Decay mechanisms of single particle excitations in bulk metals and at metal surfaces

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Outline

1. Motivation
2. Sketch of theory
3. Decay mechanisms
4. Results
5. Conclusions

Motivation

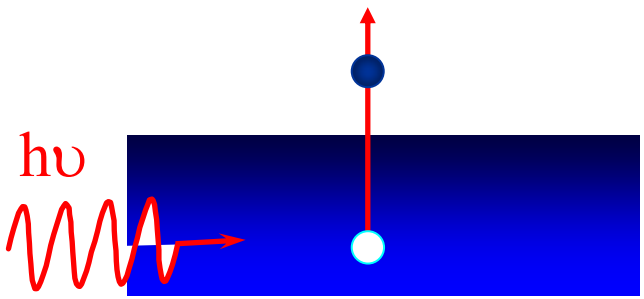
The accurate description of electronic structure is of paramount importance for understanding many properties of different materials. This description usually consist of ***two*** steps.

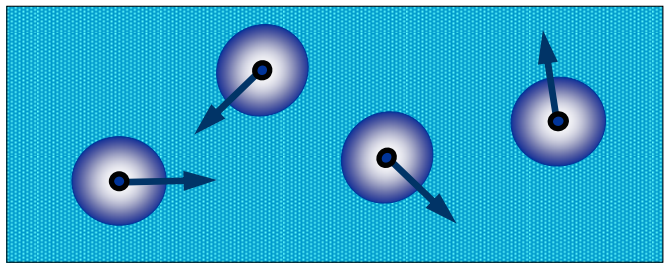
First, electronic structure is calculated in terms of "non-interacting" electrons. Common practice is the use of DFT (LDA, GGA,…) or some model hamiltonians.

Second, by using the DFT one-electron energies and wave functions the electron self-energy (Σ) is evaluated to correct the DFT electronic structure.

Majority of the Σ calculations have been done for $\mathrm{Re}\Sigma$ while $\mathrm{Im}\Sigma$ has been addressed significantly less.

Lifetime of quasiparticles





Interactions between quasiparticles limit how long the corresponding quantum states retain their identity: a quasiparticle is said to have a ***lifetime*** which sets the duration of the excitation. In combination with the velocity, this lifetime determines the ***mean free path***, a measure of influence of the excitation

Importance of lifetime

- charge and spin transport in bulk materials, across interfaces, and at surfaces
- electron dynamics and energy transfer
- localization
- surface photochemistry and catalitical reactions

In general case the decay rate (lifetime broadening) of a quasiparticle measured experimentally can be written as

$$\Gamma = \Gamma_{e\text{-}e} + \Gamma_{e\text{-}ph} + \Gamma_{e\text{-}def} + \Gamma_{corr}$$

$\Gamma_{e\text{-}e}$ - the inverse lifetime contribution due to inelastic electron-electron scattering

$\Gamma_{e\text{-}ph}$ - the contribution from electron-phonon interaction

$\Gamma_{e\text{-}def}$ - the contribution from electron-defect scattering events

$\Gamma_{e\text{-}corr}$ - energy and momentum corrections due to the finite experimental resolution

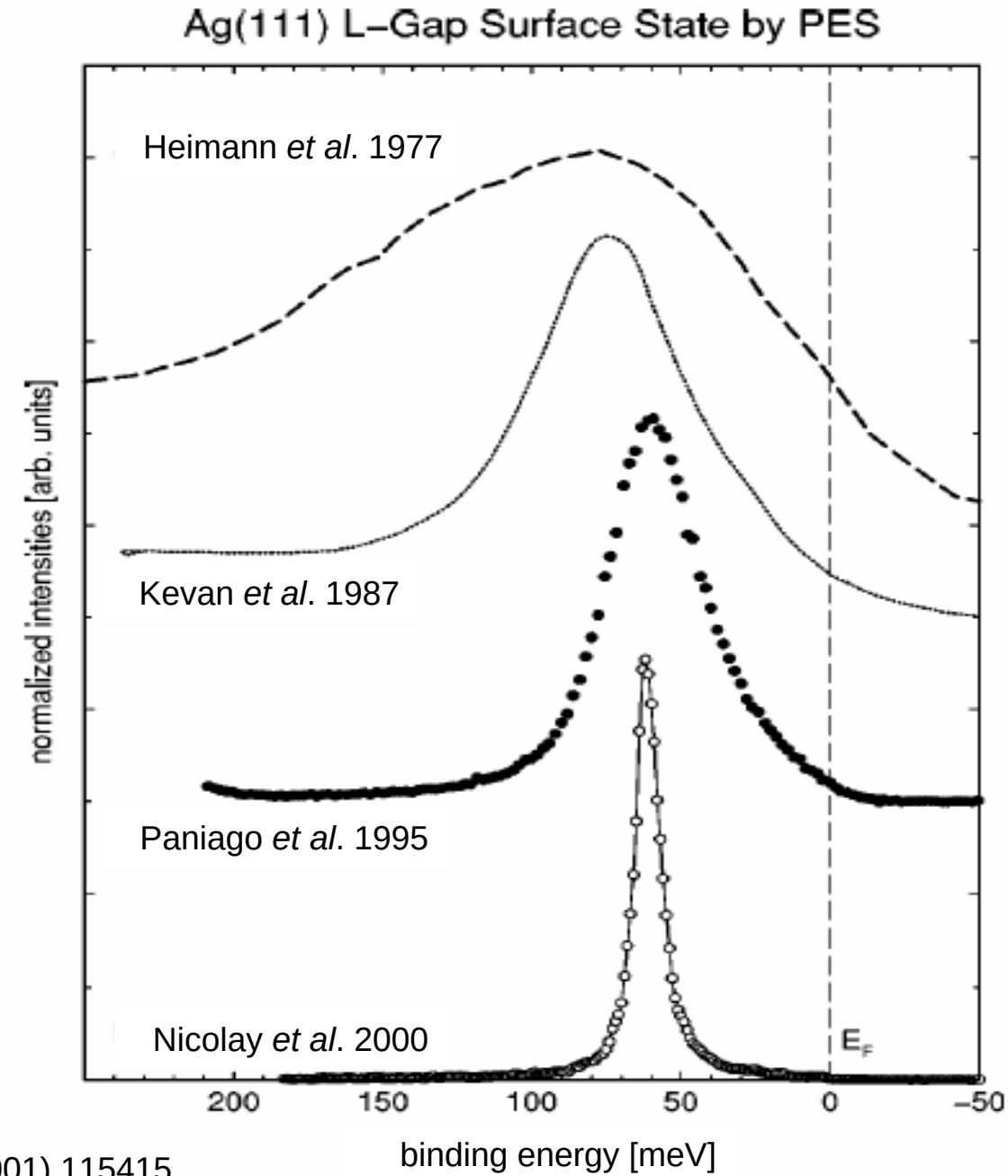
In all spectroscopies, there are two levels of interpretation. The lower level focuses on positions of spectral features. The higher, and more problematic, level focuses on intensities and shapes...

My mood of skepticism applies largely to quantitative interpretations of linewidths in terms of quasiparticle lifetimes...

The moral here is that, even on a material as well understood and easy to prepare as Cu, a very high degree of sample perfection is required if we are to avoid extraneous broadening mechanisms.

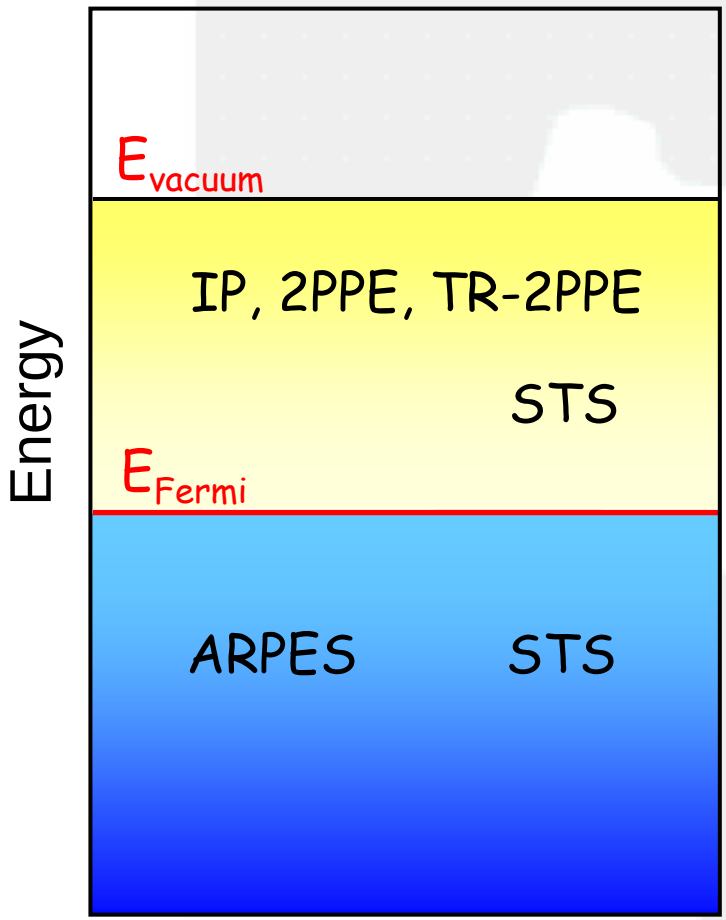
N.V.Smith. Comments Cond. Mat. Phys. 1992. Vol 15, Nos. 5&6, pp. 263-272

Experimental linewidths change quickly with time!



from F.Reinert *et al*., PRB **63** (2001) 115415.

