

Surface Electronic Band Structure of Aluminium (111)

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We calculate the surface band structure for Al(111) for $\bar{\Gamma}$ to \bar{M} using a scattering approach and semi-infinite crystal. The surface states and strong resonances agree with a comprehensive finite-layer density-functional calculation and experiment. This suggests that our method can provide a reliable connection between surface bands both above and below the vacuum level. This is because our method can be extended to above the vacuum level while other methods are not applicable.

1. Introduction

We aim to calculate the surface energy band structure of metal systems, here Al(111) for energies over their entire energy range including above the vacuum level, E_v . In this work the energy range is to 5 eV above E_v . As well as providing information about surface potentials, knowledge of the surface band structure at these energies is needed to unravel features in many above-vacuum spectroscopies that also contain other unknown surface properties.

2. Details of the calculation

We use the 2D layer Green's function scattering approach to calculate the surface band structure [1]. It requires partial wave phase shifts to describe the bulk Al potential which we calculate from the muffin-tin potential for Al from Moruzzi et al [2]. Reflection and transmission scattering amplitudes from atomic layers are matched to plane waves between layers and 5 phase shifts and up to 9 plane waves were included in the present calculation. A semi-empirical surface barrier potential is added to form the metal-vacuum interface. The scattering properties of each layer are combined to form a semi-infinite crystal. We prefer to locate the Fermi energy E_f from experimental location of bulk Al bands but those that are edges of 2D gaps for $\bar{\Gamma}$ and \bar{M} (see Fig. 1) do not appear to have been measured [3]. We therefore estimate E_f from the calculation in Ref. 2 to be 8.5 eV above the muffin-tin zero (MTZ). With an experimental bulk lattice constant of $a = 7.60$ a.u. and experimental work function $\phi = 4.24$ eV [4], the energy of the vacuum level E_v is 12.74 eV above the MTZ. We use a surface barrier with image tail and cubic polynomial saturation as suggested by Malmström et al [5].

The values of (k_{\parallel}, E) for which a “standing wave” is set up from multiple scattering between the crystal potential and surface barrier potential map the surface energy band structure. This requires examining the singularities in the determinant of scattering matrices as explained elsewhere [6].

A Rydberg $n = 1$ image surface resonance on Al(111) at $\bar{\Gamma}$ has been detected by k -resolved inverse photoemission spectroscopy (KRIPES) [7,8] and scanning tunnelling spectroscopy (STS) [8]. It was found to be at +3.75 eV with respect to E_f (taken as the zero of energy in the following unless stated otherwise) or ~ 0.5 eV with respect to E_v . It was found that an image plane origin $z_0 = -1.1$ a.u. from the centre of the first row of atoms at 0 a.u. and saturation starting at -2.0 a.u. and continuing to 0 a.u. at the MTZ produced this resonance in

our calculation at +3.73 eV. Once fixed from this one experimental point no further change to the surface barrier potential was made.

3. Previous Calculations

There have been a number of calculations of Al(111) surface bands [9-13] but the most comprehensive which gives a quantitative dispersion for all the bands up to E_v is by Heinrichsmeier et al [14,15] using the density-functional (DF) method. They used the local density approximation (LDA) in Ref. 14 and also the non-local density approximation (non-LDA) in Ref. 15 to obtain the $1/z$ image tail of the surface barrier and hence the image resonances.

4. Results

The calculated surface band structure for $\bar{\Gamma}(\bar{\Sigma})\bar{M}$ in this work is shown in Fig. 1. At $\bar{\Gamma}$ we find the surface state at -4.44 eV in the 2D band gap bounded by the $L_{2'}$ and L_1 bulk band energies. It arises from just the 00 plane wave incident at a region of the surface barrier 8.68 eV below E_v . It agrees sufficiently with the experimental result from high-resolution angle-resolved photoemission spectroscopy (ARPES) [16] of -4.56 ± 0.04 eV and also the recent result of the DT [14,15] calculations of -4.6 eV. Such a surface state has been called a crystal-induced state or Shockley state. It would be labelled S_0 in the Smith et al [17] notation. We prefer a terminology where states are classified as intrinsic or extrinsic [18] in the present context. All states and resonances in this work are of the intrinsic type. Three members $n = 1, 2$ and ∞ of the Rydberg series of image barrier resonances are calculated. The $n = 1$ member arises from just the 00 plane wave incident at a region of the surface barrier ~ 0.5 eV below E_v . It is to be noted that the energy position of the $n = 1$ Rydberg resonance and surface state at $\bar{\Gamma}$ are not particularly sensitive to the image potential origin or the barrier saturation. This is

