The Abdus Salam
International Centre for Theoretical Physics

1936-33

Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

7 - 25 April 2008

Very low-photoemission spectroscopy.

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Very low-energy photoemission spectroscopy

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Sincrotrone Trieste S.C.p.A.

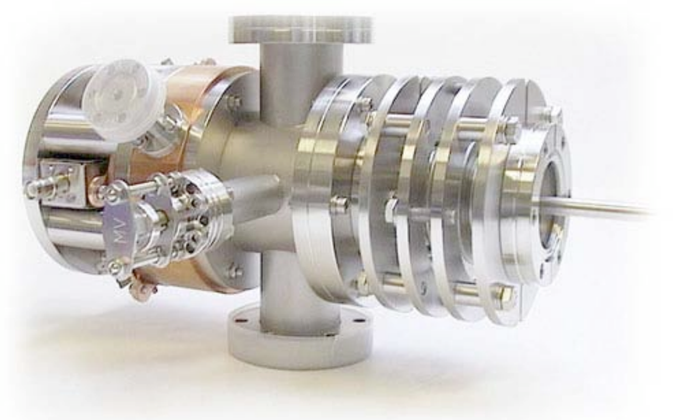
Outline

- How low photon energy are produced
- The Bad ElPh beamline
- Reasons for low photon energy: bulk sensitivity, higher momentum resolution, good energy resolution easier
- Sudden Approx still valid?
- Final state effects?
- Other problems

How low photon energies can be obtained ?

1) Gas discharge lamp (He=21.22 eV, Ne=16.85 eV, Ar= 11.62-11.83 eV, H_2= 10.2 eV)

Large spot size (several mm), ~ 10^{14} photons/s, intrinsic linewidth ~ 1-2meV
satellite lines



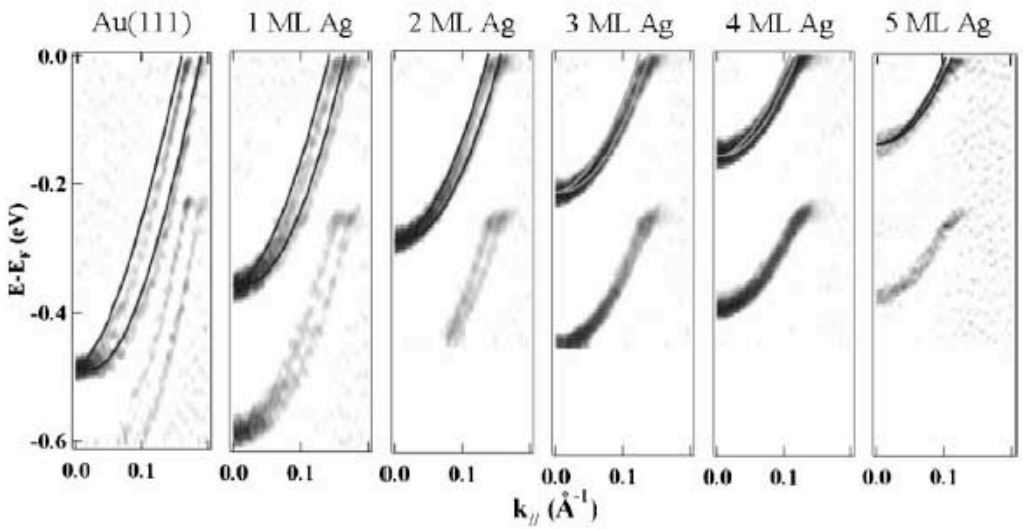


FIG. 2. Surface state dispersion changes with silver coverage taken with Ar I. The grey-scale maps represent the second derivative of the measured intensity. The calculations of the Shockley state (black lines) have been shifted for each coverage to fit the measured binding energies. The replica at higher BEs is due to the Ar satellite.

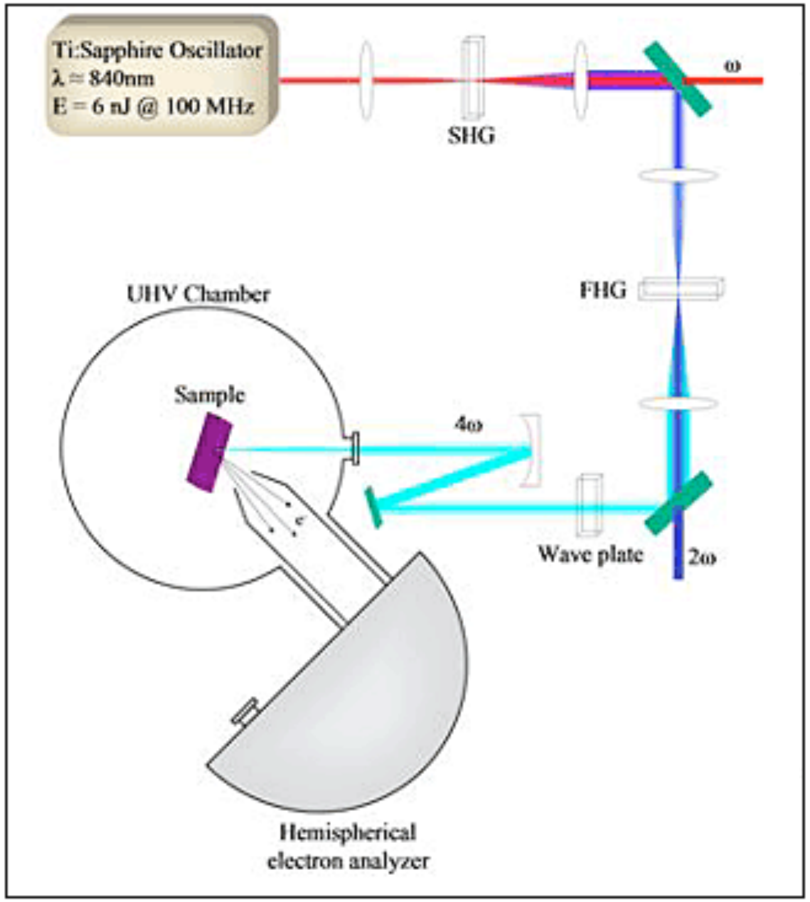
How low photon energies can be obtained ?

2) Laser systems (6 - 7 eV)

Spot size 1-500μm, > 10^{15} photons/s on the sample, intrinsic linewidth 0.26-0.1meV, only one energy

S. Shin, RIKEN, Tokyo Univ. (Jap)
D.S. Dessau, Univ. Colorado (USA)

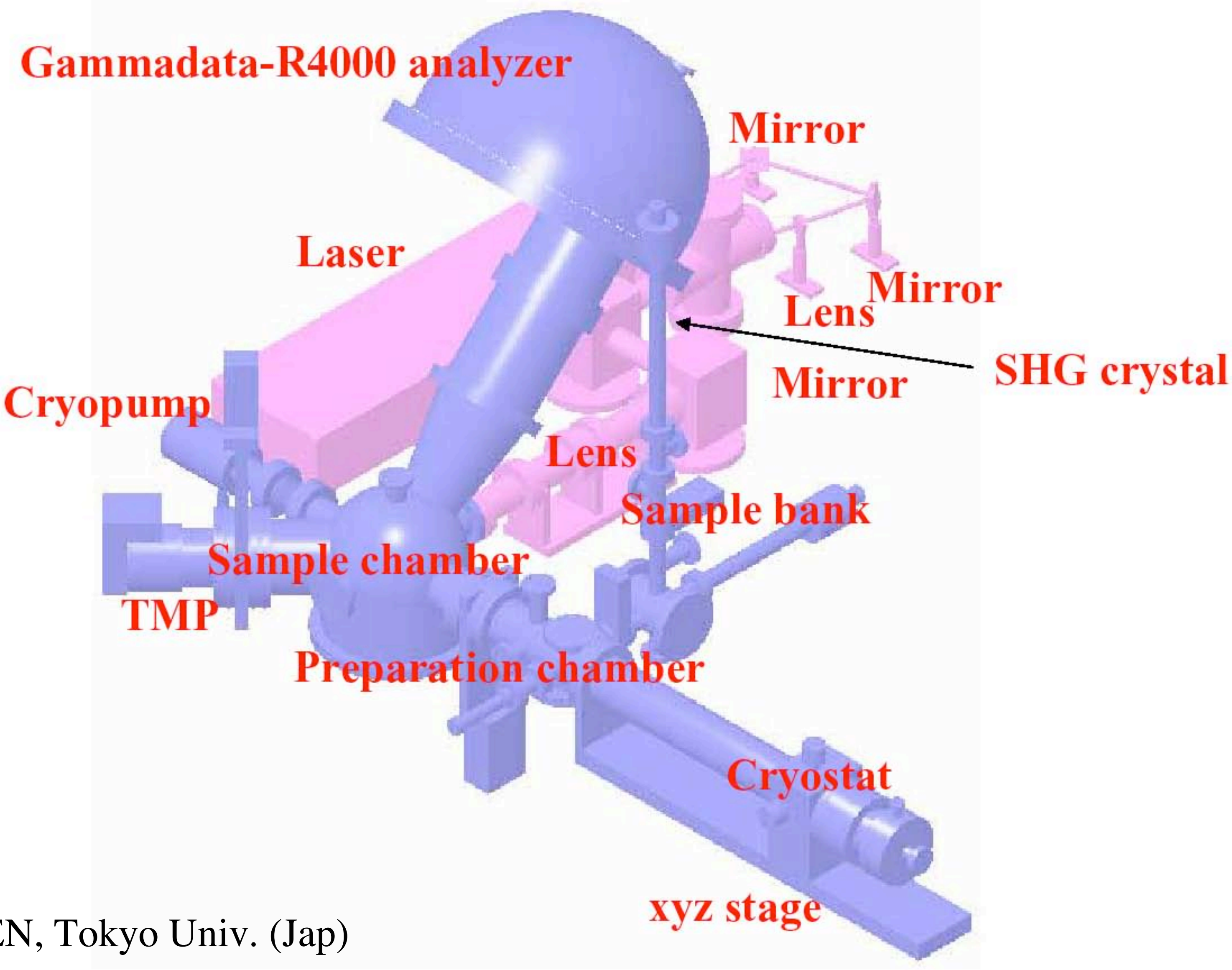
Schematic of a system for performing photoemission spectroscopy based on a frequency quadrupled Ti:sapphire oscillator (6 eV) running at 100 MHz.



Note the high repetition rate:
Needed for a high signal to noise while keeping the instantaneous electron emission rate low.

This last aspect is critical for keeping the electronic response of the sample in the linear regime and to minimize space-charge and other spurious effects.

Laser excitation photoemission spectrometer

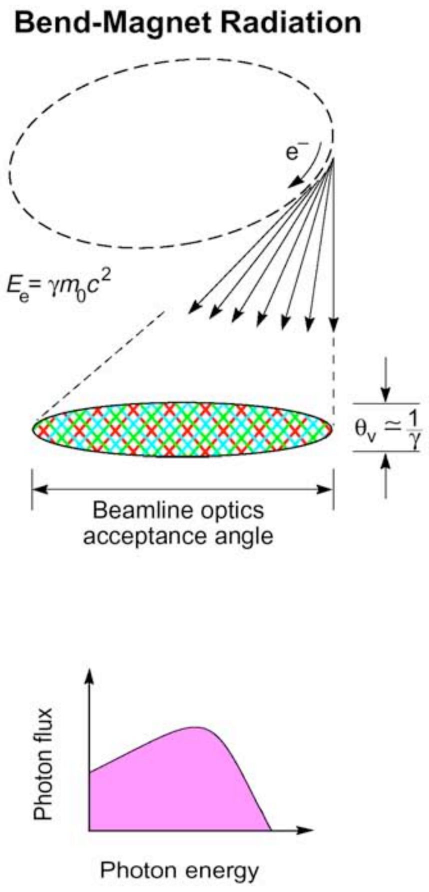


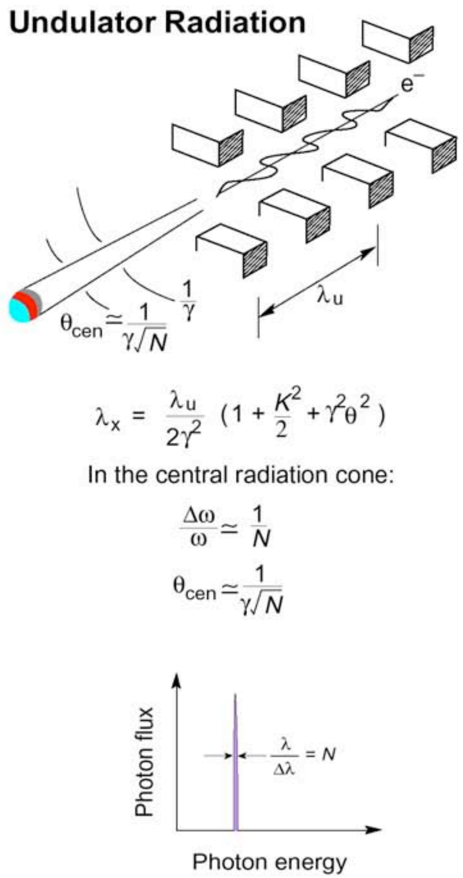
S. Shin, RIKEN, Tokyo Univ. (Jap)

How low photon energies can be obtained ?

3) Synchrotron radiation

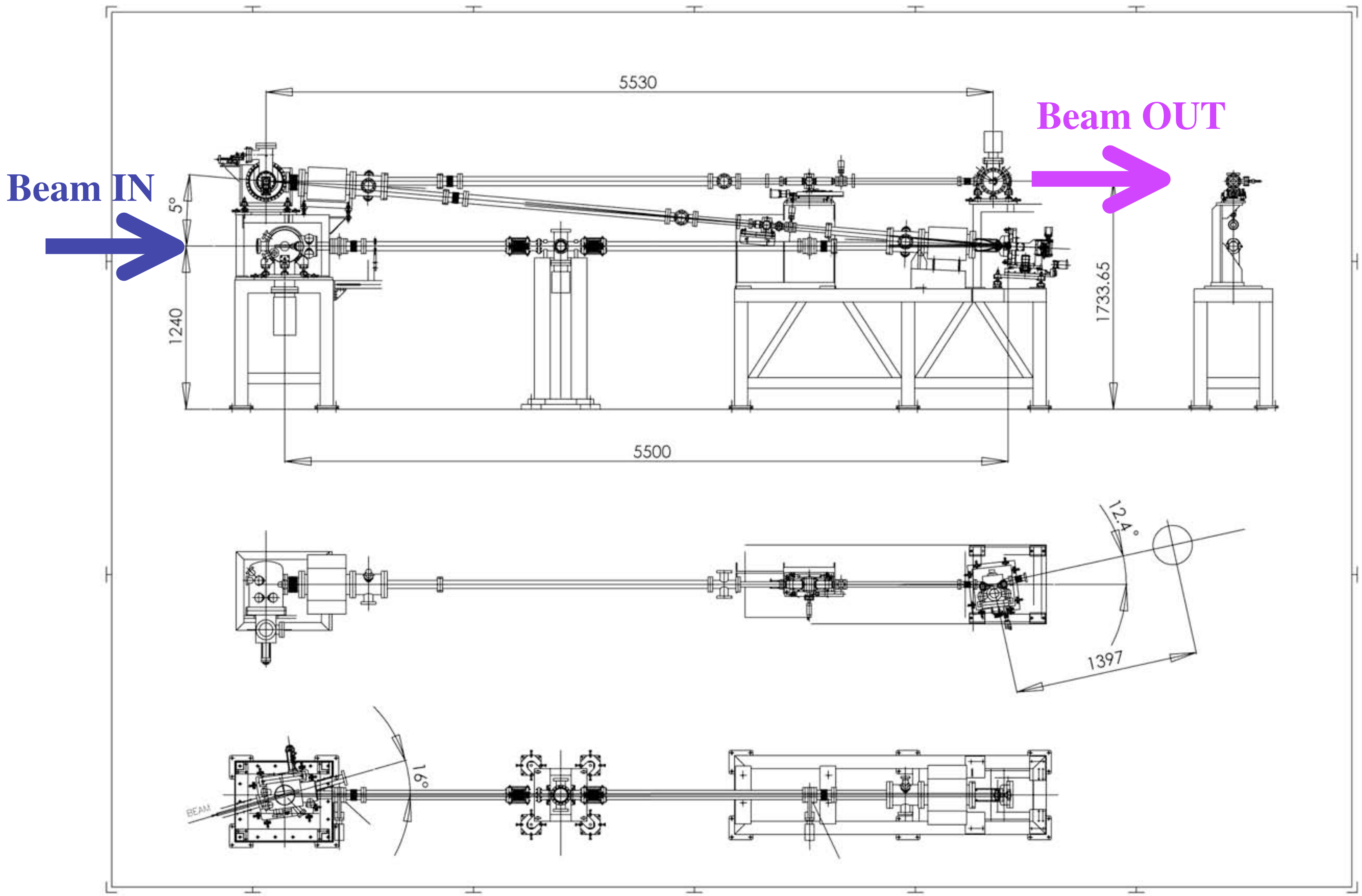
Spot size 10-400μm, > 10^{12} photons/s on the sample, intrinsic linewidth < 1meV, continuous energy range





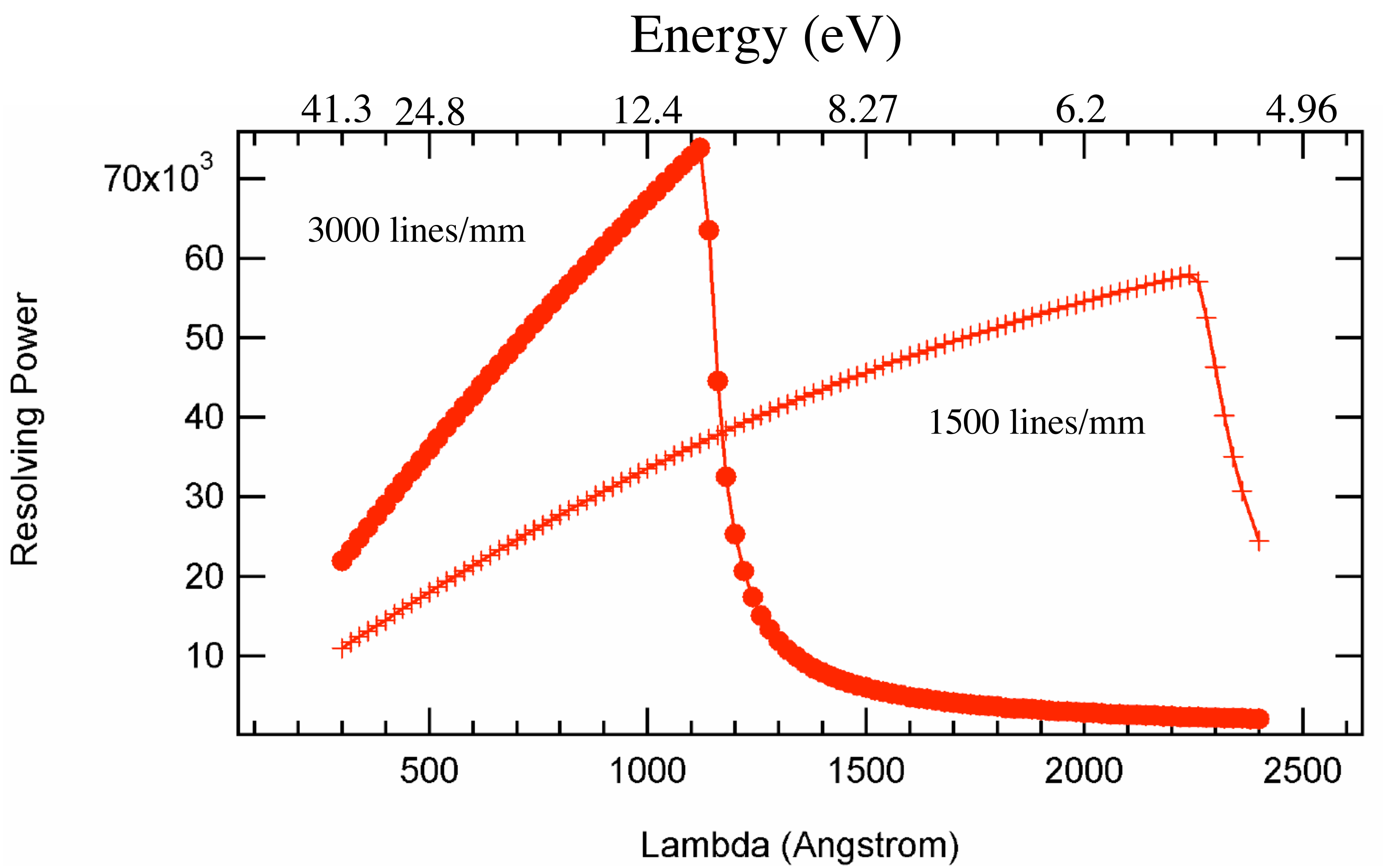
BaD ElPh Layout

4m Normal Incidence Monochromator: 5°



Energy range: 5 - 23 eV with two gratings, a third grating foreseen for 23-35 eV

The monochromator performances



20 eV, resolving power 45000 (10 μm)
12 eV, resolving power 75000 (10 μm)
8 eV, resolving power 50000 (10 μm)

Expected performances:

Cryostat/manipulator
T ~ 4 K

Total energy resolution
~ 3 meV

Momentum resolution
< 0.005 Å^{-1}

Actual performances:

Cryostat/manipulator
T ~ 11 K (on the sample)

Total energy resolution
~ 5.7 meV

Momentum resolution
< 0.005 Å^{-1}

GAMMADATA
—SCIENTA—

ELECTRON SPECTROMETER

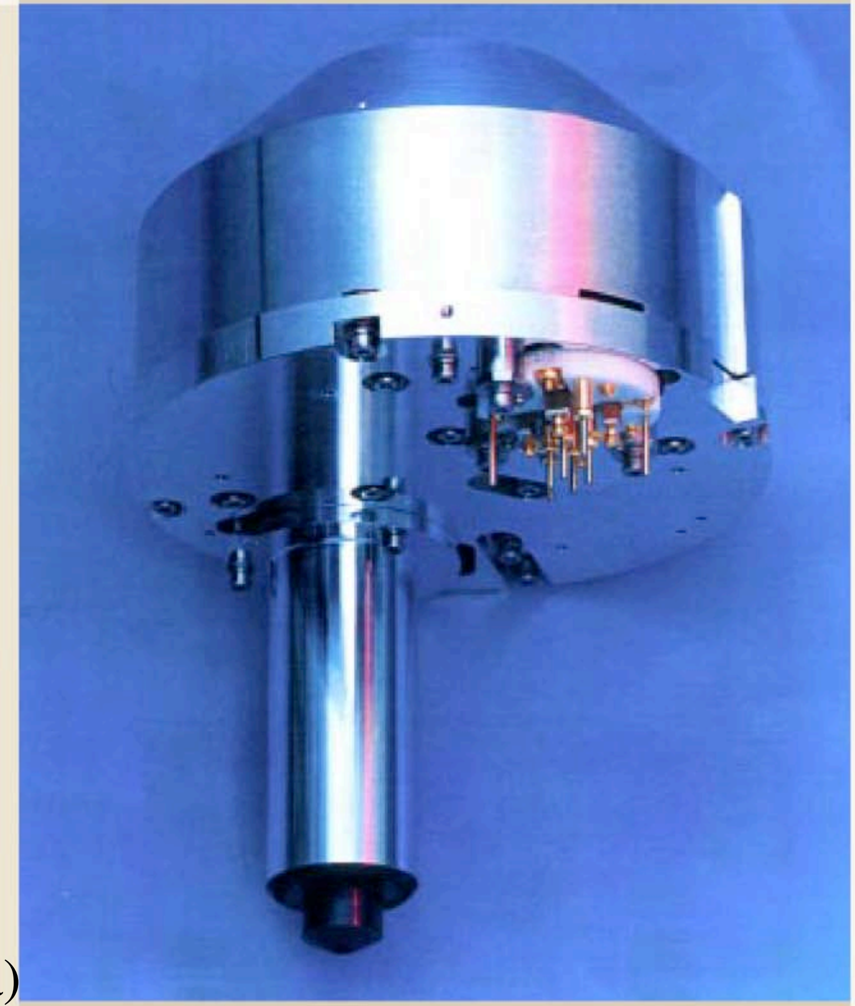
SCIENTA SES 50

Features:

