Role of bulk and surface phonons in the decay of metal surface states

A. Eiguren¹, B. Hellsing², F. Reinert³, G. Nicolay³, E. V. Chulkov¹,4, V. M. Silkin⁴, S. Hüfner³ and P. M. Echenique¹,4

1. Departamento de Física de Materiales and Centro Mixto CSIC-UPV/EHU,
Facultad de Ciencias Químicas, Universidad del País Vasco/Euskal Herriko Unibertsitatea,
Adpo. 1070, 20018 San Sebastián/Donostia, Basque Country, Spain
2. Department of Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden
3. Fachrichtung Experimentalphysik, Universität des Saarlandes, 66041 Saarbrücken, Germany and
4. Donostia International Physics Center, Paseo de Manuel Lardizabal, 4, 20018 San Sebastián/Donostia, Spain
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We present a comprehensive theoretical investigation of the electron-phonon contribution to the lifetime broadening of the surface states on Cu(111) and Ag(111), in comparison with high-resolution photoemission results. The calculations, including electron and phonon states of the bulk and the surface, resolve the relative importance of the Rayleigh mode, being dominant for the lifetime at small hole binding energies. Including the electron-electron interaction, the theoretical results are in excellent agreement with the measured binding energy and temperature dependent lifetime broadening.

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Understanding the temporal evolution of quasi particles (electron and holes) on metal surfaces is of paramount importance to describe many important phenomena such as the dynamics of charge and energy transfer, quantum interference, localization and many others. This temporal evolution is characterized by a finite lifetime, τ, which refers to the time the quasi particle retains its identity. While the lifetime of an excited electron or hole is determined by many-body interactions, namely electron-electron (e-e) and electron-phonon (e-p) scattering processes, the peak width in an experiment might also be influenced by electron-defect scattering on crystal or surface imperfections. However, it was demonstrated in recent STM and photoemission experiments that these defect contributions can be minimized, making it possible to analyze the pure lifetime broadening due to the formation of a hole in the sp surface state band in the L-gap of the (111)-surface of noble metals.

These Shockley-type surface states form a two-dimensional (2D) electron gas and the e-e contribution to the hole lifetime has been rationalized in terms of a dominant contribution from intraband transitions within the 2D surface state band, screened by the underlying 3D bulk electron system, and in terms of interband transitions (bulk states → surface state). On the other hand an appropriate calculation of the e-p contribution to the lifetime broadening of surface states is still lacking. The present work is an attempt in this direction.

The strength of the e-p coupling is described by the electron mass enhancement parameter λ, which is, in general, energy and momentum dependent. Many properties of metals, such as resistivity, specific heat and superconductivity, reflect the e-p coupling and can be expressed in terms of the Fermi surface-averaged λ-value. It also reflects the high temperature behavior of the broadening Γ_e_p = 2πλkB T, and the e-p contribution to the renormalization of the mass m^∗ = m(1 + λ). The anisotropy of λ is well known and is revealed in e.g. cyclotron resonance measurements.

Typically, the phonon contribution to the decay of surface states is estimated using the Debye phonon model. Within this model the Eliashberg spectral function of the e-p interaction is proportional to the quadratic density of phonon states α^2 F(ω) = λ(ω/ω_D)^2, where ω_D is the Debye energy, λ is usually obtained from measurements or theoretical calculations of bulk properties. However, it is not obvious that this approach should be adequate for surface states or holes when the surface state itself, as well as the surface phonon modes, are not taken into account and furthermore, the low temperature Γ_e_p will depend on the model used. A more rigorous treatment of the e-p contribution is needed especially for surface states close to the Fermi level, because for these states the e-e contribution is small and the electron-phonon interaction becomes dominant even at low temperatures.

In this letter we present an analysis of the e-p coupling contribution to the lifetime broadening of surface electron states taking into account all electron and phonon states involved in the electron-phonon scattering process, in comparison to new energy and temperature dependent high-resolution photoemission data. The theoretical analysis is based on a calculation of the full Eliashberg spectral function. With this approach we are able to resolve in details the contributions from different phonon modes, in particular from the Rayleigh surface mode and bulk phonons and the general temperature dependence. We also obtain the high temperature behavior represented by λ, which is given by the first reciprocal moment of the Eliashberg function. We show that an approach based on (i) Thomas-Fermi screened Ashcroft ion-electron potentials, (ii) one-electron states with first principles quality and (iii) a simple model phonon calculation give results in good agreement with
recently published experimental data \[1, 2, 3, 4\] and data presented here.

