance at the center of the surface Brillouin zone,  $\bar{\Gamma}$ . The intensities of both peaks relative to the bulk are functions of photon energy and exhibit maxima for final-state momentum values as predicted by the theory of Louie *et al.* The intensities of both peaks are very sensitive to oxygen contamination of the surface, and their energy positions and dispersions are in good agreement with theoretical predictions. Changes in the polarization of the exciting radiation show that the two states have  $\Delta_1$ - and  $\Delta_5$ -like symmetry, respectively, suggesting that they originate from the *s-d*-hybridized  $\Delta_1$  band at the bottom of the Cu *d* band, and from the  $\Delta_5$  band, respectively.

### I. INTRODUCTION

We report here the results of an extensive study of the electronic structure of a Cu{001} surface which confirm the existence of a surface state and a surface resonance at the center of the surface Brillouin zone,  $\bar{\Gamma}$ . The surface state is located 5 eV below the Fermi level in the *s-d*-hybridization gap, while the surface resonance is located 2.2 eV below the Fermi level. A surface resonance is distinguished from a surface state in that its position is not in a band gap of the projected band structure. Both this surface state and this surface resonance have been discussed and questioned in recent reports in the literature.

Experimentally, several surface states have been observed on Cu{001},<sup>1-4</sup> and their energy dispersion relations have been found to be in qualitative or semiquantitative agreement with the results of calculations.<sup>5-8</sup> However, theoretical predictions of the number and energy location of surface states have been controversial. Thus, Gurman and Pendry<sup>9</sup> find a single surface-state band in the *s-d*-hybridization gap. Kasowski<sup>10</sup> finds no surface state on Cu{001}. Louie *et al.*<sup>11</sup> concluded from a high-resolution experimental study that a 5-eV peak in the photoemission spectrum of Cu{111} is a surface state, and claimed that a 5-eV peak in the photoemission spectrum of Cu{001} should have the same surface-state properties as that on Cu{111}. By contrast, Nilsson *et al.*<sup>12</sup> concluded, on the basis of a theoretical analysis of the band structure around 5 eV below the Fermi level, that the energy of the observed state is not located in a band gap, but rather coincides with the lowest bulk band near the *L* point of the Brillouin zone. Our experiments support the claim of Louie *et al.* for Cu{001} and suggest that the surface state is split off from the *s-d*-hybridized  $\Delta_1$  band at the bottom of the *d* band.

The surface resonance examined in this work is located at the top of the *d* band about 2.2 eV below the Fermi level. In the late 1970s several experiments were per-

formed which studied the changes in photoemission spectra caused by the chemisorption of a number of gases on Cu{001}.<sup>13-15</sup> A universal feature of the results of these experiments is that a sharp peak in the Cu{001} photoemission spectrum at the top edge of the 3*d* band is substantially attenuated when foreign atomic species are chemisorbed on the surface. Gay *et al.*<sup>5</sup> carried out an elaborate self-consistent electronic-structure calculation for a nine-layer Cu slab with {001} surfaces, and found a number of surface-state and/or surface-resonance bands which are expected to be strongly attenuated by the chemisorption of impurities, thereby explaining the experimental observations. However, these theoretical conclusions have not been widely accepted, partly because the existence and the energy of surface states located near or in the *d* band are usually not well predicted by calculations. Essentially all *d*-like surface states are predicted to be at too high an energy relative to experiment. The experiments reported herein involve changes in polarization and energy of the light which could not have been easily done in the 1970s. Thus, we find a very strong and narrow surface resonance located at the top edge of the *d* band which is indeed sensitive to surface contamination. Studies of the symmetry of the wave function and of the dispersion relation of the state involved show that this state originates from the  $\Delta_5$  branch of the Cu 3*d* band.

The structure of this paper is as follows: Sec. II outlines the experimental technique; Sec. III presents the results pertinent to the 5-eV surface state; Sec. IV describes the results relating to the 2.2-eV surface resonance; and Sec. V summarizes our conclusions with regard to the origin of these states.

