One-Step Theory of Photoemission: Band Structure Approach

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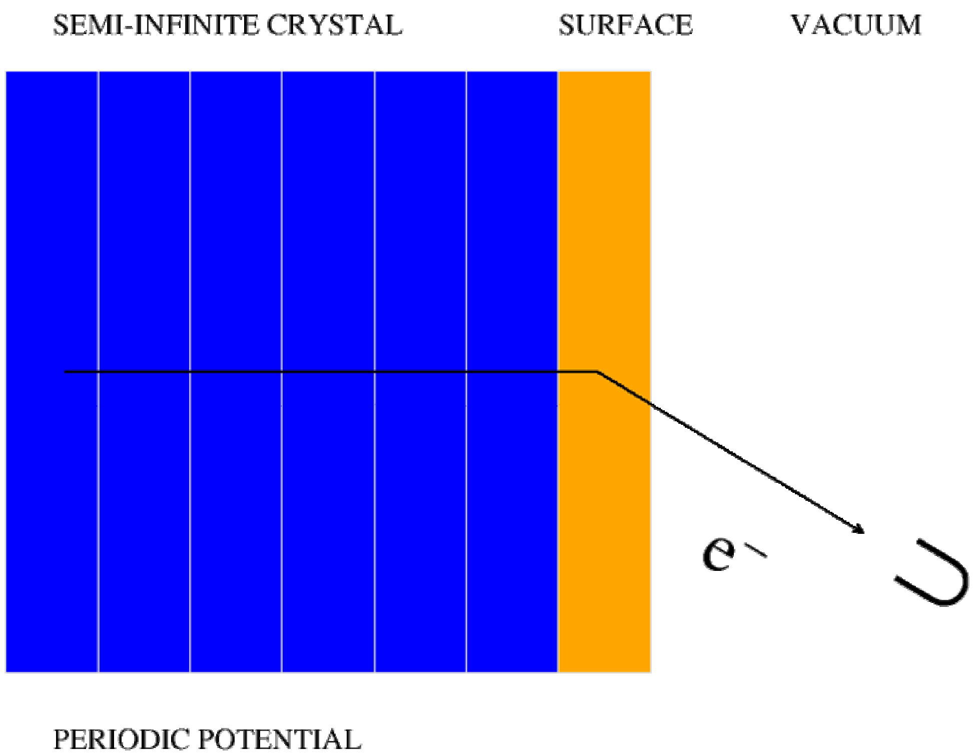
CONTENTS

- One-Step Theory
- Theory of Band Mapping
- Valence band photoemission from Al(111) and Al(100)
- Photoemission from surface states
- Photoemission from layered crystals $TiTe_2$ and VSe_2
- Two photon photoemission

Angle Resolved Photoemission: the Presence of Detector



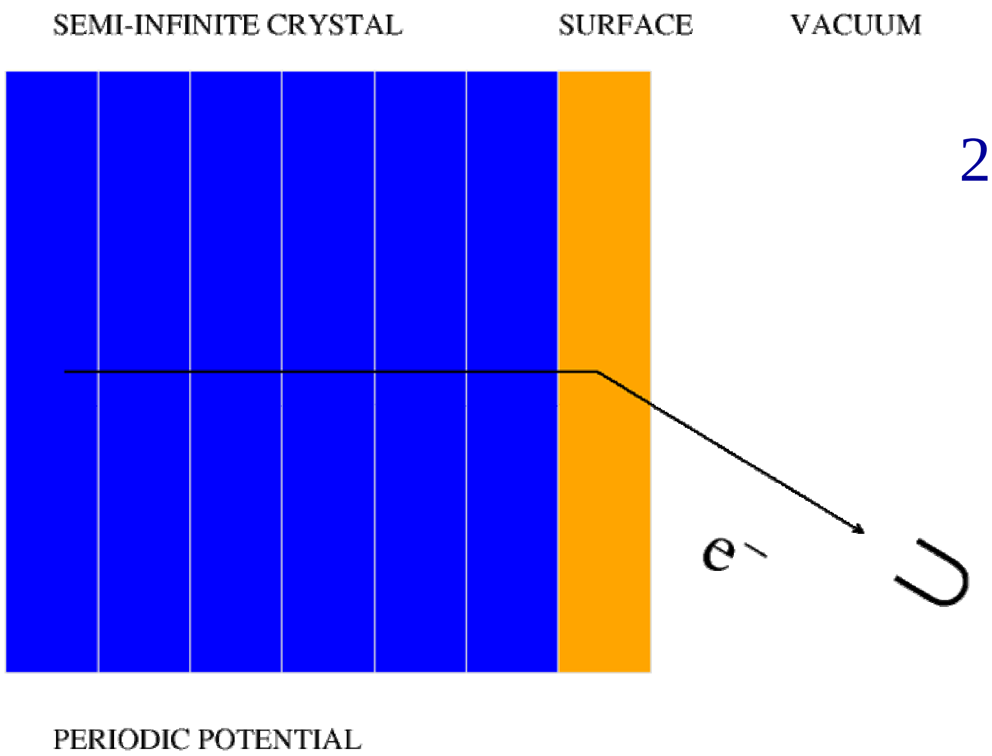
1. Semi-infinite geometry (surface)

2. Surface sensitivity (damped waves)

Surface sensitivity: computational implications

Photoemission is formulated as an initial value problem

(in contrast to bulk properties - optics, XPS - that reduce to a boundary value problem)



1. Semi-infinite geometry:
   scattering states

2. Inelastic effects:
   non-Hermitean Hamiltonian

One-Step Theory: Formalism

First-order perturbation theory:

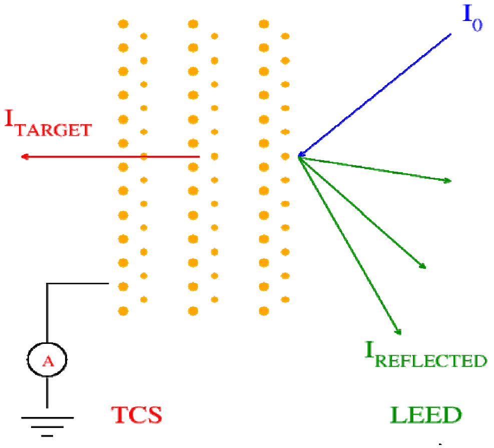
$$\psi(\vec{r};\epsilon+\hbar\omega) = \int d\vec{r}\,'\, G(\vec{r},\vec{r}\,';\epsilon+\hbar\omega)\,[-i\nabla]\,\phi(\vec{r}\,';\epsilon)$$

Asymptotics at the detector $r \rightarrow \infty$

$$\begin{aligned}\psi(\vec{r};\epsilon+\hbar\omega) &= \int d\vec{r}\,'\, \Phi_{\mathbf{LEED}}(E_{\mathbf{fin}},\vec{r}\,')\,[-i\nabla]\,\phi(\vec{r}\,') \\ &= \langle\, \mathrm{LEED}^* \,|-i\nabla\,|\,\phi\,\rangle\end{aligned}$$

Time reversed LEED state

= final state (loosely speaking)

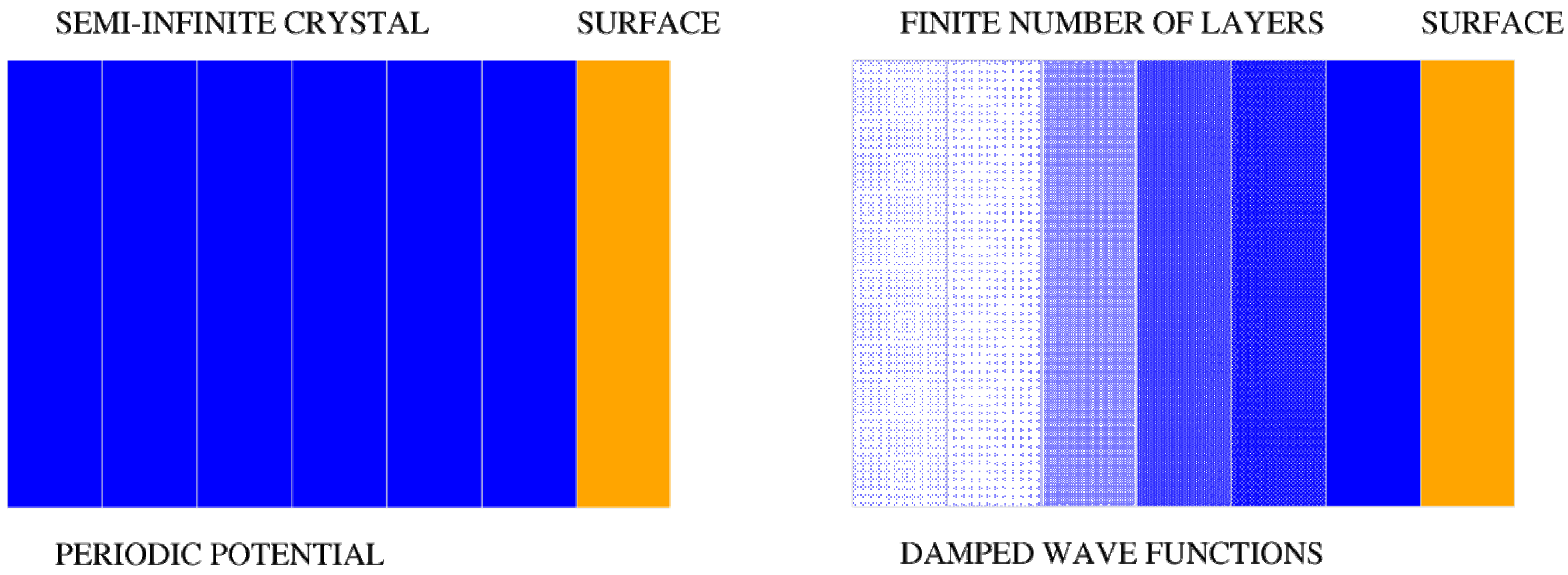


Computational approaches to scattering:
Layered Method *vs.* Bloch States

J.B. Pendry: *Low Energy Electron Diffraction* (1974)

M.A. van Hove, S.Y. Tong: *Surface Crystallography by LEED* (1979)

present approach



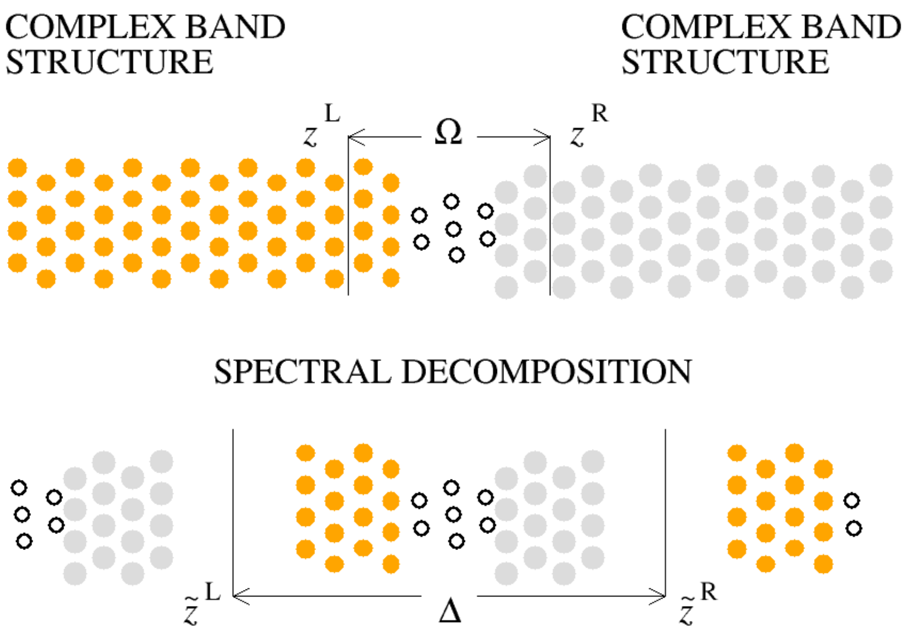
Bloch waves approach to scattering

Two crystal half-spaces separated by a scattering region:

- Partial waves (= complex band structure) representation in each half-space
- Complete basis set in the scattering region

Basis set domain:

repeated slab



Variational embedding method for scattering

Given initial conditions at z_s the function is continued up to z_V by solving the equation

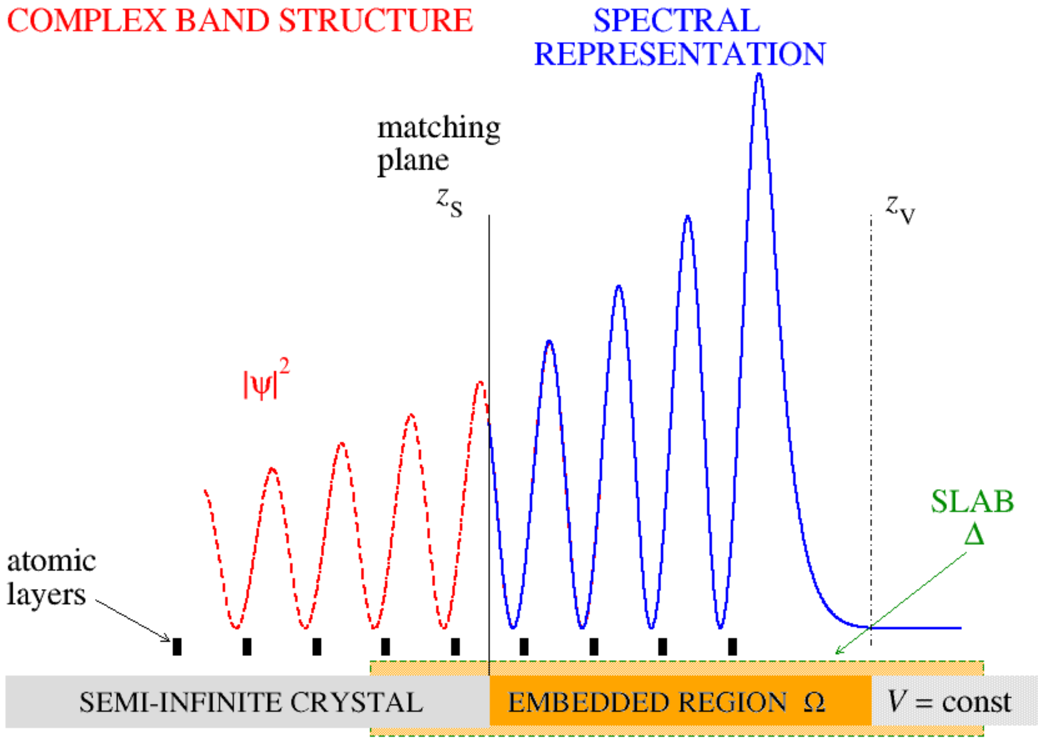
$$(\hat{H} - E)\Psi = 0$$

$$\Downarrow$$

$$\hat{\gamma}(\hat{H} - E)\Psi = 0$$

$$\Downarrow$$

$$\min \left\| \hat{\gamma}(\hat{H} - E)\Psi \right\|$$



method: Extended Linear APW

EK, Phys. Rev. B **70**, 245322 (2004)

