

**Observation of a one-dimensional state on stepped Cu(775)**

X. J. Shen, H. Kwak, D. Mocuta, A. M. Radojevic, and S. Smadici  
*Columbia Radiation Laboratory, Columbia University, New York, New York 10027*

R. M. Osgood, Jr.\*  
*Columbia Radiation Laboratory, Columbia University, New York, New York 10027,  
 Brookhaven National Laboratory, Upton, New York 11973*

(Received 20 July 2000; revised manuscript received 2 January 2000; published 27 March 2001)

We report on using high-resolution angle-resolved two-photon photoemission to observe a one-dimensional surface state 0.27 eV below the Fermi level on a stepped Cu(111) surface. The state is dispersive along the step direction but localized perpendicular to the step orientation. The origin of the state may be explained by confinement due to the step-edge potential.

DOI: 10.1103/PhysRevB.63.165403

PACS number(s): 73.20.At, 73.21.-b

**I. INTRODUCTION**

The study of the electronic and magnetic behavior of quantum-confined electrons is important for fundamental condensed matter physics and for its technical applications. For example, considering the former, the quasiparticle-based Fermi-liquid theory is known to break down for one-dimensional electron systems because of the Peierls divergence in the particle-hole bubble and the charge-spin separation.<sup>1</sup> Instead in one-dimensional systems, the Luttinger-liquid model is applicable. This theory predicts several new phenomena, such as the vanishing of the Fermi edge, the appearance of charge and spin-density waves, and the enhancement of electron-electron correlations.<sup>1</sup> As a consequence, the search for an ideal one-dimensional electronic system, with which to observe low-dimensional electron energy structure and dynamics, has recently been the object of extensive theoretical and experimental research. For example, electrons in one-dimensional metallic carbon nanotubes have been reported to show the signature of a Luttinger liquid.<sup>2</sup> In addition, one-dimensional confinement of surface-state states has been observed on H/Ni(110),<sup>3</sup> the Fe(100)-c(2×2)Si surface alloy,<sup>4</sup> as well as between the surface-oxide domains on Cu(110).<sup>5</sup> Finally, the collective excitations of spin and charge modes predicted by Luttinger theory were recently observed in one-dimensional Au chains formed on vicinal Si(111).<sup>6</sup>

Monoatomic steps on surfaces offer an interesting possibility for the study of a one-dimensional system, since these steps may be prepared with nearly ideal geometry and in the dense arrays needed for probing with photoemission. On a stepped surface, the two-dimensional symmetry of a flat surface is broken in the direction perpendicular to the step orientation and, as shown in several recent experiments, steps may localize surface states into one dimension.<sup>7-10</sup> Decorations of these steps with an adsorbate may be used to adjust the degree of this localization.<sup>10</sup> For example, confined step-edge states have been found on stepped Au(111) by analyzing STM images of the electronic states and measuring the  $dI/dV$  spectra of the confined states.<sup>7</sup> Similarly, localized electronic states at step edges on Ni(7, 9, 11) have been observed with angle-resolved ultraviolet photoelectron

spectroscopy.<sup>8</sup> Finally, evidence of an unoccupied isolated step-induced image state on stepped Cu(001) has been reported by Ortega *et al.*,<sup>9</sup> in this case electron movement perpendicular to the steps was believed to be confined by the potential trough at the step edge.

In the work reported here, a new surface state on stepped Cu(775) was investigated to determine if any evidence of reduced dimensionality is present in its electronic structure. The experiments used high-resolution angle-resolved two-photon photoemission (AR2PPE) in conjunction with a high-repetition-rate femtosecond optical source to examine the dispersion and energy distribution curves of this surface state on the stepped surface. Comparative dispersion measurements along and perpendicular to the step edges show that one of these surface states was occupied and had a one-dimensional character; this state apparently results from step-potential confinement. The surface of the single-crystal sample was probed under a variety of surface conditions. For example, introduction of a low-coverage of adsorbed oxygen was found to enhance the photoemission signal.

**II. EXPERIMENT**

The experimental measurements relied on the use of angle-resolved two-photon photoemission, a technique described in detail, for example, in Ref. 11. Briefly the technique is able to probe the energies and dispersions of both occupied and unoccupied surface and bulk bands. Although not used here, AR2PPE can also measure the electron dynamics in these bands through the use of a variable-time-delay pump-probe technique. Our apparatus utilized the femtosecond output of a mode-locked Ti:sapphire oscillator. The laser output consisted of 70 fs pulses at a repetition rate of 89 MHz and had an average power of ~500 mW; its wavelength was tunable between 760 and 840 nm. The third harmonic ( $3\omega$ , ~4.68 eV, spectral width of 30 meV) and second harmonic ( $2\omega$ , ~3.13 eV, spectral width of 40 meV) pulses were generated in nonlinear crystals and compressed by two four-prism configurations. These two beams were used either together as a ( $3\omega$ ) pump and probe ( $2\omega$ ) beam or as both ( $2\times 2\omega$  or  $2\times 3\omega$ ) for two-photon photoemission; see Sec. III B and III C, respectively. These two beams were aligned

collinearly and focused onto a single-crystal (775), copper surface.

The stepped surface was formed by making an  $8.5^\circ$  miscut to a single-crystal Cu(111) surface; the reverse side of the same crystal was cut to provide flat Cu(111). After repeated cycles of sputtering and annealing, the LEED pattern exhibited sharp split spots at its hexagonal corners, indicating a regular step array. Details of the morphology and preparation procedures for the sample can be found in Ref. 12. An electrostatic spherical-sector energy analyzer, with an energy resolution  $\sim 80$  meV, was used for the detection of the photoelectrons. The analyzer was rotatable about a vertical axis through the crystal face and in a plane that is perpendicular to the sample surface. The detector had a  $0.5^\circ$  angular resolution.