### II. EXPERIMENTAL PROCEDURE

The photoemission experiments were carried out at beam line U7 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton,

NY). A plane-grating monochromator was used to disperse the synchrotron light, and the experiments were carried out in the range of photon energies from 13 to 130 eV. Two different photoemission spectrometers were used in order to optimize the range of available polarizations of the synchrotron light. For measurements with pure or strongly *s*-polarized radiation an angle-resolved double-pass cylindrical mirror analyzer was used with an angular resolution of  $2^\circ$ . For measurements with strongly *p*-polarized radiation a hemispherical analyzer (Vacuum Generators) featuring a  $2.4^\circ$  acceptance angle was used. The total resolution was 0.3 eV (0.2 eV) as determined at the Fermi level of Au with 25 eV (10 eV) pass energy in the analyzer and 40 eV photon energy.

Clean Cu{001} surfaces were prepared by sequences of argon-ion bombardment and annealing cycles. The cleaning process was continued until Auger-electron-spectroscopy spectra of the surface showed no C, O, or S signals. The crystallinity of the surface was checked by low-energy electron diffraction.

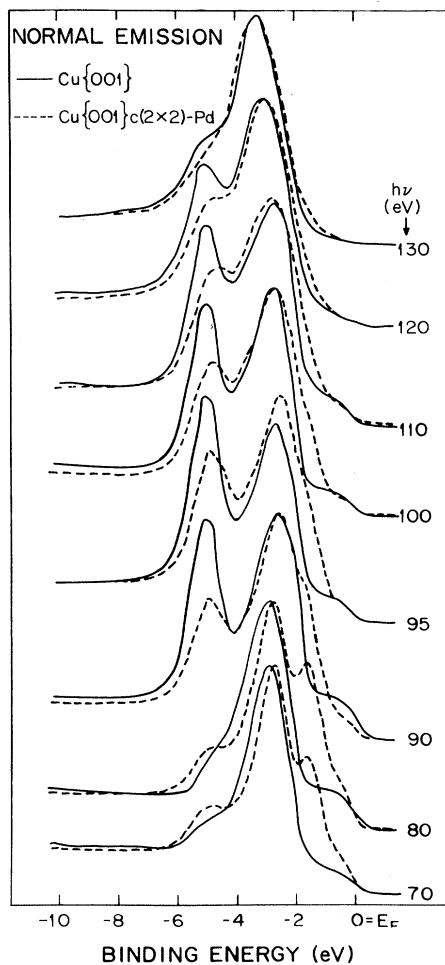


FIG. 1. Angle-resolved electron-distribution curves for normal emission from Cu{001} (solid) and Cu{001}c(2×2)-Pd (dashed) measured with photon energies between 70 and 130 eV with 70%-*p*-polarized light.

### III. THE 5-eV SURFACE STATE

The experimental identification of surface states is based on the verification of recognized properties of such states, namely (i) absence of energy dispersion with respect to the momentum component perpendicular to the surface ( $k_{\perp}$ ), (ii) energy location in band gaps of the projected band structure, and (iii) sensitivity to the presence of foreign atoms (most photoemission peaks due to surface states are strongly reduced in intensity when impurities are adsorbed on the surface).

Figure 1 depicts normal-emission electron-distribution curves (EDC's) from clean Cu{001} (solid curves) as measured with photon energies between 70 and 130 eV and about 70%-*p*-polarized radiation. We note the presence of two peaks: one located between 2 and 4 eV below the Fermi level  $E_F$ , the other at about 5 eV below  $E_F$ . We discuss in the following the nature and the origin of both these peaks.

The lower-binding-energy peak exhibits some energy dispersion with momentum perpendicular to the surface ( $k_{\perp}$ ) and reaches a minimum in binding energy when the photon energy  $h\nu$  is about 95 eV. In the free-electron approximation the final-state momentum at normal emission is given by the formula

$$k_{f\perp} = 0.512(h\nu - E_b + |V_0|)^{1/2}, \quad (1)$$

where  $E_b$  and  $V_0$  are the binding energy of the initial state and the inner potential in eV, respectively. For  $h\nu = 95$  eV, choosing  $E_b = 2.5$  eV and  $V_0 = -8.6$  eV,<sup>16</sup> we calculate from Eq. (1) that  $k_{f\perp} = 5.15 \text{ \AA}^{-1}$ . Assuming that the free-electron approximation is valid and comparing the calculated  $k_{f\perp}$  with the distance  $\Gamma X$  between the  $\Gamma$  and  $X$  points of the bulk Brillouin zone (for Cu,  $a_0 = 3.61 \text{ \AA}$ ; hence  $\Gamma X = 1.74 \text{ \AA}^{-1}$ ), we find that