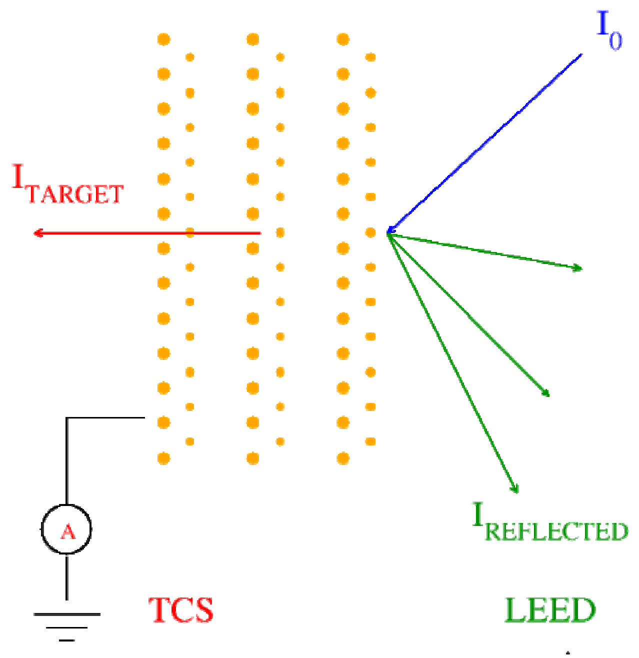
Application to Electron Diffraction at Very Low Energies

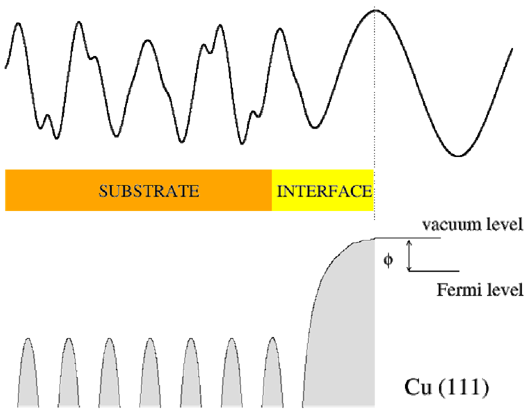
Treatment of inelastic effects

with optical potential

Very Low Energy Electron Diffraction: kinetic energies 0 – 50 eV

EXPERIMENT: Transmitted current (TCS)
or reflected current (VLEED)



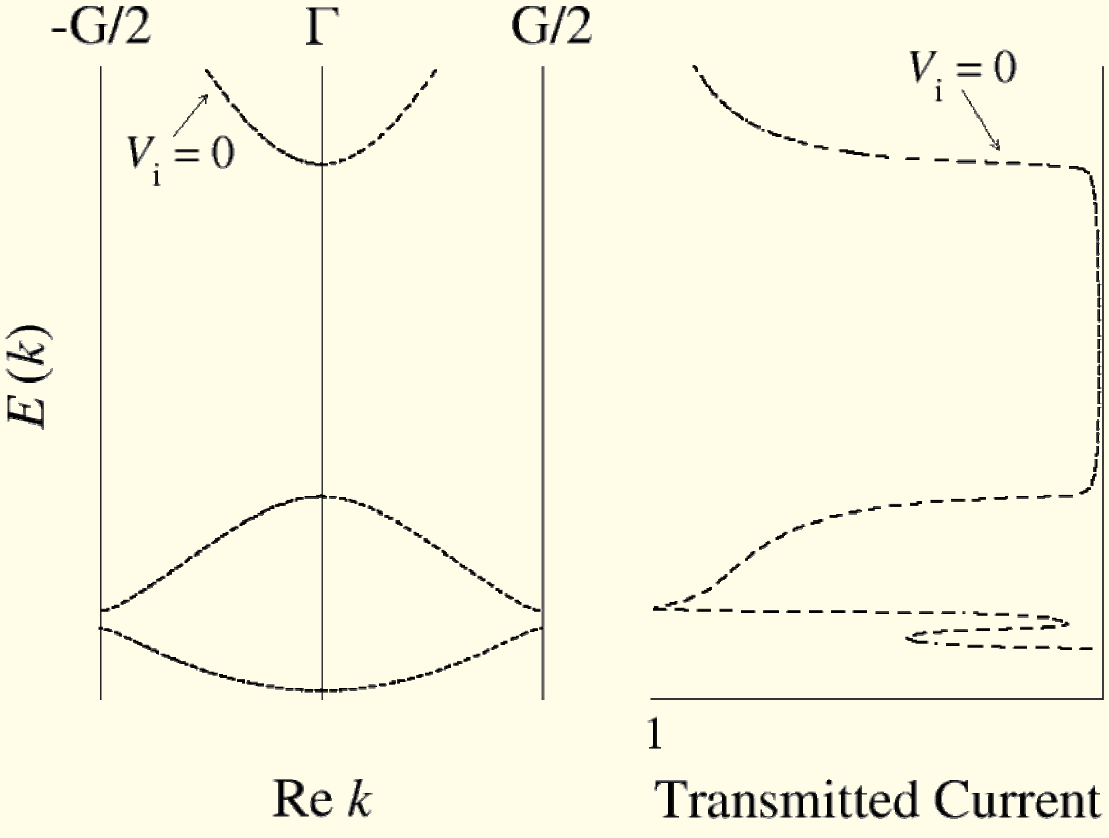


THEORY: Scattering problem for a
plane wave incident from vacuum

Band signatures in the low-energy-electron reflectance spectra of fcc metals.
R.C. Jaklevic and L.C. Davis, Phys. Rev. B **26**, 5391 (1982)

Electron Transmission Spectra in Band Structure Theory

Band Structure Target Current Spectrum



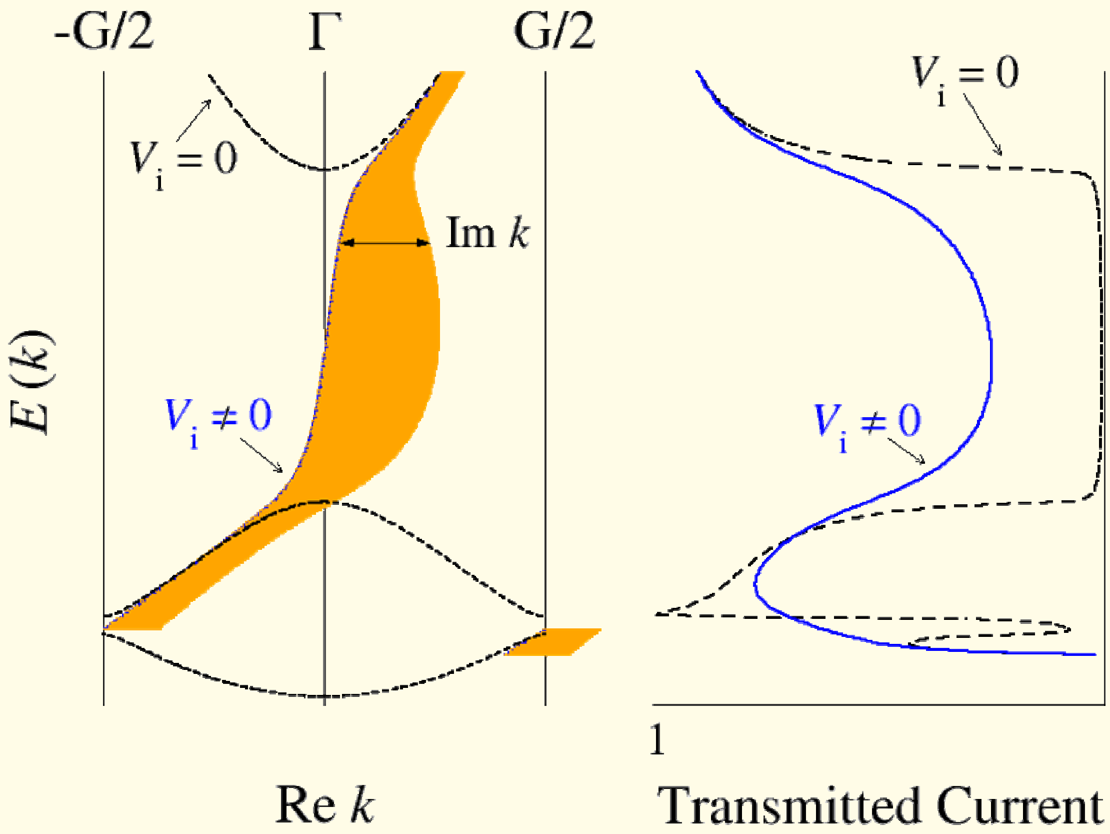
Elastic case:

Hermitean Hamiltonian

Sharp Decrease of Transmission

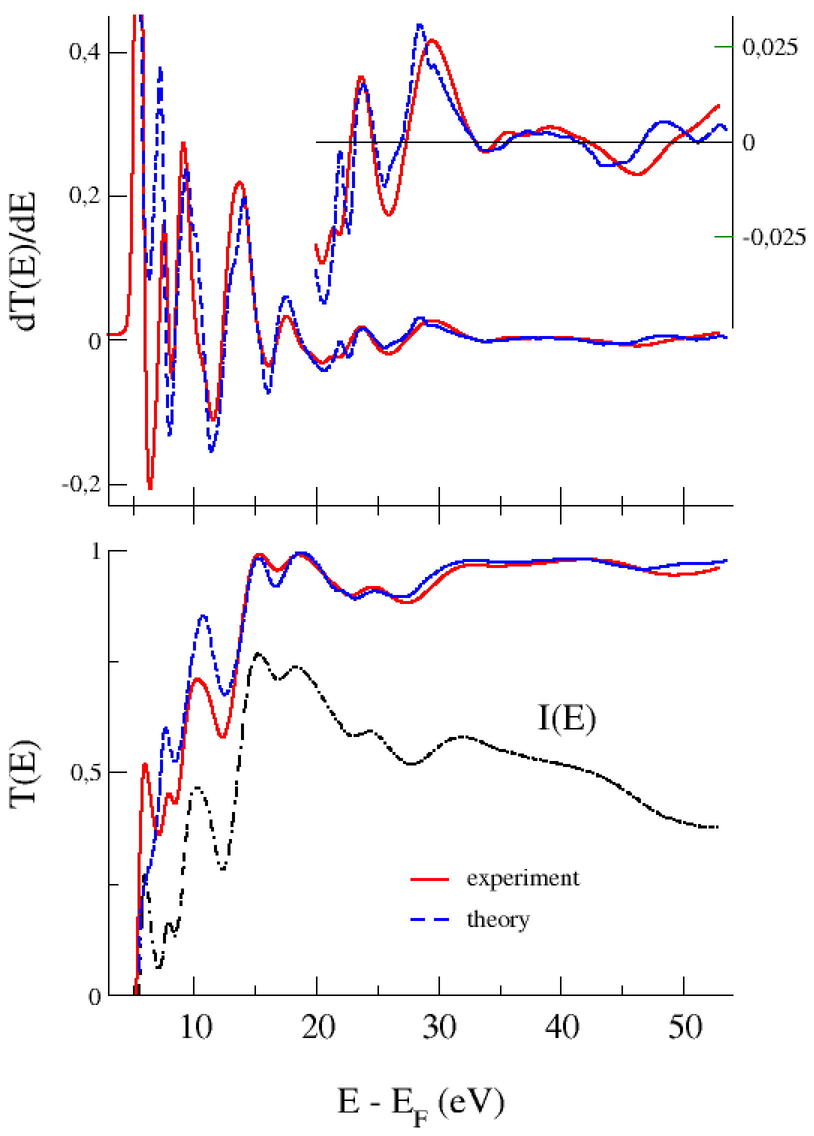
Electron Transmission Spectra in Band Structure Theory

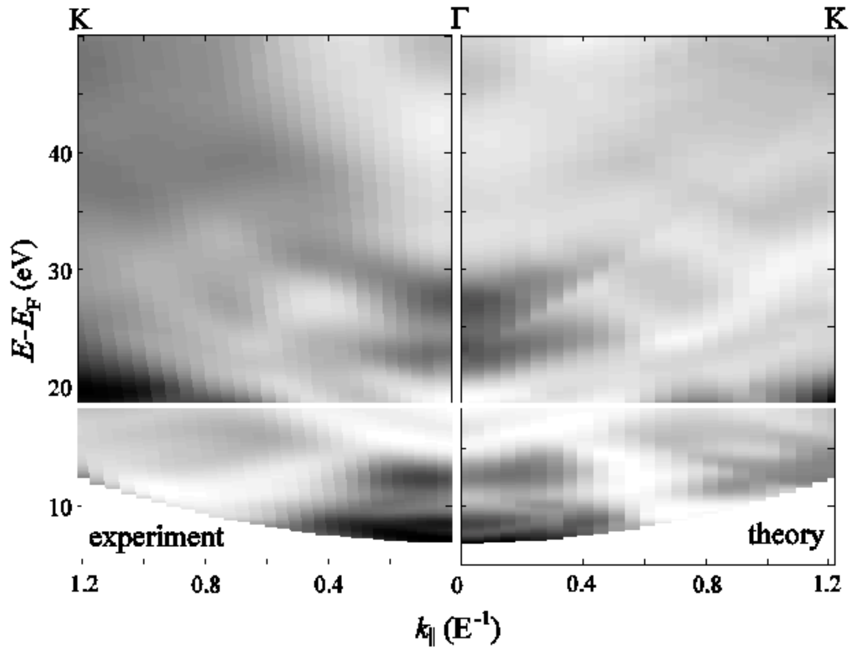
Damped Electron Waves in Crystals. Phys. Rev. **51**, 840 (1937)



