Surface electron band structure and VLEED reflectivity for Al(111)

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We calculate the above vacuum-level surface energy-band structure for Al(111) at $\overline{\Gamma}$ for 0 – 27 eV using a 2D layer Green function scattering method. This *above* vacuum surface band structure does not appear to have been calculated before. We find Tamm surface resonances at 6.9 and 8.3 eV, a Shockley surface resonance at 14.3 eV and a series of Rydberg (image) resonances starting at 23.9 eV. We also calculate very low-energy electron diffraction (VLEED) reflectivity profiles that probe this region of the surface band structure and have not been calculated before.

1.   Introduction

We have recently used the 2D layer Green function scattering method of Kambe-McRae to calculate the below vacuum-level, E_v, surface band structure of Al(111) [1]. The energy positions of surface states and strong resonances agree with a comprehensive density-functional calculation and experiment. Advantages of the present method are that it includes a semi-infinite crystal, can accurately deal with more localized bulk bands, can incorporate inelastic interactions and be extended to energies above the vacuum level. Here we examine the above vacuum-level surface-state resonances for Al(111) at $\overline{\Gamma}$ for 0 – 27 eV above E_v.

2.   Details of the method

Surface-projected bulk-band gaps correspond to total reflection from the crystal substrate and are determined [2] from values of energy, *E,* and crystal momentum parallel to the surface, $\mathbf{k}_\parallel$, for which

$$\det [\mathbf{M}'] = 1. \tag{1}$$

$\mathbf{M}'$ is the scattering matrix of propagating plane waves from the semi-infinite crystal substrate with no inelastic scattering [3].

Surface states and resonances are located [4] by determining values of $(E, \mathbf{k}_\parallel)$ for which

$$\det [\mathbf{I} - \mathbf{S}^{\mathrm{II}} \mathbf{M}] \qquad \text{is a minimum.} \tag{2}$$

$\mathbf{M}$ is the full semi-infinite crystal substrate scattering matrix (propagating and evanescent plane waves) and $\mathbf{S}$ is the surface barrier potential scattering matrix [5]. Both matrices may include inelastic scattering. The sub-matrix $\mathbf{S}^{\mathrm{II}}$ describes internal scattering at the surface barrier potential from inside the crystal surface. The above condition determines at which energies the amplitude of the wave-function passes through a maximum value in the surface region and corresponds to the electron being permanently or temporarily trapped in a surface state or resonance.

3.   Results for energy of surface states/resonances *below* the vacuum energy level

The results of the calculation from Eq. 1 for the surface–projected bulk-band energy gaps for Al(111) for $\mathbf{k}_\parallel = 0$ ($\overline{\Gamma}$ point) for energies below the vacuum level are shown in Fig. 1(a) for energies below 0 eV. All energies are referred to the vacuum level unless specified

otherwise. These gaps are calculated from the Moruzzi *et al.* [6] crystal potential with lattice constant 4.0496 Å corresponding to 300 K and with no relaxation of the surface atomic layers.

In this method the surface barrier potential is modeled by an empirical form. It is described in detail by Malmström and Rundgren [7] and it has an 'image' $1/(z - z_0)$ form where z_0 is the image-plane position. This form joins smoothly to a cubic polynomial-type saturation at a point z_1 closer to the metal surface. The z axis is perpendicular to the surface plane with origin $z = 0$ at the centre of the top row of atoms and the crystal is located at positive z values. The inner potential or barrier height, U_0, is 12.74 eV for the Moruzzi *et al.* bulk potential and was determined from the experimental surface core-level shifts (which are negligible) and the experimental work function. The values of $z_0 = -1.1$ a.u. and $z_1 = -2.0$ a.u. were found in our previous calculation [1] by matching trial calculations of the surface band energies below vacuum level to the two experimentally determined values of Shockley state and Rydberg resonance at $\bar{\Gamma}$. The result of this calculation using Eq. 2 is shown in Fig. 1(b) (and (c)) for energies below 0 eV. Here the minima occur at energies corresponding to the surface state and resonance found experimentally at -8.80 ± 0.04 eV [8] and $-$

Fig. 1. Calculations in the present work for surface–projected bulk-band gaps from Eq. 1 (frame (a)) and energy positions of surface states and resonances from Eq. 2 (frames (b) and (c)) for Al(111) and $\boldsymbol{k}_\parallel = 0$ ($\bar{\Gamma}$ point). The values of inelastic bulk scattering potential, $U_{in}(E)$, in frame (c) are given in the text. The termination of $U_{in}(E)$ at the surface is specified by a Gaussian function with half-width a. The downward arrows in frame (c) indicate the energy of surface resonances above the vacuum level. The two vertical lines indicate the energies at which the first degenerate set of non-specular plane waves become propagating in the crystal (dotted line) and in the vacuum (dashed line).