$$k_{f\perp} \cong 3\Gamma X. \quad (2)$$

This result means that at  $h\nu \cong 95$  eV the momentum value is at or near the  $X$  point. According to the dipole selection rule<sup>17</sup> at normal emission only initial states which have  $\Delta_1$  or  $\Delta_5$  symmetry can be excited. From studies of the Cu band structure<sup>18</sup> we know that there is no  $\Delta_1$  band near the  $X$  point in the energy range between 2 and 4 eV below  $E_F$ ; hence we conclude that the initial state producing the photoemission peak in this energy range is the bulk  $\Delta_5$  band.

We now discuss several properties of the other peak that appears in Fig. 1—the peak located about 5 eV below  $E_F$ , which for brevity we will call  $s_1$ . We begin by noting that the  $s_1$  peak exhibits no energy dispersion in the photon-energy range between 70 and 130 eV. Since the data presented in Fig. 1 were collected at normal emission, no dispersion means that the  $s_1$  peak is independent of  $k_{\perp}$ .

Next, we note that the intensity ratio of  $s_1$  to the adjacent bulk peak (2–4 eV below  $E_F$ ) is a function of photon energy and reaches a maximum at  $h\nu \cong 98$  eV. This general behavior is characteristic of surface states, as was originally explained by Louie *et al.*<sup>11</sup> and discussed by others.<sup>3</sup> The theory predicts that the peak intensity of a

surface state that is derived from a single band is periodic in  $k_{f1}$ , and has maxima at photon energies corresponding to the  $k_{f1}$  value at which the energy of the bulk band is closest to the surface-state energy. In the present case, at  $h\nu=98$  eV the free-electron approximation (1), with  $E_b=5$  eV and  $V_0=-8.6$  eV, gives  $k_{f1}=5.16 \text{ \AA}^{-1}=2.97\Gamma X$ . We claim that this result is consistent with Louie's theory of surface states. In fact, Cu band-structure studies show that in the energy range around 5 eV below  $E_F$  there are only two bulk bands: one is  $\Delta_2$ , the other is  $\Delta_1$ . According to the dipole selection rule, excitation from the  $\Delta_2$  band is forbidden; hence the surface state  $s_1$  can only be derived from the  $\Delta_1$  band. Since the  $\Delta_1$  band has its highest energy near the  $X$  point, the distance between  $s_1$  and the  $\Delta_1$  band is minimum near the  $X$  point. We conclude that the photon-energy dependence of the intensity of  $s_1$  is indeed consistent with Louie's theory of surface states.

Finally, we examine the sensitivity of the intensity of the  $s_1$  peak to the presence of foreign atoms on the sur-

face. In Fig. 1 the dashed curves were measured after deposition of 0.5 layers of Pd on the Cu{001} surface. It is obvious that the intensity of the  $s_1$  peak decreases much faster than that of the bulk peak. In Fig. 2 the EDC's were measured with 30%- $p$ -polarized light; the solid curves are from a clean Cu{001} surface, the dashed curves from a surface exposed to 4000 L of oxygen gas. [1 langmuir (L) $\equiv 10^{-6}$  Torr sec.] Comparison of the ratios of  $s_1$  to the adjacent bulk peak in Fig. 1 (70%  $p$ ) and Fig. 2 (30%  $p$ ) shows that the ratio decreases when the  $p$  component of the light is reduced. Thus, according to the dipole selection rule,<sup>17</sup> the wave function of  $s_1$  has  $\Delta_1$ -like symmetry. This result confirms the assertion that the  $s_1$  peak is derived from the  $\Delta_1$  band. In fact, examination of the Cu band structure as calculated by Janak, Williams, and Moruzzi<sup>19</sup> shows that  $s_1$  is located just above the top of the lowest  $\Delta_1$  band in the  $s$ - $d$ -hybridization gap. We conclude that all the properties listed above are supportive of the surface-state character of the  $s_1$  peak.