- < 3 meV energy resolution
- Angle multiplexing recording from small area samples
- Extremely low noise, high stability power supplies
- Customized lens design
- Multi-channel resistive anode detector

Main application:

- High resolution electron spectroscopy
- High resolution photo-electron diffractionion
- High resolution angular resolved spectroscopy

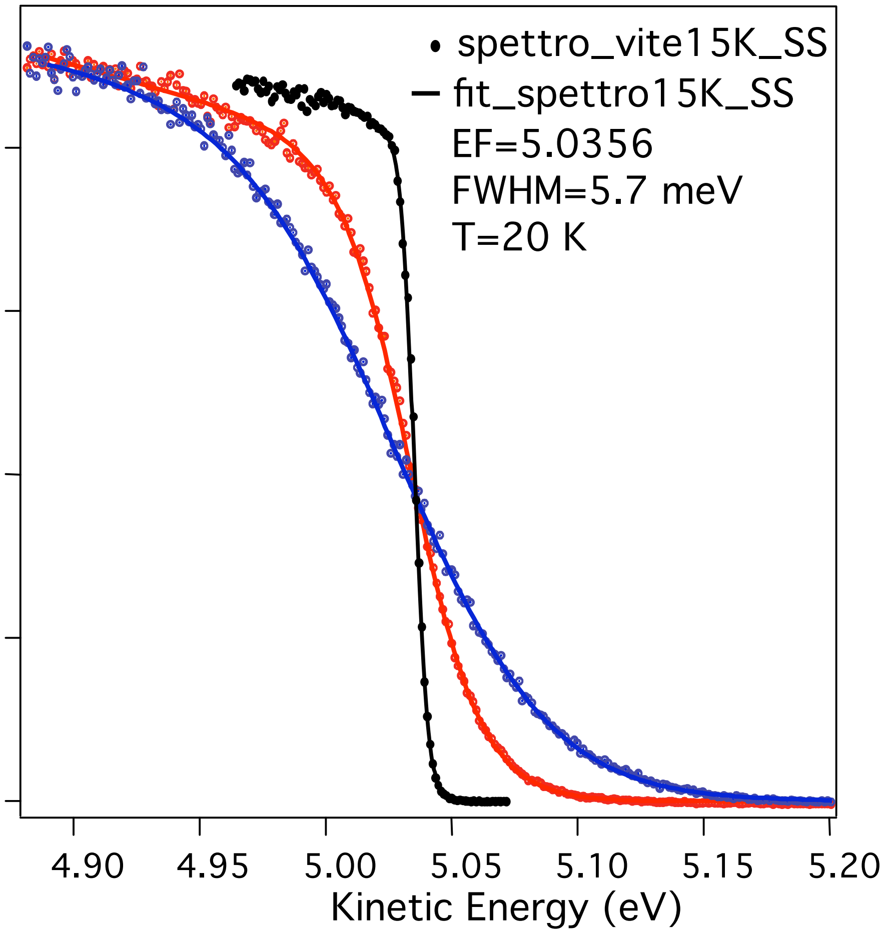


256x256 pixels
128 slices (spectra)
3 MHz count-rate

Mounted on a two-axis goniometer

Courtesy of R. Claessen (Univ. of Wuerzburg)

$h\nu$ = 9 eV PE=2 eV



somma_vite 160K

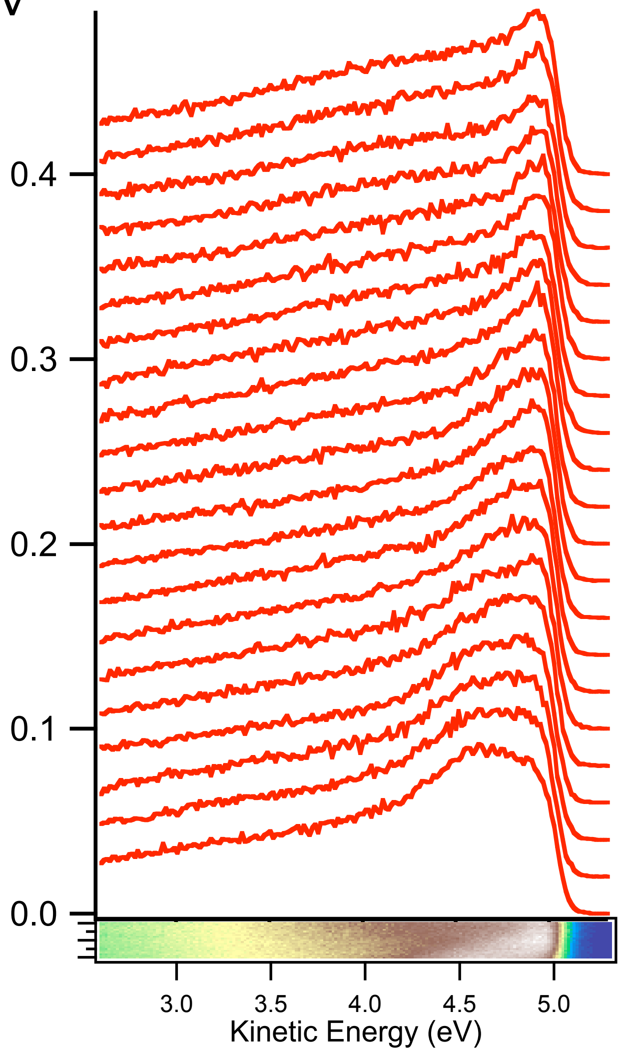
fit_somma_vite 160K

EF=5.03563; FWHM:5.8meV; T=164 K

somma_vite 300K

fit_somma_vite 300K

EF=5.0356; FWHM:5.8meV; T=300 K



θ range = 5°

21 slices; $\Delta\theta \sim 0.25°$

$\Delta K < 0.005$ Å^{-1}

A. Goldoni et al., unpublished

Why going to very low photon energies?

4 eV$<$ hν $<$ 20 eV

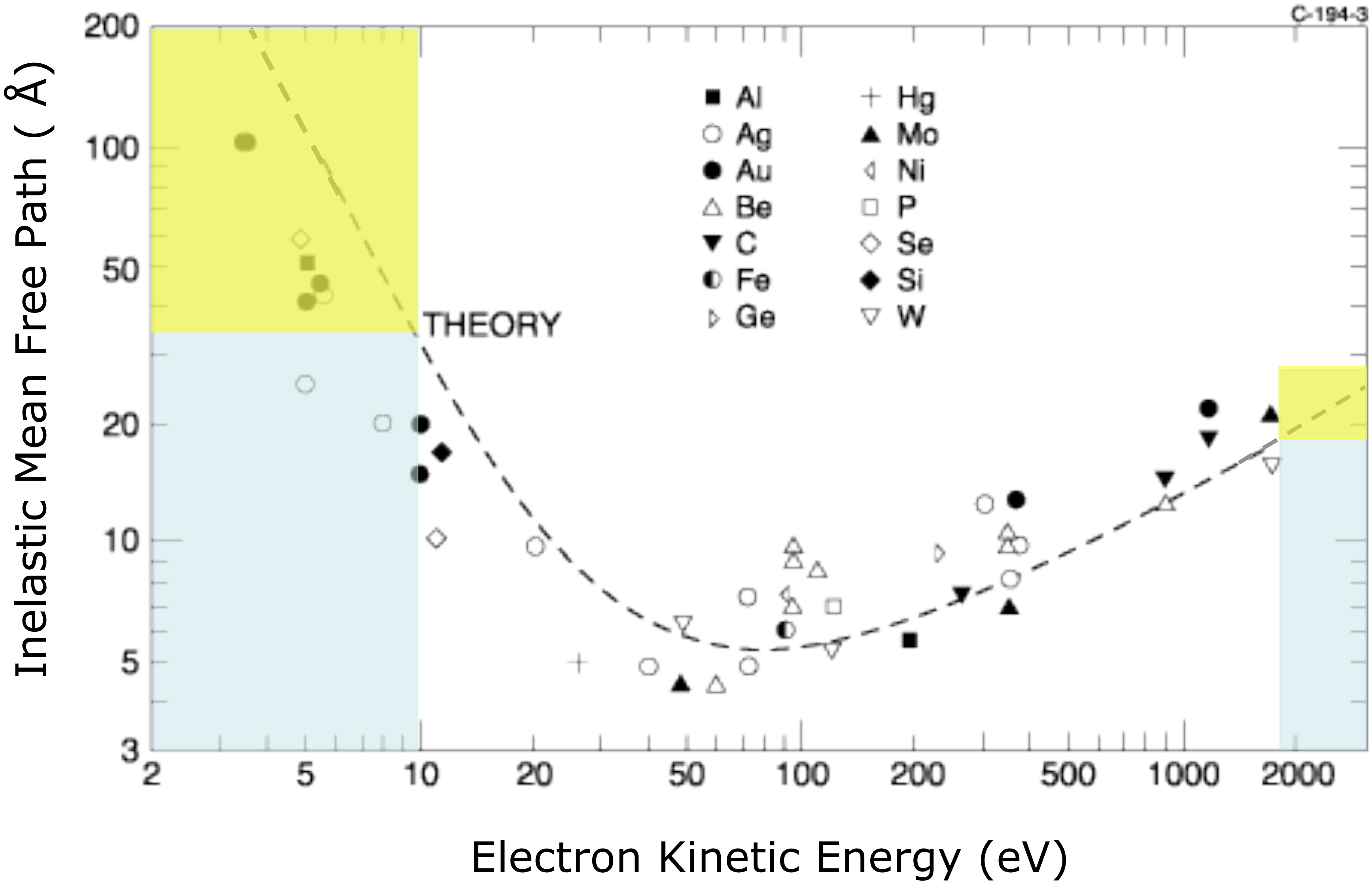
1) Bulk sensitivity
2) Higher momentum resolution
3) Good energy resolution easier

Why going to very low photon energies?

$4\ \mathrm{eV} < h\nu < 20\ \mathrm{eV}$

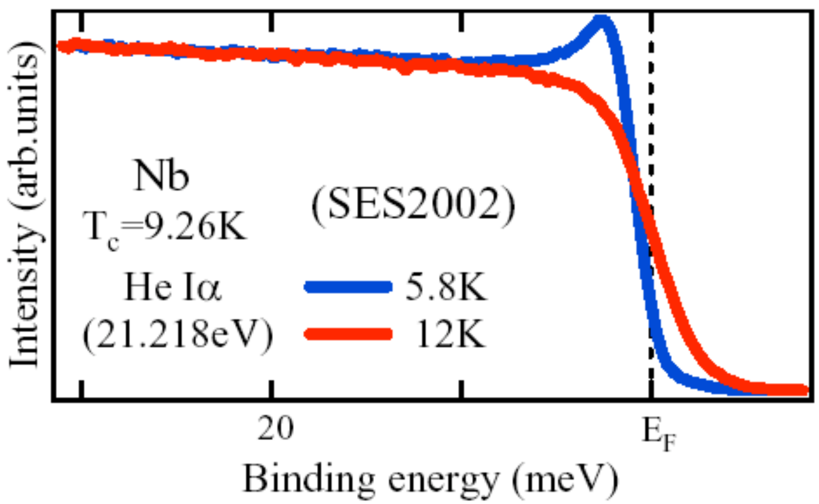
1) **Bulk sensitivity**
2) Higher momentum resolution
3) Good energy resolution easier

Electrons photoemitted with low photon energies are the most bulk sensitive

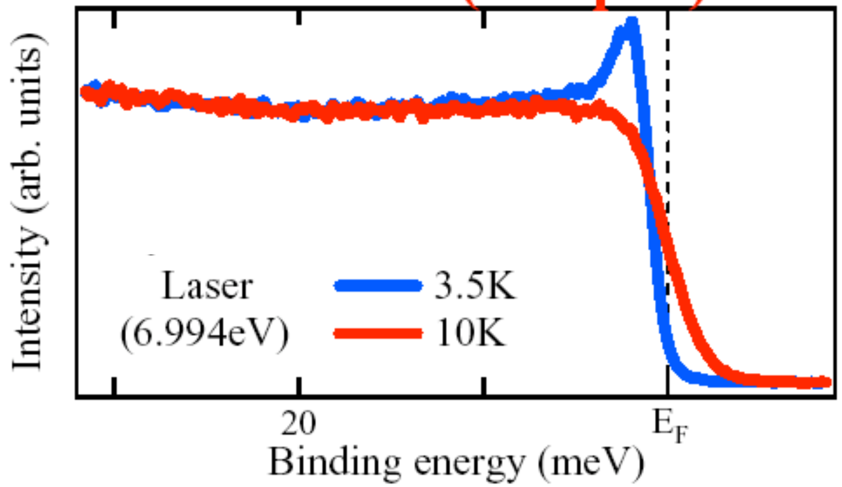


Superconducting gap of Nb

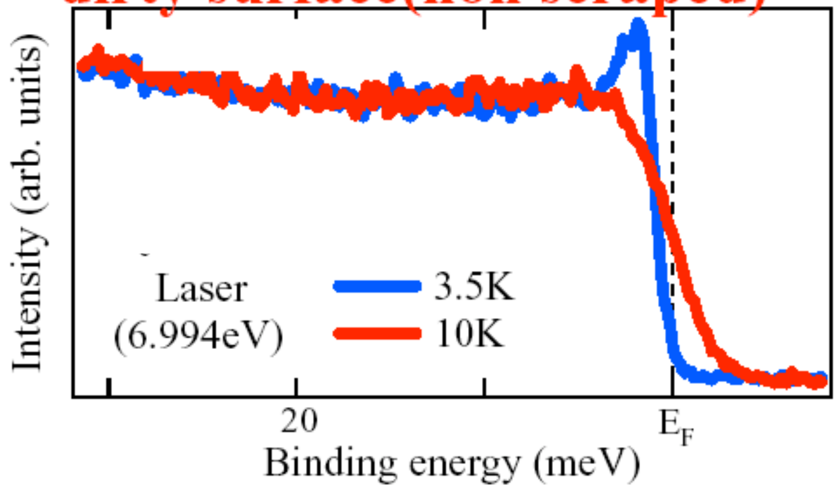
Chainani et.al., PRL, 85(2000)1966



clean surface(scraped)



dirty surface(non scraped)



We can measure superconducting gap without clean surface

T. Kiss et al.,JESRP 144-147, 953 (2005)

Fermi surface of Bi(111): Bulk vs Surface states

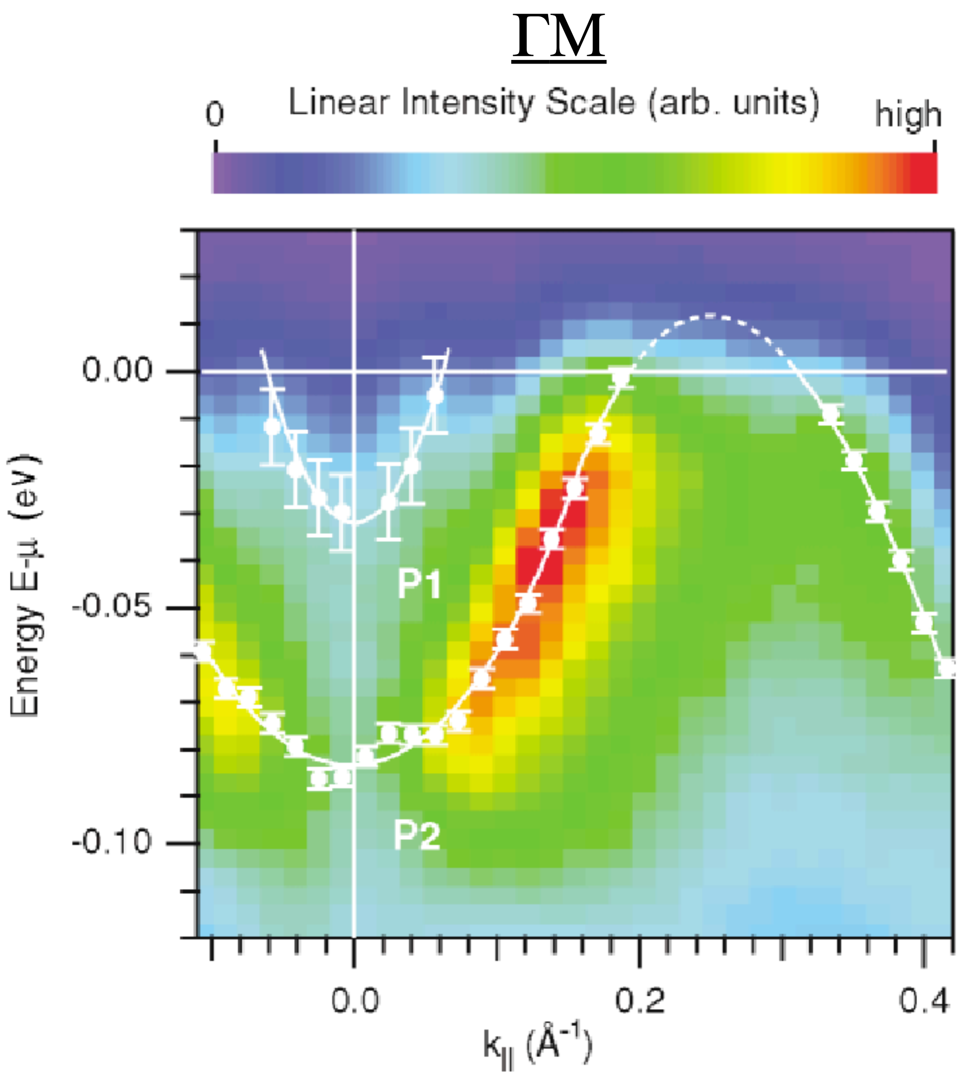
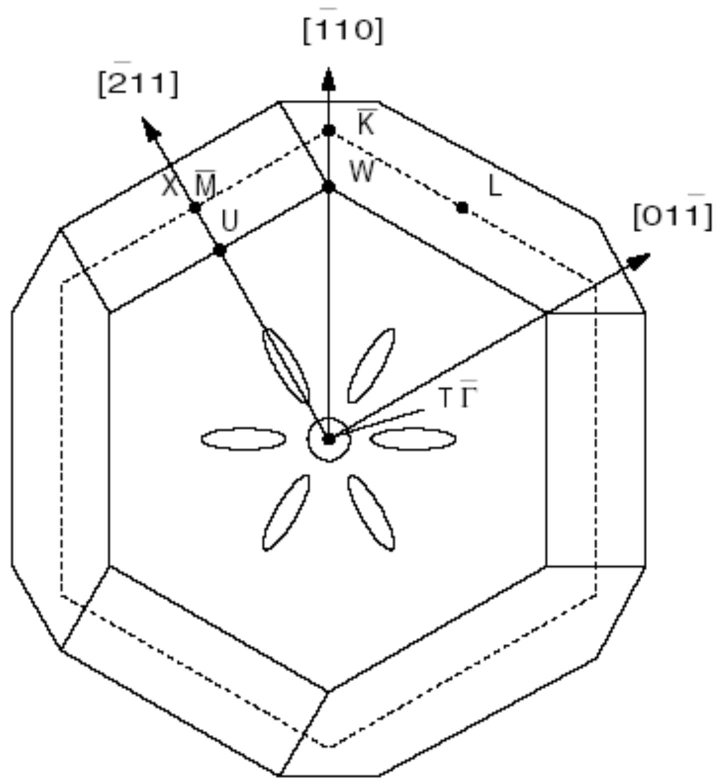


FIG. 4 (color). Band structure of Bi(111) at $h\nu = 18$ eV. $k_{\|}$ along $\overline{\Gamma M}$. Solid lines: Polynomial fit to peak positions. Energies relative to chemical potential μ.



C.R. Ast, H. Hochst, PRL 87, 177602 (2001)

