Observation of empty bulk states on Cu(100) by two-photon photoemission

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Two-photon photoemission is observed from Cu(100) in normal emission. The energy-distribution curve shows a structure which originates from the d band at X_5 as a fixed initial state 2.13 ± 0.04 eV below the Fermi level. A resonance of this structure at a photon energy of 3.61 ± 0.02 eV is associated with a transition to the X_4' state as an intermediate state 1.48 ± 0.06 eV above the Fermi level.

A complete comprehension of the electronic system in a solid requires the knowledge of the empty states as well as the occupied states. Experimentally the regime below the Fermi level is accessible by direct measurement of an excited electron, i.e., one-photon photoemission (1PPE). In the past few years inverse photoemission spectroscopy and spectroscopy by two-photon photoemission (2PPE) have been developed as new methods to study empty states. While inverse photoemission can give a complete survey of the unoccupied states,[1] 2PPE is limited to the energy range below the vacuum level and to a small part of the surface Brillouin zone around its center. In this range, however, 2PPE yields considerably more accurate results than inverse photoemission. The advantages of this method have been demonstrated for image-potential states on a number of metal surfaces[2] and for oxygen-induced adsorbate states on Cu(111).[3] In this paper we report on the determination of an unoccupied bulk state on Cu(100) by 2PPE spectroscopy.

The 2PPE process considered in this paper can be explained as follows: An electron is excited from a fixed occupied bulk state to an intermediate state by the first photon and further to a state above the vacuum level by a second photon. The excitation probability of this process depends on the density of states and on the lifetime of the intermediate state. If this product exhibits a maximum in the energy range between Fermi level and vacuum level the 2PPE intensity becomes resonant when the photon energy is tuned to the transition energy between the fixed initial state and this intermediate state. The energy distribution curve (EDC) gives information on the position of the initial state while the intermediate state can be determined by the resonance photon energy.

The experiments were carried out with a tunable dye laser pumped by a XeCl excimer laser with 10 nsec pulse length and a repetition rate up to 30 Hz. For photon energies up to 3.8 eV a uv dye was used and the energy range above 3.75 eV was reached by frequency doubling. Care was taken to avoid a distortion of the spectra by space charge effects which lead to a deviation from the quadratic dependence of this signal on the light intensity. The EDC's of the 2PPE were normalized to the square of the light intensity. The photoelectrons were detected with an angle-resolving (narrower than $\pm2°$) hemispherical energy analyzer operated at a resolution of 160 meV. The Cu(100) surface oriented better than 0.5° was sputtered and annealed up to 500 °C in repeated cycles. The quality of the surface was controlled by low-energy electron diffraction and by 1PPE measured *in situ* using an Ar-resonance lamp. This enabled us to determine the Fermi level and the work function of the sample with an accuracy of 10 meV.

In Fig. 1, spectra of 2PPE normal to the surface are shown for different photon energies. The sample was irradiated with p-polarized light under an angle of 45° in the ΓKWX symmetry plane. The EDC exhibits a structure with a linewidth [full width at half maximum (FWHM)] of ~330 meV, which is marked by an arrow. The shift of this structure with photon energy is shown in Fig. 2. The data lie on a straight line with slope $2h\nu$ which indicates that the structure is caused by a fixed initial state.[3] This straight line intersects the abscissa at a photon energy $h\nu_0=3.38$ eV. From the 1PPE data we obtained a work function $\Phi=4.63$ eV. The position of the fixed initial state relative to the Fermi energy $E_B=\Phi-2h\nu_0$ is determined to -2.13 ± 0.04 eV. Figure 3(a) shows how the peak height of the EDC marked in Fig. 1 depends on photon energy. A pronounced resonance occurs at a photon energy $h\nu_r=3.61\pm0.02$ eV with a width of ~180 meV. This resonance is due to an intermediate state with energy $E_i=h\nu_r+E_B$ at 1.48 ± 0.06 eV above the Fermi level.

The intermediate state that we have found in our experiment could be a bulk state or a surface state. In order to distinguish between these two possible assignments we have repeated the experiment with a monolayer of oxygen adsorbed at the surface of our sample. The result is shown in Fig. 1 by the dashed curve ($h\nu=3.66$ eV). Since this photon energy is close to the resonance energy the process should involve the intermediate state under consideration. The structure is seen to persist in the signal from the oxygen-covered sample, although slightly weakened. Since a surface state should be strongly suppressed by an oxygen coverage,[1] we conclude that the intermediate state is a bulk state. It is obviously not identical with the surface state at 1.15 eV above the Fermi level found in inverse photoemission measurements.[4] This surface state could not be detected in our experi-