We have also measured the dispersion of this surface state. Figure 3 shows experimental EDC's measured with  $h\nu=90$  eV and about 30%- $p$ -polarized light along the  $\bar{\Gamma}\bar{\Delta}\bar{X}$  line. The inset of Fig. 3 shows the experimental dispersion relation along the  $\bar{\Gamma}\bar{\Delta}\bar{X}$  line for the  $s_1$  surface state (solid circles) and the theoretical dispersion relation as calculated by Gay *et al.*<sup>5</sup> (open circles and solid line). The experimental trend is in good agreement with the theoretical, although the energy positions reveal

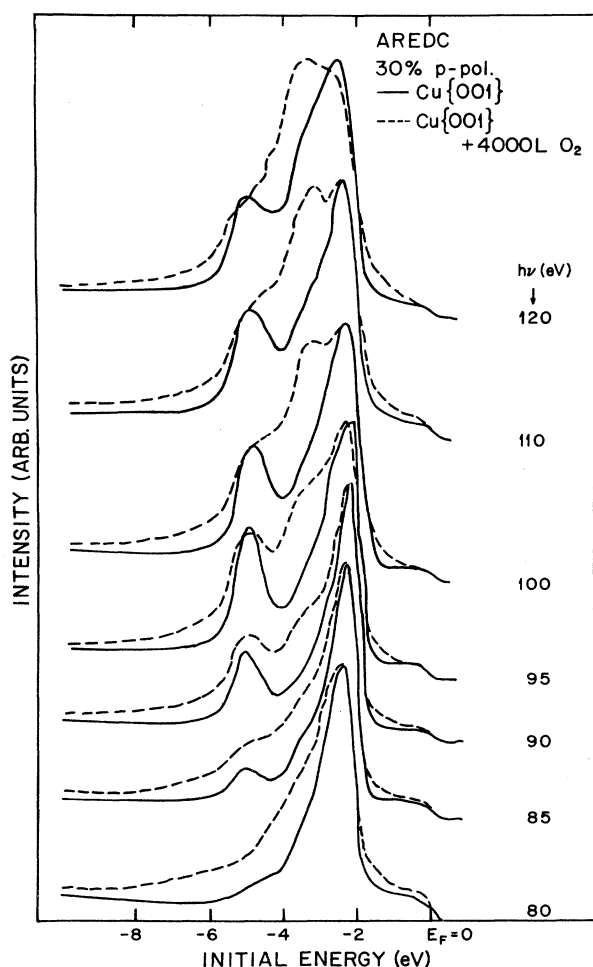


FIG. 2. Angle-resolved electron-distribution curves for normal emission from Cu{001} (solid) and Cu{001} + 4000 L of oxygen (dashed) measured with photon energies between 80 and 120 eV with 30%- $p$ -polarized light.

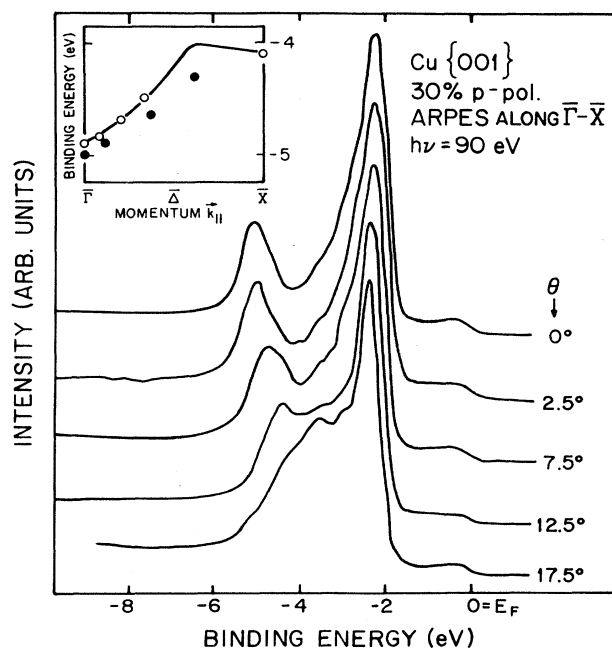


FIG. 3. Angle-resolved electron-distribution curves measured for emission at different polar angles  $\theta$  along  $\bar{\Gamma}\bar{X}$  with  $h\nu=90$  eV and 30%- $p$ -polarized light. The value  $\theta=0^\circ$  corresponds to normal emission. The inset shows the dispersion of the surface state (solid circles) compared with the calculation of Gay *et al.* (Ref. 5) (open circles and solid line).

