Bulk, Surface and Thermal Effects in Inverse Photoemission Spectra from Cu(100), Cu(110) and Cu(111)

W. Jacob, V. Dose, U. Kolac, and Th. Fauster
Max-Planck-Institut für Plasmaphysik, EURATOM-Association, Garching, Federal Republic of Germany

A. Goldmann
Laboratorium für Festkörperphysik der Universität, Duisburg, Federal Republic of Germany

Received February 25, 1986

We have performed a study of empty electronic bulk and surface states on the three low indexed copper surfaces employing momentum resolved inverse photoemission. The bulk electronic features may be well understood in the framework of the bulk direct transition model using state of the art band structure calculations. Surface states of both, the crystal derived and the image potential induced type have been identified and were found to agree with previous work. Several radiative transitions into unoccupied bands were also investigated at elevated temperatures. Characteristic temperatures of an exponential attenuation law are distinctly different between surface and bulk transitions. However, no systematic behaviour of bulk transitions at different points of the Brillouin zone could be established.

I. Introduction

Angle-resolved electron spectroscopies have become the most successful techniques for the investigation of the electronic properties of ordered solids. This holds in general for both the electronic structure of the bulk and at the surface. In particular angular resolved photoemission techniques [1–3] have made larger progress in recent years. While these can in principle yield information about the occupied electron states and those empty states that are located energetically above the vacuum level $E_v$, most photoemission studies concentrate on the analysis of the occupied states [1, 2]. This restriction results from the difficulties associated with the determination of the electron momentum in the solid. Upon penetration of a single-crystal surface only $k_{||}$, the wave-vector component parallel to the surface, is conserved and directly obtainable from the kinematical parameters, while $k_{\perp}$ remains unknown in general. This is of course no problem if two-dimensional surface or absorbate bands are studied, where the energy eigenvalues $E(k_{||})$ depend only on $k_{||}$. However, the investigation of bulk electronic states requires additional information to deduce the full energy band dispersion $E(k_{||}, k_{\perp})$. Various methods have been proposed to determine the full wave vector $k = (k_{||}, k_{\perp})$ by experiment. A detailed discussion of these methods has been presented recently [3] and shall not be repeated here. They have in common, that they are generally rather tedious and time consuming. Therefore in most photoemission studies performed up to date, reasonable assumptions were made about $k_{\perp}$, for example “free-electron-like” final state bands. In consequence not too much experimental information is generally available about $E(k)$ of unoccupied bulk bands. Moreover, the energy region between the Fermi energy $E_F$ and $E_v$ is not at all accessible to photoemission. Most important, empty surface bands inherent to the clean surface and/or empty states derived from adsorbates cannot be observed by the standard (one photon absorption) photoemission techniques.

This methodological gap was bridged with the recent advent of angle-resolved ultraviolet inverse pho-
toemission [4–10]. This technique observes radiative transitions into empty surface and/or adsorbate states or between two empty bulk bands. The obtainable information is then mostly just complementary to the photoemission results. Of course, the limitations with respect to the determination of $k_f$ are the same for both methods. In order to check the general understanding as well as the inherent experimental limitations of inverse photoemission, the new technique was first applied to those materials that were best known from various photoemission experiments. In this context Cu is probably the best studied material at all, and the available knowledge about its electronic structure was summarized recently in considerable detail [3]. In particular, Cu is one of the very few materials, where a lot of both experimental and theoretical information about empty bulk band dispersions and about empty surface states is available. Therefore several inverse photoemission studies focused on the low-indexed Cu surfaces. It is the aim of the present paper to summarize available knowledge from several studies already published [11–26], to present new experimental results, and to review critically all that material in the light of our present understanding of electron states in bulk Cu and at its surfaces.

Section II below describes briefly the experimental techniques employed in this work. Section III presents and summarizes, in the form of $E(k_{l1})$ plots, inverse photoemission results from Cu(100), Cu(110), and Cu(111) along different azimuths. The experimental bulk band results are discussed in the context of calculated bands in Sect. IV. Inverse photoemission spectra were also measured for samples at elevated temperatures and typical results are presented and interpreted in Sect. V. A summary of the understanding of empty surface bands is given in Sect. VI. Finally our conclusions are presented in Sect. VII.

II. Experimental

All our results are obtained by measuring spectra in the “isochromat” mode: Electrons with kinetic energy $E_{\text{kin}}$ impinge on the sample at an angle $\theta$ (with respect to the surface normal) in a mirror plane of the substrate crystal. The isochromat spectra register the emitted photon intensity at a fixed photon energy $h\omega = 9.7$ eV during a scan of $E_{\text{kin}}$. The experimental details have been described in detail elsewhere [10, 27]. The photon spectrometer is based on an energy-selective ultraviolet Geiger-Müller counter which is iodine filled and has a CaF$_2$ entrance window. This combination of counting gas and window acts as a bandpass filter which detects photons at $h\omega = 9.7$ eV with an overall resolution (FWHM) of 0.8 eV.