Experimental Methods



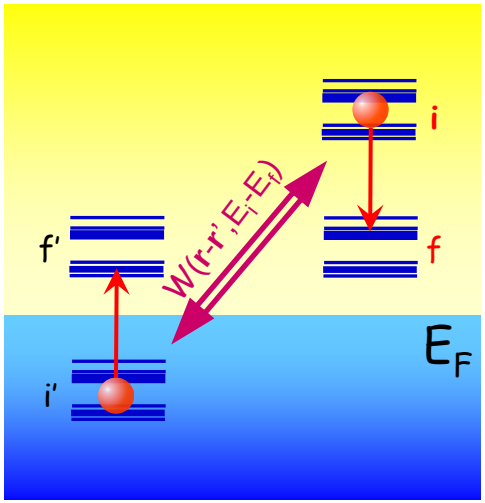
- Time-Resolved Two-Photon Photoemission (TR-2PPE)
- Two-Photon Photoemission (2PPE)
- Inverse Photoemission (IP)

- Scanning Tunneling Spectroscopy (STS)

- Angle-Resolved Photoemission Spectroscopy (PES)

2. Sketch of theory: e-e interaction

- Lifetime $\tau^{-1} = -2 \int d\mathbf{r}\, d\mathbf{r}'\, \phi_i^*(\mathbf{r})\, \mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i)\, \phi_i(\mathbf{r}')$



- Lifetime – Screened interaction

$$\tau^{-1} = -2 \sum_f{}' \int d\mathbf{r} \int d\mathbf{r}'\, \phi_i^*(\mathbf{r})\, \phi_f^*(\mathbf{r}')\, \mathrm{Im}W(\mathbf{r},\mathbf{r}';\omega)\, \phi_i(\mathbf{r}')\, \phi_f(\mathbf{r})$$

- Self-energy

$$\mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i>E_F) = \sum_{E_F\le\varepsilon_f\le\varepsilon_i}{}' \phi_f^*(\mathbf{r}')\, \mathrm{Im}W(\mathbf{r},\mathbf{r}';\varepsilon_i-\varepsilon_f)\, \phi_f(\mathbf{r})$$

- Screened Interaction

$$W(\mathbf{r},\mathbf{r}';\omega) = V(\mathbf{r}-\mathbf{r}') + \int d\mathbf{r}_1 \int d\mathbf{r}_2 [V(\mathbf{r}_1-\mathbf{r}_2)+K^{xc}(\mathbf{r}_1,\mathbf{r}_2,\omega)]\chi(\mathbf{r}_1,\mathbf{r}_2,\omega)V(\mathbf{r}_2-\mathbf{r}')$$

- Response function

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \chi^o(\mathbf{r},\mathbf{r}';\omega) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi^o(\mathbf{r},\mathbf{r}_2,\omega)\, [V(\mathbf{r}_1-\mathbf{r}_2)+K^{xc}(\mathbf{r}_1,\mathbf{r}_2,\omega)]\chi(\mathbf{r}_2,\mathbf{r}';\omega)$$

where

$$\chi^o(\mathbf{r},\mathbf{r}';\omega) = 2\sum_{i,j} \frac{\theta(E_F-\varepsilon_i)-\theta(E_F-\varepsilon_j)}{\varepsilon_i-\varepsilon_j+(\omega+i\eta)}\, \phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}')\phi_i^*(\mathbf{r}')$$

2. Sketch of theory: Electron-phonon (e-ph) interaction

Electron-phonon coupling matrix element

$$g_{\vec{q},\nu}^{i,f} \equiv \sqrt{\frac{1}{2\cdot M\cdot \omega_{\vec{q}}^{\nu}}}\cdot\left\langle \varphi_i^0 \left| \sum_{\mu} \vec{\varepsilon}_{\vec{q}}^{\,\nu,\mu}\cdot\vec{\nabla}_{\vec{R}_\mu} V_{e-ion}^{\vec{q}} \right| \varphi_f^0 \right\rangle$$

Eliashberg function

$$\alpha^2 F_{\vec{k}_i}(\omega) \equiv \sum_{f,\vec{q},\nu} \left| g_{\vec{q},\nu}^{i,f} \right|^2 \cdot \delta(\varepsilon_{\vec{k}_i}^{el} - \varepsilon_{\vec{k}_f}^{el}) \cdot \delta(\omega - \omega_{\vec{q}}^{\nu})$$

Quasi-elastic approximation

$$\delta(\varepsilon_{\vec{k}_i}^{el} - \varepsilon_{\vec{k}_f}^{el} \pm \omega_{\vec{q}}^{\nu}) \approx \delta(\varepsilon_{\vec{k}_i}^{el} - \varepsilon_{\vec{k}_f}^{el})$$

E-ph contribution to the electronic linewidth

$$\Gamma_{\vec{k}_i} = 2\pi \cdot \int_0^{\infty} \alpha^2 F_{\vec{k}_i}(\omega) \cdot [2\cdot n_B(\omega) + 1 + f(\varepsilon_{\vec{k}_i} + \omega) - f(\varepsilon_{\vec{k}_i} - \omega)] \cdot d\omega$$

E-ph contribution at high temperatures ($T \to \infty$)

$$\Gamma_{\vec{k}_i} \cong 2\pi \cdot K_B \cdot T \cdot \lambda$$

E-ph contribution at T=0 K

$$\Gamma_{\vec{k}_i} \cong 2\pi \cdot \int_0^{\varepsilon_{\vec{k}_i}} \alpha^2 F_{\vec{k}_i}(\omega) d\omega$$

E-ph coupling constant

$$\lambda = 2 \cdot \int_0^{\infty} \frac{\alpha^2 F_{\vec{k}_i}(\omega)}{\omega} \cdot d\omega$$

Calculations of a lifetime for excited electrons (holes) in

Bulk states

Surface states

Image states

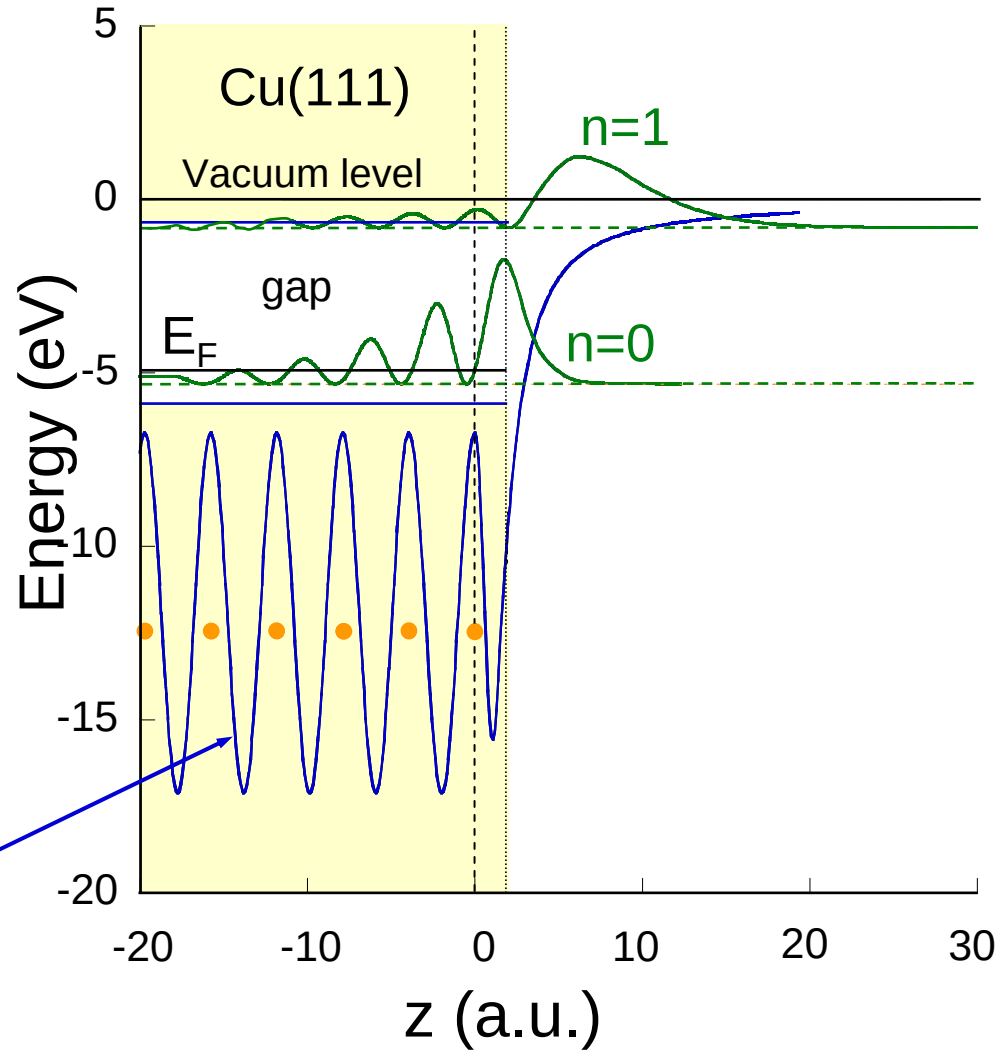
Quantum well states

and at Adsorbates

Contributions to the quasiparticle decay rate:

Electron-electron

Electron-phonons



Model potential

Surf. Sci. **391**, L1217 (1997); **437**, 330 (1999)

PHYSICS OF LIFETIME

3. Decay mechanisms

(electron-electron contribution)

$$\tau^{-1} = -2 \sum_{f}{}' \int d\mathbf{r} \int d\mathbf{r}' \, \phi_i^*(\mathbf{r}) \, \phi_f^*(\mathbf{r}') \, \mathrm{Im}W(\mathbf{r},\mathbf{r}';\omega) \, \phi_i(\mathbf{r}') \, \phi_f(\mathbf{r})$$

1) Initial State $\phi_i(\mathbf{r})$, Final State $\phi_f(\mathbf{r})$ } Overlap of the initial and final states wave functions. Important difference between intra-band and inter-band transitions arises.

2) Final States Effect

a) "Phase space": number of final states in momentum space

b) Density of final states: distribution of final states in momentum space

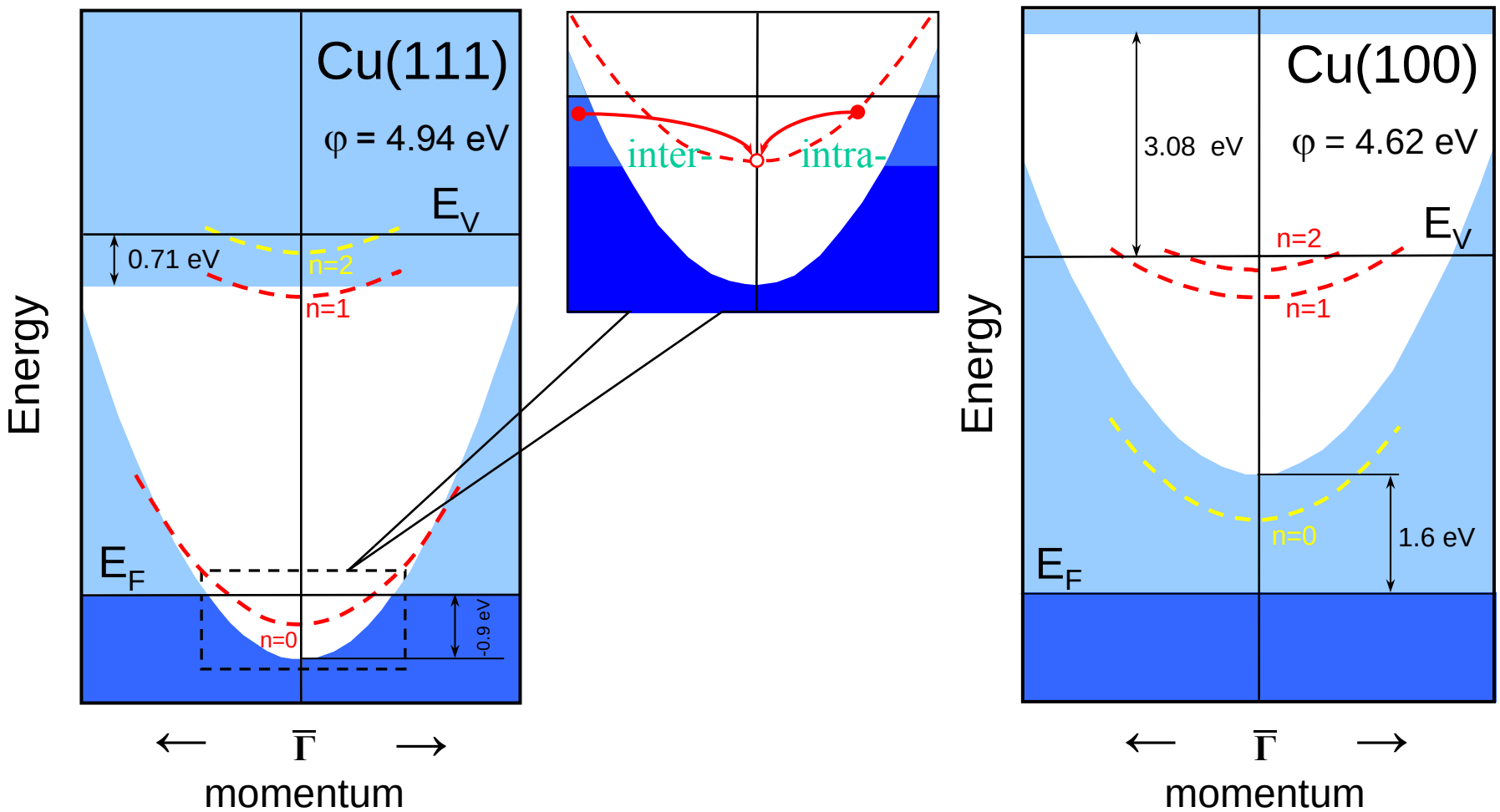
3) Screening: Response Function

$$\mathrm{Im}W(\mathbf{r},\mathbf{r}';\omega) = \mathrm{Im}\varepsilon^{-1}(\mathbf{r},\mathbf{r}';\omega) \cdot V(\mathbf{r}-\mathbf{r}')$$

$\mathrm{Im}\varepsilon^{-1}(\mathbf{r},\mathbf{r}';\omega)$ is the well known loss function

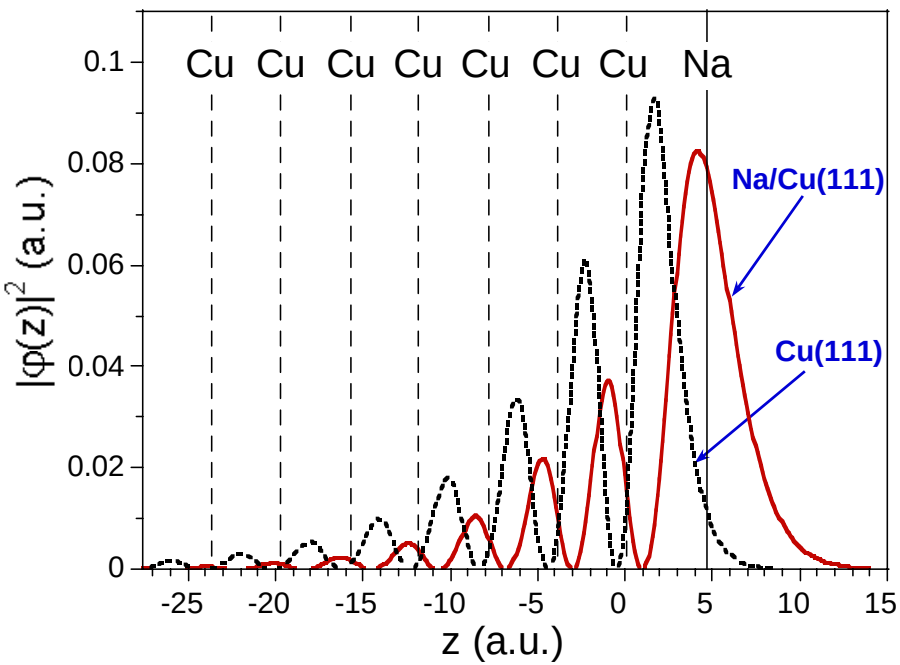
1) Overlap effect: intra- and inter-band transitions

