



Surface-state electron dynamics in noble metals

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Abstract

Theoretical investigations of surface-state electron dynamics in noble metals are reported. The dynamically screened interaction is computed, within many-body theory, by going beyond a free-electron description of the metal surface. Calculations of the inelastic linewidth of Shockley surface-state electrons and holes in these materials are also presented. While the linewidth of excited holes at the surface-state band edge ($\mathbf{k}_{\parallel} = 0$) is dominated by a two-dimensional (2D) decay channel, within the surface-state band itself. The calculations indicate that major contributions to the electron–electron interaction of surface-state electrons above the Fermi level come from the underlying bulk electrons. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Shockley surface states are known to exist near the Fermi level in the Γ -L projected bulk band gap of the (1 1 1) surfaces of the noble metals Cu, Ag and Au [1–3]. The wave functions of these crystal-induced surface states [4–6] are localized near the surface and decay into the solid, in contrast to the Bloch waves propagating into the bulk. Hence, these states form a quasi two-dimensional (2D) electron gas, which overlaps in energy and space with the three-dimensional (3D) substrate and represent a playground for lifetime investigations.

Various techniques have been used to measure the lifetime broadening of surface-state electrons and holes near the Fermi level. High-resolution angle-resolved

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photoemission spectroscopy (ARPES) has been used to investigate the lifetime of surface-state holes [7–12]. In contrast to this technique, which is restricted to lifetime measurements of occupied states, it has been demonstrated that scanning tunneling spectroscopy (STS) offers the possibility to measure the lifetime of long-living surface states above and below the Fermi level [13–15]. The lifetime of excited holes at the band edge of the partially occupied Shockley surface states on Ag(1 1 1), Cu(1 1 1) and Au(1 1 1) was accurately determined by Li et al. [13] and by Kliewer et al. [14] with the use of STS. Recently, STS has been used to measure lifetimes of hot surface-state and surface-resonance electrons, as a function of excess energy [15].

On the (1 1 1) surfaces of Cu, Ag and Au, the Shockley surface-state at the center of the surface Brillouin zone ($\mathbf{k}_{\parallel} = 0$) lies just below the Fermi level, with $E - E_F = -445$, -67 and -505 meV, respectively [14], E and E_F representing the surface-state energy and the Fermi level. The dispersion relation of these states is displayed in Fig. 1, which shows that they are free-electron-like with effective masses of 0.42, 0.44 and $0.28m_e$ (m_e is the free-electron mass) that account for the potential variation parallel to the surface. This figure clearly shows that the decay of Shockley surface-state electrons and holes in these materials may proceed either through the coupling with bulk states (3D channel) or through the coupling, within the surface-state band itself, with surface states of different wave vector parallel to the surface (2D channel).

While 3D free-electron calculations of the decay rate of excited holes at the surface-state band edge ($\mathbf{k}_{\parallel} = 0$) of the noble metals are known to predict significantly longer lifetimes than those observed with either ARPES [7–12] or STS [13,14], recent measurements [15] have shown that, in the case of surface-state electrons above the Fermi level, the experimental values are comparable to the calculated lifetimes of bulk free-electrons with the same energy. That the decay of surface-state holes is dominated by 2D electron–electron interactions, but screened by the underlying 3D electron system, has been demonstrated recently [14,16], showing an excellent agreement with experiment. In this paper, we extend these theoretical investigations to the case of hot surface-state and surface-resonance electrons in Cu(1 1 1), and show that major contributions to the electron–electron interaction of surface-state electrons above the Fermi level come from the underlying bulk electrons. We also present self-consistent calculations of the screened interaction, and investigate the role that both the partially occupied 2D surface-state band and the underlying 3D electron gas play in the relaxation mechanism.

The contribution to measured lifetimes of surface-state electrons in the noble metals arising from electron–phonon interactions has been discussed in [14]. Here, we focus on the investigation of the energy-dependent inelastic lifetimes that are due to electron–electron interactions.

2. Theory

We take an arbitrary Fermi system of interacting electrons and consider an excited electron or hole interacting with the Fermi sea. The electron–hole decay rate, i.e., the