differences of about 0.2 eV. We note that both the position and the dispersion of  $s_1$  are also in good agreement with the calculation of Gurman and Pendry.<sup>9</sup>

#### IV. THE 2.2-eV SURFACE RESONANCE

Figure 4 depicts normal-emission EDC's from Cu{001} as measured with photon energies between 70 and 110 eV and pure  $s$ -polarized light. The main peak  $A$ , which is located about 2.2 eV below  $E_F$ , exhibits no energy dispersion in the photon-energy range considered. Since the EDC's were collected at normal emission, no energy dispersion means independence of  $k_{\perp}$ . Figure 5(a) shows two sets of normal-emission EDC's taken at  $h\nu=75, 90,$  and  $110$  eV—one set from clean Cu{001}, the other from a Cu{001} surface that had been exposed to 600 L of oxygen. Figure 5(b) shows difference curves obtained by subtraction of the clean-surface EDC's from those of the oxygenized surface. For this subtraction we have assumed that the photoemission intensities near the Fermi level and at energies larger than 7 eV were not affected by the exposure to oxygen. The figure shows

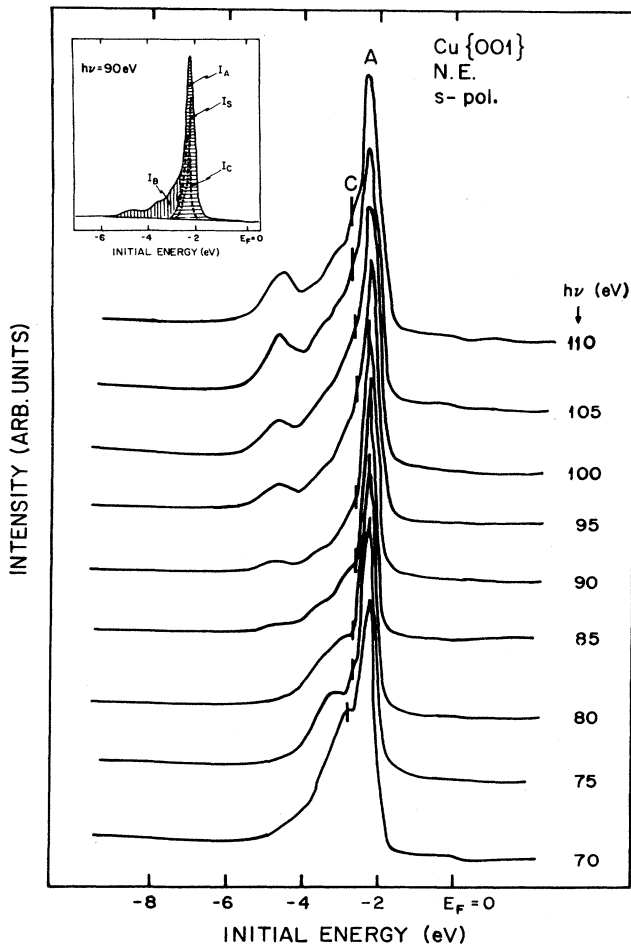


FIG. 4. Angle-resolved electron-distribution curves for normal emission from Cu{001} measured with photon energies between 75 and 110 eV with pure  $s$ -polarized light.

that the most striking consequence of this exposure is the severe attenuation of the main peak  $A$ . Thus, both the absence of dispersion with  $k_{\perp}$  and the sensitivity to impurities indicate that the state producing peak  $A$  is localized at the surface. However, this state is not in a band gap of the projected bulk band structure; hence it is more properly called a surface resonance rather than a surface state.