Cu(111) and **Cu(100)** Surface Band Structures

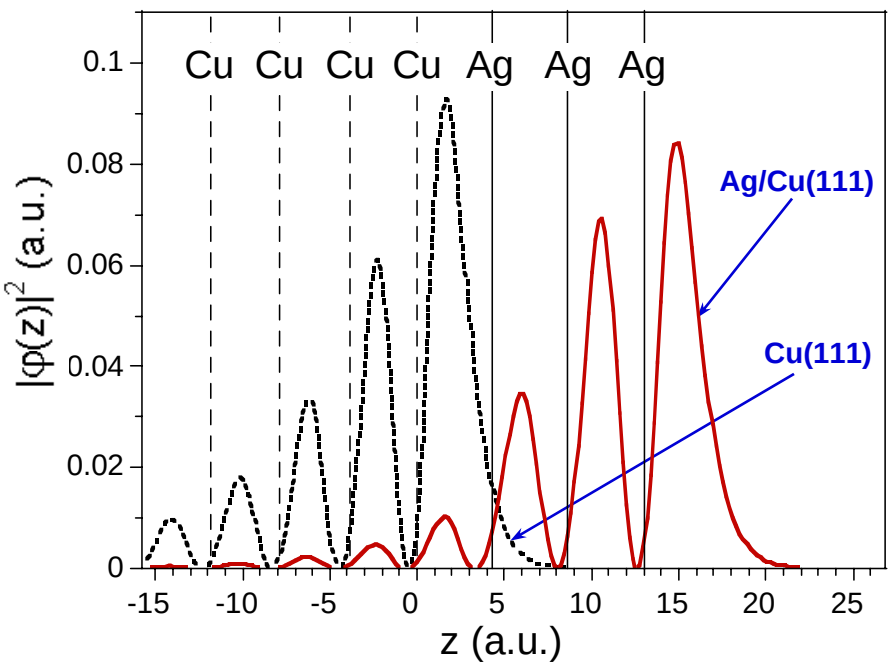


Quantum Well State Charge Density

1ML Na/Cu(111)



3ML Ag/Cu(111)

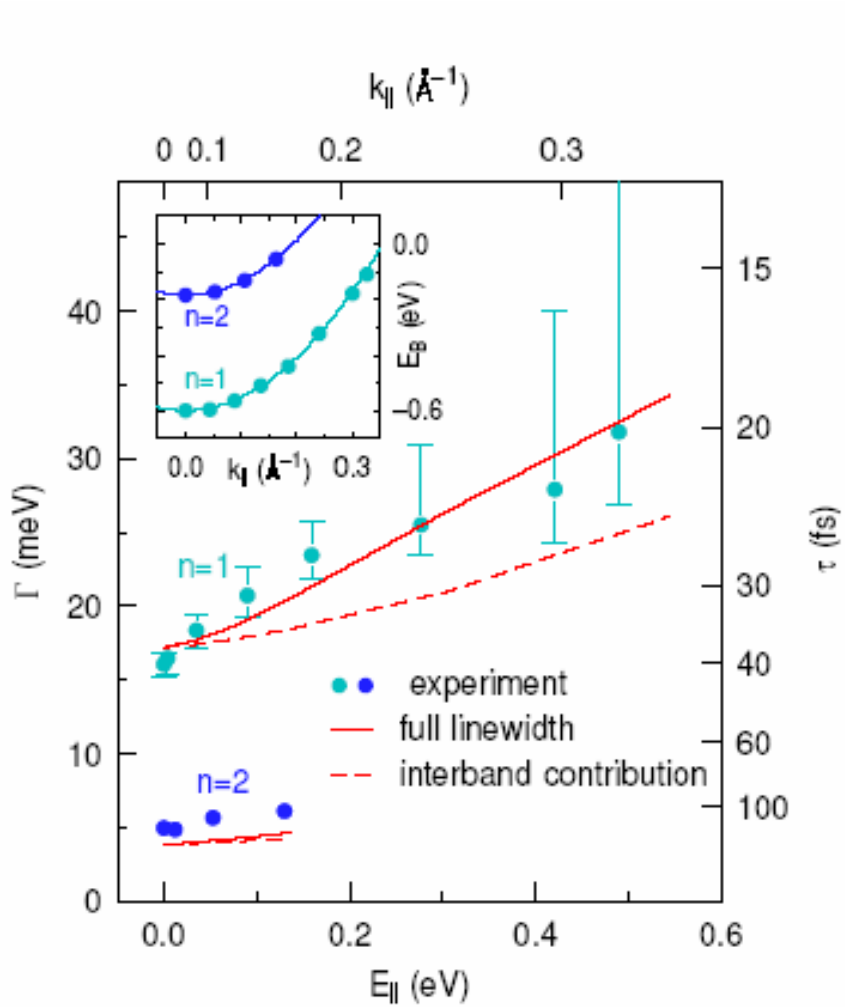


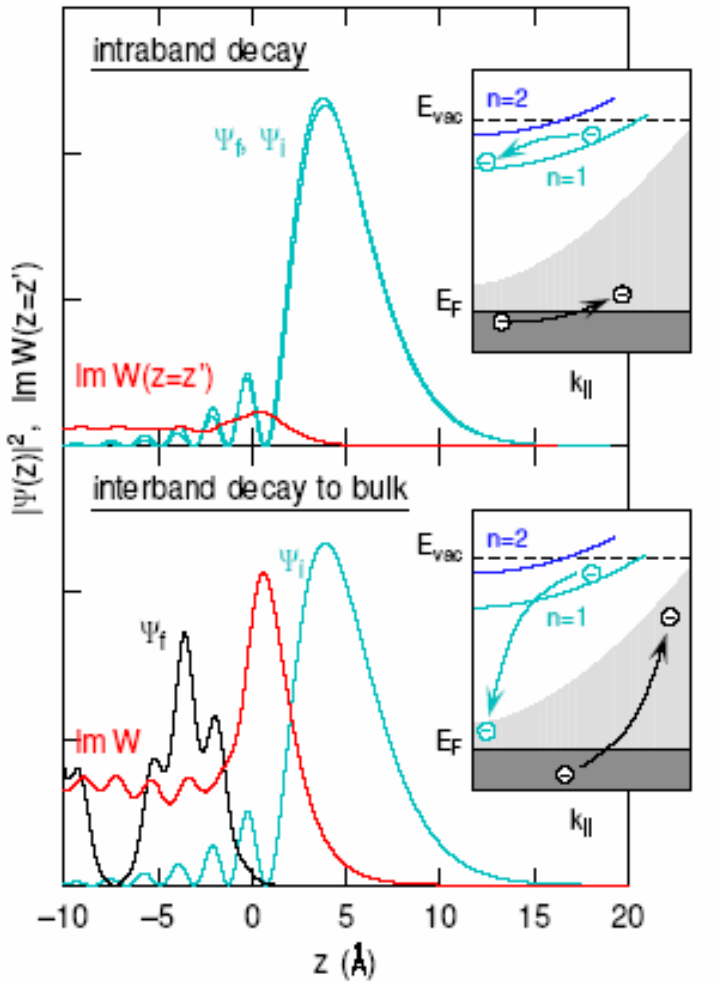
Calculated and measured **inverse lifetime** of the **s-p_z** surface state at the $\bar{\Gamma}$ point on **Cu(111)**. Surface state (**2D**) contribution is indicated in parenthesis. Dominant **2D** effect is also obtained for Ag(111), Au(111), Be(0001), Be(1010). For Mg(0001), Al(111) and Al(100) the **2D** effect is not dominant.

Temperature	Experimental surface state energy (eV)	**Theory** Quinn (meV)	**Theory** Model potential (meV)	**Experiment** (meV)
0 K **5 K**	**-0.44**[a] **-0.445**[i]	**5** no d-screened **5.1**[i] d-screened **2.2**[i]	**25(19)** no d-screened **25(19)**[i] d-screened **13.7(11.1)**[i]	Electron contribution **22**[b]; **16**[i] **15**[j]**; 21±5**[c] Electron+phonon contribution **24**[i]**;30**[b]
Troom	**-0.39**[a,d]	**4**	**23(18)**	electron+ phonon+defect contributions **55 ±5**[b,e]; **65 ± 5**[f,,g] **62 ± 4**[h]

[a]Surf.Sci. **336**, 113 (1995); [b]Phys.Rev. B**51**, 13891 (1995); [c]Phys.Rev. B**56**, 3632 (1997); [d]Phys.Rev. B**36**, 5809 (1987); [e]Phys.Rev.Lett. **50**, 526 (1983); [f]Phys.Rev. B**54**, 14807 (1996); [g]Surf.Sci. **374**, 44 (1997); [h]J.Electron.Spectrosc.Relat.Phenom.**88-91**, 577 (1988); [i]Science, **288**, 1399 (2000); [j]Phys.Rev. B **63**, 1154815 (2001)

Momentum-dependent lifetimes of Cu(100)-image-potential states





PRL **88**, 056805 (2002)

