



## Model Eliashberg functions for surface states

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### ABSTRACT

We present a simplified procedure for the analysis of the phonon-induced lifetimes of surface states. The model includes information about the electron and phonon structure and is thus more reliable than procedures based on phonon Debye models. We apply the model to calculate the lifetime broadening of Cu(1 1 1) and Al(0 0 1) surface states. The obtained Eliashberg functions and lifetimes are in reasonable agreement with previous detailed studies.

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## 1. Introduction

In many ultra-fast processes on surfaces such as vibrational damping or decay of surface or quantum-well states, electron–phonon coupling plays a crucial role. Recent progress in experimental techniques in surface science reveals the quantitative importance of the electron–phonon coupling in such surface dynamics [1–5]. For the analysis of experimental results theoretical investigations are indispensable. In many of previous works the analysis of the phonon-induced lifetime broadening is based on the Debye model or Einstein model [3]. In the Debye model, the phonon density of states is determined by the Debye frequency and in addition the electron–phonon coupling matrix elements are assumed to be independent of both electron and phonon momentum. In this procedure the importance of the coupling between electronic surface states and surface phonon modes are ignored. One would for example expect that localized electronic

surface states couple more strongly to surface localized phonon modes than to bulk phonon modes. This fact has been shown in detailed theoretical investigations of phonon-induced lifetime broadening of several metal surfaces [6,7]. However, *first principles* calculations based on the density functional perturbation theory (DFPT) [8] are computationally highly demanding and so reliable simplifications are desirable.

The approximation of the Eliashberg spectral function presented in this paper, includes the most important features of the surface electronic state and the phonon structure. We apply this procedure to calculate the lifetime broadening of surface states of Cu(1 1 1) and Al(0 0 1) in the  $\bar{\Gamma}$ -point and show reasonable agreement with previous more elaborate studies. The surface state of Cu(1 1 1) is localized around the surface layer while that of Al(0 0 1) is more delocalized deeply penetrating into the bulk [9]. This difference should result in the qualitative difference of the Eliashberg functions for these two surface states, which is shown in previous studies [7]. Because of this reason we choose the surface states of Cu(1 1 1) and Al(0 0 1) as examples for the test of our proposed procedure in this study.

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## 2. Theory

The general expression for the phonon-induced lifetime broadening  $\Gamma_{ep}(T)$  is [1]

$$\Gamma_{ep}(T) = 2\pi\hbar \int_0^{\omega_m} \alpha^2 F(\omega) [1 + 2n(\omega; T) + f(-\varepsilon_b + \omega; T) - f(-\varepsilon_b - \omega; T)] d\omega \quad (1)$$

where  $f$  and  $n$  are the electron and phonon distribution functions,  $\omega$  is the phonon frequency,  $\omega_m$  is the maximum phonon frequency.  $T$  is the temperature of the system and  $\varepsilon_b$  is the binding energy of the surface states.  $\alpha^2 F(\omega)$  is the electron–phonon coupling Eliashberg function

$$\begin{aligned} \alpha^2 F(\omega) &= \sum_{\nu, \vec{q}, \vec{k}} |g_{\nu, \vec{q}}^{\vec{k}}|^2 \delta(\omega - \omega_{\nu, \vec{q}}) \\ &= \sum_{\nu, \vec{q}} \sum_{\vec{k}} \langle \psi_{ss} | A_{\nu, \vec{q}} | \psi_{\vec{k}} \rangle \langle \psi_{\vec{k}} | A_{\nu, \vec{q}}^\dagger | \psi_{ss} \rangle \delta(\omega - \omega_{\nu, \vec{q}}) \end{aligned} \quad (2)$$

where  $g_{\nu, \vec{q}}^{\vec{k}}$  is the electron–phonon coupling matrix element,  $\psi_{\vec{k}}$  is the wavefunction of the final state and  $\psi_{ss}$  is the wavefunction of the surface state. The summation is performed over the possible final states with the momentum  $\vec{k}$  and the phonon mode  $\nu$  with the momentum  $\vec{q}$ .  $A_{\nu, \vec{q}}$  is defined as

$$A_{\nu, \vec{q}} = \sum_l \sqrt{\frac{\hbar}{2N_l M_l \omega_{\nu, \vec{q}}}} \sum_j \vec{e}_{\nu, \vec{q}}(j) \vec{\nabla}_{\vec{R}} V(j, \vec{r}) \quad (3)$$

where  $l$  is the layer index and  $j$  is the atom index in each layer.  $N_l$  is the number of the ions in each layer and  $M_l$  is the ion mass.  $\vec{R}$  and  $\vec{r}$  are the nuclei and electron coordinate, respectively.  $\vec{e}_{\nu, \vec{q}}(j)$  is the phonon polarization vector and  $V(j, \vec{r})$  is the screened electron-ion potential.