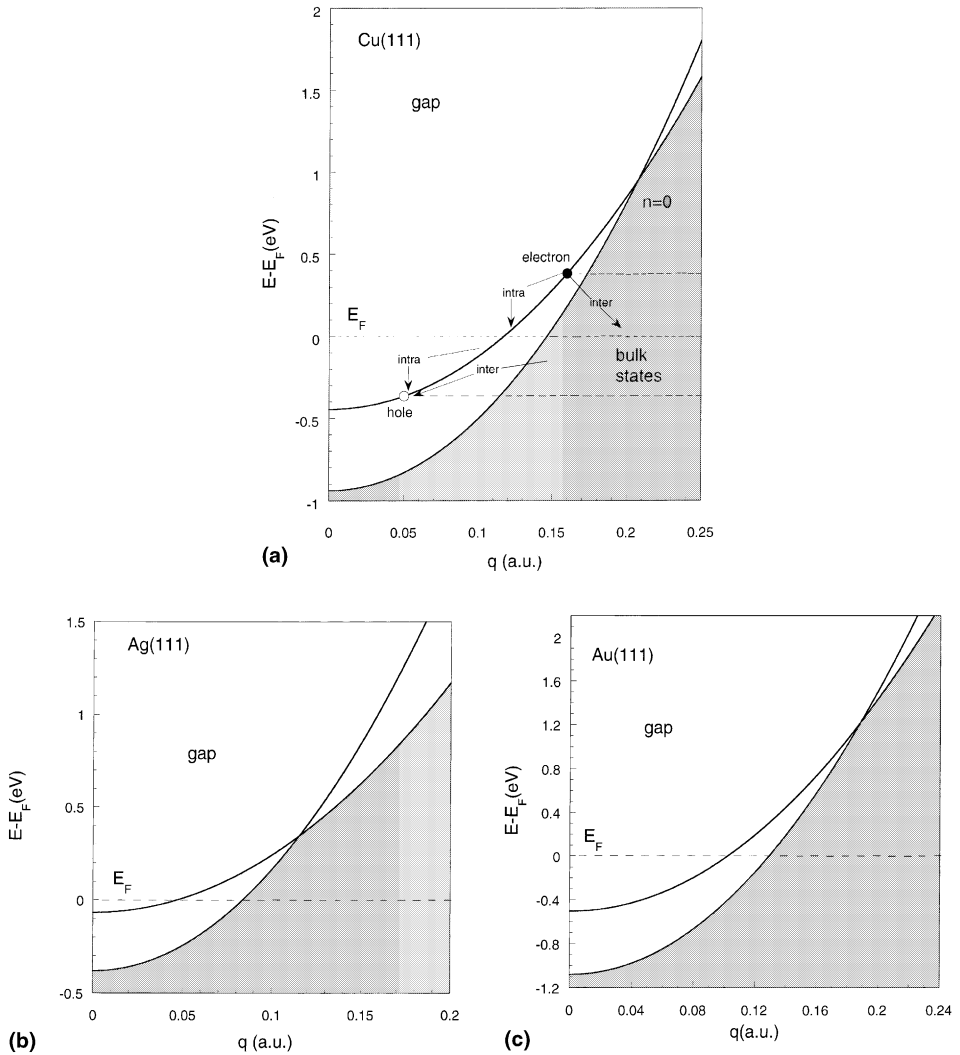


Fig. 1. Dispersion of Shockley surface state and bottom of projected band-gap on the (111) surfaces of: (a) Cu, (b) Ag, (c) Au. Shaded areas represent areas outside the band-gap, where bulk states exist. Relaxation of Shockley surface-state electrons and holes may proceed either through interband coupling with bulk states (3D channel) or through intraband coupling, within surface state itself, with surface states of different wave vector parallel to surface (2D channel).

probability per unit time for the probe particle to scatter from an initial state $\psi_i(\mathbf{r})$ of energy E_i to some available final state $\psi_f(\mathbf{r})$ of energy E_f ($|E_f - E_F| < |E_i - E_F|$), by carrying the Fermi gas from the many-particle ground state to some excited many-particle state, may be obtained by using the *golden rule* of time-dependent perturbation theory [17]. By keeping terms of first-order in the screened interaction, one finds (we use atomic units throughout, i.e., $e^2 = \hbar = m_e = 1$):

$$\tau^{-1} = 2 \sum_{\mathbf{f}} \int d\mathbf{r} \int d\mathbf{r}' \psi_{\mathbf{i}}^*(\mathbf{r}) \psi_{\mathbf{f}}^*(\mathbf{r}') \text{Im}[-W(\mathbf{r}, \mathbf{r}'; |E_{\mathbf{i}} - E_{\mathbf{f}}|)] \psi_{\mathbf{i}}(\mathbf{r}') \psi_{\mathbf{f}}(\mathbf{r}), \quad (1)$$

where $W(\mathbf{r}, \mathbf{r}'; \omega)$ is the frequency-dependent dynamically screened interaction

$$W(\mathbf{r}, \mathbf{r}'; \omega) = v(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}_1 \int d\mathbf{r}_2 v(\mathbf{r}, \mathbf{r}_1) \chi(\mathbf{r}_1, \mathbf{r}_2; \omega) v(\mathbf{r}_2, \mathbf{r}'), \quad (2)$$

$v(\mathbf{r}, \mathbf{r}')$ and $\chi(\mathbf{r}_1, \mathbf{r}_2; \omega)$ being the bare Coulomb interaction and the *exact* density-response function of the Fermi system, respectively.

