Self-energy Effects and the Unbound Electronic Structure of the Cu(111) Surface

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There are very few calculations of unbound surface electron energy bands above the vacuum level for any system where self-energy effects are significant. We calculate the surface and bulk bands for Cu(111) at $\bar{\Gamma}$ for the above energy range using a scattering method. A number of surface resonance states are predicted. Experimental confirmation could lead to new techniques in photoemission spectroscopies.

1.   Introduction

The identification of surface states arising from the surface barrier continues to be important for explaining phenomena and possible technological application [1]. We use the semi-empirical scattering method for a semi-infinite crystal to calculate the unbound excited surface electronic band structure for Cu(111) to energies 140 eV above the vacuum level for $k_{\parallel} = 0$ ($\bar{\Gamma}$). These surface state resonances have not been calculated previously and may take part in many surface electron spectroscopies. The energy and momentum variations of the quasi-particle electron self-energy due to many-body effects in this energy range are significant and are included here. *Ab initio* calculations of these variations do not exist or have not been tested experimentally. It is necessary to first demonstrate that the present method is capable of reproducing the experimentally determined surface band structure for the ground state below the vacuum level.

2.   Scattering method

Full details of the scattering method are given elsewhere [2]. Surface states/resonances are identified from the condition for sustained multiple scattering between the bulk crystal plus surface atomic layers and the surface barrier. This corresponds to the electron being trapped in this surface region. The condition involves the matrices S^{II} and M that contain reflection coefficients of barrier and crystal respectively. When one or other of the eigenvalues of the matrix $S^{\mathrm{II}}M$ approach unity we have the condition for the above sustained multiple scattering. This can be expressed as

$$| 1 - \lambda_v | \; \rightarrow \; \text{minimum} \tag{1}$$

where λ_v is the vth eigenvalue of the matrix $S^{\mathrm{II}}M$. For computational purposes it is convenient to re-express this condition in the form

$$| \det [\, I - S^{\mathrm{II}}M \,] | \; \rightarrow \; \text{minimum} \tag{2}$$

where I is the identity matrix.

3.   Calculations for the ground state below vacuum level E_{v}

3.1   Method

We use the bulk muffin-tin potential of Chodorow since it has been found to reliably account for the measured bulk band structure [3]. The potential of the top atomic layer at the surface is less attractive than bulk layers because of the reduced atomic coordination. This is

expected to slightly narrow the width of the $3d$ bands and the $4sp$ band and to reduce the binding energy of the centroid of these band widths and also reduce the binding energy of the ion-core states [4]. Additionally there is the outflow of the valence electrons from the top atomic layer into the vacuum producing the surface barrier. There are no modern measurements of d-band or sp-band narrowing or any measurements of surface-core-level-shifts for Cu(111). The present method allows for the inclusion of surface atomic potentials obtained from *ab initio* self-consistent theoretical calculations although the significant uncertainty in the approximations used in these calculations for the exchange-correlation potential U_{xc} in this surface region does not ensure they are realistic. Here the top atomic-layer potential for Cu(111) is determined empirically by applying a Madelung-type shift [4] to reduce the magnitude of the bulk atomic potential. This shifts the potentials of valence and ion-core electrons to higher energies by the same amount.

The surface barrier potential $U_b(z)$ is not accurately determined in *ab initio* self-consistent calculations using local approximations for U_{xc} and is determined here from an empirical image potential with cubic-type saturation joined smoothly to the zero of potential at the centre of the top atomic layer at $z = 0$ where z is normal to the surface. This join point agrees with expectations of the start of significant charge outflow to form the surface potential. The image position z_o and saturation point z_1 from $z = 0$ are determined from the experimental energy position of barrier-sensitive Shockley-type and Rydberg surface states/resonances at $\bar{\Gamma}$ below E_v [3,5]. The ground state work function is found from experiment [6]. The geometric structure of the surface is found from low-energy electron diffraction (LEED) analysis that finds an approximately 0% dilation of the (1x1) top atomic layer [7]. Self-energy effects beyond the one-electron approximation are negligible in this energy range.