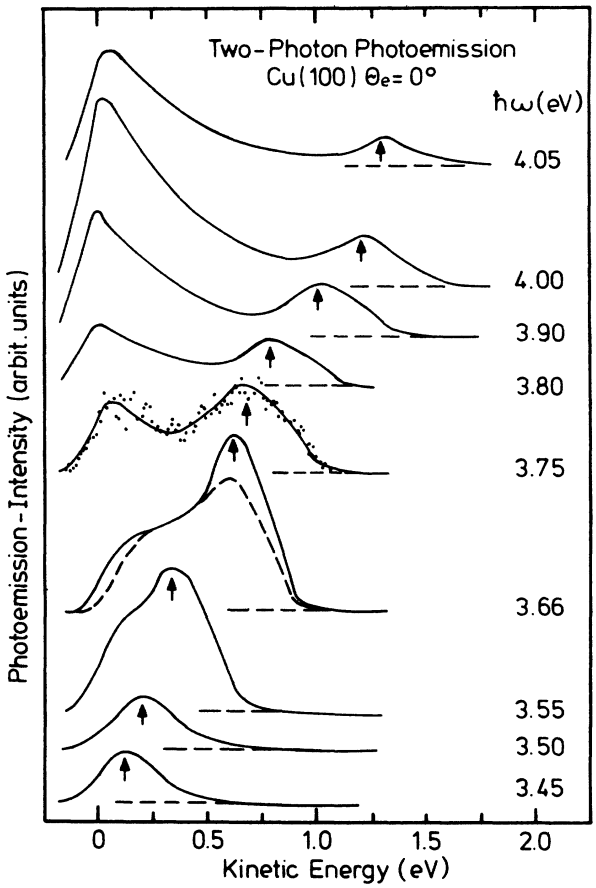

FIG. 1. Energy-distribution curves of two-photon photoelectrons for various photon energies. The emission is normal to the surface and the light is p polarized. The dashed curve for $h\nu=3.66$ eV gives the energy distribution after exposure of the sample to about 2000 L oxygen. [1 langmuir (L)$\equiv 10^{-6}$ Torr sec.]

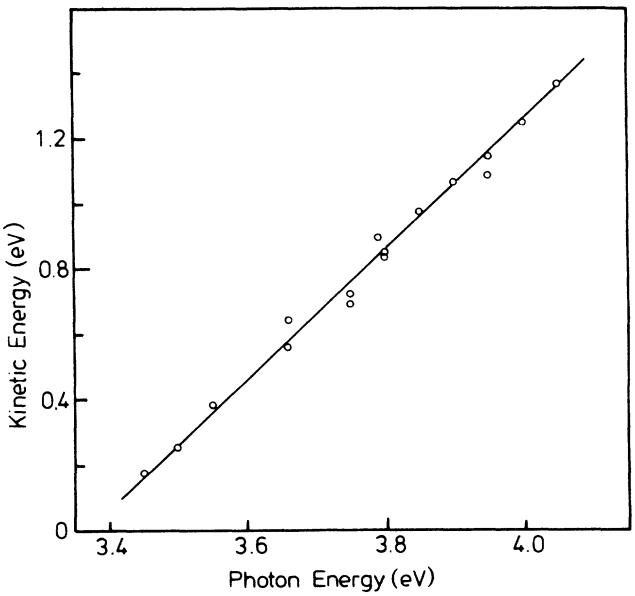

FIG. 2. Kinetic energy of the structure marked by an arrow in Fig. 1 as a function of photon energy. The slope of the straight line is $2h\nu$, which shows that the structure is due to a fixed initial state.

ment, since the excitation energy from the fixed initial state is too small to ionize this intermediate state.

The band structure [Fig. 3(b)] shows that in the photon-energy range of our experiment the intermediate state lies on the Δ_1 band or at the X_4' point. Dipole-transition rules exclude the Δ_2 band and the X_2 point as initial states;[6] therefore, the fixed initial state has to be the flat Δ_5 band or the X_5 point. The transitions $\Delta_5 \rightarrow \Delta_1$ and $X_5 \rightarrow X_4'$ can be excited with an A vector of the light parallel to the surface. For normal emission the final state has to be totally symmetric, i.e., Δ_1 or X_1 in our case.[7] The transition from the intermediate state to this final state can only be excited with an A vector normal to the surface. The combination of the two dipole selection

