Two-photon excitation processes and linewidths of surface and image states on Cu(111)

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Abstract

The occupied surface state and the first image state on Cu(111) have been observed by high-resolution, two-photon photoemission as a function of photon energy. A pronounced narrowing of the linewidth is found for the resonant excitation from the occupied surface state into the first image state. The product of two Lorentzians convoluted with a Gaussian leads to a satisfactory description of the complete series of spectra. The intrinsic linewidth of the first image state on Cu(111) is obtained as 85 ± 10 meV, in agreement with recent time-resolved measurements. The occupied surface state has an intrinsic linewidth of 65 ± 15 meV, as also observed in one-photon photoemission experiments. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the advent of lasers the experimental investigation of higher-order optical processes has been a field of continuous expansion. A particularly simple process is the consecutive absorption of two photons, as illustrated in Fig. 1. In solids the \( k \) vector of the initial state below the Fermi energy \( E_F \) is transferred to the electron in the final state, \( E_f \), through momentum-conservation in the direct optical transitions. If \( E_f \) is above the vacuum energy, \( E_{\text{vac}} \), the electron can leave the solid and its energy and direction can be measured. This information is sufficient to determine the components of the wave-vector parallel to the surface \( k_i \). For surface states this characterizes the states completely. Of particular interest is a specific type of unoccupied surface state below \( E_{\text{vac}} \), which exists in the potential well created by the attractive long-range image potential and bulk-band gaps in the direction of the surface normal, which forbids penetration into the crystal [1]. These image states have been studied on many single-crystal surfaces by two-photon photoelectron spectroscopy [2,3]. Their binding energy relative to \( E_{\text{vac}} \) can be related to the energetic position relative to the band gap. The small overlap of the wave function with bulk states leads to a long lifetime of the image states, which is advantageous for the two-photon process. The lifetime or energy relaxation time \( T_1 \) can be measured directly by introducing a time delay between two photon pulses of femtosecond duration [4]. The high energy resolution of two-photon photoelectron spectroscopy permits a determina-
Fig. 1. Two-photon photoemission excitation processes involving the occupied surface state \( n=0 \) and the first image state \( n=1 \) on Cu(111). For the processes shown at the left (right), the photon energy \( 2h\nu \) is below (above) the energy for resonant excitation from the \( n=0 \) into the \( n=1 \) state (center).

The above considerations apply to the case of excitation into the image state from bulk bands which form a continuum of states due to the dispersion along the direction perpendicular to the surface. A surface state acts as a discrete initial state and two different processes can be distinguished: (i) excitation into the image state \( (n=1) \) and subsequent ionization; (ii) excitation from the occupied surface state \( (n=0) \) and subsequent ionization without occupation of the image state. These processes lead to two different final-state energies, \( E_F \), for a given photon energy, as illustrated in the right and left part of Fig. 1. The photon-energy dependence of the peak in the spectra can be used to distinguish between occupied initial states and unoccupied intermediate states \([3]\). For a photon energy equal to the energy difference between initial and intermediate state only one peak is observed (Fig. 1 center) and a resonant enhancement of the measured signal might be observed \([2]\).

The energetics of the processes are well understood, but the linewidth of the observed peaks has not been studied as a function of photon energy with high resolution so far. The intrinsic linewidth of the occupied surface states close to \( E_F \) on fcc(111) surfaces \([7-9]\) is comparable to the intrinsic linewidth of the \( n=1 \) image states \([5]\). The similar lifetimes of the involved states might lead to interesting effects around the resonance photon energy. A narrowing of the linewidth in resonance has been reported for Ag(111) \([10]\). For Cu(111) a rather small intrinsic linewidth of \( 16\pm4 \) meV has been reported at the resonance photon energy \([5]\). Time-resolved measurements quoted lifetimes \( \tau_i \) between 10 and 18 fs \([6,11,12]\), corresponding to linewidths \( \Gamma \) larger than 66 and 37 meV, respectively. In order to resolve these discrepancies, we chose Cu(111) to study the linewidth of the peaks with high-resolution two-photon photoelectron spectroscopy as a function of photon energy. The energy of the occupied surface state, 0.39 eV below \( E_F \), permits for Cu(111) the observation of the peaks corresponding to the two different processes over a large photon energy range both below and above the resonance photon energy.

2. Experiment

The experiments were carried out in an ultrahigh vacuum system described elsewhere \([13,14]\) at a base pressure better than \( 1\times10^{-8} \) Pa. Frequency-doubled laser pulses of 15 ns duration and photon energy \( 2h\nu \) were used to excite electrons from occupied states below \( E_F \) into unoccupied states below \( E_{\text{vac}} \) (see Fig. 1). A second photon of energy \( h\nu \) lifts these excited electrons above the vacuum level. Electrons leaving the sample within 0.6° of the surface normal were detected and analyzed using an electron spectrometer with an energy resolution of \( \approx 50 \) meV. The analyzer function can very well be approximated by a Gaussian for the lineshape analysis of the experimental spectra \([5]\).