Clean samples of Cu(100), Cu(110) and Cu(111) were prepared by standard procedures of argon ion etching and annealing. Typical experimental parameters were set as follows: kinetic ion energy between 800 and 1000 eV at ion current densities between 3 and 15 $\mu$A/cm$^2$, annealing temperatures ranging from about 500 to about 600 K for times between 5 and 15 minutes. After that treatment the samples were characterized using the standard Auger and low-energy-electron-diffraction (LEED) techniques, and the preparation cycles were repeated until an excellent LEED pattern was obtained and no traces of S, C, O or other contaminants could be observed.

III. Results

The Cu(100) surface has attracted the most experimental attention yet and several groups have published inverse photoemission results. We shall therefore skip the reproduction of experimental spectra here. Normal incidence isochromat spectra were obtained at $h\omega = 9.7$ eV by Woodruff et al. [11, 12] and by Dose and coworkers [15, 16, 18, 22]. Woodruff et al. also report on isochromat spectra taken at $h\omega = 9.5$ eV, 10.3 eV, and 11.0 eV, respectively [20]. Straub and Himpsel [17] have studied normal incidence at fixed electron kinetic energies between 9.8 eV and 18.3 eV. In this constant initial state mode, one records the intensity of the emitted bremsstrahlung as a function of $h\omega$ [17]. Angle-dependent isochromat spectra along both the $\Gamma X W K$ bulk azimuth (corresponding to the $\Gamma M$ direction of the surface Brillouin zone, for definitions see e.g. [1]) and the $\Gamma X U L$ azimuth ($\Gamma X \bar{X}$) are reported by several authors [12, 15, 18] and experimental attempts have been made to distinguish between bulk band transitions [12–15] and transitions into surface-specific electron states [16–18, 20, 22]. If we account for differences in energy-resolution and angular resolution, we conclude, that all experimental results summarized above are in reasonable to excellent agreement.

The complete set of data obtained in our work for Cu(100) is presented in Fig. 1 as a plot of observed final state energies $E(k_{l1})$ versus $k_{l1}$. The final state energy is given in terms of the initial state energy $E_i$ by

$$E = E_i - h\omega = E_{\text{kin}} + \Phi - h\omega$$

where $\Phi$ is the sample work function. The value of $k_{l1}$ is $k_{l1} = k_{l1} - g_{l1}$, where the index $i$ denotes the momentum $h k_{l1,i}$ of the incoming electron and $g_{l1}$ is a surface reciprocal lattice vector. With the usual assumption [1, 2] that $g_{l1} = 0$ we obtain

$$k_{l1} = \sin \theta (2m E_{\text{kin}}/h^2)^{1/2}$$
Fig. 1. Final state energies $E$ as a function of $k_{\|}$ for isochromat emission peaks observed from Cu(100). The electrons were incident in the $\Gamma XUL$ (left side) and $\Gamma XWK$ (right) bulk mirror planes, respectively. Unshaded areas indicate a gap of the projected bulk band structure. Dashed lines: kinematically allowed bulk band transitions, see text. Solid lines through $B_1$-band: results from one-step-model calculations [14, 18].

where $m$ is the free electron rest mass. The assumption $g_{\|}=0$ means that surface umklapp scattering (a “secondary cone” effect in Mahan’s [28] sense) contributes only weakly to the observed emission intensity, while “primary cone” incidence ($g_{\|}=0$) dominates the spectra. The dominance of $g_{\|}=0$ effects is a general observation in photoemission [1-3].

Our results summarized in Fig. 1 are labeled according to their identification as bulk to bulk transitions (label B) or transitions into surface bands (label S). Details will be discussed in Sect. IV and VI below. Except from our group [15, 16, 18] $E(k_{\|})$-results have been reported earlier by Woodruff et al. [12], which observed the bands labeled $B_1$ in Fig. 1 in a smaller $k_{\|}$ interval. Their data agree in general with our results.

Much less is known about Cu(110) and Cu(111) from earlier work. A sample of angle-dependent Cu(110) isochromat spectra taken at $h\omega=9.7$ eV along $\Gamma KLU$ ($\tilde{\Gamma} \tilde{\gamma}$, for definition see e.g. Ref. 1) is reproduced in Fig. 2. Similar results obtained along $\Gamma KWX$ ($\tilde{\Gamma} \tilde{x}$) are shown in Fig. 3. In both azimuths we observed prominent bulk band transitions ($B_1, B_2$) as well as prominent surface state transitions ($S_1, S_2$).