The phonon induced lifetime broadening of a surface band state with momentum $\vec{k}_i$ and energy $\omega_i$ is given by

$$
\Gamma_{\text{ep}}(\omega_0) = 2\pi \int_{0}^{\omega_m} \left\{ \alpha^2 F_{\text{ep}}^{2}(\omega) \right\} \left[ 1 + 2 n(\omega) + f(\omega_0 + \omega) - f(\omega_0 - \omega) \right] d\omega ,
$$

(1)

where $\omega_m$ is the maximum phonon frequency and

$$
\alpha^2 F_{\text{ep}}^{2}(\omega) = \sum_{\vec{q},\nu,f} \left| g_{\vec{q},\nu,f}^{\alpha}(\vec{R}_\mu) \right|^2 \delta(\omega - \omega_{\vec{q},\nu}) \delta(\epsilon_{\vec{k}_i} - \epsilon_{\vec{k}_f}),
$$

(2)

where the sum is over final electron states $\vec{k}_f$ of band $f$ and phonon modes $\nu$ with momentum $\vec{q}$.

In Eq. (2) we also make use of the quasi elastic scattering approximation. The $e-p$ coupling constant is given by

$$
g_{\vec{q},\nu,f}^{q,\nu} = \frac{1}{2MN\omega_{\vec{q},\nu}} \times \langle f | \sum_{\mu} \tilde{e}_{\vec{q},\nu}(\vec{R}_\mu) \cdot \tilde{\nabla}_n \tilde{V}_n^\nu(\vec{q}) | i \rangle ,
$$

(3)

summing over the layers $\mu$ of the slab. $M$ and $N$, are the atomic mass and number of ions in each layer of the slab, respectively. $\tilde{e}_{\vec{q},\nu}(\vec{R}_\mu)$ denotes the complex phonon polarization vectors normalized over the slab and $\tilde{V}_n^\mu$ is the screened ion-electron potential. The electron states, of the form $\psi_{n,\vec{k}}(\vec{x}, z) = (z|n) \exp(-\vec{k} \cdot \vec{x})$, where $\vec{k}$ and $\vec{x}$ is the electron momentum and electron coordinate parallel to the surface, respectively are derived from a slab model calculation. This model potential scheme by Chulkov et al. \[8, 9, 10\] produces wave functions in good agreement with those obtained from \textit{ab initio} calculations and energy spectra reproducing experimental data.

The Umklapp processes can be neglected as the Fermi momentum of the noble metal surface states are small (< 0.12 a.u.) in comparison with half the minimum reciprocal vector (< 0.75 a.u.). Furthermore, the maximum Fermi momentum vector of the final bulk states is < 0.74 a.u., which implies that the final states are all confined to the first Brillouin zone. Thus, the contribution from Umklapp processes is less than 10% for small binding energies and vanishes completely approaching the $\Gamma$-point. To obtain the phonon dispersion relations and polarization vectors we perform a calculation using the same force constant model as I of Black et al. \[1\], but in addition, we expand the dynamic matrix in Gottlieb polynomials \[12\] in order to minimize the representation of the surface phonon modes. The force constant is fitted to reproduce elastic constants and bulk phonon frequencies, with surprisingly good agreement with He scattering experiments \[13\].

The screened ion-electron potential is determined by the static dielectric function and the bare pseudo potential, $\tilde{V}_n^\nu(z) = \int d\omega' \tilde{\varepsilon}^{-1}(\omega', q') \tilde{V}_n^{\nu\text{bare}}(z'; q')$, where $q$ is the modulus of the phonon momentum wave vector parallel to the surface and $V_n^{\nu\text{bare}}$ is the 2D-Fourier transform parallel to the surface of the bare ion-electron Ashcroft pseudo potentials \[4\]. We have investigated the quality of the screening using the dielectric function according to Thomas-Fermi and within RPA (constructed from the eigen wave functions and eigen energies of a 31-slab calculation). The difference is about 1% for both $\lambda$ and $\Gamma_{\text{ep}}$ due to a compensating effect. Referring to the surface layer, Thomas Fermi screening is symmetric while RPA yields a screening slightly stronger below and slightly weaker above.

