Unoccupied electronic states and surface barriers at Cu surfaces

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Abstract. The surface potential barrier shape of the low-index faces of copper was determined by an analysis of inverse photoemission and two-photon photoemission measurements making use of the one-step model of photoemission. The barrier potentials obtained in this way allow for a consistent description of the energetic positions and effective masses of all known surface states for the various faces. It is found, in agreement with previous theoretical predictions, that the most open surface, Cu(110), exhibits the strongest saturation of the image potential with an image plane lying nearest to the topmost atomic layer and with the weakest image force outside the crystal. A comparison with theoretical slab calculations shows that in these calculations the position of the image plane is always significantly further outside the crystal than derived in the present study. Dynamical effects in the effective potential are found to be negligible for electronic states up to 6 eV above the Fermi level $E_F$, but are probably responsible for systematic discrepancies between theory and experiment for unoccupied bulk states in the energy range 10–15 eV above $E_F$.

1. Introduction

Inverse photoemission (1PE), two-photon photoemission (2PPE) and very-low-energy electron diffraction (VLEED) have recently led to a renewed interest in the study of unoccupied electronic surface states in the local energy gaps of metals. In this context the variation of the potential near the metal–vacuum interface has been central to the discussions.

The effective potential felt by an electron in the surface region is mediated by the electrons self-energy $\Sigma(r, r', E)$, which represents a non-Hermitean, non-local, energy-dependent operator [1]. The self-energy $\Sigma$ is usually defined within the Green function formalism of elementary excitations in interacting many-particles systems in such a way, that it takes into account all the dynamical exchange and correlation effects beyond the Hartree approximation [2]. For electron states exactly at the Fermi level $E_F$, it can be shown in the framework of density functional theory (DFT), that the total effect of $\Sigma(r, r', E_F)$ can be incorporated exactly by means of an effective local static potential $V_{XC}(r)$ [3]. Within the usual local density approximation (LDA) for $V_{XC}(r)$ DFT allows for an $ab\text{-}initio$ calculation of the total effective potential, which near the metal-vacuum interface is then termed the surface barrier potential $V_B(r)$ [4].
For occupied and unoccupied electronic surface states at metals with energies near $E_F$ the DFT surface barrier $V_B$ in principle gives an excellent description. Unfortunately, however, the LDA in DFT results in an incorrect asymptotic behaviour of $V_B(r)$ in the vacuum region. For large distances $|z|$ from the metal surface $V_B(r)$ in LDA decays exponentially, instead of behaving proportional to $|z|^{-1}$, which in turn is required by simple electrostatic arguments. This shortcoming of the usual LDA–DFT barrier potential has led some authors to work in practical calculations with parametrized models for the surface barrier.

In this contribution we study occupied and unoccupied surface states at the three low-index surfaces of Cu. We will use a parametrized surface barrier and calculate both the energetics and corresponding IPE spectra for surface states on the basis of the dynamical one-step model of photoemission [5–7].

The aim of this paper is to extract as much information as possible about the barrier potential of Cu by comparing our calculated results with the wealth of experimental information on Cu surface states available in the literature.

2. One-step model: surface contribution

The general theory for the surface contribution in the one-step model has already been described in a very compact form elsewhere [8]. In the following we present the full details of its derivation. For a clean and unreconstructed surface the effective static barrier potential takes the form [9],

$$V_B(r) = \sum_g V_{Bg}(z)e^{ig \cdot r_B}. \quad (1)$$

Here $g$ denotes a two-dimensional reciprocal lattice vector and $r_B$ is parallel to the surface. Self-consistent electronic structure calculations for solid metal films in the framework of DFT [4] have demonstrated that $V_B(r)$ has a distinctly three-dimensional character. The periodic variation of $V_B$ in the lateral directions is commonly referred to as corrugation. At the present level of accuracy in VLEED and IPE corrugation effects seem, however, to be of relative insignificance [10,11]. Thus all terms with $g \neq 0$ in (1) are usually disregarded and $V_B$ is approximated in one-dimensional form $V_B(z)$.

In the framework of the one-step model of angular resolved ultraviolet photoemission (ARUPS) and inverse photoemission [5–7] the electron (photon) current is described by the following expression:

$$I(k_{\|}, \epsilon_f) = -(1/\pi)\text{Im}(k_{\|}, \epsilon_f | G^+_2 \Delta G^+_1 \Delta^1 G^-_2 | \epsilon_f, k_{\|}). \quad (2)$$

The propagators for the final- and for the hole-state are denoted by $G^\pm_2$ and $G^+_1$, respectively, and calculated from standard layer Korringa–Kohn–Rostoker (KKR) multiple scattering techniques for the semi-infinite crystal [5,7,12]. The operator $\Delta$ mediates the coupling to the electromagnetic field. In atomic units ($e = \hbar = m = 1, c = 137.036$) it follows:

$$\Delta = (1/2c)A_0 \cdot p. \quad (3)$$

$A_0$ denotes the spatially constant amplitude of the electromagnetic vector potential and $p$ the momentum operator. In the case of photoemission $\epsilon_f$ is the single-particle
energy of the outgoing electron and $k_{||}$ denotes its wavevector component parallel to the surface.

