Angular distributions of VUV photoelectrons from Cu(001)

U. Thomann, G. Rangelov, Th. Fauster *,1
Sektion Physik, Universität München, Schellingstrasse 4, 80799 München, Germany
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Abstract

A He resonance lamp and synchrotron radiation in the energy range from 15 to 60 eV were used to excite the valence band electrons on Cu(001) surfaces. The complete angular intensity distributions of the photoelectrons within 45° away from the surface normal were recorded with a two-dimensional display-type analyzer. The symmetry of the observed patterns permits an easy identification of the different character of the initial states as a function of energy. Additional information is obtained by exploiting the tunability and the polarization of the synchrotron radiation.

Keywords: Angle resolved photoemission; Copper; Low index single crystal surfaces; Visible and ultraviolet photoelectron spectroscopy

1. Introduction

The valence bands of copper have been the drosophila of photoelectron spectroscopy since its beginning [1]. Most of the fundamental achievements in the development of angle-resolved photoemission and its relation to the electronic properties have been reached on copper surfaces [2]. The energy and momentum conservation permits the extraction of the complete information about the dispersion and symmetry of the states of the electronic band structure from experimental data. This process is rather complicated and requires a huge number of spectra taken at many angles and photon energies [3]. Therefore, the dispersion of the energy bands of copper has been measured along a few lines in k space only. In this paper we will present a view of the electronic bands of copper from which many features can be seen in a direct and intuitive way. The method relies on the angular distribution of the photoelectron intensity instead of the presentation of energy spectra and dispersion curves.

2. Experiment

The Cu crystals were cleaned by sputtering and annealing. Surface cleanliness and crystallographic order were verified with Auger electron spectroscopy and low-energy electron diffraction. The samples were then transferred to the analyzer chamber. For the photoemission experiments a He resonance lamp (He I 21.2 eV) and synchrotron radiation in the energy range from 15 to 60 eV from the TGM-3 beam line at the BESSY storage ring were employed. The angular distribution patterns of the photoelectrons were recorded by a two-dimensional display-type electron spectrometer [4]. It consists of an ellipsoidal mirror serving as a low-pass filter and a set of retarding grids acting as a high pass for the electrons. The complete an-
angular distributions in an acceptance cone of 88° are registered. The data processing and the normalization with respect to the spatial analyzer efficiency followed the procedure developed for forward-scattering experiments at high kinetic energies [5–7]. For the valence-band studies an average of the spatial analyzer efficiency over the whole energy range was used. The energy resolution was 200 meV in the angle-integrating mode and up to 100 meV for angle-resolved spectra [8].

3. Angular distributions of photoelectrons

The angular distributions of the photoelectrons are shown as gray-scale pictures in Fig. 1 in a slightly distorted polar diagram with the surface normal approximately in the center and with the maximum polar angles of ~ 45° [5–7]. In order to show the structures as clearly as possible, the lowest (highest) intensity of each pattern is shown in the picture as black (white). The unpolarized He I (21.2 eV) radiation from the resonance lamp enters along the direction near the top left corner of the patterns. It can be recognized by a reduced intensity and worsened statistics. The light reflected from the sample leads to electron emission from the ellipsoidal mirror. The resulting intensity in the patterns near the bottom left corner cannot be corrected completely by the image processing procedure and leads to irregularities in this area.

The patterns shown in Fig. 1 show a considerable variation with initial state energy. At the Fermi level $E_F$ a diamond-shaped pattern is seen which contracts when going to lower energy. The image of the Fermi surface agrees well with previous measurements [9]. Below ~2 eV additional structures appear which exhibit considerable variation with initial state energy. The most obvious change is the transition from a ‘x’ to a ‘+’ shape around ~3 eV. All images show a clear fourfold symmetry as expected for a fcc (001) surface. An exception occurs below ~3.5 eV where the intensity of the emission at the bottom is stronger than the symmetrically equivalent emission at the top. The light incidence is in a mirror plane of the crystal which ensures a left/right symmetry. The lower intensity at the left is due to experimental problems with the analyzer efficiency in this area.

4. Discussion

The emission into a small angular range at fixed energy and the pronounced changes of the size of the structure between 0 and ~2 eV without a change of the diamond shape indicates that it results from transitions between strongly dispersing bands. In the energy range only one nearly-free-electron band is accessible as initial state $E_i$. For a qualitative understanding of the features we assume a free-electron dispersion $E_i = \hbar^2 k^2 / 2m + V_0$. This describes a sphere in k space around the origin with a radius which increases with energy. The energy scale is relative to the constant potential $V_0$ which is given by the bottom of the valence bands [3]. The final state energy can be written as $E_f = \hbar^2 (k - g)^2 / 2m + V_0$. This is a sphere in k space centered at the reciprocal lattice vector $g$. The radius is restricted by the photon energy $\hbar\omega$ due to energy conservation $E_f = E_i + \hbar\omega$. The intersection of the two spheres yields a circle with the axis along the direction of $g$. In Fig. 1 we observe straight lines which implies that we are looking along the plane of the circles. From the orientation of the sample we identify the reciprocal lattice vectors (in units of $2\pi/a$, with the lattice constant $a = 3.61$ Å) as $(\pm 2, 0, 0)$ and $(0, \pm 2, 0)$ producing the observed diamond. In the geometry used here the contribution from the $(0, 0, \pm 2)$ reciprocal lattice vectors can be excited only by the $p$ component of the light which seems to contribute less. Plugging in numbers into the above equations one sees that the $E_f$ spheres enclose the point $k = 0$. For fixed initial energy the $E_f$ sphere contracts with decreasing photon energy resulting in a shift of the lines towards the center. This is observed in the experiments with synchrotron radiation (not shown here). A reduction of the initial state energy (at fixed photon energy) shrinks the $E_i$ and the $E_f$ spheres resulting in the same qualitative behavior as seen in Fig. 1. For a detailed interpretation one has to keep in mind that the size of the $k$ patterns plotted in the angular net changes also with the kinetic energy of the final state. This is only a minor correction in the cases shown here where the kinetic energy varies by ~ 10%.