We want to point out that in almost all investigations of the $e-p$ interaction, the relevant electron scattering takes place close to the Fermi surface and only the mean $e-p$ coupling, averaged over the Fermi surface, comes into play. When considering the lifetimes of surface states, the situation is quite different. The $e-p$ coupling becomes state dependent as the probed initial electron state is fixed. For the surface states of the studied noble metal surfaces Cu(111) and Ag(111), not only the Fermi surface is of importance because the binding energy of the initial hole state ranges from zero (Fermi level) to about 0.4 eV.

The intraband electron scattering $(f=i)$ in Eq.(3) can be neglected with the following argument. In the case of intraband transitions in the long wavelength limit, the matrix element of the gradient of the screened ion-electron potential is approximately the expectation value of the force acting on the ions in the direction perpendicular to the surface $\langle \psi_{i,\vec{R}} \cdot \tilde{\nabla}_n \tilde{V}_n^\nu(\vec{x}, \tilde{z}) \rangle \approx \tilde{F}_n \approx |i|\partial \tilde{V}_n^\nu(0) / \partial z |i| \tilde{z}$. It is well known that within linear response, the sum over the forces acting on the ions induced by the electron (hole) must be zero \[15, 16, 17, 18\], thus the matrix element of the sum of gradients of the screened ion-electron must be equal to zero $\sum_n \tilde{F}_n = 0$. Furthermore, the ion displacements forming the phonon modes in the surface region, associated with small $q$ are locally rigid with a coherence length of $2\pi/q$ isotropically in all directions, in parallel and perpendicular to the surface \[15\] From Eqs. (3)—(4), it can be seen that this restriction and the reduced phase space in the intraband scattering process makes this contribution negligible compared to interband contribution.

From Eq. (3) we see that the Eliashberg function is given by the phonon density of states weighted by the electron-phonon coupling strength $g$. In Fig. 1. the calculated phonon dispersion and the Eliashberg function is presented for Cu(111). The Rayleigh surface mode is split of from the bulk phonon band, which gives a lower energy peak in the Eliashberg function, at about ~13 meV in Cu(111). The oscillations in the Eliashberg function reflects the finite number of layers of the model potential (31 layers) in the calculation of electron wave functions and thus have no physical significance.
The high-resolution photoemission experiments presented here were performed with an energy and angular resolution of $\Delta E \approx 3$ meV and $\Delta \Theta \approx 0.3^\circ$, respectively, at VUV photon energy of $h\nu = 21.23$ eV (He I). A detailed description of experimental conditions and sample preparation can be found in Ref. [2]. A complete data set at one temperature, consisting of the photoemission data over an angular range of $\pm 6^\circ$ off normal, was measured within the first 15 min after the last annealing step at $\approx 600^\circ$C. As an example, the inset in Fig. 3 demonstrates the temperature dependence of the normal emission ($\Gamma$ point) spectra on Cu(111) at three different temperatures. For the quantitative analysis we fitted the individual spectra of a temperature series as described in Ref. [17]. The resulting Lorentzian lifetime widths $\Gamma$ (full widths at half maximum: FWHM) are given as open symbols in Fig. 3. The binding energy dependence of the linewidth at low temperature (cf. Fig. 2) was determined from MDC (momentum distribution curve) cuts at the respective energy and are given relative to the linewidth at the Fermi level $E_F$, which is nearly completely determined by the finite angular resolution.

The most interesting hole binding energy region is of course very close to the Fermi level, in particular when the binding energy is less than the maximum phonon energy (see Tab. I). The binding energy dependence is completely determined by the the $e$-p coupling. The contribution from $e$-e interaction is very small, for Cu(111) and Ag(111), $\Gamma_{ee} < 0.2$ meV.