In general we have for the surface contribution of the current the formula

$$I_{\text{surf}}(k_{||}, \epsilon_f) = -\frac{1}{\pi} \text{Im} \int \langle k_{||}, \epsilon_f | G_2^+ | r \rangle \Delta(r | G_1^+ \Delta^+ G_2^- | \epsilon_f, k_{||}) \, dr$$

(4)

derived from equation (2).

In the region between the surface barrier and the first layer of the bulk crystal the wavefields for the initial and final states can be written in plane-wave representations, since it is assumed, that the potential is constant between the non-overlapping muffin-tin-spheres and the surface barrier potential $V_B(z)$. The plane wave representation gives for the initial state

$$\langle r | G_1^+ \Delta^+ G_2^- | \epsilon_f, k_{||} \rangle = \sum_g \left( [a_{1_g}^+ + r_{1_g} d_{1_g}^-] e^{ik_{||}z(r-c_i)} + d_{1_g}^- e^{ik_{||}z(r-c_i)} \right)$$

(5)

and for the final state

$$\langle k_{||}, \epsilon_f | G_2^+ | r \rangle = \sum_g \left( u_{1_g}^+ e^{ik_{||}z(r-c_i)} + u_{1_g}^- e^{ik_{||}z(r-c_i)} \right).$$

(6)

With the coefficient $a_{1_g}^+$, which is emitted by the barrier, we take into account the reflection of the initial state wavefield by the surface potential. $r_{1_g}$ denotes the barrier-reflection coefficient for the hole-state.

According to the $z$-dependence of the barrier potential we have to calculate the initial and final state wavefield numerically in the surface region. It follows for the initial state

$$\langle r | G_1^+ \Delta^+ G_2^- | \epsilon_f, k_{||} \rangle = \sum_g \phi_{1_g}(z) e^{ik_{||}z(r-c_i)}$$

(7)

with

$$\phi_{1_g}(c_{1_z}) = a_{1_g}^+ + r_{1_g} d_{1_g}^- + d_{1_g}^-$$

(8)

and again for the final state

$$\langle k_{||}, \epsilon_f | G_2^+ | r \rangle = \sum_g \psi_{2_g}(z) e^{ik_{||}z(r-c_i)}$$

(9)

with

$$\psi_{2_g}(c_{1_z}) = u_{1_g}^+ + u_{1_g}^-.$$  

(10)

Here $\phi_{1_g}$ and $\psi_{2_g}$ denote the regular solutions of the Schrödinger equation for $V_B(z)$ in the range $-\infty < z < c_{1_z}$. The value $c_{1_z}$ defines the point, where the surface potential goes smoothly into the inner potential of the bulk crystal.

Inserting (7) and (9) into equation (4) and rewriting the surface contribution for the current, we arrive at the following expression:

$$I_{\text{surf}}(k_{||}, \epsilon_f) = -\frac{1}{\pi \omega e} \text{Im} \left( e^{i k_{||} \cdot c_{||}} \sum_g \int_{-\infty}^{c_{1_z}} dz \psi_{2_g}(z) \frac{dV_B}{dz} \phi_{1_g}(z) e^{i k_{||}z} \right)$$

(11)
where $A_z$ is the $z$-component of the amplitude $A_0$ and $q$ is the wavevector of the photon field.

The problem that remains, is the calculation of the coefficient $a_{1g}^+$ which belongs to the initial state wavefield emitted by the surface barrier. The initial state matrix element $\langle \mathbf{r} | G_1^+ \Delta^\dagger G_2^- | \epsilon_f, k_{||} \rangle$ can be manipulated to a form more appropriate to a direct calculation:

$$
\langle \mathbf{r} | G_1^+ \Delta^\dagger G_2^- | \epsilon_f, k_{||} \rangle = \int \langle \mathbf{r} | G_1^{+(0)} + G_1^{+(0)} r_1 G_1^{+(0)} | \mathbf{r}' \rangle \Delta^\dagger \langle \mathbf{r}' | G_2^- | \epsilon_f, k_{||} \rangle \, d\mathbf{r}'
$$