In the case of a bounded 3D electron gas that is translationally invariant in the plane of the surface, which we assume to be normal to the z -axis, the probe-particle initial and final states are of the form

$$\psi_{\mathbf{i}}(\mathbf{r}) = \phi_{\mathbf{i}}(z) e^{i\mathbf{k}_{\parallel} \cdot \mathbf{r}} \quad (3)$$

and

$$\psi_{\mathbf{f}}(\mathbf{r}) = \phi_{\mathbf{f}}(z) e^{i(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel}) \cdot \mathbf{r}}, \quad (4)$$

with energies

$$E_{\mathbf{i}} = \varepsilon_{\mathbf{i}} + \frac{\mathbf{k}_{\parallel}^2}{2m_{\mathbf{i}}} \quad (5)$$

and

$$E_{\mathbf{f}} = \varepsilon_{\mathbf{f}} + \frac{(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel})^2}{2m_{\mathbf{f}}}, \quad (6)$$

where the one-particle wave functions $\phi(z)$ and energies ε describe motion normal to the surface. Using these wave functions and energies in Eq. (1), one easily finds

$$\tau^{-1} = 2 \sum_{\mathbf{f}} \int \frac{d\mathbf{q}_{\parallel}}{(2\pi)^2} \int dz \int dz' \phi_{\mathbf{i}}^*(z) \phi_{\mathbf{f}}^*(z') \text{Im}[-W(z, z'; \mathbf{q}_{\parallel}, |E_{\mathbf{i}} - E_{\mathbf{f}}|)] \phi_{\mathbf{i}}(z') \phi_{\mathbf{f}}(z), \quad (7)$$

$W(z, z'; \mathbf{q}_{\parallel}, \omega)$ being the 2D Fourier transform of the screened interaction.

3. Screened interaction

The main ingredient in the evaluation of electron–hole decay rates in a bounded 3D electron gas is the screened interaction $W(z, z'; \mathbf{q}_{\parallel}, \omega)$. When both z and z' are fixed far from the surface, a few atomic layers within the bulk, there is translational invariance in the direction normal to the surface, and $W(z, z'; \mathbf{q}_{\parallel}, \omega)$ can then be easily obtained from the knowledge of the dielectric function of a homogeneous electron gas $\epsilon(q, \omega)$:

$$W^{\text{bulk}}(z, z'; \mathbf{q}_{\parallel}, \omega) = \int \frac{dq_z}{2\pi} e^{iq_z(z-z')} v(q) \epsilon^{-1}(q, \omega), \quad (8)$$

where $v(q)$ represents the 3D Fourier transform of the bare Coulomb interaction, and $q^2 = q_{\parallel}^2 + q_z^2$. In the random-phase approximation (RPA), $\epsilon(q, \omega)$ is the Lindhard dielectric function [18,19].

Shockley surface-state electrons and holes are found to be very close to the Fermi level ($|E - E_F| \ll E_F$). Hence, as the energy transfer $|E_i - E_f|$ entering Eq. (7) cannot exceed the value $|E - E_F|$, one can use the low-frequency form of the Lindhard dielectric function, which yields the energy-loss function

$$\text{Im}[-\epsilon^{-1}(q, \omega)] = \frac{2}{q^3} \epsilon^{-2}(q, 0) \omega \Theta(2q_F - q), \quad (9)$$

where $\Theta(x)$ represents the Heaviside function and q_F is the Fermi momentum. If one further replaces the static dielectric function $\epsilon(q, 0)$ by the Thomas–Fermi (TF) approximation, then one finds,

$$\text{Im}[-\epsilon^{-1}(q, \omega)] = \frac{2q}{(q^2 + q_{\text{TF}}^2)^2} \omega \Theta(2q_F - q), \quad (10)$$

$q_{\text{TF}} = \sqrt{4q_F/\pi}$ being the TF momentum.

