

## Lifetime in a two-dimensional image-potential-induced electron band

P. de Andrés

*Departamento de Física del Estado Sólido and Instituto de Física del Estado Sólido,  
Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

P. M. Echenique

*Cavendish Laboratory, Madingley Road, Cambridge, CB30HE, United Kingdom  
and Euskal Herriko Unibersitatea, Donostia, Euskadi, Spain*

F. Flores

*Departamento de Física del Estado Sólido and Instituto de Física del Estado Sólido,  
Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

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Lifetimes in a two-dimensional image-potential-induced electron band have been evaluated. Realistic wave functions, allowing penetration of the electron into the crystal, have been used. This results in a shorter lifetime for image electrons in the (111) noble-metal faces than in the (100) faces. Our results agree well with the recent experimental data of Giesen *et al.*

Electrons can be trapped by an attractive potential at a crystal surface. The Coulombic nature of the interaction, i.e., the classical image potential, allows an infinite Rydberg series to exist. The resulting appropriately scaled hydrogenic series converges toward the vacuum level for zero parallel momentum. These states were first observed at the surface of liquid helium and offer the possibility of studying a two-dimensional electron gas confined by a very simple potential.<sup>1</sup> Echenique and Pendry<sup>2</sup> discussed the detection and existence of these states at metal surfaces and showed that in spite of the different possible mechanisms leading to energy broadening, the Rydberg series could be resolved, i.e., that the energy difference between levels is, in a wide range of experimental situations, larger than the energy broadening of the levels. States of this kind play a role in the vacuum tunneling process through a gap at the sample surface.<sup>3</sup>

Recently, the technique of inverse photoemission<sup>4</sup> has provided a great deal of experimental information about the binding energy, width, and energy dispersion of image-potential-induced surface states.<sup>5-7</sup> Recent theoretical work has been concerned with the binding energy and dispersion of such states, both from a phase-shift multiple-scattering point of view<sup>2,8</sup> and from a many-body self-energy approach.<sup>9</sup> The energy resolution of inverse photoemission allows for only one state to be well resolved, and a precise energy determination of the lifetime of the state is difficult. In an experiment using the technique of two-photon photoemission Giesen *et al.*<sup>10</sup> determined the binding energies and lifetimes of the first two image states at the silver (111) surface. In these experiments intense laser radiation is used to populate a normally unoccupied state with the first photon and to photoionize this intermediate state with the second photon. As pointed out by Giesen *et al.*,<sup>10</sup> image-potential-induced surface states are ideally suited as intermediate states because, as a result of

their long lifetime,<sup>2</sup> a significant population can be built up. The occurrence of these strong two-photon photoemission processes shows that a high population density of image-potential states is possible, thus stressing the importance of a detailed understanding of the main mechanisms contributing to the finite lifetime of such electrons. This understanding is also relevant to the study of new states of matter that possibly occur in two-dimensional electron systems.<sup>1</sup>

In this paper we shall be concerned with the lifetime of electrons localized in a Rydberg-like series at metal surfaces. The first calculation of the lifetime of image states<sup>2</sup> was more concerned with establishing the possibility of resolving the Rydberg series than with actual quantitative estimations. For emphasis and simplicity Echenique and Pendry established an upper limit to the energy width of these states by assuming that only the electronic charge inside the solid sees an effective optical potential  $V_{oi}$ . This method can only be used as a qualitative guide, since there are no experimental data on the optical-potential values and, in any case, the detailed nature of the localized electron wave function and allowed final states does not allow this method to be used quantitatively. It does, however, provide very useful qualitative guidance and can be used to obtain useful upper limits. At the energies of the inverse photoemission and two-photon experiments two processes are responsible for the inelastic width: Decay into empty bulk states can occur via excitation of some quasiparticle, mainly an electron-hole pair excitation, and for finite momentum parallel to the surface the electron can also decay into image surface states having smaller parallel momentum.

A calculation of inelastic lifetimes, valid for the (100) noble-metal surfaces, was made by Echenique, Flores, and Sols.<sup>9</sup> In these cases, where penetration of the wave function into the crystal can be realistically neglected, the two

processes give comparable energy broadening of the order of 10 meV. A more complicated situation arises for the (111) faces, for which the only experimental data exist,<sup>11</sup> in which wave-function penetration results in additional bulk and interference terms in the many-body lifetime calculation.

In this paper we shall first be concerned with the linewidths of image states for the (111) faces of Ag and Cu. A discussion of the relevance of our results to the formation of a two-dimensional electron gas will follow. Two different effects will be analyzed: First of all, we shall discuss inelastic effects associated with electron-hole pair excitations; in a second step, we shall consider elastic linewidths due to the fact that some image states [ $n \geq 2$  for the (111) face of Ag and Cu] are located outside the gap and resonate with the continuum of energy near the band edge.