The high-repetition rate of the laser pulses gave an excellent signal-to-noise ratio, while allowing the flux intensity for both pump and probe beams to remain relatively low at the sample surface ( $\leq 20 \mu\text{J}/\text{cm}^2$ ); thus space-charge distortion of the electron energy distribution was negligible. A bias voltage of  $-4$  V was applied between the sample and the analyzer in order to reduce any stray-field-induced drift of low-energy electrons. Such a bias can, in principle, affect the measurement of dispersion. Thus, a series of dispersion measurements were carried out for different values of bias voltage, between  $-1$  and  $-8$  V, and it was found that, while the signal intensity varied with the bias, the measured dispersion curves had the same effective mass for each value of bias voltage. Finally, all experiments were conducted at room temperature.

### III. RESULTS

#### A. Bichromatic spectra on clean Cu(775)

Angle-resolved, two-photon-photoemission measurements were performed on the Cu(775) surface. In these experiments, two-color, or bichromatic, 2PPE was used because its use gives higher signal-to-noise than monochromatic 2PPE.<sup>11</sup> The 2PPE signal from a clean Cu(111) surface, in the range of pump energies used here, is known to be dominated, in the first step of the process, by resonant excitation from the  $s$ - $p$   $n=0$  band to the  $n=1$  image state. However, for a stepped (775) surface, the  $n=0, 1,$  and  $2$  bands are displaced from each other in  $k_{\parallel}$  space by the miscut and stepped surface slopes which give rise to different reference planes for these three bands.<sup>12</sup> This displacement is shown in Fig. 1, which presents data obtained using nanosecond 2PPE;<sup>12</sup> these measurements had lower signal-to-noise than that obtained in the present experiment. Note also that the  $s$ - $p$  state shown in Fig. 1 exhibits a normal dispersion for a direction perpendicular to the step edge; a result consistent with other measurements on stepped surfaces by photoemission<sup>12-13</sup> and scanning tunneling microscopy.<sup>14</sup>

Figure 2(a) shows a set of bichromatic 2PPE spectra on clean Cu(775) for detection angles of  $\theta=0^\circ$  to  $+21^\circ$ , measured with a pump photon energy  $h\nu_{\text{pump}}$  of 4.68 eV and a probe energy  $h\nu_{\text{probe}}$  of 3.13 eV. The spectra in Fig. 2(a) were taken in a direction perpendicular to the step edge; the

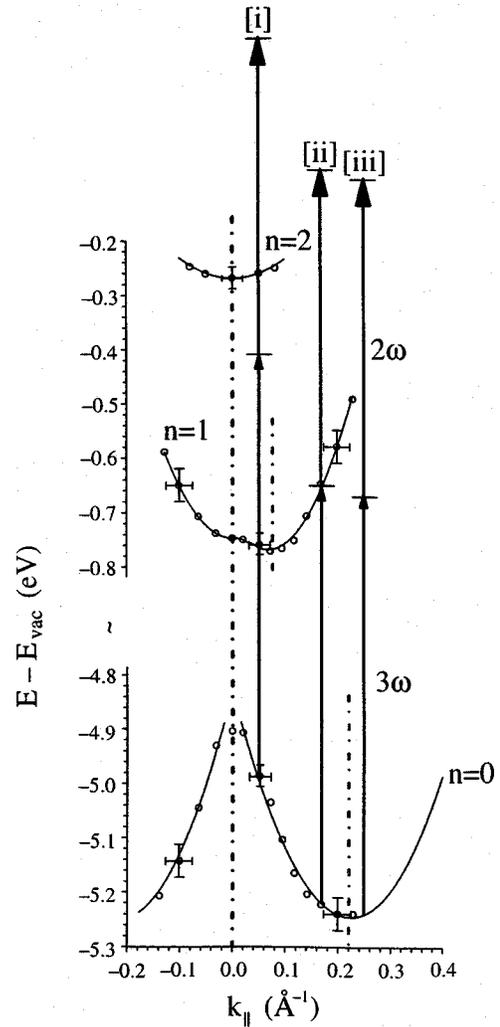


FIG. 1. Dispersion curves of the  $n=0, 1,$  and  $2$  states on stepped Cu(775); from Ref. 12. Note that these curves were obtained with a nanosecond source and, thus, have a lower signal-to-noise ratio than that obtained using the femtosecond source used in this paper. Excitation processes for the  $n=0$  surface state at three different angles are also displayed, corresponding to spectra (i), (ii), and (iii) in Fig. 2(a).

positive angles correspond to detection in the “uphill” direction, as indicated in Fig. 2(b). The pump wavelength chosen here allows resonant excitation between the  $s$ - $p$  surface state and the  $n=1$  image state for a value of parallel momentum corresponding to  $\theta \sim 8^\circ$ . This resonance manifests itself through a higher intensity for the  $n=1$  signal in the spectrum at  $\theta=9^\circ$  than for that at other angles, i.e., case (ii) in Figs. 2(a) and 1. As indicated in Fig. 2(b)  $k_{\parallel}=0$  is defined with respect to [775]. Similar signals were seen for negative detection angles. Because of the different reference planes for the  $n=1$  and  $2$  states, as shown in Fig. 1, both of these states are energetically accessible from the  $n=0$  state at the uv-pump photon energy used here, for small detection angles, i.e.,  $\theta < 12^\circ$ . However, notice that the signal of the  $n=2$  image state disappears at large angles because the photon energy is not sufficient to excite electrons below the Fermi level to the  $n=2$  image state. The dispersion, apparent

