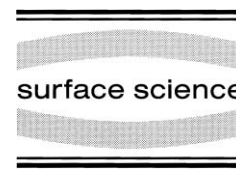




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Surface Science 433–435 (1999) 882–885



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Surface screening and lifetime of image states on Li(110)

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Abstract

We here present the calculation results of the lifetime $\tau = \hbar/\Gamma$ of the $n=1, 2$ image states on the Li(110) surface. The linewidth Γ of an image state is evaluated as the imaginary part of the electron self-energy Σ projected over the state itself. The GW approximation is utilized for the calculation of Σ . Different approximations are used to clarify the role of the surface screening on the lifetime of image states. The $n=1$ image state lifetime is found to be of 18 fs, which is very close to both theoretical and experimental predictions of the lifetime of the first image state on Cu(111). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Low index single crystal surfaces; Surface electronic phenomena

1. Introduction

Image potential states form a Rydberg-like series which converges towards the vacuum level [1,2]. The binding energies of these states have been measured on a variety of metal surfaces [3–6]. Very recently, high precision measurements of the lifetimes of a few image states on the (100) and (111) surfaces of Cu and Ag have been performed with time-resolved two-photon photoemission (TR2PPE) [7–10]. These experiments have shown that the $n=1$ image state lives 15–55 fs, i.e. substantially longer than bulk states with the same energy. First calculations of the linewidth Γ of image states demonstrated that Γ is crucially influenced by the penetration of an image state

into the bulk [11,12]. Recent calculations performed for the Cu(100) and Cu(111) surfaces [13] within the self-energy formalism [11,14] have shown that the use of a realistic one-dimensional potential [15] allows one to predict lifetimes of image states that are in good agreement with TR2PPE measurements [7–10]. In this paper we present the results of a calculation of the self-energy and the lifetime of image states on the Li(110) surface. This surface has been chosen for two reasons. The first is that lithium has no d-electrons and one can treat it as a simple metal. Another reason is that just above the Fermi level the electronic structure of Li(110) is very similar to that of Cu(100), whereas just below the vacuum level it is similar to that of Cu(111) [15]. As a result, the present calculations may be compared with available theoretical [13] and TR2PPE experimental [7–10] data for the lifetime of the $n=1$ image state on copper surfaces.

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2. Calculation method

Image state wave functions lie mainly in the vacuum region, where charge density and potential have little variation in the plane parallel to the surface (this plane is chosen to be normal to the z axes). Hence, we assume independence of these values on the x, y coordinates. Within this model, wave functions may be presented in the form $\psi_{nk_{\parallel}}(\mathbf{r}) = \exp(i\mathbf{k}_{\parallel}\mathbf{r}_{\parallel})\phi_n(z)$ and the corresponding energies are $E_{nk_{\parallel}} = E_n + k_{\parallel}^2/2$ (atomic units are used throughout). For the image state at the $\bar{\Gamma}$ point the inverse lifetime can be expressed through the two-dimensional Fourier-transform of the electron self-energy

$$\tau_i^{-1} = \Gamma = -2 \int \int dz dz' \phi_i^*(z) \times \text{Im}\Sigma(z, z'; \mathbf{q}_{\parallel} = 0, E_i)\phi_i(z'). \quad (1)$$

Subindex i indicates here an image state. Within the GW approximation, which we use, only the first term of the expansion of the self-energy in the screened Coulomb interaction is taken into account. We also replace the one-particle Green function of many body theory G , by the zero-order approximation G_0 and obtain

$$\text{Im}\Sigma(z, z'; \mathbf{q}_{\parallel} = 0, E_i) = \sum_{E_F \leq E_n \leq E_i} \phi_n^*(z')\phi_n(z) \times \int \frac{d\mathbf{k}_{\parallel}}{(2\pi)^2} \text{Im}W^{\text{ind}}\left(z, z'; E_i - E_n - \frac{k_{\parallel}^2}{2}\right), \quad (2)$$

