Polarization Dependence of Angular-Resolved Photoemission from *d* Bands of Cu†

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We find strong polarization effects in the angular-resolved energy distribution of photoelectrons emitted from a Cu(111) surface using plane polarized light at normal incidence with $\omega = 10.2$ eV. This polarization dependence reveals the symmetry and $\vec{k}$ vector of the states involved, in particular for excitation from *d* states. The spectra can be interpreted assuming direct transitions between bulk states and subsequent elastic emission. No evidence for many-body effects or modification of the states at the surface is observed.

The polarization dependence of the angular-resolved photoemission for Cu at low energies, i.e., for transitions between the *sp* bands, agrees with the simple volume model of photoemission.[1] However, it has been suggested that many-body effects might be of importance for transitions from the relatively flat *d* bands.[2] Furthermore, the small escape depth of the electrons at higher energies might restrict the region contributing to photoemission to a thin surface layer with a local density of states appreciably different from that in the volume.[3] It is thus surprising that the one-electron volume model still accounts for the major features of the spectra given in Figs. 1 and 2 which were obtained with a photon energy of $\omega = 10.2$ eV. The model simply assumes perfect periodicity in the volume and at the surface, with $\vec{k}$ conserving transitions between Bloch states and subsequent transport to and emission through the surface without scattering of the excited electron. The periodicity at the surface requires conservation of the tangential component of $\vec{k}$ ($\vec{k}_t$) in the emission process. We refer to this model as elastic photoemission. Since the light hits the surface of the single-crystalline sample at *normal* incidence, surface photoemission connected with the steplike potential at the surface and the polarization dependence of Fresnel's equations are eliminated.

The experimental setup for taking the energy distribution of the photoelectrons emitted in different fixed directions is similar to the system described earlier.[1] However, we now use an electrodeless rf hydrogen discharge lamp together with a windowless optical system consisting of an ion-pumped Seya-Namioka monochromator and two gold-coated cylindrical mirrors mounted at 60° angle of incidence. The system provides linearly polarized light (degree of polarization > 96%) focused onto the sample within a spot of approximately 1 mm diameter.[4] Using a universal feedthrough, we adjust the (111) surface of the electropolished sample to be *perpendicular* to the incident radiation and select either the $(1\bar{1}0)$ or the $(11\bar{2})$ plane to be parallel to the fixed plane of polarization. The fixed analyzer provides one plane of observation parallel to the plane of polarization and another perpendicular to it. The sample can also be positioned for argon-ion bombardment and subsequent annealing to about 350°C under ultrahigh vacuum conditions (partial pressure of $O_2 < 10^{-10}$ Torr). Without this cleaning procedure, no sharp structure or polarization effects can be observed. Once clean, the surface gives identical spectra with only minor degrading within three days after cleaning. During the present measurements a potential of 0.8 V is applied to the sample thereby compensating the contact potential between the sample and the analyzer.[1]

Figure 1 shows the energy distribution of the photoelectrons excited from Cu(111) at *normal* incidence of the light and a polar angle of detection of $\bar{\vartheta} = 30°$, i.e. $\vartheta = 30° \pm 7°$. The upper portion of the figure corresponds to the $(1\bar{1}0)$ plane of emission with $\vec{k}_t$ parallel to $[11\bar{2}]$. The labels $\perp$ and $\parallel$ denote the orientation of the electric field vector perpendicular and parallel to the plane of emission, respectively. The lower portion of the figure corresponds to the $(11\bar{2})$ plane of emission. Figure 2 shows the appropriate data for a polar angle of $\bar{\vartheta} = 60°$, i.e. $\vartheta = 60° \pm 7°$.

