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Three-photon photoemission from Cu(100): observation of an unoccupied surface state near $\bar{\Gamma}$

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The photon energy dependence has been measured for three-photon photoemission from Cu(100). A narrow resonance (FWHM = 0.02 eV) was observed centered at 2.02 eV photon energy. The resonance can be explained by the presence of an unoccupied surface state near the center of the surface Brillouin zone at $\bar{\Gamma}$ and 2.0 eV above E_F .

1. Introduction

Two-photon photoemission has been shown to be a useful method for obtaining highly accurate measurements of the energy and dispersion of unoccupied electronic states between the Fermi level and the vacuum level [1-5]. In this process electrons from an occupied state below the Fermi level are excited to an intermediate unoccupied state by one photon followed by ionization from the intermediate state by a second photon. Recently we have also reported on the observation of remarkably strong three-photon photoemission from a clean Cu(100) surface in UHV [6,7]. The excitation process is envisioned to be similar to the two-photon photoemission process except now two intermediate states may be involved. In the present paper we report the observation of a narrow resonance centered at 2.02 eV as a function of photon energy in the three-photon photoemission electron yield from Cu(100). We assign this resonance to the existence of a narrow surface state located in a gap in the bulk band structure near $\bar{\Gamma}$ of the surface Brillouin zone.

2. Experimental

The experiments were conducted in an ultra-high vacuum chamber with a base pressure of 10^{-11} Torr. The Cu(100) surface was prepared by Ar⁺ sputtering, followed by annealing. The resulting surface was clean as evidenced by Auger electron spectroscopy, and yielded a $p(1 \times 1)$ low energy electron diffraction (LEED) pattern.

The output of an excimer pumped dye laser was focussed to a 4×10^{-3} cm² spot (FWHM) on the room temperature surface. The laser had a 12 ns pulse width (FWHM), was incident to the sample at 45°, and was s-polarized. The geometry of the experiment is shown in fig. 1. Typical pulse energies used were 5 mJ resulting in an energy density of $5 \text{ mJ} / 4 \times 10^{-3} \text{ cm}^2 = 1.3 \text{ J/cm}^2$. At 2.02 eV the reflectivity of Cu is approximately 0.9 [8]. Using this value, a maximum laser-induced surface temperature of 650 K is calculated using the method of Burgess et al. [9]. This method has been shown to work well in the present regime of pulse energy and duration. At this temperature surface melting will not occur.

Electrons emitted from the surface were detected using pulse counting LEED optics [10] which subtend a cone angle of $\pm 16^\circ$ about the surface normal. Electrons emitted from the surface were accelerated toward the detector with a

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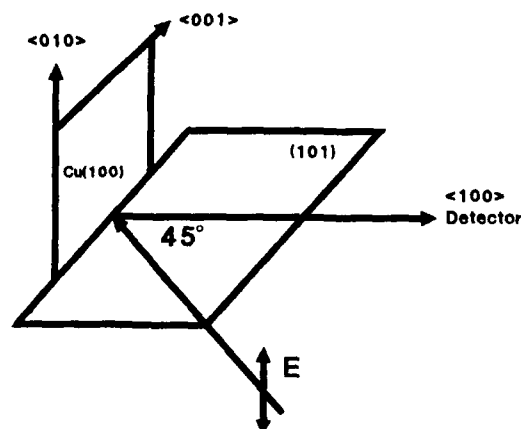


Fig. 1. Geometry of experiment. Incident beam is in (101) plane, 45° to normal and s-polarized. Detector subtends cone of $\pm 16^\circ$ about $\langle 100 \rangle$.

50 V bias such that emission from the entire hemisphere excluding 1° about the normal was collected. Electrons are not collected within 1° of the surface normal because the LEED electron gun occupies the center axis of the LEED optics. A set of grids functioned as a retarding field analyzer, and a microchannel plate electron multiplier provided gain up to 10^6 for single electron counting. A computer recorded the electron yield and pulse energy for each laser pulse. The emitted charge densities in the present experiments are below the level where space charge effects become important. The emission current density in our experiment $[(0.2-6) \times 10^{-6} \text{ A/cm}^2]$ is comparable to the density in two-photon photoemission experiments [5] $(0.3 \times 10^{-6} \text{ A/cm}^2)$ where space charge effects have been shown to not be significant. More details of our experimental apparatus can be found elsewhere [7].

3. Results and discussion

The electron yield has been shown in ref. [7] to follow the cubic dependence on laser power density expected for the three-photon photoemission process. Fig. 2 shows the photon energy dependence of the electron emission yield from 1.94 to 2.16 eV for a constant incident photon density of $4.3 \times 10^{18} \text{ photons/cm}^2$. Two different laser dyes

were used to scan this region. The two data sets were normalized to each other at 2.09 eV where data from both dyes were available. The electron yield shows a strong dependence on photon energy in this region with the peak yield at 2.02 eV being 16 times the yield at either wavelength extreme.

