Resonant bound states for simple metal surfaces

S. Å. Lindgren and L. Walldén
Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
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Using a simple model potential, a truncated image barrier, for the Al(111) surface, one obtains a resonant bound surface state at an energy that agrees surprisingly well with recent observations by inverse photoemission.

For a metal that, due to a band gap, is highly reflecting to electrons, there will appear a Rydberg-like series of surface states, all with energies within around an electron volt of the vacuum level. It is the image form of the potential in the outer parts of the surface barrier that makes the series Rydberg-like. For a metal surface modeled by an image barrier in front of an infinite barrier, the binding energies are reduced by a factor of 16 compared with the Rydberg energies. That states of this type may appear was evident from the measured and calculated electron reflectivities.[1–4] Later direct spectroscopic observations have been made by inverse photoemission[5] and two-photon photoemission.[6]

The observations made so far by these two methods include states which appear at energies within a band gap or resonances which are outside the band gap but only slightly outside such that the crystal reflectivity is still appreciable.[5,7] In a third category we rank one—as far as we know it is unique— observation of a resonance a few tenths of an electron volt below the vacuum level of a free-electron-like metal, namely Al.[8,9] These inverse photoemission measurements are for the direction normal to the (111) surface in which case the band gaps are far away from the interesting final-state energy range around the vacuum level.[10] If the peak is associated with the final states of the inverse photoemission process it thus seems to give an example of a pure surface barrier resonance formed by electrons which are reflected back and forth between different parts of the surface barrier *and not* between the surface barrier and the bulk potential. The purpose of the present paper is to point out that using a simple model potential and assuming that the inverse photoemission spectrum reflects the surface density of states the energy as well as the width and line shape can be predicted quite well.

Before proceeding we consider the possibility that the structure is due to the initial states of the inverse photoemission process. With the detector used by Heskett *et al.*[8,9] the initial states are around 9.5 eV above the final states. Close to the initial energies of interest, around 13 eV above E_F, there is a bulk band gap in the Γ-L direction.[10] The gap produces a 5% intensity peak in electron reflectivity spectra.[11] One expects that any structure in the inverse photoemission induced by the gap has a width similar to that of the electron reflectivity peak. This peak is around 2 eV wide while for the inverse photoemission peak the width is around 0.6 eV. Taking into account that the experimental resolution is around 0.4 eV (Refs. 8 and 9) this means that the expected initial-state effect is much too broad to explain the peak in the inverse photoemission spectrum.

Our model potential is a truncated image barrier (Fig. 1). The cutoff level is obtained by adding the work-function value of 4.24 eV measured for Al(111) (Ref. 11) and the free-electron Fermi energy. The density of states in the barrier region for electrons with zero parallel wave vector, $n_s(E,q_{11}=0)$, is given by $n_s(E,q_{11}=0)dE = dk\, N_k \int_z^\infty |\Psi_k|^2\, dz$, where N_k is the density of states along a k axis. The integral gives the amount of charge deposited in the barrier by a state with wave number k. For an evaluation we may use the results obtained by Paasch and Wonn[12] for a well with a constant potential between two barriers. Since $N_k = (L + d\Phi_B/dk)/\pi$ the density in k space increases with the well thickness L, but this increase is balanced by a decrease by the same factor of the square of the amplitude of the state. Φ_B is the phase shift at the vacuum barrier. If E is the energy relative to the bottom of the well, the density of electronic states in the barrier with zero parallel wave vector is given by

$$n_s(E,q_\parallel=0)=\frac{1}{2\pi}\left[\frac{d\Phi_B}{dE}+\frac{1}{2E}\sin\Phi_B\right].$$

This result applies for any barrier. For our image barrier

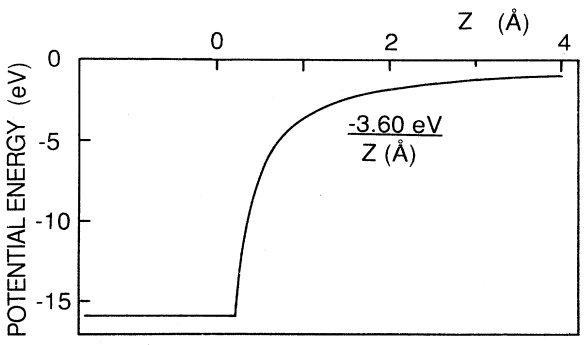

FIG. 1. Truncated image barrier used as model potential for the Al(111) surface.

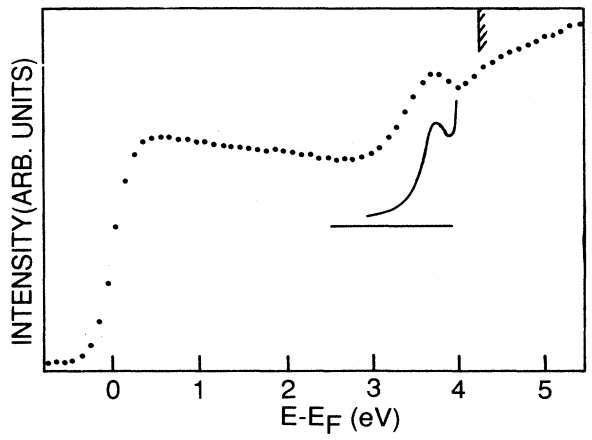

FIG. 2. Inverse photoemission spectrum measured by Heskett *et al.* (Ref. 8) (dotted) compared with the calculated surface density of states with zero parallel wave vector.