We interpret the experimental data by means of Fig. 3. In this figure various contours of constant energy[1] are plotted in the neighborhood of the Λ axis. The plane of the figure is the $(1\bar{1}0)$ mirror plane. $\vec{k}_t$ conservation requires electrons observed in the $(1\bar{1}0)$ plane to originate from states with $\vec{k}$ vectors in this plane. The experimental data in the upper portions of Figs. 1 and 2 can thus be compared directly with the energy contours in Fig. 3. The contours are plot-

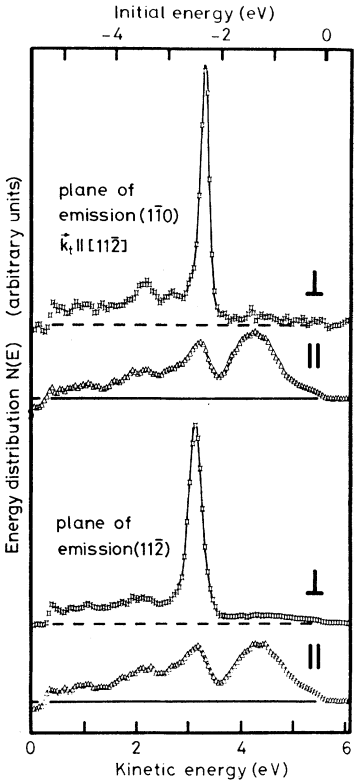

FIG. 1. Angular-resolved energy distribution of photoelectrons emitted from a Cu(111) surface at normal incidence of plane polarized light with 10.2-eV photon energy and $\vartheta = 30° \pm 7°$.

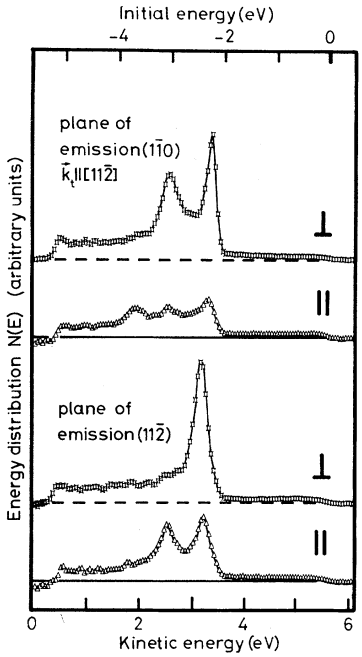

FIG. 2. Angular-resolved energy distribution for $\vartheta = 60° \pm 7°$, with the remaining parameters identical to those of Fig. 1.

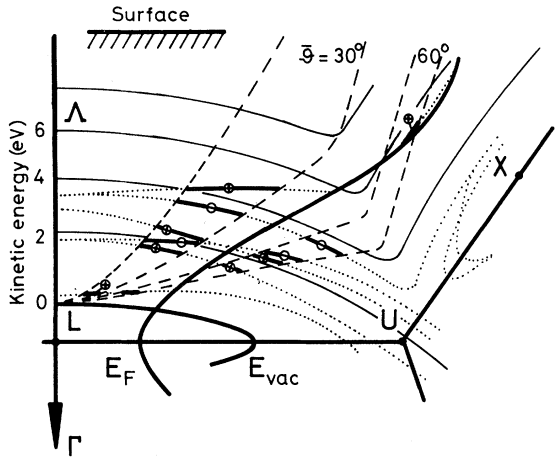

FIG. 3. Contours of constant energy for Cu characterizing direct optical transitions observable in the spectra shown in the upper portion of Figs. 1 and 2.

ted using the combined interpolation scheme with the set of parameters published earlier.[1] The heavy solid line gives the Fermi energy E_F and the vacuum energy E_{vac}, respectively, where $E_{vac} = E_F + 4.5$ eV is assumed. The light solid lines represent contours of constant final energy of the lowest unoccupied band in steps of 2 eV above E_{vac}. The dotted lines correspond to direct transitions from the five d bands and the half-occupied sp bands to the lowest unoccupied band for $\omega = 10.2$ eV. The dashed lines enclose the two areas of final states from which electrons detected under $\bar{\vartheta} = 30°$ and 60° must originate for elastic emission. These lines are calculated using the relation $E_{kin} = \hbar^2 k_t^2/(2m \sin^2\vartheta)$. The width of the respective area represents the finite angular resolution. The broad bars within these areas therefore give those final states excited by $\omega = 10.2$ eV which may contribute to the emission under the respective polar angle, with kinetic energies of the final states above E_{vac} as given in the figure. The labels $\oplus$ and $\ominus$ give the parity of the corresponding initial states with respect to the (1$\bar{1}$0) mirror reflection. Since the final state has positive parity, the selection rules require parallel polarization of the incident light for $\langle \oplus | \times \vec{A} \cdot \vec{p} | \oplus \rangle \neq 0$ and perpendicular polarization for $\langle \ominus | \vec{A} \circ \vec{p} | \oplus \rangle \neq 0$. Comparing the spectra in the upper portion of Fig. 1 with the calculated energy contours in Fig. 3, it is evident that the broad hump in the perpendicular spectrum centered at 4.2-eV kinetic energy corresponds to the uppermost transition in the $\bar{\vartheta} = 30°$ cone in Fig. 3 with the initial band being of sp type. The observed polarization dependence agrees with the selection rules given above since for perpendicular polar-