Their dispersion, immediately recognized upon inspection of Figs. 2 and 3, is summarized as an $E(k_{\|})$-plot in Fig. 4. An additional rather faint step labeled $S_3$ in Fig. 2 is due to a transition into an image potential bound state, see Section VI below for details. Spectra along $\Gamma KLU$ ($\tilde{\Gamma} \tilde{\gamma}$) have also been reported by other authors. Bartynski et al. [24] report the band labeled $S_3$ in Fig. 4 to be located $2.5 \pm 0.2$ eV above $E_F$ at $\tilde{\gamma}$. Reihl and Frank [25] derive a binding energy of $E-E_F=2.0 \pm 0.4$ eV at $\tilde{\gamma}$, in excellent agreement with our result of $1.8 \pm 0.2$ eV. On the other hand the dispersion of $S_1$ observed in [25] is much weaker than that observed in [24]. Bartynski et al. [24] report an effective mass of $m^*/m=1.1$, in good agreement with our value of $m^*/m=0.8 \pm 0.2$. The weak feature labeled $S_3$ in Fig. 2 appears better resolved in Fig. 1 of Ref. [25]. The latter authors also observed a more pronounced emission peak near $E_F$ at $\theta=0^\circ$ (labeled $B_3$ in Fig. 4). The reason for the different intensities...
might well be due to light-polarization effects. Such differences are to be expected if the photon collection geometries differ in the experimental arrangements, see e.g. Fig. 2 of [15] for a convincing example. A high energy peak observed in this work [15] in normal incidence at $E - E_F = 14.3 \pm 0.3$ eV ($\hbar \omega = 9.7$ eV) was also reported in [25] at 14.5 eV above $E_F$. Since it was observed only at $\bar{F}$ it is not included in Fig. 4, but will be discussed further in Sect. IV.

Isochromat spectra from Cu(111) taken at $\hbar \omega = 10.2$ eV along the $\bar{F}K$ azimuth, which is symmetrical with respect to $\pm \theta$, have been reported by Hulbert et al. [19, 21]. These data are included in Fig. 6. We have measured isochromat spectra at $\hbar \omega = 9.7$ eV along $\bar{F}M'$ ($\Gamma LUX$) and $\bar{F}M$ ($\Gamma LKL$), respectively, and sample spectra are reproduced in Fig. 5. Although our intensities differ considerably from those observed in [21] – which could be due to the combined effects of different photon detection energies, different angular resolution, different photon collection geometry and different sample quality – the $E(k_F)$-results are very similar. Our results are reproduced in Fig. 6 as full dots. Note that $\bar{F}M$ and $\bar{F}M'$ are not equivalent with respect to bulk transitions, but equivalent with respect to the surface Brillouin zone [1] which is exclusively defined by the geometry of the topmost atomic layer. As discussed in detail in references [19, 21] and [26] the band labeled $S_1$ is the continuation above $E_F$ of the well known [31–33] occupied surface state observed 0.4 eV below $E_F$ at $\bar{F}$, while $S_2$ is due to the image potential surface state. Comparison of our data in Fig. 6 with those obtained by Hulbert et al. [19, 21] gives the following result: although there seems to be a slight (0.2...0.3 eV) overall downward shift of the energy scale – probably due to a different location of $E_F$ – the observed dispersions of both $S_1$ and $S_2$ are remarkably equal. This indicates that within the error margins neither $S_1$ nor $S_2$ depend on the specific azimuths chosen.

Fig. 4. Final state energies $E$ as a function of $k_F$ for isochromat emission peaks observed from Cu(110). The electrons were incident in the $\Gamma KLU$ (left side) and $\Gamma KWX$ (right) bulk mirror planes, respectively. Unshaded areas indicate a gap of the projected bulk band structure. Dashed lines: kinematically allowed bulk band transitions, see text. Dash-dotted lines: predicted surface state bands [29]. Dotted line around $\bar{F}$ below $E_F$: photoemission results [30].

Fig. 5. Isochromat spectra from Cu(111) for electrons incident at several polar angles $\theta$ in the $\Gamma XULK$ bulk mirror plane.