J. C. Slater

Target Current Spectroscopy of $NbSe_2$





high

low

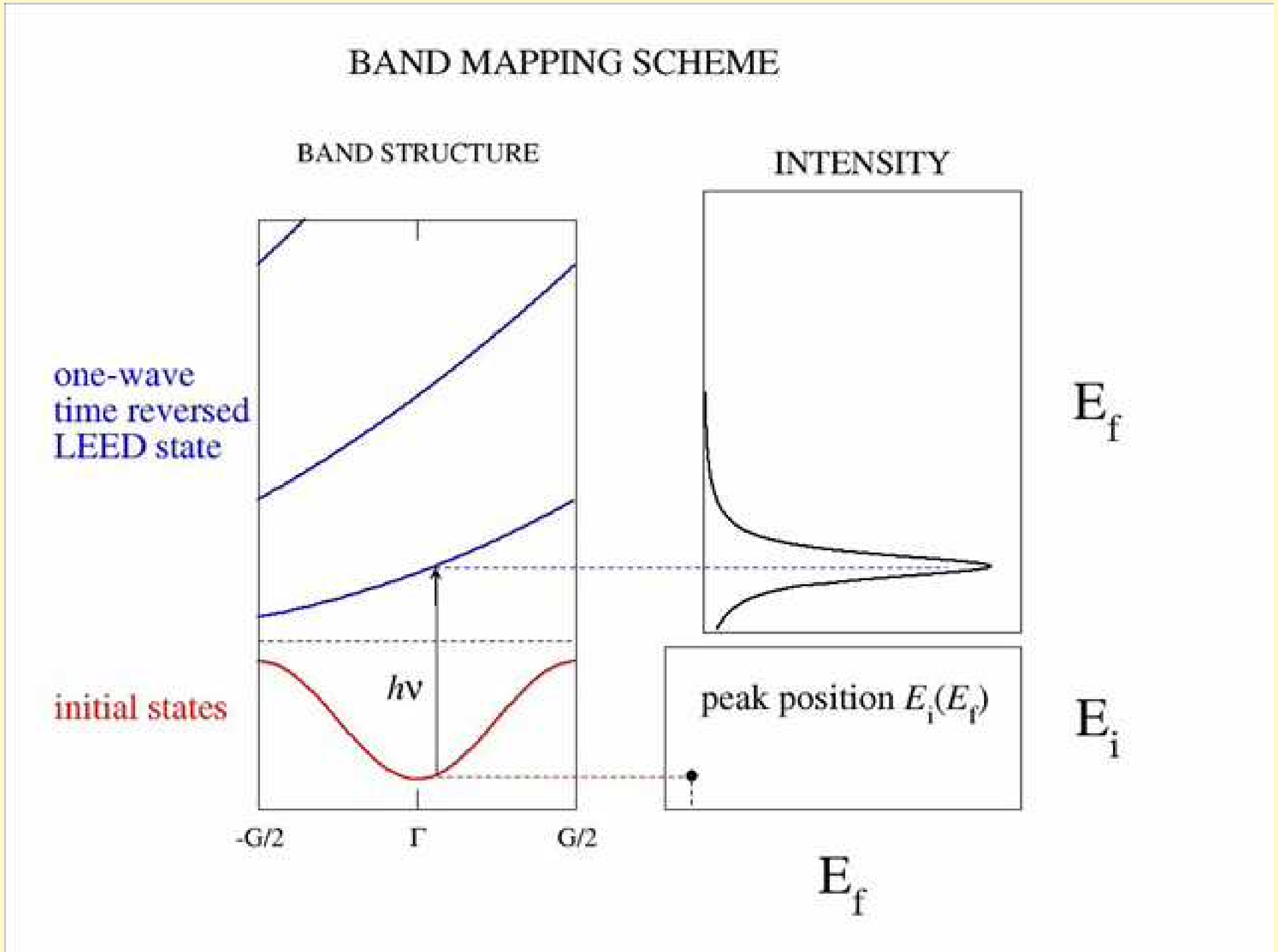
Electron transmission as a function of electron incidence angle and energy

E.K., W. Schattke, V.N. Strocov, and R. Claessen, Phys. Rev. B **66**, 235403 (2002)

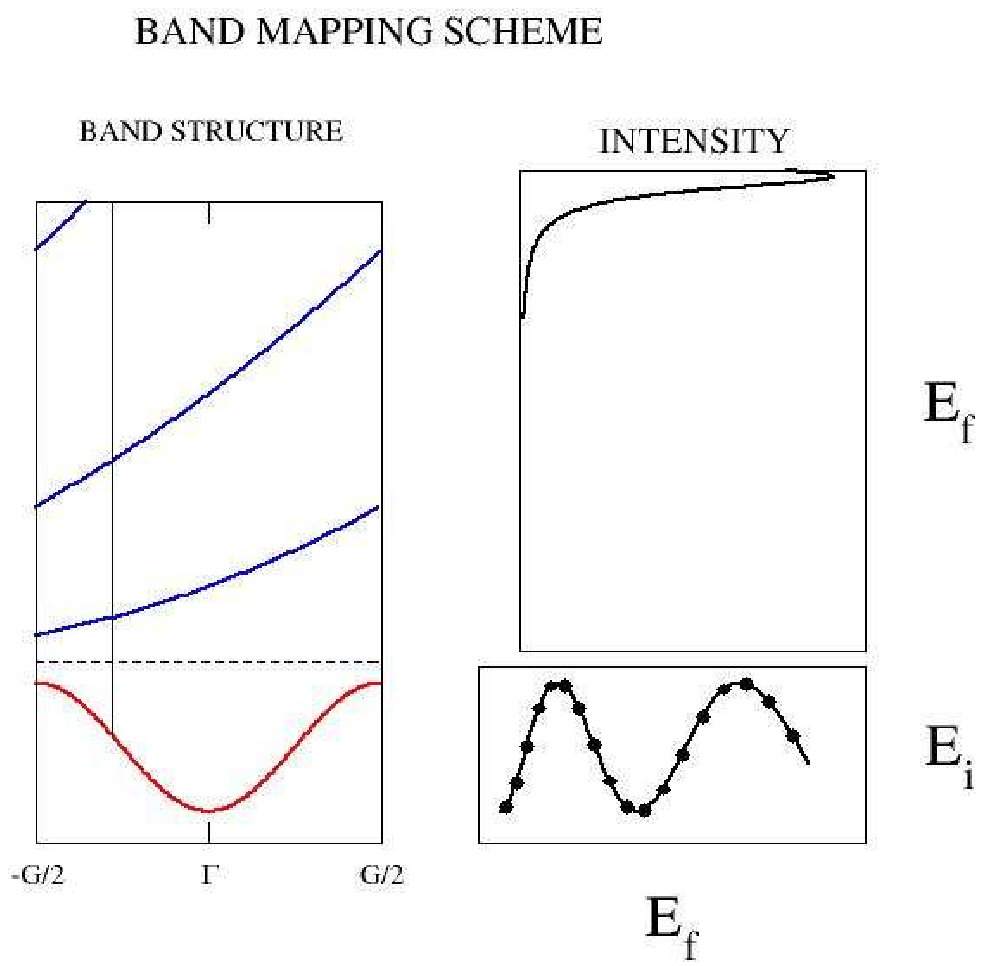
Band Mapping by Angle Resolved Photoemission

How to determine the bulk band structure with a surface sensitive method.

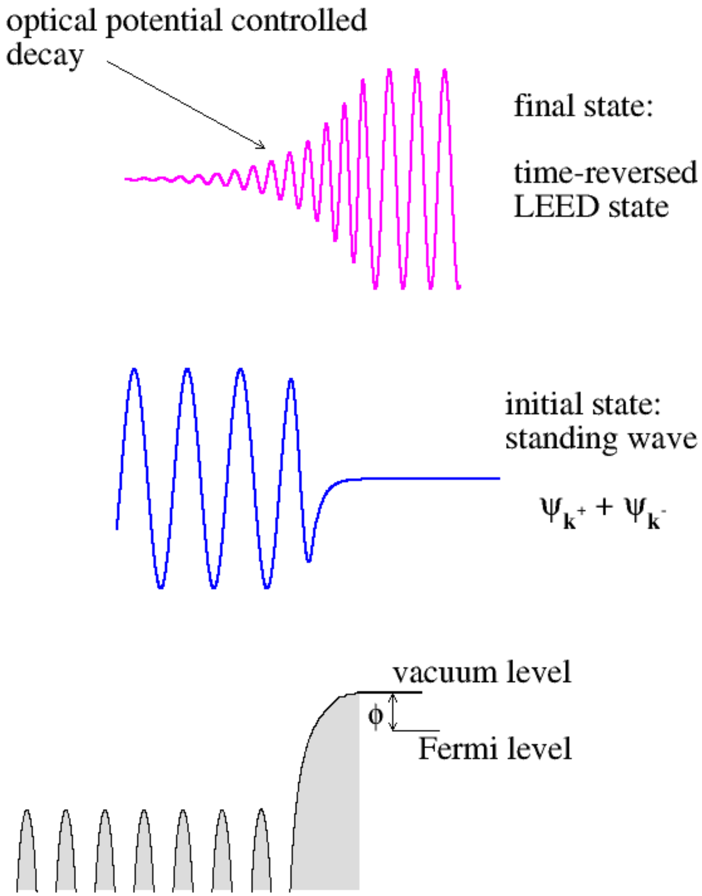
Geometric Band Mapping: Direct Transitions Picture



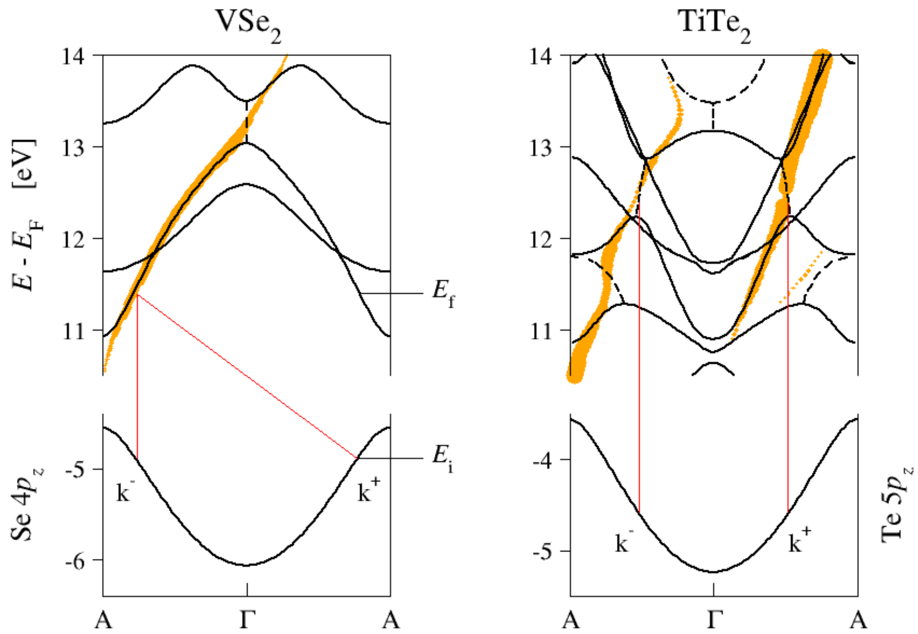
Geometric Band Mapping: Direct Transitions Picture



One-Step Theory of Photoemission

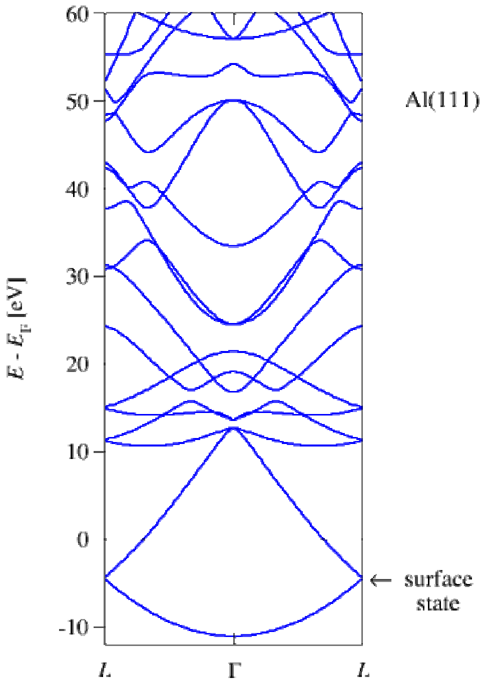


Conducting complex band structure

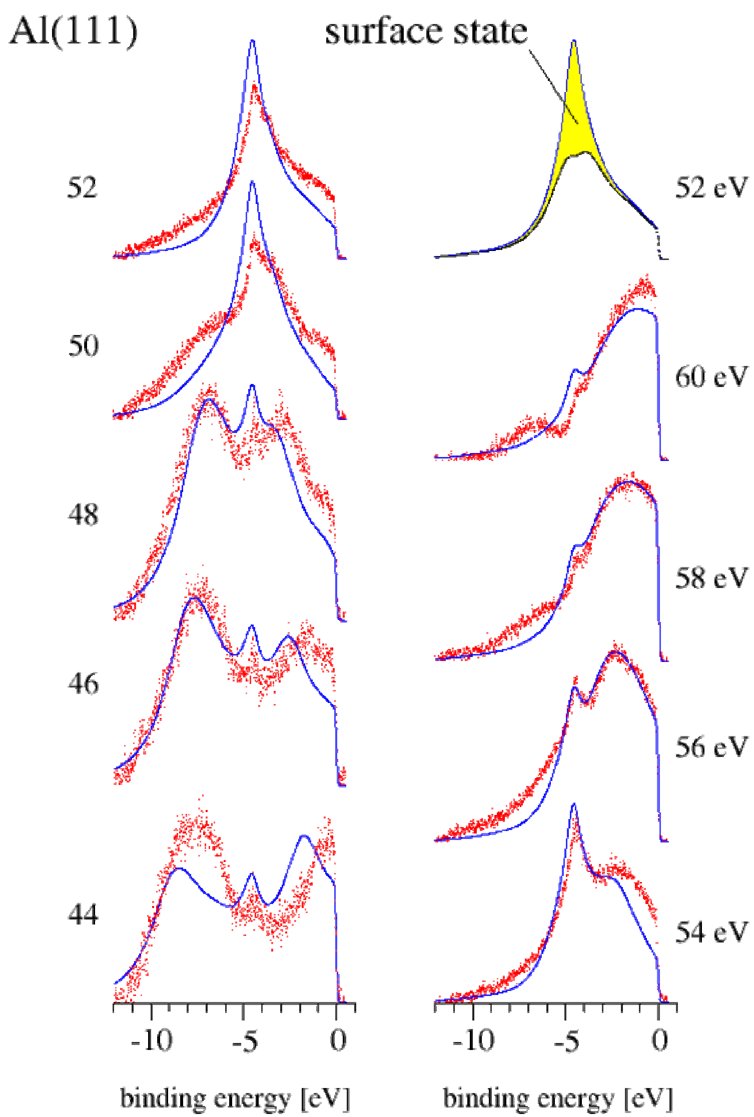


Example: Al(111) – a textbook free-electron-like system

- ARUPS on large binding energy scale
- Surface state intensity enhancement at $\hbar\omega$= 50 eV



