

# Observation of a direct transition in the sp-band of Cu(111) and $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$ in one- and two-photon photoemission

D. Velic, E. Knoesel, M. Wolf \*

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

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## Abstract

One- and two-photon photoemission (1PPE and 2PPE) spectroscopy has been employed to characterize electronic states of the Cu(111) and  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  systems. A 2PPE process with an unusual wavelength dependence ( $\Delta E_{\text{kin}} = 1.4\Delta h\nu$ ) is observed and assigned to a direct transition from the lower to the upper branch of the copper sp-band. Good agreement (within  $\pm 25$  to  $\pm 35$  meV) between the experimental transitions and a two-band model for the Cu(111) band structure is obtained. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Photoemission measurements generally determine the initial electronic states below the Fermi level and the final states above the vacuum level [1,2]. In order to investigate the unoccupied electronic structure, particularly in the range between the Fermi and the vacuum levels, inverse photoemission has been used [3]. An alternative technique to inverse photoemission is two-photon photoemission (2PPE) spectroscopy [2,4], which probes both occupied and unoccupied states. The nature of the 2PPE process for transitions involving fixed initial, intermediate and final states is illustrated schematically in Fig. 1a–c, respectively. Fig. 1 shows the expected wavelength dependence

of these states; i.e., how the kinetic energy of a peak in 2PPE shifts with the photon energy. To illustrate this dependence we use two different photon energies,  $h\nu_1$  and  $h\nu_2$ . Fig. 1a shows that the kinetic energy of the photoemitted electron from a discrete occupied initial state below the Fermi level varies with twice the photon energy ( $\Delta E_{\text{kin}} = 2\Delta h\nu$ ). Fig. 1b shows that, for a peak arising from a fixed intermediate state, the kinetic energy varies with once the photon energy ( $\Delta E_{\text{kin}} = 1\Delta h\nu$ ). Finally, Fig. 1c indicates that the energy of a fixed (non-dispersing) final-state peak will not vary with photon energy in 2PPE [5]. The wavelength dependence of these three processes has been used to distinguish occupied and unoccupied states in 2PPE spectra [2]. However, the scenario of Fig. 1 implicitly assumes that there is no dispersion along the normal component of the electron wave vector ( $k_\perp$ ). This is valid in the case of surface states or adsorbate-induced states, but

\* Corresponding author. Fax: +49-30-8413-5106;  
e-mail: wolf\_m@fhi-berlin.mpg.de.

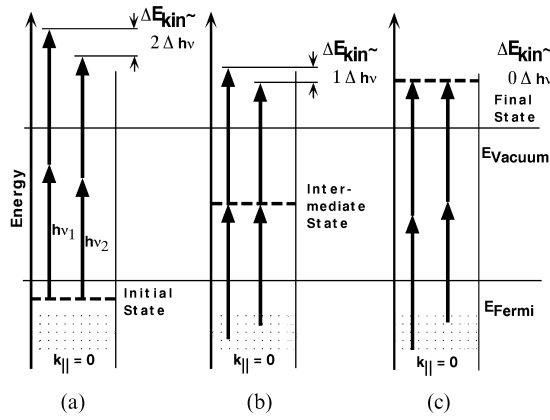


Fig. 1. Variation of the kinetic energy in 2PPE with the photon energy ( $h\nu_1$  and  $h\nu_2$ ). (a) An initial-state peak varies with twice the photon energy ( $2\Delta h\nu$ ); (b) an intermediate state with once the photon energy ( $\Delta h\nu$ ); and (c) a final state peak does not vary with photon energy.

not for transitions in the bulk band structure [1]. Recently, an additional 2PPE process to the one shown in Fig. 1b has been proposed by Pawlik et al. [6] for Ag/Cu(100). 2PPE and one-photon photoemission (1PPE) were compared, showing that a wavelength dependence with a slope of approximately unity (as in Fig. 1b) is not a sufficient criterion for the assignment of an intermediate state [6]. The 2PPE feature observed on Ag/Cu(100) [6] was proposed to originate from a direct transition in the silver sp-band, a process which has been previously reported for 1PPE from Ag(111) [7]. Similar results have been found also in 1PPE from Cu(111) [1,8]. In this paper we report 2PPE and 1PPE measurements from Cu(111) and  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  [9,10]. An unknown feature is observed for both Cu(111) and  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$ , assigned to direct transitions between the lower and the upper branch of the copper sp-band, and compared with the calculated band structure. After Pawlik et al.'s proposal of this process in 2PPE, we provide a more rigorous proof that the observed electronic feature arises from a direct (one- or two-photon) transition from the lower to the upper branch of the Cu(111) sp-band. This assignment is fully consistent with the results of 1PPE from copper [1,8]. In 2PPE spectroscopy the wavelength dependence of this transition exhibits a slope of 1.4