As long as  $\hbar\omega \ll k_B T$ , the width is approximately linear in temperature [1]

$$\Gamma_{ep} = 2\pi\lambda_0 k_B T \quad (4)$$

where the low temperature lambda value,  $\lambda_0$  is given by

$$\lambda_0 = 2 \int_0^{\omega_m} \frac{\alpha^2 F(\omega)}{\omega} d\omega \quad (5)$$

From fitting to measured width at high temperatures, assuming a temperature independent additional non-phonon-induced lifetime broadening, we can obtain the lambda value  $\lambda_0$  applying Eq. (4). If we then apply a Debye phonon model [3] and assume a constant electron–phonon coupling function, we obtain an analytical expression for the Eliashberg function, which is linearly dependent on  $\lambda_0$ . We can then determine the  $\Gamma_{ep}$  value at  $T = 0$  from Eq. (1), which is

$$\Gamma_{ep}(0) = 2\pi\hbar \int_0^{\omega_m} \alpha^2 F(\omega) d\omega \quad (6)$$

However, this procedure ignores the importance of in particular low energy surface phonon modes, which are expected to couple strongly to the electronic surface state. As will be shown in this work, this fitting procedure will in general overestimate the lifetime broadening. Furthermore, we gain no understanding of the variation of measured line widths, referring to particular properties of electron and phonon structures.

The main approximations in our modeling of the Eliashberg function are that (i) the deformation potential is localized within the atomic volume of each atom [1,10] and (ii) the initial electronic states  $\vec{k}$  in Eq. (2) form an approximative complete set within this

volume. Finally, after some additional approximations [11] we have

$$\alpha^2 F(\omega) = \sum_{\nu, \vec{q}} B_{\nu, \vec{q}} \delta(\omega - \omega_{\nu, \vec{q}}). \quad (7)$$

$$B_{\nu, \vec{q}} = \Delta V^2 \frac{\hbar^2}{2\omega_{\nu, \vec{q}}} \sum_l \frac{I_l}{N_l M_l} \sum_j \vec{e}_{\nu, \vec{q}}(l, j) \otimes \vec{e}_{\nu, \vec{q}}^*(l, j) \quad (8)$$

where

$$I_l = \int_{z_{l+1}}^{z_l} \left( \int \int |\psi_{ss}(z)|^2 dx dy \right) dz \quad (9)$$

where  $z_l$  is located in the middle between the layer  $l$  and  $l + 1$ .  $\Delta V$  is an overall average of the atomic deformation potential.

Except for a constant factor  $\Delta V^2$ , we have obtained a reasonable approximation of the energy dependence of the Eliashberg function which can be calculated relatively easily. The inputs are the dispersion relation  $\omega_{\nu, \vec{q}}$  with corresponding polarization vector fields  $\vec{e}_{\nu, \vec{q}}$  and in addition the electronic surface state wavefunction.

## 3. Results and discussion

Applying the scheme presented in the previous section, we have calculated the phonon-induced lifetime broadening of the surface states of Cu(1 1 1) and Al(0 0 1) at the  $\bar{\Gamma}$ -point. The phonon structures are obtained with the single force constant model [12,13] and the surface state wavefunctions are obtained from the one-dimensional potentials proposed by Chulkov et al. [9]. In the calculations of electronic surface state wavefunctions and phonon structure, a 31 layers thick slab is used. In Fig. 1, where we plot  $I_l$ , the deep penetration depth of the surface state wavefunction of Al(0 0 1) is clearly seen in comparison with that of Cu(1 1 1).