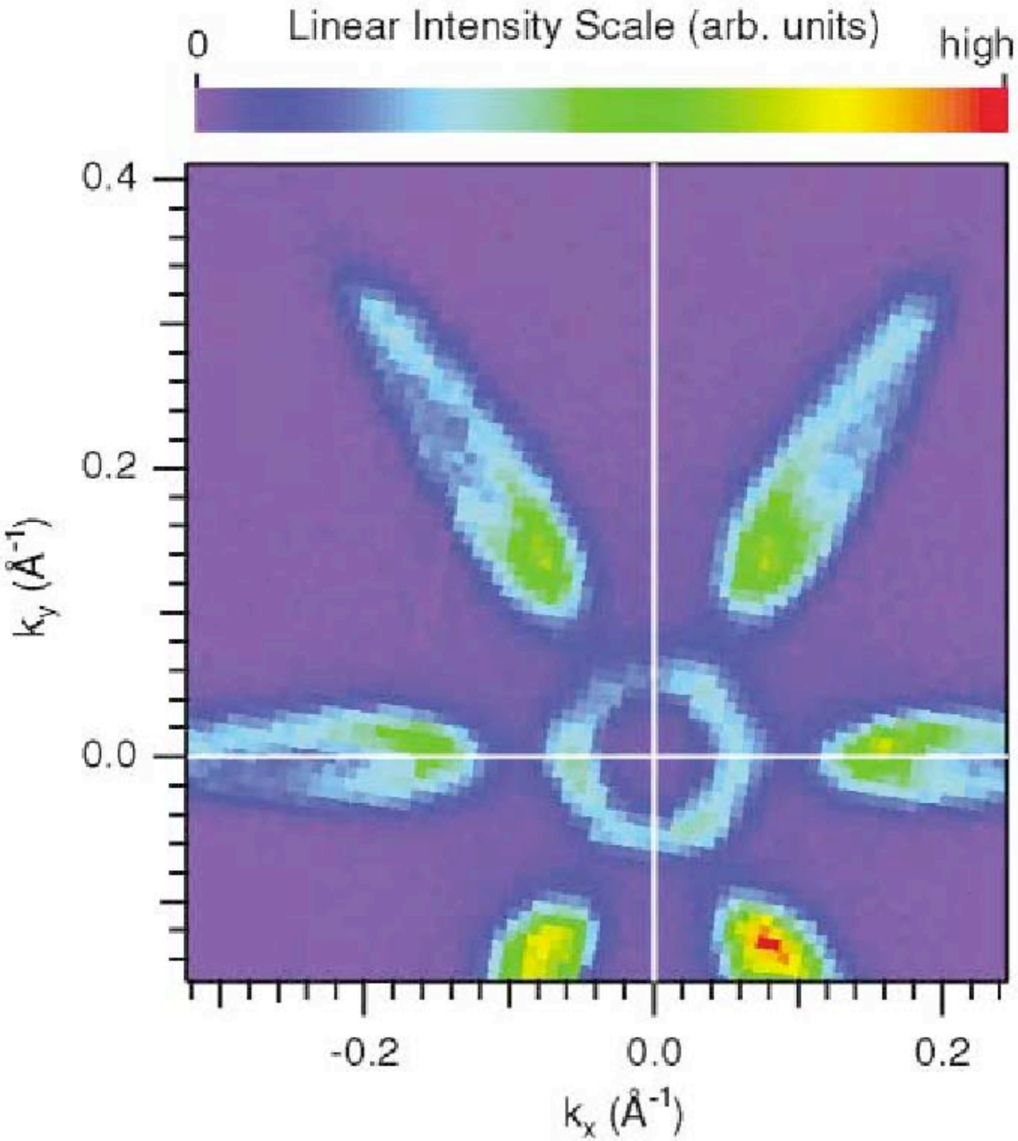
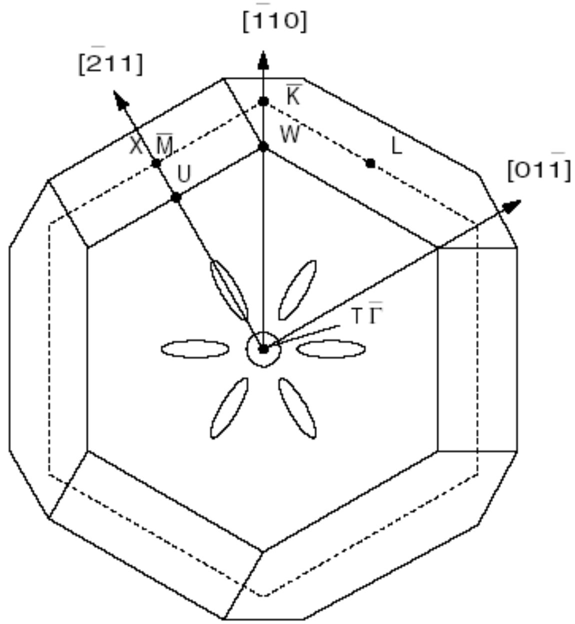
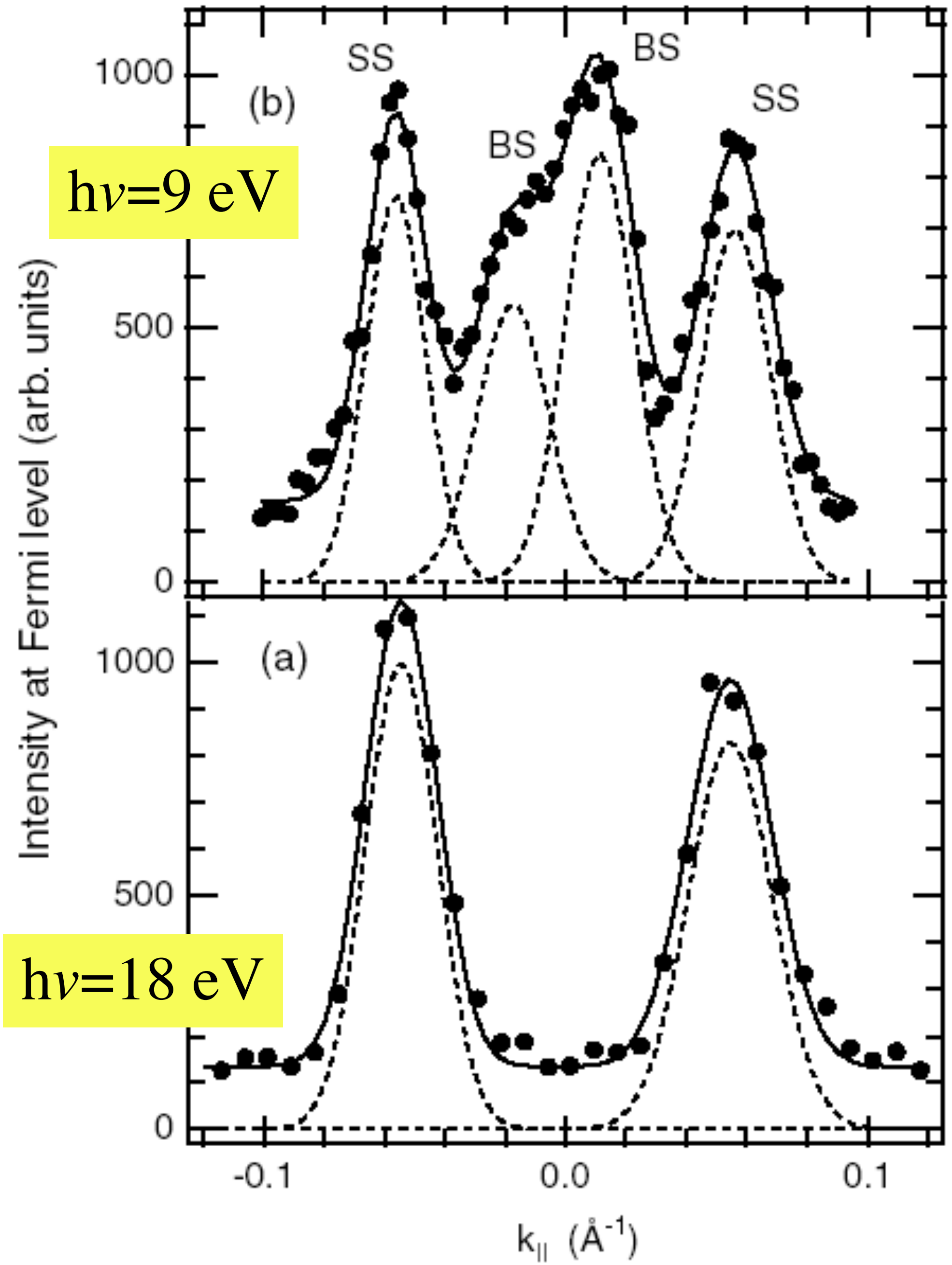


FIG. 1 (color). Intensity map at the Fermi level of Bi(111) measured at $h\nu = 18$ eV. The angular steps were 0.25°. k_x and k_y are the parallel components of the electron momentum along the $\overline{\Gamma M}$ and the $\overline{\Gamma K}$ direction, respectively.



C.R. Ast, H. Hochst, PRL 87, 177602 (2001)

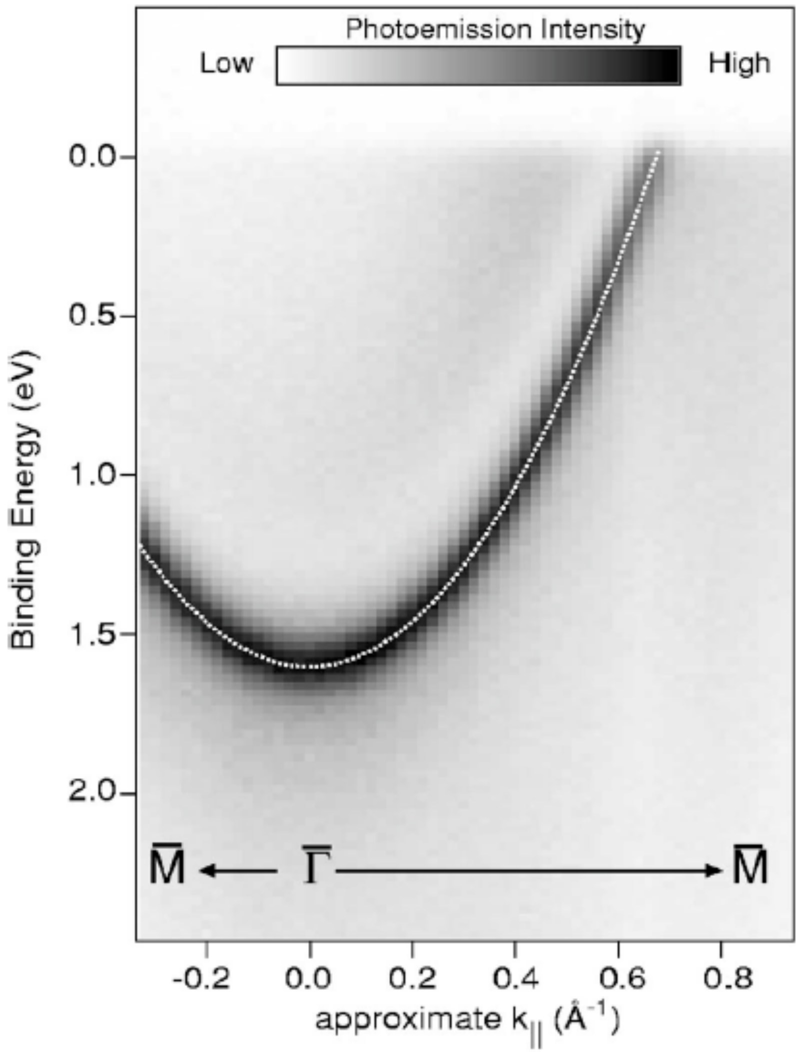


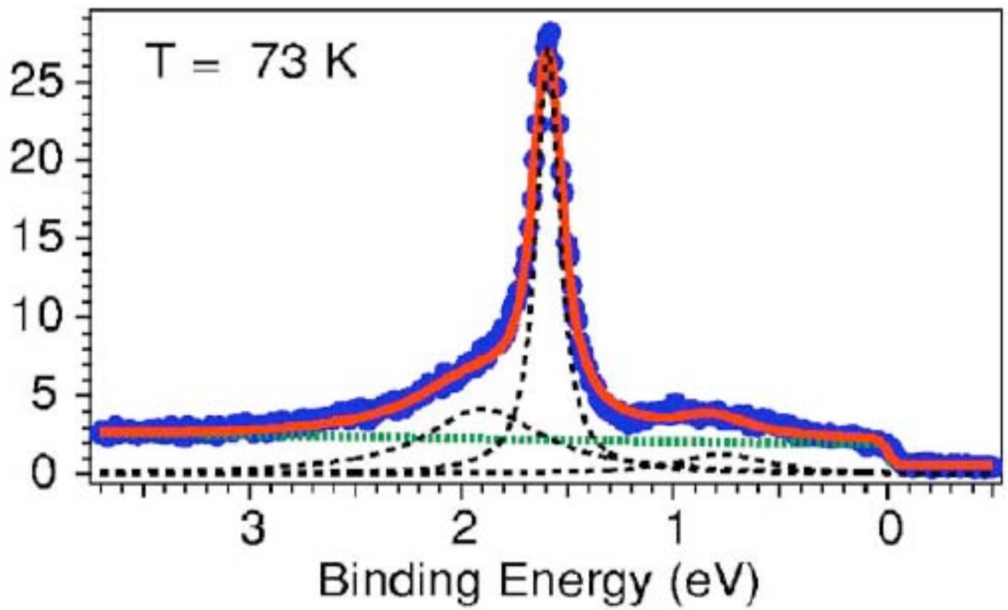
Momentum Distribution Curves at E_F for Bi(111) along the ΓK

Note:
bulk states (BS) appear at low photon energies

C.R. Ast, H. Hochst, PRL 87, 177602 (2001)

Photoemission from Mg(0001): surface *vs* bulk states



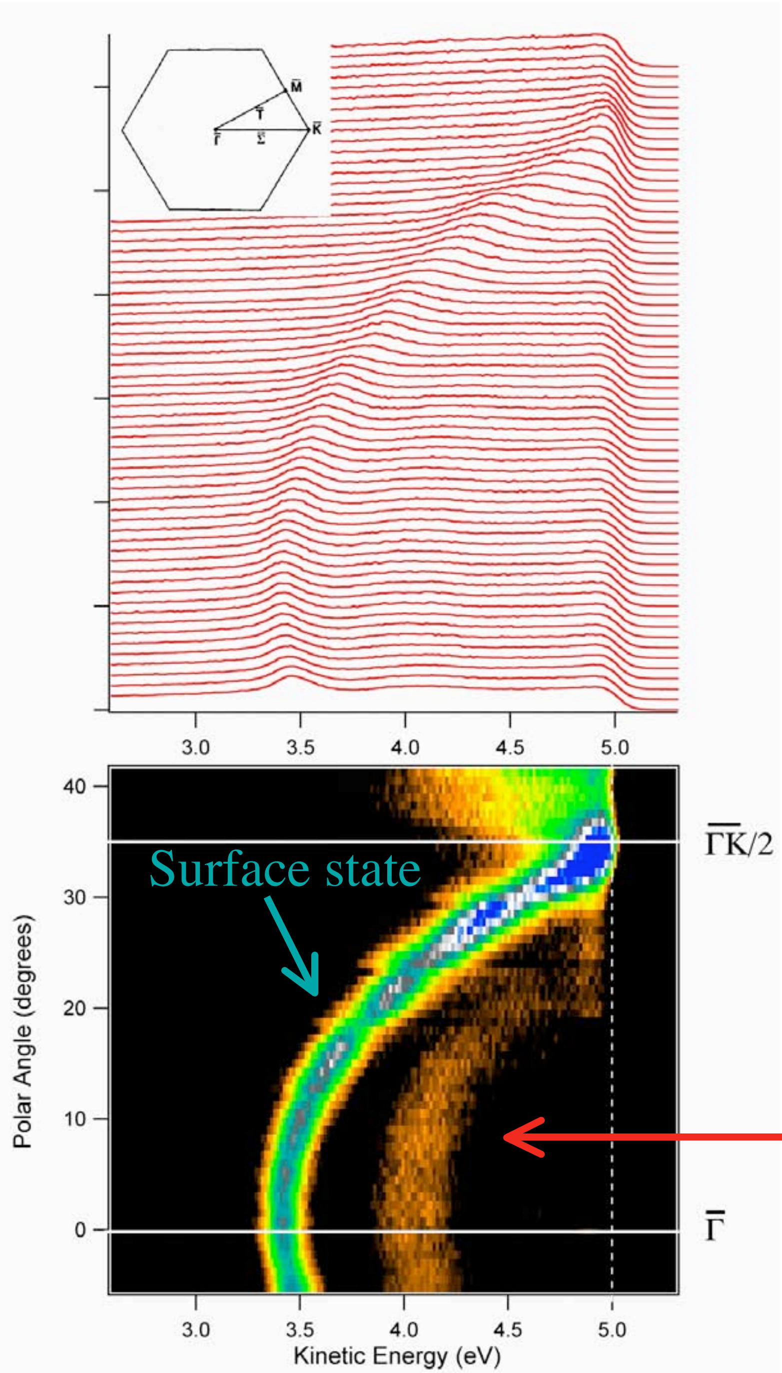


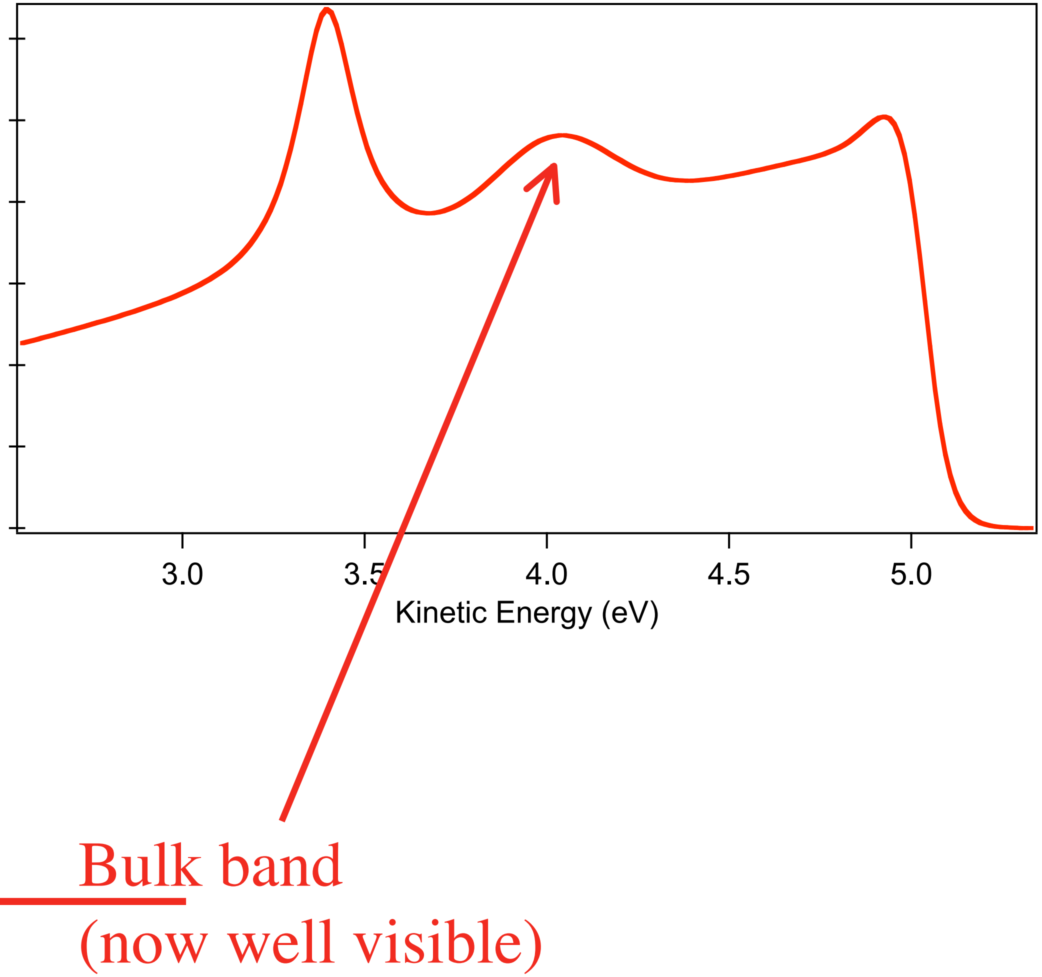
Measured at hν=44 eV
Bulk states intensity very very small

T. Kim et al., PRB 72, 075422 (2005)

Mg(0001) measured at hν = 9 eV

Enhanced bulk sensitivity at low photon energy





P. Vilmercati et al., Notiziario Neutroni e Luce di Sincrotrone (2008)

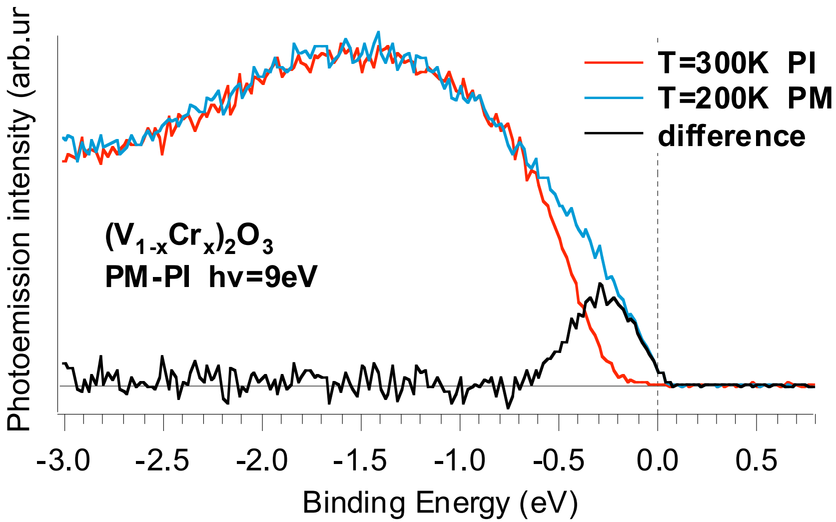
Mott transition in V_2O_3

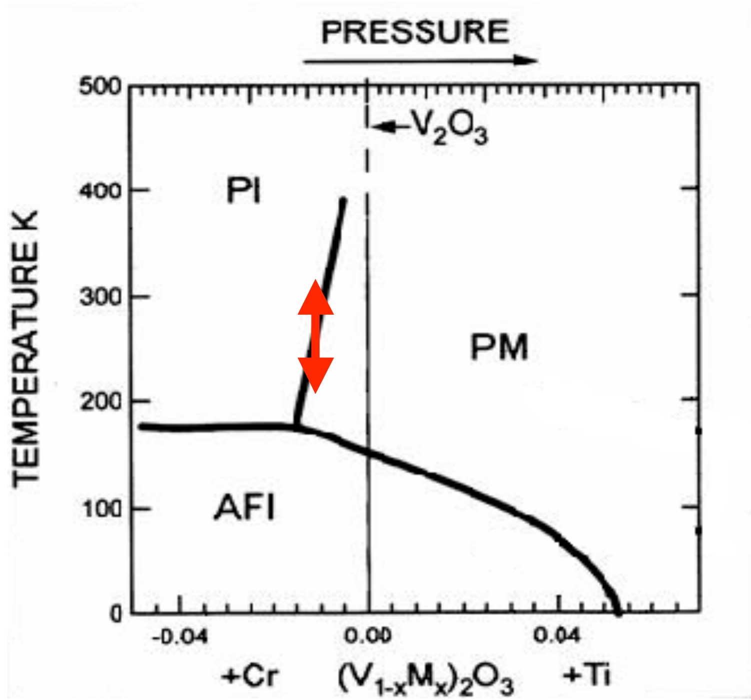
M. Marsi et al., submitted to PRB
(similar experiment made by R. Claessen et al.)

$(V_{1-x}Cr_x)_2O_3$ prototype system for isostructural metal-insulator transition induced by electron correlations

$(V_{1-x}Cr_x)_2O_3$ x =0,011

T=300K paramagnetic insulator
T=200K paramagnetic metal





Mott transition in V_2O_3

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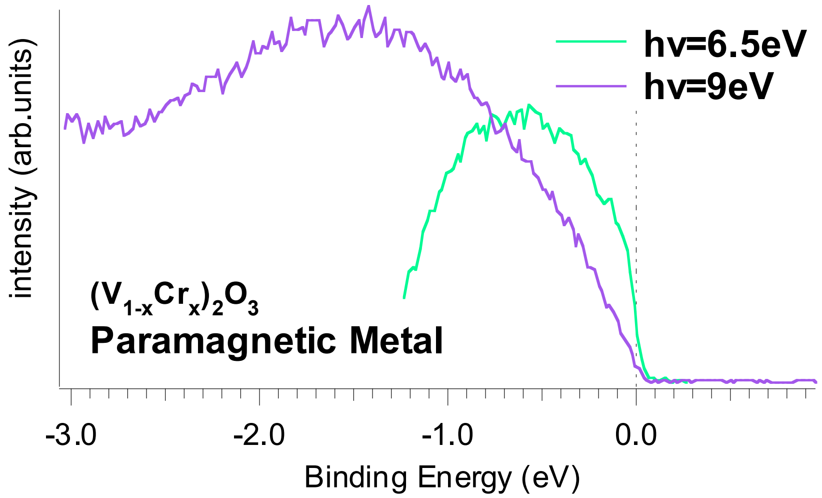
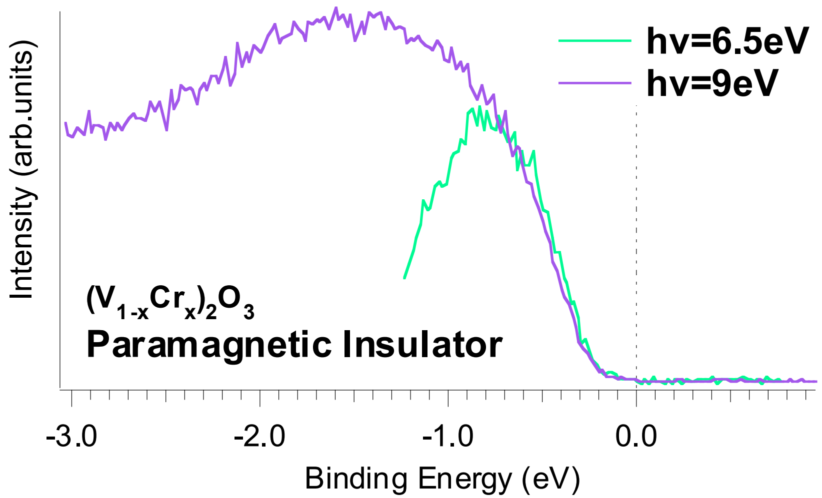




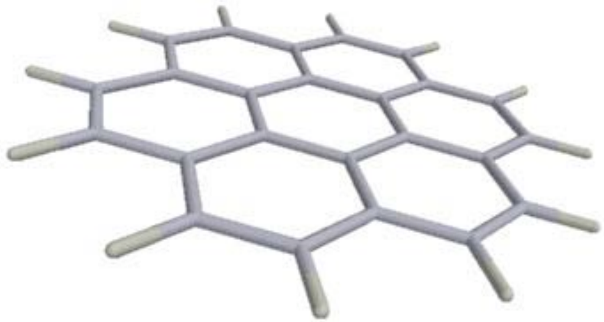
Photoemission on BaD ElPh
Low photon energy
Normal emission

metallic phase shows larger difference between surface and bulk

➔ Surface is more correlated than bulk

➔ True also for other strongly correlated systems ?

