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# Lifetime of holes and electrons at metal surfaces; electron–phonon coupling

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## Abstract

Surface chemical reactions are influenced by inherent dissipative processes which involve energy transfer between the conduction electrons and the ionic motion. We will discuss how it is possible to model this electron–phonon coupling in order to estimate its importance. A relevant quantity for this investigation is the lifetime of surface localized electron states. A surface state, quantum-well state or surface image state is located in a surface projected band gap and becomes relatively sharp in energy. This makes a comparison between calculations and experimental data most attractive, with a possibility to resolve the origin of the lifetime broadening. We point out the importance of taking into account the phonon spectrum, electron surface state wave functions and the screening of the electron–ion potential.

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## 1. Introduction

Lately, experimental surface science techniques have been used to reveal the fundamental interactions in solids, such as the electron–electron ( $e-e$ ) and the electron–phonon ( $e-p$ ) interactions. An understanding of these interactions is important in nanoscale physics, as quantum size effects become important and the  $e-e$  and  $e-p$  interactions will limit the lifetime of excited one-electron states. In surface

chemistry, a reaction often proceeds via an intermediate electronically excited state. A relevant question is then if the lifetime of this intermediate state is compatible with the time it takes for the reactants to complete the reaction, or at least long enough that a significant fraction will. For this reason, it is important to find the parameters that determine the lifetime of the excitation. The decay channel of an excited electronic state via excitations of secondary electrons has been investigated theoretically in detail for many systems [1–3]. In this paper, we summarize some calculations of lifetimes of surface localized states with focus on the  $e-p$  scattering mechanism. In addition, we discuss the possibility to obtain

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information on phonons and  $e$ - $p$  coupling strength from experiments.

Today, several ways to experimentally investigate lifetimes of surface localized electron states have been presented: angular resolved photoemission electron spectroscopy (ARPES) [4–10], two-photon photoemission (2PPE) techniques [11,12], time resolved two-photon photoemission technique for direct determination of excitation lifetimes [13–24] and different methods based on scanning tunneling spectroscopy [25–31].

## 2. Lifetime broadening

Considering the fact that in general phonons in metals introduce a small perturbation to the ground state electron structure, the corresponding spectral function  $A(\omega, \mathbf{k})$  takes the form of a Lorentzian with respect to energy with the Full Width at Half Maximum (FWHM) given by  $\Gamma_{ep} = 2|\text{Im} \Sigma_{ep}|$ , where  $\Sigma_{ep}$  is the self-energy introduced by the  $e$ - $p$  interaction. Considering a metal slab calculation we have one-electron wave functions and energies

$$\begin{aligned} \psi_{n,\mathbf{k}_{\parallel}}(z, \mathbf{x}) &= \frac{1}{\sqrt{A}} \phi_n(z) e^{i\mathbf{k}_{\parallel} \cdot \mathbf{x}}, \\ \varepsilon_n(\mathbf{k}_{\parallel}) &= \varepsilon_n^0 + \hbar^2 k_{\parallel}^2 / 2m_n, \end{aligned} \quad (1)$$

where  $n$  is the band index,  $\mathbf{k}_{\parallel}$  the momentum parallel to the surface and  $A$  the surface area. In the following, we will suppress the  $\parallel$  index. The  $z$  coordinate is along the surface normal and  $\mathbf{x}$  in the surface plane.

The  $e$ - $p$  coupling function includes the matrix element between the initial ( $i$ ) and final ( $f$ ) electron band

$$\begin{aligned} g_{i,f}^{\nu}(\mathbf{q}) &= \sqrt{\frac{1}{2MN\omega_{\nu}(\mathbf{q})}} \\ &\times \left\langle f \left| \sum_{\mu} \boldsymbol{\varepsilon}_{\mathbf{q}\nu}(\mathbf{R}_{\mu}) \cdot \nabla_{\mathbf{R}_{\mu}} \tilde{V}_q^{\mu} \right| i \right\rangle. \end{aligned} \quad (2)$$

We neglect the frequency dependence of the coupling  $g_{\nu}$  and thus consider the static screening of the electron–ion potential. The approximation is acceptable since the phonon frequencies are in general small in comparison with the energies of the scattered electrons. The coupling function in Eq. (2) is

the result of the standard first-order expansion of the screened electron–ion potential,  $\tilde{V}_q^{\mu}$ , with respect to the vibrational coordinate  $\mathbf{R}_{\mu}$ .  $N$  is the number of ions in each layer,  $M$  is the ion mass,  $\mu$  is the layer index and  $\boldsymbol{\varepsilon}_{\mathbf{q}\nu}(\mathbf{R}_{\mu})$  are the phonon polarization vectors.

