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Dynamics of electrons and holes at surfaces

E.V. Chulkov [a,b,*], A. Leonardo [b], I.Yu. Sklyadneva [b,c], V.M. Silkin [b]

[a] Departamento de Física de Materiales, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián/Donostia, Basque Country, Spain
[b] Donostia International Physics Center 20018 San Sebastian/Donostia, Basque Country, Spain
[c] Institute of Strength Physics and Materials Science, pr. Academicheskii 2/1, 634021 Tomsk, Russia

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Abstract

We present *ab initio* calculation results for electron–phonon (e–ph) contribution to hole lifetime broadening of the $\bar{X}$ surface state on Al(0 0 1). We show that e–ph coupling in this state is significantly stronger than in bulk Al at the Fermi level. It makes the e–ph decay channel very important in the formation of the hole decay in the surface state at $\bar{X}$. We also present the results for e–e lifetime broadening in a quantum-well state in 1 ML K/Cu(1 1 1). We show that this contribution is not negligible and is much larger than that in a surface state on Ag(1 1 1).

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1. Introduction

Electron excitations in metal systems play an important role in many chemical and physical phenomena. They are essential for energy transfer in photochemical reactions, for excitation mediated desorption and oxidation of molecules at surfaces [1]. Electronic excitations have a profound impact on molecular motion induced by femtosecond laser pulses and play a large role in catalytic reactions [2,3]. They are of paramount importance for spin transport within bulk metals, across interfaces, and at surfaces [4]. The key quantity for the electron excitation is the lifetime of the excited electron which sets the duration of the excitation and in combination with the velocity determines the mean free path of the excited particle. In the last decade the excited electron and hole lifetimes have extensively been studied both theoretically and experimentally in bulk metals, at clean metal surfaces, at surfaces covered with single adatoms and with metal adlayers [5–25]. Despite these studies some important aspects of the excited hole decay are still missed. For instance, nothing is known about decay mechanisms of holes in surface states located in a very narrow energy gap at the border of the Brillouin zone (BZ). Up to now little is known about the hole decay in quantum-well states (QWS) of alkali metal adlayers on metals except for the Na/Cu(1 1 1) system which has been studied in detail both theoretically and experimentally [26–32].

The decay of the excited electrons and holes occurs via electron–electron (e–e), electron–phonon (e–ph) or/and electron–defect (e–def) scattering. The (e–def) scattering can be, in principle, avoided in scanning tunneling spectroscopy (STS) measurements [10,19,23] and strongly reduced in photoemission spectroscopy (PES) study [11]. Finally, the study of electron (hole) lifetimes is reduced to the calculation of e–e and e–ph interactions. In this paper we give the results of *ab initio* calculations of electron–phonon coupling and the contribution of this coupling to the hole decay rate in a surface state at the $\bar{X}$ point for the Al(0 0 1) surface. We show that despite a bulk-like character of this state localized in a very narrow energy gap [33] the e–ph coupling parameter for this state is significantly larger than that in bulk Al at the Fermi level (E_F). It makes the e–ph contribution Γ_{e-ph} important in the formation of the hole lifetime, especially at room and higher temperatures. We also

* Corresponding author at: Departamento de Física de Materiales, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián/Donostia, Basque Country, Spain. Tel.: +34 943 01 82 20; fax: +34 943 01 56 00.
E-mail address: waptctce@sq.ehu.es (E.V. Chulkov).

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analyse the e–e contribution Γ_{e-e} to the hole lifetime in QWS for 1 monolayer (ML) of K on Cu(1 1 1). We show that this contribution is not negligible for the hole decay rate even though the state is very close to E_F and together with the e–ph contribution Γ_{e-ph} it provides the hole decay rate well comparable to that for a clean Cu(1 1 1) surface where the surface state is located much father from E_F.

2. Theory

The phonon-induced lifetime broadening of a hole (electron) state with momentum $\mathbf{k}_i$ and energy $\epsilon_{\mathbf{k}_i}$ is defined as [34]:

$$\Gamma_{e-ph}(\epsilon_{\mathbf{k}_i}) = 2\pi\hbar \int_0^{\omega_m} \alpha^2 F_{\mathbf{k}_i}(\omega) \times [1 - f(\epsilon_{\mathbf{k}_i} - \omega) + f(\epsilon_{\mathbf{k}_i} + \omega) + 2n(\omega)]\mathrm{d}\omega. \quad (1)$$

where f and n are the Fermi and Bose distribution functions, respectively, and ω_m is the maximum phonon frequency. In the quasielastic approximation the Eliashberg spectral function and e–ph coupling parameter are given by

$$\alpha^2 F_{\mathbf{k}_i}(\omega) = \sum_{\mathbf{q},\nu,f} \delta(\omega - \omega_{\mathbf{q},\nu}) \times |g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, \nu)|^2 \delta(\epsilon_{\mathbf{k}_i} - \epsilon_{\mathbf{k}_f}), \quad (2)$$

$$\lambda_{\mathbf{k}_i} = 2\int_0^{\omega_m} \frac{\alpha^2 F_{\mathbf{k}_i}(\omega)}{\omega}\,\mathrm{d}\omega, \quad (3)$$

where $g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, \nu)$ is the e–ph matrix element. The sum is carried out over final electron states $\mathbf{k}_f$ and phonon modes $(\mathbf{q}, \nu)$. When initial and final electronic states remain on E_F and $\lambda_{\mathbf{k}_i}$ is averaged over all initial electron states one obtains the e–ph coupling parameter $\lambda(E_F)$ which determines the electronic mass enhancement. The calculations have been performed within the local density approximation using a linear response approach in a plane-wave pseudopotential representation [35]. The plane-wave basis set is restricted by the kinetic energy cutoff of 16 Ry. To describe the surface we have considered fully relaxed 11-layer Al slabs separated by 7 atomic layers of vacuum. The Brillouin zone (BZ) integrations are performed by using 45 special points in the irreducible surface BZ.