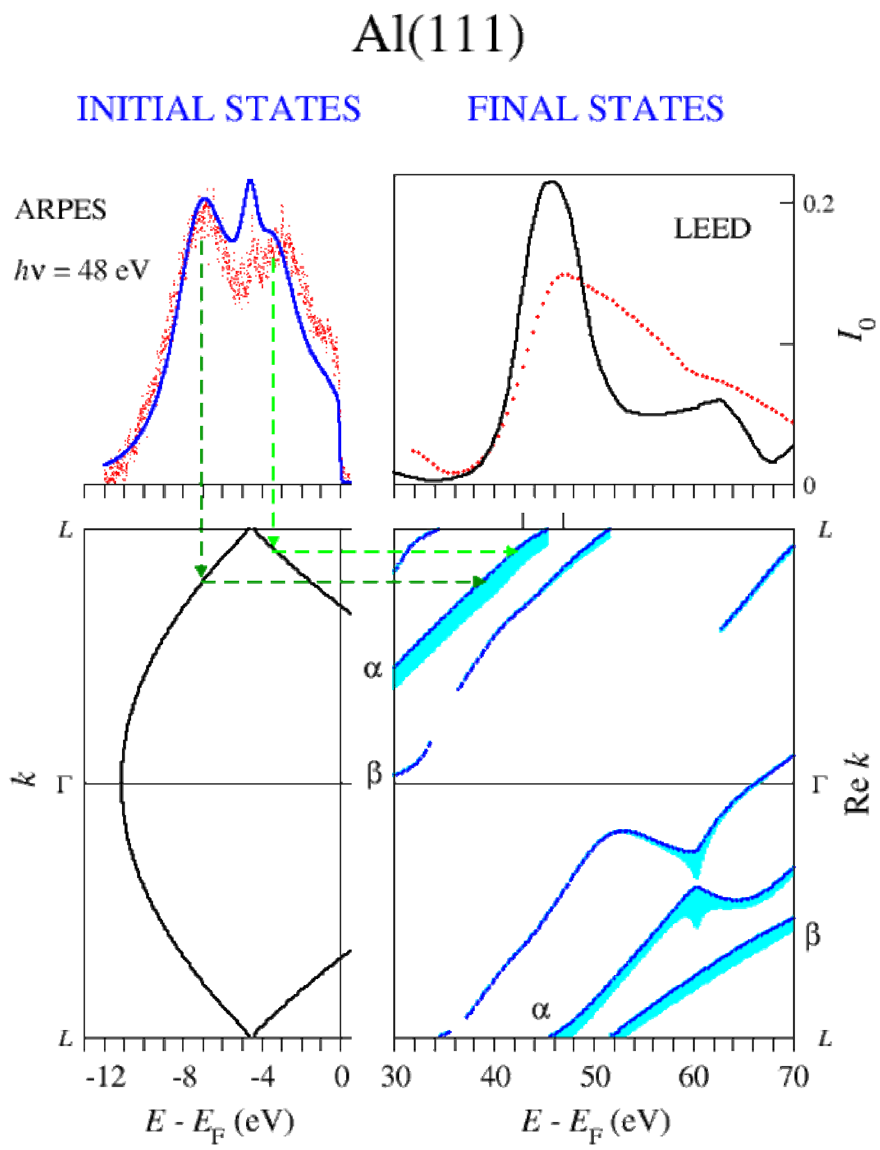
Experiment by Jiříček, Dudr, Bartoš (2006)



Band structure interpretation of photoemission: Al(111)

Photoemission final states are time-reversed LEED states.

Complex band structure constituents serve as partial waves.

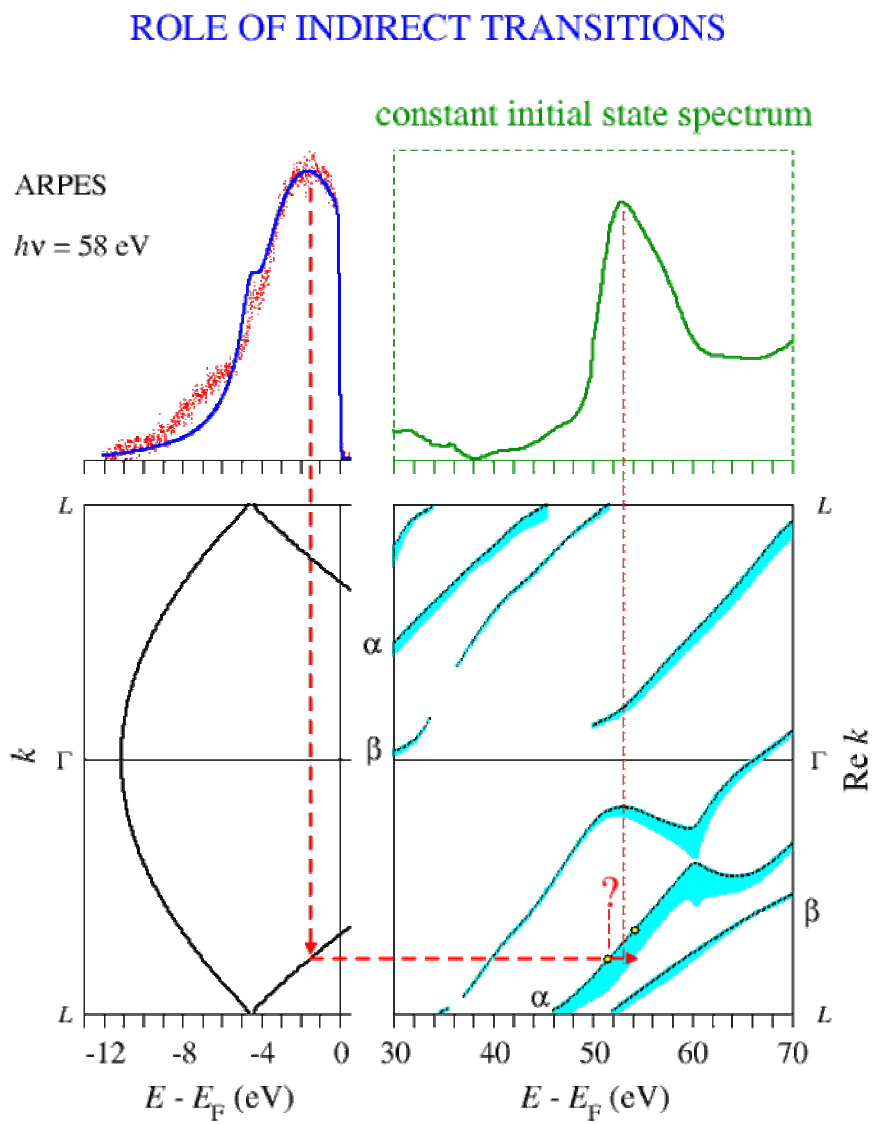


Band structure of Al(111) is far from free-electron-like.

EK, Schattke, Jiříček, Dudr, Bartoš (2006)

Al(111) – a free-electron-like system?

Even for aluminium the ‘geometric’ band mapping may be misleading.



EK, Schattke, Jiříček, Dudr, Bartoš (2006)

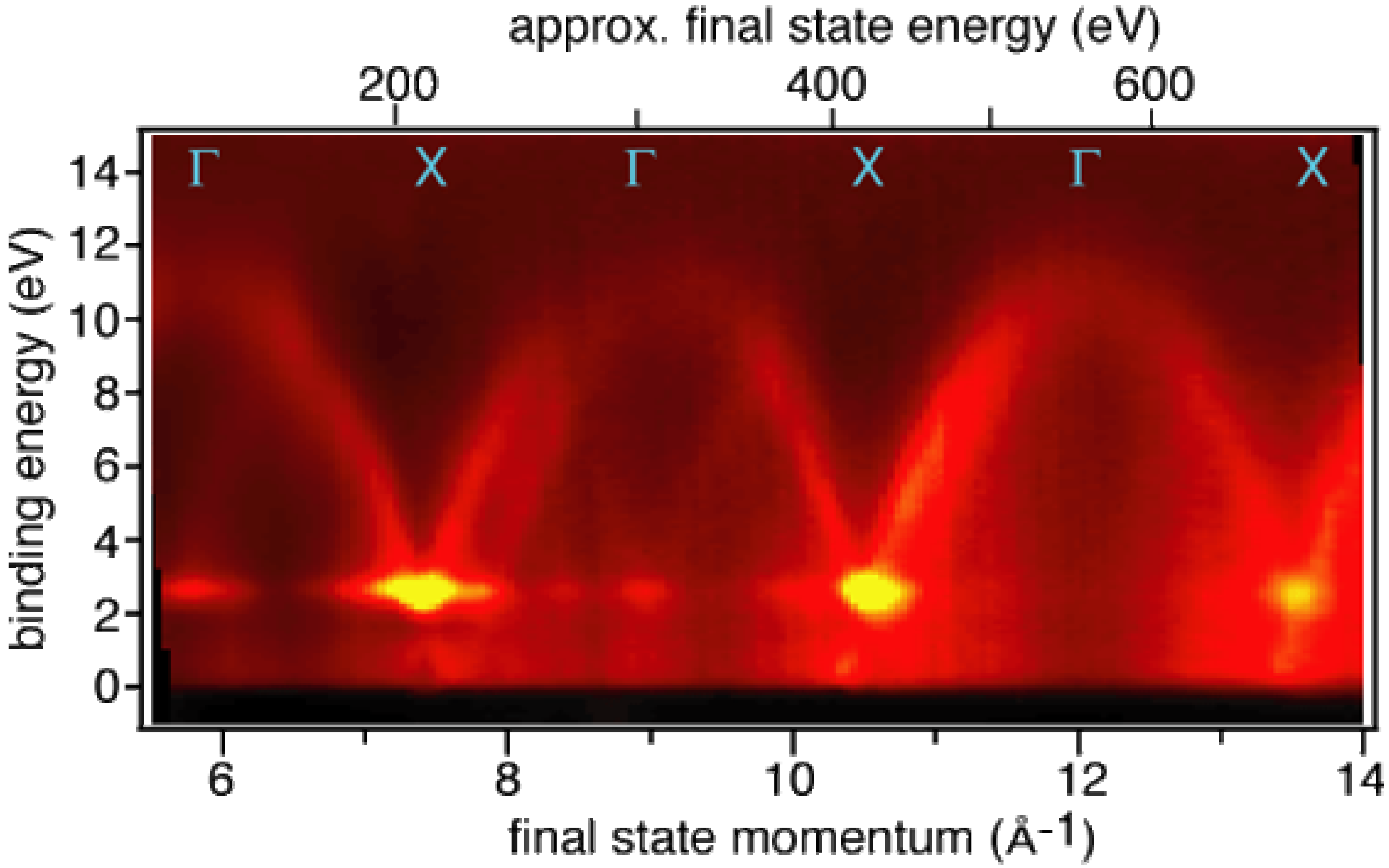
INTERMEDIATE CONCLUSIONS

- The one-step theory works.
- Final states cannot be expected to be free-electron-like.
- Direct transitions picture is too optimistic.