In Fig. 2 we present the calculated $\Gamma_{ep}$, at $T = 30K$, for Cu(111) and Ag(111) together with the experimental results. From a simple Debye model we would expect a cubic binding energy dependence in the region below $\omega_m$, which obviously is not the case. The saturation of $\Gamma_{ep}$ for binding energies exceeding $\omega_m$ is clearly seen in experimental data. Adding the contribution from the $e$-$e$ interaction, values close to the experiment are obtained (see Tab. I). We note from Fig. 2, that the contribution from only the Rayleigh mode gives about 38% of $\Gamma_{ep}$ beyond the maximum phonon frequencies, indicating that bulk phonons give most of the contributions in this range. But for binding energies below the maximum of the Rayleigh mode energy, this mode alone represent on average about the 85% of $\Gamma_{ep}$.

The main signature of the $e$-$p$ contribution to the lifetime broadening is the temperature dependence. For binding energies exceeding $k_BT$ we can neglect the temperature dependence of the $e$-$e$ scattering. The temperature dependence of $\Gamma_{ep}$ was calculated for the hole state in the $\Gamma$ point for Cu(111) and Ag(111). For a comparison with the experimental temperature dependence we show in Fig. 3 the sum of the constant contribution from $\Gamma_{ee}$ and the $T$-dependent $\Gamma_{ep}$. The calculated broadenings are in good agreement with the experimental data points, except for the highest temperature data point for Cu(111).

In the Tab. I we summarize the calculated and measured low temperature results for the lifetime broadening for the surface states of Cu(111) and Ag(111). Summing up the calculated contribution from $e$-$e$ interaction $\Gamma_{ee}$ and the results of the present work for the $e$-$p$ interaction $\Gamma_{ep}$ show the proper trend in comparison with both STM [6] and ARUPS [3] data.

In summary we have presented results from a theoretical and experimental study of the inherent phonon induced lifetime broadening of surface states of the noble metal surfaces Cu(111) and Ag(111). Taking into account the electron and phonon states, including surface states is crucial for the understanding of experimental findings in particular for states close to the Fermi level. The Rayleigh surface phonons are shown to give an important contribution to the phonon-induced lifetime broadening of surface states, in particular for small binding energies. We have demonstrated that for noble metal surface states, simple Thomas Fermi screening of Ashcroft pseudo potentials gives very similar results as a more rigorous treatment of the screening. We find excellent agreements with experiments both with respect to the binding energy and the temperature dependence of the lifetime broadening.

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FIG. 1: (a) The phonon dispersion from a 31 layer slab calculation in the $\Gamma-M$ direction of the S.B.Z. (b) The Eliashberg function of the hole state in the $\Gamma$ point (solid line) and the contribution from the Rayleigh mode to the Eliashberg function (dashed line).

FIG. 2: (a) Lifetime broadening of the Cu(111) surface hole state as a function of binding energy, $\Gamma_{ee} + \Gamma_{ep}$ (solid line), $\Gamma_{ep}$ (dotted line), the Rayleigh mode contribution to $\Gamma_{ep}$ (dashed line) and photoemission data (diamonds). (b) The same as in (a) for Ag(111).

FIG. 3: Lifetime broadening of the Cu(111) and Ag(111) surface hole states as a function of temperature (solid line), $\Gamma_{ee}$ (dotted line) photoemission data (open circles). The inset shows the energy distribution curves (EDC) on Cu(111) for selected temperatures.

### Tables

| Material | $\Gamma_{ee}$ | $\Gamma_{ee} + \Gamma_{ep}$ | $\Gamma_{STM}$ | $\Gamma_{ARUPS}$ | $\lambda$ |
|----------|---------------|-----------------------------|----------------|-------------------|---------|
| Cu(111)  | 6.6           | 14.0                        | 20.0           | 24                | 23 ± 1.0| 0.16   |
| Ag(111)  | 3.6           | 2.0                         | 5.5            | 6                 | 6 ± 0.5| 0.12   |

*This value for $\Gamma_{ee}$ is a lower limit, because the used model does not take into account the confinement of $d$ electrons.*
Cu(111) and Ag(111) binding energy graphs.
Cu(111)

Ag(111)