We have calculated the Eliashberg functions according to Eqs. (7) and (8) and then fitted the deformation potential parameter  $\Delta V$  in order to reproduce the experimentally determined  $\lambda_0$  values [14–16] (as we have no reliable experimental value for Al(0 0 1), we used a calculated value [17]). The obtained Eliashberg functions as well as the Eliashberg functions obtained with several different Debye models are shown in Fig. 2. The three- and two-dimensional-based Debye models used in this analysis are denoted 3D, 2D and 3D + 2D. For the 3D + 2D Debye model, the surface Rayleigh mode is added to the 3D model. The expressions of the Eliashberg functions of these models are [3]

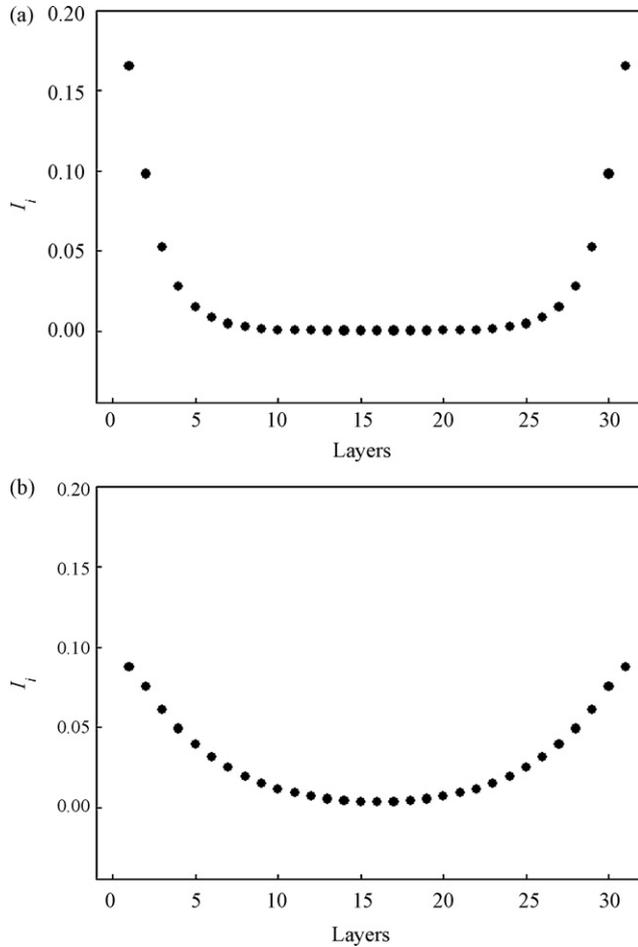
$$\lambda_0 \left( \frac{\omega}{\omega_{DB}} \right)^2 \theta(\omega_{DB} - \omega) \quad (10)$$

$$\left( \frac{\lambda_0}{2} \right) \left( \frac{\omega}{\omega_{DS}} \right) \theta(\omega_{DS} - \omega) \quad (11)$$

$$\left( \frac{1}{2} \right) \lambda_0 \left( \frac{\omega}{\omega_{DB}} \right)^2 \theta(\omega_{DB} - \omega) + \left( \frac{1}{2} \right) \left( \frac{\lambda_R}{2} \right) \left( \frac{\omega}{\omega_R} \right) \theta(\omega_R - \omega) \quad (12)$$

for the 3D, 2D and 3D + 2D Debye model, respectively.  $DB$ ,  $DS$  and  $R$  denote the bulk Debye, the surface Debye and the Rayleigh mode, respectively. Here we assume that  $\lambda_0 = \lambda_R$ . We use 27 meV (Cu(1 1 1)) and 37 meV (Al(0 0 1)) for bulk and surface Debye mode frequencies and 13 meV (Cu(1 1 1)) and 18 meV (Al(0 0 1)) for Rayleigh mode frequencies.

For Cu(1 1 1) there is a prominent peak at 13 meV in the Eliashberg function obtained in this study. This peak is due to the Rayleigh mode, which of course is completely absent in the 3D and