Photoemission from Surface States

Another Method to Study Final States

Surface state photoemission: Al (100)



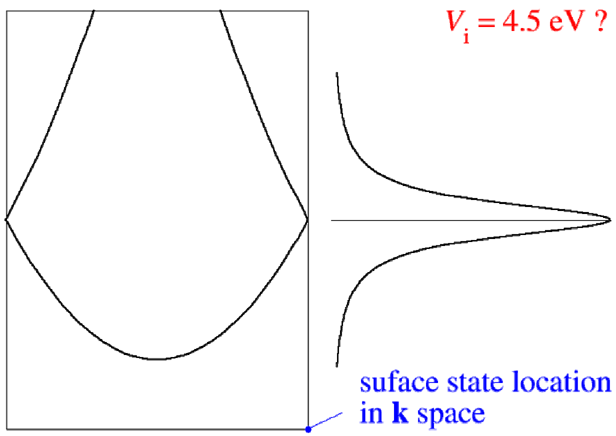
Hofmann *et al.* Phys. Rev. B **66**, 245422 (2002)

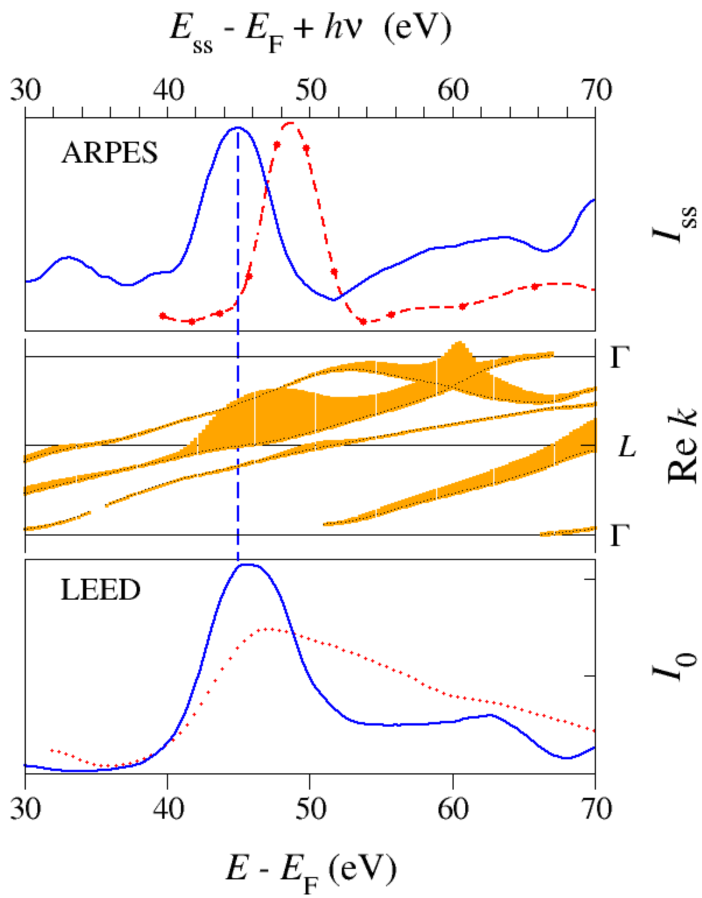
from http://whome.phys.au.dk/~philip/photoemgroup/photoemhome.htm

Surface state photoemission: Al (111)

Emission from surface states shows strong photon energy dependence: emission windows are separated by wide regions of low intensity

First observed by Kevan, Stoffel and Smith (1985). An explanation: final state broadening due to inelastic scattering





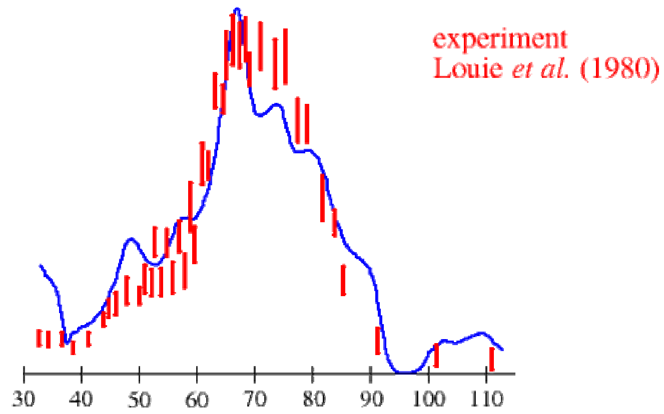
EK, Schattke, Jiříček, Dudr, Bartoš (2006)

Surface state photoemission: Cu (111) and Al(100)

Complicated band structure at high energies:

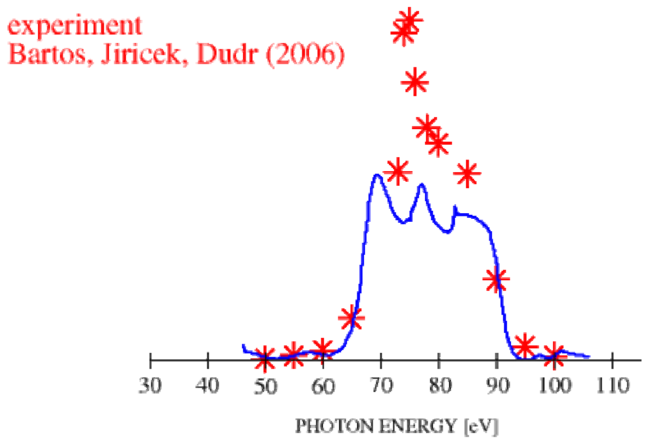
Emission intensity grows by orders of magnitude.

Emission from the surface state at -0.55 eV on Cu(111)

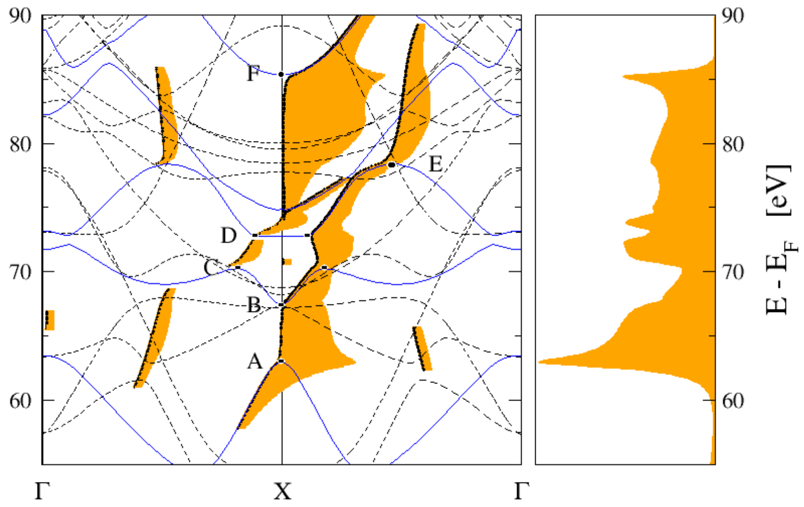


$V_i = 2$ eV; $E_f \rightarrow E_f + 2.5$ eV

Emission from the surface state at -0.265 eV on Al(100)

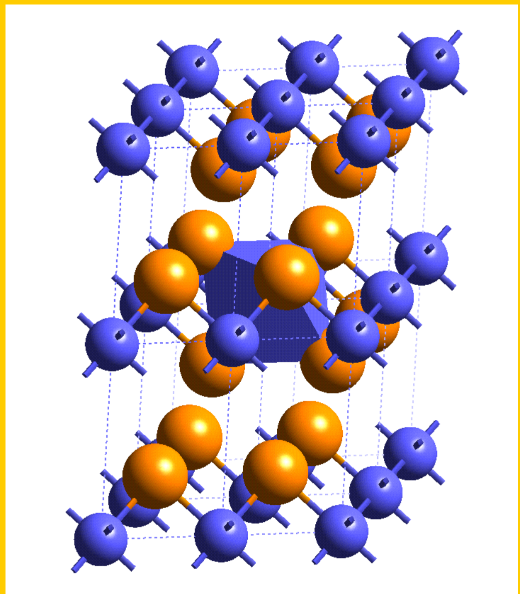


Partial contributions to the surface state photoemission intensity

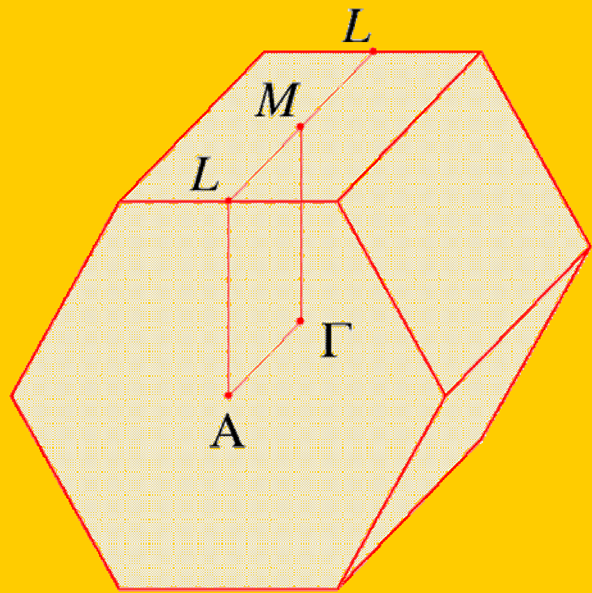


EK and W. Schattke, Phys. Rev. Lett. **93**, 027601 (2004)

Valence band photoemission from layered dichalcogenides $TiTe_2$ and VSe_2



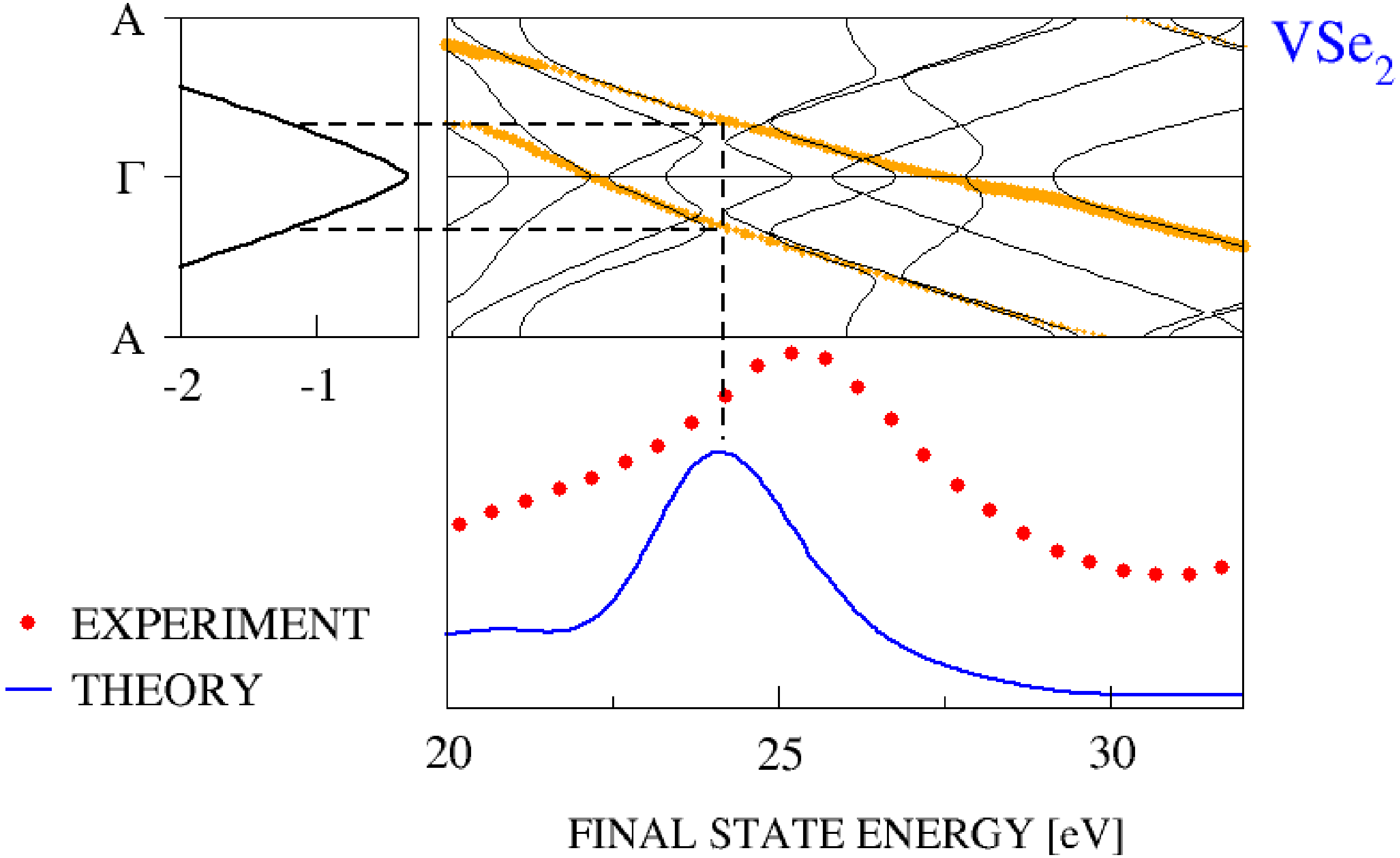
Crystal structure CdI_2



Brillouin zone

Normal emission from VSe_2: double-Bloch-wave final states

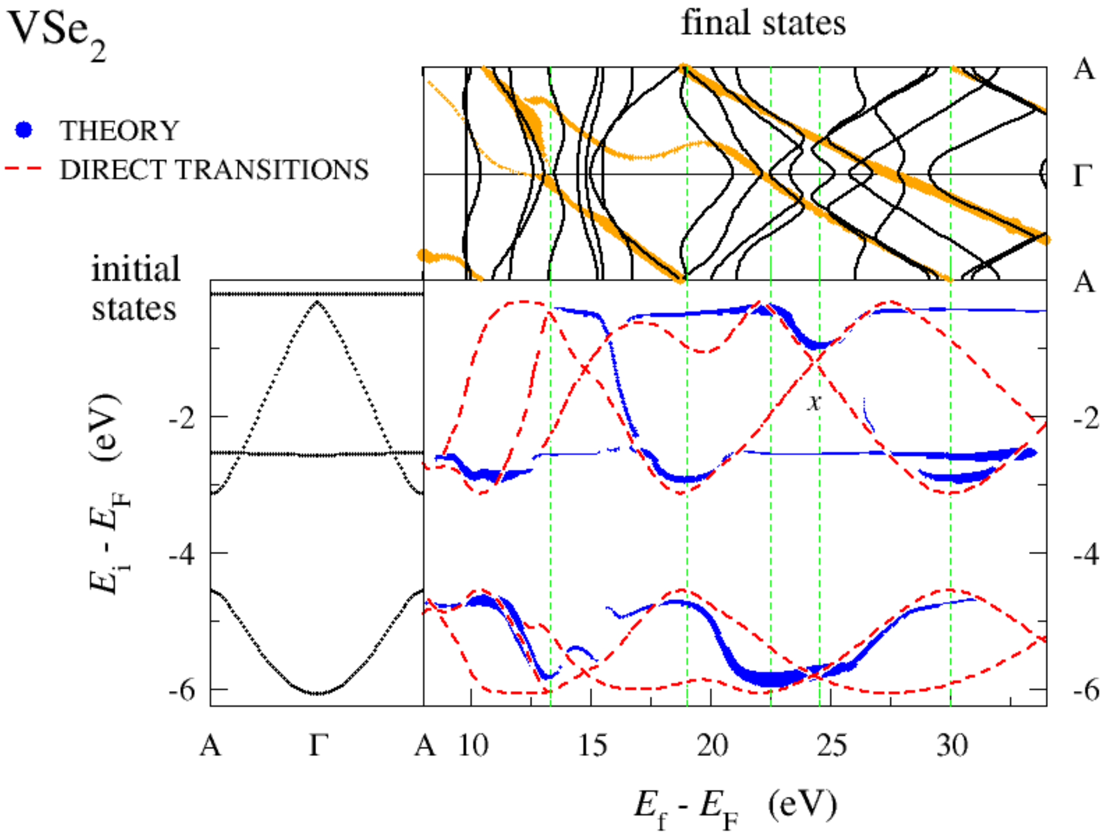
Interference effects in constant initial state spectrum