The inelastic linewidth of a state is calculated in terms of the imaginary part of the self-energy  $\Sigma$  projected over

$$\Delta_1 = -i/(2\pi)^2 \sum_f \int d^2Q \int d\omega \int dz \int dz' \psi_f(z) \psi_0^*(z) \psi_0(z') \psi_f^*(z') [1/(\omega - \Delta E + i\delta)] \times (e^{Qz} e^{Qz'}/Q) [\epsilon_s^{-1}(Q, \omega) - 1] / [\epsilon_s^{-1}(Q, \omega) + 1], \quad (2b)$$

$$\Delta_2 = -i/(2\pi)^2 \sum_f \int d^2Q/Q \int d\omega \int dz \int dz' \psi_f(z) \psi_0^*(z) \psi_0(z') \psi_f^*(z') [1/(\omega - \Delta E + i\delta)] \times \left[ \int dq' \frac{1}{k'^2} \cos[q'(z - z')] [1/\epsilon(k', \omega) - 1] + \int dq' \cos[q'(z + z')] / [k'^2 \epsilon(k', \omega)] + (2Q/\pi) \left( \frac{\int dq' \cos(q'z) / [k'^2 \epsilon(k', \omega)] \int dq'' \frac{\cos(q''z)}{k''^2 \epsilon(k'', \omega)}}{1 + \epsilon_s^{-1}(Q, \omega)} \right) \right], \quad (2c)$$

$$\Delta_3 = -i/(2\pi)^2 \sum_f \int d^2Q/Q \int d\omega \int dz \int dz' \psi_f(z) \psi_0^*(z) \psi_0(z') \psi_f^*(z') [1/(\omega - \Delta E + i\delta)] \times \left[ e^{Qz'} \int dq' \cos(q'z) / [k'^2 \epsilon(k', \omega)] \right], \quad (2d)$$

where  $\epsilon_s^{-1}(Q, \omega) = (Q/\pi) \int dq / [k^2 \epsilon(k, \omega)]$ ,  $\mathbf{k} = (\mathbf{Q}, q)$ ,  $\psi_0$  and  $\psi_f$  are the initial and final states in the direction perpendicular to the surface, and  $\Delta E = E_{fz} - E_{0z} + Q^2 - \mathbf{p} \cdot \mathbf{Q}$ ,  $E_{fz}$  and  $E_{0z}$  being the energies of  $\psi_0$  and  $\psi_f$  perpendicular to the surface and  $\mathbf{p}$  the momentum parallel to the surface associated with the initial state  $\psi_0$ . Notice that the different contributions to  $\Delta$  [Eq. (2a)] are associated with the interactions between an electron at  $\mathbf{r}$  and another at  $\mathbf{r}'$ , depending on whether  $\mathbf{r}$  and  $\mathbf{r}'$  are outside or inside the solid (see Fig. 1).

Equations (2) are calculated using a step model in order to obtain the bulk final wave function.<sup>9</sup> As regards the initial state, for the  $n=1$  wave function, we match a hydrogenic state which behaves like  $(z+a)\exp(az)$  for  $z < 0$ , to a decaying wave function in the crystal calculated within a narrow-gap approximation.<sup>15</sup> The parameter  $a$  in the hydrogenic state is adjusted to yield the observed level for  $n=1$ .

We have also calculated, for  $n=1$ , the extra contribution due to the fact that the initial state has a momentum

the state itself:<sup>9</sup>

$$\Delta = \int \psi_0^* \Sigma(\mathbf{r}, \mathbf{r}', E_0) \psi_0 d\mathbf{r} d\mathbf{r}', \quad (1)$$

where  $\psi_0$  is the state wave function and  $E_0$  its energy.  $\Sigma$  has been calculated with a  $GW$  approximation;<sup>12</sup>  $G$  is the Green's function and  $W$  the screened interaction calculated using the specular-reflection model of Ritchie and Marusak<sup>13</sup> (in Ref. 9 we showed this to be a good approximation to the surface response function;<sup>14</sup> this approximation is even better for the contribution coming from the electron penetrating into the bulk). In this paper, the specular-reflection model has been evaluated using the Lindhard dielectric function.

Assuming translational invariance for the surface response, we find that  $\Delta$  is given by the following equations:

$$\Delta = \Delta_1 + \Delta_2 + 2\Delta_3, \quad (2a)$$

where

parallel to the surface  $\mathbf{p}$ ; in that case the  $z$  dependence of the final state is taken equal to that of the initial state, and Eqs. (2) yield the extra broadening associated with that intraband transition.

Table I shows our results for the first image state of the (111) faces of Ag and Cu. For  $\mathbf{p}=\mathbf{0}$ , we find that the

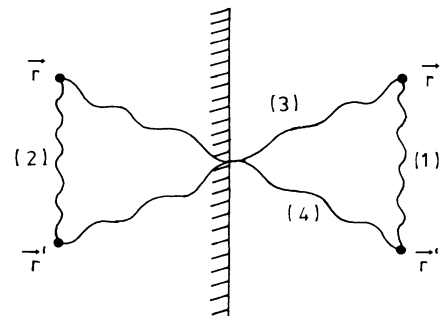


FIG. 1. Different interactions introduced in  $\Delta$ .