(12)

where $G_1^{+(0)}$ is the free electron Green function for the initial state. After integrating over $d\mathbf{r}'$ in equation (12), we can describe the matrix element by a plane wave expansion, which is valid in the region of our interest, namely between the surface barrier and the first bulk layer:

$$
\langle \mathbf{r} | G_1^+ \Delta^\dagger G_2^- | \epsilon_f, k_{||} \rangle = \sum_g a_{1g}^+ e^{ik_{||}(\mathbf{r}-\mathbf{c}_1)}
$$

(13)

with

$$
a_{1g}^+ = - \frac{iA_z e^{-i\omega \mathbf{c}_1}}{2\omega c k_{1g}^+} (1 + r_{1g}) \int_{-\infty}^{c_1z} dz e^{-i\mathbf{q}_z \cdot \mathbf{k}_{1g}^+} \left( \phi_1^-(z) \frac{dV_B}{dz} \psi_{2g}(z) \right).
$$

(14)

For a step barrier $V_B(z) = V_0 \Theta(z - c_{12})$, where $\Theta$ is the unit step function, we obtain Pendry's result [5]. $V_0$ denotes the constant inner potential of the bulk crystal.

In calculating the matrix element for the surface contribution by itself we follow Pendry's original ansatz. The main effect from a $z$-dependent surface barrier results in a strong variation of the barrier reflection coefficient $r_{1g}$. For that reason we use for the evaluation of this coefficient a potential model for $V_B(z)$, which has been introduced first by Rundgren and Malmström [13] in LEED calculations.

3. Results for Cu surfaces and discussion

The spectra of electronic surface states on Cu surfaces have been calculated with the theoretical model of section 2. For the bulk muffin-tin potential of Cu the potential due to Chodorow [14,15] was used. Damping processes within the one-step model are described by adding a constant imaginary part $V_{0i}$ to the inner potential $V_0$. For the high-lying electron states we took $V_{0i2} = -1$ eV, which is in accordance with LEED experience, for the low-lying states near $E_F$ $V_{0i1}$ was chosen as a small quantity $V_{0i1} = -0.02$ eV.

3.1. Cu(100)

In figure 1 we present the projected bulk bandstructure for Cu(100) together with all calculated and experimentally observed IPE data. The shape of the surface barrier [13]
giving rise to the surface states $S$ in figure 1 will be discussed below in a systematic comparison of all three low-index surfaces of Cu.

In addition to our former work on surface states at Cu(100) [8,16], which concentrated on the $\Gamma XULK$ azimuth, here we give also the results for $\Gamma XWK$. Along $\Gamma XULK$ so far four empty surface states $S_{R}, S_{1}, S_{2}, S_{3}$ and two unoccupied bulk states $B_{1}, B_{2}$ have been detected in IPE experiments. SR denotes a crystal-induced surface resonance, $S_{1}$ the first image-potential state, both being associated with the $X_{2p}-X_{1}$ gap. $S_{2}$ and $S_{3}$ represent crystal-induced surface states derived from the $L_{2p}(\Sigma_{1})-L_{4}$ gap. $S_{2}$ becomes an occupied surface state near $X$ and has been detected there in high-resolution photoemission spectroscopy [17].

When compared to our former work [8,16], an interesting new feature in figure 1 is the existence of an additional bulk state $B_{3}$ at $-0.35$ eV ($X$) in the occupied regime near $X$. This state lies at $X 0.28$ eV below $S_{2}$ and just at the $\Sigma_{1}$ bulk edge. In our former work [8,16] $B_{3}$ did not show up for two reasons. Those calculations had been restricted to the energy range above $-0.1$ eV, since no additional state had been expected. Moreover, those calculations concentrated on the $z$-component $A_{z}$ of the photon field $A_{0}$. For $B_{3}$ it turns out, however, that the calculated orientation of the electric dipole axis in the $\Gamma XULK$ azimuth is rotated $\sim 45^\circ$ away from the surface normal. In a pure $z$-polarized spectrum $B_{3}$ therefore becomes suppressed.

The question, whether $B_{3}$ has been observed in corresponding high resolution photoemission experiments [17] in addition to $S_{2}$, is not clear. In these experiments a doublet of surface states $S', S$ is seen both for excitation energy $h\omega = 16.85$ eV (NeI) and $h\omega = 11.85$ eV (ArI), but the presence of the second component $S'$ was attributed to the NeI ($\Delta = 0.177$ eV) and ArI ($\Delta = 0.210$ eV) satellite line in the exciting photon field. This satellite splitting, however, is comparable to the calculated $B_{3}-S_{2}$ splitting in the occupied regime which is of the order of 0.15–0.28 eV. Moreover, the fact that both energetic separation and relative intensity in the $S', S$ doublet vary slightly in the experiment as a function of $\Theta$ (cf figure 2 in [17]) suggests that the existence of an additional state near $X$ might be a real effect.