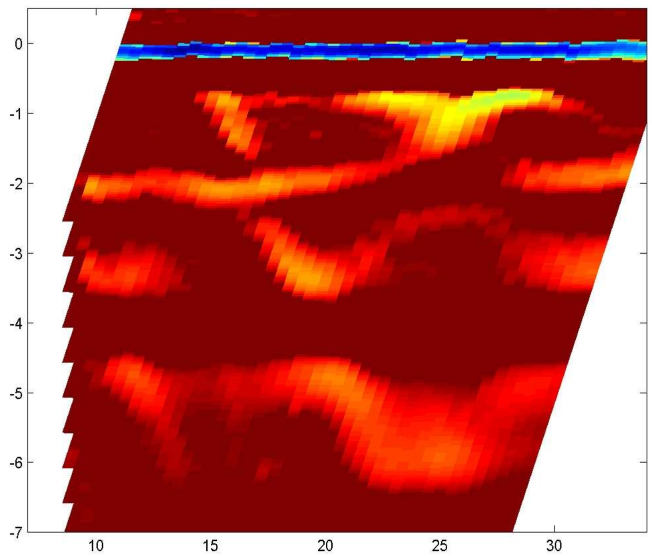


E.K., V.N. Strocov, N. Barrett, H. Berger, W. Schattke, R. Claessen, Phys. Rev. B **75**, 045432 (2007)

Interference effects: band mapping of Se 4*p* states in VSe_2

Theoretical peak dispersion deviates from direct transitions lines: can the band structure be derived from the measured spectra?





E.K., V.N. Strocov, N. Barrett, H. Berger, W. Schattke, R. Claessen, Phys. Rev. B **75**, 045432 (2007)

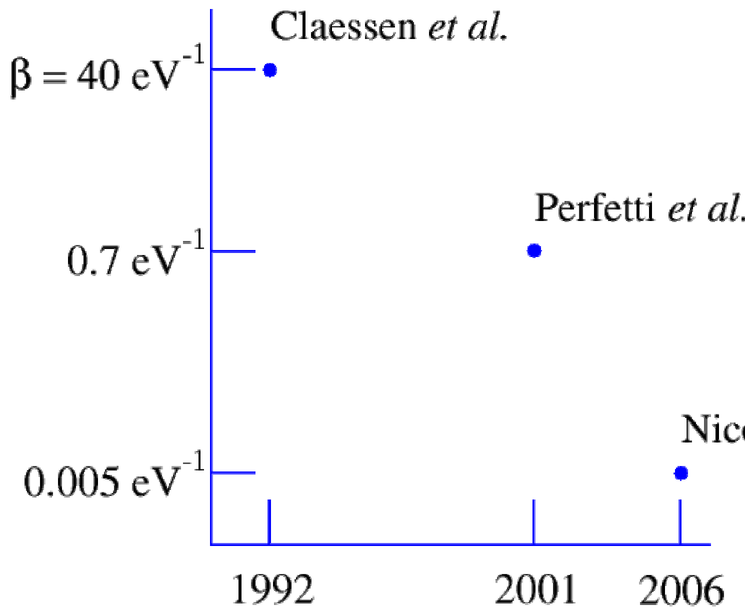
Do our senses deceive us?

Spectroscopy of the Ti 3d band in 1T - $TiTe_2$

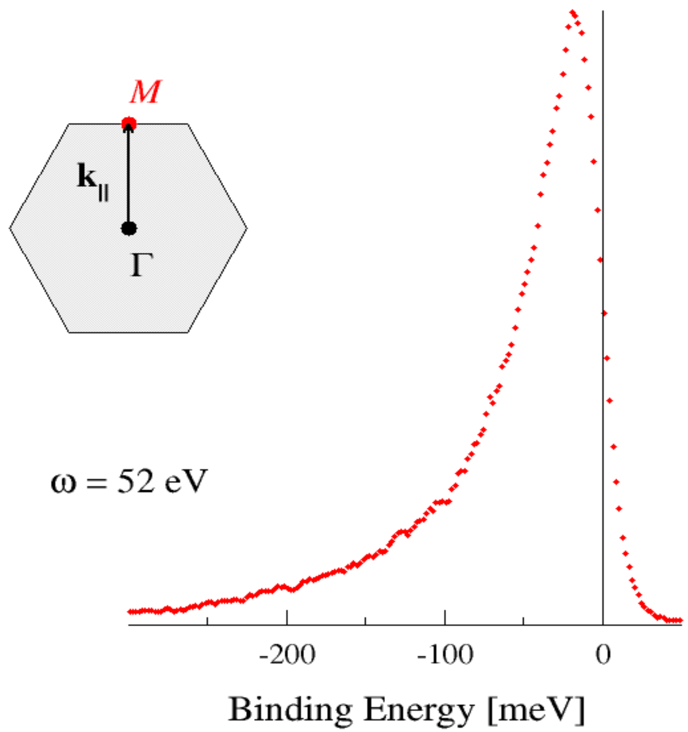
Does the line shape reflect the initial state spectral function?

Energy dependence of hole lifetime in Fermi liquid $\Gamma(E) = \beta E^2$

Fermi liquid parameter β for Ti 3d states of $TiTe_2$



Off-normal emission from $TiTe_2$

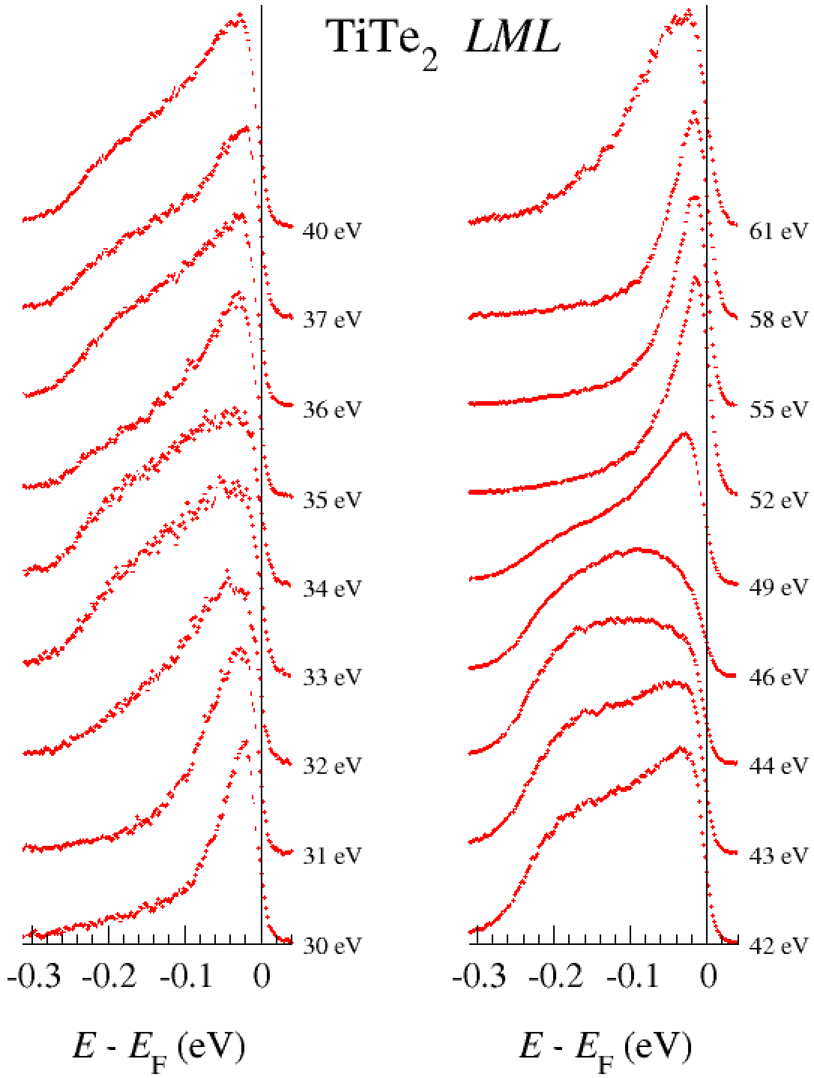


Spectroscopy of the Ti 3*d* band in 1*T* - $TiTe_2$

Line shape changes dramatically with photon energy

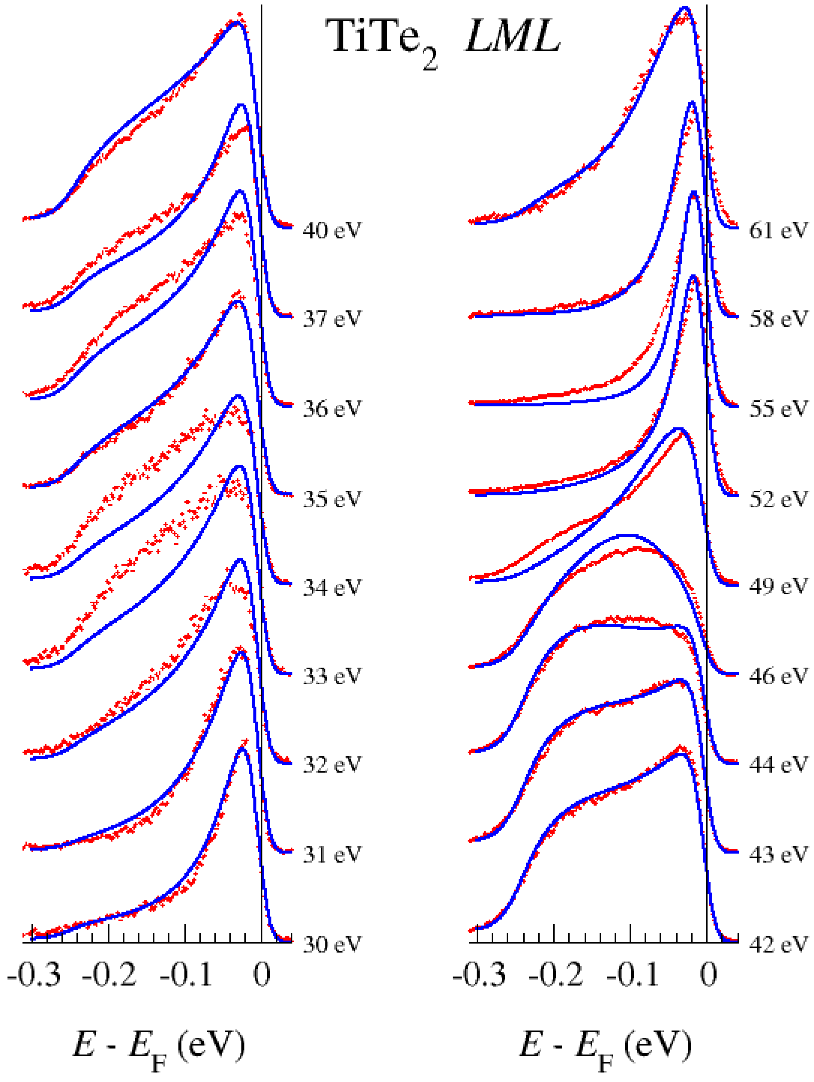
What is the effect of the momentum broadening in the final state?

E.K., K. Roßnagel, A. Fedorov, W. Schattke, L. Kipp (2007)



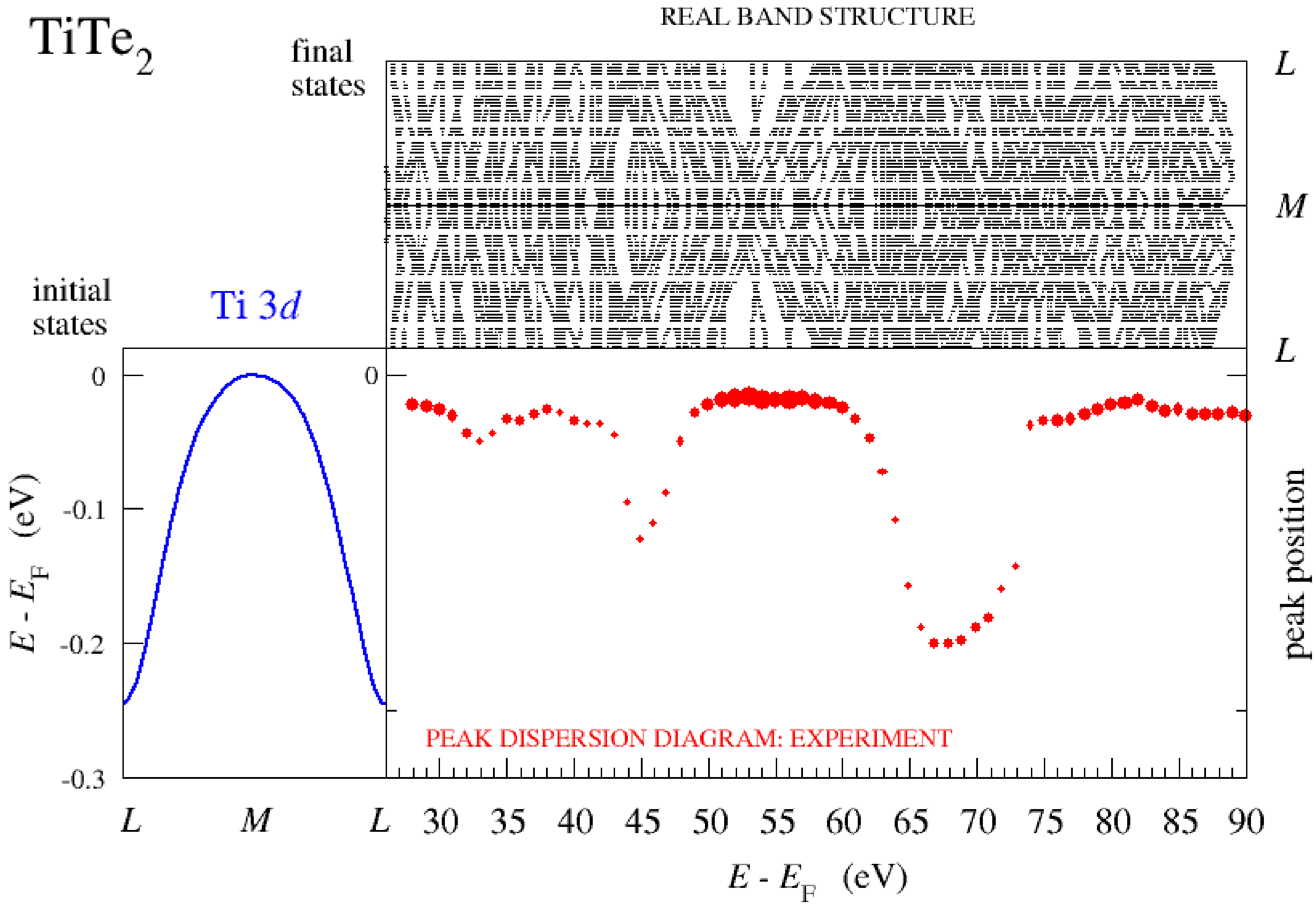
Spectroscopy of the Ti 3*d* band in 1*T* - $TiTe_2$

