Angular distribution of the inverse photoemission from Cu(100)

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We have measured the intensity distribution of the light emitted in inverse-photoemission transitions in the $\Gamma X U L$ mirror plane of a Cu(100) crystal. The distributions are in good agreement with the dipole-transition model for inverse photoemission. The orientation of the dipole axis for bulk transitions follows qualitatively calculations with a combined interpolation scheme. The applicability of the Fresnel formulas for the transmission and refraction of light emitted in the surface region is discussed.

I. INTRODUCTION

Within the last ten years the energy bands of copper have been determined by photoemission and inverse-photoemission experiments with high accuracy and considerable detail.\textsuperscript{1–3} The measured energy bands agree very well with the results from first-principles band-structure calculations.\textsuperscript{4,5} This agreement is found not only for bulk energy bands but also for surface states.\textsuperscript{6,7} It can, therefore, be stated that the energy bands of copper and its low-index surfaces are understood. An investigation of the transition-matrix elements adds a further test to this understanding. The transition-matrix elements for photoemission are generally believed to be determined by the dipole operator $\mathbf{A} \cdot \mathbf{p}$, the scalar product of the vector potential $\mathbf{A}$, and the momentum operator $\mathbf{p}$. A straightforward way to test the transition-matrix element would be the measurement of intensities. Intensities are difficult to measure quantitatively and they also contain the reflection and transmission of the electron through the surface barrier, which is unknown from experiment. In most studies, therefore, the matrix element is tested only by the use of symmetry selection rules, which forbid certain transitions.\textsuperscript{8,9} A more extensive test of the dipole-transition model is the determination of the angular dependence of the intensity of a specific transition on the direction of the photon. This should be described by a $\sin^2 \alpha$ law, where $\alpha$ is the angle between the dipole axis and the direction of the photon. Only a few photoemission studies of this type have been performed.\textsuperscript{10–13} In inverse photoemission only measurements for two different photon detection angles have been reported.\textsuperscript{13} In this paper we present results of a detailed study of the angular dependence of the inverse photoemission on a Cu(100) surface. The following section describes the experimental setup and procedures. Section III presents data for a surface state and the analysis for these data. In Sec. IV, we compare the experimental results to calculations and show that the orientation of the dipole axis provides a good test for the matrix elements in inverse photoemission. A summary and discussion of the implications of the results for the application of Fresnel’s formulas is given in Sec. V.

II. EXPERIMENT

The measurement of the angular distribution of the light emitted in an inverse-photoemission experiment could be done, in principle, simply by rotating the detector around the sample. This is, not practical since the usual Geiger-Müller counters are rather bulky and require a vacuum connection to the outside.\textsuperscript{14} We used, therefore, a fixed detector and an electron gun rotatable around the sample similar to the setup of Royer and Smith.\textsuperscript{15} For the measurement of the angular distribution of the light, we need a fixed angle of incidence for the electrons. This means we have to rotate the sample simultaneously with the electron gun around a common axis in the sample surface. The coincidence of the centers of rotation of electron gun and sample can be tested by the absence of variations in the sample current during simultaneous rotation of sample and electron gun, especially for the grazing angle of incidence. Since we deal with electrons of very low kinetic energy ($< 10$ eV), we have to eliminate all magnetic parts in the region of our electron beam and we have to compensate for the remaining earth magnetic field by Helmholtz coils. Even for carefully compensated magnetic fields it is necessary to determine the angle of incidence $\theta$ of the electron beam relative to the sample surface. The usual way of doing this is the measurement of the dispersion of inverse-photoemission transitions. For measurements perpendicular to a mirror plane of the crystal, extrema are observed in the dispersion at the center of the surface Brillouin zone. In our case this procedure is not very efficient because we would have to do this for several sample positions. We, therefore, developed a quicker method of determining the normal incidence of the electron beam. We simply measure the sample current as a function of incidence angle $\theta$. Changes in the reflectivity for the electrons produce minima and maxima in the angular scans, which are symmetric with respect to the surface normal for scans perpendicular to a mirror plane of the crystal. The sensitivity of this method is greatly enhanced by the measurement of the first derivative of the sample current with modulation techniques. The detection angle $\alpha$ for the emitted photons is defined in the
same way as $\theta$ and is calibrated by autocollimation through the entrance window of the Geiger-Müller counter. The minimum angle between the detector and the electron gun is $30^\circ$ due to geometrical restrictions; otherwise, any combination of $\alpha$ and $\theta$ is accessible. The rotations of sample and electron gun are motorized and are controlled by a personal computer which is also used for the data acquisition. The Cu(100) crystal was cleaned by sputtering and annealing. The cleanliness was checked by ion-scattering spectroscopy and the inverse-photoemission spectra. The crystallographic orientation was determined in situ by impact-collision ion-scattering spectroscopy.\textsuperscript{16} The sample surface was found to be better than $0.5^\circ$ within the (100) orientation.