The experimental EDC's depicted in Fig. 4 allow the evaluation of the ratio  $I_A/I_B$  between the intensity  $I_A$  of peak  $A$  (horizontal shading in the inset of Fig. 4) and the intensity  $I_B$  of the emission on the high-energy side of peak  $A$  between approximately 2.5 and 6 eV (vertical shading in the inset of Fig. 4). The experiment shows that  $I_A/I_B$  is maximum for a photon energy of 90 eV. This observation seems to contradict two facts, one theoretical and one experimental. The theoretical fact is that the theory of Louie *et al.*<sup>11</sup> predicts a maximum for the intensity ratio between a surface-state (or surface-resonance) emission and bulk emission at  $k_{f\perp}=3\Gamma X$ , see Eq. (2), which in the present case [using Eq. (1) with  $k_{f\perp}=5.22 \text{ \AA}^{-1}$ ] corresponds to a photon energy of 97 eV, not 90 eV. The experimental fact is that, upon exposure of the surface to oxygen, the attenuation of the intensity of peak  $A$  relative to that of the bulk is *not* maximum at 90 eV, as it should be if peak  $A$  were wholly due to the surface resonance, but is larger at 75 and at 110 eV than at 90 eV, see Fig. 5(b).

These contradictions are only apparent. In Fig. 4 we note the presence of a small shoulder  $C$  which disperses with photon energy and is closest to peak  $A$  at 90 eV. The fact that peak  $C$  disperses tells us that it is caused by interband transitions, and the fact that it is closest to peak  $A$  at 90 eV tells us that at this photon energy there is a substantial contribution to the intensity of peak  $A$  by bulk interband transitions. Such contribution is obviously larger at 90 eV than at 75 or 110 eV, because at these latter energies the shoulder  $C$  is farther away from peak  $A$ . In general, we can write that  $I_A=I_S+I_C$ , where  $I_S$  and  $I_C$  are the contributions from the surface resonance and shoulder  $C$ , respectively (see dashed and dotted curves in the inset of Fig. 4). Hence,  $I_A/I_B=(I_S+I_C)/I_B$ . Only  $I_S$  is sensitive to oxygen exposure, and  $I_C$  is larger at 90 eV than at either 75 or 110 eV. Hence the relative attenuation of peak  $A$  is larger at 75 or 110 eV than at 90 eV, as observed in Fig. 5(b). Furthermore, we can calculate the ratio  $I_S/(I_B+I_C)$ , and find that it has indeed a maximum near 97 eV, as predicted by the theory of Louie *et al.*<sup>11</sup>

We have also measured the dispersion relation of the surface-resonance peak along the  $\bar{\Gamma}\bar{\Delta}\bar{X}$  line. Figure 6 shows EDC's of the Cu valence band measured at  $h\nu=90$  eV with pure  $s$ -polarized light and for different photoelectron emission angles  $\theta$  along the  $\bar{\Gamma}\bar{\Delta}\bar{X}$  line. For  $\theta=10^\circ$ ,  $k_{\parallel}\cong 0.5\bar{\Gamma}\bar{X}$ , and the increase in binding energy of peak  $A$  is less than 0.1 eV. This small dispersion of the surface-resonance peak is consistent with the results of the calculations of Gay *et al.*,<sup>5</sup> although the energy position is different by 0.05 Ry.