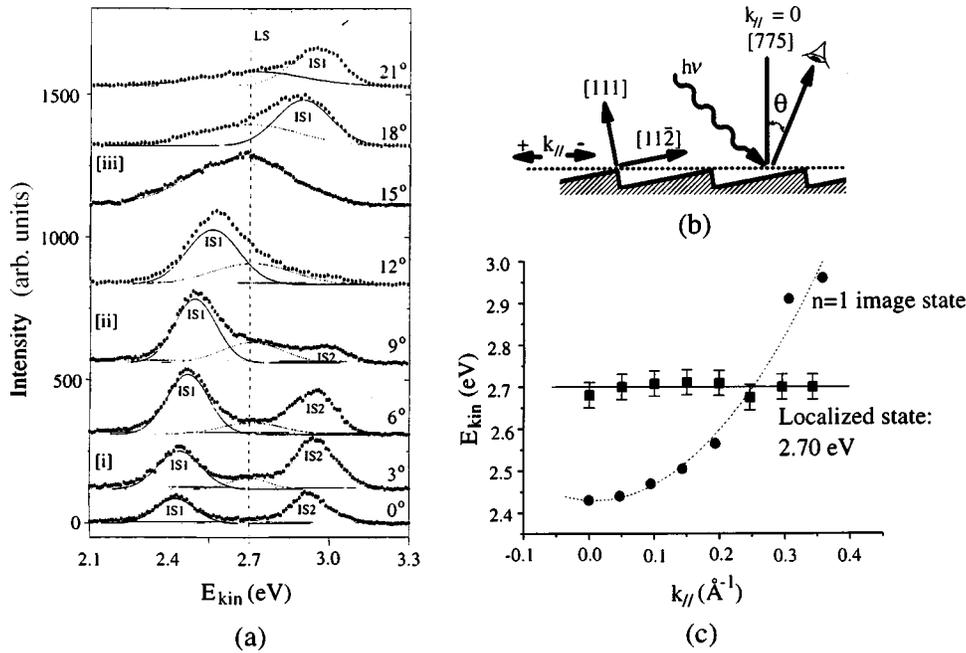


FIG. 2. (a) Bichromatic angle-resolved spectra on clean Cu(775): detection perpendicular to the step orientation. (IS1:  $n = 1$  image state, IS2:  $n = 2$  image state, LS: localized state.) The pump photon energy is 4.68 eV and the probe photon energy is 3.18 eV. (b) The geometry for angle-resolved photoemission experiment. (c) Dispersion curves of the  $n = 1$  image state and the newly observed “flat” band state: detection perpendicular to the step orientation.

in the data of Fig. 2(a), was measured and was found to be in good agreement in energies and parallel momenta with the earlier measurements made using a nanosecond probe<sup>12</sup> and shown in Fig. 1. Note that the  $s$ - $p$  surface-state dispersion curve, which is displayed in Fig. 1, was measured via a different approach than described here for the  $n = 1$  and 2 curves.<sup>12</sup> However, the fact that in Fig. 2 resonant excitation for  $n = 1$  using  $3\omega$  was at  $\theta \sim 9^\circ$  is, for the reasons described above, consistent with the  $s$ - $p$  dispersion curve shown in Fig. 1.

The measured energy distribution curves (EDC) were carefully fit (see Fig. 2) with a Gaussian profile or a Gaussian profile convoluted with a Fermi function at the Fermi edge, using a standard nonlinear least-squares fitting algorithm. As just mentioned, the  $n = 1$  and  $n = 2$  image-state peaks were the most prominent features in the angular-dependent spectra. These features exhibited the normal, i.e., parabolic dispersion with an effective mass of  $m^* \sim m_e$ , the mass of a free electron. In addition, a careful analysis of each spectrum also revealed the presence of a weak feature midway between the  $n = 1$  and  $n = 2$  features. This feature was not observed in our earlier measurements using nanosecond sources;<sup>12</sup> the reason is given at the end of this section. The kinetic energy of electrons emitted from this new band was  $2.70 \pm 0.04$  eV, indicating that the state was located at  $0.27 \pm 0.04$  eV below the Fermi level. The dispersion curves of the  $n = 1$  image state and the new band cross each other at a  $15^\circ$  detection angle, thus causing the EDC to have only a single broad peak at this angle, as shown in Fig. 2(a). Figure 2(c) shows the dispersion curve of the  $n = 1$  image state as well as that of the new band, obtained from the angle-dependent EDC’s. Note that this band does not disperse for detection in the plane perpendicular to the step edges. Finally an examination of Fig. 2(a) also shows that the width of both the image and localized state appear to broaden as the detection angle increases. Broadening of both the image and the  $s$ - $p$  surface states with detection angle has been observed by

several groups previously and attributed to electron confinement by surface scattering.<sup>15</sup> This angle-dependent broadening of the localized state seems to be significantly larger than for the image or  $s$ - $p$  states. At present we do not have an explanation for this observation.

Further, 2PPE measurements were made for the electrons emitted parallel to the step edges on the same Cu(775) surface, with the same pump and probe photon energies as given above. The data are shown in Fig. 3 for detection angles  $\theta$  from  $-10^\circ$  to  $11^\circ$ . The  $n = 1$  and 2 image states showed the same dispersion, as that of a flat surface. In contrast to the nondispersive behavior across the steps seen for perpendicular photoemission, the newly observed band is dispersive in the direction parallel to the step edges with an effective mass  $m^* = 0.39 \pm 0.13 m_e$ . The presence of a state,

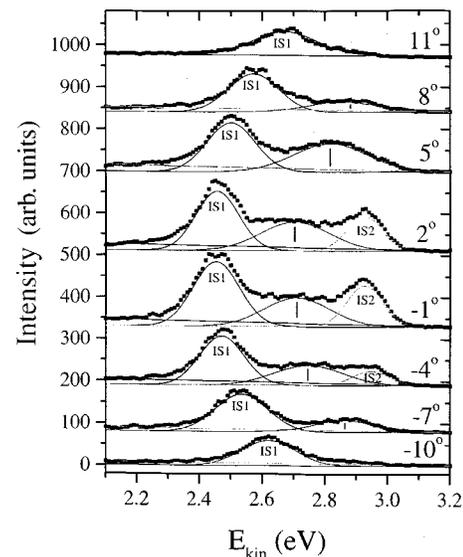


FIG. 3. Bichromatic angle-resolved spectra on clean Cu(775): detection parallel to the step edge.