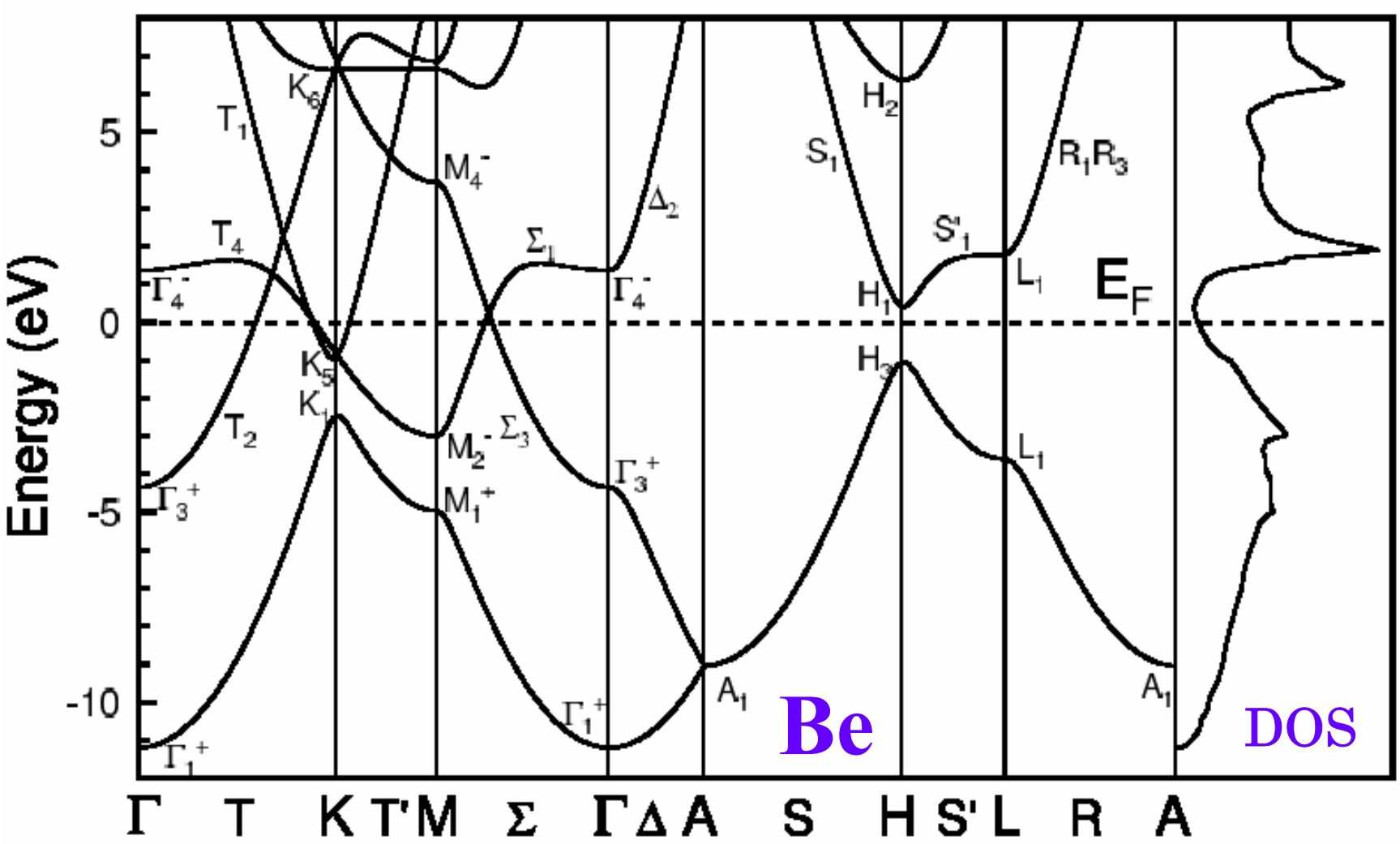
2) Final States Effect

$\Gamma_4^- \rightarrow \Gamma_{e\text{-}e} = 1$ meV

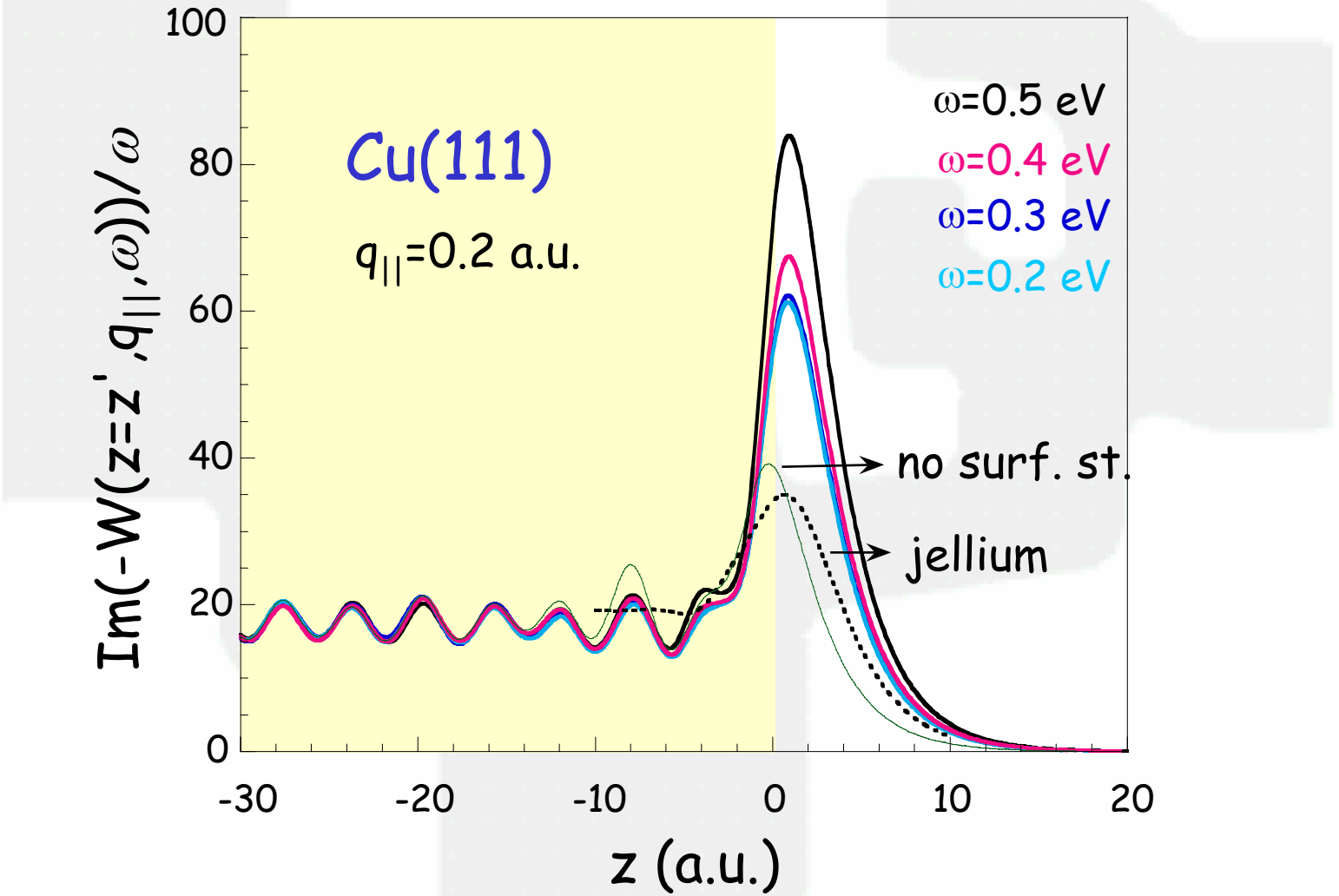
$\Gamma_3^- \rightarrow \Gamma_{e\text{-}e} = 124$ meV

$M_2^- \rightarrow \Gamma_{e\text{-}e} = 95$ meV

$M_1^+ \rightarrow \Gamma_{e\text{-}e} = 221$ meV

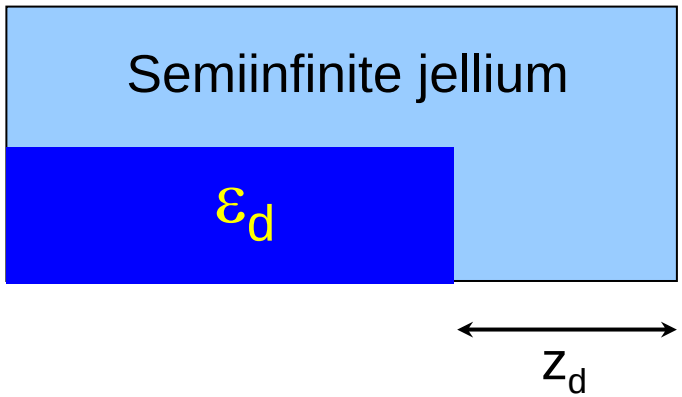


3) Screening: 3D with a mixture of 2D



3) Screening effect: one more aspect

s-d polarization model



A.Liebsch, PRL **71** (1993) 145
(jellium model)