3.2   Results

Experimentally a Tamm-like surface state is found at 0.08 eV above the top of the d-bands at $\bar{M}$ [3]. We did not produce a surface state in this position when all atomic-layer potentials were the same as the bulk. Calculations were performed using trial top atomic-layer potentials that were formed by applying a Madelung-type shift of the bulk potential to higher energies. A shift of 0.1 eV produced the above Tamm state at the experimental position with negligible change to the calculated position of all the other experimentally determined surface states. This top atomic-layer potential was used in all final calculations. These potentials produce a surface band structure that agrees with the experimental results available for all the symmetry directions of the surface Brillouin zone. We show elsewhere these calculations of the near-surface complex band structure $E(\mathbf{k}) = E(\mathbf{k}_{\parallel}, k_{\perp})$ for $\mathbf{k}_{\parallel} \equiv \bar{\Gamma}$, $\bar{M}$, $\bar{K}$ [8].

4.   Calculations for energies above vacuum level E_v

4.1   LEED calculations

The energy variation of the quasi-electron self-energy for $\mathbf{k}_{\parallel} = 0$ can be found from an analysis of the experimental normal-incidence LEED reflectivity profiles that are shown in [7]. We calculated these LEED profiles using the method of McRae [9] for energies to, 140 eV above E_v that we show elsewhere [8]. The same atomic bulk and surface potentials were used as for the ground state calculation in section 3 and room temperature thermal vibrations were included. By comparison of calculated and experimental profiles we determined the energy variation of the surface barrier height U_o, and hence the energy variation of the dynamic work function. We also obtained the energy variation of the bulk inelastic potential U_{in} that corresponds to the imaginary part of the self-energy. These variations are shown with respect to the crystal zero potential in Fig. 1(b) and (c) where they join onto the values previously determined for energies below E_v in section 3. A significant surface-barrier
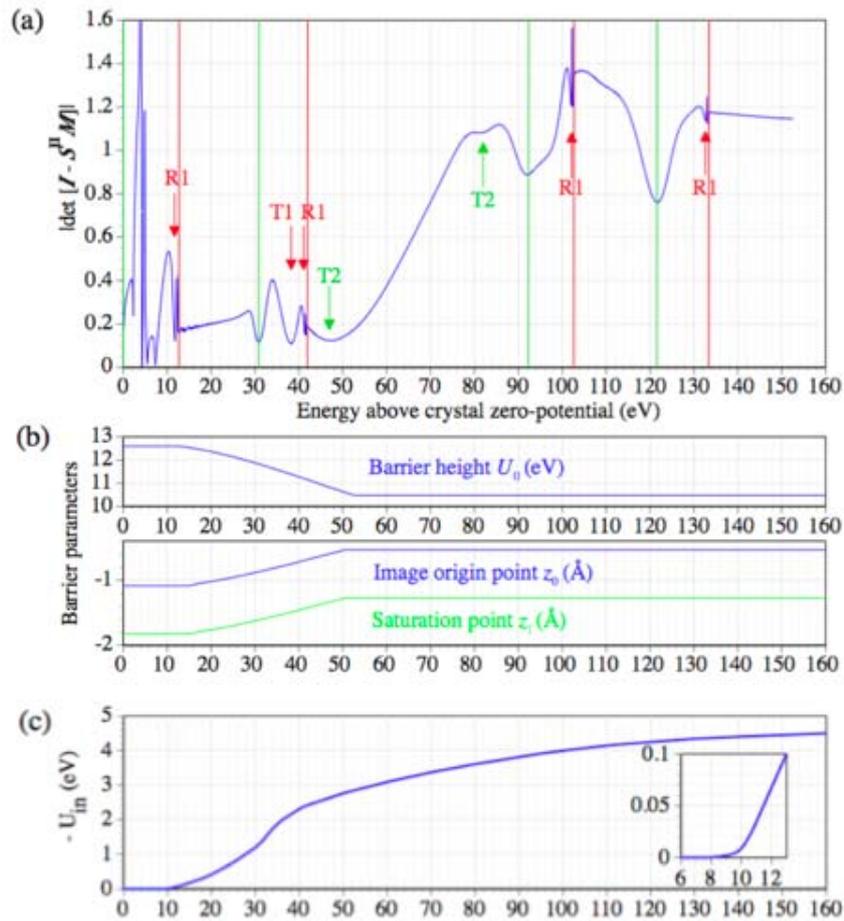
Fig. 1. (a) Calculation of surface state resonances for Cu(111) at $\bar{\Gamma}$ from Equ. (2).
(b) Energy variation of barrier parameters. (c) Energy variation of bulk inelastic potential.
The insert shows the same variation for 6 to 13 eV.

scattering feature was found near 90 eV in the {01} beams that had not been identified in previous LEED analyses. This allowed determination of the barrier image potential origin z_o and saturation position z_1 for the energy range above ~ 50 eV. The termination of the bulk inelastic potential within the surface barrier region $U_{b,in}(z)$ was found using a Gaussian function of half-width $\alpha = 2.6$ Å. The determined variations of these barrier quantities from the values below E_v are also shown in Fig. 1(b).