Typical calculated IPE-spectra and corresponding experimental data ($h\omega = 9.7$ eV) for different angles $\Theta$ of electron incidence and photons emitted within the azimuth
in different directions $\alpha$ with respect to the surface normal $z$ are shown in figure 2 for $\Gamma XUL$ and in figure 3 for $\Gamma XWK$, respectively. The spectra are raw spectra, convoluted with a Gaussian of 0.275 eV full width at half-maximum, to take the experimental resolution into account. Apart from the fact that the experimental spectra show a large fraction of secondary emitted photons, which are not taken into account in the calculations, the agreement between theory and experiment is generally very good. In particular the polarization dependence of the intensity of the various peaks is well reproduced in the theory.

Figure 2. Experimental (left) and theoretical (right) inverse photoemission spectra ($h\omega = 9.7$ eV) for Cu(100) along the $\Gamma XUL$ bulk mirror plane. $\Theta$ denotes the angle of electron incidence and $\alpha$ the photon detection angle.

Figure 3. Experimental (left) and theoretical (right) inverse photoemission spectra ($h\omega = 9.7$ eV) for Cu(100) along the $\Gamma XWK$ bulk mirror plane. $\Theta$ denotes the angle of electron incidence and $\alpha$ the photon detection angle.

A systematic comparison of all calculated surface states at the zone centre $\Gamma$ and boundary $\bar{X}$ with experimental data for Cu(100) is included in table 1. The agreement between theory and experiment for the energetic positions and effective masses is within the error bars of the experiment. A recent inverse photoemission study of Cu(100) at variable photon energy reported a surface state at the zone boundary $\bar{X}$ with energy $\simeq 0.5$ eV [18] (not included in table 1). We have calculated the corresponding 1PE spectrum ($h\omega = 22.7$ eV), but have been unable to find a
surface state at $\bar{X}$ in this energy range. At present the origin of this discrepancy is not clear.

Table 1. Comparison of experimental and calculated binding energies and effective masses of surface states on Cu(100), Cu(110) and Cu(111).

<table>
<thead>
<tr>
<th>Surface normal</th>
<th>Symmetry point</th>
<th>Type</th>
<th>$E - E_F$ (eV) (theory)</th>
<th>$m^*/m_e$ (theory)</th>
<th>$E - E_F$ (eV) (experiment)</th>
<th>$m^*/m_e$ (experiment)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) $\bar{\Gamma}$</td>
<td>S$_1$</td>
<td>4.10</td>
<td>0.990</td>
<td>4.13 ± 0.20</td>
<td>4.00 ± 0.20</td>
<td>1.2 ± 0.20</td>
<td>40</td>
</tr>
<tr>
<td>(100) $\bar{\Gamma}$</td>
<td>S$_1'$</td>
<td>4.48</td>
<td>1.010</td>
<td>4.45 ± 0.02</td>
<td>1.15</td>
<td>1.20 ± 0.30</td>
<td>41</td>
</tr>
<tr>
<td>(100) $\bar{\Gamma}$</td>
<td>S$_R$</td>
<td>1.50</td>
<td>0.427</td>
<td>1.48 ± 0.06</td>
<td>0.086 ± 0.025</td>
<td>0.067 ± 0.01</td>
<td>42</td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_2$</td>
<td>3.52</td>
<td>0.630</td>
<td>3.60 ± 0.20</td>
<td>3.45 ± 0.20</td>
<td>0.70 ± 0.20</td>
<td>43</td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_3$</td>
<td>4.54</td>
<td>0.98</td>
<td>4.28 ± 0.35</td>
<td>4.39 ± 0.15</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_2'$</td>
<td>4.74</td>
<td>0.99</td>
<td>-0.393 ± 0.025</td>
<td>2.50 ± 0.20</td>
<td>1.91 ± 0.25</td>
<td>45</td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_3$</td>
<td>2.38</td>
<td>0.94</td>
<td>1.80 ± 0.20</td>
<td>1.80 ± 0.20</td>
<td>0.80 ± 0.20</td>
<td>46</td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_4$</td>
<td>1.96</td>
<td>0.248</td>
<td>2.09 ± 0.20</td>
<td>2.00 ± 0.40</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>(110) $\bar{\Gamma}$</td>
<td>S$_5$</td>
<td>5.30</td>
<td>1.49</td>
<td>5.63 ± 0.20</td>
<td>5.40 ± 0.40</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