Fig. 6. Final state energies $E$ as a function of $k_F$ for isochromat emission peaks observed from Cu(111). Solid dots: this work. The electrons were incident in the $\Gamma LUX$ (left side) and $\Gamma LKL$ bulk mirror planes, respectively. Triangles: data obtained in [21] along $\Gamma K$. Unshaded areas indicate a gap of the projected band structure. Dotted line below $E_F$ around $\bar{F}$: photoemission result [33]. Dashed line extends the photoemission result above $E_F$ using the effective mass determined in [33].
IV. Discussion of the Bulk Band Transitions

The observation of bulk band transitions requires to satisfy simultaneously three conditions:

(i) energy- and momentum conservation: “kinematically allowed” transitions can occur only at $k$-points where $E_i(k) = E(k) + \hbar \omega$ (thus neglecting the momentum of the photon). Clearly $k = (k_\parallel, k_\perp)$ is restricted to a line $k_\parallel = \text{const.}$ as defined by the parameters of the particular experiment;

(ii) the transition matrix element must not vanish due to symmetry constraints, or become very small accidentally;

(iii) the probability for the incoming electron to couple to the initial Bloch band at $E_i(k)$ must not be too small or zero. At normal incidence only initial bands totally symmetric with respect to the point group operations of the surface normal are allowed [34], in mirror-plane geometries the initial band must be even with respect to the mirror plane [34]. However, not all initial bands allowed by these symmetry-selection rules contribute equal intensity: A large coupling probability is to be expected [12] only if the band in question exhibits a large amplitude of that partial plane wave associated with the bulk reciprocal-lattice vector directed along the surface normal. Clearly, in normal incidence this condition is best met by “free-electron-like” bands, with a dispersion according to

$$E_i = \frac{\hbar^2}{2m^*} k^2 + V_0$$

where $k^2 = k_\parallel^2 + k_\perp^2$ is considered in the extended zone scheme. For Cu an effective mass $m^* = m$ and an inner potential $V_0 = -7.5 \text{ eV}$ are typical “best choice” parameters [3] for the range of energies of interest here.

To analyze our results we have first calculated the kinematically allowed transitions according to condition (i) above. They are indicated in Figs. 1 and 4 by the dashed lines. Our calculation is based on an unpublished band structure kindly supplied by Bross and coworkers [35]. Although several other band structures have been published for Cu [3] they are often restricted to high-symmetry $k$-space directions or concentrate on the occupied bands. The convenience and computational merit of the band structure used here lies in the fact, that it offers 413 energy eigenvalues $E(k)$ and the corresponding gradients $\nabla E(k)$, distributed uniformly over the irreducible $1/48$ wedge of the Brillouin zone. We mention that this band structure [35] is in very good agreement with that obtained recently by Eckardt et al. [36]. For Cu(100) direct transitions had already been calculated before [14, 18] on the basis of the one-step-model of inverse photoemission and these results are reproduced by solid lines through the $B_1$ data points along both azimuths in Fig. 1.

Inspection of Fig. 1 shows that only one bulk transition ($B_1$) occurs at $\Gamma$, corresponding to the $\Gamma - \Delta - X$ line of the bulk Brillouin zone, and this transition is easily identified with the vertical solid arrow between $F - T$ in Fig. 7. Nonrelativistic dipole selection rules [34] dictate a photon polarization of the corresponding $A - A$ transition along the surface normal, and this polarization effect has been verified experimentally [15]. Increasing quantum energies will shift the required final state band below $E_F$, and the disappearance of the $B_1$ peak is nicely demonstrated in [17]. Going off normal in Fig. 1, both branches of band $B_1$ are almost perfectly reproduced by the one-step-model results (solid lines). In particular we note that for larger $k_\parallel$ along $FXUL$ obviously $B_1$ splits off the bulk into the projected gap, in excellent agreement with theory. As is evident from Fig. 4 all other bulk transitions ($B_2 - B_4$) are consistent with the kinematical predictions. Of course, not all such predicted transitions can be observed, due to the constraints (ii) and (iii) mentioned above.

A detailed inspection of Fig. 7 shows that several
kinematically allowed transitions are predicted along the \( \Sigma/S \)-line, which corresponds to \( \vec{F} \) of Fig. 4. Only three out of nine in total are shown in Fig. 7. According to Fig. 4, however, only one transition \( B_1 \) is observed for \( E < 8 \) eV, appearing only very weak in the spectra of Figs. 2 and 3. The reason for the reduced intensity is obvious from Fig. 7: Although the initial band is of symmetry allowed \( \Sigma_1 \) character [34], its dispersion is not free-electron-like as discussed above. In consequence it couples only weakly to the incoming electron. Therefore the emission intensity is small, despite of the fact that the subsequent \( \Sigma_1 \rightarrow \Sigma_1 \) radiative transition is clearly dipole allowed. Going off normal along \( \Gamma K L U \) in Fig. 4, band \( B_1 \) may be consistent with the dashed lines for \( k_\parallel \lesssim 0.4 \) Å\(^{-1}\), but definitely adopts appreciable surface character at larger \( k_\parallel \) and finally gets a pure surface state band in the projected bulk band gap. A detailed and quantitative explanation for this behaviour is still missing. A similar trend is indicated with band \( B_2 \) along \( \Gamma K W X \): while clearly explainable by the kinematical calculation (dashed line) for \( k_\parallel \lesssim 0.9 \) Å\(^{-1}\), it tends to move into the projected bulk band gap near \( \bar{X} \).