One-step photoemission theory accurately describes the changes of line shape

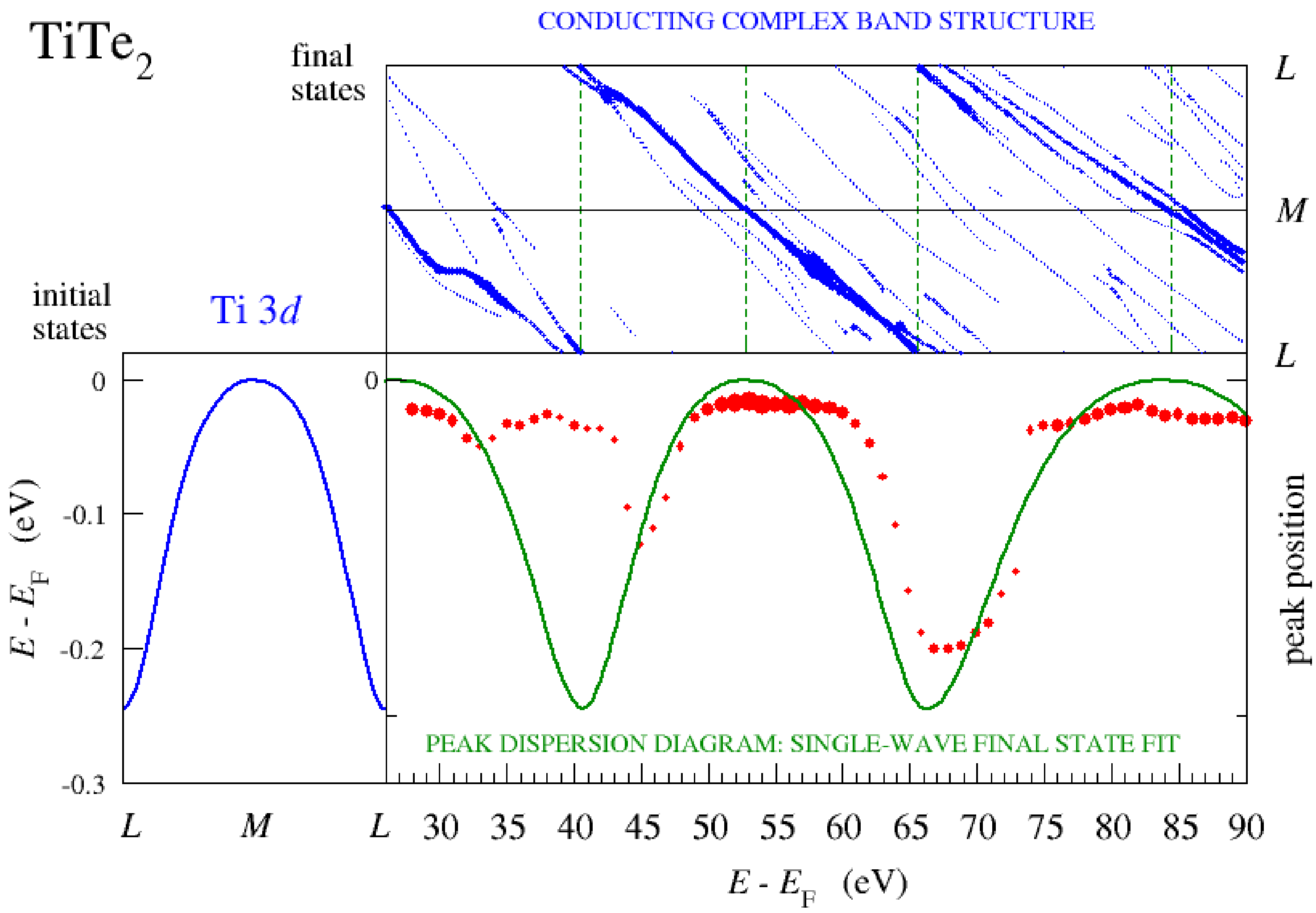


E.K., K. Roßnagel, A. Fedorov,
W. Schattke, L. Kipp (2007)

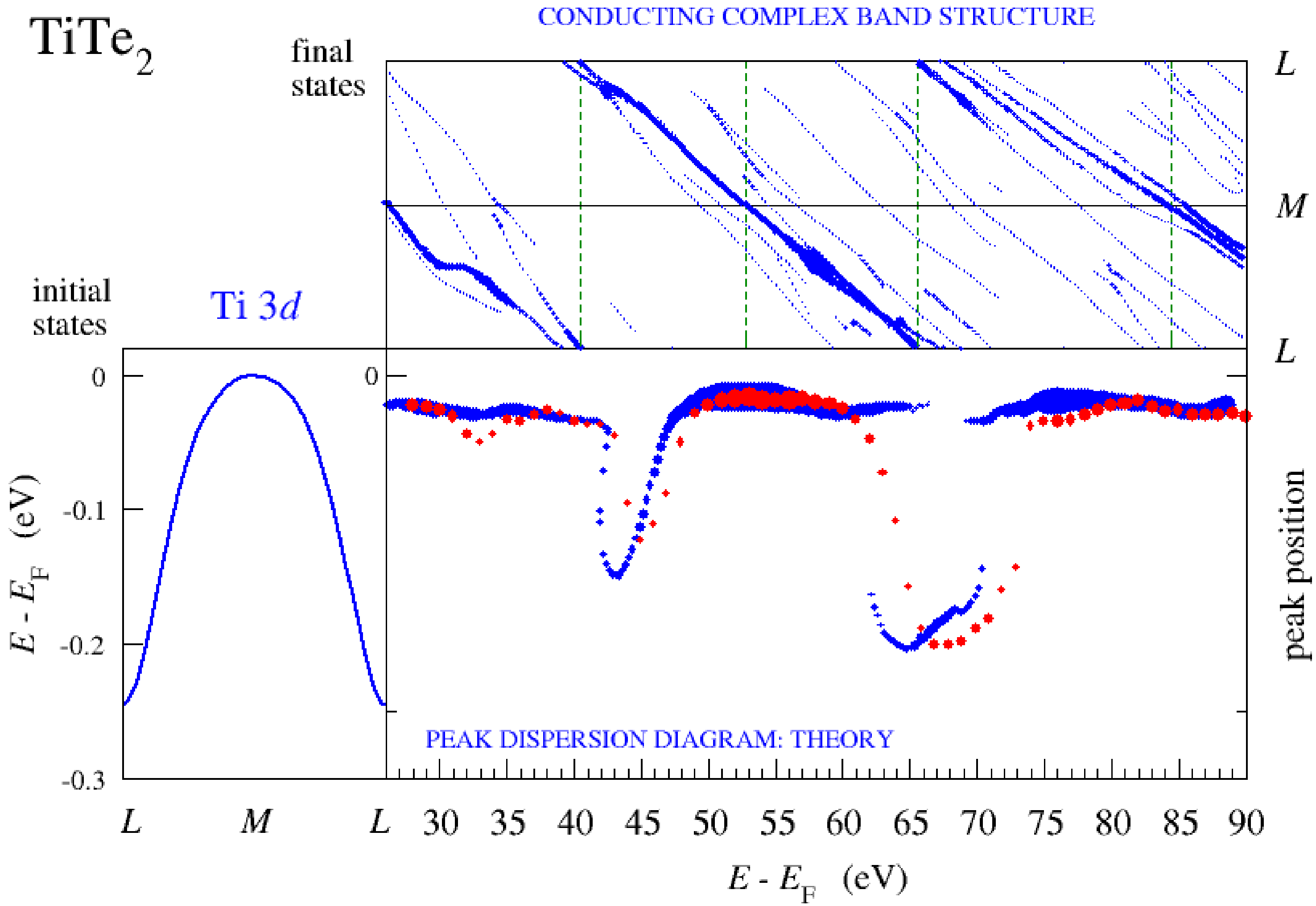
Band mapping of Ti 3d states in $TiTe_2$



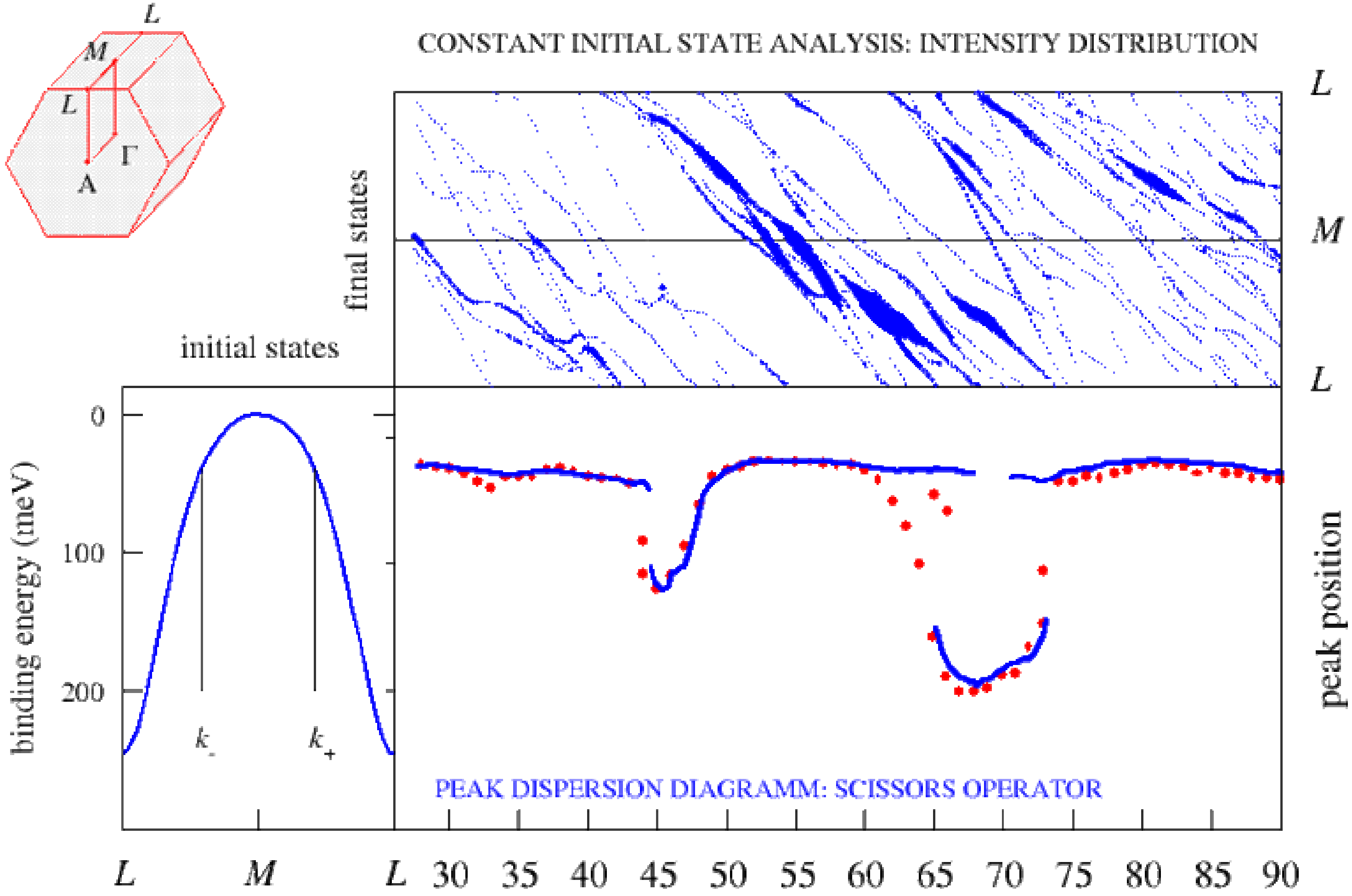
Band mapping of Ti 3*d* states in $TiTe_2$