In the bulk, the maximum magnitude of $\text{Im}[-W(z, z'; \mathbf{q}_{\parallel}, \omega)]$ occurs at $z = z'$ and is independent of the actual value of z . Fig. 2 shows this quantity for Cu(111), as

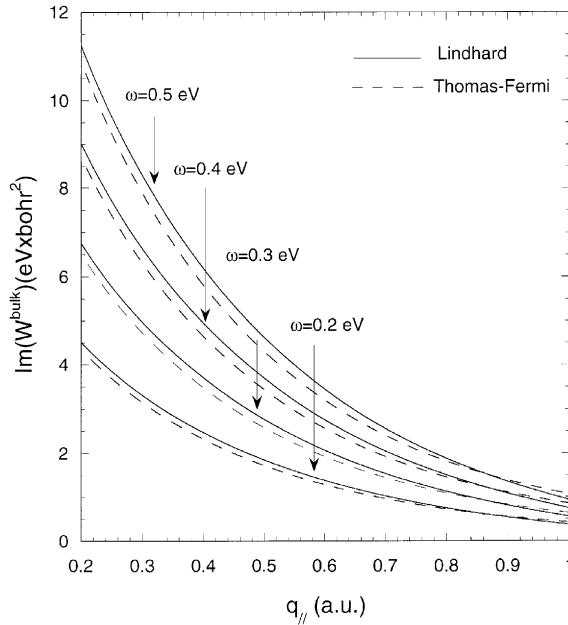


Fig. 2. Imaginary part of bulk screened interaction $\text{Im}[-W^{\text{bulk}}(z, z; \mathbf{q}_{\parallel}, \omega)]$ of Eq. (8), as a function of $q_{\parallel}$ for various values of ω : 0.2, 0.3, 0.4 and 0.5 eV. Solid and dashed lines represent the result of introducing into Eq. (8) either Lindhard dielectric function (solid lines) or the approximated energy-loss function of Eq. (10) (dashed lines).

obtained from Eq. (8) with either the Lindhard dielectric function or the approximated energy-loss function of Eq. (10), versus $q_{\parallel}$ for fixed values of ω [$\omega = 0.2, 0.3, 0.4, 0.5$ eV]. One clearly sees that for the momentum and energy transfers of interest (see Fig. 1), the approximated form of Eq. (10) yields a screened interaction which is close to that obtained with use of the Lindhard dielectric function, small differences being mainly due to the fact that the static dielectric function $\epsilon(q, 0)$ has been replaced by the TF approximation. Contributions to the surface-state decay rate coming from the penetration of the surface-state wave function into the solid are, therefore, expected to be well described by Eq. (10).

Nevertheless, coupling of Shockley surface states with the crystal may also occur, either through the evanescent tails of bulk states near the surface or within the surface-state band itself. These contributions to the surface-state decay rate are both dictated by the screened interaction at z points near the surface, where the representation of Eq. (8) is not accurate.

For a realistic description of the screened interaction, we proceed along the lines reported in [20,21]. First of all, we compute the single-particle eigenfunctions and eigenvalues of a 1D model potential [22,23]. This model potential, which reproduces far outside the surface the classical image potential, is chosen so as to describe the width and position of the energy gap at the Γ point ($\mathbf{k}_{\parallel} = 0$) and, also, the binding energies of both the Shockley surface state at Γ and the first ($n = 1$) image-potential induced state. We then introduce these eigenfunctions and eigenvalues into Eq. (7), we also use them to compute the non-interacting density-response function [24], and finally solve an integral equation to derive the RPA density-response function $\chi(z, z'; \mathbf{q}_{\parallel}, \omega)$ and the screened interaction $W(z, z'; \mathbf{q}_{\parallel}, \omega)$.

As the maximum magnitude of $\text{Im}[-W(z, z'; \mathbf{q}_{\parallel}, \omega)]/\omega$ near the surface still occurs at $z \sim z'$ (only far from the surface into the vacuum, where the Shockley surface-state amplitude is negligible, does the maximum of this quantity occur at $z \neq z'$ [25]), we choose $z = z'$ and show $\text{Im}[-W(z, z; \mathbf{q}_{\parallel}, \omega)]/\omega$ in Fig. 3, as a function of z going from the bulk to the vacuum, for $q_{\parallel} = 0.2a_0^{-1}$ (a_0 is the Bohr radius) and for various values of ω . We find that at the surface $\text{Im}[-W]/\omega$ is enhanced, for the smallest values of ω , by a factor of 3, relative to the bulk. This is mainly due to the strong anisotropy at the surface, which enhances the electron-hole pair creation probability.¹ We also find that for frequencies smaller than 0.2–0.3 eV, the strong anisotropy of the surface does not modify the linear frequency scaling characteristic of the *bulk* screened interaction [see Eq.(9)]. However, for the larger but still small frequencies explored in Fig. 3, the screened interaction at the surface exhibits an important enhancement due to corrections to the linear scaling that are not present within the bulk. As a result, for the largest values of ω that we have considered, $\text{Im}[-W]/\omega$ is enhanced at the surface by a factor as large as 4.