Up to now our analysis was based on a calculated band structure. A simplified analysis, relying on the free electron initial band approximation, was chosen to interpret the emission peak observed [15] at \( E - E_F = 14.3 \pm 0.3 \) eV on Cu(110) at normal incidence. From Eq. (1) we calculate \( k_L = (2.86 \pm 0.02) \) Å\(^{-1}\). This result localizes the transition (label \( e \)) in Fig. 7, and we realize very good agreement with the calculated band structure. If a given direct transition can be observed from (at least) two differently oriented surfaces, “triangulation” [41] allows an absolute experimental determination of \( k_L \), without the need to resort to a calculated band structure or to specify particular assumptions about the initial state involved. Such a triangulation has been performed [23] for some of the \( B_1 \) transitions observed on Cu(100) in the \( \Gamma X W K \) plane (see Fig. 1). The same transition can also be identified in isochromat spectra taken from Cu(210), and the resulting location of \( k \) is shown by the dots in Fig. 8. The dashed lines reproduce the kinematically allowed transitions. We realize excellent agreement between the \( k \)-space loci determined absolutely with those derived from the band structure calculation. Transitions which satisfy the “free-electron-like-behaviour” requirement (iii) discussed above, manifest themselves in a plot like Fig. 8 by the fact that the dashed line runs essentially parallel to the zone boundary [12]. Radiative transitions between two free-electron-like bands require \( k_L = \) const. when \( k_\parallel \) is changed. This condition is obviously met by the curves paralleling the data points. On the other hand, Fig. 8 clearly shows that the dashed line labeled \( b \) crossing \( X - W \) near \( X_{002} \) does not exhibit the required behaviour. In consequence the corresponding transition along \( X - W \), compare arrow \( b \) in Fig. 7, is not observed experimentally, although the initial band (Fig. 7) clearly is of “allowed” [34] mirror plane symmetry \( \Sigma_1 \).

We conclude that the various results of isochromat spectroscopy are in good to excellent agreement with the calculated bands [35, 36]. The consistency of our results and those obtained by several other authors with data obtained by different spectroscopic techniques is demonstrated in Fig. 7, where we have included experimental points from photoemission [3], low-energy-electron reflectance [37], de Haas – van
Alphen effect [3] and secondary electron emission [38-40]. To make this comparison more quantitative, we have collected several experimental and theoretical critical point energies in Table 1. Obviously the bulk-related properties discussed in our context may be well explained on the basis of the band structure calculations within typically ±0.5 eV. We conclude that the empty Cu bands up to about 25 eV above \( E_F \) are well understood.

V. Thermal Effects: Results and Discussion

Spectra obtained by angle-resolved electron spectroscopies may be modified at elevated sample temperatures in four respects [48]: peak intensity changes, peak broadening, peak energy shifts and appearance of new peaks resulting from phonon-assisted processes. Several experimental photoemission studies have investigated such effects [49-55] and theoretical efforts are reported to obtain a quantitative understanding [48, 56, 57]. The dominating effect in the range of temperatures and electron energies of our measurements is the reduction of peak intensities. The other three effects appear to be thermal effects of higher order, at least for Cu. The attenuation of direct transition peaks at elevated sample temperature is easily understood qualitatively. Although phonon energies are generally small as compared to electron energies, the scattering of the outgoing (or incoming) electrons by phonons is associated with momentum transfers comparable to the size of the Brillouin zone. Consequently the electron-phonon interaction tends to randomize the electron \( k \)-vector and direct transition features observed at fixed angle will lose intensity. In case of surface state transitions – where the electron states are residing essentially at the outermost atomic layer – the strongly anisotropic surface potential causes enhanced vibrational motion of the surface atoms and we therefore expect an even stronger temperature sensitivity than for bulk transitions. This fact has clearly been demonstrated in photoemission experiments [52, 54, 55] and provides a means to discriminate between bulk and surface effects. We have therefore checked for the temperature dependence of peak intensities in isochromat spectra and will now present and discuss typical results.

Temperature dependent spectra obtained from Cu(110) at \( \theta = 35^\circ \) along \( \Gamma K L U \) are reproduced in Fig. 9. The surface peak \( S_1 \) (compare Fig. 4) is considerably attenuated at elevated temperatures, while the bulk state transition \( B_1 \) (compare Fig. 4) is much less affected. A more detailed study of the same two bands has been performed at \( \theta = 31^\circ \) along the same azimuth and the peak intensities, corrected for background which was shown to be independent of sample temperature \( T \), are plotted against \( T \) in Fig. 10. Clearly the observed behaviour parallels the results presented in Fig. 9. If we assume a simple exponential temperature dependence [48, 54] according to

\[
I(T) = I_0 \exp\left(-\frac{T}{T_c}\right)
\]

we can obtain a characteristic temperature \( T_c \). A fit of equation (2) to the data points is shown by the
Table 2. Experimental characteristic temperatures $T_c$ for bulk and surface derived transitions observed on Cu surfaces by photoemission (P) and inverse photoemission (IP), respectively.