The phonon induced lifetime broadening  $\Gamma_{ep} = 2|\text{Im} \Sigma_{ep}|$  is calculated considering a self energy taking into account the lowest order one-phonon Feynman diagram

$$\begin{aligned} \Gamma_{ep}(\omega, \mathbf{k}_i) &= 2\pi \sum_{\nu,\mathbf{q},f} |g_{i,f}^{\nu}(\mathbf{q})|^2 \{ [1 + n(\omega_{\nu}) \\ &\quad - f(\xi_{f,\mathbf{k}_i+\mathbf{q}})] \delta(\omega - \xi_{f,\mathbf{k}_i+\mathbf{q}} - \omega_{\nu}) \\ &\quad + [n(\omega_{\nu}) + f(\xi_{f,\mathbf{k}_i+\mathbf{q}})] \delta(\omega - \xi_{f,\mathbf{k}_i+\mathbf{q}} \\ &\quad + \omega_{\nu}) \}. \end{aligned} \quad (3)$$

To relate to a conceptually simpler picture of the phonons we introduce the Eliashberg function  $\alpha^2 F(\omega)$  [32] which is the phonon density of states weighted by the  $e$ - $p$  coupling function  $g$

$$\alpha^2 F_{\mathbf{k}_i}(\omega) = \sum_{\nu,\mathbf{q},f} |g_{i,f}^{\nu}(\mathbf{q})|^2 \delta(\omega - \omega_{\nu}(\mathbf{q})) \delta(\varepsilon_f - \varepsilon_i), \quad (4)$$

where the last delta function indicates that we consider the quasi-elastic approximation, neglecting the change in the energy of the scattered electron due to absorption or emission of a phonon. Thus we can write  $\Gamma_{ep}$  as an integral over phonon energies. If we consider an initial hole state  $(\omega, \mathbf{k}_i)$  and take into account phonon absorption and emission processes (Fig. 1) we obtain

$$\begin{aligned} \Gamma_{ep}(\omega, \mathbf{k}_i) &= 2\pi \int_0^{\omega_n} \alpha^2 F_{\mathbf{k}_i}(\varepsilon) [1 + 2n(\varepsilon) + f(\omega + \varepsilon) \\ &\quad - f(\omega - \varepsilon)] d\varepsilon, \end{aligned} \quad (5)$$

We then obtain the  $T = 0$  result ( $\Rightarrow n = 0$ ) for  $\Gamma_{ep}$  as a function of hole binding energy  $|\omega|$ .

$$\Gamma_{ep}(\omega, \mathbf{k}_i) = 2\pi \int_0^{|\omega|} \alpha^2 F_{\mathbf{k}_i}(\varepsilon) d\varepsilon. \quad (6)$$

The mass enhancement parameter  $\lambda$  is determined by the derivative of the real part of the self-energy.