¹ Band-structure effects on the screened interaction are found to be of minor importance, i.e., the screened interaction is not very sensitive to whether the single-particle wave functions and energies entering the calculation of the non-interacting density-response function are the eigenvalues and eigenfunctions of our model potential or the Kohn–Sham LDA *jellium* hamiltonian.

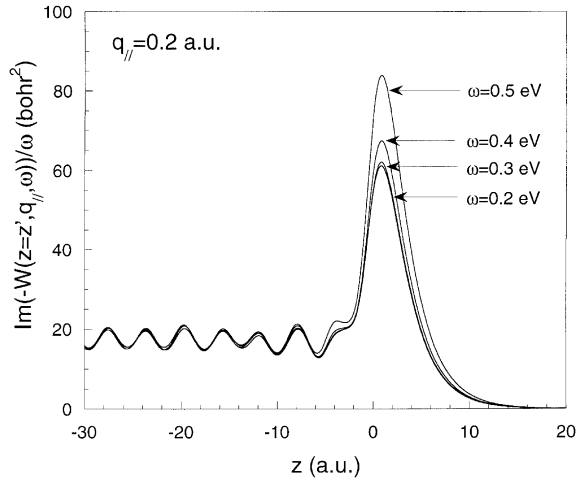


Fig. 3. Imaginary part of the scaled RPA screened interaction $\text{Im}[-W(z, z; \mathbf{q}_{\parallel}, \omega)]/\omega$ of Eq. (7) versus z , for $q_{\parallel} = 0.2a_0^{-1}$ (a_0 is the Bohr radius) and various values of ω : 0.2, 0.3, 0.4 and 0.5 eV.

Fig. 4 displays $\text{Im}[-W(z, z; \mathbf{q}_{\parallel}, \omega)]/\omega$ as a function of z , for $\omega = 0.2$ eV and for various values of $q_{\parallel}$. While $\text{Im}[-W]/\omega$ is enhanced at the surface, for the smallest values of $q_{\parallel}$, by a factor of 3 or 4 in the frequency range $\omega = 0.2$ –0.5 eV, this enhancement becomes very small for the largest values of $q_{\parallel}$ that we have explored. These calculations indicate that only transitions with $q < 0.4a_0^{-1}$ are affected by the strong anisotropy at the surface.

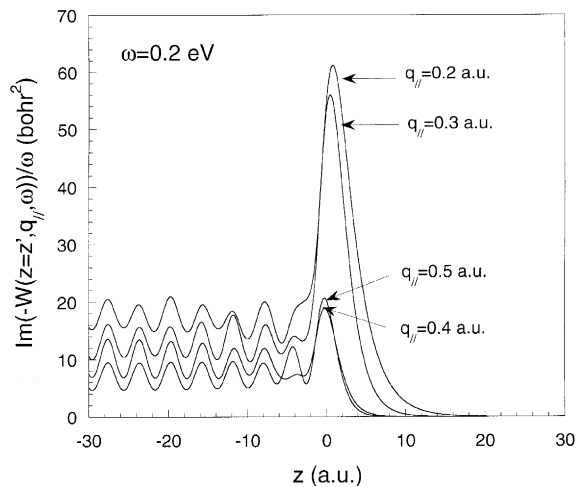


Fig. 4. As in Fig. 3, for $\omega = 0.2$ eV and various values of $q_{\parallel}$: 0.2, 0.3, 0.4 and $0.5a_0^{-1}$.

4. Lifetime broadening

We compute the lifetime broadening of Shockley surface states from Eq. (7) with a realistic description of the RPA screened interaction, as described in the previous section. Although Eq. (7) has been derived by assuming that our electron system is translationally invariant in the plane of the surface, we account for the potential variation parallel to the surface through the introduction of a realistic effective mass into Eqs. (5) and (6), and also through the introduction into Eq. (7) of initial and final wave functions that change along the actual dispersion curve of each state. The effective mass of bulk states has been chosen to increase from our computed values of 0.31, 0.25 and 0.21 m_e at the bottom of the gap in Cu(1 1 1), Ag(1 1 1) and Au(1 1 1), respectively, to the free-electron mass m_e at the bottom of the valence band. The z -dependent initial and final wave functions $\phi_i(z)$ and $\phi_f(z)$ have been recalculated for each value of $\mathbf{k}_{\parallel}$ and $\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel}$, respectively, as was done at the Γ point, with use of the 1D hamiltonian described in the previous section.