Within a many-body theory the inelastic electron–electron contribution, Γ_{e-e}, to the lifetime broadening of a hole ($E < E_F$) in a quantum state $\psi(\mathbf{r})$ with energy E is obtained as the projection of the imaginary part of the self-energy $\sum(\mathbf{r}, \mathbf{r}; E)$ onto the state itself

$$\Gamma_{e-e} = 2\int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\psi^*(\mathbf{r})\,\mathrm{Im}\sum(\mathbf{r}, \mathbf{r}'; E)\psi(\mathbf{r}'). \quad (4)$$

The self-energy is calculated by using the GW approximation. For details of this kind of calculations we refer to Ref. [30]. Wave functions $\psi(\mathbf{r})$ and energies E for 1 ML K/Cu(1 1 1) have been evaluated using one-dimensional potential proposed for alkali metal adlayer on paramagnetic metals [30]. Parameters of this potential were determined by reproducing the energy gap of Cu(1 1 1) [36] and the experimental energies of QWS and the first image state of 1 ML K/Cu(1 1 1) [26].

3. Results and discussion

3.1. e–ph interaction at Al(0 0 1)

In Fig. 1 we show surface electronic structure of Al(0 0 1) in the $\overline{\Gamma X}$ and $\overline{XM}$ directions. As follows from the figure the $\bar{X}$ surface state is located at energy −4.63 eV at the bottom of a very narrow energy gap. This makes the state very bulk like one in contrast to a very clear surface state at the $\bar{\Gamma}$ point and surface states on Be and (1 1 1) noble metal surfaces [36–39]. In Fig. 2 the calculated Eliashberg function is plotted as a function of phonon energy. The contribution from surface phonon states is also shown. One can see that for phonon energies $\omega \gtrsim 7$ meV the Eliashberg function is mostly determined by the hole interaction with bulk phonons. However, the contribution from surface phonons is not negligible, especially for 5 meV $\lesssim \omega \lesssim$ 23 meV. The obtained e–ph coupling parameter $\lambda = 0.75$ is significantly larger than $\lambda = 0.51$ calculated at the $\bar{\Gamma}$ point for Al(0 0 1) [40]. However, it is well comparable to e–ph coupling in surface states on Be [41,42] and on Bi [43,44]. On other simple metal and noble metal surfaces this coupling is significantly smaller, $\lambda = 0.10$–0.30 [9,45–47].

The calculated Γ_{e-ph} for the $\bar{X}$ surface state is equal to 45 meV at $T = 0$ K and 123 meV at T_{room}. The latter value is well comparable to Γ_{e-e} for the $\bar{\Gamma}$ surface state on Al(0 0 1) ($\Gamma_{e-e} = 131$ meV) and Al(1 1 1) ($\Gamma_{e-e} = 336$ meV) [25]. Since the $\bar{X}$ surface state is of bulk-like character our Γ_{e-ph} can also be compared to Γ_{e-e} for bulk electron states of Al. *Ab initio* calculations [18,48,49] give for excited electron lifetime broadening at $E = 4.6$ eV a value of 100–200 meV. These results show that the e–ph interaction is an important ingredient in the linewidth of the $\bar{X}$ surface state on Al(0 0 1).

3.2. 1 ML K/Cu(1 1 1)

As was shown by Fischer et al. [26] the 1 ML K/Cu(1 1 1) QWS at the $\bar{\Gamma}$ point is located at −60 meV with respect to E_F.

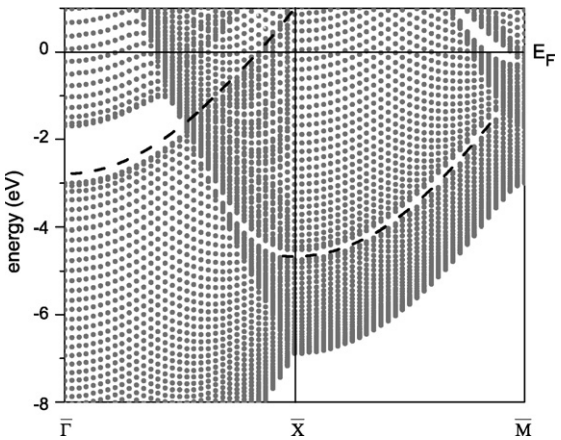

Fig. 1. Calculated Al(0 0 1) electronic structure. The dotted area is a continuum of bulk electron states, the dashed lines trace the $\bar{\Gamma}$ and $\bar{X}$ surface electron states.