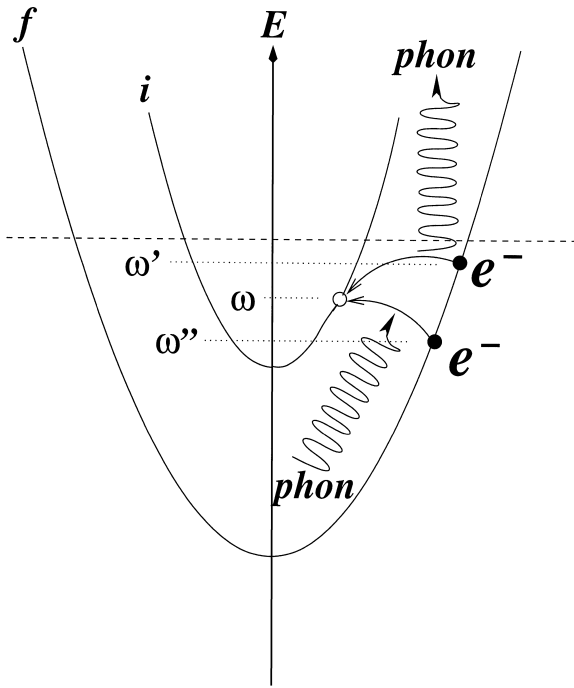


Fig. 1. Schematic drawing of the phonon mediated interband scattering from a band  $f$  (final state of the hole to the band  $i$ , initial state of the hole with energy  $\omega$ ). Both phonon emission and absorption are pictured.

In terms of the Eliashberg function [33],  $\lambda$  is just the first reciprocal moment of the Eliashberg function

$$\lambda(\mathbf{k}_i) = 2 \int_0^{\omega_m} \frac{\alpha^2 F_{\mathbf{k}_i}(\omega)}{\omega} d\omega. \quad (7)$$

If the high  $T$ -limit ( $k_B T \gg \hbar \omega_m$ ) of Eq. (5) is considered, Grimvall [34] has pointed out a very useful result which enables an experimental determination of the mass enhancement parameter

$$\Gamma_{ep}(\omega, \mathbf{k}_i) = 2\pi\lambda(\mathbf{k}_i)k_B T. \quad (8)$$

We thus conclude that the Eliashberg function  $\alpha^2 F$  is a basic function to calculate. Given this function, most of the interesting quantities can be calculated, such as the temperature and also binding energy dependence of the lifetime broadening and the mass enhancement parameter. However, this is no simple task, as all the physics connected to the  $e$ - $p$  interaction is buried in  $\alpha^2 F$ , the phonon dispersion

relation, phonon polarization vectors, one-electron wave functions and last but not least, the gradient of the screened electron-ion potential—the deformation potential.

### 3. Calculations

We now present results from numerical calculations of the phonon induced lifetime broadening  $\Gamma_{ep}$ . Different simple models, based on Debye phonon models, have been discussed in a recent publication [35]. First we consider the quantum-well state (QWS) and the lowest image state (IS) for 1 ML Na on Cu(111) and then the surface states of the clean noble metal surfaces Cu(111) and Ag(111).

#### 3.1. Na/Cu(111)

According to He scattering experiments on the system 1 ML Na on Cu(100) [36], the phonon dispersion relation is flat, referring to the phonon energy versus momentum parallel to the surface. Furthermore, the observed vibrational modes are consistent with ‘organ pipe’ type of modes normal to the surface [36]. Assuming the conditions are similar for 1 ML of Na on Cu(111), we adopt the Einstein model for the transverse overlayer vibrational mode polarized normal to the surface with an energy denoted  $\hbar\Omega_0$ .

The  $e$ - $p$  coupling includes intraband and interband scattering. For the two separately investigated states, the QWS hole and the IS electron in the  $\bar{\Gamma}$ -point, intraband scattering only involves phonon emission for the QWS, while for the IS only, phonon absorption. Interband transitions will include both phonon absorption and emission, illustrated in Fig. 1. In the case of the decay of the IS electron in  $\bar{\Gamma}$ -point (parallel electron momentum equals zero), the narrow energy window for the final states, given by two times the phonon energy, is shown in Fig. 2.

Important quantities for a theoretical estimate of  $\Gamma_{ep}$  are the deformation potential  $\partial V_{ei}/\partial R_z$  and the vibrational energy  $\hbar\Omega_0$ . We evaluate the deformation potential and the vibrational energy from a *first principles* Density Functional Theory (DFT) calculation [37,38] using the Generalized Gradient Approximation (GGA) for the exchange-correlation func-