( $\Delta E_{\text{kin}} = 1.4\Delta h\nu$ ) as a result of the  $k_{\perp}$ -dispersion of the copper sp-band along the (111) direction. We obtain good agreement ( $\pm 25$  to  $\pm 35$  meV) between the measured values and the calculated sp-band structure. These results provide a more complete picture of the wavelength dependence of 2PPE spectroscopy.

## 2. Experimental

The 2PPE and 1PPE experiments were performed in an ultra-high vacuum chamber ( $2 \times 10^{-10}$  mbar) combined with a femtosecond laser system as described elsewhere [11]. Briefly, a 200 kHz femtosecond titanium:sapphire oscillator/amplifier (Coherent, Mira 900/RegA 9000) pumped by an argon-ion laser (Coherent, Innova 400) is employed to pump an optical parametric amplifier (Coherent, OPA 9400). Tunable visible pulses of the OPA and also RegA output are used to generate ultraviolet pulses at  $2\omega$  and  $4\omega$ , respectively. Photoemitted electrons are detected in an electron time-of-flight spectrometer within an acceptance angle of  $\pm 3.5^\circ$ . The p-polarized laser beams (electric field vector parallel to the plane of incidence) are incident under  $45^\circ$  with respect to the spectrometer axis. For measurements of the dispersion, the sample is rotated with respect to the axis of the time-of-flight spectrometer. The Cu(111) surface was cleaned by standard sputtering-annealing and the CO gas was dosed through a pin-hole doser at 85 K. The different coverages of CO on Cu(111) were prepared after saturation with the CO at 85 K and subsequent annealing to specific temperatures.

## 3. Results and discussion

Fig. 2 shows 2PPE spectra of clean Cu(111) at 300 K plotted as the 2PPE intensity versus kinetic energy of the final state which were recorded (at  $k_{\parallel}=0$ ) with different photon energies, varying from 3.37 to 3.90 eV. Three features are observed: the copper d-band appearing with increasing photon energy, an unknown peak A and the (initially occupied)  $n=0$  surface state. The maxima

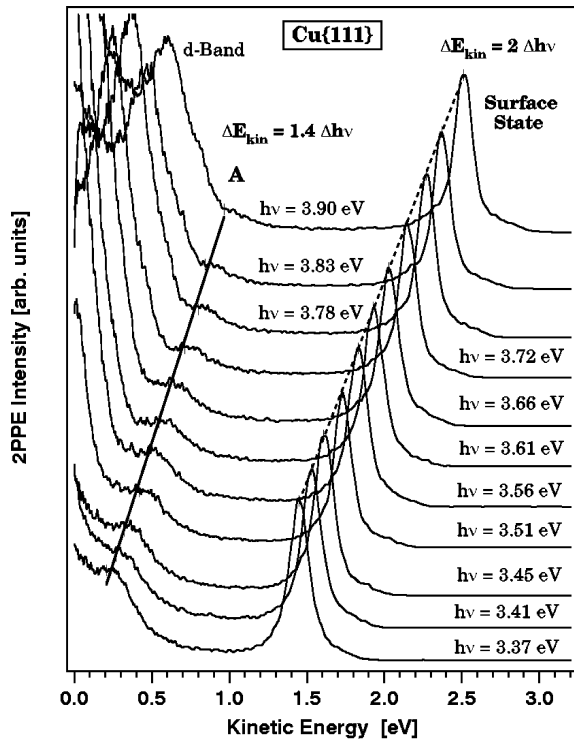


Fig. 2. 2PPE spectra recorded from Cu(111) at 300 K and  $k_{\parallel}=0$ . Note the superposition of the state A with the copper d-band at photon energies above 3.61 eV.

of the A-state and surface-state peaks are determined by single Gaussian fits. The wavelength dependence shows that the peak of the surface state varies with twice the photon energy, which is in agreement with the two-photon process in Fig. 1a. The kinetic energy of peak A varies with approximately 1.4 times  $\Delta h\nu$ , which suggests that it does not correspond to any of the processes described in Fig. 1. Assuming that the observed slope of 1.4 would be approximately either one or two, we might hypothetically consider the state A as either an intermediate unoccupied or an initial occupied state in 2PPE. From the measured work function of copper of 4.9 eV [5] and the photon energies used, one would calculate the binding energies of these hypothetical states to be approximately either 3.1 eV below the vacuum level or 1.8 eV below the Fermi level, respectively. Such states have not been either experimentally observed nor theoretically predicted for Cu(111) [2,4]. We

thus conclude that the peak A in Fig. 2 does not originate from either the 2PPE process shown in Fig. 1a or in Fig. 1b.