The Cu(111) sample was cleaned by Ne⁺ sputtering (energy 600 eV) at room temperature and subsequent annealing to 800 K for about 600 s.
The preparation was checked with Auger electron spectroscopy, ultraviolet photoemission spectroscopy, low-energy electron diffraction and two-photon photoemission spectroscopy.

3. Results

Two-photon photoemission spectra from a Cu(111) surface for various wavelengths of the ionizing light are shown in Fig. 2. Each spectrum is normalized to maximum height and plotted versus the kinetic energy (i.e. energy relative to $E_{\text{vac}}$) of the detected electrons. The resonant excitation of electrons out of the occupied $n=0$ surface state [14] into the unoccupied $n=1$ image state occurs at a wavelength around 553 nm, corresponding to a photon energy $h\nu=2.24$ eV. At longer wavelengths electrons out of the $n=0$ surface state are detected at lower kinetic energy than electrons out of the $n=1$ image state. At shorter wavelengths this situation is reversed. This behavior can be easily understood with the help of Fig. 1. At the wavelength limits of 535 and 585 nm the two peaks are clearly resolved. The energies of the states relative to $E_F$ are $-0.39$ eV for the occupied surface state and $4.10$ eV for the $n=1$ image state, in agreement with previous work [5,14,15]. This applies also to the work function ($E_{\text{vac}}-E_F$) of $4.93$ eV. The dependence of the kinetic energy of the two peaks on the photon energy is shown in the lower part of Fig. 3. The kinetic energy of the occupied $n=0$ surface state varies with a slope of $3.17\pm0.10$ $h\nu$ while the kinetic energy of the unoccupied $n=1$ image state has a slope of $1.14\pm0.09$ $h\nu$. These values are obtained from linear fits to the data points and are close to the expected slopes of $3$ $h\nu$ and $1$ $h\nu$, respectively.

Where two peaks can be identified in the spectra of Fig. 2, the peak at a higher kinetic energy always has the higher relative intensity. An experimental influence such as an energy-dependent transmission of the energy analyzer can be excluded, because the analyzer was operated at

![Fig. 2. Series of two-photon photoemission spectra of Cu(111) for different wavelengths of the ionizing light. The spectra are normalized to maximum height and plotted as a function of the kinetic energy of the detected electrons.](image)

![Fig. 3. Upper part: Intrinsic linewidth of the states obtained from fitting the product of two Lorentzians to the spectra of Fig. 2. The average values (horizontal lines) are $85\pm10$ and $65\pm15$ meV for the image and surface state, respectively. Lower part: Dependence of the kinetic energy of the detected electrons out of the $n=1$ image state (filled diamonds) and the $n=0$ surface state (open circles). The straight lines are the result of linear fits to the data.](image)
constant pass energy. In addition, the relative difference of the kinetic energies of the two peaks is in all cases quite small.

The lineshape of peaks in two-photon photoemission spectra is commonly represented by a Lorentzian for the intrinsic linewidth convoluted with a Gaussian for the experimental resolution [5]. The spectrum for the resonance wavelength of 553 nm shows the smallest linewidth of the whole series. In the spectra for 535 and 585 nm, two peaks can be resolved and both peaks show linewidths larger than the one observed in the resonance spectrum. All spectra were measured with the same pass energy of the analyzer and, consequently, the same experimental resolution. Previous experiments proved that the intrinsic linewidth of the n=1 image state on Cu(111) measured at the resonance photon energy is independent of the pass energy [14]. The spectral bandwidth of the laser is negligible and is not expected to vary with photon energy. Excluding these experimental influences, we are led to the conclusion that the intrinsic linewidth and, consequently, the lifetime of the states depends on the photon energy used in the two-photon photoemission process.

This seems rather unlikely and we have to look for a new interpretation of the data. We note that the peaks in the spectra for 535 and 585 nm, corresponding to the n=0 surface state or the n=1 image state, have similar linewidths regardless of the photon energy. This is also confirmed by fitting the spectra at the limits of the series with the sum of two Lorentzians for the two peaks convoluted with a Gaussian for the experimental resolution [5]. An intrinsic linewidth around 60 and 85 meV is obtained for the n=0 and n=1 state, respectively. The spectrum at resonance can be fitted with a single Lorentzian of 16±4 meV width [5]. This is a large discrepancy and we are forced to reconsider the interpretation of the spectrum at the resonance photon energy. In this case the initial state and the intermediate state contribute to a single peak in the spectrum. A peak narrowing at resonance can be achieved by modeling the spectra by a product of two Lorentzians at energies E_0 and E_1 and full-width at half-maximum (FWHM) \( \Gamma_0 \) and \( \Gamma_1 \) for the initial state and the intermediate state, respectively
\[
\frac{1}{(E-E_0)^2+(\Gamma_0/2)^2} \cdot \frac{1}{(E-E_1)^2+(\Gamma_1/2)^2}.
\]