By definition a surface state must contribute to the surface current $I_{surf}$ in equation (11), i.e. its intensity for $z$-polarized light should be non-zero. Mirror symmetry of the three low-index surfaces in FCC crystals then induces that for a surface state at $\bar{\Gamma}$ the intensity for $x$- or $y$-polarized light must vanish as long as spin–orbit interaction is disregarded. In such a case the dipole orientation $\Theta_z$ of the surface state thus will be exactly parallel to $z$, i.e. $\Theta_z = 0^\circ$. Here $\Theta_z$ denotes the angle between the vector formed from $I(A_x)$, $I(A_y)$, $I(A_z)$ and the surface normal. Similarly for a surface state in an azimuth, which represents a mirror plane of the crystal, the intensity for $y$-polarized light perpendicular to the azimuth must vanish. The vector formed from $I(A_x)$, $I(A_y)$, $I(A_z)$ thus will lie within the mirror plane, but its orientation $\Theta_z$ for a surface state away from $\bar{\Gamma}$ can in principle now span the range $0^\circ \leq \Theta_z < 90^\circ$. Increasing values of $\Theta_z$ then indicate an increasing bulk
contribution to the surface state. In our calculation for Cu(100) we found significant non-zero values of $\Theta_z$ only for the surface state $S_2$ at $\bar{X}$. This result shows that this state could be sensitive to corrugation in the effective barrier potential $V_B(r)$ of equation (1), an effect which is not taken into account here.

In addition to the transitions discussed so far, the experimental IPE-spectra contain dispersionless features in the range 0–1.5 eV above the Fermi level. These features, which show up at all three low-index surfaces of Cu, must be attributed to transitions into weak maxima of the three-dimensional density-of-states (DOS) in this energy range.

3.2. Cu(110)

The projected bulk bandstructure for Cu(110) together with all calculated and experimentally observed IPE data is shown in figure 4. In addition to the first and second image-potential states $S_1$ and $S_1'$ near $\Gamma$, two crystal-induced surface states $S_2$, $S_3$ ($\Gamma$KLU) and $S_4$, $S_5$ ($\Gamma$KWX) are clearly identified in the $L_2$–$L_1$ and $X_4$–$X_1$ derived band gaps. Furthermore three unoccupied bulk states $B_1$, $B_2$, $B_3$ have been detected in IPE experiments. In analogy to the (100) surface, $S_2$ becomes an occupied surface state near $\bar{Y}$ and has been detected there in high-resolution photoemission spectroscopy [19].

![Complex diagram illustrating the bulk bandstructure and projected bands for Cu(110)]

Figure 4. Bulk bandstructure of Cu, projected onto the $\Gamma$–$\bar{X}$ and $\Gamma$–$\bar{Y}$ directions of the surface Brillouin zone. Solid circles (open squares with error bars) denote calculated (measured) band dispersions. The size of the symbol indicates the intensity of the transition. The band gaps of the projected bulk band structure are bounded by solid lines.

Calculated IPE-spectra and measured data ($\hbar\omega = 9.7$ eV) are shown in figure 5 for the $\Gamma$KLU azimuth and in figure 6 for $\Gamma$KWX. Theory and experiment agree very well. As in the case of Cu(100) the peaks in the experimental spectra are often obscured by a large fraction of secondary emitted photons. Energy and effective mass of all surface states at Cu(110) are included in table 1. With the exception of the second image-potential state $S_1'$ at $\bar{\Gamma}$, which so far has not been observed experimentally, we find essentially agreement between theory and experiment within the experimental error bars. Significant non-zero values for the electric dipole orientation $\Theta_z$ of surface states at Cu(110) were found for $S_2(\bar{Y})$ and $S_4(\bar{X})$, i.e. these states could also be sensitive to corrugation effects in the effective barrier potential.
3.3. Cu(111)

Figure 7 shows the projected bulk bandstructure for Cu(111) together with all calculated and experimentally observed IPE data. Three bulk states B₁, B₂, B₃, two image-potential surface states S₁, S₁' above the L₂'–L₁ derived gap and two crystal-induced surface states S₂, S₃ in the L₂'–L₁ and X₄'–L₁ derived gap are identified. Again S₂ becomes an occupied surface state near \( \bar{\Gamma} \) and is observable in high-resolution photoemission spectroscopy [20,21].