In the two-band model of the nearly-free electron approximation the transition matrix element is given by $\langle \psi_f | A \cdot p | \psi_i \rangle \propto A \cdot g$. This implies vanishing emission with the polarization vector $A$ normal to the reciprocal lattice vector $g$. The experimental proof is
Fig. 1. Angular distributions of valence-band photoelectrons from Cu(001) excited with unpolarized HeI (21.2 eV) radiation. Normal emission is approximately in the center of the patterns which span polar angles up to $\sim 45^\circ$. The orientation of the crystal and the appropriate angular net are shown at the bottom right. The separation of the lines is $10^\circ$ and $15^\circ$ in the polar and azimuthal direction, respectively.
seen in the top row of Fig. 2 which shows the emission patterns at −0.9 eV for the Cu(001) sample rotated by 45° compared to Fig. 1. From the square seen with HeI radiation only the left and right sides are clearly visible using synchrotron radiation with the (horizontal) s-polarization vector. The reduced intensity at the left is observed in all synchrotron data and is due to problems with the sample and beam alignment relative to the retardation stage of the display analyzer [4].

For lower initial state energies the structures seen in the patterns of Fig. 1 are smeared out and show mainly a redistribution of the intensity with energy. These patterns represent emission into a wide angular range at fixed energy and correspond to the slowly dispersing Cu d-bands. The change in the symmetry of the patterns from a ‘×’ to a ‘+’ shape around −3 eV can be understood in the following model. The matrix element for a dipole transition from a localized orbital \( \psi_i(r) = f(r) \psi_{lm}(\theta, \phi) \) into a free-electron final state \( \psi_f(r) = \exp(ik \cdot r) \) can be written as

\[
\langle \psi_i | A \cdot p | \psi_f \rangle = \int dr f(r) \psi_{lm}(\theta, \phi) A \cdot h k \exp(ik \cdot r).
\]

The momentum operator causes the derivative of the final-state wave function and we obtain the Fourier transform of the initial-state wave function [10]. Using the expansion of a plane wave into spherical harmonics and their orthogonality relation we obtain

\[
\langle \psi_i | A \cdot p | \psi_f \rangle \propto A \cdot k R_i(k) \psi_{lm}(\theta_k, \phi_k),
\]

where \( R_i(k) = 4\pi i \int_0^\infty dr j_i(kr) f(r) \). The above expression shows that the intensity distribution \((\theta_k, \phi_k)\) of the electron emission shows the same angular symmetry as the initial orbital in real space. This statement is also true if we replace the initial-state wave function by a Bloch sum in a tight-binding basis. We can immediately see from the patterns that the \( d_{x^2-y^2} \) basis function contributes in the energy range from −3 eV to −2 eV, whereas the \( d_{xy} \) derived bands appear at lower energies. This assignment agrees with the well-known properties of the Cu band structure.

With the expression for the matrix element we can explain the top/bottom asymmetry in the patterns below −3.5 eV. The intensity is reduced for the electrons traveling close to the direction of the incident light. Because of the transverse polarization of the light the term \( A \cdot k \) vanishes. For electrons seen at the bottom of the pattern the p-polarized component has an \( A \) vector almost parallel to the wave vector \( k \) leading to a strong emission. Measurements with pure s-polarized synchrotron radiation show the top/bottom symmetry as expected and illustrated in the bottom row of Fig. 2. In these experiments one would expect zero intensity in the plane of incidence in contrast to the experiments. This is due to the assumption of a free-electron final state. A plane-wave expansion adds further terms \( k + g \) to the matrix element which can be regarded as diffracted beams.

5. Summary and outlook

We have presented angular distribution patterns of valence-band photoelectrons from a Cu(001) surface. From these patterns the character and symmetry of the initial states can be extracted in a very simple and intuitive way. A refinement of the model yielding the Fourier transform of a localized orbital should include
the orbitals centered at neighbor atoms. The inversion of the data would then yield the charge density as well as the position of the atoms. The practical implementation of this valence-charge holography requires measurements over a wide range of photon energies to obtain \( f(r) \) from \( R_i(k) \). The variation of \( k \) across the d bands is rather small. Problems may arise from the contributions of diffracted beams and the polarization of the light leading to extinction along certain directions. In this context it should be mentioned that single-scattering calculations agree surprisingly well with measurements of the angular distributions of the photoelectrons at Cu surfaces integrated over the whole 3d bands [11]. This indicates that only the nearest and next-nearest neighbors are important for the development of the band structure [12] and a holographic inversion might be possible.

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References