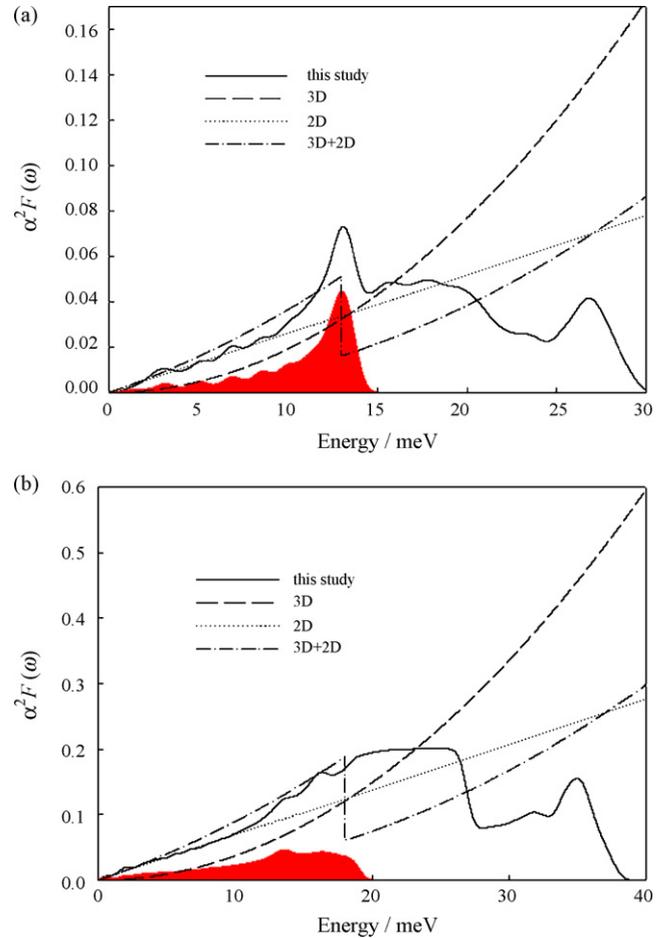
**Fig. 1.**  $I_l$ , the slab layer  $l$  resolved normalization integral of the surface state: (a) Cu(1 1 1) and (b) Al(0 0 1).

2D Debye model. In contrast, such a distinct peak is not observed for Al(0 0 1), due to the surface state less localized at Al(0 0 1) in comparison with Cu(1 1 1). The lifetime broadening at  $T = 0$  is calculated applying Eq. (6). The results, as well as values obtained with Debye models and more elaborate calculations are presented in Table 1.  $\Gamma_{ep}$  values obtained from our model Eliashberg functions are close to the values by 3D + 2D model. In the 3D + 2D Debye model, the contribution from the Rayleigh mode is explicitly taken into account while other Debye models include no information about the surface phonon modes. Thus, the obtained Eliashberg function with the 3D + 2D Debye model is qualitatively similar to the one obtained in this study. This is clearly shown in Fig. 2. The difference between  $\Gamma_{ep}$  and  $\lambda_0$  is the factor of  $1/\omega$  in the integrand (see Eqs. (5) and (6)). Thus low frequency phonon modes have larger contribution in the integration for  $\lambda$  than for  $\Gamma_{ep}$ , which yields a smaller  $\Gamma_{ep}$  value for a fixed  $\lambda_0$  value. The difference in the lifetime broadening (Eq. (1)) of the surface state hole between

**Table 1**  
Calculated  $\Gamma_{ep}$  at  $T = 0$  for Cu(1 1 1) and Al(0 0 1)

	3D	2D	3D + 2D	[7]	DFPT [17]	This study
Cu(1 1 1)	7.9	5.9	5.4	6.9	–	5.7
Al(0 0 1)	40	30	27	18	35	26

We use 27 meV (Cu(1 1 1)) and 37 meV (Al(0 0 1)) for bulk Debye frequencies and 13 meV (Cu(1 1 1)) and 18 meV (Al(0 0 1)) for surface Debye frequencies.  $\lambda_0$  values are 0.14 for Cu(1 1 1) [14–16] and 0.51 for Al(0 0 1) [17].



**Fig. 2.** Calculated Eliashberg functions for the surface state bands in the  $\Gamma$ -point for (a) Cu(1 1 1) and (b) Al(0 0 1). Contributions from Rayleigh modes are shown by red-colored areas. The Eliashberg functions obtained with Debye models are also presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Cu(1 1 1) and Al(0 0 1) can be explained by the difference of the penetration depth of the surface state wavefunctions into the bulk. From Fig. 1, it is clear that the surface state wavefunction of Cu(1 1 1) is more localized near the surface layer and thus more efficiently couples to surface phonon modes (here Rayleigh mode). The obtained Eliashberg functions are in reasonable agreement with previous more elaborate calculations and *first principles* calculation results [7,17], reproducing the difference between Cu(1 1 1) and Al(0 0 1) as a consequence of the difference in electron and phonon structures.

#### 4. Summary

In summary, we present a new approximative calculation scheme for the phonon-induced lifetime broadening of surface states. Results are presented for Cu(1 1 1) and Al(0 0 1) and compared with the Debye model-based methods. The Eliashberg functions are in reasonable agreement with previous detailed studies, revealing the characteristic features of its frequency dependence. We would like to point out that with this calculation scheme, we will be able to study more complex systems, e.g. phonon-induced lifetimes of quantum-well states in overlayers on metals [10], which still is extremely demanding applying *first principles* methods.

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