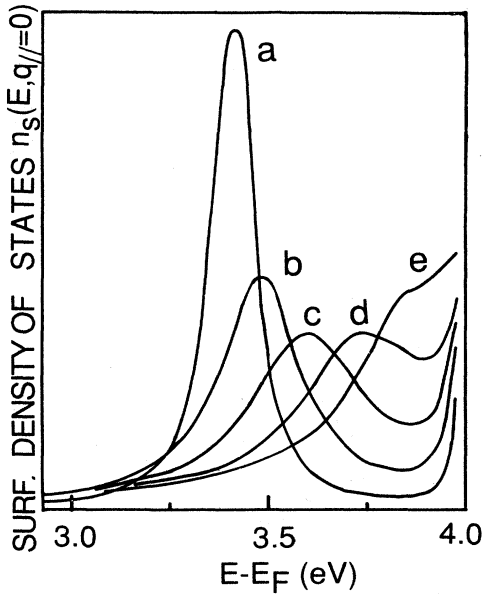

FIG. 3. Surface density of states with zero parallel wave vector calculated for truncated image potentials with different depths, namely (a) 2500 eV, (b) 250 eV, (c) 50 eV, (d) 15.8 eV, and (e) 6 eV.

and for energies near the vacuum level, the first term dominates.

The barrier phase shift is obtained from the Whittaker function solution of the wave equation for an image potential. To evaluate the Whittaker function and its derivative at the cutoff of the image barrier we use an integral representation valid for binding energies higher than 0.85 eV.[13] To get into the energy range of greater present interest closer to the vacuum level, we use a relation between the Whittaker functions $W_{\kappa+1,m}(x)$ and $W_{\kappa,m}(x)$.[13] Considering the simple potential used, the calculations reproduce the observed structure with surprising accuracy regarding energy and line shape, Fig. 2. The calculated width is somewhat smaller than the measured width, which may be explained by the limited experimental resolution. No broadening is included in the calculation.

The calculated surface density of states peak is the lowest-energy member of a Rydberg-like series of similar resonant bound states. This should be clear from Fig. 3 which shows how, as the image-potential cutoff level is lowered, the surface density of states peak becomes narrower and approaches the binding energy of 0.85 eV (3.39 eV above E_F in Fig. 3) characteristic of the unlimited image potential. If the model potential is useful also for simple metals with a lower electron density than that of Al then one expects that for these the lowest resonant bound state will be more difficult to resolve. The curve labeled *e* in Fig. 3 corresponds to a jellium with the density of *Na* and in this case one would expect to find a shoulder rather than a peak.

An obvious question concerns how the present resonant bound states are affected when a more sophisticated potential is used. As a check of this one may calculate the surface density of states for the potential constructed by Jennings *et al.*[14] This is a three-parameter potential which well reproduces potentials obtained from first-principles calculations. The potential is given by the expression

$$U_1(Z) = -\frac{1}{2(Z-Z_0)}(1-e^{-\lambda(Z-Z_0)}), \quad Z > Z_0$$

$$U_2(Z) = -\frac{U_0}{Ae^{B(Z-Z_0)}+1}, \quad Z < Z_0$$

with

$$A = -1+2U_0/\lambda, \quad B = U_0/A \ .$$

U_1 and U_2 join smoothly at the reference plane $Z = Z_0$. The authors find that with $\lambda = 1.25$ a.u. the potential agrees well at close range with the potential obtained

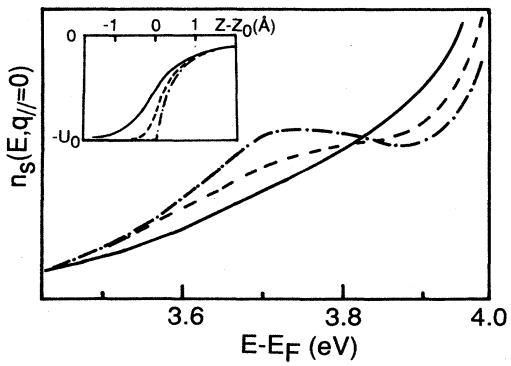

FIG. 4. Surface density of states calculated for a potential suggested by Jennings *et al.* (Ref. 13) for an $r_s = 2$ jellium surface and the different values of the parameter λ: 1.25 a.u. (solid), 1.75 a.u. (dashed), and 2.4 a.u. (dash-dotted). The potentials obtained for these λ values are shown in the inset.

with the local-density approximation[15] for a jellium with the approximate density of Al. It is therefore of some interest and concern to note that, when this potential is used, we find no peak in the surface density of states in the energy range of the observed inverse photoemission peak. If the value of λ is increased this means that the potential becomes more like the image potential. To get a peak in the surface density of states a value for λ of around 1.75 a.u. or more is needed (Fig. 4).

It is not easy to accept that a truncated image barrier is a better approximation to use for a prototypical free-electron-like metal surface such as Al(111) than the potential suggested by Jennings *et al.*[14] The difference of present interest between the two potentials is that the image barrier is steep enough to provide a sufficient reflectivity for electrons returning from the outer parts of the surface barrier. If the potential, which is believed to be more realistic, is not providing a sufficient reflectivity to produce a resonant bound state then one has to look for some other mechanism that could turn the electrons around close to the surface. Until this mechanism is found and a proper description can be made it appears from the present results that a truncated image barrier can be used to simulate the potential encountered by electrons at a simple metal surface.

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