As the relaxation of Shockley surface-state electrons and holes may proceed either through the *interband* coupling with bulk states (3D channel) or through the *intra-band* coupling, within the surface state itself, with surface states of different wave vector parallel to the surface (2D channel), we also consider the decay of electrons and holes in 3D and 2D uniform systems. Introduction of Eq. (10) into Eq. (8) and then Eq. (8) into Eq. (7), with both $\phi_i(z)$ and $\phi_f(z)$ replaced by plane waves, yields [26]

$$\tau_{3D}^{-1} = \frac{\sqrt{\pi q_F}}{8q_F^2} \left[\tan^{-1} \sqrt{\pi q_F} + \frac{\sqrt{\pi q_F}}{1 + \pi q_F} \right] \frac{(E - E_F)^2}{k}, \quad (11)$$

k being the momentum of the excited electron or hole. On the same level of approximation, the 2D decay rate is given by [27,28],

$$\tau_{2D}^{-1} = \frac{E_F}{4\pi} \left[-\ln \frac{|E - E_F|}{E_F} + \frac{1}{2} + \ln \frac{2q_{2D}^{TF}}{q_F} \right] \left(\frac{E - E_F}{E_F} \right)^2, \quad (12)$$

where $q_{2D}^{TF} = 2m$ is the TF screening wave vector in 2D, and m is the electron mass.

4.1. Surface-state holes at Γ

The partially occupied Shockley surface-state band forms a uniform 2D electron gas, with the 2D Fermi energy being given by the band-edge of the surface state, i.e., $E_F = 445, 67$ and 505 eV for the (1 1 1) surfaces of Cu, Ag and Au, respectively. Our full calculation for the intraband linewidth of the band-edge surface-state hole on the (1 1 1) surfaces of Cu, Ag and Au is presented in Fig. 5 by full squares, together with the linewidth of Eq. (12) with $E = 0$ and the electron mass m chosen to be either the free-electron mass (solid line) or the surface-state effective mass (full circles). We find that calculations based on a pure 2D electron gas are larger than the actual intra-band contribution to the linewidth by a factor of ~ 7 . This large discrepancy is due to the fact that electron–electron interactions within the actual Shockley surface-state

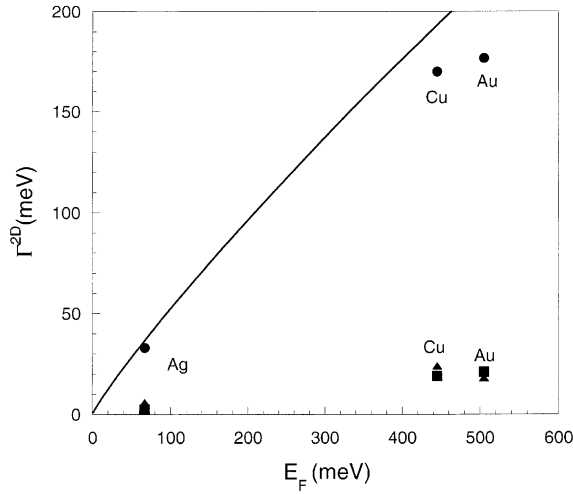


Fig. 5. Solid line represents linewidth of holes at the bottom ($E = 0$) of a 2D free-electron gas, as obtained from Eq. (12) with $m = 1$ versus the the 2D Fermi energy. Squares represent our full calculation for the intraband contribution to the linewidth of band-edge ($\mathbf{k}_{\parallel} = 0$) Shockley surface-state holes on the noble metals Cu, Ag and Au. 2D free-electron gas predictions of Eq. (12) with $E_F = 445$ meV and $m = 0.42$ (Cu), $E_F = 67$ meV and $m = 0.44$ (Ag) and $E_F = 505$ meV and $m = 0.28$ (Au) are represented by circles. Triangles represent experimentally determined inelastic linewidths taken from [14] (after subtraction of estimated electron–phonon linewidth of 8, 5.2 and 5.2 meV for Cu(111), Ag(111) and Au(111), respectively).

2D band are strongly screened by the underlying 3D bulk electron system, thereby, reducing the scattering probability.

Separate intraband and interband contributions to the linewidth of Shockley surface-state holes at the Γ point of the projected bulk band-gap of the (111) surfaces of Cu, Ag and Au are displayed in Table 1. The 3D linewidth of bulk free holes with the same energy, as obtained from Eq. (11), is also shown in this table. Differences between our full interband calculations and those obtained from Eq. (11) arise from (a) the enhancement of $\text{Im}[-W]$ at the surface, which increases the linewidth, (b) localization of the surface-state wave function in the direction perpendicular to the surface and (c) the restriction that only bulk states with energy lying below the projected band-gap are allowed. Both localization of the surface-state wave function and the presence of the band-gap reduce the linewidth, and therefore,

Table 1
Decay rates, in linewidth units (meV), of the Shockley surface-state hole at the Γ point of the noble metals^a

Surface	Energy	3D	Inter	Intra	Total
Cu(111)	–445	5.9	6	19	25
Ag(111)	–67	0.18	0.3	2.7	3
Au(111)	–505	10	8	21	29

^a Decay rates in a 3D free-electron gas of holes with the energy of the Shockley surface-state at Γ are also displayed.

tend to compensate the enhancement of $\text{Im}[-W]$ at the surface. In the case of Cu(111) this compensation is nearly complete, thereby yielding an interband linewidth that nearly coincides with the 3D linewidth of free holes. However, this is not necessarily the case for other materials, depending on the surface band structure.