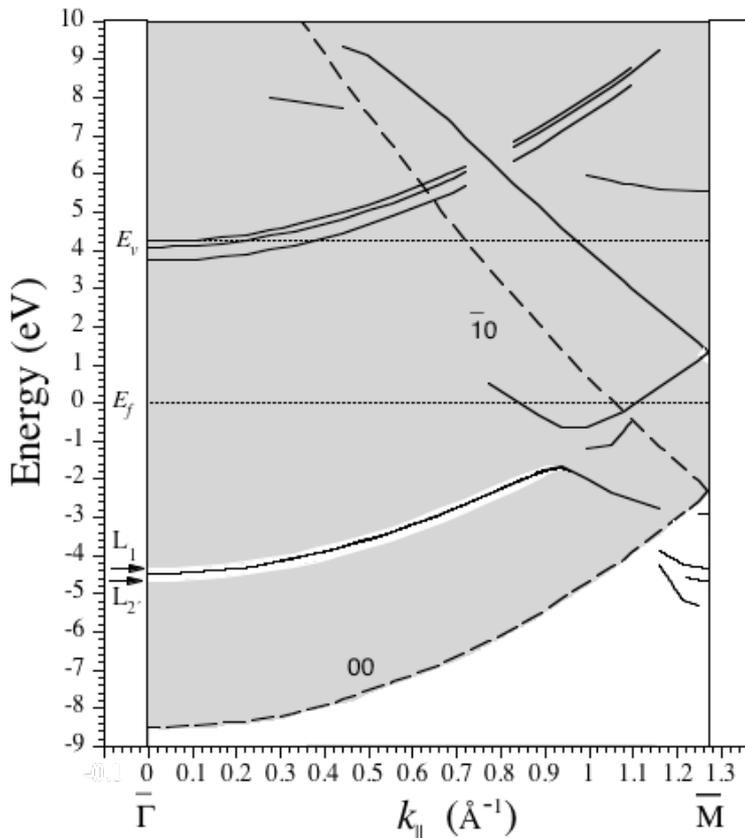


Fig. 1. Surface band structure for Al(111) from the present calculation. Full lines are the surface bands. E_f is the Fermi energy and E_v is the vacuum level. The dashed lines show the free-electron surface band structure. Unshaded regions show surface-projected bulk-band gaps from this calculation except below the dashed line marked 00. This is because the method does not directly indicate gaps in this region where all wave functions are evanescent. Bulk band edges of the 2D gaps are indicated in the margins.

mostly because the rapid phase changes near the narrow 2D gap edges at $\bar{\Gamma}$ tend to pin the location of the surface state in this energy region.

At \bar{M} we reproduce the two surface states in the small 2D gap formed between E_f and E_v . These surface states are at +1.34 and +1.37 eV from our calculation and +1.11 and +1.22 eV from the DF calculation. Of the other previous calculations Caruthers et al [10] and Mednick and Kleinman [13] produced one surface state in this gap at +1.29 eV and +1.09 eV respectively. Since two very different approaches of the present and the DF calculation, both produce two states here with their dispersions also in agreement, one can be confident that this same result will be obtained from experiment. Unfortunately there is no experimental determination of the above E_f bulk band energies or search for surface states at \bar{M} near the above energy range. The two states in this calculation arise from interaction of the two propagating plane waves 00 and $\bar{1}0$ forming even and odd combinations which would be labelled S_0^- (lower energy) and S_0^+ in the Smith et al [17] notation. Below E_f at \bar{M} , the DF calculation also produces a surface resonance at -4.68 eV and a broad resonance between ~ -2.0 and -3.0 eV. We also find a resonance at -4.68 eV and in addition we find two other weak resonances at -2.9 and -4.34 eV as well as another weak resonance near \bar{M} with minimum energy -5.33 eV. These four resonances arise from interaction of only evanescent (decaying) 00 and $\bar{1}0$ plane waves that leak into the potential well at the crystal-vacuum interface. There is experimental investigation in this region [19] but most features lie very close to energies corresponding to direct transitions into bulk bands and their interpretation is ambiguous.