TABLE I. Half-widths (in meV) for the first image states of Ag and Cu (111) faces as a function of the wave-function penetration into the crystal.

Penetration	$\Gamma/2^a$	(meV)	$\Gamma/2^b$	(meV)
	Cu	Ag	Cu	Ag
10%	9.7	10.8	0.5	0.5
20%	19.4	21.8	1.7	1.9
30%	30.2	33.1	3.8	4.1
99%	83.0	91.7	37.4	40.4

<sup>a</sup>Values for  $\mathbf{p}=0$ .

<sup>b</sup>Contributions associated with intraband transitions for  $\mathbf{p}=0.2$  a.u.

linewidth of the state depends strongly on the penetration of the wave function into the crystal (the results shown in Table I are given as a function of that penetration). They are not very sensitive to the detailed form of the wave function. For Cu, this penetration is expected to be<sup>7</sup> about 10%; for this value the half-width is 9.7 meV. For Ag, the wave-function penetration is expected to be somewhat larger;<sup>4</sup> if we take it to be about 20%, the corresponding half-width is 21.8 meV. Notice that the half-widths are practically proportional to the penetration of the wave function into the crystal: For a 99% penetration, the half-width appears to be about 90 meV for both cases, in good agreement with other calculations.<sup>16</sup>

At the (111) surfaces of Ag and Cu, the second image state ( $n=2$ ) lies in the continuum, and therefore the surface state presents an elastic linewidth. We have obtained this width by matching the wave function of a narrow-gap approximation to the image-state wave function. The wave function inside the crystal is written as follows:<sup>15</sup>

$$\Psi(z) \sim \sin[(q + \frac{1}{2}g)z + \eta] + a \sin[(-q + \frac{1}{2}g)z + \eta], \quad (3)$$

where  $g$  is the reciprocal vector of the potential  $V$ , creating the gap,  $q$  is the momentum with respect to the one-dimensional Brillouin-zone edge, and  $a = [e - (e^2 - V^2)^{1/2}]/V$ ,  $e$  being the energy measured with respect to the mid-gap. In Eq. (3),  $\eta$  is a phase shift, so far arbitrary.

The surface image potential is characterized by the following interface wave function:<sup>15,17</sup>

$$\Phi(z) \sim \sin[(\frac{1}{2}g - q)z + \phi], \quad (4)$$

where  $\phi$  is given<sup>2</sup> by  $[\pi/\sqrt{32E} - \pi/2]$ ,  $E$  being the energy with respect to the vacuum level. By matching Eqs. (3) and (4), we obtain  $\eta$  as a function of  $\phi$ , and the interface density of states is given by<sup>15</sup>  $-(1/\pi)d\eta/dE$ . From this analysis we find that the elastic half linewidth is given by

$$(1/128\pi)(1-a)/(1+a) \text{ in a.u.} \quad (5)$$

From this equation we obtain the following elastic half-widths for the second image state: 26 meV for Ag and 20 meV for Cu.

This elastic structure is associated with the image surface state spread in energy over the linewidth of the resonance, while no other contribution to that structure comes from the electron states of the crystal. Accordingly, in order to analyze how inelastic processes broaden the elastic resonance, we have to consider as the initial state in Eq. (2), the wave function of the image state neglecting any penetration into the crystal. Notice that for this case we also have the possibility of an electron jumping from the second to the first image state; this has been evaluated with Eq. (2) by taking the first state  $n=1$  as  $\psi_f$ . Proceeding in this way, we have found an inelastic broadening for the second image state of 2.7 meV for Ag and 2.2 meV for Cu (most of this broadening,  $\approx 90\%$ , is associated with the transition from the second to first image states).

Summarizing all the previous results, we have found that (i) for the first image state, the total half-width is 22 meV for Ag and 10 meV for Cu, while (ii) for the second image state, the half-width for Ag is 29 meV and for Cu 22 meV. In the case of the first image state, the broadening is determined by an inelastic process where the penetration of the wave function into the crystal plays the main role. In this sense, notice that the penetration is strongly reduced for other faces like the (110) and the (100) ones. In these cases, the half linewidths can be expected to resemble the values found in Ref. 9 very much. As regards the second image state, let us finally stress that it is the elastic resonance between the surface state and the continuum density of states of the bulk, the main process controlling the broadening of the image state. Finally, a comment should be added on the relevance of our results to the existence of a two-dimensional electron band. The (100) faces are obviously better candidates than the (111) faces of noble metals, but even in the (100) faces, the intraband lifetime is of the same order of magnitude as the one associated to decay into the crystal. Better candidates will be materials with a well-defined gap in the projected band structure over a range of parallel momentum, such as diamond, where decay into crystal states is severely restricted.

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