Figure 2 confirms the sensitivity of the surface reso-

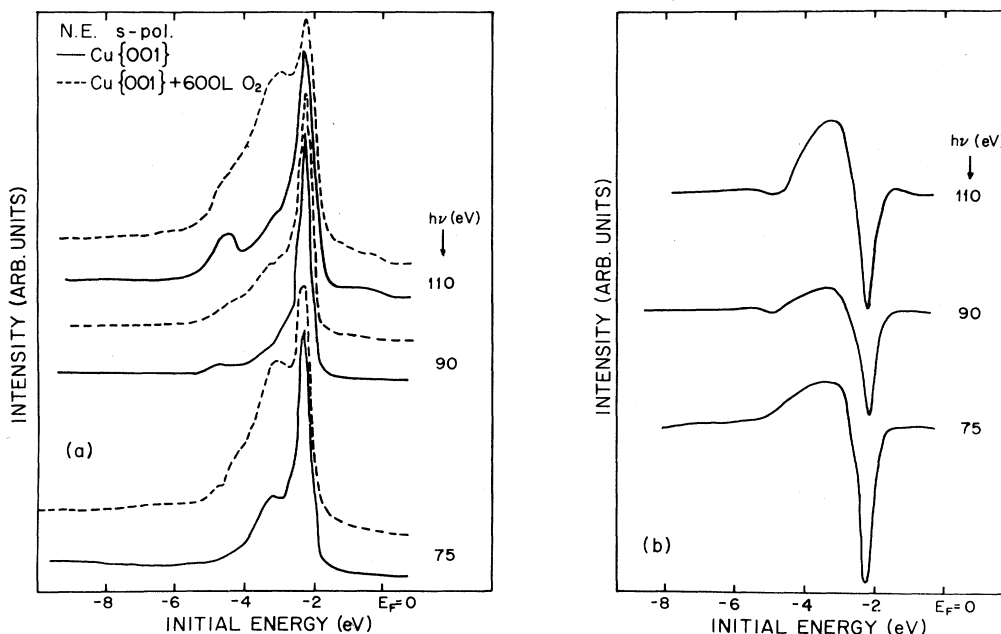


FIG. 5. (a) Angle-resolved electron-distribution curves for normal emission from Cu{001} (solid) and Cu{001} + 600 L of oxygen (dashed) measured with photon energies 75, 90, and 110 eV. (b) Difference curves between the two curves in (a).

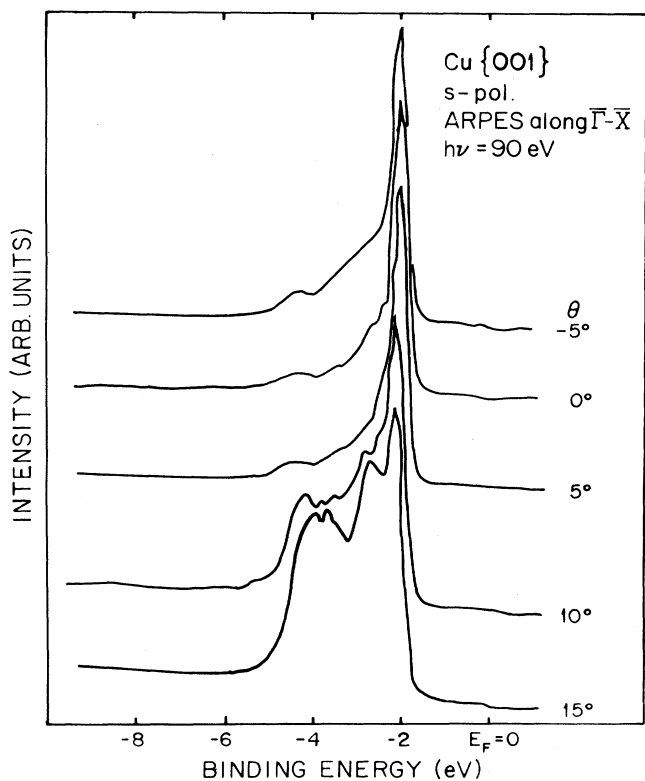


FIG. 6. Angle-resolved electron-distribution curves measured from Cu{001} for emission at different polar angles  $\theta$  along  $\bar{\Gamma}-\bar{X}$  with  $h\nu=90$  eV and pure  $s$ -polarized light. The value  $\theta=0^\circ$  corresponds to normal emission.

nance to chemisorption of impurities by showing that after exposure to 4000 L of oxygen the intensity of the 2.2-eV peak relative to the rest of the valence band decreases. Comparison of Fig. 4 with Fig. 2 shows that the intensity of the surface-resonance peak decreases when the  $s$  component of the light decreases, suggesting that the wave function of the surface resonance has  $\Delta_5$  symmetry. Reference to the calculated band structure<sup>8</sup> and to experimental results<sup>19</sup> further suggests that the surface resonance is located at or just above the top of the  $\Delta_5$  band. Thus, indications are that the surface resonance is derived from the bulk  $\Delta_5$  band.