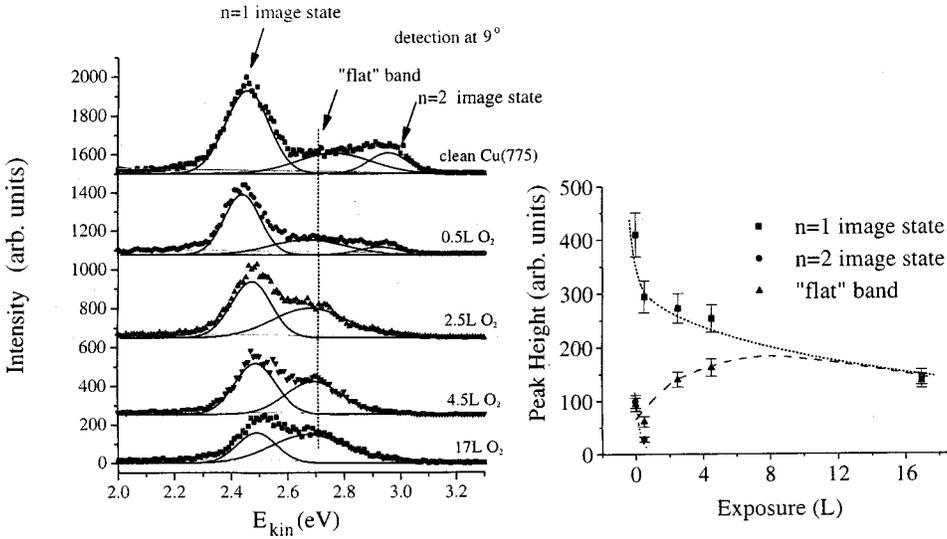


FIG. 4. Effects of  $O_2$  exposure on the signal intensities of the two image-states and the nondispersive state. The spectra were taken at  $9^\circ$  from the surface normal and in a plane perpendicular to the step edge. The inset shows the dependence of the peak height of the three states on  $O_2$  exposure in Langmuir.

which is normally dispersive along the step edge and nondispersive perpendicular to the step edges, indicates that the state is localized in one dimension. It is also interesting that this value of the effective mass is, within experimental error, that for the  $s$ - $p$  surface state on stepped Cu(111), which has  $m^* \sim 0.38m_e$  (Ref. 14) as measured by STM, and  $\sim 0.49m_e$  (Ref. 12) as measured by resonance excitation in 2PPE. Note also that in those measurements the  $s$ - $p$  surface state was dispersive both perpendicular and parallel to the step edges. Our measurements throughout this paper indicate a similar behavior for the usual  $s$ - $p$  surface state.

To test the sensitivity of these observations to a specific Cu(775) surface many independently prepared surfaces were formed; each exhibited a sharp LEED pattern. The nondispersive state seen in Fig. 2(a) was seen repeatably on each surface. This state was not seen, however, on flat Cu(111). In addition, we have considered why our prior measurements<sup>12</sup> on the same stepped surface, using a nanosecond pump and probe pulses, did not detect such a band. We believe that the current experiments were able to detect the nondispersive band because the very high-repetition-rate femtosecond pulses used here enabled us to achieve a much higher signal-to-noise ratio and, thus, a much higher energy resolution (80 vs 150 meV), compared to that available from the earlier nanosecond system.

### B. Cu(775) surface after $O_2$ exposure

Additional experiments were made to clarify the origin of the flat band. The first of these involved exposure of the surface to  $O_2$  since oxygen is known to affect image and  $s$ - $p$  surface states. Specifically, oxygen exposure quenches the  $n=0$ , 1, and 2 surface states. Dosing the stepped surface with  $O_2$  should, thus, permit a comparison of the sensitivity of the flat-band state to  $O_2$  exposure with the sensitivity of other surface states. Additional effects of oxygen on copper surface will be discussed in Sec. IV B.

In the experiment, the surface was first exposed to  $O_2$  and any changes in spectra, obtained with bichromatic 2PPE, were examined. Figure 4 shows our observation of the ef-

fects of oxygen exposure on both the image-state and the flat-band peaks at  $9^\circ$ . A slight increase of the work function of  $\sim 40$  meV was observed on this stepped surface due to oxygen adsorption—a contrast with previously reported observations that showed no change in work function after oxygen-adsorption on flat Cu(111).<sup>16–18</sup> The inset in Fig. 4 shows the dependence of signal intensity on  $O_2$  exposure in Langmuirs.

Although not shown in the figure, our measurements showed that the sensitivity of the  $s$ - $p$  state to oxygen exposure was approximately the same as that for the  $n=1$  state. The  $n=2$  image-state signal was the most sensitive to  $O_2$  and, in fact, was essentially quenched after 0.5 L  $O_2$  exposure. There appear to be two possible contributing factors to this behavior. First, there is most probably a greater probability for inelastic scattering for the higher lying  $n=2$  state on the  $O_2$ -disordered surface than for the  $n=1$  state because of the smaller binding energy of the former. This would cause the state to be quenched at lower oxygen coverage than for the  $n=1$  state. In addition, a diminution of the  $n=2$  signal could also be expected to result from the small increased work function on the  $O_2$ -covered surface. This reduction would decrease the degree of resonance between the  $n=0$  state and the  $n=2$  state and the pump photon energy as the  $O_2$  coverage was increased. Specifically since the image states are pinned to the vacuum level while the surface state is fixed relative to the Fermi level, an increase in the surface work function would increase the energy spacing between the  $n=2$ , which lies above the Fermi level, and  $n=0$  state. Thus, the degree of resonance for the fixed photon energy used here would be reduced. It is interesting that the intensity of the  $n=1$  image-state signal was less sensitive to  $O_2$ ; thus, it was only reduced by  $\sim 2$  for the 4.5 L  $O_2$  exposure shown in the figure. This reduced sensitivity, compared to that for  $n=2$  is consistent with the above arguments for  $n=2$ , since the  $n=1$  state has a higher binding energy and would be less prone to inelastic scattering and since an increase in work function would cause the energy spacing between the  $n=1$ , which lies below the vacuum, and  $n=0$  state to increase and the resonance between the two levels to increase.