The appropriate energy-scale is chosen to reproduce the peaks at E_0 and E_1 in the experimental spectrum. This description can be extended over the whole photon energy range. Note that the energy is conserved only for the overall two-photon process and not for each excitation step. For photon energies far away from resonance we retrieve, approximately, the sum of two independent Lorentzians, because at the position of the one Lorentzian the variation of the other Lorentzian is rather small.

The experimental spectra contain the experimental broadening, which is taken into account by convoluting the lineshape of Eq. (1) with a Gaussian. A non-linear least-squares fitting procedure with the proper statistical weighting of the least-squares sums was used. Typical fit curves are shown in Fig. 4. The results for the product (solid lines) and sum (dashed lines) are compared. The width of the Gaussian was around 50 meV, as expected from the chosen analyzer resolution. In all cases the data points are fitted quite well. The individual fit functions show considerable differences for the two models. For the spectrum at resonance the single narrow Lorentzian has higher intensity than the product of the Lorentzians, owing to the area normalization of the convolution procedure. In the off-resonance spectra the peak shapes and the peak positions exhibit differences for the two models. The product model yields an energy relative to \( E_F \) of 4.10±0.015 eV for the image state, whereas the fit with the sum of two Lorentzians shows a considerable shift with photon energy. The energies E_0 and E_1 from the fits are plotted in the lower part of Fig. 3. The upper part shows the Lorentzian widths for the n=1 image state and n=0 surface state. Near resonance, the two peaks cannot be resolved and it becomes difficult to fit the widths \( \Gamma_0 \) and \( \Gamma_1 \) independently. For these spectra we fixed the parameter \( \Gamma_1 \) to the average value 85 meV and obtained reasonable values for \( \Gamma_0 \) and the Gaussian width. The upper
part of Fig. 3 shows that, with the product-model, we can describe the whole series of spectra with intrinsic linewidths of $65 \pm 15$ meV for the $n=0$ surface state and $85 \pm 10$ meV for the $n=1$ image state.

The ansatz of the product model Eq. (1) contains only one amplitude and the intensity ratio of the two peaks is determined by the widths. The peak with the larger intrinsic linewidth always has lower intensity compared to the one with the smaller intrinsic linewidth. The relative peak intensities can be seen most clearly in the spectra far away from resonance where the two peaks are well separated. At 535 nm the broader image state shows a smaller intensity than the surface state (Fig. 2). The situation is reversed in the spectrum at 585 nm, where the broader image state shows a higher intensity than the surface state. For the purpose of the fit procedure an additive Lorentzian contribution to the image state was included at the position $E_1$ with the width $\Gamma_1$. For wavelengths below resonance this contribution had no statistically significant amplitude. For longer wavelengths the amplitude increased. This is in agreement with the spectra, which show a larger height for the broader $n=1$ peak compared to the height of the narrower $n=0$ peak for the spectra with photon energies below resonance.

In order to explain the additional intensity in the $n=1$ image state for photon energies below resonance, we have to consider the band structure of the Cu(111) surface at parallel momentum $k_z=0$ for normal emission. The occupied $n=0$ surface state at $E_F = -0.39$ eV lies half way between the Fermi energy and the bottom of the band gap at $E_F = -0.85$ eV [14]. This implies that $k_z$-conserving optical excitations should be possible only at the resonance photon energy. The off-resonance intensity is rather small as confirmed experimentally [14,15]. Possible explanations of the observed peaks off-resonance involve excitations from states with $k_z \neq 0$. The necessary momentum transfer can be achieved through scattering by phonons or surface defects. The first possibility can be excluded, because the additional intensity is also observed after cooling the sample from 300 down to 140 K. The number of phonons decreases with temperature and should lead to a reduced intensity for electrons out of the $n=1$ image state, if the excitation into this state is phonon assisted. This is clearly ruled out by the experimental results and the additional intensity must be due to scattering by defects such as steps or impurities at the surface.

The remaining question is whether the defect scattering involves electrons from surface or bulk states. This can be answered by considering the energy dependence of the additional intensity in the image state. It is only observed for photon energies below resonance, i.e. from states with energies between the surface state and the Fermi level. Bulk states with $k_z \neq 0$ are available up to several eV below $E_F$ and no characteristic energy dependence should be expected. The upward-dispersing surface-state band provides states in the right energy range. These states require only small momentum transfer from the defect scattering and have similar character as the $n=0$ surface state at the bottom of the band, which couples strongly to the image state in optical excitations.

