

IMAGE STATES: IDEA AND THEORETICAL DEVELOPMENT

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Abstract

The concept and theoretical development of image states is reviewed. A brief summary of calculations of binding energies and effective masses is presented together with a more detailed discussion of the lifetime of such states. A brief discussion of the dependence of the linewidths with the surface response function is presented.

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Acknowledgements

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Abbreviations

LEED Low Energy Electron Diffraction.

1. Introduction

It has long been recognized that electrons can be trapped by the image potential in front of a solid surface if the electron reflectivity of the material is high for energies below the vacuum level.

Hydrogenic states of this kind were studied on theoretical grounds by Sommer [1], Cole and Cohen [2,3] and Shikin [4] who noted that liquid helium showed total reflectivity to electrons near the vacuum zero in energy and therefore should trap electrons in Rydberg States. A great deal of theoretical and experimental work has been made on the properties of such electrons localized on the surface of liquid helium [5,6] and on the two-dimensional system of electrons suspended above the surfaces by the image force and by an external electrostatic field [7,8].

Another example of this sort of state is provided by surface polarons, electrons bound to the surface region of a dielectric by coupling to the phonon fields [9,10]. Localized states of positron at surfaces have also been studied [11-16].

In metals a high electron reflectivity occurs in a gap, or near by in energy, of the projected band structure. Structure related to image states on metals were detected experimentally by LEED fine structure analysis [17-19]. Johnson and Smith [20] pointed out that these states could be observed in a more direct way by angle-resolved inverse photoemission [21,22]. Many workers have reported experimental measurements of binding energies and effective masses of image states [23-28].

Resolution in inverse photoemission is currently limited to about 260 meV [29,30] in energy and 0.05\AA^{-1} in momentum; two-photon photoemission [31-33] provides better resolution both in energy and momentum. Recent two-photon photoemission experiments have an energy resolution of $\sim 30\text{meV}$ [34-35].

2. Binding Energy and Effective Masses

A simple way to understand the main physics involved in calculations of binding energies and effective masses of image states at metal surfaces is provided by the phase shift model [36]. In this picture the surface state is considered as a wave trapped between the bulk crystal and the surface barrier and the condition for a surface state is written as the one for the poles of the total amplitude of the wavefunction at the surface

$$\frac{1}{1 - r_B r_C e^{i(\phi_C + \phi_B)}} \quad (2.1)$$

where $r_{C,B}$; $\phi_{C,B}$ are the modulus and the phase of the crystal and the surface barrier. In this model the binding energy of the Rydberg series depends on the position of the vacuum level with respect to the top of the gap. The model predicts that in the (111) faces of some fcc metals, where the vacuum level occurs at the top of the gap the image states would be more tightly bound than in the (100) faces, where the vacuum level occurs at the middle of the gap [37]. This trend has been corroborated in two photon photoemission experiments [31-32]. Smith [38,39] and Smith and coworkers [40,41] have presented an elegant study, within the nearly free electron two band model for the crystal reflectivity, of the trends that should be expected for the binding energy and effective masses for a variety of surface states on different surfaces.

A comparison between the results of the simple phase shift model and the experimental ones both for binding energies and lifetimes has been presented by Steinmann [33].

When the vacuum level is situated above the energy gap of the metal band structure image states may appear as well. They appear at the maxima of the amplitude, eq.(1), of the wave function at the surface. Such resonances have been studied by several authors at the (111) surfaces of some fcc metals [42-48]. Surface states shifts have been used as probes for surface reconstructions [49]. Barrier resonances have also been studied in the presence of an external electric field [50]. Magnetic splitting of image states at ferromagnetic surfaces of Fe, Co and Ni have been investigated recently [51-53]. Attempts of a description of the binding energy of image states based on a many body description of the real part of the surface self-energy, which incorporates the dynamic response of the metal surface have been presented [54-63].