In contrast to the monotonic decrease of the  $n=1$  image state (and the  $s$ - $p$  surface state) with  $O_2$  exposure, the intensity of the flat band state, observed here, initially increased with  $O_2$  exposure. This increase resulted in a factor of  $\sim 2$  enhancement in the flat band signal at an exposure of the 4.5 L. Larger values of exposure led to a decrease in signal at a rate approximately equal to that of the  $s$ - $p$  signal. The photoemission signals for all surface states were extinguished, i.e., unobservable, after an exposure of  $>30$  L. Thus, while the flat-band state is enhanced by low oxygen coverage, its sensitivity to oxygen exposure at higher coverage, is nearly that of the  $s$ - $p$  surface band. There are several possible explanations for the pronounced enhancement of the flat-band state at low oxygen coverage. However, the most obvious is that it is well known that chemisorbed surface oxygen in Cu(111) gives rise to an unoccupied surface band located at 2.9 eV above the Fermi level.<sup>17-19</sup> This band would provide a near-resonant intermediate path for excitation from the flat-band state with the 3.1 eV,  $2\omega$  photon. In this case the photoemission process would be due to a bichromatic  $2\omega$  plus  $3\omega$  process, see Secs. III C and IV below for additional comments on  $O_2$  chemisorption.

Finally, mild Ar-ion sputtering of the clean surface, e.g., 30 sec at  $0.05 \mu\text{A}$ , was sufficient to destroy all surface states. Subsequent, brief annealing led to the recovery of all features reported above. These same measurements were repeated on flat Cu(111), i.e., the surface on the reverse side of the stepped sample. No extra state was observed either before or after  $O_2$  exposure on the flat surface. These observations indicate that the newly observed state is a real step-induced one-dimensional state, rather than a defect- or adsorbate-induced artifact.

Finally in this section, we have concentrated on describing the  $O_2$  exposure from the point of view of a diagnostic technique for understanding the properties of the flat-band surface state. In fact, a trace, i.e., 3–6 L, exposure of the surface to  $O_2$  also had the important advantage of permitting simplification of the signal, since it selectively weakened the nearby image-state signal, while also enhancing the flat-band signal. This technique was used, for example, for the experiments that are described in the following section. Note that although there was a slight work-function-induced shift of the peak energy, when  $O_2$  was present, the energy relative to the Fermi level and the dispersion of the flat-band was identical to that for the clean surface.

### C. Monochromatic ( $2\omega$ ) spectra on Cu(775)

The photoemission spectrum can also be simplified via the use of monochromatic angle-resolved 2PPE. Specifically, if only a  $2\omega$  ( $\sim 3.1$  eV) beam is used to excite and probe the Cu(775) surface, this choice of a single pump wavelength eliminates the normally unoccupied image state in the spectrum, since this photon energy is not sufficient to excite electrons from the  $s$ - $p$  surface state or the bulk states to the image state. As a consequence, only a signal from the occupied states will be present in the spectra.

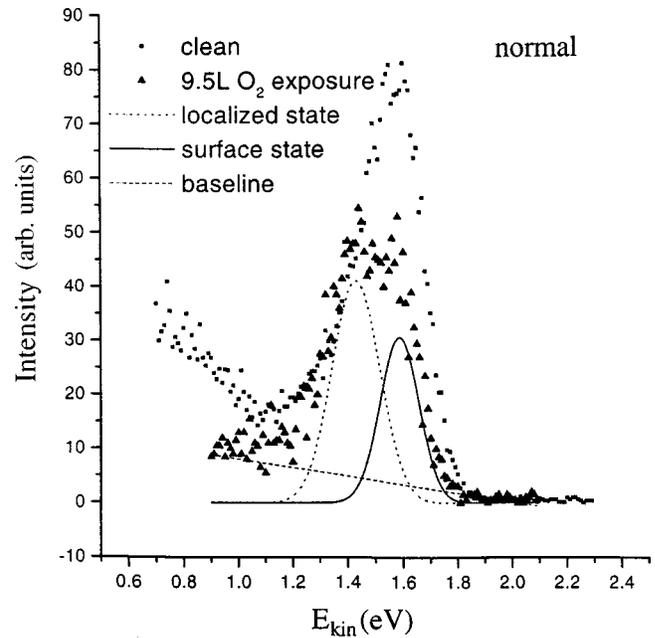


FIG. 5. Monochromatic spectra at 3.1 eV, taken at the surface normal. The data show the comparison between the clean surface and the surface for 9.5 L  $O_2$  exposure.

Note that for the photon energies used in this monochromatic-excitation experiment, an additional oxygen-related feature must be considered. Specifically, as mentioned above, an unoccupied surface band can also be induced by the presence of  $\sim 500$  L of oxygen adsorbed on Cu(111);<sup>17-19</sup> for a stepped surface which is more reactive the needed coverage would be expected to be lower. This band is located  $\sim 2.9$  eV above the Fermi level and would provide a resonance of the  $2\omega$  photon energy used in our experiment between our observed occupied flat band and this unoccupied band. The dispersive properties of this band appeared not to have been reported for a stepped surface; it does disperse on flat Cu(111).<sup>17</sup> Because of the possibility of resonant excitation, this state might be expected to enhance the signal intensities of states lying below the Fermi level.

Figure 5 shows monochromatic 2PPE spectra taken in the direction of the surface normal, before and after oxygen exposure, with the  $2\omega$  beam present. The signal from the  $s$ - $p$  surface state was more sensitive to oxygen and was reduced by  $\sim 2$  after 9.5 L exposure, while the signal from the newly observed state was close to its maximum value.