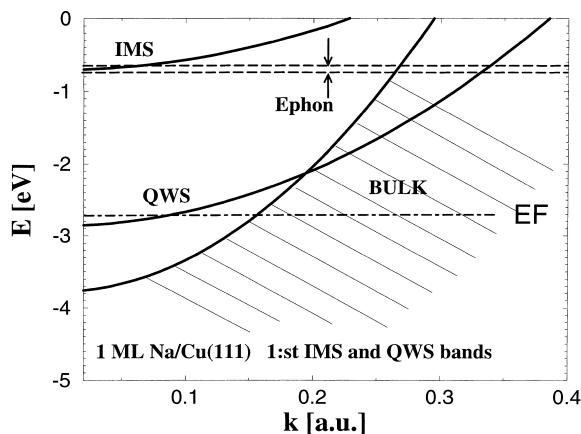


Fig. 2. The one-electron bands of the quantum-well state (QWS) and the first image state (IS) for the system 1 ML Na on Cu(111). Energies are given with respect to the vacuum level. The shaded region shows the region of the bulk bands. The region denoted Ephon show the energy range of possible final states for the scattered IS electron.

tional [39], applying a plane wave basis and ultra soft pseudo potentials [40] for both Na and Cu [41,42]. Applying a total energy analysis, we determined the vibrational energy  $\hbar\Omega_0 = 21$  meV [42]. In an EELS experiment, the vibrational energy has been measured in the coverage range 0–0.35 ML and found to be rather constant  $\approx 21$  meV [43]. Experimental data are available for 1 ML Na on Cu(100) and in this case, the vibrational energy is,  $\hbar\Omega_0 = 18$  meV [36].

Due to the Einstein phonon approximation, the  $e$ - $p$  coupling function in Eq. (2) simplifies considerably. The binding energy in the  $\bar{\Gamma}$ -point of the QWS hole is about 100 meV and the excitation energy (relative to the Fermi level) of the IS electron is 2 eV (Fig. 2). Thus, for any reasonable temperature, the final states for the IS electron will be unoccupied and the final states of the QWS hole will be occupied. The temperature is thus completely determined by the phonon occupation numbers  $n(T, \Omega_0)$ .

To compare with normal photoemission experiments for the QWS decay we add the contribution from the decay channel due to  $e$ - $e$  scattering,  $\Gamma_{ee}$ , in Fig. 3. The reported normal photoemission data [44]

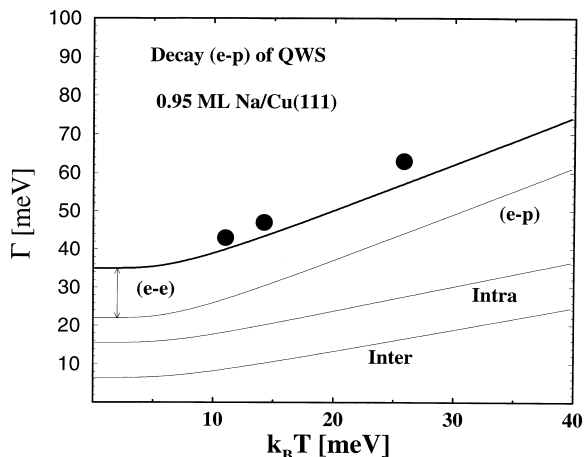


Fig. 3. The lifetime broadening of the QWS of 0.95 ML Na on Cu(111) in the  $\bar{\Gamma}$ -point calculated as a function of temperature. The contribution to  $\Gamma_{ep}$  from intraband and interband scattering is denoted INTRA and INTER. The normal photoemission data are from Ref. [44] (filled circles). The size of the filled circles corresponds to the experimental resolution of about 5 meV.

is taken for 0.95 ML Na on Cu(111). For this coverage, the hole binding energy is 80 meV [44]. The calculated mass enhancement factor  $\lambda = 0.23$  agrees well with the experimentally determined value from the  $\Gamma$  slope versus temperature,  $\lambda = 0.22$  [44]. Adding  $\Gamma_{ee}$  and  $\Gamma_{ep}$  we obtain reasonable agreement with experiment as seen in Fig. 3.

High-resolution two-photon photoemission measurements have been used to determine the lifetime broadening of the three IS of the system 1 ML Na/Cu(111) [12]. The lowest lying IS was reported to have a FWHM of 140 meV [12]. In Fig. 4 we show our results for  $\Gamma_{ep}$  versus temperature. First of all, in comparison with experiment, the decay of the IS due to absorption or emission of phonons seems unimportant with less than a 10 meV contribution to the broadening. We find that the most efficient decay channel for the excited electron is to scatter into the QWS band [35].