III. SURFACE STATE DATA

Figure 1 shows a set of inverse-photoemission spectra for various photon takeoff angles $\alpha$ normalized to equal intensity at a final-state energy $E_f$ of 5.7 eV. The electrons impinging at an angle $\theta=-60^\circ$ relative to the surface normal of the Cu(100) crystal. Electrons, as well as photons, traveled parallel to the (011) mirror plane, commonly known as the $\Gamma XUL$ plane. We can identify two peaks in the spectra at 0.6 and 3.5 eV above the Fermi level. These transitions have been observed previously\textsuperscript{13} and are surface states in the band gap of the projected bulk band structure near the $\overline{X}$ point of the surface Brillouin zone. We note that the peaks do not shift with changing photon takeoff angle $\alpha$ but show strong intensity variations. The higher-energy peak vanishes completely for $\alpha=-20^\circ$. Similar effects have been reported for these transitions in a previous study, but only for two different photon takeoff angles.\textsuperscript{15} With our rotatable electron gun setup we can now do the following experiment: For a fixed electron energy $E_f$ and fixed angle of incidence $\theta$, we measure the intensity of a particular transition as a function of photon takeoff angle $\alpha$. The top curve of Fig. 2 shows such a scan for the surface state at 3.5 eV (see Fig. 1). We see a broad maximum around $30^\circ$. The dropoff for large angles $\alpha$ is similar to the behavior of the background measured at 5.7 eV. We assume that the angular dependence of the background gives a good picture for the transmission probability of the photons through the solid-vacuum interface. If we normalize the intensity of the surface state relative to the background, we obtain the dotted curve in the bottom of Fig. 2. This curve should represent the emission probability for this transition as a function of photon takeoff angle. It can be fitted very well with a squared sine function, as expected for a dipole transition. Since we know from Fig. 1 that this transition disappears completely for $\alpha=-20^\circ$, we conclude that the dipole axis must lie in the $\Gamma XUL$ plane. This is in agreement with the symmetry selection rules for dipole transitions for a mirror plane. The initial state coupling to the vacuum must always be even under reflection with respect to the mirror plane.\textsuperscript{8} Since the matrix element must be invariant under the symmetry operation, even final states have a dipole axis lying in the mirror plane; whereas, odd final states have a dipole axis.

![Cu(100) $\Gamma XUL$](image1)

**FIG. 1.** Inverse-photoemission spectra for various photon takeoff angles $\alpha$ and fixed angle of incidence $\theta=-60^\circ$ in the $\Gamma XUL$ mirror plane of a Cu(100) surface.

![Cu(100) $\Gamma XUL$](image2)

**FIG. 2.** Intensity of a direct transition at $E_f=3.5$ eV and the background at $E_f=5.7$ eV as a function of the photon takeoff angle $\alpha$. The bottom part shows the intensity of the direct transition normalized to the background. This curve can be fitted with a squared sine function (solid line).
oriented normal to the mirror plane. When observed in the mirror plane, the transitions into even (odd) states show up with $p$- ($s$-) polarized light. Our data show conclusively, therefore, that this particular transition can be described as a dipole transition into an even final state and that there is no odd state at the same energy. The dipole axis encloses an angle of $\sim 45^\circ$ with the surface normal. At the first glance this is somewhat surprising for a surface state which owes its existence mainly to the potential step at the surface and should, therefore, have a dipole axis normal to the surface. For a surface state at the boundary of the surface Brillouin zone, however, the corrugation of the surface potential is not negligible, leading to two different surface states$^6$ and a dipole axis tilted away from the surface normal. The dipole axis is oriented approximately parallel to the incident (or refracted) electron beam, reminiscent of the classical picture of bremsstrahlung emission by a decelerated electron.