The ΓXUL and ΓLKL azimuths shown in figure 7 are equivalent, if only the surface layer is taken into account, but become non-equivalent for the bulk crystal. Pure surface states thus should behave symmetrically in both azimuths, whereas bulk states can exhibit an asymmetry. This is indeed the case in figure 7. For the surface states this means that the dipole orientation \( \Theta₂ \) is nearly zero up to the zone boundary. For the Cu(111) surface there is thus no indication for corrugation effects in the effective barrier potential, a result which is compatible with the densely packed structure of this surface.
Calculated IPE-spectra and measured data ($h\omega = 9.7$ eV) for Cu(111) are shown in figures 8 and 9 for the azimuths ΓXUL and ΓKL, respectively. Again theory and experiment agree very well. The non-equivalence of both azimuths for bulk states is clearly seen. In addition this non-equivalence also exists for larger values of $\Theta$, i.e. near the zone boundary, in the intensity of the surface state $S_3$. In fact $S_3(\vec{M},\vec{M}')$ exhibits the largest non-zero value for the dipole orientation ($\Theta = 3.9^\circ$) among the surface states at Cu(111). Energy and effective mass of surface states at Cu(111) are included in table 1 and again show an agreement with the experiment essentially within experimental error bars. Note that the energetic position of $S_3$ at the zone boundary is not known exactly. Like in the case of Cu(100) and Cu(110) the experimental IPE data show weak dispersionless features in the energy range 0.5–1.5 eV above the Fermi level which correspond to DOS transitions.

3.4. Corrugation effects

In the present paper corrugation is defined as the lateral variation of the barrier potential $V_B(r)$ in equation (1) with $r$. This effect is neglected in our calculations. Note, however, that the total bulk crystal potential will exhibit a trivial lateral variation and that this effect is of course taken into account by our formalism.

The relative importance of corrugation in the barrier potential can be judged by inspection of the angles $\Theta_z$ of the dipole orientation of the various surface states. The maximum $\Theta_z$ values at the various surfaces are: $\Theta_z = 10.3^\circ$ for $S_4(\vec{X})$ at Cu(110), $\Theta_z = 9.5^\circ$ for $S_2(\vec{X})$ at Cu(100) and $\Theta_z = 3.9^\circ$ for $S_3(\vec{M},\vec{M}')$ at Cu(111). The relative importance of corrugation thus decreases with increasing density of atoms in the surface unit cell. This was to be expected.

To judge the absolute importance of corrugation effects in the barrier, it is necessary to resort to the occupied surface state $S_2$ at the various surfaces, since this state has been measured with the highest resolution. A comparison of theory and experiment for $S_2$ is shown in figure 10. The calculated energetic position of $S_2$ at the various symmetry points is always within the error bars of the experiment. Only the calculated effective mass of $S_2$ at Cu(110) and Cu(111) lies slightly outside the
error bars, but we hesitate to interpret this as a clear-cut indication for the importance of surface corrugation.

Another group of surface states, which is known with high precision, are certain image-potential states, which are accessible to two-photon photoemission. In the case of Cu this is the case for $S_i$ and $S_i'$ at the (100) and the (111) surface [21, 22, 42]. From the agreement between theory and experiment in table 1 for these states we conclude, that an influence of surface corrugations is not detectable in these cases. This conjecture is in agreement with a recent theoretical study of this problem [11].

3.5 Effective surface barrier

The effective $z$-dependent surface barriers $V_B(z)$ for the various Cu surfaces are shown in figure 11. They are plotted with respect to the vacuum level $E_{vac}$ utilizing the values of the work function $\Phi$ as given in table 2. The zero of the $z$ scale lies in the uppermost layer of atoms. As mentioned above, $V_B(z)$ is of the Rundgren-Malmström (RM) type [13]. For its real part we have:
\[ V_B(z) = \begin{cases} \frac{1}{4}(z - z_{im})^{-1} & z < z_A < z_{im} \\ s_0 + s_1(z - z_A) + s_2(z - z_A)^2 + s_3(z - z_A)^3 & z_A < z < z_E \\ \text{or} & z > z_E \end{cases} \]

Here \( z_{im} \) denotes the position of the classical image plane. The asymptotic regime \( z < z_A \) is connected to the bulk muffin-tin zero \( V_0 \) by a third-order polynomial in \( z \), spanning the range \( z_A < z < z_E \). The polynomial coefficients \( s_0, s_1, s_2, s_3 \) are fixed through the requirement of continuity of \( V_B(z) \) and its derivative. The parameters \( z_{im}, z_A, z_E \), the polynomial range \( \Delta z = |z_A - z_E| \), the size \( A_E \) of the surface unit cell and one-half of the interlayer distance \( d_{1/2} \) are listed in Table 2 for the various surfaces.