The impact of the enhanced $\text{Im}[-W]$ at the surface on both interband and intraband contributions to the Shockley surface-state hole linewidth at the Γ point in Cu(111) is illustrated in Fig. 6. In this figure, our full calculations of the interband and intraband contributions to the total inelastic linewidth (full circles) are compared to the results we have also obtained from Eq. (7), but with the actual screened interaction replaced by that of Eq. (8) (full triangles). 3D and 2D free-electron gas calculations, as obtained from Eqs. (11) and (12), are represented by open squares. We find that the impact of the surface anisotropy on $\text{Im}[-W]$ (difference between full circles and triangles) is to largely increase both interband and intraband contributions to the linewidth. Fig. 6 clearly shows that the agreement, in the case of Cu(111), between our interband linewidth (full circle) and that obtained from Eq. (11) (open square) is due to a fortuitous cancellation between both localization of the surface-state wave function and the presence of the band-gap, on the one hand, and the enhancement of $\text{Im}[-W]$ at the surface, on the other. We also note from this figure that a large contribution from intraband transitions, strongly screened by the underlying 3D bulk electron system, is responsible for the large differences between the 3D free-electron gas prediction and the experimental results (represented by open triangles), as discussed in [14].

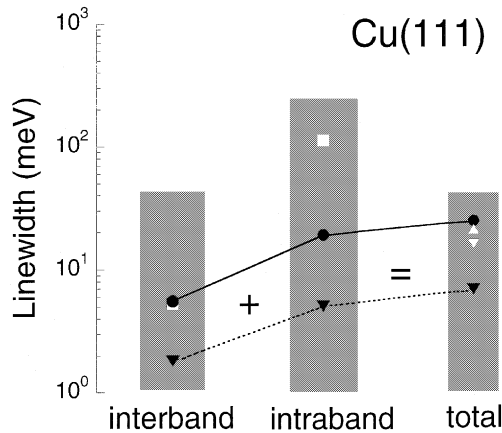


Fig. 6. Band-edge ($k_{\parallel} = 0$) Shockley surface-state hole linewidths in Cu(111). Full circles: Separate interband and intraband contributions to total inelastic linewidth, as obtained from Eq. (7) with our full surface calculation of $W(z, z'; \mathbf{q}, |E_i - E_f|)$. Full triangles: Separate interband and intraband contributions to the total inelastic linewidth, as obtained from Eq. (7) with $W(z, z'; \mathbf{q}, |E_i - E_f|)$ replaced by that of Eq. (8). Open squares: 3D and 2D free-electron gas calculations of interband and intraband linewidths, as obtained from Eqs. (11) and (12), respectively. Experimentally determined inelastic linewidths of [9] (after extrapolation of ARP linewidth to zero defect density) and [14] (after subtraction of estimated electron-phonon linewidth of 8 meV) are represented by the open triangle and the inverted open triangle, respectively.

4.2. Surface-state electrons and holes with $\mathbf{k}_{\parallel} \neq 0$

Our full calculation of the total inelastic linewidth of Shockley surface-state electrons and holes on Cu(111), as obtained from Eq. (7), is shown in Fig. 7 (solid line with circles) versus the surface-state energy. Separate interband and intraband contributions to the linewidth are also represented in this figure, by solid lines with triangles (interband) and inverted triangles (intraband), and the linewidth of bulk free-electrons with the same energy, as obtained from Eq. (11), is represented by a dotted line. Measurements of the linewidth of excited holes at the surface-state band edge ($\mathbf{k}_{\parallel} = 0$) are represented by open triangles, and the STS measurements for surface-state electrons reported by Burgi et al. [15] ($\mathbf{k}_{\parallel} \neq 0$) are represented by full squares.