3. Lifetimes

The image state's wave function lies mainly in the vacuum side. Thus the Rydberg states are effectively decoupled from the crystal wave functions and would be affected very little by scattering processes at the crystal region and therefore image states are expected to have longer lifetimes (and hence smaller intrinsic linewidths) than bulk states of comparable energy (which

have a linewidth of 0.5-1eV). Time resolved photoemission [64-66] and energy resolved two-photon photoemission [34,35,53,67,68] have allowed experimental determination of lifetimes of image states; Intrinsic linewidths vary from 16 meV (Cu(111) to 130 meV (Fe(110)). Quantitative predictions of the lifetimes of image states using a self-energy formalism have been made [69-72].

The formalism describes the linewidth of image states through the imaginary part of the self-energy [61,72]. Echenique and co-workers used strong approximations in order to make the calculations tractable. Schuppler, Steinmann and coworkers provide in a very recent paper [67] a thorough discussion of the approximations involved. The detailed description of the density of final states as a function of the parallel momentum is necessary. A detailed calculation of the penetration of the image state wavefunction into the crystal is needed to calculate the image state's lifetime. According to Schuppler et al. fairly recent experimental results indicate a greater penetration on Cu(111) than on Ag(111). This does not go in the right direction to understand the greater width of the image states on Ag(111) with respect to Cu(111).

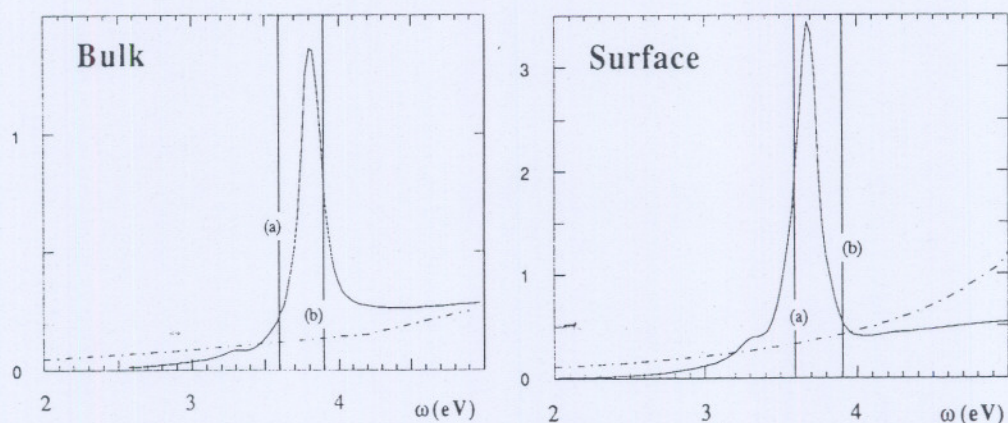


Fig. 1 Imaginary part of the bulk and surface Ag response functions used in this work. Continuous lines correspond to the experimental data [75], and the broken ones to the Mermin dielectric function at $q_{\parallel}=0$. ($r_s=3.02$, damping constant $\gamma=0.2\omega_p$). Vertical lines (a) and (b) indicate the upper limits of the energy of the transitions to bulk states for both (111) and (100) surfaces respectively.

The surface dielectric functions used so far have been very simplified models based on free electron gas models. The bulk dielectric Mermin [73]

response has been used, the surface being introduced via the specular reflection model [74]. This may not be very appropriate in situations where the d-bands play a role, or when the surface or bulk plasmon are allowed channels of decay.

In fig.1 we show the imaginary part of the bulk and surface response functions of silver both in the Mermin approximation for a free electron gas of density parameter $r_s = 3.02$, and the experimental ones [75]. The top of the allowed transition energy windows are 3.9 eV and 3.6 for the faces (100) and (111) respectively.