Figure 6 shows data taken from angle-resolved measurements, including the dispersion curves of the newly observed state, measured after 3 L  $O_2$  exposure, both perpendicular and parallel to the step edge. The surface was first exposed to 3 L of oxygen to boost the intensity of the flat-band or newly observed state. A typical angle-resolved spectrum for a measurement made perpendicular to the step and showing both the  $s$ - $p$  surface state and the newly observed state is given in the inset. The dispersion data in Fig. 6 do not include, however, our measured data for the  $s$ - $p$  surface states. This spectral data showed that the  $n=0$  surface state and the localized state coexist on our sample. The angular sequence of these

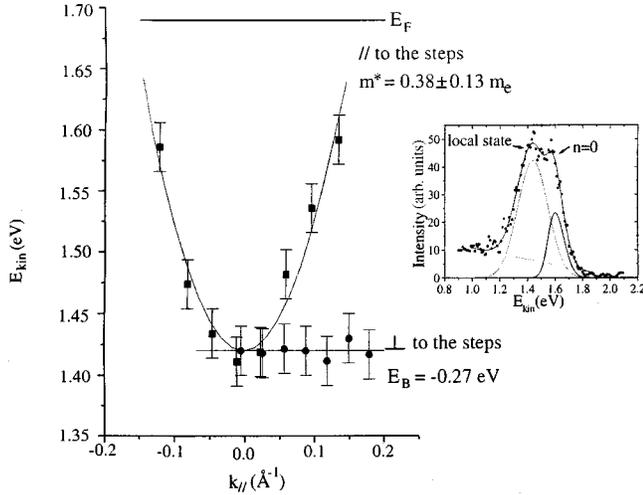


FIG. 6. Dispersion of the newly observed occupied band perpendicular and parallel to the step. Monochromatic 2PPE at 3.1 eV is used. The inset provides one typical EDC, taken at  $\theta=9^\circ$  which shows the coexistence of both the localized state and the  $n=0$  surface state.

data showed that the  $n=0$  surface state exhibited a downward dispersion with an effective mass that, within experimental error, was equal to its value on a flat surface.<sup>12,20</sup> More discussion regarding the  $s$ - $p$  state will be given in Sec. IV A. Regarding the flat-band state shown in Fig. 6, the data shows that the state is nondispersive in a direction perpendicular to the steps and is located 0.27 eV below the Fermi edge. On the other hand, the state is dispersive parallel to the step orientation with an effective mass of  $0.38 \pm 0.13 m_e$ .

We can now crosscheck the location of the state shown in Fig. 6 with that seen in the bichromatic photoemission experiments discussed in Sec. III A. In that case, the pump energy was 4.68 eV and the probe energy was 3.13 eV. For those photon energies, an occupied one-dimensional state located 0.27 eV below the Fermi level would result in a feature with  $E_{\text{kin}}=2.7$  eV, exactly the value obtained in the data shown in Fig. 2. The effective mass for the dispersion curves measured along the step direction for both bichromatic and monochromatic photoemission were also the same within experimental error. The results indicate that the flat band observed in Fig. 2 came from excitation of the same occupied one-dimensional state as probed in this section. Finally, note that this same band has also been observed in the data obtained from the separate ( $3\omega$ ) monochromatic 2PPE experiment in which only  $3\omega$  ( $\sim 4.65$  eV) beam was used to pump and probe the surface while all other experimental conditions were kept the same as in bichromatic experiment.

As mentioned earlier in this section, the existence of an unoccupied oxygen-induced state at 2.9 eV above the Fermi level must be considered in interpreting our data. Clearly the presence of this state on the bare surface in Sec. III B argues that, in the absence of unknown impurities, it is not important for our flat-band state. However, in addition, the photon-energy independence of results further supports this point. In particular, the photoemission data in the case of monochromatic  $2\omega$  2PPE show a band, which is identical in location

and dispersion to that obtained using monochromatic  $3\omega$  2PPE. In the latter case, for which  $3\omega$  was used as a pump, the oxygen state could not be important since it is not resonant at this pump photon energy. Thus, the similarity of the two sets of data, as well as the bichromatic results in Secs. III B and III C, indicates that the flat-band state observed is not affected by this oxygen-induced unoccupied state. However an adsorbed oxygen state, even if not directly in resonance, could enhance the intensities of the pumping process by providing a nearby lying intermediate state.

## IV. DISCUSSION

### A. Clean surface

#### 1. Prior observations

Even though the observation of localized states on several systems has been recently reported, the exact origin of these states still remains unclear.<sup>21–23</sup> For example, the observations described above are consistent with at least one other observation of a localized state on vicinal Cu(111). Specifically, using occupied-state photoemission spectroscopy, Speller *et al.*<sup>21</sup> have recently observed a one-dimensional state on several stepped Cu(111) surfaces; this state also dispersed only along the step orientation. In their experiment the  $s$ - $p$  surface was also present and had the same dispersive properties as on the flat surface. The energy position of the local state was  $\sim 250$  meV below the Fermi level, a position within experimental error of our flat-band state. These authors attributed the origin of this state to Anderson localization.

#### 2. Our observations

Consider first the effect of a simple change in the surface potential in the vicinity of the step edge, as discussed in Ref. 9. In principle, a stepped surface can be viewed as an array of regular, correlated potential perturbations to an ideal two-dimensional surface. However it is best to consider, first, a single, isolated step edge on a perfect flat surface. In general terms, such a step interacts with the bulk crystal in a manner similar to a line defect.<sup>24</sup> Thus, new surface states would be expected to develop around this defect, just as surface states develop at the two-dimensional termination of a bulk crystal. The wave function of the new state should have translational symmetry along the step edge while being localized in a direction perpendicular to the edge by the step-edge potential. This confinement is similar to the localization of image-state electrons by the work-function discontinuity on the perimeter of two-dimensional adsorbate islands, described in Ref. 25.

The degree of the confinement of a one-dimensional electronic state depends on the details of the step-edge dipole. Specifically, the binding energy of the localized state would be expected to be modified by the local dipole potential at the step site, which also lowers the local work function.<sup>26</sup> Consider the analogous case of the surface barrier formed by the image potential. In this connection, Bartels *et al.*<sup>23</sup> have used scanning tunneling microscopy to observe a one-

dimensional image state, trapped at an isolated, straight, step edge on a Cu(111) surface. The authors attributed this localization of an image electron to the dipole potential at the step edge. The binding energy of such a state was calculated by numerically solving the Schrödinger equation at the step site. We anticipate that the occupied state, described here, could be localized in a similar way. To obtain a qualitative insight, let us consider only the change in the surface barrier due to the dipole potential. For simplification, we neglect any effect of the step dipole on the crystal potential. Since the surface state is located just below the surface plane,<sup>12</sup> the static dipole-charge interaction would lead to a lowering of the surface barrier for the surface-state electrons, and a concomitant reduction in the binding energy of the  $s$ - $p$  surface state. This line of reasoning is in agreement with our measurement of a reduction in the binding energy for the localized, occupied state, i.e., 270 meV below the Fermi level, compared to a binding energy of 390 meV at the bottom of the  $s$ - $p$  surface band on the flat surface. Previous experimental measurements of the  $n=0$  surface state binding energy on stepped Cu(211) (Ref. 27) reported a similar reduction for the stepped surface. A quantitative understanding awaits a more rigorous calculation.