Model potential

+

ε_d d-component of dielectric function

z_d boundary of d electron medium

Ag: z_d=-1.5 a.u. Reproduces the experimental surface plasmon dispersion

Inverse lifetime Γ of n=1 image state on Ag(100)

Without d-electron effect	With d-electron effect	Experiment
Γ = 18.3 meV	Γ = 12.0 meV	Γ = 12 meV

PRL **89,** 096401 (2002)

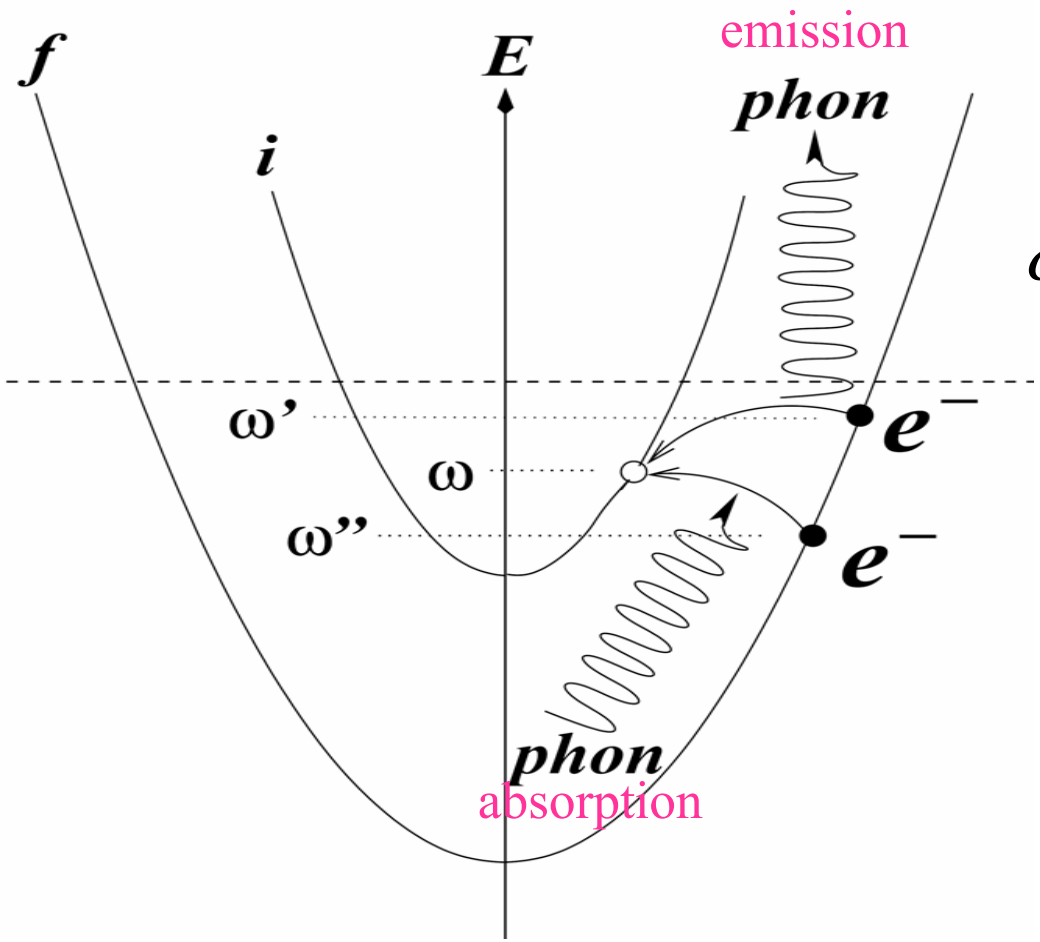
3. Decay mechanisms

PHYSICS OF LIFETIME

(electron-phonon contribution)