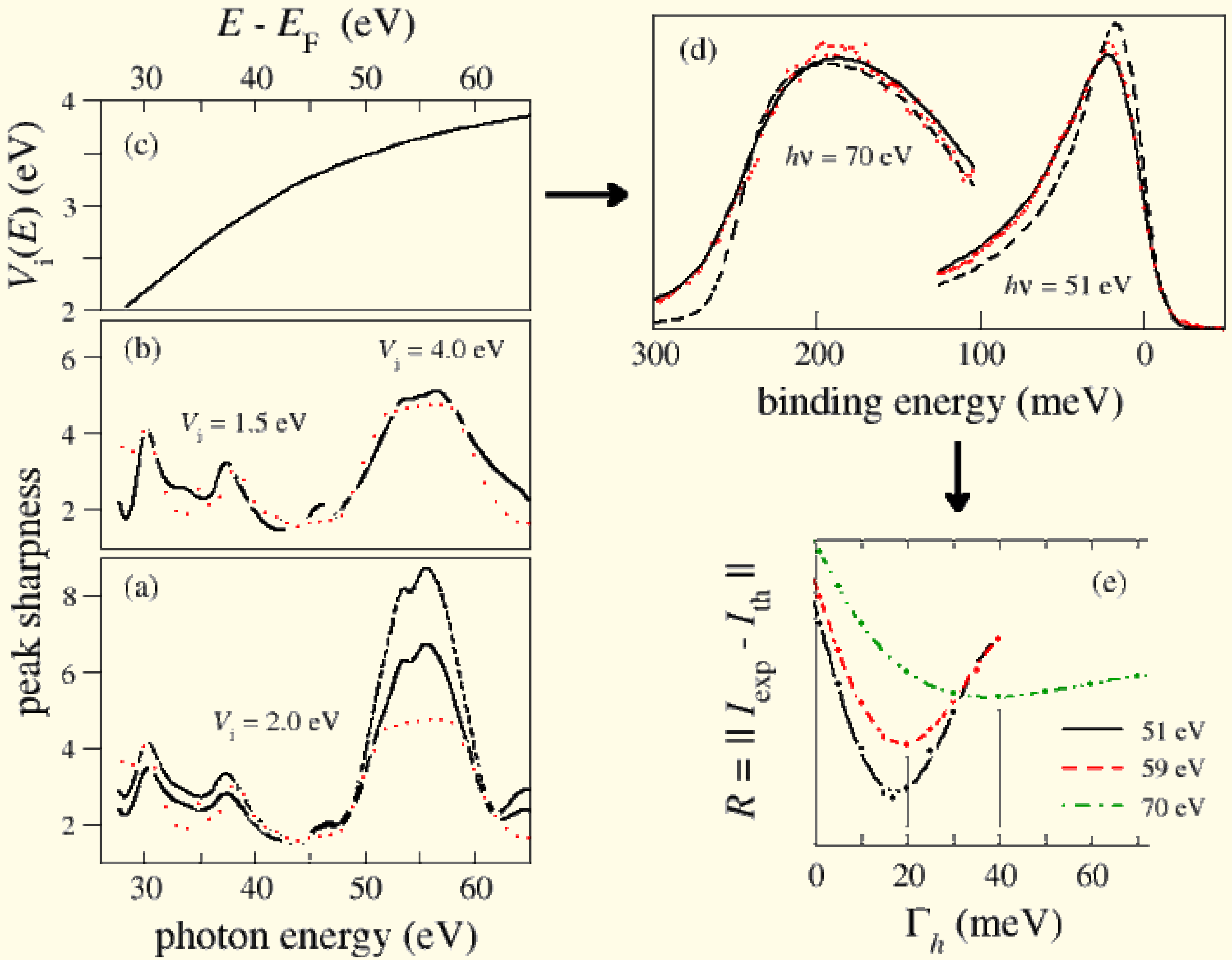
Band mapping of Ti 3*d* states in $TiTe_2$



Band mapping of Ti 3d states in $TiTe_2$

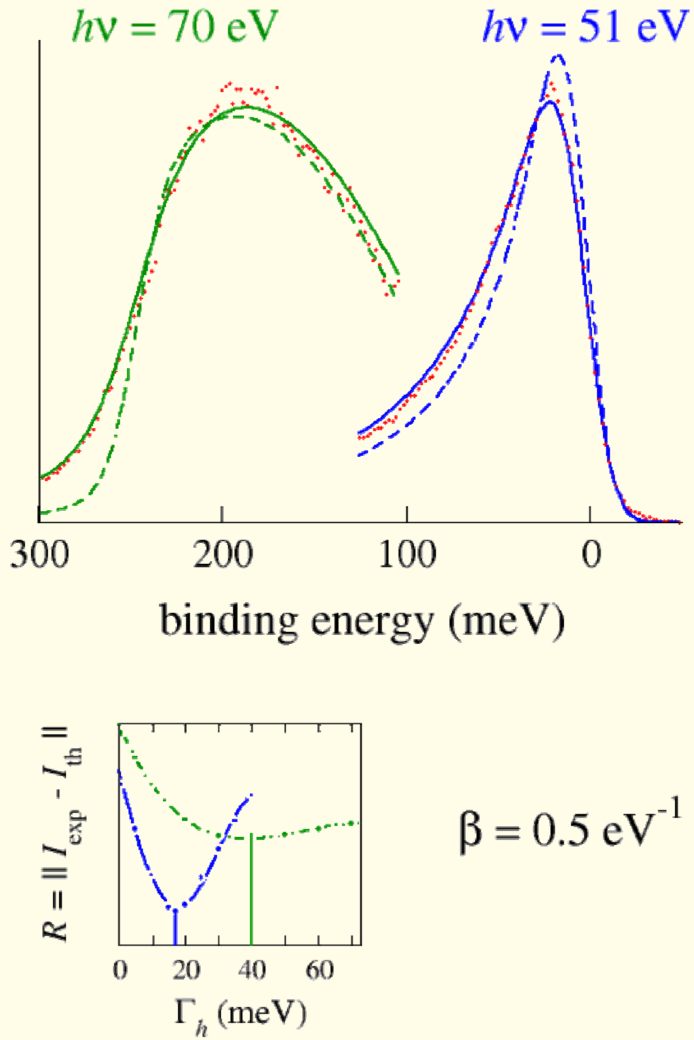


Ti 3*d* states in $TiTe_2$: line shape dynamics



INTERMEDIATE CONCLUSIONS

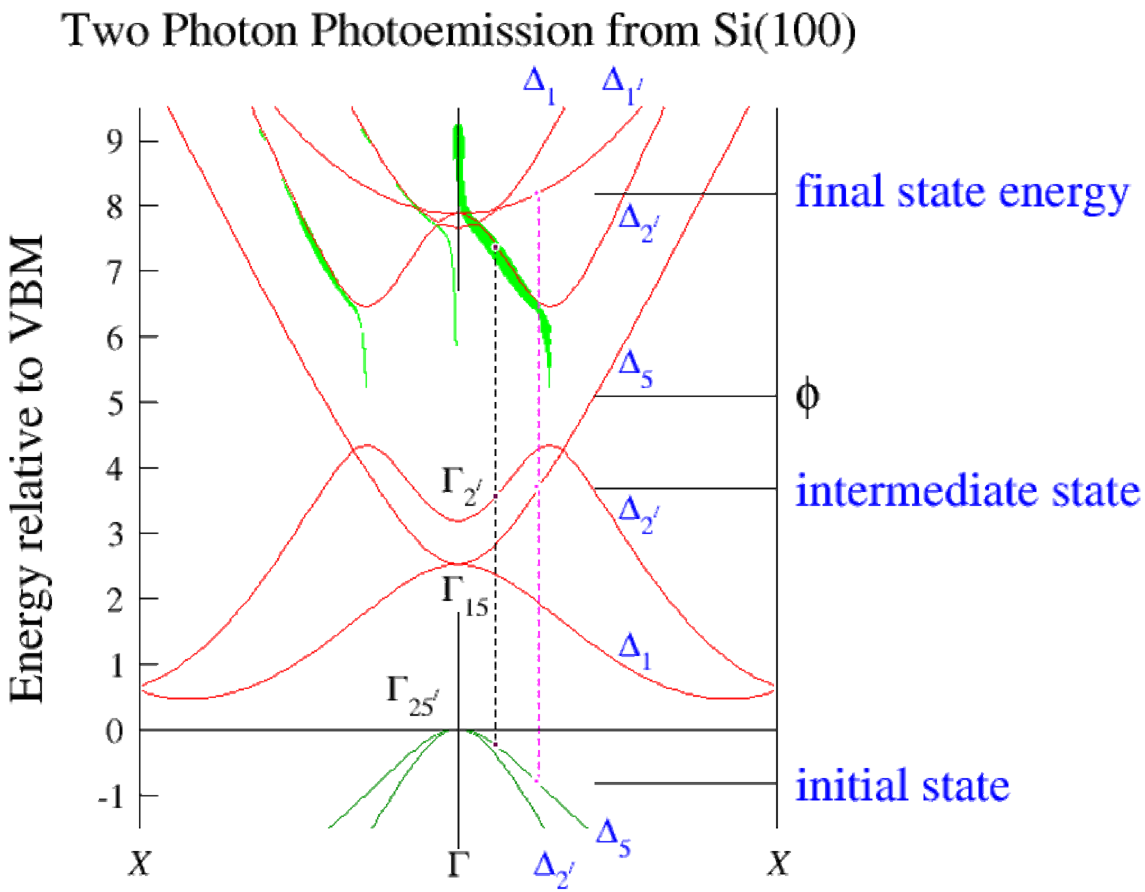
- It is not the spectral function that is seen in the photoemission experiment.
- The spectral function can be inferred from the experiment based on the one-step theory. In particular, the hole lifetime can be determined.



Aspects of Two-Photon Photoemission

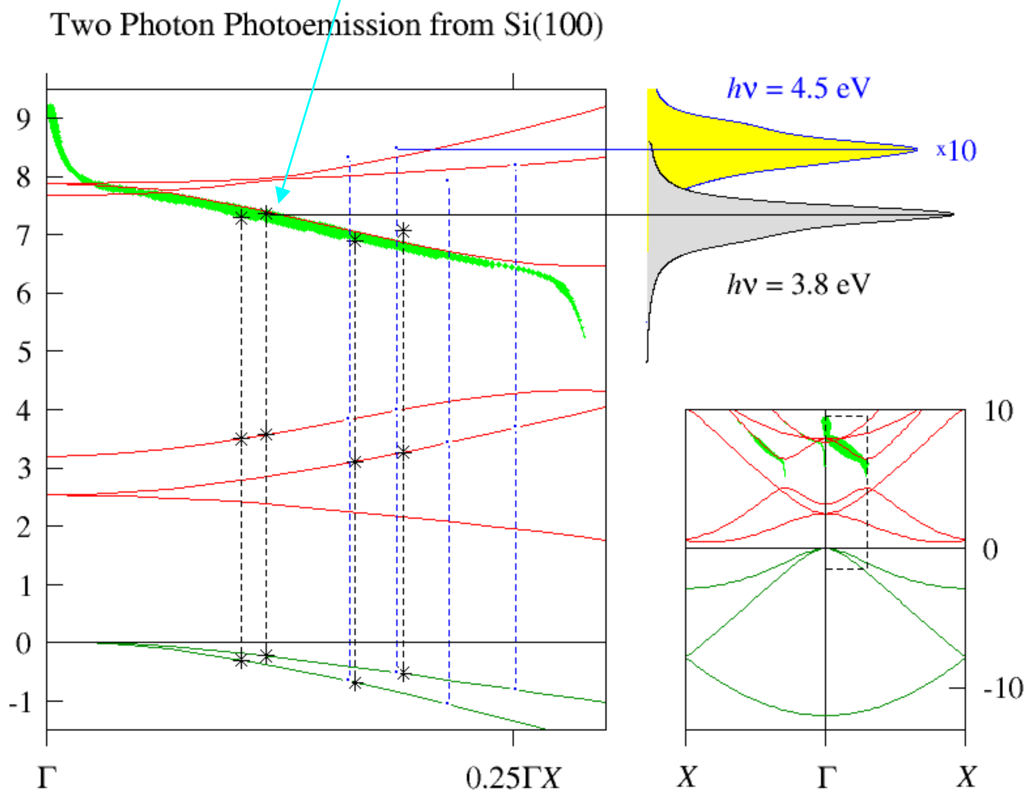
$$|\,\epsilon + 2\hbar\omega\,\rangle = \hat{G}(\epsilon_a + 2\hbar\omega)\Delta\hat{H}\,\hat{G}(\epsilon_a + \hbar\omega)\Delta\hat{H}\,|\,a\,\rangle$$

- Effect of final states on the line width is strongly reduced → sharp peaks.
- Final states affect the intensity of two-photon photocurrent.



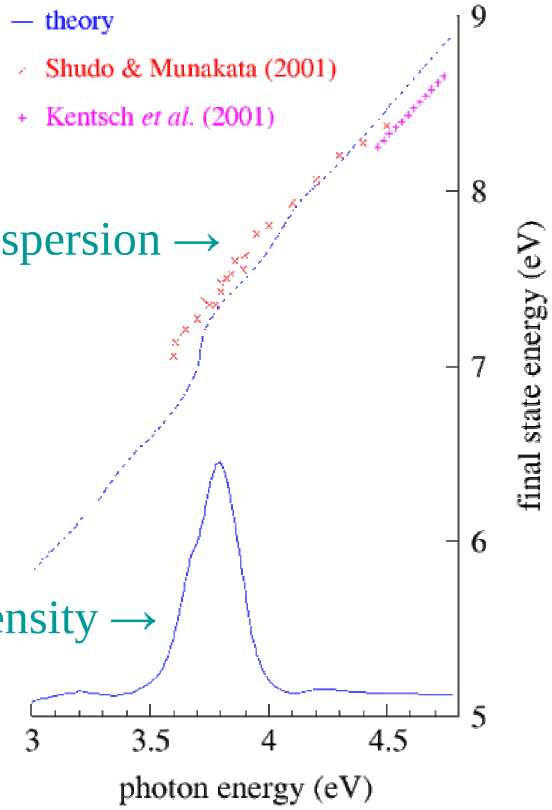
Resonance Two-Photon Photoemission from Si(100)

resonance due to dispersion of final state



peak dispersion →

peak intensity →



CONCLUSIONS

- The wave functions formalism for semi-infinite systems is a sound basis for *ab initio* treatment of excitations at surfaces.
- Multiple scattering is important up to 100 eV, and band structure can be resolved.
- The damped waves model of inelastic scattering provides a detailed description of measured spectra.
- Spectra are most conveniently interpreted in terms of conducting complex band structure, but band mapping should allow for the interference between Bloch states.

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