<table>
<thead>
<tr>
<th>States involved</th>
<th>Face</th>
<th>$T_c$/K</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image potential</td>
<td>100</td>
<td>$&gt; 20,000$</td>
<td>IP</td>
<td>this work: $S_1$(100)</td>
</tr>
<tr>
<td>Surface (Shockley)</td>
<td>110</td>
<td>590</td>
<td>IP</td>
<td>this work: $S_1$(110)</td>
</tr>
<tr>
<td>Surface (Shockley)</td>
<td>111</td>
<td>670</td>
<td>P</td>
<td>[54]</td>
</tr>
<tr>
<td>Surface (Tamm)</td>
<td>100</td>
<td>625</td>
<td>P</td>
<td>[58]</td>
</tr>
<tr>
<td>Surface (Tamm)</td>
<td>111</td>
<td>560</td>
<td>P</td>
<td>[54]</td>
</tr>
<tr>
<td>Bulk (s, p)</td>
<td>100</td>
<td>1,510</td>
<td>IP</td>
<td>this work: $B_{11}(100)$</td>
</tr>
<tr>
<td>Bulk (s, p)</td>
<td>100</td>
<td>1,430</td>
<td>P</td>
<td>extracted from [50]</td>
</tr>
<tr>
<td>Bulk (s, p)</td>
<td>110</td>
<td>3,700</td>
<td>IP</td>
<td>this work: $B_{11}(110)$</td>
</tr>
<tr>
<td>Bulk (s, p)</td>
<td>110</td>
<td>$\approx 1,000$</td>
<td>P</td>
<td>[59]</td>
</tr>
<tr>
<td>Bulk (s, p)</td>
<td>111</td>
<td>5,900</td>
<td>P</td>
<td>[54]</td>
</tr>
<tr>
<td>Bulk (d)</td>
<td>110</td>
<td>1,000...2,500</td>
<td>P</td>
<td>[55]</td>
</tr>
<tr>
<td>Bulk (d)</td>
<td>111</td>
<td>1,220...1,670</td>
<td>P</td>
<td>[54]</td>
</tr>
</tbody>
</table>

straight lines in Fig. 10. The results for $T_c$ are summarized in Table 2. Another experimental result is presented in Fig. 11. In that case we studied the $T$-dependence of features $B_1$ and $S_1$ observed at normal incidence on Cu(100), compare also Fig. 1. A typical spectrum taken at $T=380$ K is reproduced in the insert of Fig. 11. In contrast to the data shown in Fig. 10, where the surface peak decayed much faster than the bulk emission, we now find a clear attenuation of $B_1$, but no temperature effect at all for $S_1$. The characteristic temperatures $T_c$ are also given in Table 2. Further included in this table are $T_c$ values obtained from photoemission on different surfaces of Cu. We mention that peak broadening effects and peak energy shifts could not be uniquely identified. Obviously such effects are within or below our resolution limits. In fact, a photoemission study [50] of transitions from the occupied $A_{6(1)}$ band along $\Gamma-X$ (slightly below $E_F$, see Fig. 7) to the empty $A_{6(1)}$ band starting about 7.5 eV above $E_F$ at $X_{S+}(1)$ (the photoemission final states are indicated by open circles along that band in Fig. 7) showed no resolvable thermal shift (<25 meV) in this k-space region. This was explained [50] by compensating energy shifts of the upper and lower band, respectively. Therefore no such shift was to be expected for the $B_1$ isochromat transition along $\Gamma-X$ in agreement with our experimental results.

From Fig. 4 of that work [50] we can estimate the intensity-attenuation of the direct $A_{6(1)} \rightarrow A_{6(1)}$ transition observed at $h \nu=11$ eV. The corresponding final state is the open circle identified by the small arrow in Fig. 7. Photoemission spectra were taken in [50] at 300 K and 775 K and from the observed decrease we derive $T_c=1430$ K. The two points (normalized to our data at 300 K) are plotted as squares in Fig. 11 and perfect agreement with our results is obvious.