where summation is performed over the final states $\phi_n(z)$. The induced interaction W^{ind} is determined from the two-dimensional Fourier-transforms of the bare Coulomb potential $V(z, z'; \mathbf{k}_{\parallel})$ and the density response function $\chi(z, z'; \mathbf{k}_{\parallel}, E)$

$$W^{\text{ind}}(z, z'; \mathbf{k}_{\parallel}, E) = \int \int dz_1 dz_2 V(z, z_1; \mathbf{k}_{\parallel}) \times \chi(z_1, z_2; \mathbf{k}_{\parallel}, E)V(z_2, z'; \mathbf{k}_{\parallel}). \quad (3)$$

Within the random phase approximation (RPA) the density response function satisfies the integral equation

$$\chi(z, z'; \mathbf{k}_{\parallel}, E) = \chi^0(z, z'; \mathbf{k}_{\parallel}, E) + \int \int dz_1 dz_2 \times \chi^0(z, z_1; \mathbf{k}_{\parallel}, E)V(z_1, z_2; \mathbf{k}_{\parallel})\chi(z_2, z'; \mathbf{k}_{\parallel}, E), \quad (4)$$

where χ^0 represents the density response function of non-interacting electrons. An explicit expression for χ^0 can be found in Ref. [16], in terms of both eigenfunctions $\phi(z)$ and eigenvalues E_n of the one-electron Hamiltonian. The results presented below have been found to be well converged and have been obtained for a 31 layer film of Li(110) by summing over all one-electron states (including image potential ones) up to an energy of 80 eV above the vacuum level. These wave functions and energies have been obtained as the solutions of the one-dimensional Schrödinger equation with the model potential [15] which approaches, far outside the surface, the classical image potential. This model potential reproduces the width and position of the energy gap at the $\bar{\Gamma}$ point and, also the binding energies of both the crystal-induced surface state at $\bar{\Gamma}$ and the first image state. As was shown in Ref. [15] this potential reproduces accurately the wave function of the $n=1$ state derived from the first-principles calculation [15].

3. Calculation results and discussion

In Table 1 we show the calculated linewidth (lifetime) values of the first and second image states for Li(110). These results have been obtained within two models to describe the screened interaction and final states. First, the screened Coulomb interaction has been evaluated within RPA, and final states have been calculated as explained above. Secondly, the specular reflection model (SRM) [17] has been used, in which the charge density is assumed to be abruptly terminated at the jellium edge, and a step model is utilized to evaluate the final states [11,12]. In Table 1 we also present the various contributions to the linewidth as determined by splitting the linewidth into three terms: $\Gamma = \Gamma_{\text{vv}} + \Gamma_{\text{ss}} + \Gamma_{\text{vs}}$. Γ_{vv} , Γ_{ss} , and Γ_{vs} , which represent vacuum, bulk, and interference contributions respectively, have been obtained by carrying out the integration of Eq. (1) over either vacuum ($z > 0, z' > 0$), bulk ($z < 0, z' < 0$) or vacuum–bulk ($z > 0, z' < 0$ and $z < 0, z' > 0$) coordinates. For comparison, we also give the results of calculation of the Cu(111) and Cu(100) surfaces, as obtained at the same level of

Table 1

Calculated total linewidth (meV), including Γ_{vv} , Γ_{ss} , and Γ_{vs} contributions and lifetime (fs) for the $n=1, 2$ image potential states on Li(110), and for $n=1$ state on Cu(111) and Cu(100)