We conclude that when comparing the calculated  $\Gamma_{ep}$  for the IS and the QWS, the latter is an order of magnitude greater. The physical reason is that the IS wave function has its center of gravity further out towards vacuum in comparison with the wave func-

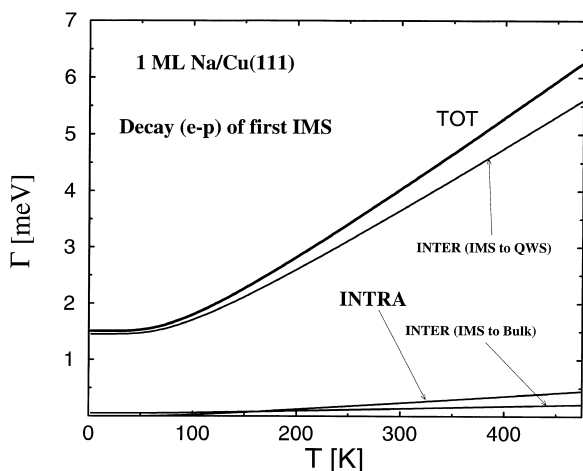


Fig. 4. Phonon induced lifetime broadening of the first image state of 1 ML Na on Cu(111) in the  $\bar{F}$ -point calculated as a function of a temperature.

tion of the QWS. This yields a much smaller overlap with the deformation potential and the bulk states (in the case of interband scattering).

### 3.2. Cu(111) and Ag(111)

We present results here from a recent calculation of the lifetime broadening of the intrinsic surface states of the noble metal surfaces Cu(111) and Ag(111) compared to high resolution ARPES data [45]. In Fig. 5, the schematic band structure is presented.

Considering the  $e$ - $p$  interaction, the aim was to take into account in some detail the phonons, both bulk and surface modes. To achieve the phonon dispersion and the phonon polarization vectors we carried out a slab calculation [45]. In comparison with the Na/Cu(111) study described above, we applied a simpler description of the electron-ion potential which determines the deformation potential that drives the electron scattering. We adopted the Ashcroft pseudo potentials as bare electron-ion potentials, parameterized according to Ashcroft and Langreth [46]. We have investigated the screening of the bare potentials by applying the dielectric function according to both Thomas-Fermi and RPA (con-

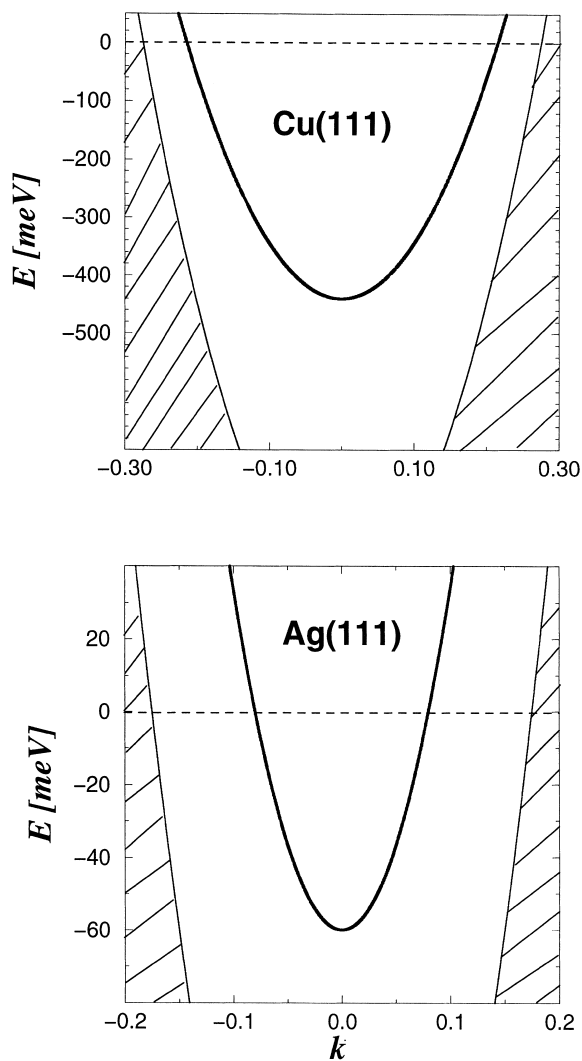


Fig. 5. Schematic drawing of the band structure of Cu(111) and Ag(111) versus parallel momentum in units of  $\text{\AA}^{-1}$ . The solid line indicates the surface state band, the dashed horizontal line the Fermi level and the shaded regions the bulk band region.

structed by the eigen wave functions and energy eigen values from a 31-layer slab calculation). The two different types of screening gave a difference of about 1% for the mass enhancement factor ( $\lambda$ ) and the phonon induced lifetime broadening ( $\Gamma_{ep}$ ) due to compensating effects [35].