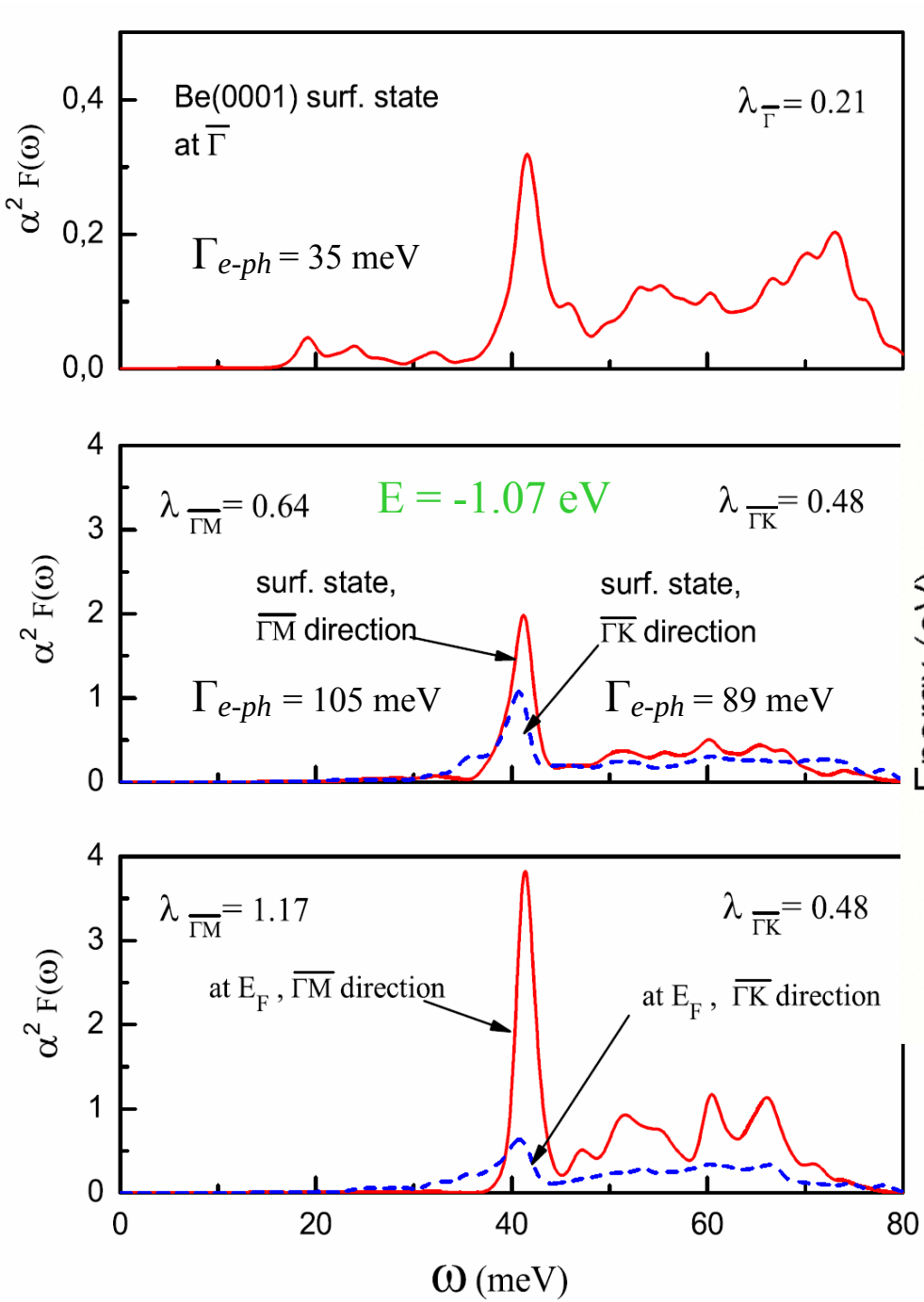
Eliashberg function

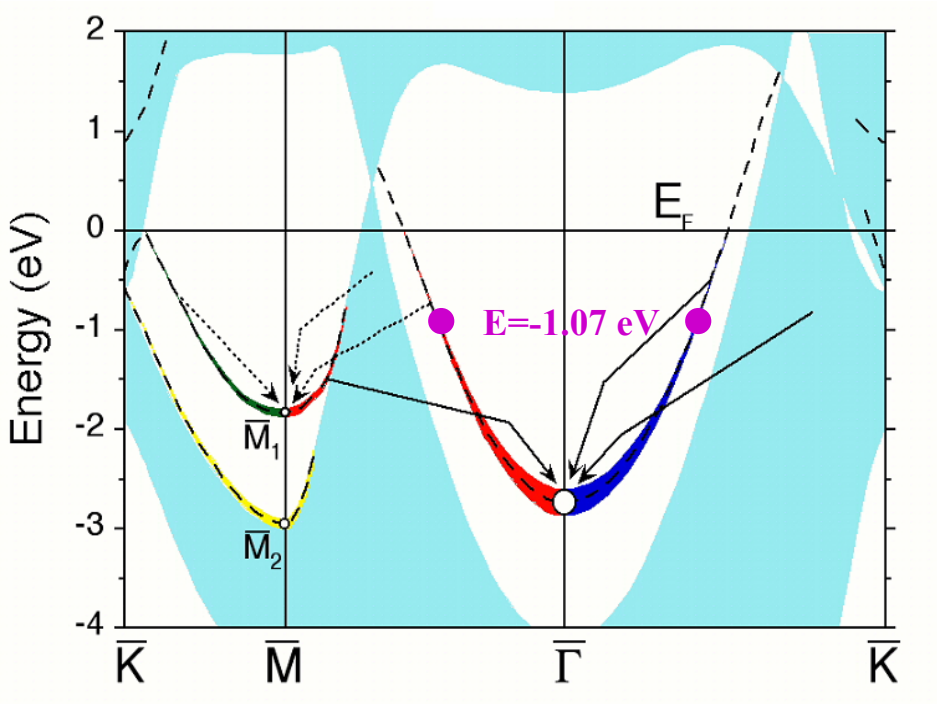
$$\alpha^2 F_{\vec{k}_i}(\omega) \equiv \sum_{\vec{f},\vec{q},\nu} \left| g^{i,f}_{\vec{q},\nu} \right|^2 \cdot \delta(\varepsilon^{el}_{\vec{k}_i} - \varepsilon^{el}_{\vec{k}_f}) \cdot \delta(\omega - \omega^{\nu}_{\vec{q}})$$

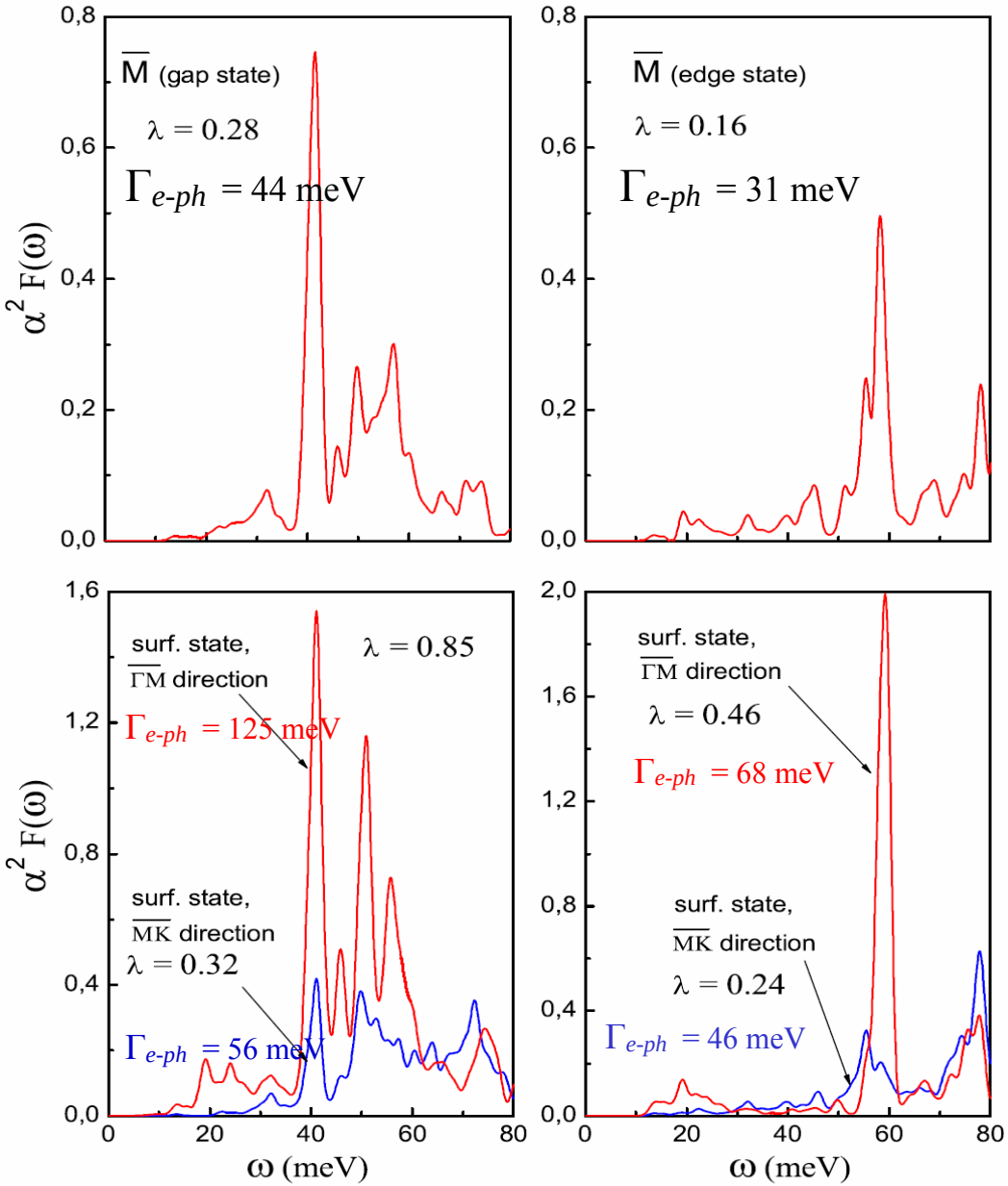


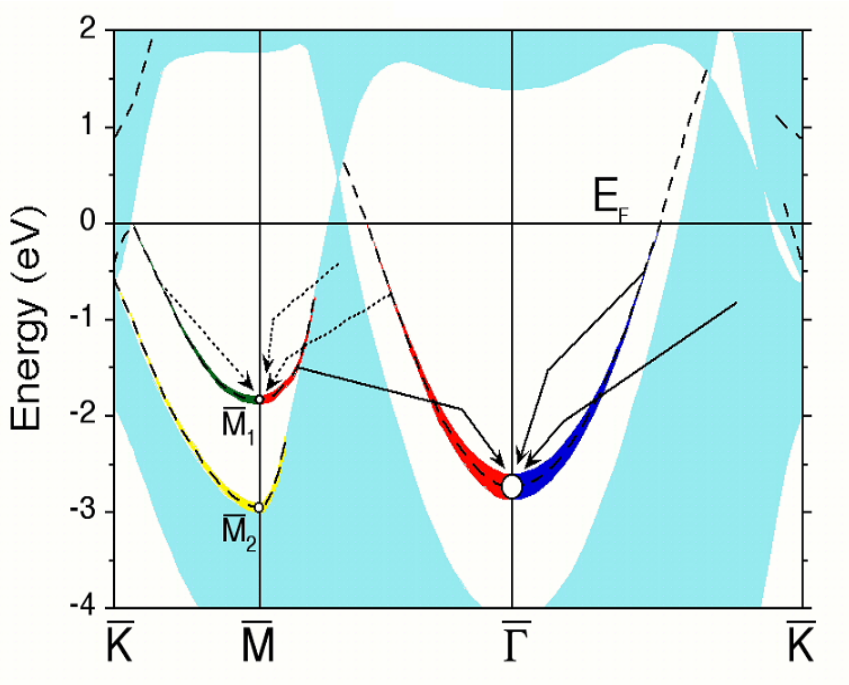
Quasi-elastic approximation

$$\delta(\varepsilon^{el}_{\vec{k}_i} - \varepsilon^{el}_{\vec{k}_f} \pm \omega^{\nu}_{\vec{q}}) \approx \delta(\varepsilon^{el}_{\vec{k}_i} - \varepsilon^{el}_{\vec{k}_f})$$