We find that the fortuitous agreement between the actual interband linewidth and that derived from Eq. (11) is present not only for surface-state holes at the Γ point, but also for surface-state electrons and holes near the Fermi level. Hence, the

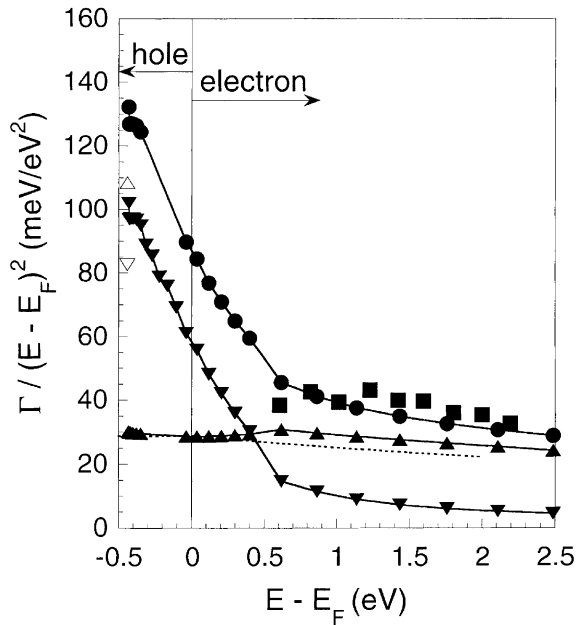


Fig. 7. Scaled inelastic linewidth of Eq. (7), $\tau^{-1}/(E - E_F)^2$, of Shockley surface-state electrons and holes in Cu(111), as a function of surface-state energy. Total linewidth is represented by a solid line with circles. Intraband and interband contributions to the linewidth are represented by solid lines with triangles (interband) and inverted triangles (intraband). 3D free-electron gas prediction of Eq. (12) is represented by a dotted line. Experimentally determined inelastic linewidths of [9] (after extrapolation of the ARP linewidth to zero defect density) and [14] (after subtraction of an estimated electron–phonon linewidth of 8 meV) are represented by the open triangle and the inverted open triangle, respectively, as in Fig. 6. Full squares represent STS measurements of linewidth (with no subtraction of electron–phonon contribution) of surface-state and surface-resonance electrons reported in [15].

interband linewidth shows the $(E - E_F)^{-2}$ energy dependence that is present in the case of a 3D free-electron gas.

Fig. 7 shows that at the surface-state band edge ($k_{\parallel} = 0$) the intraband linewidth represents an 80% of the total linewidth (see also Table 1). Nevertheless, as the surface-state wave vector parallel to the surface increases, the surface-state wave function acquires a bulk-like character, with a larger penetration into the bulk, and the intraband contribution to the linewidth decreases very rapidly. This conclusion explains the experimental observation that while 3D free-electron gas predictions of surface-state hole lifetimes are too large, they are in the case of surface-state electrons (above the Fermi level) comparable to measured lifetimes.

Open triangles in Fig. 7 represent the inelastic contribution to measured linewidths of Shockley surface-state holes at the Γ point, which are to be compared with our calculated linewidth at this point (full circle). Since our model, which correctly reproduces the behaviour of the s–p valence states, does not include screening from *d* electrons, differences between measured linewidths (open triangles) and our calculations (full circles) are expected to be due to the effect of virtual transitions, giving rise to additional screening by *d*-electrons [29], as discussed in [14].

The STS measurements represented in Fig. 7 by full squares include both inelastic and electron–phonon contributions to the surface-state linewidth. Hence, one must be cautious in the comparison of these measurements with our calculations. Electron–phonon linewidths of typically 8.0 in Cu(111) [30], which are essentially independent of the surface-state energy, yield theoretical predictions for the total linewidth that are above the experimental observation, especially for the lowest surface-state energies explored. This discrepancy between theory and experiment could be partially compensated by the screening of *d*-electrons, which as in the case of surface-state holes at the Γ point, reduce the inelastic linewidth.

5. Summary and conclusions

We have reported theoretical investigations of surface-state electron and hole lifetimes in the noble metals Cu, Ag and Au. We have also presented self-consistent calculations of the screened interaction, and have investigated the role that the partially occupied 2D surface-state band and the underlying 3D electron gas play in the relaxation mechanism.

We have reached the conclusion that, while the linewidth of surface-state excited holes at the Γ point of the (111) surfaces of the noble metals is dominated by a 2D decay channel, major contributions to the electron–electron interaction of surface-state electrons above the Fermi level come from the underlying bulk electrons. This key dependence of the relative contribution of intraband transitions to the total decay rate explains the experimental observation that while 3D free-electron gas predictions of surface-state hole lifetimes are too large, they are in the case of surface-state electrons (above the Fermi level) comparable to measured lifetimes.

Acknowledgements

We acknowledge partial support by the University of the Basque Country, the Basque Hezkuntza, Unibertsitate eta Ikerketa Saila, and the Spanish Ministerio de Educación y Cultura and the Max Planck Research Award funds.

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