<table>
<thead>
<tr>
<th>Table 2. Potential parameters for the barrier potentials of Cu(111), Cu(100) and Cu(110).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Workfunction: ( \Phi ) (eV)</td>
</tr>
<tr>
<td>Reference</td>
</tr>
<tr>
<td>Surface barrier potential: ( V_0 ) eV</td>
</tr>
<tr>
<td>Beginning of the polynomial region: ( z_A ) a.u.</td>
</tr>
<tr>
<td>End of the polynomial region: ( z_E ) a.u.</td>
</tr>
<tr>
<td>Length of the polynomial region: ( \Delta z =</td>
</tr>
<tr>
<td>Size of the surface unit cell: ( A_E ) 10^{-2} a.u.</td>
</tr>
<tr>
<td>One-half of interlayer distance: ( d_{1/2} ) a.u.</td>
</tr>
<tr>
<td>Position of the image plane: ( z_{im} ) a.u.</td>
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</tbody>
</table>

The shape of the surface barrier depends on the parameters \( z_{im}, z_A, z_E \) that were determined in the following manner. To receive an approximate value for the
position of the image plane $z_{im}$, we started the variational procedure with one-half of the interlayer distance $d_{1/2}$ and fixed the value for $z_{im}$ roughly by comparison of the experimental and theoretical peak positions for normal emission ($k_{||} = 0$). In determining the beginning $z_A$ and the end of the polynomial region $z_E$, these parameters were varied from $+1.0$ to $-5.0$ a.u. In this way, as well as for the exact fixing of $z_{im}$, the peak positions and effective masses of all surface states in the whole projected bulk bandstructure were taken into account, to receive the best fit for the surface potential. The quality of the surface potential depends on the accuracy of the experimental measurements. To reproduce the measured data within the experimental resolution, especially the results from the high resolution photoemission experiments [17,19,20] and two-photon photoemission experiments [21,22,42,44], it was necessary to vary the most sensitive parameter $z_{im}$ up to the third digit.

It should be noted that no relaxation of the outermost atomic surface layer has been taken into account in the present calculation. This neglect of relaxation effects seems to be justified on the basis of various thin film calculations for Cu surfaces and LEED fine structure analysis cited below.

From the data in table 2 it is seen, that $z_{im}$ moves toward the first layer of atoms and the polynomial range $\Delta z$ becomes larger, if $A_E$ increases. This means, that the most open surface, Cu(110), exhibits the strongest saturation of the image potential with an image plane lying nearest to the topmost layer. As a further consequence the image force for a given value of $z$ outside the crystal is strongest for Cu(111) and weakest for Cu(110).

This behaviour is in agreement with calculated surface barrier parameters for the semi-infinite jellium model for varying density of the conduction electrons [23–25]. Moreover it agrees with the results of density functional calculations for thin films of Cu(100) and Cu(110) [26,27]. However, the absolute value of $z_{im}$ for Cu surfaces in these calculations was significantly larger than in the present study. For Cu(100) the results are $z_{im} = -2.40$ a.u. [26], $-2.33$ a.u. [27] compared to $-1.93$ a.u. in table 2, for Cu(110) $z_{im} = -2.17$ a.u. [26], $-2.28$ a.u. [27] compared to our result $-1.76$ a.u.

It has been argued [26] that this systematic deviation is due to different choices of the barrier model. In fact in the calculations of [26,27] the self-consistent static effective potential of LDA–DFT in the surface region was planar-averaged and then fitted to an expression (III) [28]

$$V_B(z) = \begin{cases} \frac{1}{4(z - z_{im})} \{1 - \exp[\lambda(z - z_{im})]\} & z < z_{im} \\ -V_{or}/\{A \exp[-B(z - z_{im})] + 1\} & z > z_{o}. \end{cases} \tag{16}$$

Here $A$ and $B$ are constants determined by matching $V_B(z)$ and its derivative at the image plane $z = z_{im}$.

We have also used the III barrier in our calculations for Cu(100). With parameters $V_{or} = -0.896$ Ry, $z_{im} = -1.93$ a.u., $\lambda = 1.34$ one obtains a description of all surface states at Cu(100), which is of similar accuracy as that discussed in subsection 3.3 on the basis of the RM barrier. The conjecture, that the III and RM barriers result in similar values for $z_{im}$, when fitted to the same data base, is furthermore corroborated by recent work of Smith et al [27]. These authors fitted the III barrier for the various Cu surfaces to corresponding surface state energies, making use of a simple phase-accumulation model. The simplicity of this model does not allow for the derivation of a definite set of barrier parameters, which works for all observed surface states.
at a given surface. What can be obtained, however, are parameters averaged over the surface states included in the fitting procedure. In this way the authors derived \( \langle z_{im} \rangle = -2.27 \) a.u. for Cu(111), \( \langle z_{im} \rangle = -2.18 \) a.u. for Cu(100) and \( \langle z_{im} \rangle = -1.70 \) a.u. for Cu(110). One notices that these JJJ fits to the experiment still yield values for \( z_{im} \) smaller than the corresponding JJJ fits to the theoretical potentials in [26,27]. Moreover, these averaged parameters are in very nice agreement with our RM fits to a data base of similar quality. The fact, that the face dependence in these \( \langle z_{im} \rangle \) values is more pronounced than in our \( z_{im} \) parameters, is understandable, since the two procedures work at quite different levels of theoretical refinement.