A notable feature in our calculation is the above E_v surface resonance at \bar{M} at +5.54 eV. The DF calculation does not extend past E_v . We find this resonance somewhat pinned to the narrow 2D pseudogap near this energy in our calculation. Yang et al [20] using KRIPES have identified a surface resonance at \bar{M}' at +4.1 eV. There is a ~ 1.4 eV difference in energy here and further analysis is warranted. We have also included inelastic scattering electron-electron interactions above E_f via absorption potentials in this calculation according to the data from McRae [21]. We find that up to 10 eV above E_f , after which surface plasmons become excited, there is little effect on any of the surface bands calculated in this work. We have also found that displacement of the top row of atoms by $\pm 0 \rightarrow 5\%$ has no significant effect on the energy of any of the surface bands in the present calculation.

At $0.65 \bar{\Gamma}\bar{M} \rightarrow 0.8 \bar{\Gamma}\bar{M}$ there is a difference between our calculation and the DF one in that we obtain discrete resonance bands while DF obtain mostly a broad resonance ending at \bar{M} between ~ -2.0 and -3.0 eV. This is a region where a 2D pseudogap occurs bounded at \bar{M} by the X_4 and X_1 bulk band energies and traversed by a continuum of plane-wave-like bulk states. This pseudogap is plotted in Refs. 19 and 22. The lower energy surface band at \bar{M} above E_f flattens and bends upward below E_f in our calculation and also in the DF calculation. The dispersion below E_f is also clearly confirmed in the experimental data of Grepstad and Slagsvold [19]. In all three cases the flattening occurs near -0.7 eV and for $\sim 0.75 \bar{\Gamma}\bar{M}$. This agreement tends to confirm the dispersion of this surface band below E_f . Above E_f this band continues to follow the upper energy bound of the pseudogap above E_f in our calculation but is the broad resonance in the DF calculation. Our calculation has the surface state at $\bar{\Gamma}$ below E_f bending down at $\sim 0.75 \bar{\Gamma}\bar{M}$ into a weak resonance which tends to follow the lower energy bound of the 2D pseudogap. Again the interpretation of experimental data in this region [19,22] is ambiguous. These above mentioned resonance

bands arise from the interaction of the propagating $\bar{00}$ and evanescent $\bar{10}$ plane waves in our calculation and tend to follow part of the pseudogap energy bounds.

The DF calculation has the broad resonance straddling this pseudogap extending to ~ -2.0 and -3.0 eV at \bar{M} . Both the DF and present calculations have a resonance near -3.0 eV at \bar{M} near the lower bound of the pseudogap but the DF calculation also has one near -2.0 eV at \bar{M} where we do not. Our semi-infinite number of layers in the crystal allows for a continuum surface-projected bulk bands and the finite-layer DF calculation yields closely spaced discrete bulk bands. This may be the reason for our sharp resonances near this pseudogap.

5. Conclusion

This scattering method reproduces all surface states and strong resonances for energies below the vacuum level in agreement with the comprehensive DF calculation and experiment. It can easily incorporate inelastic electron-electron interactions which become significant for higher energies. An advantage of our method is that it can connect surface band structure above and below the vacuum level. This allows the examination of any variation of surface potentials that might occur such as the image potential origin. Other methods cannot be applied over the above range of energies.

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