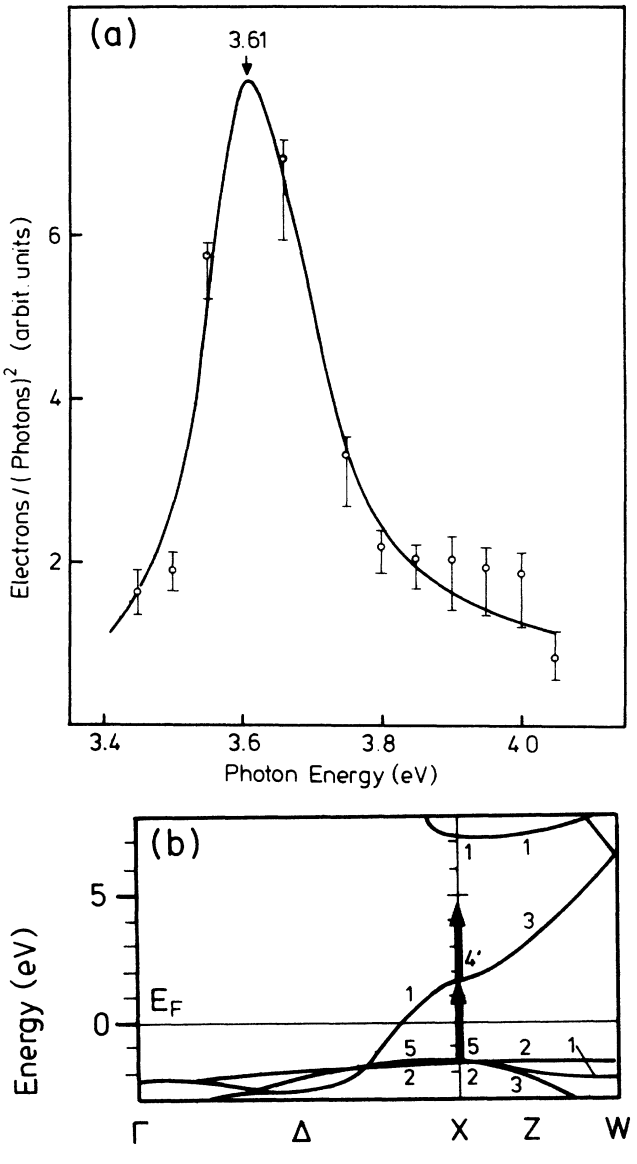

FIG. 3. (a) Peak height of the structure marked in Fig. 1 vs photon energy. (b) Part of the energy band structure of Cu (Ref. 5) relevant for our experiment. The arrows indicates the two-photon transition at resonance.

rules leads to the conclusion that this two-photon process can only be observed with p-polarized light, in agreement with our experimental observation.

The pronounced resonance which we have measured [Fig. 3(a)] has to be assigned to the $X_5 \rightarrow X_4'$ transition. The decrease of the curve above the resonance energy is due to the lack of allowed bulk states; thus only damped states in the band gap[3] are available as intermediate states above the resonance. Below the resonance-energy-allowed bulk states on the Δ_1 band are available but with decreasing density. Consequently, the low-energy side of the resonance curve is an effect of the density of bulk states.

The observed 2PPE process is confined to the surface region of the sample. The final states leading to the photoemission are not allowed bulk states since the X_1 point lies far beyond the energy range of our experiment. At resonance our final state lies in the middle of the band gap between the X_4' and X_1 point [see Fig. 3(b)]. The evanescent wave function of this final state decreases exponentially in the crystal with an exponential $k_{\perp,\mathrm{im}} \simeq 0.2$ Å^{-1}.[8] An appreciable overlap with bulk states is therefore only possible within the topmost three lattice planes limiting the probe depth of this 2PPE process close to the surface.

In Table I, our data are compared with other experimental[9–14] and theoretical results.[5,15–21] As regards the X_5 initial state, we find reasonable, and in some cases excellent, agreement with 1PPE experiments.[9–11] Theoretical values are generally smaller except for Ref. 21. The intermediate state X_4' has so far only been observed with inverse photoemission[12] but the accuracy of this measurement is not sufficient to compare the result with our data. So the energy of the X_4' state which we have measured is the first direct experimental determination with an accuracy comparable to 1PPE. The transition energy X_5-X_4' listed in the last column can be compared with experimental results of optical reflection experiments.[13,14] In the piezo-reflectance measurement our value seems to be also consistent with raw data of this experiment (see W_{44} in Fig. 8 of Ref. 13). The discrepancy with the optical data of Ref. 14 should not be taken too seriously since these experiments integrate over the whole Brillouin zone and the assignment of structure is somewhat ambiguous. The theoretical results for X_4' (with the exception of Ref. 20) are larger than our experimental result. One might argue that the surface sensitivity of our experiment is responsible for this deviation. Diffraction experiments[22]

TABLE I. Experimental and theoretical energy levels of copper at X_5 or X_7^+ and X_6^+, respectively, and X_4' or X_6^-, respectively, and the corresponding transition energy (energies are in eV, measured from the Fermi level). Numbers in parentheses are calculated from the original data for comparison.

Reference	X_5 (X_7^+ and X_6^+)	X_4' (X_6^-)	X_5-X_4'
Present work	−2.13±0.04	1.48±0.06	3.61±0.02
9	−2.05±0.1 −2.15±0.1		
10	−2.00±0.13		
11	−1.95±0.03 −2.12±0.03		
12		~2.0	
13			4.0±0.1
14			3.97
15	−1.95	2.03	(3.98)
16	−1.45	1.63	(3.08)
17	−1.81	1.86	(3.67)
18	−1.95	(2.02)	3.97
19	−1.62	1.63	(3.25)
20	−1.95	1.07	(3.02)
5	−1.54	1.66	(3.2)
21			
Exchange correlation potential	−2.01 −2.16	2.11	(4.27)
$X\alpha$ potential	−2.15 −2.31		

show that the first interlayer spacing of Cu(100) is contracted with respect to the bulk distance. This should lead to a lowering of the position of the X_4' state for the topmost layer.[16,23] This shift is, however, much smaller than the difference between our experiment and the theoretical results. As regards the transition energy X_5-X_4' the theoretical results lie both below and above our data.

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