Next we discuss the results collected in Table 2. An electron trapped in an image potential state resides far outside the crystal surface in vacuum, see also Sect. VI. Therefore the transition into an image potential state will be essentially unaffected by the thermal motion of the surface atoms, and only a weak dependence of the emission intensity on the sample temperature is to be expected. In fact, our experimental result is consistent with $T_c \rightarrow \infty$. Next we consider
surface state results, obtained for both Shockley [60] and Tamm [61]-type bands. The observed characteristic temperatures are of comparable size and appear to be consistently smaller than those observed for bulk transitions. This is clearly compatible with enhanced thermal vibrations in the surface region. In fact, our results for $S_1$ presented in Fig. 10 indicate that at $T>700$ K the negative slope increases and that the intensity decrease becomes faster than exponential. Such an effect has been observed also in photoemission both for a surface state [52] and a bulk band transition [49]. It was discussed as a beginning non-linear relation between atomic mean-square displacement and temperature in the surface region [49]. We will therefore restrict the discussion to $T<700$ K. The observed bulk transitions exhibit characteristic temperatures between 1000 K and about 5900 K. No systematic difference can be derived for transitions between $s,p$-like bands and transitions out of $d$-bands. The $T_c$ values may be converted into effective Debye-temperatures $\theta_{\text{eff}}$ [48, 54] and the general observation [54] is that $\theta_{\text{eff}} < \theta_\text{D} = 343$ K, the Debye temperature of bulk Cu. This indicates the surface sensitivity of the mechanism underlying (inverse) photoemission. Inspection of Table 2 shows that the $T_c$ values for bulk transitions at $T \leq 700$ K exhibit considerable scatter. In particular, the detailed analysis shows that they do not depend in any simple geometrical sense on electron mean free path or electron emission angle [54]. There are experimental indications [55] that $T_c$ is sensitive to the degree of localization of the involved wave-functions and/or the $k$-space localization of the transition observed, and attempts have been made to explain this [56, 57]. We conclude that the systematics of absolute $T_c$ values is not understood. However, our data clearly show, that within one energy distribution curve the relative temperature coefficients can be safely exploited in a straightforward manner to distinguish bulk, surface, and outside-surface contributions. It might be interesting to follow $T_c(k_{\parallel})$, e.g. for the $B_1$ band observed along $\Gamma K L U$ on Cu(110). Such a study could perhaps reveal the systematic change from bulk to surface character, as suggested by the data points collected in Fig. 4. Another candidate for an investigation of $T_c$ as a function of $k_{\parallel}$ is clearly the $B_1$ band, approaching the X point in Fig. 1.

VI. Discussion of Surface State Transitions

Surface states observed above the Cu $d$-band region ($-5 \ldots -2$ eV) are generally of the Shockley [60]-type. These states may be conveniently discussed within a simple model based on multiple-reflection theory. This model, originally proposed by Echenique and Pendry describes an electron trapped in a previously unoccupied surface state as a wave which is repeatedly reflected between the crystal edge and the surface barrier potential. The phases of that wave are, of course, determined by both the crystal potential near the surface and the barrier (image) potential. Depending on which contribution dominates, Echenique and Pendry distinguish “barrier induced” image potential states – these are generally located in energy just below $E_c$ and form a Rydberg-type series. Their wave functions extend far out into the vacuum whereas “crystal induced” states reside on and near the outermost atomic plane of the crystal. Clearly, image potential states are a very general property of metal surfaces, while the crystal-induced surface states reflect in detail the electronic surface structure. The model of Echenique and Pendry [62] has since been further developed by Smith [19, 21, 63, 64] and co-workers. Smith has demonstrated that a detailed qualitative understanding of crystal-induced surface state energies and a rather quantitative understanding of image-potential state energies may be achieved using some simple but reasonable assumptions about the crystal and image potential, respectively. In particular, Smith [64] has applied this type of analysis to the three low-index surfaces of Cu and the reader is referred to that work for details. The value of the phase model lies in the insight it provides into the systematics of surface state formation, and the possibility to distinguish between crystal-induced and barrier-induced features. If one is interested in quantitative results, however, and in particular in the detailed behaviour of the wave-functions, numerical calculations must be performed. Results from such calculations are contained in [65]. We only mention here, that detailed wave-function pictures are reproduced in [65] which make the distinction between “barrier-induced” and “image-potential”-derived very transparent.

Our experimental identification of surface states was generally based on various criteria: Surface derived peaks should respond more sensitively to contamination than bulk derived features. A typical example is shown in Fig. 12, which reproduces the $B_1$ and $S_1$ bands observed at $\theta=35^\circ$ along $\Gamma K L U$ on Cu(110), compare also Fig. 4, after oxygen dosing at various exposures. The rapid quenching of $S_1$ as compared to $B_1$ is clearly evident. Simultaneously an oxygen-derived feature $A$ develops, which will not be further discussed here. A second argument was the different sensitivity of surface states to temperature variation, and two clear-cut examples have been discussed in detail in Sect. V. Clearly the location of an observed intense band well within a projected gap
of the bulk Brillouin zone rules out a bulk origin. In particular the corresponding \( E(k_{\parallel}) \)-relation must then exhibit the periodicity of the surface Brillouin zone. Image potential states, in addition, are generally pinned to \( E_v \), and we have verified this behaviour in earlier papers \[16, 26\]. In \[26\] we gave a general overview on empty surface states observed on the low-index faces of Ni, Cu and Ag and we refer to that paper for a detailed discussion.