	Γ	τ	Γ_{vv}	Γ_{ss}	Γ_{vs}
Li(110)					
$n=1$ (RPA)	37	18	40	37	-40
$n=1$ (SRM)	32.8	20	0.2	35.5	-2.9
$n=2$ (RPA)	15	44	13	11	-9
Cu(111)					
$n=1$ (RPA)	38 ^a	17.5 ^a	46	43	-51
$n=1$ (SRM)	50.0	13.2	0.3	53.3	-3.6
$n=1$ (exp)	37 ^b	18 ± 5 ^b	-	-	-
$n=1$ (exp)	44 ^c	15 ± 3 ^c	-	-	-
Cu(100)					
$n=1$ (RPA)	22 ^a	30 ^a	14	24	-16
$n=1$ (SRM)	15.6	42	0.1	14.1	1.4
$n=1$ (exp)	16.5 ^{c,d}	40 ± 6 ^{c,d}	-	-	-

^a Ref. [13].

^b Ref. [9].

^c Ref. [8].

^d Ref. [7].

approximations in Ref. [13]. As one can see from Table 1, bulk contributions to the linewidth are reasonably well described within the SRM. However, this model fails to describe both vacuum and interference contributions. To clarify the origin of this difference, we show in Fig. 1 the imaginary

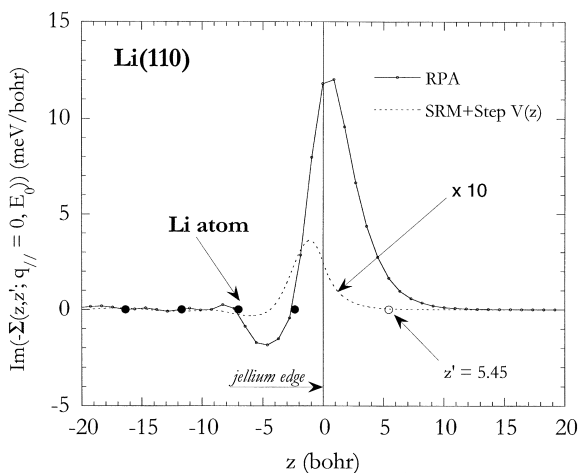


Fig. 1. The RPA (solid line) and SRM (dashed line) calculation curves of the imaginary part of the self-energy as functions of the z coordinate. Filled circles designate positions of the atomic layers

part of the self-energy ($\text{Im}\Sigma$) for the first image state on Li(110) with $q_{||}=0$ and z' being located in the vacuum region. As one can see in Fig. 1, the maximum of $\text{Im}\Sigma$ stays in the vicinity of the jellium edge and is underestimated within the SRM. As a result, the vacuum and interference contributions to the linewidth are underestimated within this approximated model for surface screening. Nevertheless, these contributions are comparable in magnitude and opposite in sign, which results in the total linewidth being (a) mainly determined by bulk contribution, and (b) reasonably well described by the simplified specular reflection model of the surface. We also note that the use, by going beyond a free electron description of the surface, of a realistic model potential in the evaluation of both initial and final states involved in Eqs. (1) and (2) is of crucial importance for an accurate prediction of the electron self-energy and the lifetime of image states. However, we find that the linewidth of the image states is not extremely sensitive to approximations used for the evaluation of the screened Coulomb interaction.

Finally, it is interesting to notice from Table 1 that the lifetime of the $n=1$ image state on Li(110) is very close to both theoretical and experimental values of the lifetime of the image state on Cu(111). The penetration of this state into the crystal is found to be of 15% and 22% for Li(110) and Cu(111) respectively, whereas for Cu(100) this penetration is of 5%. Hence, the small penetration of the $n=1$ image state on Cu(100) results in the linewidth being smaller for this surface.

In conclusion, we have calculated the lifetime for the $n=1, 2$ image states and imaginary part of the self-energy for Li(110). We have found that the lifetime of the first image state on this surface is very close to both theoretical and experimental predictions of the lifetime of the image state on Cu(111). To verify these results, it would be desirable to perform TR2PPE measurements of the image states on the (110) surface of lithium.

Acknowledgements

This work has been supported by the Ministerio de Educación y Cultura (Spain) and the

Departamento de Educación del Gobierno Vasco
(Basque Country).

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