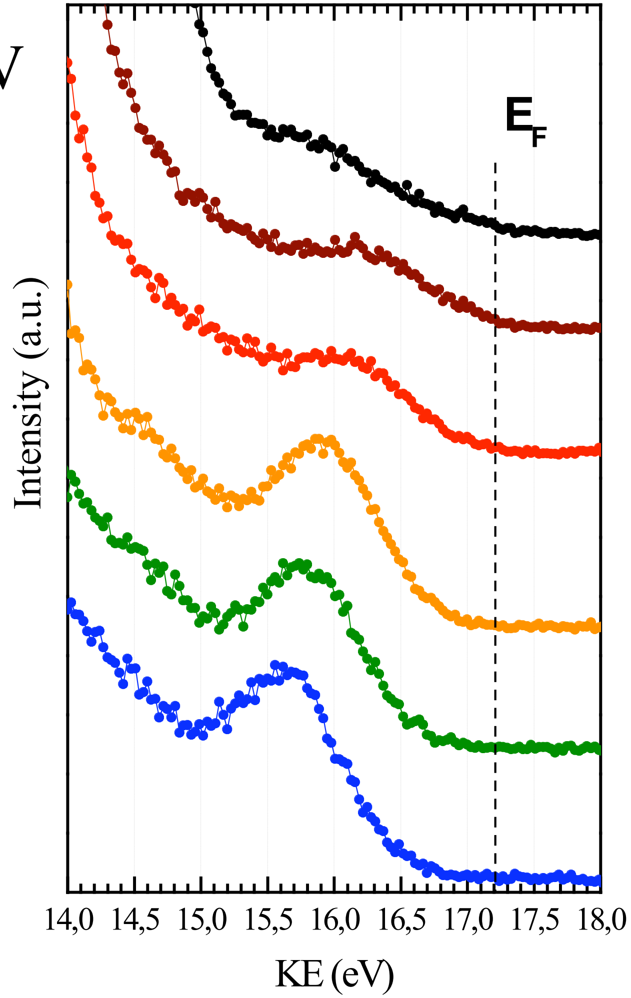
Coronene ($C_{24}H_{12}$) on Au(110), intercalated with Rb



Petra Rudolf et al.

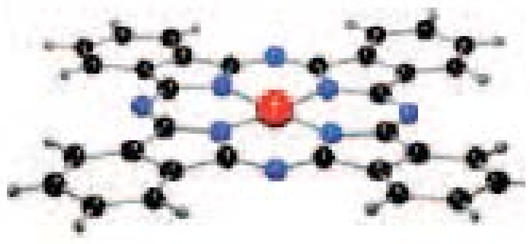
University of Groningen
Zernike Institute
for Advanced Materials

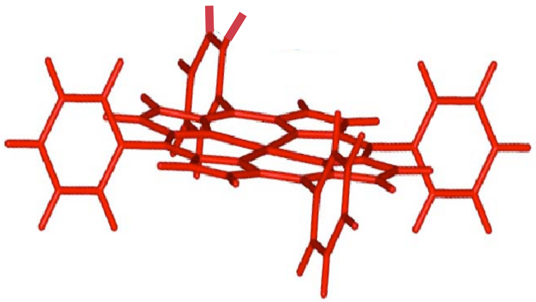
hν = 21 eV



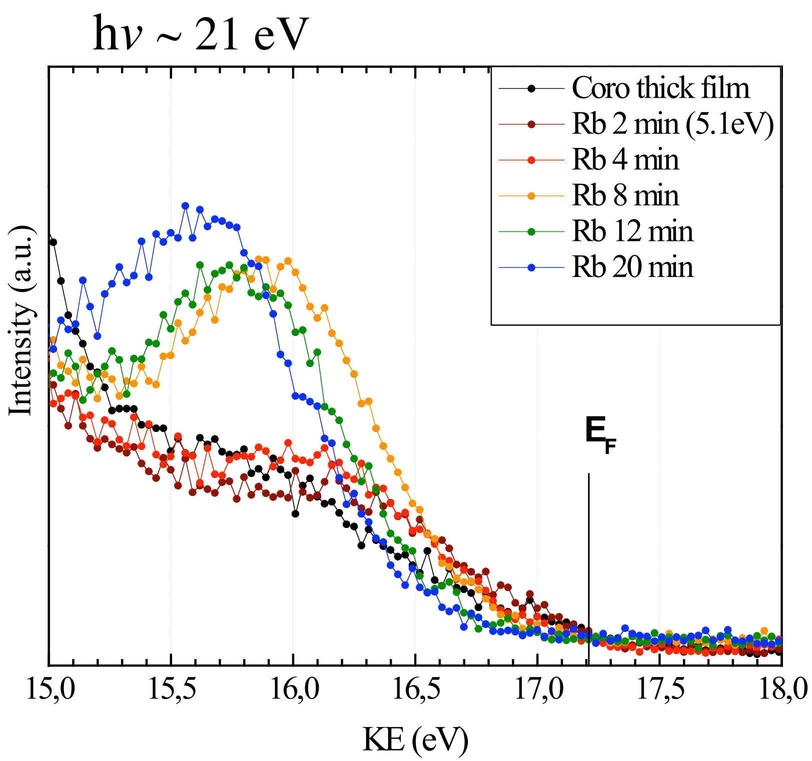
As the LUMO fills no states near E_F:
always insulating

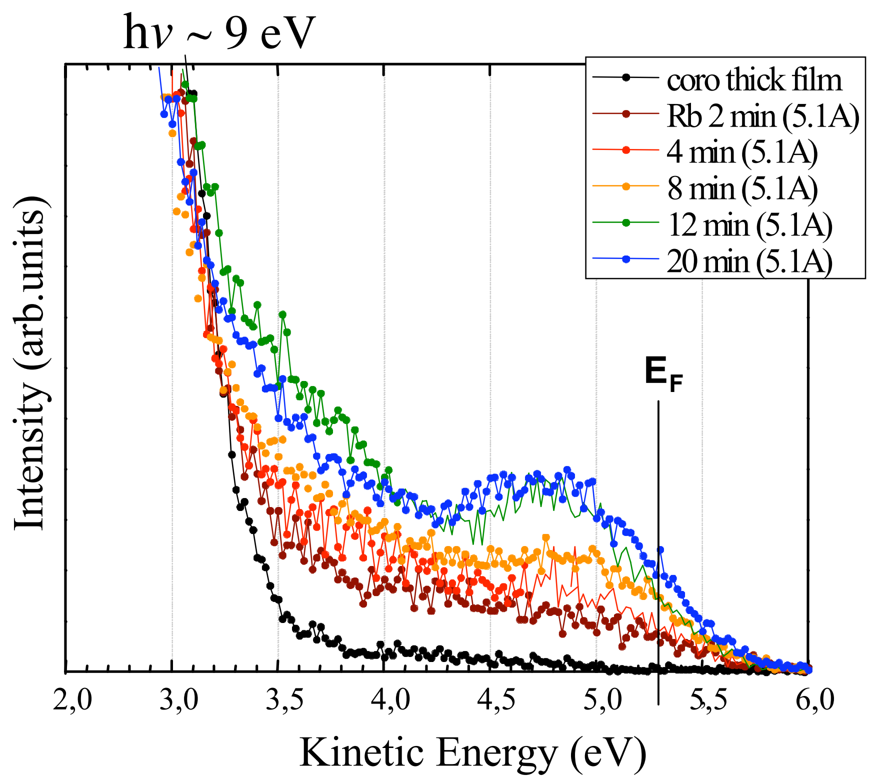
Plenty of similar photoemission examples in the literature: phtalocynins, porphyrins, …





Rb-Coronene: Fermi region with hν < 10 eV





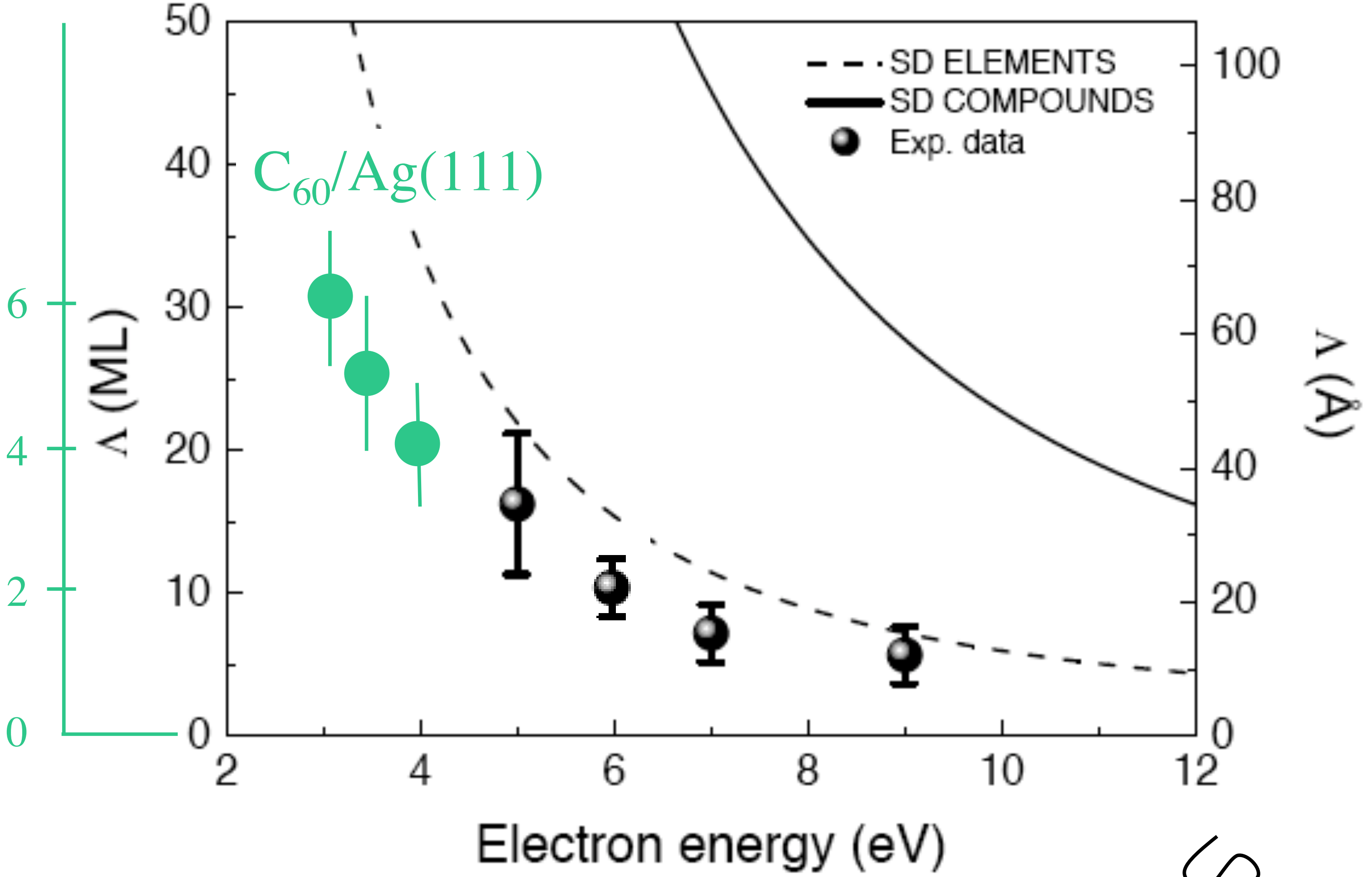
At hν =9 eV the evolution is completely different:
density of states crossing Fermi

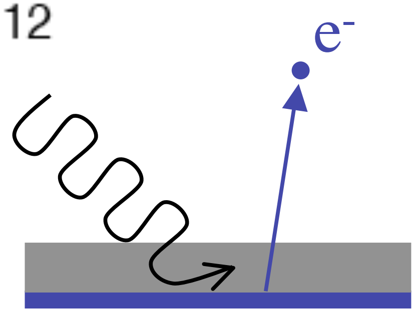
The LUMO states are closer to Fermi and crosses E_F

Petra Rudolf et al.

University of Groningen
Zernike Institute
for Advanced Materials

Attenuation length of low electron in solids: CoO/Ag and C_{60}/Ag



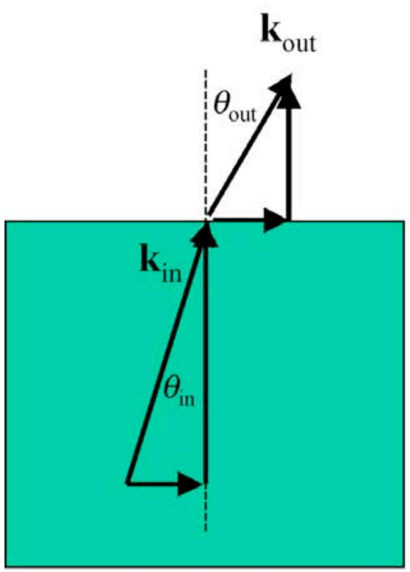


F. Offi et al., PRB (in press); A. Goldoni et al., in preparation

Why going to very low photon energies?
4 eV< hν < 20 eV

1) Bulk sensitivity

2) Higher momentum resolution



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\|} = k_{in,\|} \equiv k_{\|}$$

"Snell's Law"

$$k_{\|} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$

At the surface the crystal symmetry is conserved in the surface plane but is broken perpendicularly to the surface: the component of the electron momentum parallel to the surface plane ($k_{//}$) is conserved, but $k_{\perp}$ is not

$$k_{//} = \sqrt{\frac{2m^* E_k}{\hbar^2}} \sin\theta_{out} \approx 0.512\sqrt{E_k} \sin\theta_{out}$$

The angular resolution is defined by the electron energy analyzer. Suppose it is 0.5° and the BZ boundary is ~ 0.25 Å^{-1}.

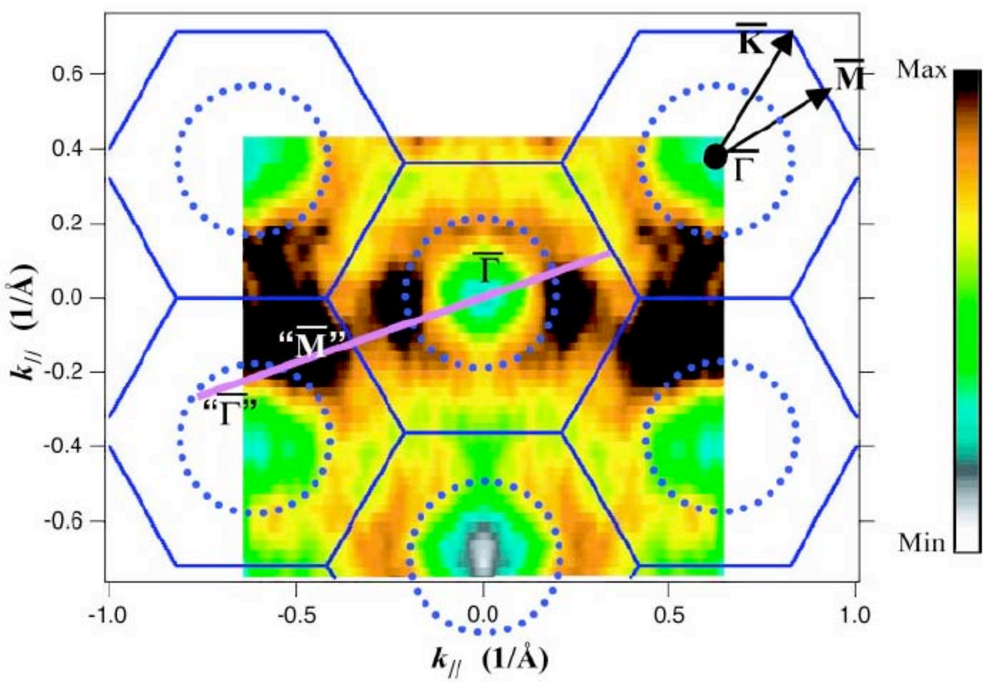
At E_k=25 eV the BZ boundary is reached after ~ 5.5°
We have 11 sampling points → $\Delta k_{//} \sim 0.025$ Å^{-1}

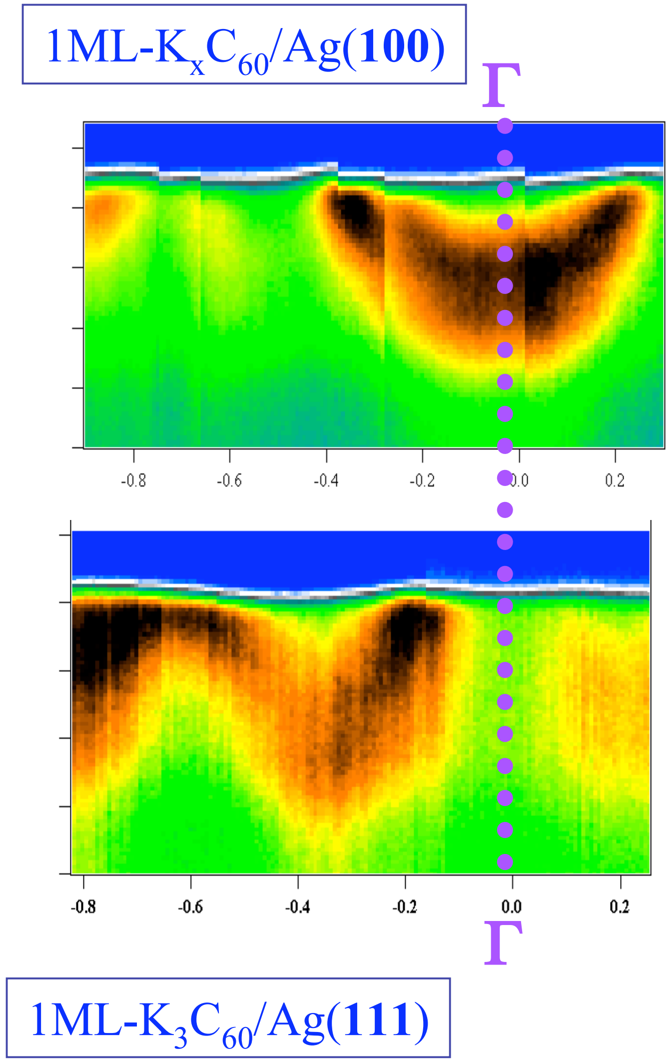
At E_k=9 eV the BZ boundary is reached after ~ 9.5°
We have 19 sampling points → $\Delta k_{//} \sim 0.014$ Å^{-1}

GOOD for systems with small BZ

Example: Band structure in fullerides

Typical hexagonal surface lattice parameter > 10 Å



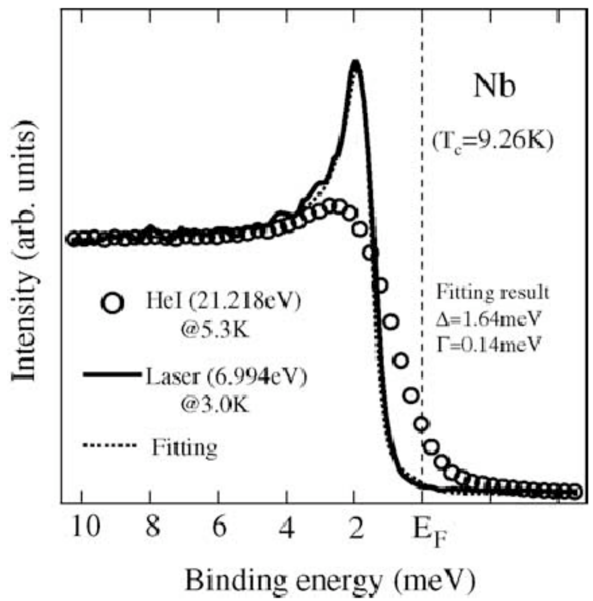


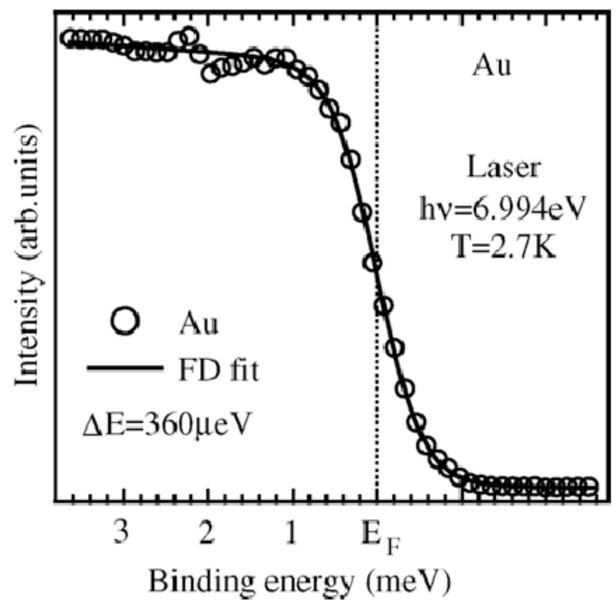
Measured at 22 eV. Lower photon energy should allow better Fermi surface mapping.

W. Yang et al., Science **300,** 303 (2003);
V. Brouet et al., PRL (2004)

Why going to very low photon energies? 4 eV< hν < 20 eV

1) Bulk sensitivity
2) Higher momentum resolution
3) **Good energy resolution easier**

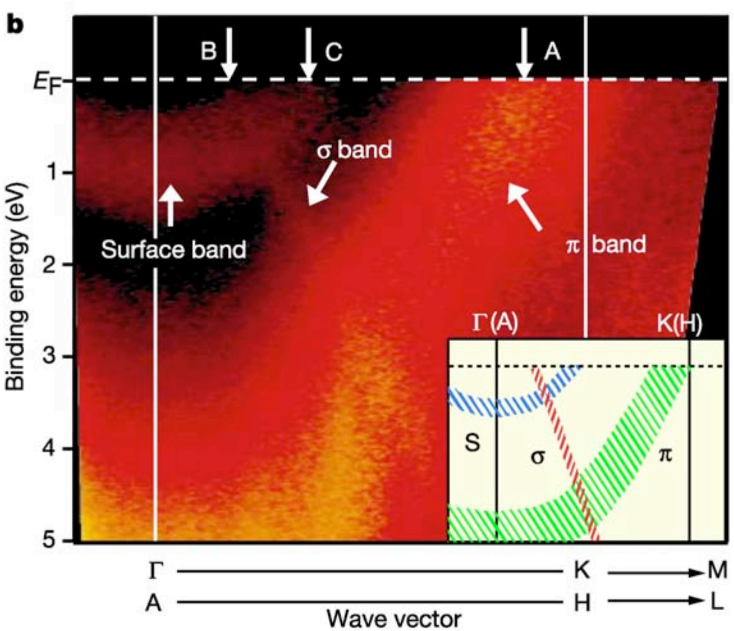




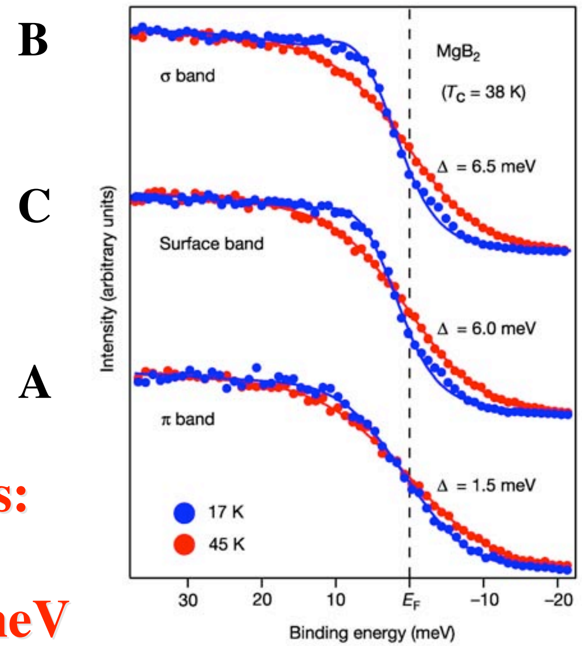
T. Kiss et al.,JESRP 144-147, 953 (2005)