## V. CONCLUSIONS

Our experiments confirm that the 5- and 2.2-eV peaks in the Cu{001} photoemission spectrum are a surface state and a surface resonance at the center of the surface Brillouin zone  $\bar{\Gamma}$ , respectively. Their energy positions and dispersions are in good agreement with the calculations of Gurman and Pendry<sup>6</sup> and of Gay *et al.*<sup>5</sup> We suggest that the 5-eV surface state originates from the  $s$ - $d$ -hybridized  $\Delta_1$  band at the bottom of the Cu  $d$  band, and the 2.2-eV resonance peak originates from the  $\Delta_5$  band.

We estimate the natural widths  $\Delta E_{NW}$  of these states as follows. First, we determine the energy resolution  $\Delta E_A$  of the analyzer from the fact that we measure, for  $h\nu=90$  eV, a width  $\Delta E_{FWHM}$  of the surface resonance peak of 0.35 eV for 10 eV pass energy in the analyzer (Fig. 4) and of 0.48 eV for 25 eV pass energy (FWHM denotes full width at half maximum). We obtain  $\Delta E_A=0.14$  eV. Then we establish the energy resolution of the monochromator, from  $\Delta E_{h\nu}/E_{h\nu}=0.0025$  eV, to

be  $\Delta E_{h\nu} = 0.22$  eV at 90 eV. Hence, from the equation  $\Delta E_{\text{FWHM}}^2 = \Delta E_{\text{NW}}^2 + \Delta E_{h\nu}^2 + \Delta E_A^2$ , we obtain  $\Delta E_{\text{NW}} = 0.2$  eV for the surface resonance at  $-2.2$  eV. We note that this value is a little smaller than the value 0.3 eV of the state at the top of the  $d$  band, as reported by Knapp, Himpsel, and Eastman.<sup>18</sup> Since in metals the electron-hole lifetimes are mostly governed by inelastic electron-electron interactions, in general one expects lifetimes to become longer (and hence the natural widths to become smaller) with increasing energy toward  $E_F$ . The surface resonance is located at or just above the top of the  $d$  band, and is localized on the surface, so that a slightly longer lifetime (smaller  $\Delta E_{\text{NW}}$ ) than that prevailing at the top of the  $d$  band is reasonable. As for the surface state at  $-5$  eV, we measure  $\Delta E_{\text{FWHM}} = 0.95$  eV at  $h\nu = 90$  and 25 eV pass energy. We then obtain  $\Delta E_{\text{NW}} = 0.9$  eV, larger than the value of 0.6 eV reported by Knapp, Himpsel, and Eastman<sup>18</sup> for states at the bottom of the  $d$  band. Since the surface state is located just above the top of the lowest  $\Delta_1$  band in the  $s$ - $d$ -hybridization gap, a shorter (larger) lifetime (energy broadening) than that applicable to bottom  $d$  states is reasonable. Finally, we note that the lifetime of a (similar) surface state at the  $\bar{\Gamma}$  point of the Cu{111} surface, which is located just above the top of the lowest  $\Lambda_1$  band also in the  $s$ - $d$ -hybridization gap ( $s_3$  state in Ref. 11), is (with  $\Delta E_{\text{FWHM}} = 0.7$  eV) longer than that found here for the state on Cu{001}. We speculate that the reason for this fact is that the  $s$ - $d$ -hybridization gap is smaller at the  $X$  point than at the  $L$  point.

The existence of both the surface state and the surface

resonance on Cu{001} can be well explained by the theory of surface-core-level shifts in noble metals.<sup>20</sup> Since the coordination number of the atoms in the first layer is smaller than that of the atoms in the bulk, the width of the valence band is narrower on the surface than in the bulk. Hence, in noble metals, in the absence of any electron charge transfer between surface and bulk, the Fermi-level position is lower for the first atomic layer than for the bulk. Therefore, there will be charge transfer from the bulk to the surface in order to align the Fermi levels. The consequence of this charge transfer is that the position of the valence band of the first atomic layer is shifted toward lower binding energies with respect to the bulk, thereby exposing the surface state and surface resonance that we have observed.

It may be interesting to note that these two states cannot easily be seen at low photon energies. For  $h\nu$  smaller than, say, 15 eV, two factors make the observation of these states very difficult: (i) the background of secondary electrons is very high, and (ii) the kinetic energy of the photoelectrons is low and, hence, their mean free path is large, reducing the surface sensitivity.

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\*Present address: Physics Department, Queens College, NY 11367.

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