4.2 Surface state resonance calculation above vacuum level E_v

Using the same method as in Sec. 3 but with the self-energy variations of relevant quantities determined from LEED and including room temperature thermal vibrations we calculated the position of the surface state resonances from Eq. (2). This is shown in Fig. 1(a) and their energies are plotted on the full near-surface complex band structure in Fig. 2. In Fig. 1(a) the region between a green line and the next highest-energy red line indicates a region where scattering occurs along the surface barrier giving Shockley-type (labelled T1 for type 1) and first-order Rydberg (image) resonances (labelled R1). Regions between red lines and the next highest-energy green line indicate regions where scattering is only occurring at the bottom of the surface barrier giving more Tamm-like (labelled T2) surface resonances. The energies of these resonances with respect to E_v are obtained by subtracting the barrier height U_o shown in Fig. 1(b) from the energy positions shown in Fig. 1(a) and Fig. 2.
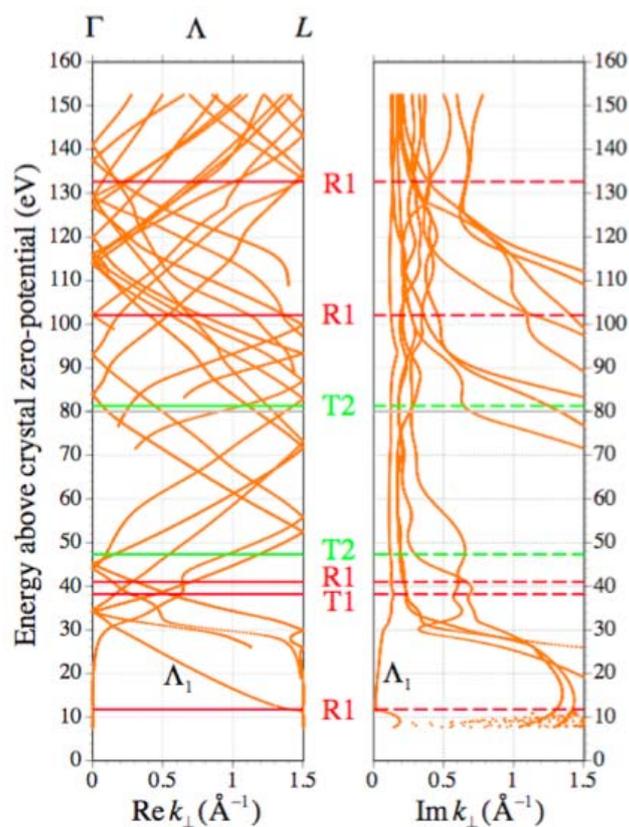
Fig. 2. Cu(111) near-surface complex band structure $E(\mathbf{k}) = E(k_{\parallel}, k_{\perp})$ for $\mathbf{k}_{\parallel} \equiv \overline{\Gamma}$ for energies extending above the vacuum level. Orange lines are surface-oriented bulk bands with least evanescent (spatially attenuating) wave functions and red and green horizontal lines are surface state resonances. The bulk band labelled Λ_1 is totally symmetric.

5.   Conclusion

With the inclusion of realistic electron self-energy effects, we have predicted surface barrier resonance states at $\overline{\Gamma}$ commonly referred to as Shockley type at 26 eV and Rydberg (image) type at 28, 90 and 120 eV above the vacuum level. Two more resonance states of a different type were found at 35 and 69 eV above vacuum level. As intermediate states in photoemission spectroscopies they have no perpendicular wave-vector dependence and barrier resonances have significantly less broadening (or inverse lifetime) than unbound bulk states. Experimental confirmation of these unbound surface resonance states could lead to new techniques to determine further details of lesser–known quantities in this energy range.

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