We propose that the peak A can be assigned to a direct transition in the copper sp-band, as illustrated in Fig. 3. The upper panel of Fig. 3 shows the copper sp-band structure along the  $\Gamma$ –L direction calculated on the basis of a one-dimensional scattering model [2] with three parameters:  $E_C$  (the bottom of the valence band),  $E_L$  (the lower band edge) and  $E_U$  (the upper band edge). Note that the experiments on Cu(111) and  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO/Cu(111) were performed at 300 K and 100 K, respectively. Therefore, both panels of Fig. 3 actually show two sp-band struc-

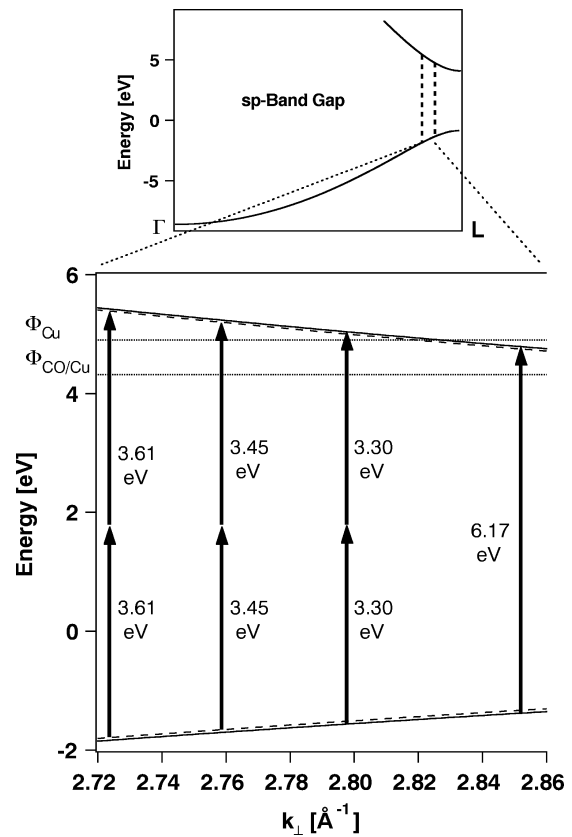


Fig. 3. The Cu(111) sp-band structure along the  $\Gamma$ –L direction, plotted as energy versus electron momentum ( $k_{\perp}$ ). The expanded region of interest shows transitions from the lower to the upper branch of the sp-band observed at 3.61 and 3.45 eV on Cu(111) and at 3.3 and 6.17 eV on  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -CO/Cu(111).

tures, although the difference between them can be only seen in the lower panel of Fig. 3 (dashed line for 300 K and solid line for 100 K). The difference is only 50 meV due to the relatively small temperature dependence of the copper band structure [12,13]. The lower panel, as an expansion of the upper panel, also, shows the work functions of Cu(111) ( $\Phi=4.90$  eV at 300 K) and  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  ( $\Phi=4.32$  eV at 100 K). The values of the model parameters  $E_C$ ,  $E_L$  and  $E_U$ , used to calculate the sp-band structures, are  $-8.6$ ,  $-0.82$  and  $4.08$  eV, and  $-8.6$ ,  $-0.85$  and  $4.1$  eV, at 300 K and 100 K, respectively [2,12,13]. In the lower panel of Fig. 3, the experimentally measured 2PPE peaks are converted into the transitions from the lower to the upper branch of the sp-band and compared with the calculated sp-band structure. For clarity, only two transitions from the spectra in Fig. 2 (at photon energies of 3.61 and 3.45 eV) are shown in Fig. 3. The conversion of the experimental peaks A and their comparison with the sp-band structure is performed as follows: (1) the kinetic energy of the A peak is measured, (2) this kinetic energy is added to the work function, (3) this final value is found on the calculated upper branch of sp-band, (4) a vertical transition is made onto the calculated lower branch of the sp-band, and (5) the difference between the upper and lower branch values is compared with twice the photon energy. This comparison was also performed starting from the lower branch of the sp-band and using the initial-state energy of peak A (kinetic energy minus  $2h\nu$ ). We find reasonably good agreement between the experimental transitions and the calculated sp-band structure within 30 meV (for  $h\nu$  between 3.37 and 3.61 eV). This good agreement is considered as proof that the peak A arises from a direct transition from the lower branch to the upper branch of the Cu(111) sp-band. Note that the agreement becomes worse ( $\pm 122$  meV) for energies above 3.61 eV, due to the energetic superposition of the A peak with the copper d-band, which hinders the determination of the exact peak position as seen in Fig. 2.