0.5 eV [9,10] respectively. The full surface band structure for $\bar{\Gamma} - \bar{M}$ below the vacuum level using this surface barrier model is shown in Ref. 1 and this is consistent with the most comprehensive calculation of the surface band structure by Heinrichsmeier *et al.* [11] using the density functional method with a finite-layer crystal slab.

4.   Results for energy of surface-state resonances *above* the vacuum energy level

While there are a number of calculations of surface bands below the vacuum level there do no appear to be any for the energy region above vacuum level. In this region the band structure is complicated because of localized 3*d* bands at ~ 15 – 20 eV and 4*f* bands at ~ 30 eV [12]. For the energy range of 0 – 27 eV we use the Moruzzi *et al.* bulk potential as before and the same surface barrier potential found from the previous analysis below vacuum level. Our calculation from Eq. 1 of the above vacuum-level surface energy-gaps from bulk bands is shown in Fig. 1(a) for energies above 0 eV. The gaps near 10 eV agree with those expected from the calculation of above vacuum bulk bands by Szmulowicz *et al.* [13]. Our calculation from Eq. 2 of the energy of surface resonances above vacuum level for no inelastic interactions is shown in Fig. 1(b) for energies above 0 eV. Here we note a number of minima in the energy range 6 – 24.49 eV indicating the occurrence of surface resonances.
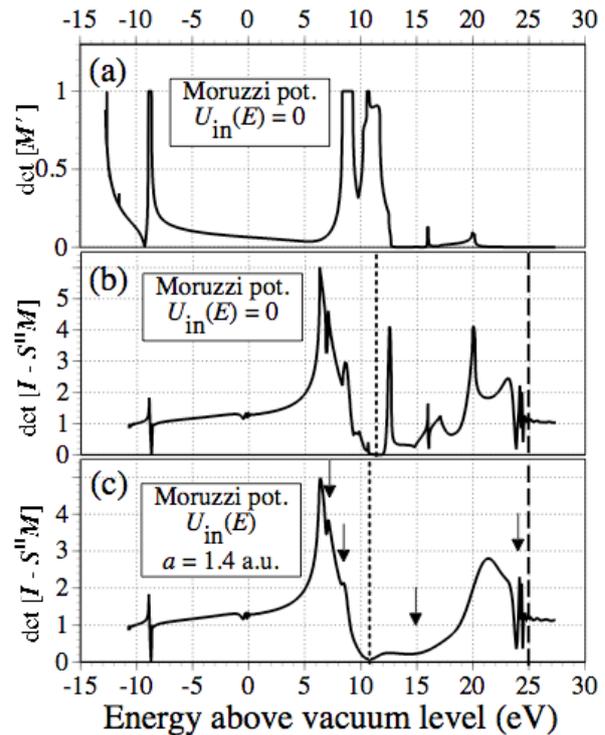
However inelastic electron-electron interactions in this energy range may damp out these resonances. We therefore introduce a bulk inelastic scattering potential, $U_{in}(E)$, from an analysis by McRae [14] from photoemission experimental data. This potential is small until 11.3 eV when it rises rapidly to 4.1 eV due to the onset of bulk plasmons. In addition inelastic processes at the surface are included by terminating the bulk inelastic potential at $z = 0$ with a Gaussian function with half-width $a = 1.4$ a.u. [15]. Fig. 1(c) above 0 eV shows the result of the inclusion of electron-electron inelastic interactions where the remaining minima indicating surface resonances are marked by downward arrows. In the range between the vertical dotted/dashed lines the resonances arise from propagating plane waves incident at the crystal-vacuum interface and scattering from the surface barrier. These resonances are of the Shockley type or of the Rydberg (or image) type if they originate from the $1/z$ image tail of the barrier. The resonance at 14.3 eV is of the Shockley type and the series of resonances starting at 23.9 eV are of the Rydberg type. In the range 6 – 11.76 eV the resonances arise from attenuated (evanescent) plane waves at the surface interface and do not depend on the surface barrier shape but occur because of the absence of further atomic layers at the surface. These may be termed Tamm-type resonances and two are found at 6.9 eV and 8.3 eV in these calculations.

5. Experimental detection of above vacuum-level surface-state resonances

Experimental techniques that may detect features due to surface-state resonances above vacuum energies include VLEED/LEEM (low energy electron microscopy), target (or total) current spectroscopy (TCS), surface soft-X-ray absorption spectroscopy (SSXA) and inverse photoemission spectroscopy (IPS).