IV. COMPARISON TO THEORY

We measured the angular intensity distributions like those shown in Fig. 2 for all accessible inverse photoemission transitions at 9.6-eV photon energy in the $\Gamma X U L$ mirror plane of the Cu(100) crystal. The dispersion of the transitions is shown as open symbols in the lower part of Fig. 3. It agrees well with previously published works.$^5,13$ The shaded area indicates the projection of the bulk energy bands onto the Cu(100) surface as obtained from calculations with a combined interpolation scheme fitted to a first-principles band-structure calculation by Bross and co-workers.$^5$ The combined interpolation scheme was also used to calculate all bulk transitions at 9.6-eV photon energy with even initial state$^8,9$ shown by the dark bands in Fig. 3. The dispersion agrees well with the measured bulk bands. The width of the bands corresponds to the calculated intensity of the transition.$^{17}$ In the upper part of Fig. 3, we plotted the angle of the dipole axis relative to the surface normal for the transitions characterized by their dispersion in the bottom part of Fig. 3. All observed transitions are into even final states which means all the dipole axes lie in the $\Gamma X U L$ mirror plane. For the experimental data the dipole axis is determined by fits like the one shown in the bottom part of Fig. 2. These fits yield also the maximum intensity of the dipole emission, which is represented by the size of the symbols. The intensities agree qualitatively with the calculations as reported previously by Woodruff and co-workers,$^{18}$ but contain a large scatter due to thermal drift of the Geiger-Müller counter and changing sample quality. For the bulk transitions the measured orientation of the dipole axis follows approximately the calculated lines, but is shifted $\sim 20^\circ$ away from the surface normal. This discrepancy remains also in a calculation with the one-step model of inverse photoemission$^1$ indicated by the solid symbols in Fig. 3. The results of the one-step model for the bulk transitions agree well with the ones from the combined interpolation scheme proving its adequacy for the interpretation of bulk states. For the surface states (data points outside the shaded regions in the bottom part of Fig. 3) only one calculated data point is available$^1$ also showing a difference of $\sim 20^\circ$ relative to the experimental value.

V. DISCUSSION

The data presented in Sec. IV, as shown in Fig. 3, prove that for bulk transitions there is good agreement between results from the combined interpolation scheme and the one-step model of inverse photoemission. The experimental dispersion follows these calculations quite well. The orientation of the dipole axis is generally found approximately $20^\circ$ further away from the surface normal than predicted by the calculations. The quality of the fits allows the determination of the angle to $5^\circ$ or better (see Fig. 2). Since this discrepancy is observed for almost all data points, we have to discuss the possibility of a systematic error or omission in our data analysis. The most critical assumption is the normalization of the data to the background as shown in Fig. 2. The transmission of light through an interface should be described by the classical Fresnel formulas.$^{19}$ For the background we can assume an isotropic intensity distribution inside the surface which would result in a curve staying almost constant up to $\sim 60^\circ$ and falling off more steeply at higher angles than the measured background curve. This holds also if we
vary the optical constants far away from the reported values for copper at 9.6-eV photon energy of $\varepsilon_r=0.35$ and $\varepsilon_i=1.75$. These optical constants give total reflection for light impinging at an angle larger than 37° onto the solid-vacuum interface. We would observe, therefore, mainly transitions with a dipole axis oriented far away from the surface normal. This is in contrast to the observation which gives strong intensity for $k_\parallel=0$ which must have, from symmetry considerations alone, a dipole axis parallel to the surface normal. If we include refraction as implied by Fresnel formulas in our data analysis procedure then we obtain considerably worse fits and an even larger discrepancy relative to the calculations. We conclude that the continuum theory contained in the Fresnel equations is not suited to describe our experimental results for inverse photoemission originating from the first few atomic layers of the surface. The local field theories of the electromagnetic field near a surface give only small corrections to the Fresnel formulas, which could not resolve our discrepancies. There is a controversial discussion about the applicability of the Fresnel equations to photoemission. For carbon monoxide and oxygen on nickel a disagreement is found for large angles of incidence of the photons. Only for bulk transitions on copper no satisfactory agreement could be found. Only for silver did the Fresnel formulas give results in agreement with experiment. It seems that more experimental and theoretical work is needed to clarify the transmission of photons through the solid-vacuum interface in inverse and regular photoemission.

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5H. Bross and B. Schiekel (private communication).