Angle Resolved Photoemission Spectroscopy of MgB_2 Single Crystals

S. Souma et al. Nature **423**, 65 (2003)

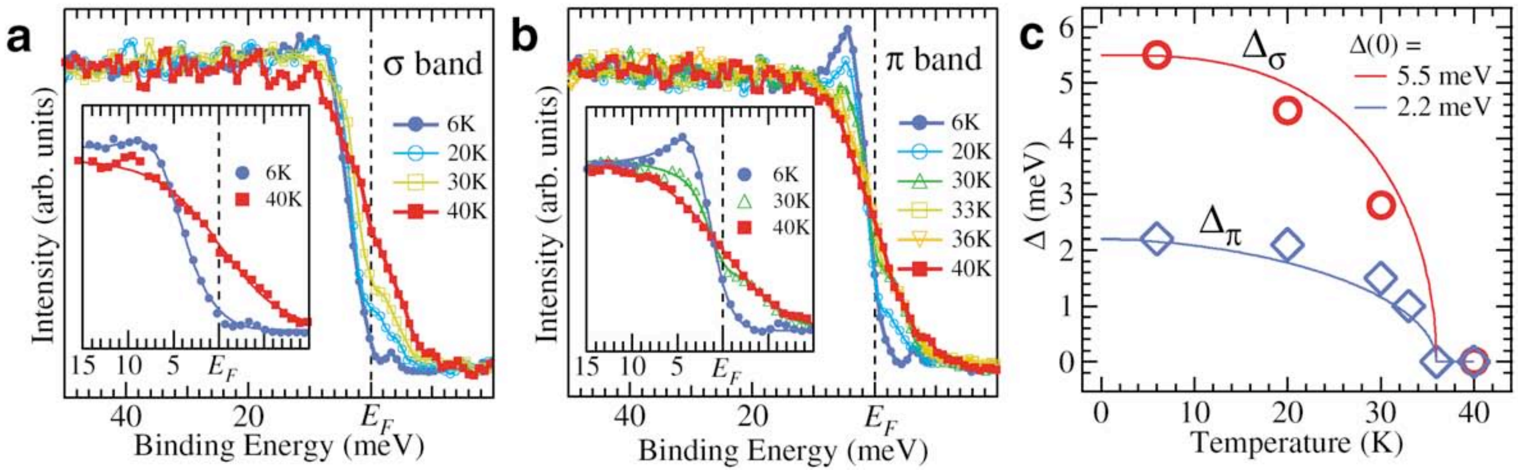


s and p superconducting gaps



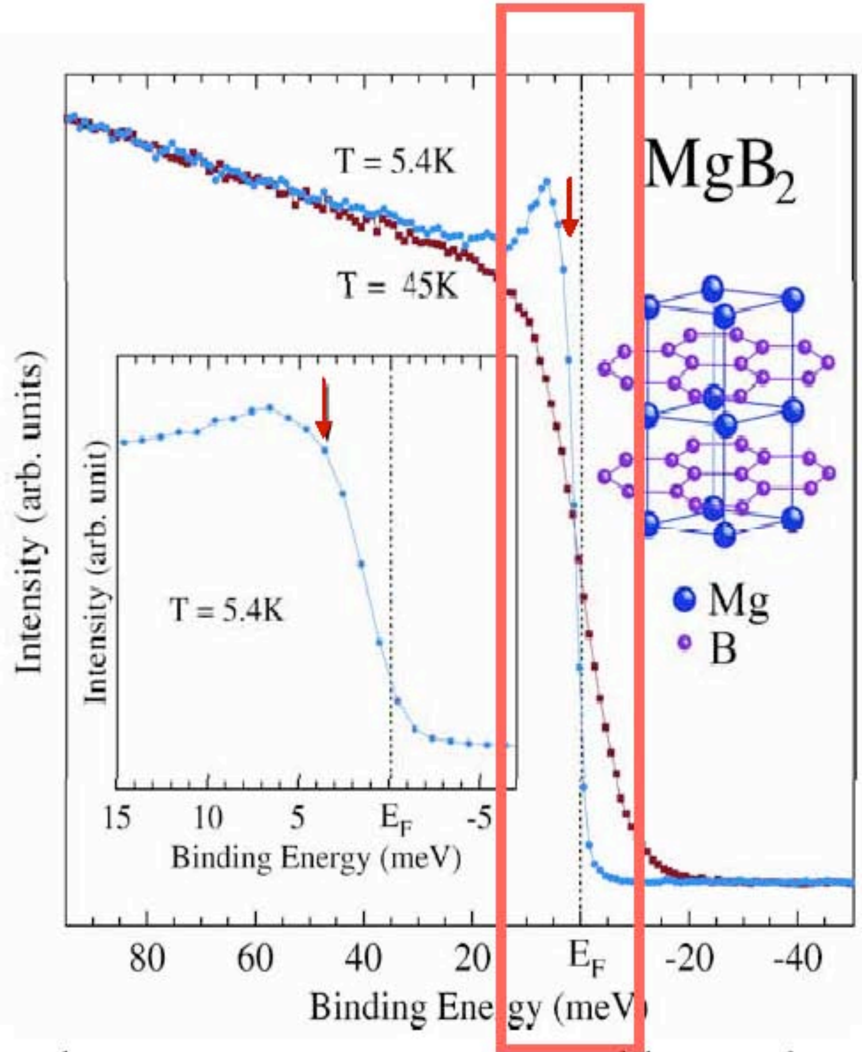
Two superconducting gaps:

D_s=5.5 meV D_p=2.2 meV

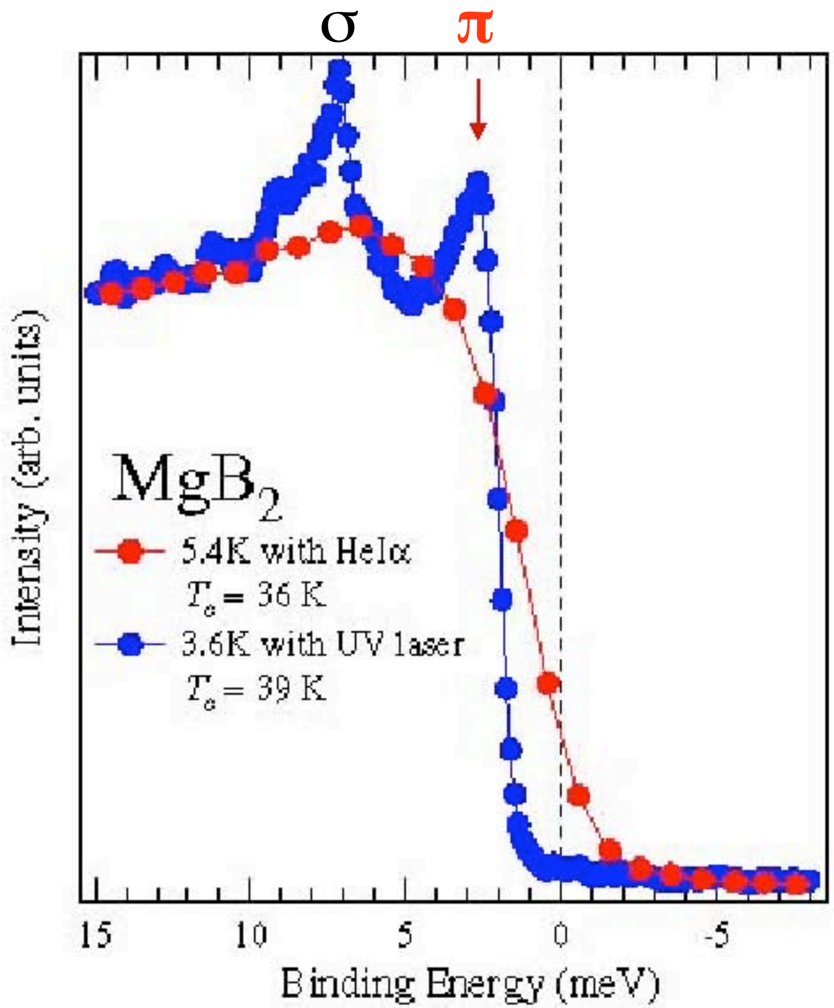


S. Tsuda et al. Phys. Rev. Lett. **91**, 127001 (2003)

"sub meV" resolution spectra on MgB_2 by laser-PES



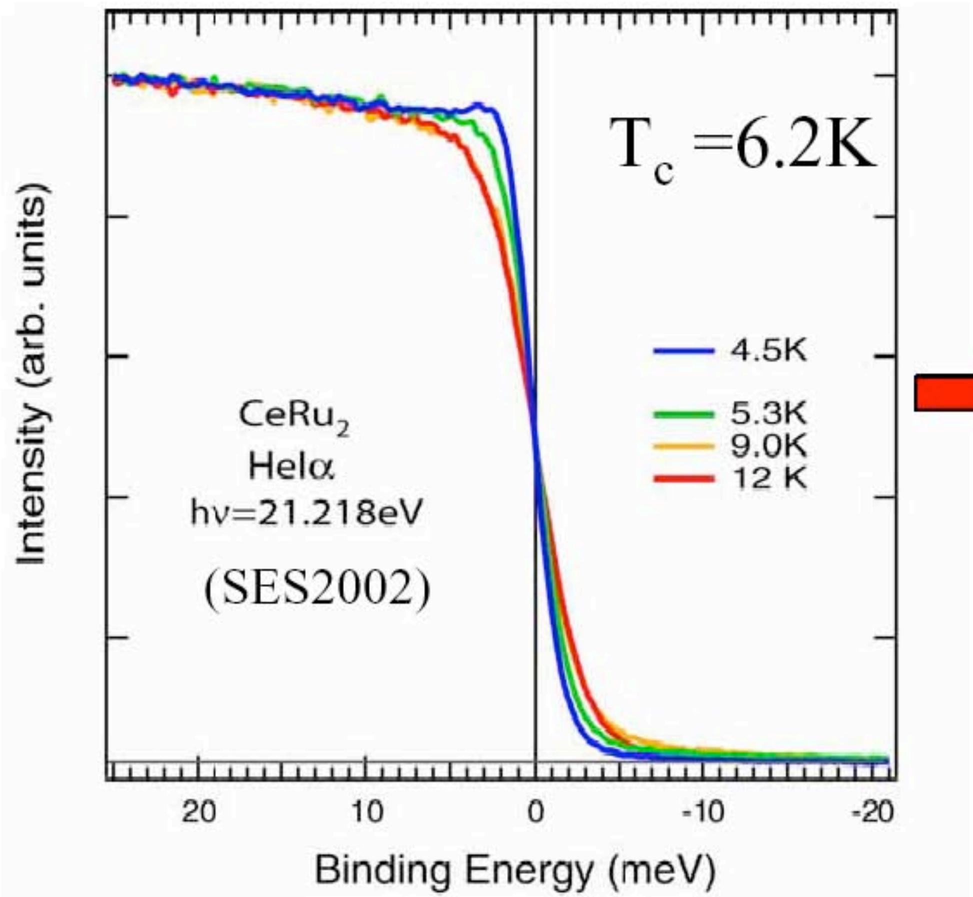
The spectrum was measured by He lamp and show the two gap structure for the first time
Tsuda et al., PRL**87**,17006(2001)

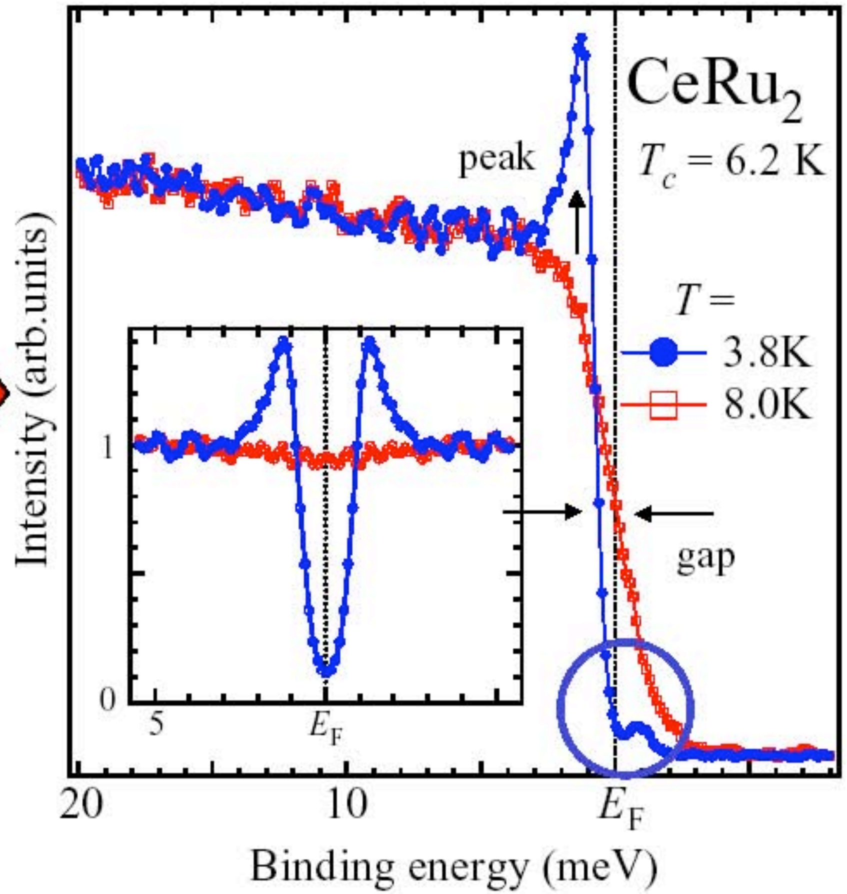


Laser-PES

Tsuda et al.

Superconducting gap of $CeRu_2$



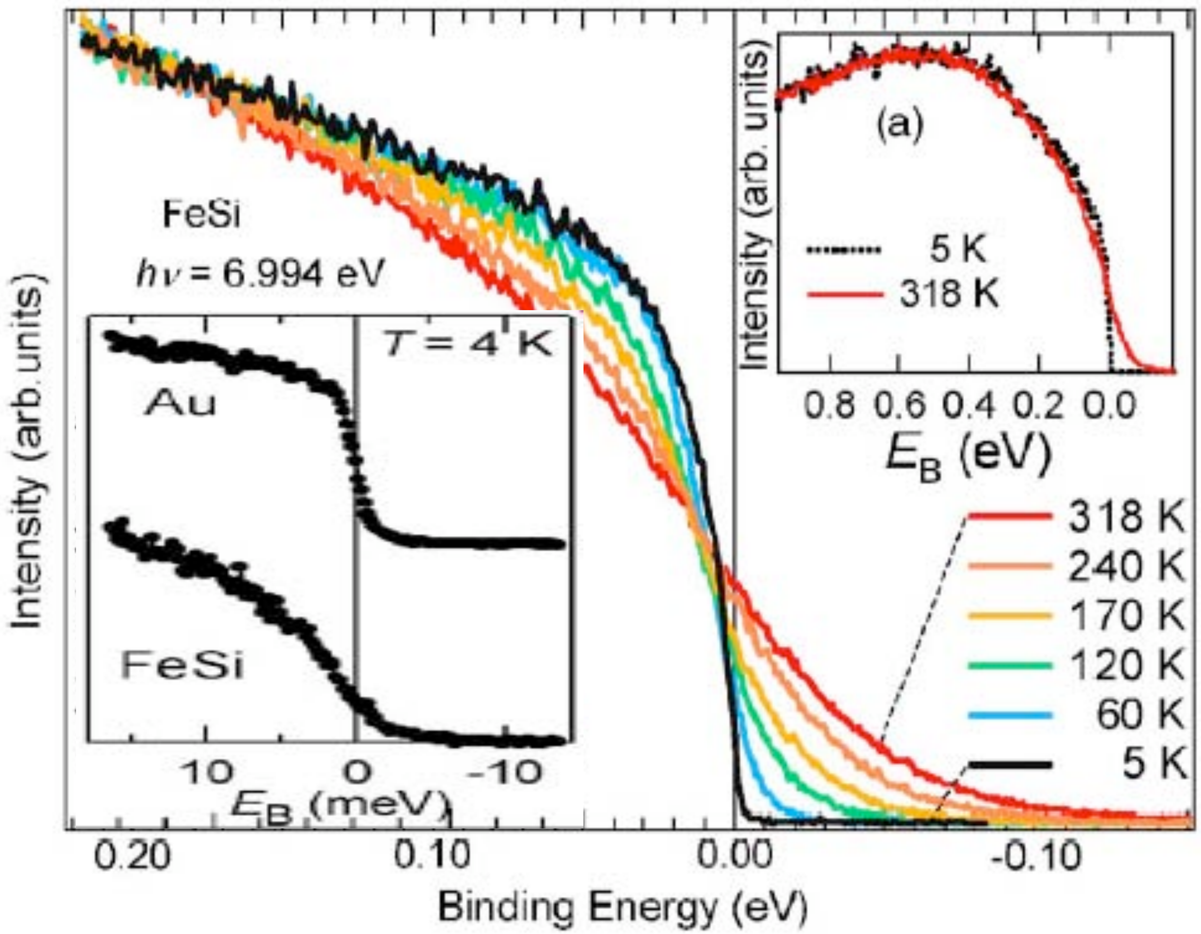


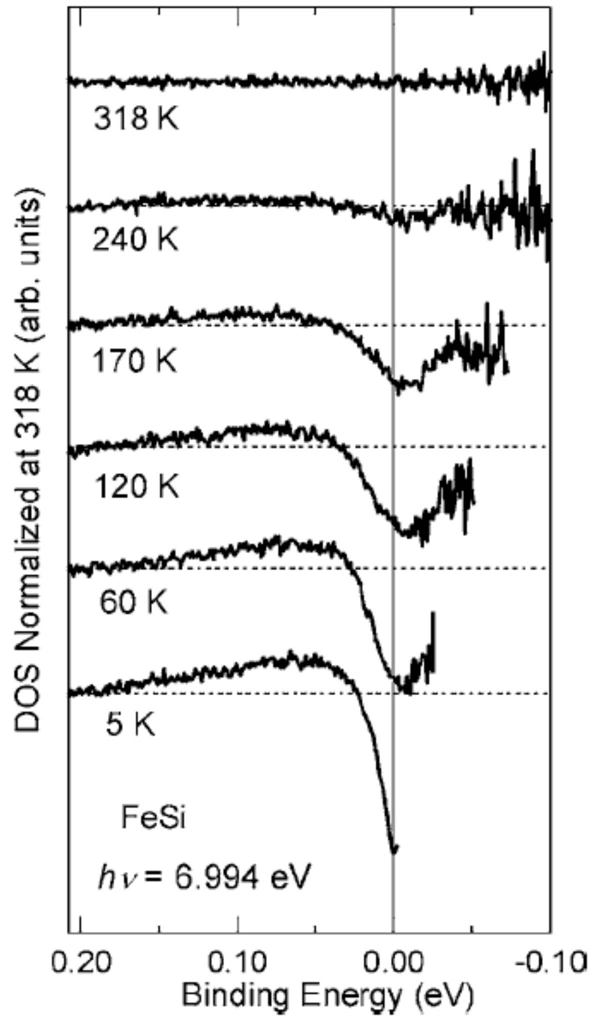
Superconducting gap was clearly observed by laser-PES

Kiss et al., PRL **94** (2005)57001

Pseudo-gap opening in FeSi

K. Ishizaka et al., PRB 72, 233202 (2005)





Critical question for ARPES at such low energies: is the Sudden Approx still valid?

Fermi´s Golden Rule for N-particle states:

$$I(\vec{k},\varepsilon) \propto \sum_s \left| \left\langle \Psi_{f,s} \middle| \hat{\Delta} \middle| \Psi_{i,0} \right\rangle \right|^2 \delta(E_{N,s} - E_{N,0} - h\nu)$$

SUDDEN APPROXIMATION:

$$\left| \Psi_{f,s} \right\rangle = \left| \vec{k}, N-1, s \right\rangle = c_{\vec{k}}^{+} \left| N-1, s \right\rangle$$

Factorization !

photoelectron

s^{th} eigenstate of remaining N-1 electron system

<u>Physical meaning</u>:
photoelectron decouples from remaining system immediately after photoexcitation, *before* relaxation sets in

This is the most important result: in the sudden approx. the photoemission spectrum is proportional to the single particle spectral density function $A(k, \omega)$

$$I(k,\omega) = I_{if}(k,\mathbf{A},\nu)A(k, \omega)\, fd(\omega, T)$$

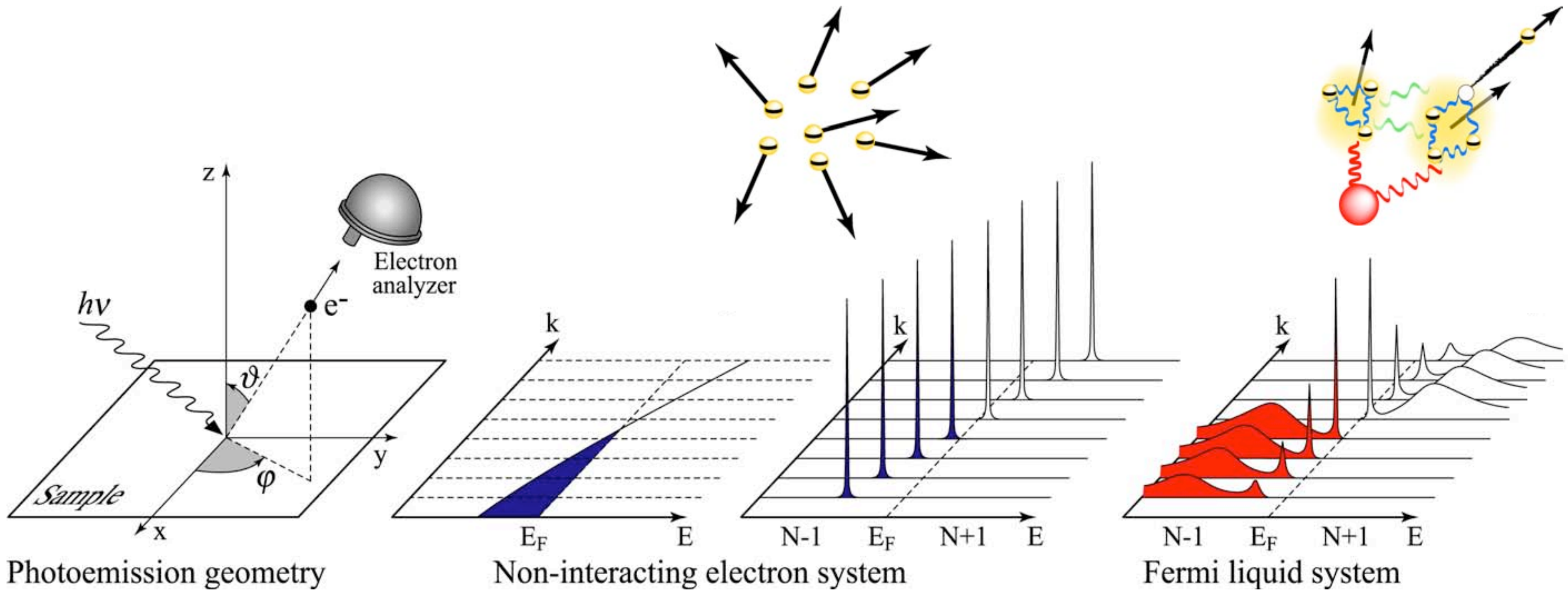
Proportional to Matrix elements

Spectral function

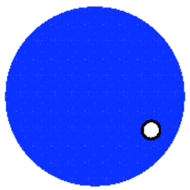
Fermi-Dirac

$$A(k,\omega) = \frac{1}{\pi}\mathrm{Im}\, G(k,\omega) = \frac{\Gamma}{\pi}\sum_s \frac{\left|\langle N-1, s|c_k|N,i\rangle\right|^2}{(\omega - E_s^{N-1} + E_i^N)^2 + \Gamma^2}$$

The single particle spectral function A(k, ω) gives the probability that the original system plus the bare hole (electron suddenly removed) will be found in an exact eigenstate of the (N-1)-system