In figure 2 we show the results of the calculations of the energy width of the image states in Ag(100) and Ag(111) for different response functions together with the experimental ones [67]. In the case of the (100) surface the image state wave function was taken to be a hydrogenic one totally outside the crystal. In the case of the (111) face, the image state lies just at the top border of the gap, and the penetration of the wave function is now relevant. We have considered in this case two approximations, the non-penetrating one, where the wave function is outside the crystal, and the penetrating wave function given by the nearly free electron two band model for the part inside the crystal, and a hydrogenic one in the vacuum region [71]. The parameters of the wave function in this case have been taken to give a realistic 10% penetration into the crystal.

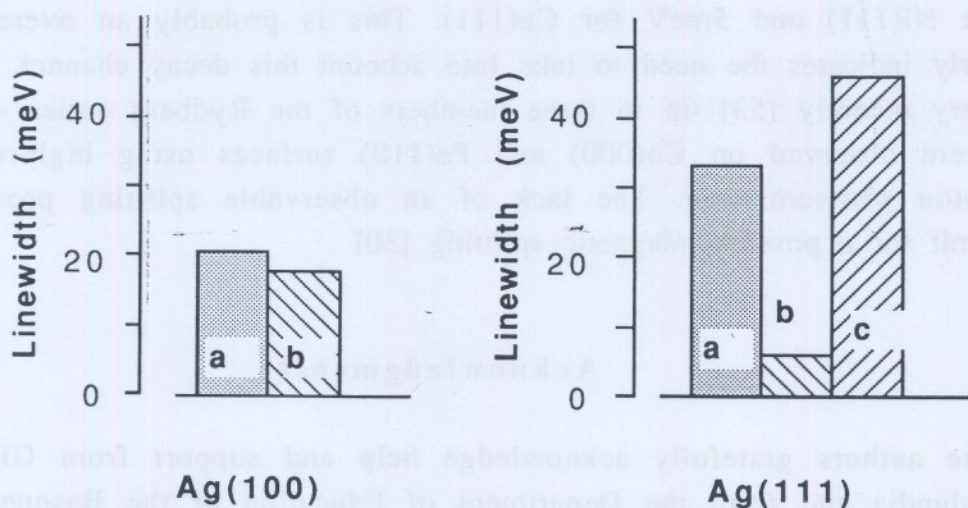


Fig. 2. Linewidth of the surface states on the faces (100) and (111) of silver. Data labeled as a are experimental values [67]. Data labeled as b correspond to theoretical values obtained by using a non-penetrating hydrogenic wave function ($\alpha=0.20$ a.u. [69]). The value labeled as c in the case of Ag(111) corresponds to a wave function penetrating 10% into the crystal:

In the case of the (100) face, our result agrees fairly well with the experimental value. Former similar theoretical estimations with RPA response function led to much smaller values (~ 3 meV) [69]. The difference among both estimations is due to the difference in the response functions shown in figure 1. The inclusion of the dispersion in the response function is not likely to be very relevant in those processes since the parallel momenta q_{\parallel} involved are small (~ 0.2 au). On the other hand the transition amplitude falls down very fast as the parallel momentum increases, working as an effective cut off on q_{\parallel} .

The non-penetrating wave function in the case of the (111) surface leads to much smaller linewidth values than the experimental one. The penetrating wave function quoted above leads to a value of 40 meV, close to the experimental one.

On the nickel surfaces the deviation from the simple free electron theory is important. The presence of the d-bands leads to a high density of states at the Fermi level and therefore to an increased width. No calculation with explicit inclusion of the d-bands as final states has been published. In addition unoccupied crystal-induced surface states provide an additional decay channel at the Ni(111) surface. Gao and Lundqvist [76] have evaluated the contribution to this width arising from transitions between surface bands. Their calculation uses a simplified wave function for the surface state and an unscreened potential for the interaction and leads to a width of the order of 40 meV for Ni(111) and 5 meV for Cu(111). This is probably an overestimation but clearly indicates the need to take into account this decay channel.

Very recently [53] up to three members of the Rydberg series of image states were observed on Co(000) and Fe(110) surfaces using high-resolution two photon photoemission. The lack of an observable splitting provides an upper limit for a possible magnetic splitting [30].

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