Consider now the effect of an *array* of steps on the electronic structure of the local state for a single step edge. Clearly for a sufficiently closely spaced array, the step states would interact. However, Ortega *et al.*<sup>9</sup> have calculated the decay length of the wave function of a step-edge localized state and concluded that the step-step interaction of the new state is very weak even for a step separation of 10 Å. This result suggests that step-state interactions can be neglected on our Cu(775) surface since the interstep spacing is 14 Å.

In one prior observation<sup>9</sup> of a step-induced state, the local state was attributed to a state, which was split off from a nearly equienergetic nonlocal (dispersive) surface state. In this specific case, the state was the  $n=1$  image state on stepped Cu(100). The local state that we observe, which has also been reported by Ortega *et al.*,<sup>21</sup> lies within 120 meV of the band minimum of the  $s$ - $p$  surface state. As a result, it seems reasonable to assume that our local state is split off from the  $s$ - $p$  state by the step-edge potential. This interpretation is further supported by our measurement of the effective mass of the localized state. Specifically, recall that our experiments showed that, in the direction parallel to the step edge, the effective mass is  $0.38 \pm 0.13 m_e$ . This value is within our experimental error, equal to the mass of the  $s$ - $p$  surface state, i.e.,  $0.49 m_e$ , on flat (111) surface<sup>20</sup> and identical to STM measurements of an effective mass of  $0.38 m_e$  on Cu(775).<sup>14</sup> This measurement, thus, further supports the identification of the local state as being split off from the  $s$ - $p$  surface state.

Thus far we have not discussed the influence of step disorder on enhancing or weakening the step localization parallel to the step edge. As mentioned above, in Ref. 21 Anderson localization, or perhaps more rigorously localization due to disorder, was invoked as a possible origin of the flat-band state located energetically in a position similar to that reported here. Given the weak interaction reported for step-localized states reported in Ref. 9, it does not seem necessary

to invoke these disorder effects to explain the localization on the clean surface.

### B. O/Cu(775)

Our measurements have also shown that the  $n=0, 1$ , and 2 states are sensitive to the surface condition and, thus, are reduced dramatically by chemisorption of oxygen on the surface. Our one-dimensional state, as shown in the inset in Fig. 4, is also sensitive to the presence of adsorbates. However, in our case, a low coverage of chemisorbed O<sub>2</sub> has been shown also to enhance the signal from the local state. Earlier in the paper, we discussed possible explanations for this effect: namely, we pointed out that the introduction of an unoccupied oxygen-induced surface state could provide possible explanations for the oxygen-induced enhancements reported here. In this section, we also wish to argue that the addition of an adsorbate should also be considered as an additional means of localizing the state via increased surface disorder.

Recently, disorder-induced localization (sometimes termed “Anderson localization”) has been invoked to explain the localization of surface states on disordered surfaces, e.g., on H/Ni(100) (Ref. 22) and on stepped Cu(111).<sup>21</sup> In such a model,<sup>28</sup> the localized state should be stronger when the correlation energy between steps becomes weak compared to the local, step-potential fluctuation. Furthermore, step bunching and doubling of the terrace widths<sup>29</sup> and weakening of the correlation between the steps would lead to stronger localization. Note that in our case such disorder may be adjustable by, e.g., exposing the stepped surface to a different coverage of oxygen.

Specifically, chemisorption of O<sub>2</sub> is also known to alter the surface structure of stepped metal surfaces.<sup>29–33</sup> For example, the chemisorption of oxygen on vicinal Cu(211), at room temperature, reconstructs the surface and leads to the formation of double steps; the reconstruction starts initially at the step edges for very low oxygen coverage.<sup>29</sup> Periodic nanostripes consisting of mesoscopic Cu(111) and Cu(110)-O(2×1) facets were also found on 5–8 L oxygen exposed vicinal Cu(443), Cu(332), and Cu(221) surfaces.<sup>33</sup> These results may be connected with our observations of the effects of oxygen adsorption on the Cu(775) surface. Specifically, the LEED patterns in our measurements showed a brighter background and more diffuse splitting of the diffraction spots after oxygen exposure, indicating that to some degree the sample was disordered, i.e., step bunching, doubling of the terrace width, and broadening of the terrace-width distribution occurred. At this point, these ideas must be considered speculative; a more definitive investigation of this model awaits additional concurrent STM photoemission experiments on the O/Cu(775) system.

### V. SUMMARY

In summary, a one-dimensional occupied state has been observed on a stepped Cu(775) surface. While this state is quenched at large values of oxygen exposure, the state appears to be enhanced by a small coverage of O<sub>2</sub>. This one-

dimensional state is consistent with a state confined by the step-edge potential.

Stepped Cu(775) surface provides a potential system for the study of one-dimensional electron systems. Further studies such as systematic time-resolved measurements on the newly observed state, STM observations of clean and oxygen exposed Cu(775) surface, step decoration with model adsorbates such as Xe, and, finally, polarization-dependence experiments may lead to new insights into the localization physics.

## ACKNOWLEDGMENT

We thank Dr. Ludwig Bartels for valuable discussions and for discussion of his STM imaging on stepped copper. We also thank Professor J. E. Ortega for communication of his new results and in their interpretation on nondispersive surface states. Financial support from the Army Research Office Contract No. DAAD19-99-1-0238, Joint Services Electronics Program Contract No. DAAG55-97-1-0166 is gratefully acknowledged.

\*Author to whom correspondence should be addressed.