Since then, however, several new results were obtained, and therefore we have prepared an updated table of observed surface state features (see \[19, 26, 64\] for details) of Cu. In that Table 3 the states are classified according to “crystal” and “barrier” origin, respectively. A wealth of experimental results is now available, and good agreement is found for results from different laboratories. Obviously two surface states are observed in each of the gaps on Cu. Results of earlier calculations by Dempsey and Kleinmann \[29\] are indicated in Fig. 4 by the dash-dotted lines around \( \bar{X} \) and \( \bar{\Gamma} \), and the overall agreement with the presently available experimental data is obviously good. The numerical analysis of Cu(111) by Thörner \[71\] is able to reproduce both states \( S_1 \) and \( S_2 \) at \( \bar{\Gamma} \) (see Fig. 6) simultaneously within one ansatz for the potential. The recent work based on the phase model has already been mentioned \[64\]. We summarize that the general aspects of surface state formation are now well understood. However, inspection of Figs. 1 and 4 reveals that additional experimental work is highly desirable. In particular on Cu(110) the movement of bands \( B_1 \) (near \( \bar{Y} \)) and \( B_2 \) (near \( \bar{X} \)) into the projected gaps as indicated by our results in Fig. 4 deserves further investigation. Since surface features must only depend on \( k_{\parallel} \) their dispersion

---

**Table 3. Summary of binding energies \( E - E_F \) and effective masses \( m^*/m \) observed for surface states connected with the low index surfaces of Cu. \( \Phi \) is the work function, \( m^*/m \) the dispersion at the respective symmetry point**

<table>
<thead>
<tr>
<th>Crystal induced</th>
<th>Barrier induced at ( \bar{\Gamma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>at ( \bar{\Gamma} )</td>
<td>at ( \bar{\Gamma} )</td>
</tr>
<tr>
<td>( \Phi = 4.39 \text{ eV} ) [70]</td>
<td></td>
</tr>
<tr>
<td>( \Phi = 4.50 \text{ eV} ) [70]</td>
<td></td>
</tr>
<tr>
<td>( \Phi = 4.98 \text{ eV} ) [70]</td>
<td></td>
</tr>
</tbody>
</table>

---

*This work, \(^*\) along \( \bar{\Gamma} \), \(^a\) along \( \bar{\Gamma} \), \(^b\) extrapolated to \( \bar{\Gamma} \) (compare Fig. 1), \(^d\) extension above \( E_F \)
been studied and their diagnostic value for angle-resolved inverse photoemission spectra is clearly recognized. Our results are discussed in the context of several other inverse photoemission studies of Cu and good agreement with other groups is observed. Experimental band dispersions $E(k_f)$ have been derived and bulk properties could be clearly distinguished from surface state features. The bulk-related emission may be well explained on the basis of calculated energy band dispersions $E(k_f)$, thereby ruling out larger relaxation effects. Several surface bands could be classified as either crystal-induced or image-potential-derived. The systemsatics of empty surface states on Cu is now either crystal-induced or image-potential-derived.

VII. Summary and Conclusions

We have investigated angle-resolved inverse photoemission spectra from Cu(100), Cu(110) and Cu(111) over extended energy and angular intervals. Our results are discussed in the context of several other inverse photoemission studies of Cu and good agreement with other groups is observed. Experimental band dispersions $E(k_f)$ have been derived and bulk properties could be clearly distinguished from surface state features. The bulk-related emission may be well explained on the basis of calculated energy band dispersions $E(k_f)$, thereby ruling out larger relaxation effects. Several surface bands could be classified as either crystal-induced or image-potential-derived. The systemsatics of empty surface states on Cu is now well established experimentally. Thermal effects have been studied and their diagnostic value for angle-resolved inverse photoemission spectroscopies is clearly recognized.

The Cu band structure used in this work has been kindly supplied by Professor H. Bross. We are indebted to C.J. Stimpfle for numerous discussions.

This work has been supported financially by the Deutsche Forschungsgemeinschaft.

References

43. Based on experimental data presented in [44]; result modified by the authors of [37]
47. Based on experimental data presented in [44]; result modified by the authors of [37]
58. Goldmann, A.: Unpublished result. Our data agree well with those reported in [52].
59. Value extracted by us from the results reported in [49].
61. Tamm, I.: Z. Phys. 76, 848 (1932)
68. Extracted by us from results of [24]

71. Thörner, G.: Unpublished results