Interestingly, we have also found an unknown feature in the CO/Cu(111) system, which is called

peak B in the following. This B state is well-resolved at a CO coverage corresponding to the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  structure as shown in Fig. 4 (left panel) with three other states labeled  $\sigma$ ,  $\pi$  and  $2\pi^*$ . The assignment and detailed investigation of the three unoccupied states is presented elsewhere [10]. Fig. 4 shows the dispersion of peak B for a series of different detection angles ( $0^\circ$  corresponds to emission along the surface normal). To ensure that peak B on  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  is not an unoccupied intermediate state induced by CO adsorption, 1PPE (one-photon photoemission) was also performed. By using 6.17 eV photon energy, the direct photoemission spectra of this state are shown in Fig. 4 (right panel) for different detection angles. Indeed, peak B is still observed while the three unoccupied intermediate state peaks ( $\sigma$ ,  $\pi$  and  $2\pi^*$ ) shown in the left panel disappear. Direct photoemission was also used to demonstrate that the state B of the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  system is not a specific CO-induced state. In Fig. 5 we display five 1PPE spectra for different CO coverages on Cu(111). The high-coverage,  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ , and low-coverage phases were prepared by CO adsorption at 85 K up to saturation coverage and subsequent annealing to 105 K, 120 K and 150 K, respectively. The spectra (measured at 100 K) are plotted as 1PPE intensity versus final-state energy above the Fermi level in order to show the change of the work function on the low-energy side. The work function changes from 4.92 eV for the clean Cu(111) surface to 4.32 eV for the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  system at 100 K. The peak B is observed at all CO coverages, suggesting that the state B is not specific for the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO}$  geometry. However, the intensity of the peak B is approximately proportional to the change of the work function (and is *not* proportional to the CO coverage). If we assume that peak B originates from a bulk transition (and not from an adsorbate-induced state) this observation can be rationalized by the change of the transmission and reflection probability of an electron at a step barrier [2]. In other words, the higher the work function (representing the top of the barrier), the higher the probability for reflection and the lower the prob-