The photon energy dependence of the electron yield cannot be explained by the copper bulk energy band structure. First, due to energy constraints the emitted electrons cannot originate from the copper d-bands. With 6.0 eV of total photon energy at the electron yield peak and a Cu(100) work function of 4.6 eV [11], the emitted electrons must originate from above -1.4 eV with respect to E_F . The d-bands high energy edge is -2.0 eV making them inaccessible in this experiment [12]. Second, the mean free path for an electron at 6.0 eV in the solid (assuming three photon excitation) is approximately 20 Å [13]. The bulk band structure predicts a maximum in the $1/e$ light penetration depth of 170 Å at 2.0 eV photon energy. However, because the photoemission is limited by the electron escape depth a maximum in the light penetration depth will not affect the electron yield. Moreover, the features of the Cu bulk band structure are too broad to be

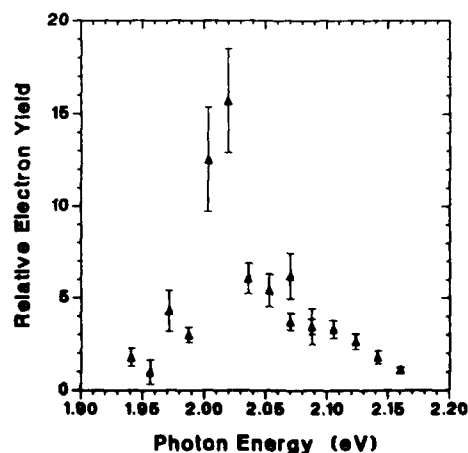


Fig. 2. Dependence of electron yield on photon energy. Yields are shown for constant incident photon flux of $3.6 \times 10^{26} \text{ photons/cm}^2 \cdot \text{s}$. Each data point is the average of approximately 25 laser shots with the error bars being equal to the standard deviation.

consistent with the width of the peak in the electron yield [4].

The photon energy dependence of the electron yield can be explained by resonant excitation between narrow surface states. A similar mechanism has been previously reported for laser-induced two-photon photoemission [1-3]. In the case of two-photon photoemission it has been shown that peaks in the electron yield versus photon energy due to resonant excitation between surface states are only 0.2 eV wide [2,3] - comparable to the width observed here. For example, resonant two-photon photoemission from Cu(111) was reported at 4.46 eV photon energy [2]. For that system the first photon is absorbed in a transition from an occupied Δ_1 surface state at -0.41 eV with respect to E_F to the $n = 1$ image potential state at 4.05 eV. A second photon couples the electron into vacuum.

We can limit the energy range and the region of the surface Brillouin zone which can contribute to the photoemission process based on the total energy of 3 photons and the work function of Cu. The electrons must have at least 4.6 eV of energy normal to the surface to overcome the surface potential barrier. Therefore, with 6.0 eV of energy, only electrons propagating within 29° of the normal will have a sufficient energy component perpendicular to the surface barrier to be emitted. In vacuum, the component of the electron momentum parallel to the surface, $k_{||}$, is given by [14]

$$k_{||} = [(2m/\hbar^2)E_{\text{KIN}}]^{1/2} \sin \theta, \quad (1)$$

where m is the electron mass, E_{KIN} is the electron kinetic energy, and θ is the emission angle with respect to the surface normal. At 29° and $E_{\text{KIN}} = 1.4$ eV, $k_{||} = 0.29 \text{ \AA}^{-1}$. Because $k_{||}$ is conserved during photoemission [14], the range of participating states is then limited to less than $0.29 \text{ \AA}^{-1}$ about $\bar{\Gamma}$ in the surface Brillouin zone.

We propose that the resonance in the three-photon photoemission involves excitation from E_F to the $n = 1$ image potential state at 4.0 eV on Cu(100) [1]. However, because there are no occupied surface states [15,16] near E_F and within $0.29 \text{ \AA}^{-1}$ of $\bar{\Gamma}$ on Cu(100), our observed photon

energy dependence is not explained by a two-photon resonant excitation from a narrow energy initial state to the $n = 1$ image potential state. Rather, the sharp photon energy dependence can be explained by transitions through an unoccupied surface state at 2.0 eV near $\bar{\Gamma}$ which then acts as a first intermediate state. In this picture resonant excitation occurs between this proposed first intermediate state and the $n = 1$ image potential state. An unoccupied surface resonance assigned to the $n = 0$ image potential state at 1.4 eV has been detected by angle-resolved inverse photoemission from Cu(100) [17]; however, this state would seem to be too low in energy to correspond to the intermediate state detected in our experiments. A surface state at 2.0 eV near $\bar{\Gamma}$ has not been reported previously, although a gap exists [18] in the bulk band projection onto the (100) surface at $\bar{\Gamma}$ from approximately 1.8 to 8.0 eV, making the existence of such a state possible.

4. Conclusion

A strong dependence on photon energy of the electron yield in three-photon photoemission has been observed. The photon energy dependence is consistent with resonant excitation between a previously unreported surface state on Cu(100) near 2.0 eV and within $0.29 \text{ \AA}^{-1}$ of $\bar{\Gamma}$. We propose a model for the photoemission process in this case to be: (1) one-photon excitation from a bulk band near E_F to the first intermediate state at 2.0 eV; (2) one-photon resonant excitation from the first intermediate surface state to the Cu(100) $n = 1$ image potential state at 4.0 eV; (3) one-photon excitation from the $n = 1$ image potential state to couple the electron into vacuum. The use of laser-induced multiphoton photoemission (both two and three photon) is increasingly becoming a useful technique for the study of surface electronic structure.

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