Calculating  $\Gamma_{ep}$ , we have to take into account

intraband and interband scattering of electrons and also possibly Umklapp processes. For the surface states of the studied noble metals, the Umklapp processes can be neglected as the Fermi momentum of the surface states are small ( $<0.12$  a.u.) in comparison with half the minimum reciprocal vector ( $|\mathbf{G}|/2 < 0.75$  a.u.) [35]. Furthermore, the intraband scattering is neglected as in this case, the ion displacements forming the phonon modes in the surface region, associated with small  $q$  are locally rigid within a large coherence length of  $2\pi/q$  isotropically in all directions, parallel and perpendicular to the surface. The maximum phonon momentum corresponds to a coherence length of about 26 a.u., which exceeds the extension of the surface state wave function in the direction of the surface normal. Also taking into account the reduced phase space for an intraband scattering process makes the intraband contribution negligible compared to interband scattering. A more detailed analysis will be presented in a coming publication [47].

We now turn to the results of the calculations concerning the hole binding energy and temperature dependence of the studied surface states. In Fig. 6, we present the calculated  $\Gamma_{ep}$ , at  $T = 30$  K, for Cu(111) and Ag(111). The calculated structure of  $\Gamma_{ep}$  in the small binding energy region, seen in Fig. 6, is determined by the Eliashberg function which reflects the real phonon density of states of the system. The high resolution ARPES data show some of these structures, indicating the possibility to experimentally obtain the Eliashberg function at low temperatures. This will be discussed further in the section below. We also note that the saturation of  $\Gamma_{ep}$  at  $\omega = \omega_m$  ( $\approx 30$  meV for Cu(111) and 20 meV for Ag(111)) is also seen in the experiment.

Adding the contribution from the  $e-e$  interaction, values close to the experiment are obtained [45]. We note from Fig. 6 that the contribution from the Rayleigh surface mode gives an important contribution in particular for very small binding energies.

The main signature of the  $e-p$  contribution to the lifetime broadening is the temperature dependence. The temperature ( $T$ ) dependence of  $\Gamma_{ep}$  was calculated for the hole state in the  $\bar{\Gamma}$  point for Cu(111) and Ag(111). The  $T$ -dependence of the full lifetime broadening is shown in Fig. 7. The calculated full lifetime broadenings for both Cu(111) and in par-

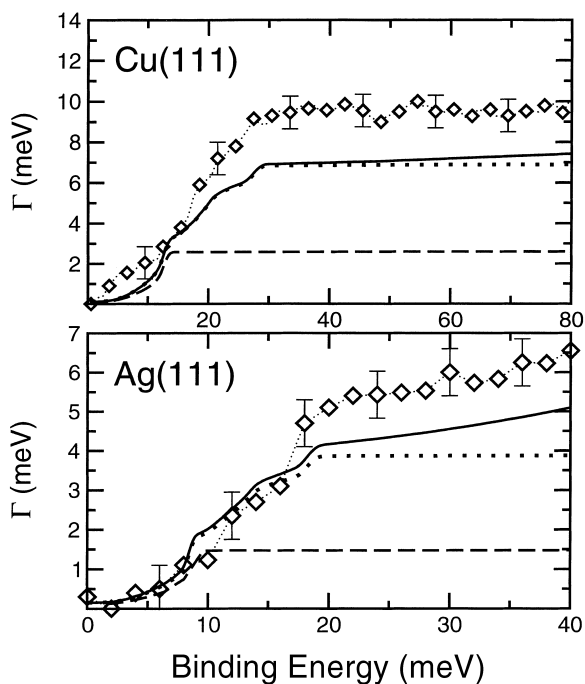


Fig. 6. Lifetime broadening of the Cu(111) and Ag(111) surface hole state as a function of binding energy,  $\Gamma_{ee} + \Gamma_{ep}$  (solid line),  $\Gamma_{ep}$  (dotted line) and the Rayleigh mode contribution to  $\Gamma_{ep}$  (dashed line).

ticular for Ag(111), are in excellent agreement with the experimental data [45].