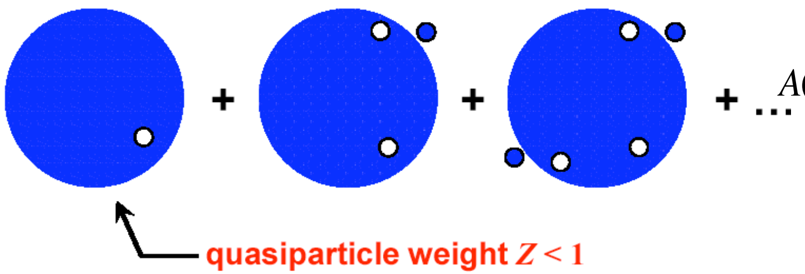


non-interacting system



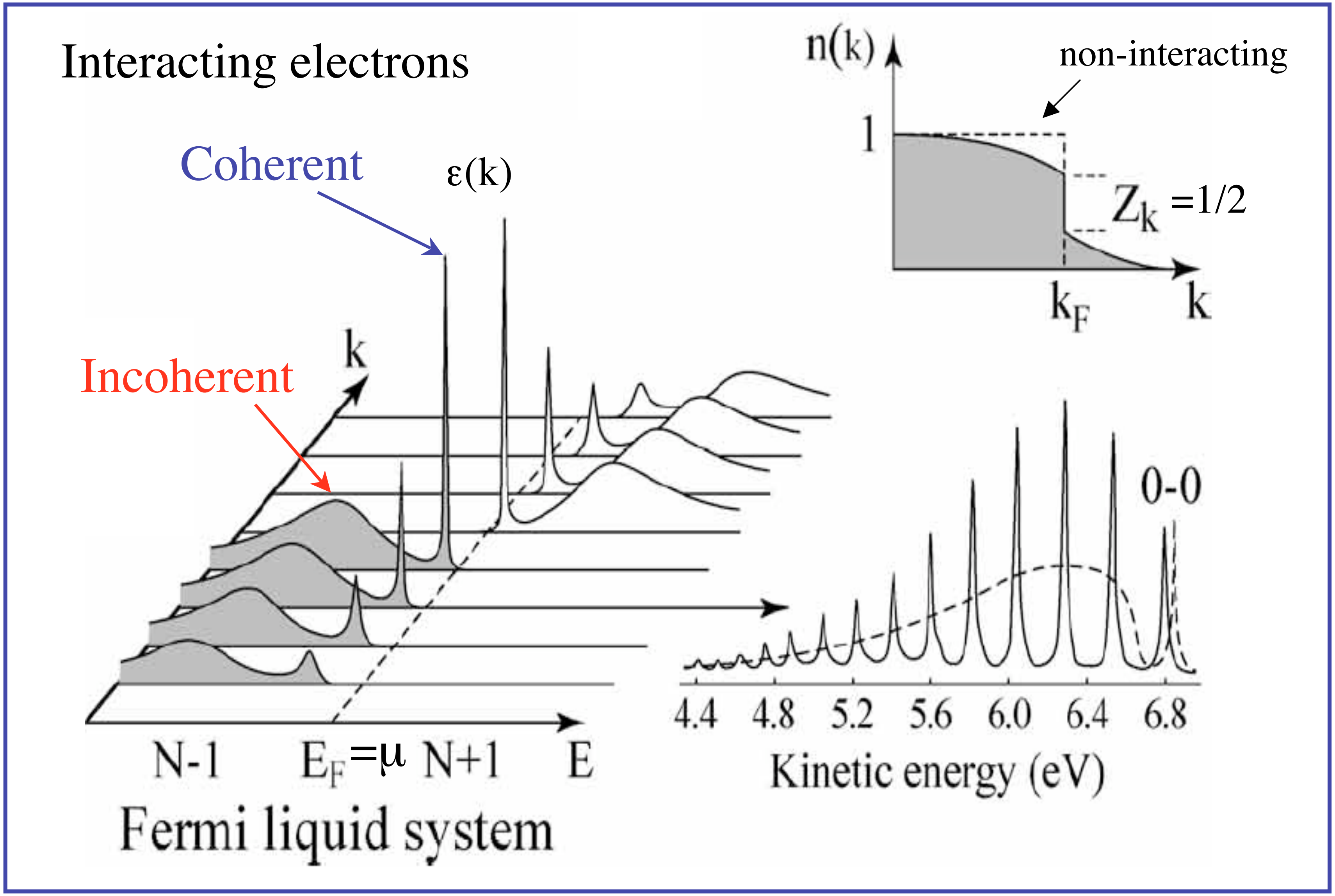
$$A(k,\omega) = -\frac{1}{\pi}\operatorname{Im} G(k,\omega) = \frac{\Gamma}{\pi}\frac{|\langle N-1,i|c_k|N,i\rangle|^2}{(\omega-\varepsilon(k))^2+\Gamma^2} = \frac{\Gamma}{\pi}\frac{1}{(\omega-\varepsilon_0(k))^2+\Gamma^2}$$

interacting system



$$A(k,\omega) = -\frac{1}{\pi}\operatorname{Im} G(k,\omega) = \frac{\Gamma}{\pi}\frac{|\langle N-1,i|c_k|N,i\rangle|^2}{(\omega-\varepsilon(k))^2+\Gamma^2} + \frac{\Gamma}{\pi}\sum_{s\neq i}\frac{|\langle N-1,s|c_k|N,i\rangle|^2}{(\omega-\varepsilon_s(k))^2+\Gamma^2}$$

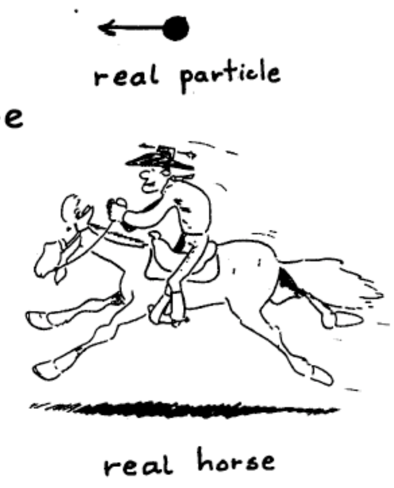
$$= A(k,\omega)_{coh.} + A(k,\omega)_{incoh}$$

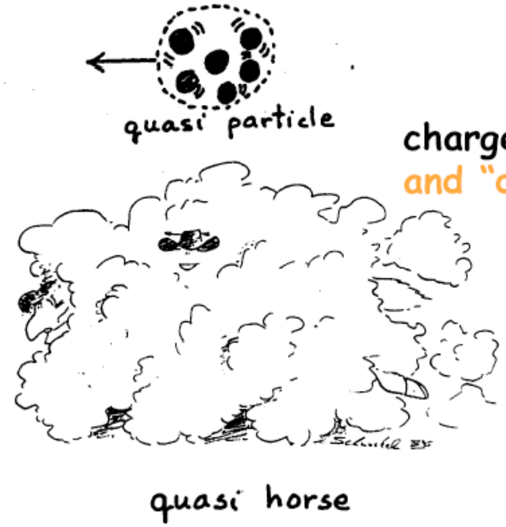


$$A(k,\omega) = \frac{\Gamma}{\pi}\frac{Z_k}{(\omega - \varepsilon(k))^2 + \Gamma^2} + \frac{\Gamma}{\pi}\sum_{s\neq i}\frac{\left|\langle N-1,s|c_k|N,i\rangle\right|^2}{(\omega - \varepsilon_s(k))^2 + \Gamma^2} = A(k,\omega)_{coh.} + A(k,\omega)_{incoh}$$

non-interacting electrons	**interacting** electrons

charge -e
spin 1/2





charge, spin
and "dressing"

band structure

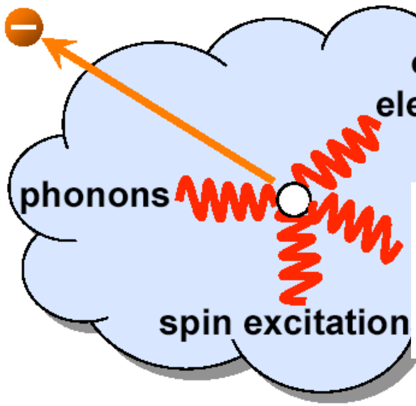
$\varepsilon_0(\mathbf{k})$

quasiparticle band structure

$$\varepsilon(k) = [\varepsilon_0(k) + \Sigma_1(k,\omega)]$$

$$\Sigma(k,\omega) = \Sigma_1(k,\omega) + i\Sigma_2(k,\omega) \quad \text{Self Energy}$$

- **photohole probes interactions** between electrons and with other dynamical degrees of freedom
  → energy shifts
  → shake-up satellites
  → line broadening
  → line shape
  (generalized Franck-Condon effect)

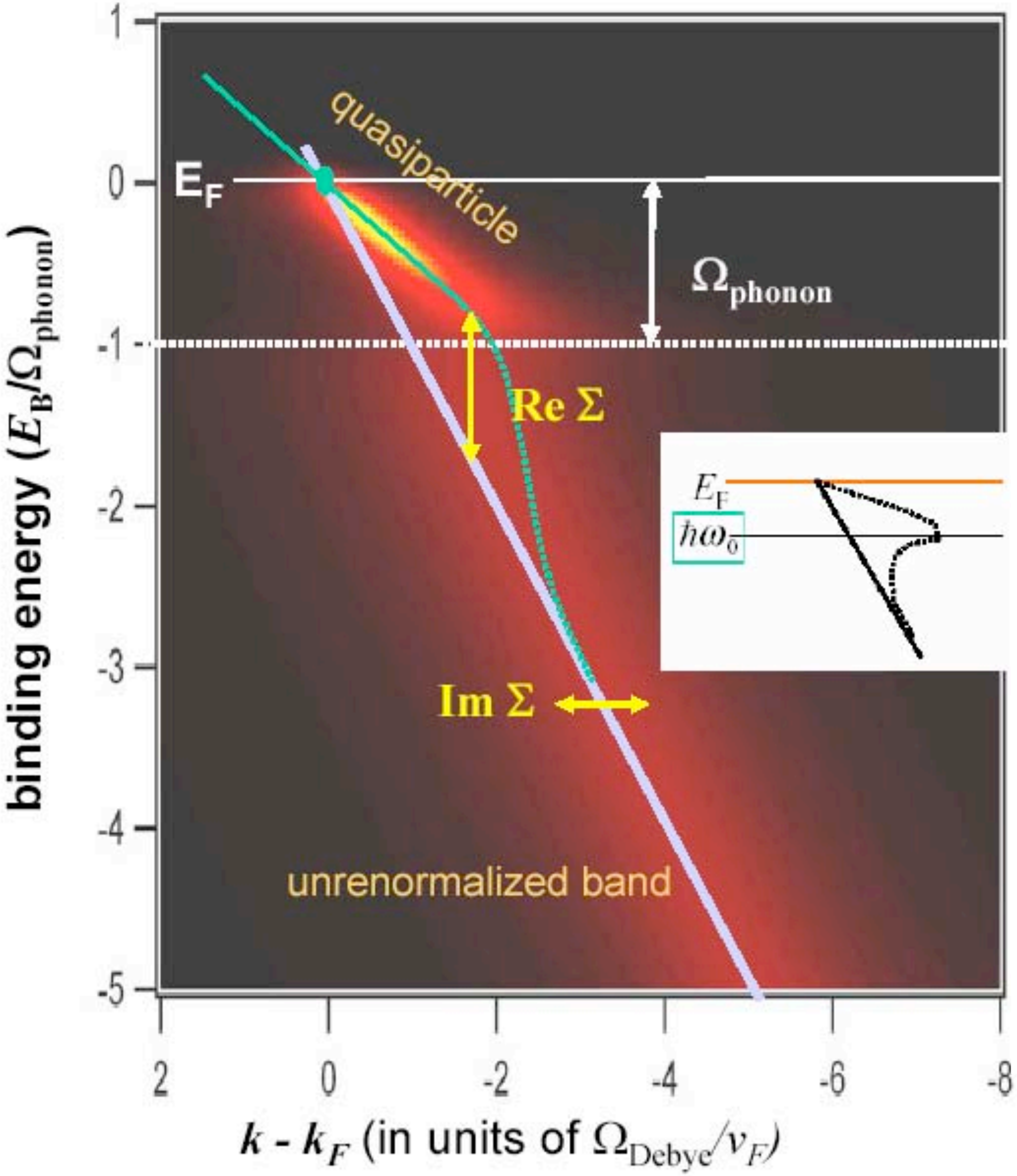


→ **lifetime broadening:** $\Gamma_{\vec{k}} = \mathrm{Im}\Sigma$

→ **quasiparticle weight:** $Z_{\vec{k}} = (1 - \frac{\partial\Sigma}{\partial\omega})^{-1} \leq 1$

$= m_o/m_{eff}$

Debye Model ($\lambda = 1$)



$$\mathrm{Im}\,\Sigma(\omega) \propto \lambda \int_0^{\omega} \rho_{phonon}(\Omega)\, d\Omega$$

energy scale Ω_{phonon}:

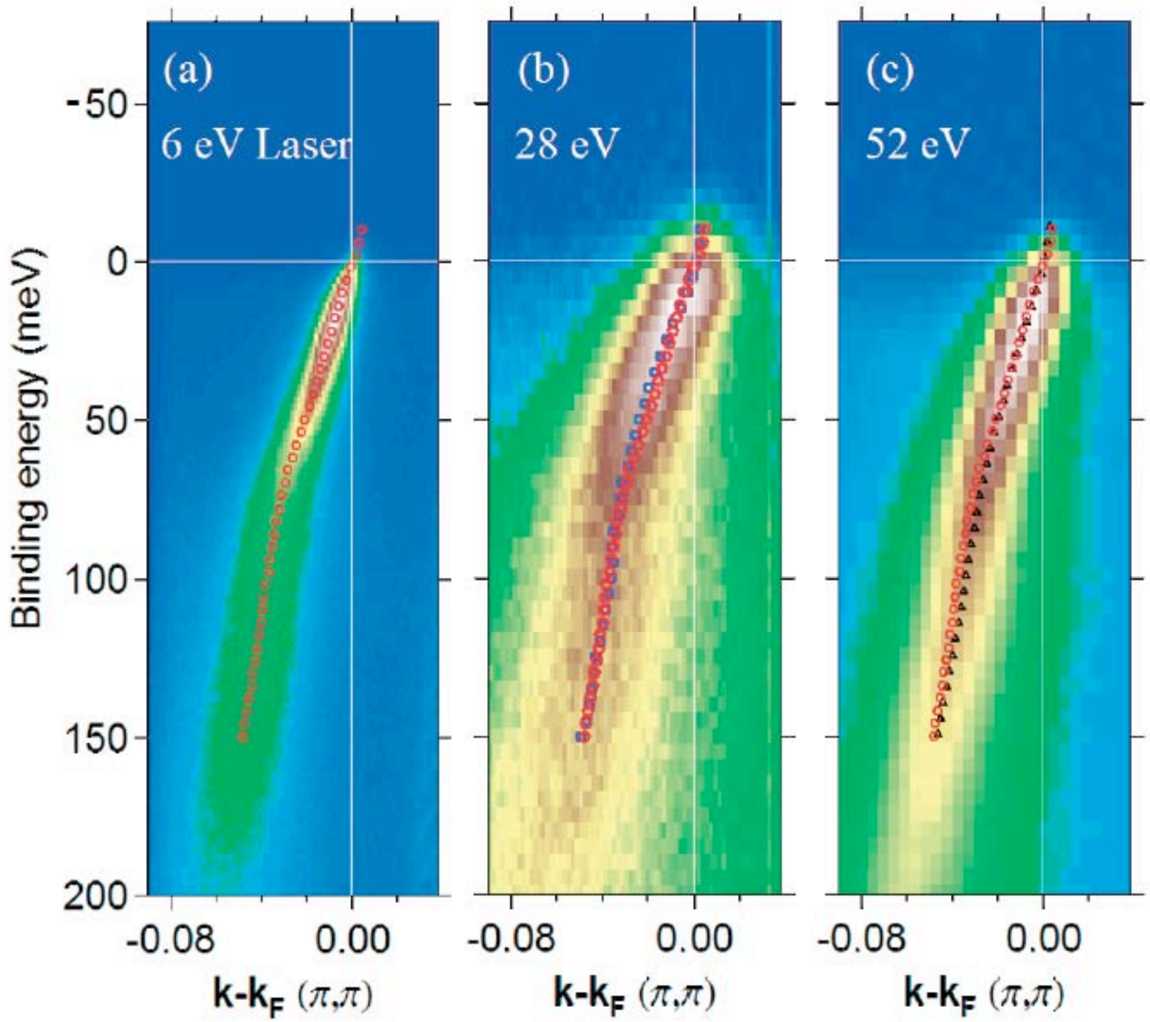
separates between *virtual* and *real* scattering processes

coupling constant λ:

effective Fermi velocity
$v_F^* = v_F^0/(1+\lambda)$

effective mass $m^* = (1+\lambda) m_0$

i.e. $Z = (1+\lambda)^{-1}$

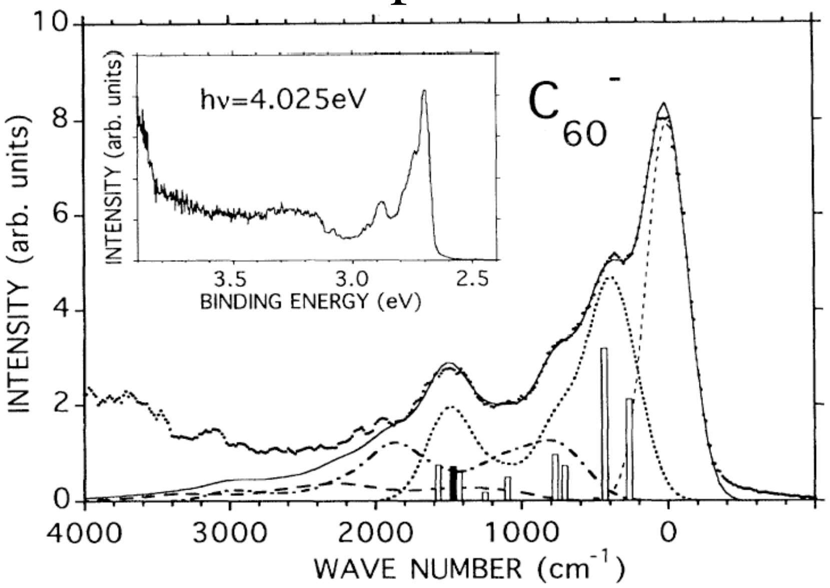


No dramatic changes in the electronic spectra near the Fermi surface. The sudden approx seems to be still valid or its breakdown may be not so important for the states near E_F.

J.D. Koralek et al., PRL76, 017005 (2005)

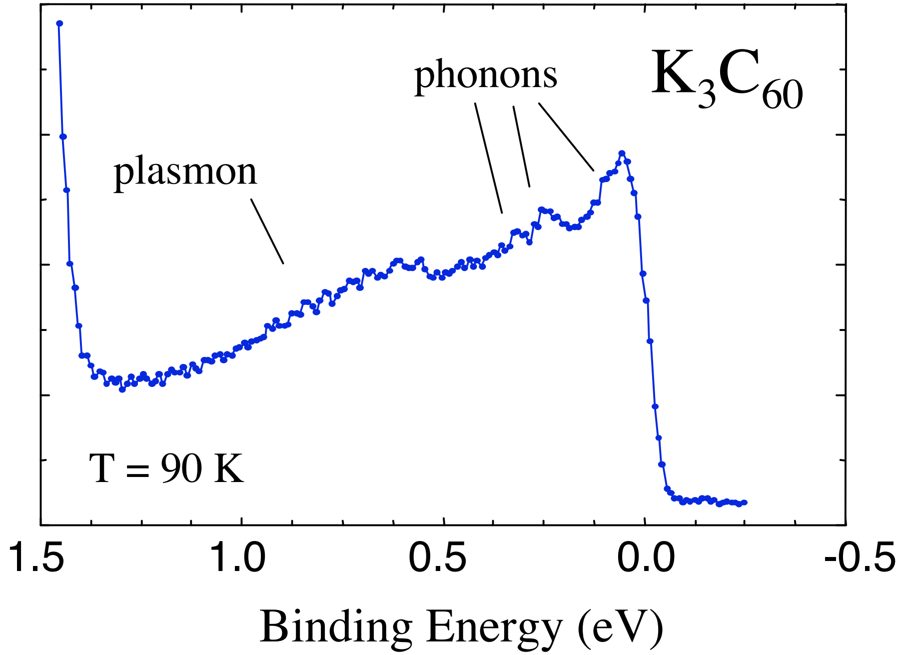
Phonon features in C_{60}

Gas phase



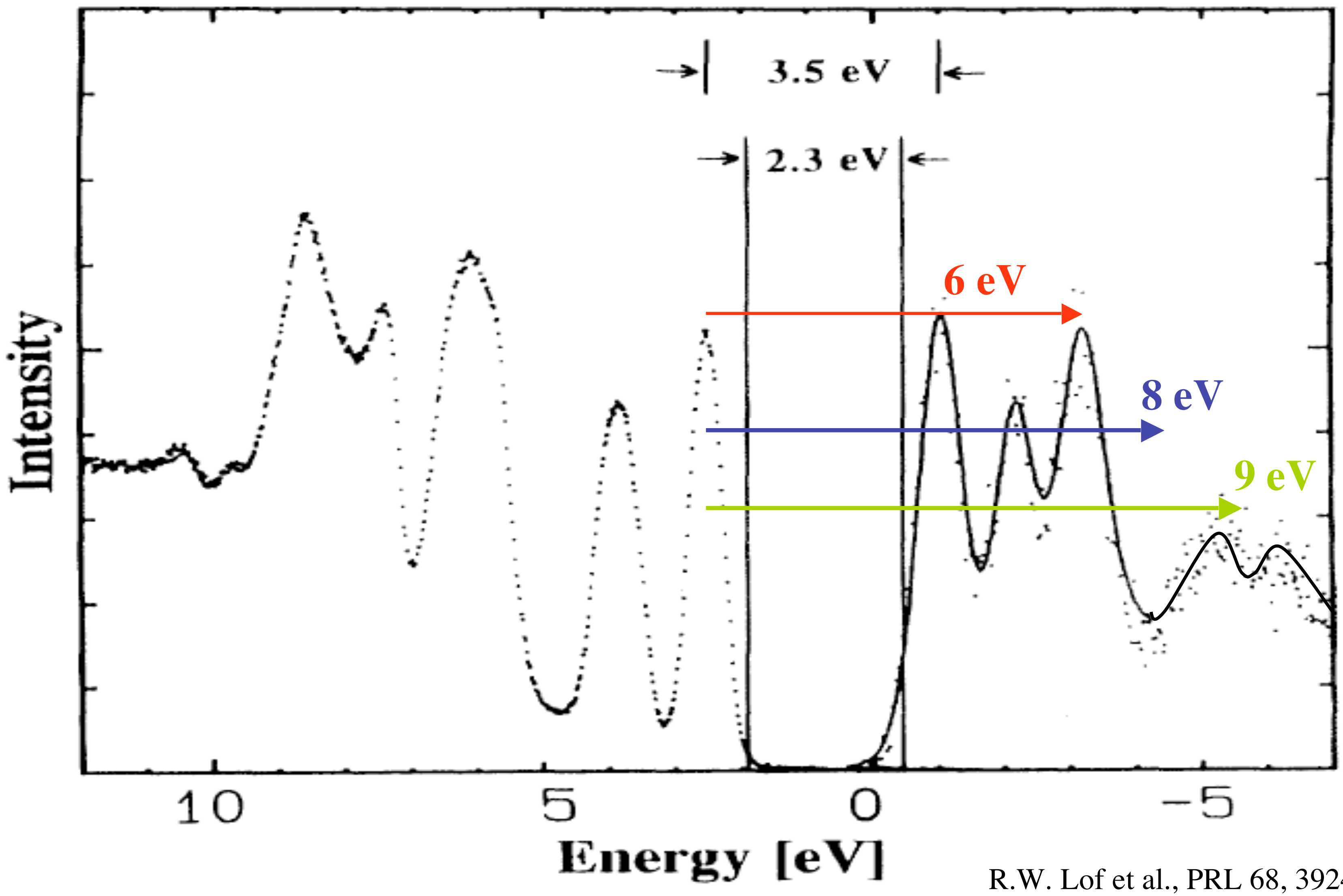
O. Gunnarsson et al. PRL74, 1875 (1995)