- <sup>1</sup>J. Voit, Rep. Prog. Phys. **58**, 977 (1995).
- <sup>2</sup>M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature (London) **397**, 598 (1999).
- <sup>3</sup>U. Bischler and E. Bertel, Phys. Rev. Lett. **71**, 2296 (1993).
- <sup>4</sup>A. Bidermann, O. Genser, W. Hebenstreit, M. Schmid, J. Redinger, R. Podloucky, and P. Varga, Phys. Rev. Lett. **76**, 4179 (1996).
- <sup>5</sup>E. Bertel and J. Lehmann, Phys. Rev. Lett. **80**, 1497 (1998).
- <sup>6</sup>P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature (London) **402**, 504 (1999).
- <sup>7</sup>Ph. Avouris and I.-W. Lyo, Science **264**, 942 (1994); Ph. Avouris, I.-W. Lyo, and P. Molinas-Mata, Chem. Phys. Lett. **240**, 423 (1995).
- <sup>8</sup>H. Namba, N. Nakanishi, T. Yamagushi, and H. Kuroda, Phys. Rev. Lett. **71**, 4027 (1993).
- <sup>9</sup>J. E. Ortega, F. J. Himpsel, R. Haight, and D. R. Peale, Phys. Rev. B **49**, 13 859 (1994).
- <sup>10</sup>Y. W. Mo and F. J. Himpsel, Phys. Rev. B **50**, 7868 (1994); F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis, Adv. Phys. **47**, 511 (1998). We have recently observed localization of a surface state and enhanced effective mass of the  $n=1$  state on quasi-one-dimensional islands of Ag on Ni(977) (work in progress).
- <sup>11</sup>Th. Fauster and W. Steinmann, in *Photonic Probes of Surfaces*, Vol. 2 of *Electromagnetic Waves: Recent Developments in Research*, edited by P. Halevi (Elsevier, Amsterdam, 1995); W. Steinmann and Th. Fauster, in *Laser Spectroscopy and Photochemistry on Metal Surfaces*, edited by H. L. Dai and W. Ho (World Scientific, 1995), pp. 184–242; R. M. Osgood, Jr. and X. Y. Wang, Solid State Phys. **51**, 1 (1998).
- <sup>12</sup>Y. Wang, X. J. Shen, and R. M. Osgood, Jr., Phys. Rev. B **56**, 7665 (1997).
- <sup>13</sup>J. E. Ortega, S. Speller, A. R. Bachmann, A. Mascaraque, E. G. Michel, A. Nürmann, A. Mugarza, A. Rubio, and F. J. Himpsel, Phys. Rev. Lett. **84**, 6110 (2000).
- <sup>14</sup>M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).
- <sup>15</sup>Ch. Reuss, I. L. Shumay, U. Thomann, M. Kutschera, M. Weinelt, Th. Fauster, and U. Höfer, Phys. Rev. Lett. **82**, 153 (1999); X. Y. Wang, R. Paiella, and R. M. Osgood, Jr., Phys. Rev. B **51**, 17 035 (1995); J. Tersoff and S. D. Kevan, *ibid.* **28**, 4267 (1983); S. D. Kevan, Surf. Sci. **178**, 229 (1986).
- <sup>16</sup>G. Witte, J. Braun, D. Nowack, L. Bartels, B. Neu, and G. Meyer, Phys. Rev. B **58**, 13 224 (1998).
- <sup>17</sup>W. Jacob, V. Dose, and A. Goldmann, Appl. Phys. A: Solids Surf. **41**, 145 (1986).
- <sup>18</sup>M. Bauer, S. Pawlik and M. Aeschlimann, Surf. Sci. **377–379**, 350 (1997).
- <sup>19</sup>D. Rieger, T. Wegehaupt, and W. Steinmann, Phys. Rev. Lett. **58**, 1135 (1987).
- <sup>20</sup>S. D. Kevan, Phys. Rev. Lett. **50**, 526 (1983); G. D. Kubiak, Surf. Sci. **201**, L475 (1988).
- <sup>21</sup>S. Speller, A. Bachmann, T. Rauch, H. Hoechst, F. Himpsel, A. Mascaraque, A. Tejada, E. Michel, A. Nürmann, and J. E. Ortega (unpublished); (private communication).
- <sup>22</sup>E. Bertel, Surf. Sci. **331–333**, 1136 (1995).
- <sup>23</sup>L. Bartels, S. W. Hla, A. Kühnle, G. Meyer, K.-H. Rieder, and J. R. Manson (unpublished).
- <sup>24</sup>Hans Lüth, *Surfaces and Interfaces of Solids*, Springer Series in Surface Sciences (Springer-Verlag, Berlin, 1993), Chap. 6.
- <sup>25</sup>R. Fischer, Th. Fauster, and W. Steinmann, Phys. Rev. B **48**, 15 496 (1993).
- <sup>26</sup>H. Wagner, in *Springer Tracts in Modern Physics*, edited by J. Holzl, F. K. Schulte, and H. Wagner (Springer, Berlin, 1979), Vol. 85, pp. 151–221.
- <sup>27</sup>R. S. Williams, P. S. Wehner, S. D. Kevan, R. F. Davis, and D. A. Shirley, Phys. Rev. Lett. **41**, 323 (1978).
- <sup>28</sup>E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. **42**, 673 (1979).
- <sup>29</sup>G. Witte, J. Braun, D. Nowack, L. Bartels, B. Neu, and G. Meyer, Phys. Rev. B **58**, 13 224 (1998).
- <sup>30</sup>K. W. Jacobsen and J. K. Nørskov, Phys. Rev. Lett. **65**, 1788 (1990).
- <sup>31</sup>O. Haase, R. Koch, M. Borbonus, and K. H. Rieder, Phys. Rev. Lett. **66**, 1725 (1991).
- <sup>32</sup>L. Niu, D. D. Koleske, D. J. Gaspar, S. F. King, and S. J. Sibener, Surf. Sci. **356**, 144 (1996).
- <sup>33</sup>S. Vollmer, A. Birkner, S. Lukas, G. Witte, and Ch. Wöll, Appl. Phys. Lett. **76**, 2686 (2000).