A temperature-dependent linewidth of the occu-
pied surface state has been observed in one-photon photoemission experiments and was explained by electron–phonon coupling [9,17]. We observed no reduction of the linewidth of the image state upon cooling the sample to 140 K. One explanation might be a somewhat poorer energy resolution in our experiment. More likely is a reduced coupling of the image state to the vibrations of the surface atoms, because the electron is a few Å away from the surface.

4. Discussion

The two-photon photoemission spectra for the surface and image state of Cu(111) can be well described by the product of two Lorentzians plus some contributions from non-$k_{\parallel}$ conserving excitations of the image state. The whole series of spectra can be fitted with one set of widths for the two states. The intrinsic linewidth of the occupied surface state of $65 \pm 15$ meV agrees with our one-photon photoemission results and previous reports: Kevan [7] finds an extrapolated intrinsic linewidth of $55 \pm 5$ meV and Schuppler et al. [5] have published a value of $54 \pm 3$ meV for the intrinsic linewidth. McDougall et al. [9] and Matzdorf et al. [17] worked with a resolution better than 20 meV and report peak widths of 55 and 65 meV, respectively. The differences between the different groups is attributed to variations in the surface quality [7,9,17]. It should be added that small deviations from $k_{\parallel}=0$ also increase the linewidth [7,17].

The obtained linewidth of the image state of $85 \pm 10$ meV corresponds to a lifetime of $\tau=8 \pm 1$ fs. This number is significantly shorter than the lifetime values, $T_{1}$, obtained by direct time-resolved measurements of $18 \pm 5$ fs [11] and $15 \pm 5$ fs [12]. Note that an earlier value of $10 \pm 3$ fs [6] has been revised in a later paper [11] using an improved model for the data analysis. The discrepancy can be reconciled by the introduction of a pure dephasing time $T_{2}^{\parallel}=2/(\tau^{-1}-T_{1}^{-1})$ attributed to elastic scattering processes [6]. The elastic scattering contributes to the observed linewidth of the energy spectra, but not to the time-resolved measurements which measure directly the population of the image state. With the given values for $\tau$ and $T_{1}$ a pure dephasing time $T_{2}^{\parallel}$ around 30 meV is obtained. It should be added that the earlier linewidth of $16 \pm 4$ meV for Cu(111) measured in resonance [5] would lead to non-physical negative values for $T_{2}^{\parallel}$.

The expected intrinsic linewidth $\Gamma$ of image states can be calculated by an heuristic approach [14] which multiplies the measured width of bulk states at the same energy by the probability of the image state electron being inside the metal. The measured linewidth analyzed by this model would lead to a rather small probability, of $\approx 15\%$, of finding the electron inside the metal. The penetration of the image-state wave function is also the main ingredient of theoretical models for the calculation of the linewidth, which describe the dynamic response of the metal electrons in front of the surface [18–20]. The energetic position of the upper edge of the band gap determines the probability of the electron being inside the crystal [3]. The energy of the $n=1$ image state is measured at 4.10 eV relative to $E_{F}$. For the upper edge of the band gap, values of 4.1 [21] and 4.25 eV [22,23] have been reported. Depending on the band edge and penetration, the calculations of de Andres et al. [19] yield linewidths of 19 [19], 40 [5], 66 – 83 meV [11]. The latter two values seem compatible with our experimental result of $85 \pm 10$ meV, which includes the additional contribution by elastic scattering that is not incorporated in the theoretical model.

5. Summary

High-resolution two-photon photoemission data for the surface and image state on Cu(111) have been measured. The spectra were analyzed with a product of two Lorentzians, which gives consistent values for the linewidths over the whole data set. The linewidths are in agreement with one-photon photoemission data and time-resolved two-photon photoemission measurements. The agreement with theoretical estimates is moderate and suffers from an insufficient knowledge of the band edge and the elastic scattering processes. The product model can be applied to the similar case of Ag(111) [10]
and to Au(111) [24]. In the latter case the linewidth of the image state is significantly larger than the one of the surface state, which makes the image state hardly observable for off-resonance photon energies. The product model holds also for the situation of excitation from a continuum of initial states outside a band gap. Integration over all initial states gives a smooth density of initial states and the measured linewidth corresponds directly to the linewidth of the image state.

Recent improvements have raised the available two-photon photoemission intensity by more than three orders of magnitude [12]. This should permit experiments with improved energy resolution, leading to a more accurate determination of the spectral lineshapes. This might give better insight into the resonant two-photon photoemission processes, which are properly described by optical Bloch equations [6].

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References