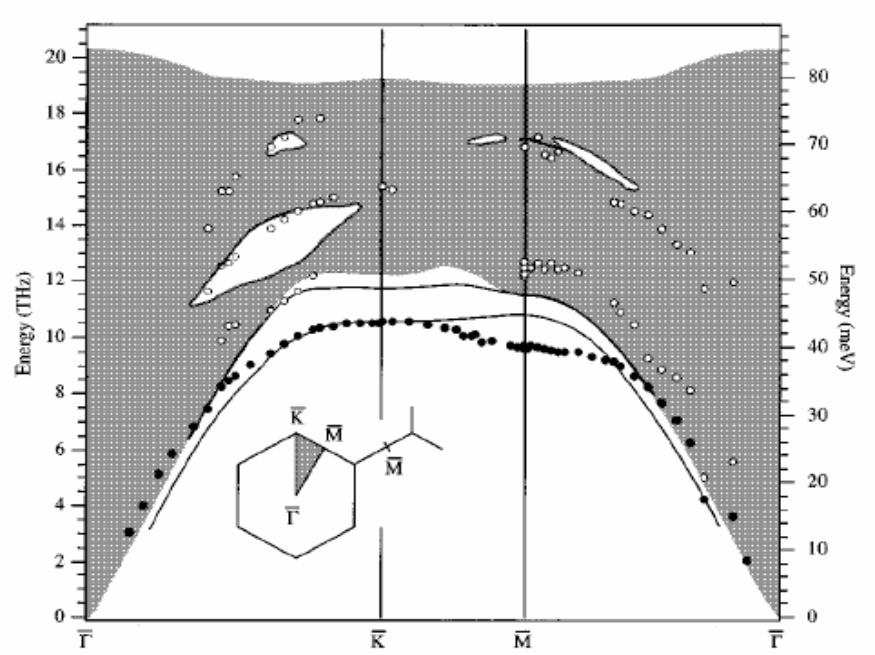

Be(0001) surf. state
at $\overline{\Gamma}$
$\lambda_{\overline{\Gamma}} = 0.21$
$\Gamma_{e\text{-}ph} = 35$ meV
$\alpha^2 F(\omega)$
$\lambda_{\overline{\Gamma M}} = 0.64$
E = -1.07 eV
$\lambda_{\overline{\Gamma K}} = 0.48$
surf. state, $\overline{\Gamma M}$ direction
surf. state, $\overline{\Gamma K}$ direction
$\Gamma_{e\text{-}ph} = 105$ meV
$\Gamma_{e\text{-}ph} = 89$ meV
$\lambda_{\overline{\Gamma M}} = 1.17$
$\lambda_{\overline{\Gamma K}} = 0.48$
at E_F , $\overline{\Gamma M}$ direction
at E_F , $\overline{\Gamma K}$ direction
ω (meV)


Energy (eV)
E_F
E=-1.07 eV
$\overline{M}_1$
$\overline{M}_2$
$\overline{K}$
$\overline{M}$
$\overline{\Gamma}$
$\overline{K}$

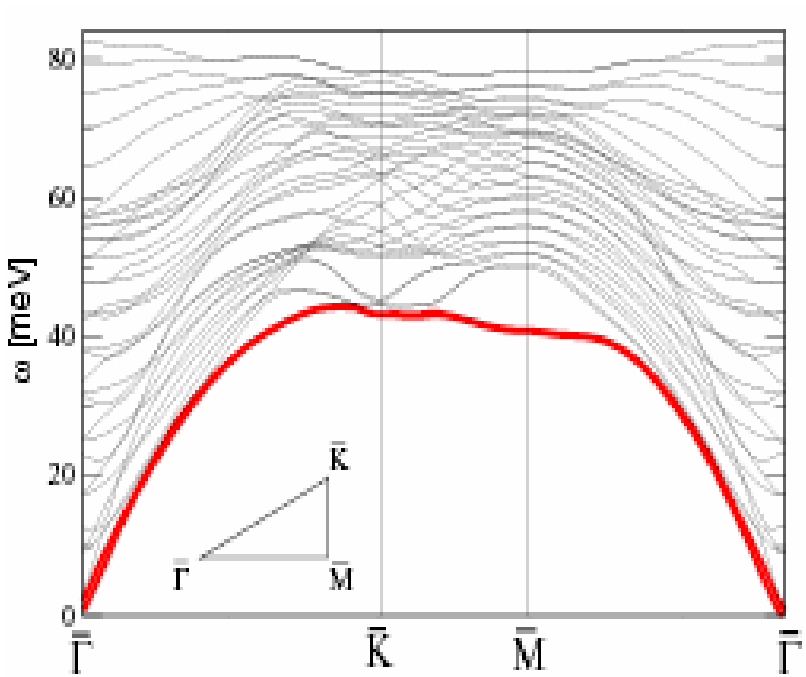

M (gap state)
λ = 0.28
Γ e-ph = 44 meV
M (edge state)
λ = 0.16
Γ e-ph = 31 meV
surf. state, ΓM direction
λ = 0.85
Γ e-ph = 125 meV
surf. state, MK direction
λ = 0.32
Γ e-ph = 56 meV
surf. state, ΓM direction
λ = 0.46
Γ e-ph = 68 meV
surf. state, MK direction
λ = 0.24
Γ e-ph = 46 meV
α² F(ω)
ω (meV)


Energy (eV)
E F
M1
M2
K
M
Γ
K

Measured (left) and calculated (right) surface phonon structure of Be(0001)



J. Hannon, E. J. Mele, and E. W. Plummer, Phys. Rev **B53**, 2090 (1996)



Our calculation

Summary for the surface states linewidth

Energies (in eV) and linewidths (in meV) for different surface states at low temperatures

Surface state		Energy	Γ_{ee}	Γ_{ep}	Γ_{calc}	Γ_{exp}	Calculated	Experimental
Cu(1 1 1)	$\bar{\Gamma}$	−0.445	14	8	22	24	[52]	[52]
		−0.435				23 ± 1		[100]
Cu(1 1 0)	$\bar{Y}$	−0.510	8			≤ 32	[295]	[127]
Ag(1 1 1)	$\bar{\Gamma}$	−0.067	2	4	6	6, 5	[52]	[52,125]
		−0.063				6 ± 0.5		[100]
Au(1 1 1)	$\bar{\Gamma}$	−0.505	14	4	18	18	[52]	[52]
		−0.484				21 ± 1		[100]
Be(0 0 0 1)	$\bar{\Gamma}$	−2.73	265	80	345	350	[143]	[143]
Be(0 0 0 1)	$\bar{M}_1$	−1.8	72	80	152	(380)	[143]	[145]
Be(1 0 $\bar{1}$ 0)	$\bar{A}$	−0.42	53	80	133	130	[146]	[146]
		−0.39				185		[147]
Mg(0 0 0 1)	$\bar{\Gamma}$	−1.6	83	25	108	(∼500)	[53]	[150]
		−1.7				(∼200)		[144]
Al(1 0 0)	$\bar{\Gamma}$	−2.75	131	18	149	(500)	[96]	[148]
			67			(450)	[295]	[149]
Al(1 1 1)	$\bar{\Gamma}$	−4.56	336	36	372	(∼1500)	[53]	[149]
Pd(1 1 1)	$\bar{\Gamma}$	+1.35	37			(54)	[225]	[225]

The calculated values (Γ_{calc}) are decomposed in electron–electron (Γ_{ee}) and electron–phonon (Γ_{ep}) contributions. Γ_{ep} values for Cu, Ag, Au(1 1 1) and Al(1 0 0) surfaces are from microscopic calculations [95,96], other values from 3D Debye model evaluations for $T = 0$ K. Values for Γ_{exp} in parentheses were measured at room temperature.

SSR **52**, 219 (2004)

Summary for electron-electron contribution to the image-potential states linewidth

Lifetimes τ_n in fs for the nth image-potential state on clean metal surfaces measured by time-resolved two-photon photoemission and calculated using the GW approximation

		τ_1	τ_2	τ_3	τ_4	τ_5	Refs.
C(0 0 0 1)	Experimental	40 ± 6					[303]
Ni(1 1 1)	Experimental	7 ± 3					[304]
Cu(0 0 1)	Experimental	40 ± 6	120 ± 15	300 ± 20	630	1200	[36,218]
	Experimental	41.3	150	406			[222]
	Theoretical	38	168	480			[69]
Cu(1 1 9)	Experimental	15 ± 5	39 ± 5	105 ± 15	200 ± 20	350 ± 40	[248]
Cu(1 1 7)	Experimental	15 ± 5	39 ± 5	95 ± 15	190 ± 20	350 ± 40	[248]
Cu(1 1 1)	Experimental	18 ± 5	14 ± 3	40 ± 6			[221,244]
	Theoretical	29					[69]
Cu(7 7 5)	Experimental	18 ± 2					[305]
Ag(0 0 1)	Experimental	55 ± 5	160 ± 10	360 ± 15			[218]
	Theoretical	55	219	658			[75]
Ag(1 1 1)	Experimental	32 ± 10	≤ 20				[260]
	Theoretical	18					[75]
Pd(1 1 1)	Experimental	25 ± 4					[225]
	Theoretical	22	89				[225]
Pt(1 1 1)	Experimental	26 ± 7	62 ± 7				[68]
	Theoretical	29	73				[68]
Ru(0 0 0 1)	Experimental	11					[267,306]
	Theoretical	14					[56]
Li(1 1 0)	Theoretical	18	44				[307]

SSR **52**, 219 (2004)

Conclusions

1. **General conclusion:**
   now we understand quite many aspects of the physics of electron and hole dynamics.

2. Future:

a) Ab initio calculations

b) GW, GW+T-matrix evaluations

c) Electron (hole) dynamics in ferromagnetic materials. New mechanism arises: spin-flip processes (PRL **93**, 096401 (2004))

d) Materials with strong spin-orbit splitting
(PRL **93**, 046403 (2004); PRL **93**, 196802 (2004))

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