### 3.3. Low- $T$ determination of $\lambda$

It is in principle possible to extract the contribution from the  $e-p$  scattering from experiments due to its temperature dependence. The strength of this coupling, represented by the electron mass enhancement factor  $\lambda$ , is typically deduced by measuring in the temperature regime well beyond the maximum phonon energy where  $\Gamma = 2\pi\lambda k_B T$ . However, for some systems, stable data are difficult to obtain at required temperatures. An alternative way to determine  $\lambda$  is instead to map out  $\Gamma$  at low temperatures for binding energies less than the maximum phonon energy. According to Eq. (6), the derivative of an experimentally measured  $\Gamma$  with respect to the binding energy determines the Eliashberg function directly and  $\lambda$  is then obtained as its first reciprocal

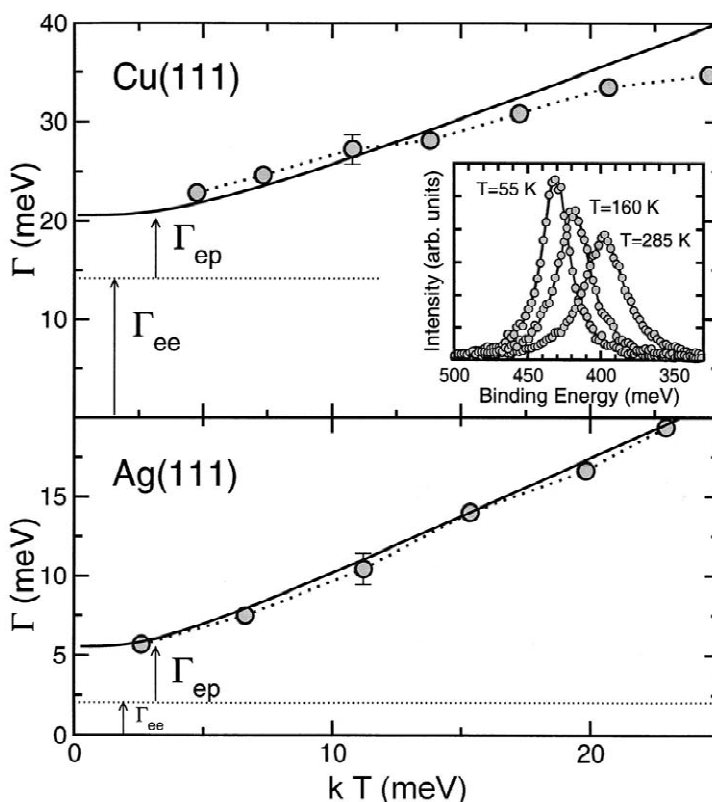


Fig. 7. Lifetime broadening of the Cu(111) and Ag(111) surface hole states as a function of temperature (solid line),  $\Gamma_{ee}$  (dotted line).

moment. In addition, the Eliashberg function also yields information on the phonon spectrum.

However, this is not an easy task as a derivative enhances all structures. In particular for very small binding energies, when  $\Gamma$  is comparable to the experimental resolution we cannot expect any reliable results. Bearing in mind the tremendous improvement in the energy resolution in PES [10], these ideas should be of future interest.

#### 4. Concluding remarks

We have demonstrated that it is possible to understand reasonably well experimental data concerning the  $e-p$  induced lifetime broadening of quantum-well states, image states and surface states. Of major importance is to take into account bulk and surface electron and phonon states.

There are presently many interesting theoretical

investigations of the  $e-p$  interaction on metal surfaces to be done. For example, to explain the observed seemingly strong  $e-p$  coupling for metallic multi-overlayer structures, taking into account properly the phonons. When it comes to methods, full scale *first principles* calculations of  $\Gamma_{ep}$  have to be done.

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