ization no electrons are observed in this energy range at all. The contour of constant photon energy intersects a wide region of contours of constant final energy thus providing a wide range of kinetic energies, as observed. On the other hand, there is the very pronounced peak at 3.2-eV kinetic energy in the perpendicular spectrum, again according to the selection rule. The initial states are at the top of the d bands. Since the related band is rather flat, the contour of constant photon energy is almost parallel to the contours of final energy in this region leading to a full width at half-maximum of only 0.2 eV for this peak. The corresponding peak in the parallel spectrum is much less pronounced; the observed width is larger than 0.4 eV. This peak grows drastically with increasing contamination of the surface. We therefore assign it to electrons excited at other places of the Brillouin zone where the top of the d bands are flat producing a large number of electrons which contribute to the angular-averaged emission. Some of these electrons will reach the detector via scattering at surface irregularities, which explains their sensitivity to surface contamination. Some of the smaller peaks in the spectra seem to have similar origin. On the other hand the amplitude ratio of the two peaks at 3.2- and 2.2-eV kinetic energy in the perpendicular spectrum tends to be constant with increasing surface contamination. The latter peak might thus result from transitions starting at the lower d band with negative parity in spite of the fact that the observed spacing of the peaks is 0.2 eV smaller than expected from the energy contours. The tight-binding parameters of the combined interpolation scheme[1] might have to be adjusted slightly to improve agreement. We actually do not observe all the structure expected from the energy contours of Fig. 3. The reason for this is probably the different transition probabilities for transitions starting from different portions of the d bands.

The spectra in the lower portion of Fig. 1 with $\vartheta = 30°$ and $(11\bar{2})$ plane of emission is rather similar to the related spectrum in the $(1\bar{1}0)$ mirror plane except for a slight shift of the main peak to lower energies. This is in agreement with the energy contours of the $(11\bar{2})$ plane which are not presented in this Letter. This energy shift was also observed by Ilver and Nilsson[5] using unpolarized light. Although the $(11\bar{2})$ plane is not a mirror plane and thus strict selection rules do not exist, we find experimentally approximate selection rules in the vicinity of the Λ axis similar to the strict rules in the mirror plane. The spectra in Fig. 2 with $\vartheta = 60°$ differ from the spectra in Fig. 1 mainly by the absence of the hump in the high-energy region, although one can still identify a small signal on an expanded scale. This is to be expected since not all of the initial states in the 60° area are occupied. Furthermore, one has to add a reciprocal-surface-lattice vector to the $\vec{k}$ vector of the leading Fourier component of the final state to achieve $\vec{k}_t$ conservation in this case, i.e., one is dealing with higher-order refraction or secondary cone emission.[6] On the other hand, the strong structure discussed before is caused by zero-order refraction which corresponds to the intense *transmitted* zero-order beam in low-energy-electron diffraction. This is not directly observed experimentally but makes itself felt by the large number of secondaries emitted after inelastic scattering of this zero-order transmitted beam.

Since the main features of the observed spectra can be interpreted by means of the bulk band structure, we conclude that the escape depth of electrons even in the region up to 10 eV above the Fermi energy is still greater than the width of the surface region where the local density of states deviates from that in the bulk. Furthermore, many-body processes like those proposed by Doniach[2] will tend to degrade the polarization effects in a fashion similar to the scattering at surface irregularities which we observed experimentally. In addition, we do not observe the low-energy tails predicted by Doniach. The polarization-dependent structure is thus not compatible with such many-body effects.

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