Solid



A. Goldoni et al. PRB 58,11023 (1998)

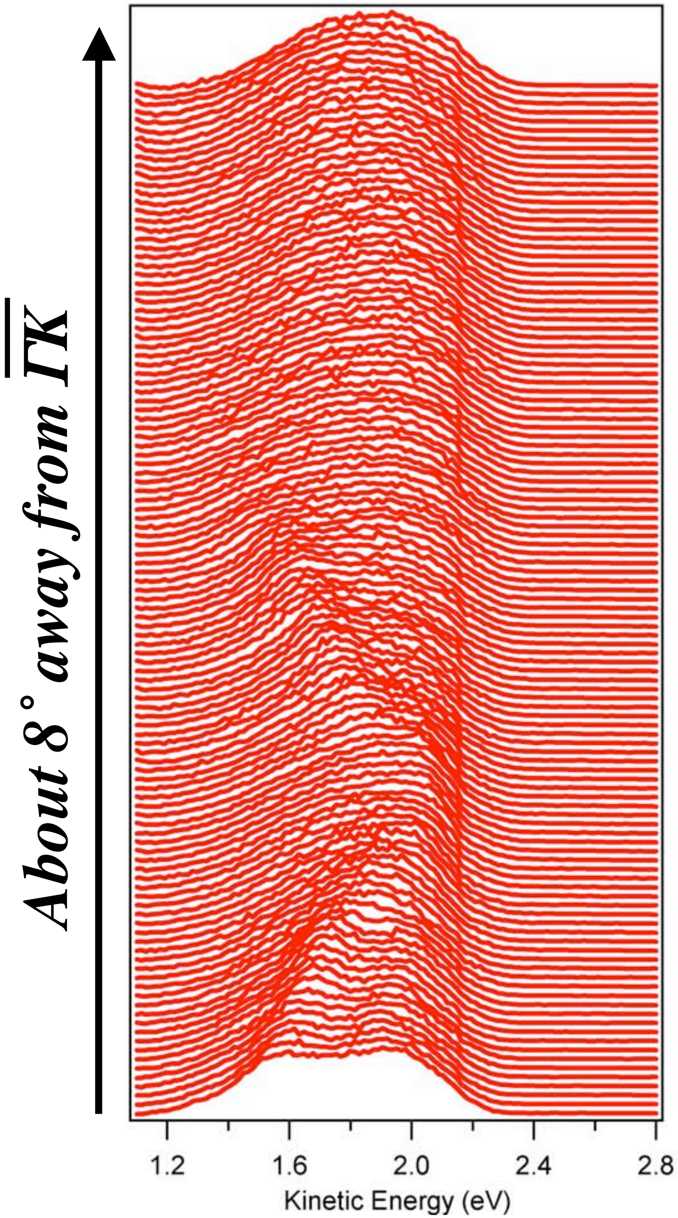
Another critical point for ARPES at low energies: "Final state" effects

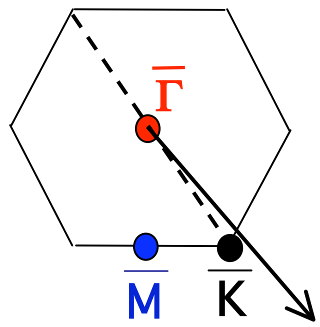


R.W. Lof et al., PRL 68, 3924 (1992)

C_{60}(111) multilayer @ RT

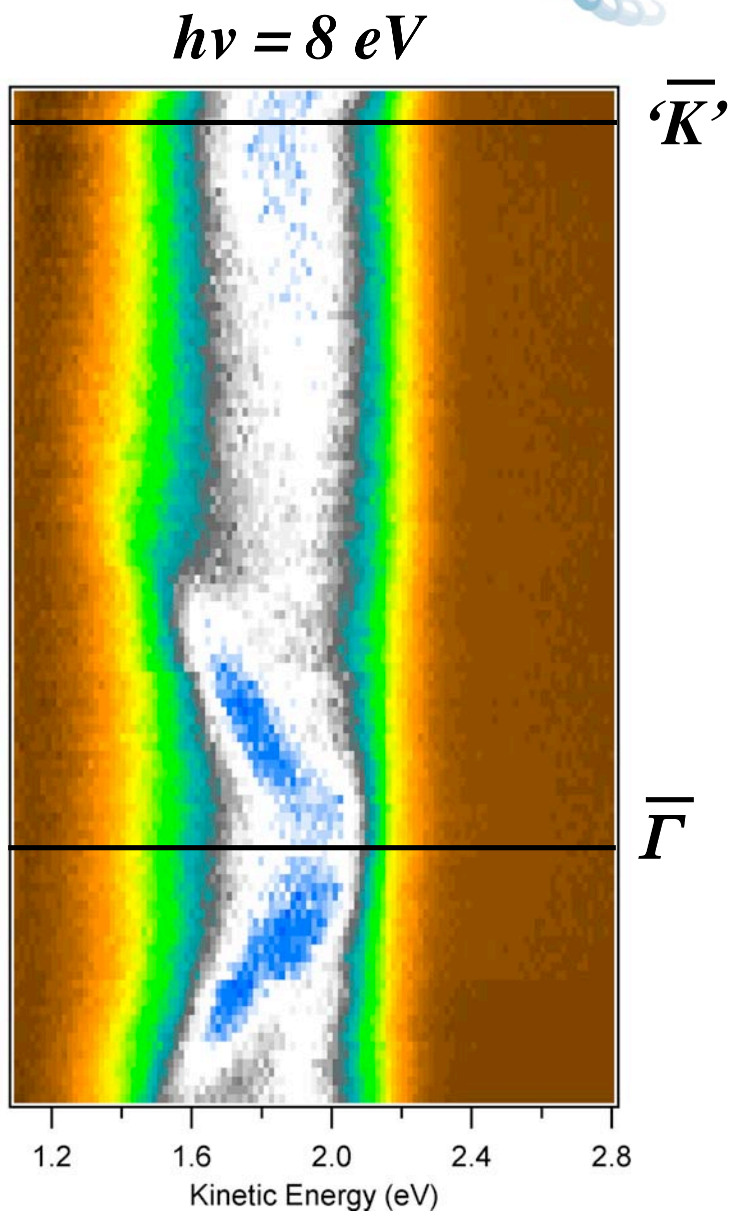
A. Goldoni et al.





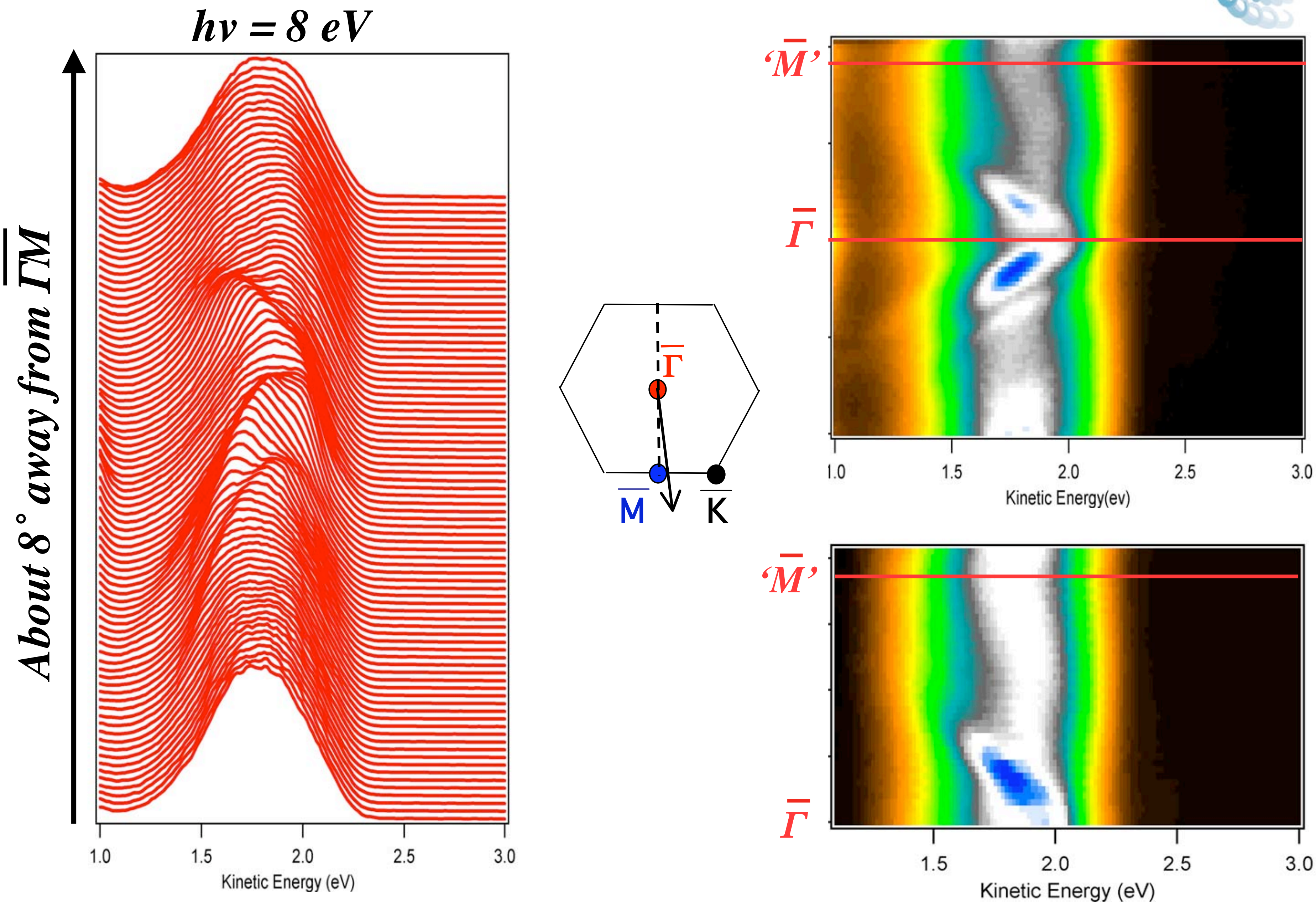
HOMO band dispersion ~ 0.6 eV

No difference @ 77 K



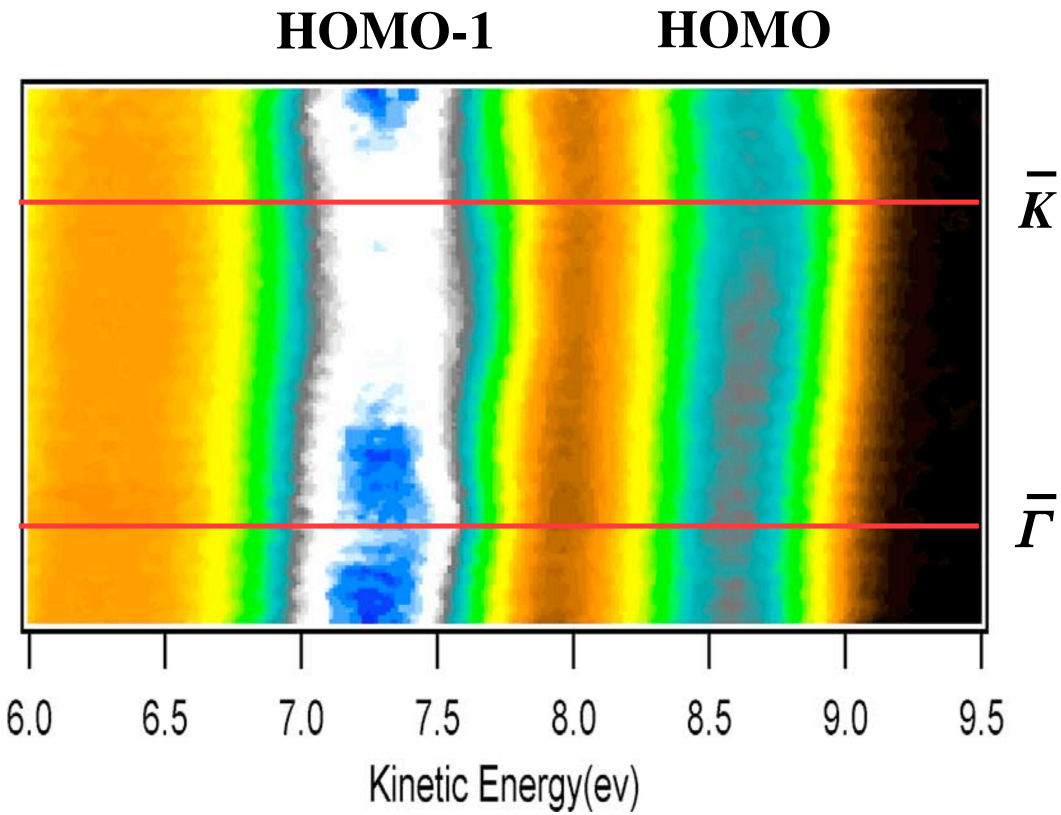
$C_{60}(111)$ multilayer @ RT

A. Goldoni et al.



C_{60}(111) multilayer @ RT

A. Goldoni et al.

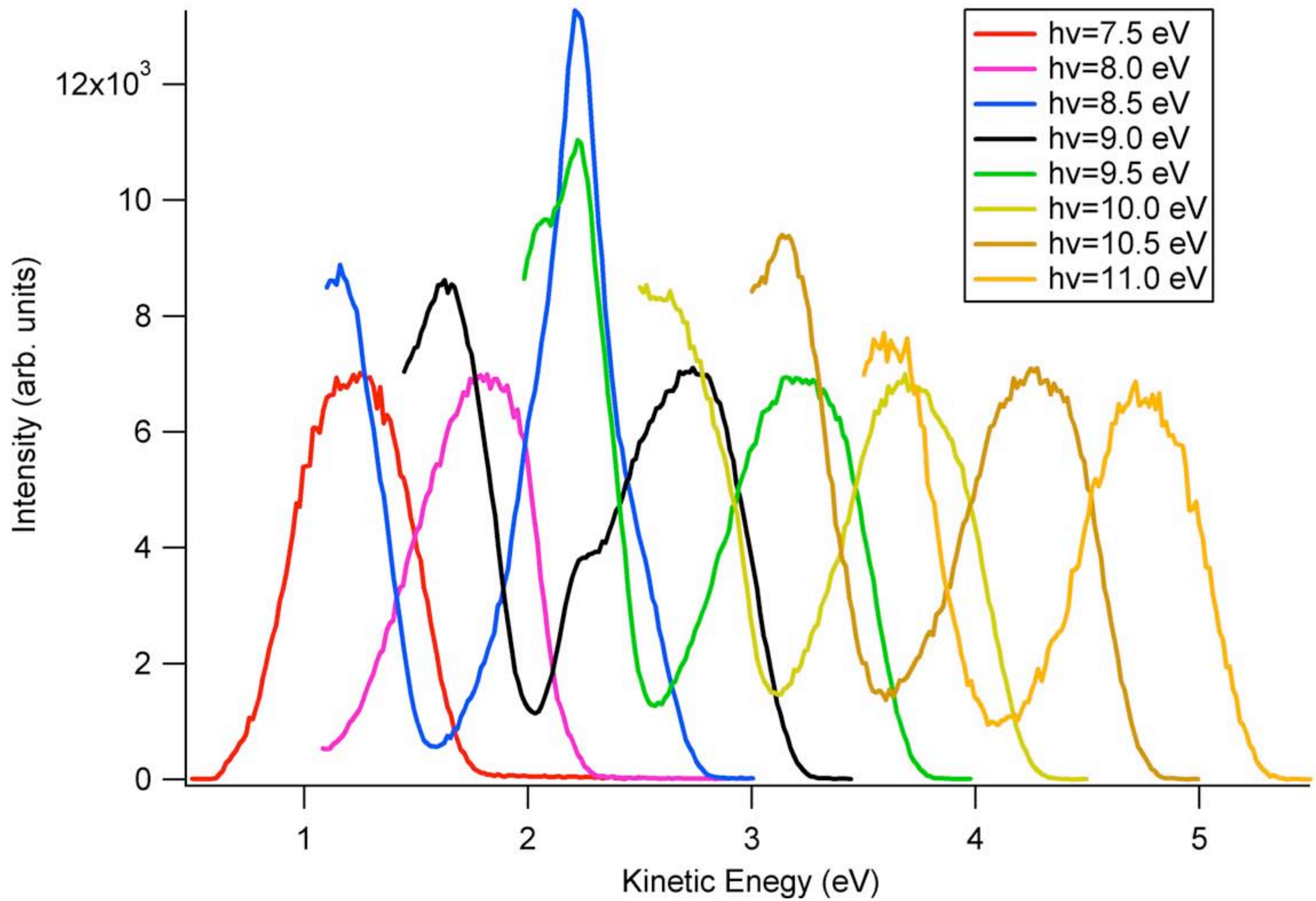


hν = 15 eV

HOMO dispersion apparently smaller than at 8 eV, but of the order of 0.2 eV ($K_{//}$ integration? Final state effects?)