The differences in \( z_{im} \) between fits to calculated first-principles LDA–DFT potentials and fits to experimental surface state data are therefore likely to have a different origin. In the introduction we have already mentioned that the effective potential felt by an electron in the surface region is in principle energy-dependent. The height \( |V_{or}| \) of the surface barrier decreases with increasing electron energy. The effective potential thus become less attractive and the effective image plane position \( z_{im} \) shifts toward the crystal, if the electron moves [29].

Such dynamical effects could in principle explain the above mentioned differences in \( z_{im} \). There is, however, a caveat: a recent very careful analysis of LEED fine structure data of Cu(001), using the JJJ barrier with \( V_{or} \) as a parameter, resulted in \( z_{im} = -2.5 \pm 0.1 \) a.u. [30]. An earlier LEED fit to the JJJ barrier of Cu(001) had given \( -2.35 \) a.u. [31]. From a comparison of these experimental fits with the fits to the theoretical potentials in [26,27] an inward shift of \( z_{im} \) as a consequence of dynamical effects cannot be deduced. Since the electron energies in such LEED fine structure experiments are usually larger than those of electrons occupying bound surface states above the Fermi level, the same would then be true for the interpretation of the corresponding IPE data. The conjecture, that dynamical effects in the effective potential should become non-negligible only for energies significantly above the vacuum level, is supported by our analysis of high lying unoccupied bulk states \( (E - E_F \approx 10-15 \) eV) in the following paragraph.

We believe that the above mentioned discrepancies in \( z_{im} \) between theory and experiment have their origin mainly in the way in which the presence of an image tail is enforced in the theoretical analysis. Fitting an ab-initio LDA–DFT barrier with incorrect asymptotic behaviour to a model barrier with correct behaviour [26,27] is a problematic task. A strategy to determine \( z_{im} \) from an ab-initio DFT barrier with correct asymptotics is clearly preferable, but so far such calculations seem to exist only for the semi-infinite jellium model [32,33] and not for real metal surfaces.

3.6. High-lying unoccupied bulk states

In figure 12 we show calculated IPE spectra and corresponding experimental data \( (\hbar \omega = 9.7 \) eV) for unoccupied bulk states of various Cu surfaces in the energy range 10–15 eV above the Fermi level. In these calculations we used \( V_{011} = -0.1 \) eV, \( V_{012} = -2.0 \) eV to account for the higher energy range. A comparison between theory and experiment shows good agreement with respect to the shape of the various spectra. The energetic positions are, however, systematically shifted by 0.5–2.5 eV in the sense, that the experimental peaks lie at higher energies above the Fermi level. We interpret this systematic effect as a consequence of dynamical effects in the effective one-electron potential felt by an electron in such an unoccupied bulk orbital. This explanation is supported by similar work of Speier et al [34]. These authors compared measured IPE peaks in an energy range 5–50 eV above the Fermi level
with calculated peaks in the density of states for various transition and noble metals, including Cu. Their conclusion was, that for Cu dynamical effects in the effective potential are negligible up to 6 eV above the Fermi level, but become of the order of 1 eV for states in the range 10–20 eV. Our result is in good agreement with their finding, though in our case the systematic shift is more pronounced. This may also be due to the different calculated muffin-tin potential entering the analysis.

4. Conclusions

The surface potential barrier shape of the low-index faces of copper can be determined by an analysis of inverse photoemission and two-photon photoemission measurements making use of the one-step model of photoemission. The barrier potentials derived here allow for a consistent description of the energetic positions and effective masses of all known surface states for the various faces. In agreement with previous theoretical predictions the most open surface, Cu(110), exhibits the strongest saturation of the image potential with an image plane lying nearest to the topmost layer. Theoretical ab-initio type slab calculations show the same trend, but in these calculations the position of the image plane is found significantly further outside the crystal. Corrugation and dynamical effects in the effective potential seem to be negligible for electronic states up to 6 eV above $E_F$. 
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References