We have calculated the LEED/LEEM 00 beam reflectivity (or intensity) for Al(111) at 300 K for normal incidence corresponding to $k_{\parallel} = 0$ to match the calculations of the surface band structure. Reflectivities for diffracted beams are calculated by the method of McRae [3] using the same $U_{in}(E)$, M and S matrices with the same Moruzzi et al. bulk potential and surface barrier potential. Fig. 2(c) shows this result. We have also calculated profiles using a non-reflection surface barrier model that allows for electron transmission and refraction at the surface but does not include reflections. It is the reflections at the surface that produce wave function maxima corresponding to surface resonances in this method. Fig. 2(a) and (b) show results for the non-reflection barrier placed at the match point $z_m = 0$ and at the jellium continuity $z_j = z_m = -2.21$ a.u. There is very little difference and the profiles show only the Bragg peaks arising from the above vacuum-level surface gaps from bulk bands shown near 10 eV in Fig. 1(a). Fig. 2(c) in addition to the Bragg peaks shows a dip-peak feature with peak at 17.5 eV and a series of similar features near 24 eV. These features
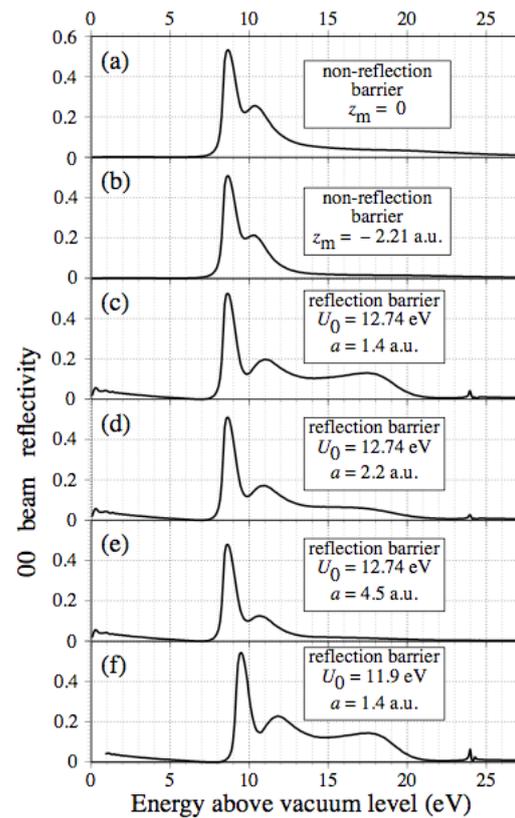

Fig. 2. Reflectivity (or intensity) of 00 beam on Al(111) at normal incidence ($k_{\parallel} = 0$) for different surface barrier models. The match point of surface barrier and crystal potentials is z_m, the crystal inner potential is U_0 and the caption of Fig. 1 describes a.

arise from scattering mechanisms involving the Shockley and Rydberg surface resonances indicated in Fig. 1(c) at energies above 0 eV. Hence experimental data that can now be obtained at normal incidence from intensity analysis in LEEM could verify the occurrence of these surface-state resonances. The Tamm-type resonances are too weak to appear in this data. Fig. 2(d) and (e) show the result of progressively increasing the inelastic scattering potential in the surface region. The surface resonance features are not completely damped out until $a = \sim 4.5$ a.u. which is far larger than the expected value. Fig. 2(f) takes into account that the crystal inner potential U_0 should decrease with increasing energy. For a decrease of 0.84 eV to $U_0 = 11.9$ eV we note in Fig. 2(f) that the Bragg peaks have moved up in energy but there is little change in the position of the Shockley resonance feature.

The only experimental data at the present time is TCS data [16] showing the main three peaks at 9.6, 11.8 and 17.3 eV with respect to the vacuum level. These energy positions agree with the calculated results here in Fig. 2(f). SSXA experimental data [17] found a surface resonance at 7.9 eV with respect to the vacuum level and this is consistent with the Tamm surface resonances at 6.9 and 8.3 eV found from calculations shown in Fig. 1(c).

6.   Conclusion

The present method of calculating the surface band structure of Al(111) above E_v predicts Tamm surface resonances at 6.9 and 8.3 eV, a Shockley resonance at 14.3 eV and a series of Rydberg resonances starting at 23.9 eV at $\bar{\Gamma}$. Before extending the calculation to all points of the surface Brillouin zone it would be desirable to have experimental confirmation for these surface-state resonances. While there are some old experimental data consistent with this result, modern measurements are desirable. The LEEM apparatus can measure the 00 beam reflectivity at normal incidence and very low energies and comparison with the calculations in Fig. 2 could verify the occurrence of the Shockley and Rydberg surface-state resonances predicted in this work.

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