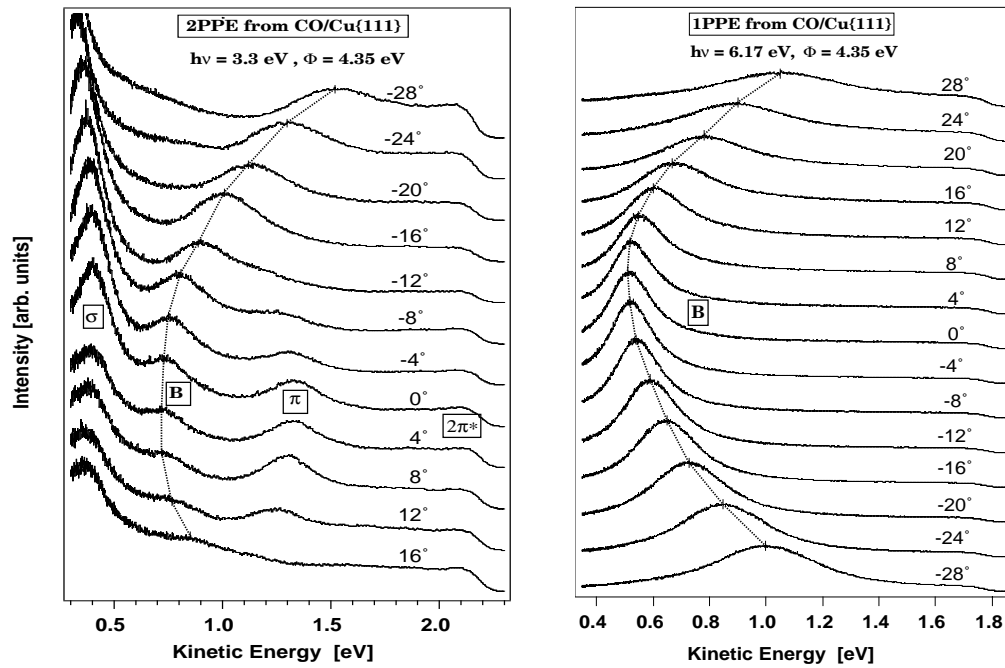


Fig. 4. 2PPE and 1PPE spectra of  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  recorded at 100 K as a function of detection angle with respect to the surface normal.

ability for transmission to the vacuum (with the latter corresponding to the 2PPE intensity). To obtain further information, the dispersions of the state B in the 1PPE and 2PPE spectra are compared. The dispersion curves are fitted by a parabolic function [5] and the fits for 1PPE and 2PPE are essentially the same ( $\pm 10\%$ ). Summarizing the results of Figs. 4 and 5, we conclude that the peak B on  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  cannot be assigned as an unoccupied CO-induced state.

The agreement between the findings for the state B in 2PPE and 1PPE is similar to those in 2PPE from Ag/Cu(100) [6] and 1PPE from Ag(111) [7]. Therefore, we propose that the origin of the B peak from  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  is a direct transition from the lower to the upper branches of the copper sp-band. The B peaks converted into the transitions as two-photon and one-photon processes using 3.30 and 6.17 eV, respectively, are shown in Fig. 3. The good agreement ( $\pm 35$  meV for 2PPE and  $\pm 25$  meV for 1PPE) of these transitions with the calculated sp-band structure proves that the feature B cor-

responds to the direct transition in the copper sp-band. We can then conclude that the B peak of the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  system and the A peak of the Cu(111) system are fundamentally identical.

#### 4. Conclusions

One- and two-photon photoemission spectroscopy has been employed to determine the electronic states of Cu(111) and  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO/Cu(111)}$  at 300 K and 100 K, respectively. New features (labeled A and B) are observed in 2PPE for both systems which are assigned to direct transitions within the sp-band of copper from its lower to its upper branch. The peaks A and B are converted to transitions in the copper sp-band structure and compared with the calculated structure based on a one-dimensional scattering model [2]. The good agreement ( $\pm 25$  to  $\pm 35$  meV) between the experimental transitions and the calculated copper sp-band reveals that both peaks arise

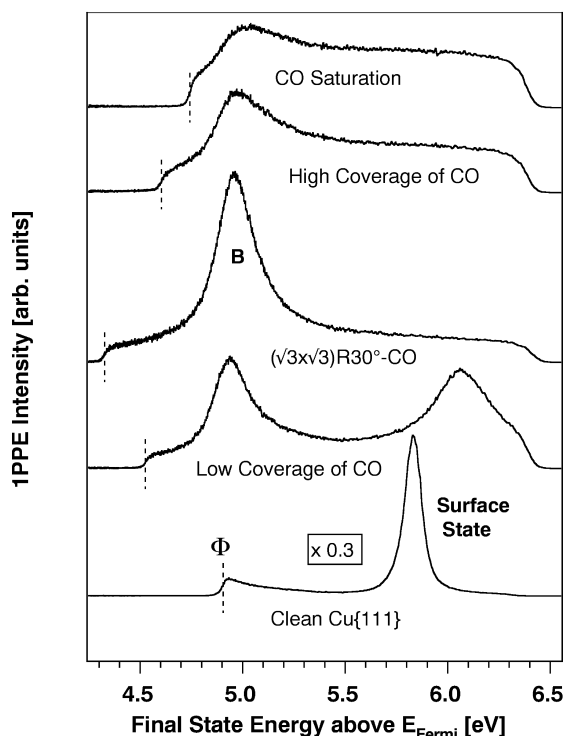


Fig. 5. 1PPE spectra of CO/Cu(111) for various coverages at 100 K ( $h\nu=6.17$  eV). The intensity of peak B is found to correlate with the change of the work function ( $\Phi$ ).

from the direct transition from the lower branch to the upper branch of the Cu(111) sp-band. Because this investigation was motivated by the observation of an unusual wavelength dependence ( $\Delta E_{\text{kin}} = 1.4\Delta h\nu$ ), these results also stress the importance of a careful analysis of the wavelength dependence in 2PPE.

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