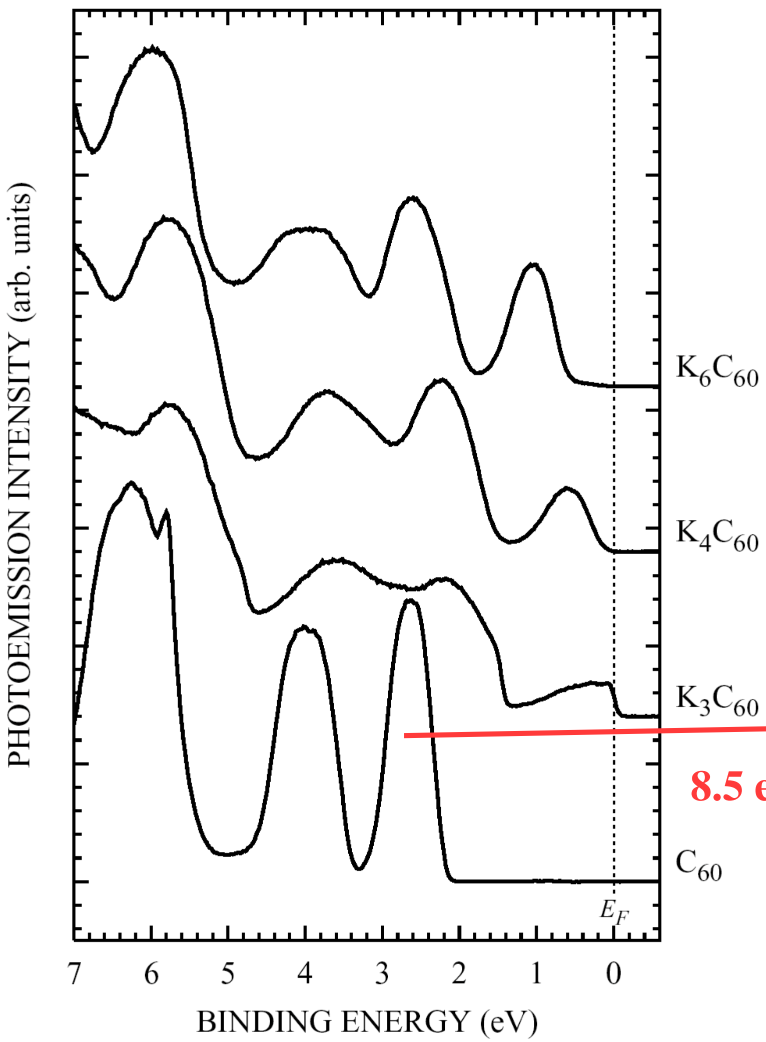
$C_{60}(111)$ multilayer

A. Goldoni et al.



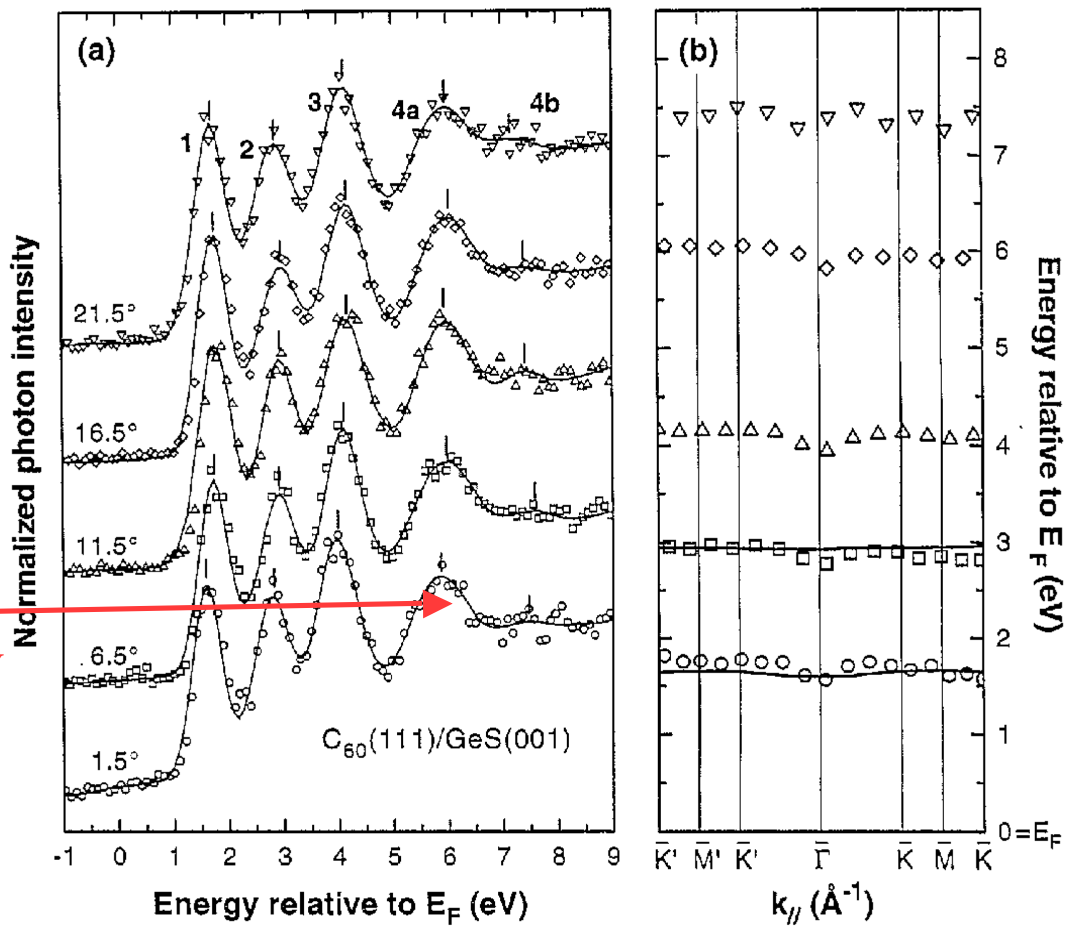
C_{60}(111) multilayer

photoemission



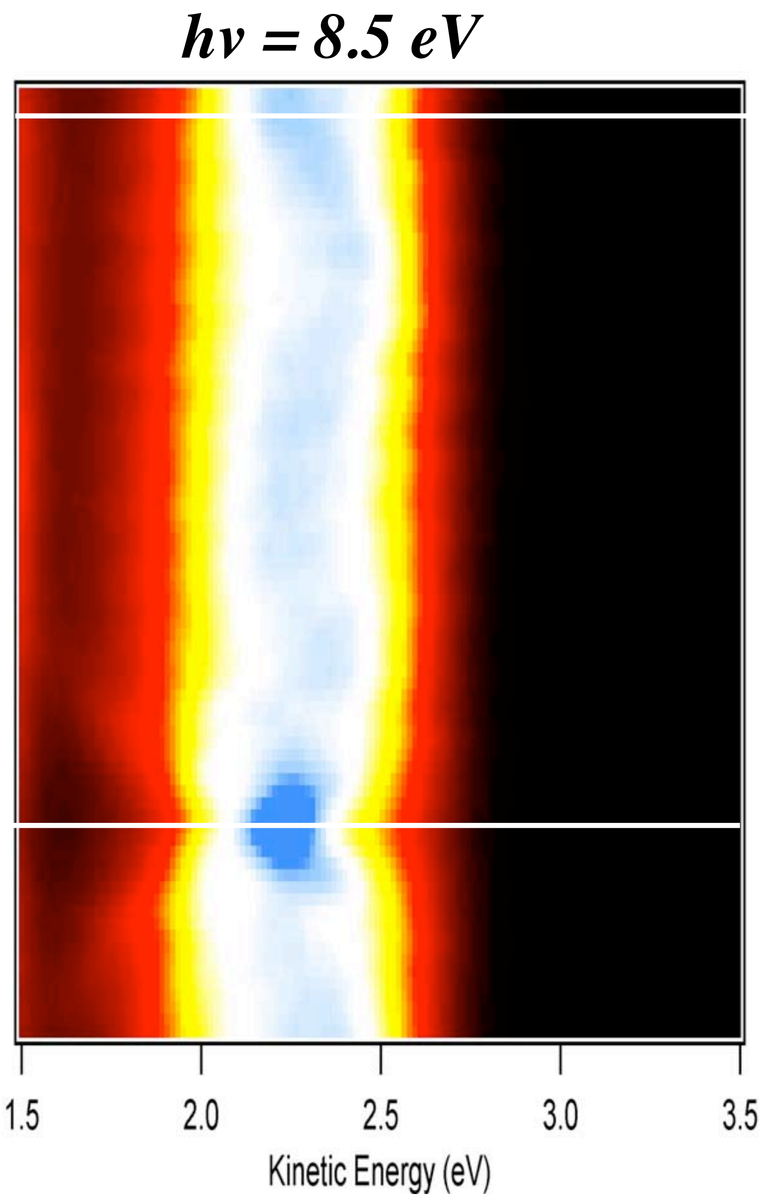
8.5 eV

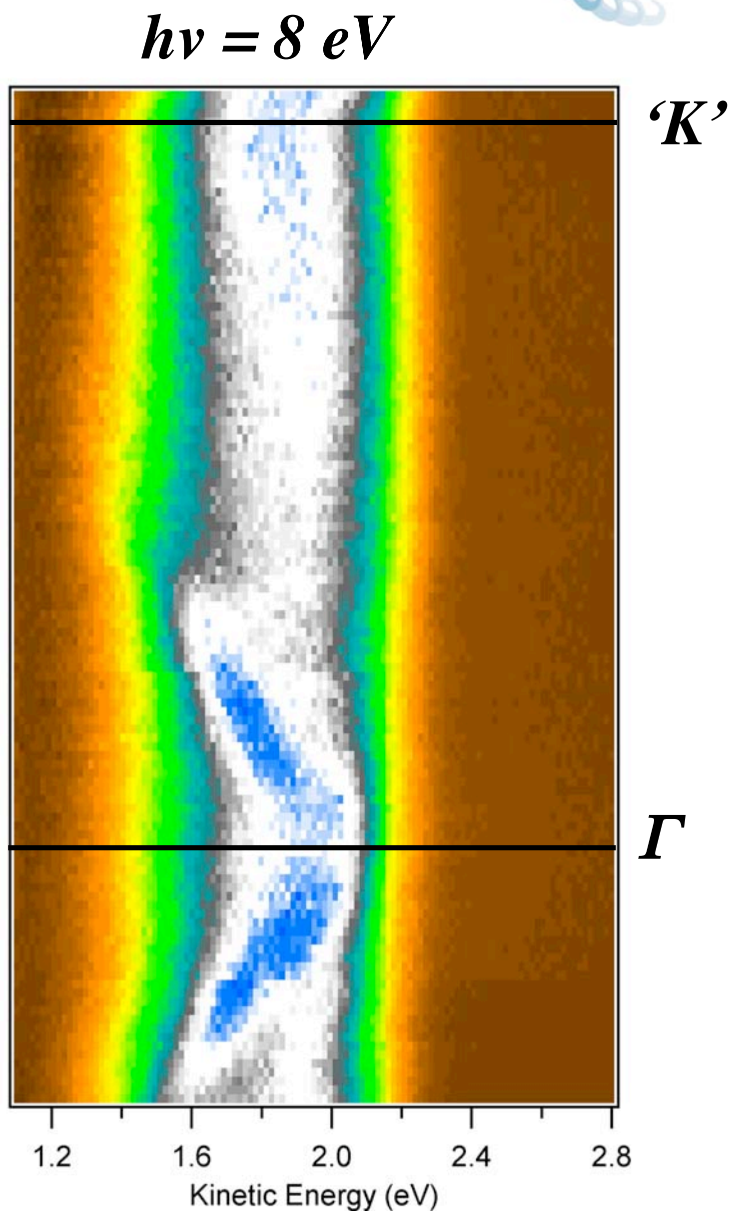
inverse photoemission



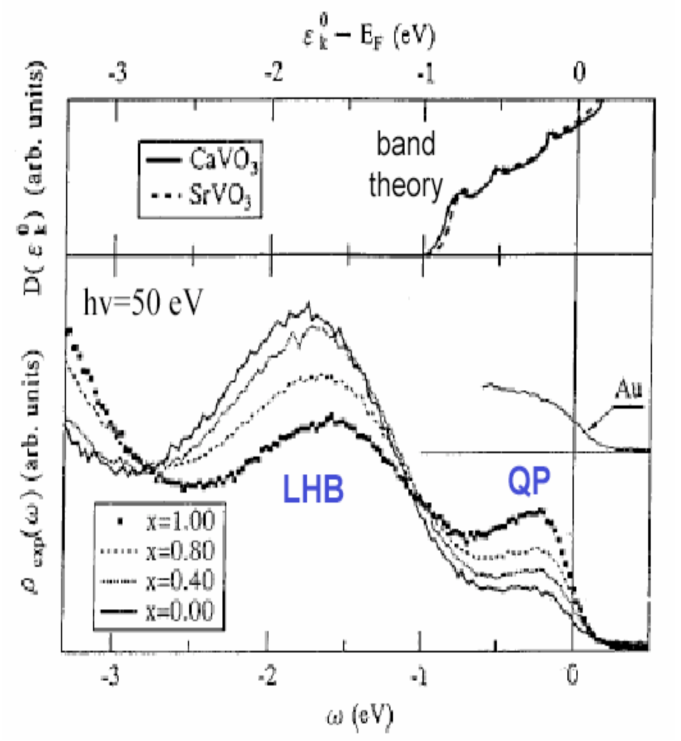
C_{60}(111) multilayer

A. Goldoni et al.

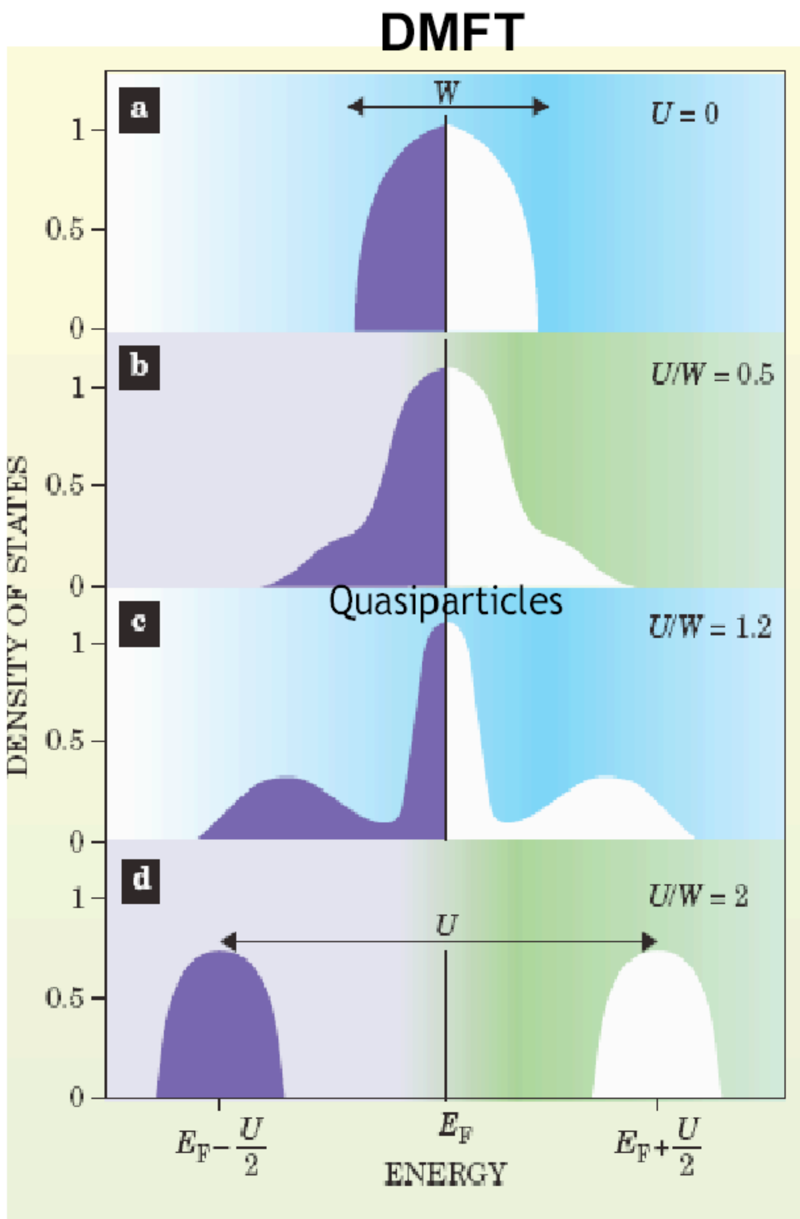




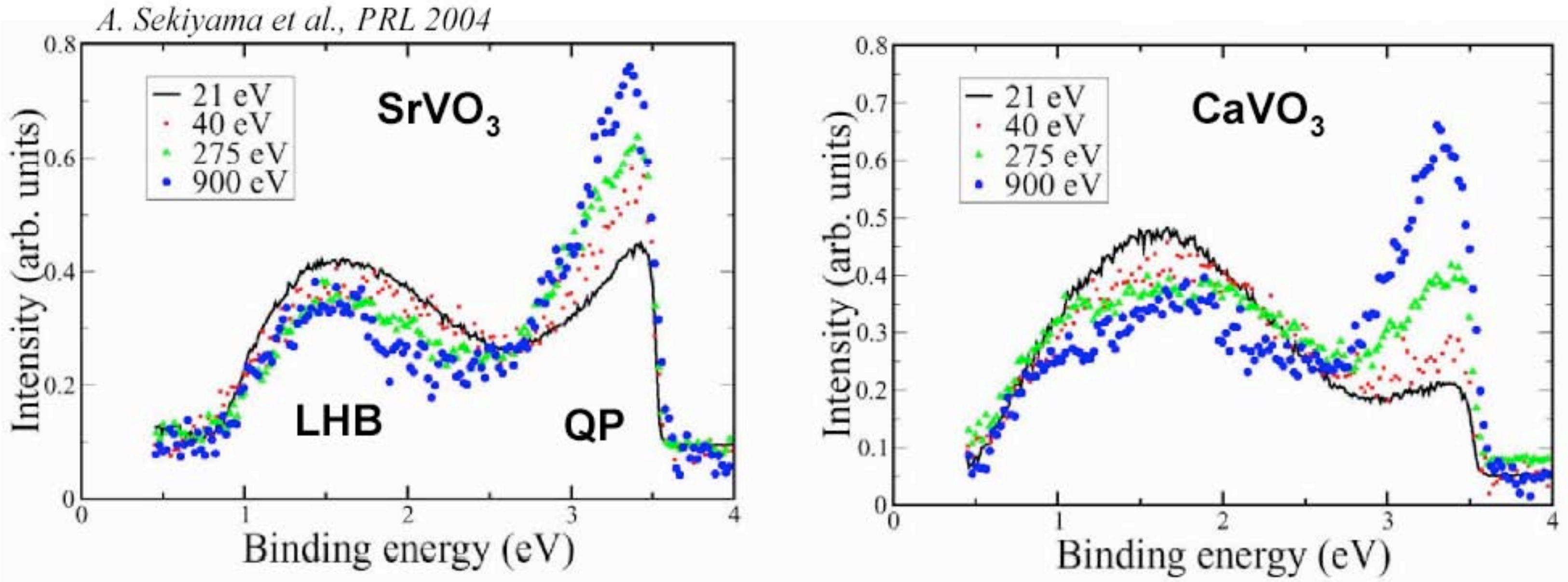
$Ca_{1-x}Sr_xVO_3$: angle-*integrated* photoemission



Inoue et al., PRL 1995



→ $CaVO_3$ more strongly correlated metal than $SrVO_3$?

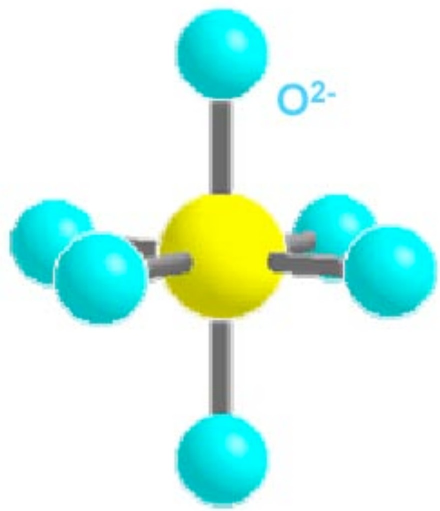


⇒ **at surface: reduced atomic coordination**

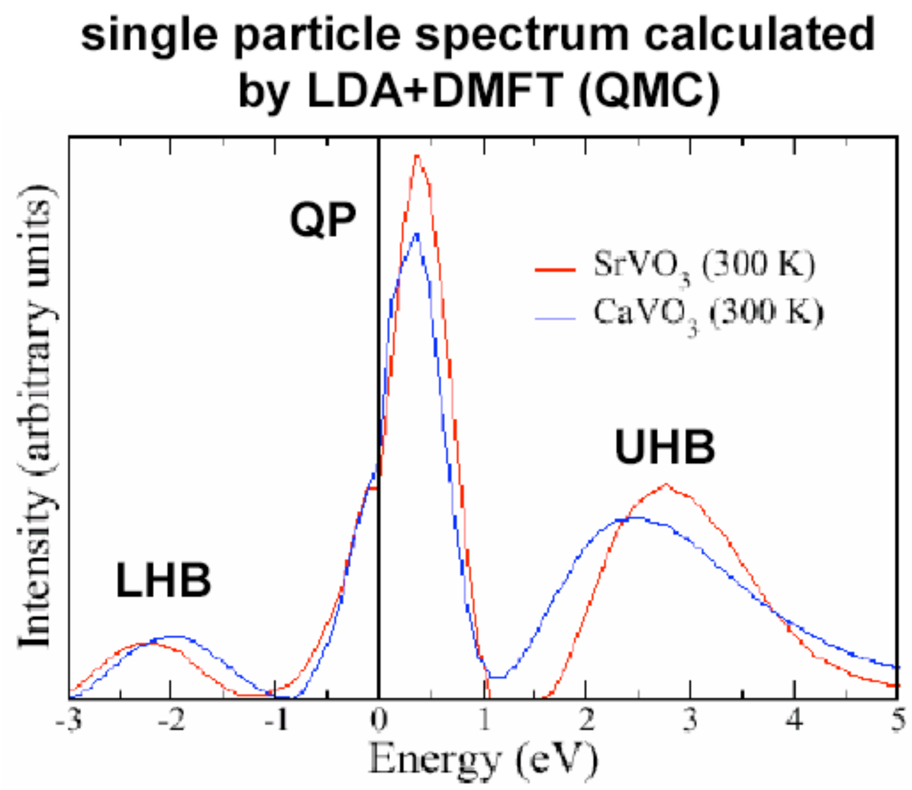
⇒ **effective bandwidth smaller:**
$W_{surf} < W_{bulk}$

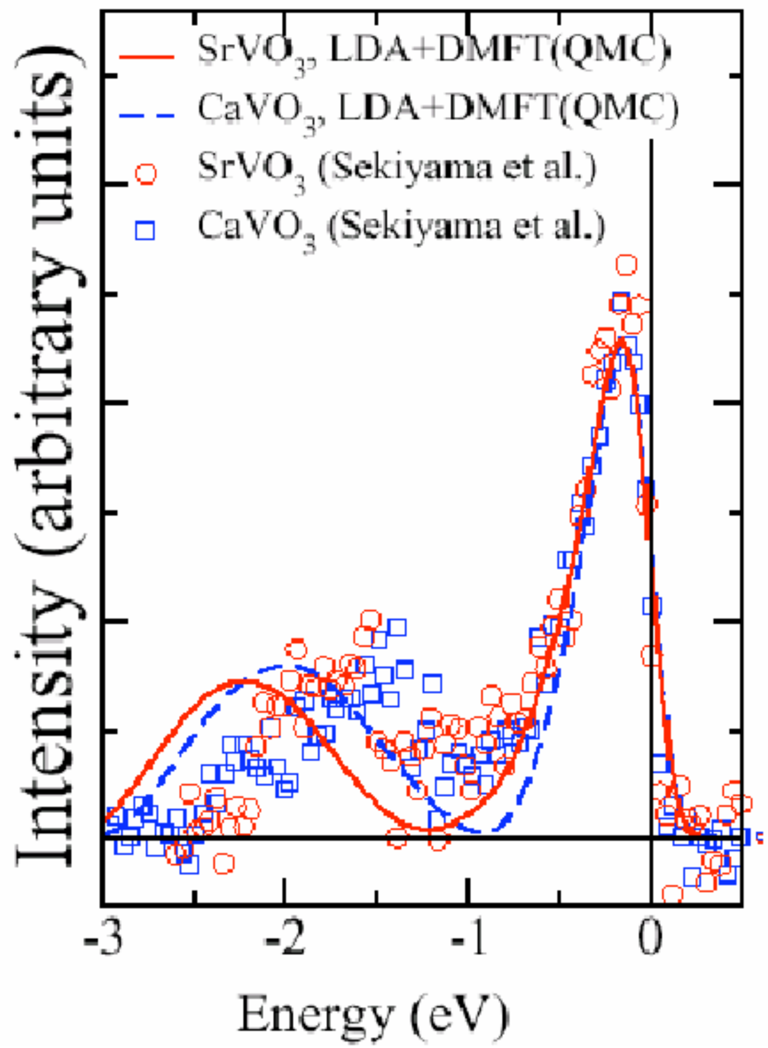
⇒ **surface stronger correlated:**
$U / W_{surf} > U / W_{bulk}$

⇒ **surface effect stronger for $CaVO_3$, but in bulk ~ identical for all compositions**



A. Sekiyama et al., PRL 2004



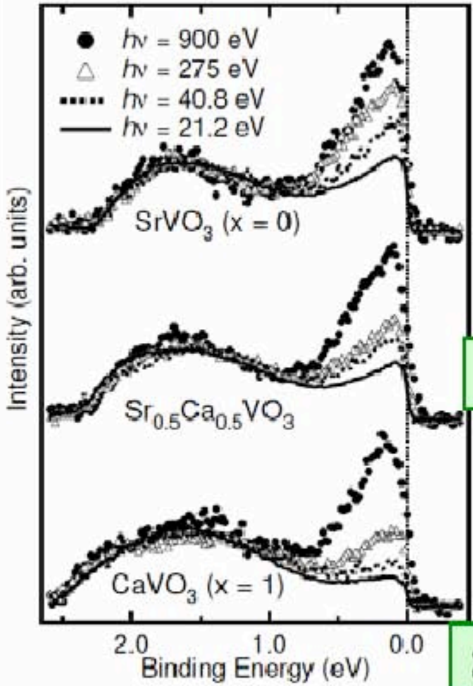


Good agreement, everything seems understood

- Incoherent peak becomes weak in SX PES
- $CaVO_3$ and $SrVO_3$ spectra are similar in SX PES

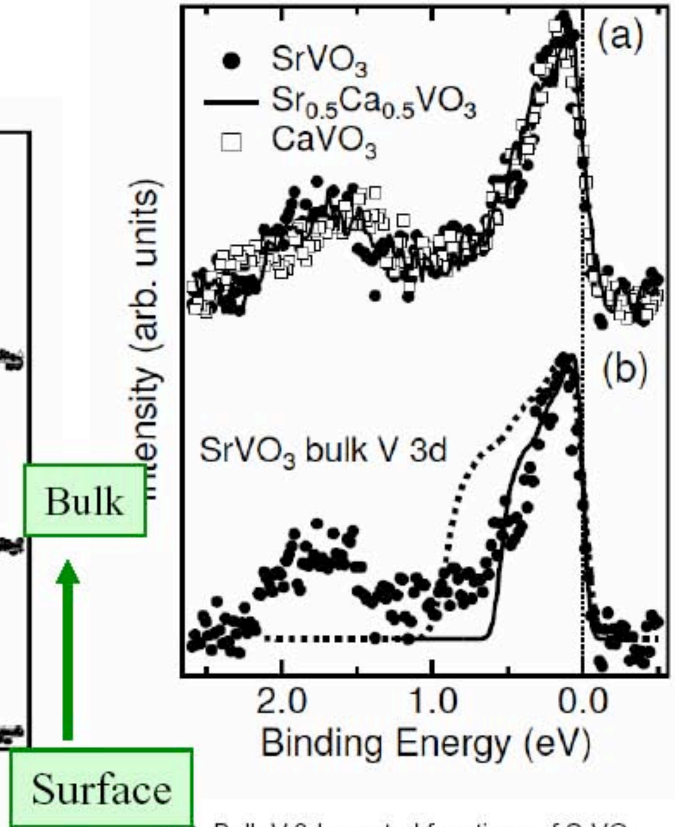
What happens in the bulk sensitive spectra using VUV laser ?

- More bulk sensitive
- much higher resolution



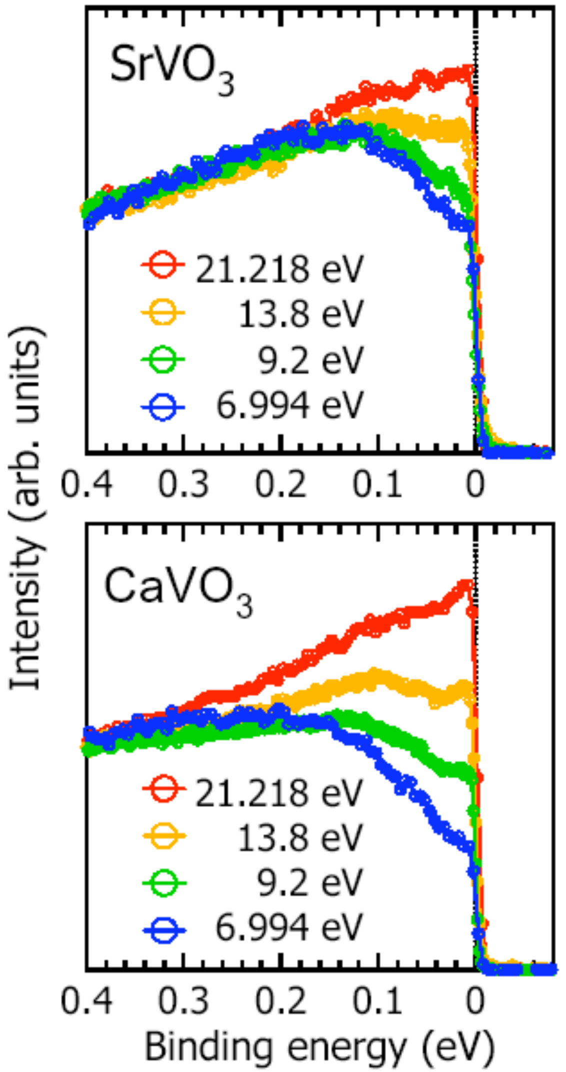
Photon-energy dependence of the V 3d spectral weights for $Sr_{1-x}Ca_xVO_3$. The V 3d spectra are normalized by the integrated intensities of the incoherent part ranging from 0.8 to 2.6 eV.

Sekiyama, PRL(2004)



(a) Bulk V 3d spectral functions of $SrVO_3$ (closed circles), $Sr_{0.5}Ca_{0.5}VO_3$ (solid line) and $CaVO_3$ (open squares).
(b) Comparison of the experimentally obtained bulk V 3d spectral function of $SrVO_3$ (closed circles) to the V 3d partial density of states for $SrVO_3$ (dashed curve) obtained from the band-structure calculation, which has been broadened by the experimental resolution of 140 meV. The solid curve shows the same V 3d partial density of states but the energy is scaled down by a factor of 0.6.

Excitation energy dependence of coherence peak

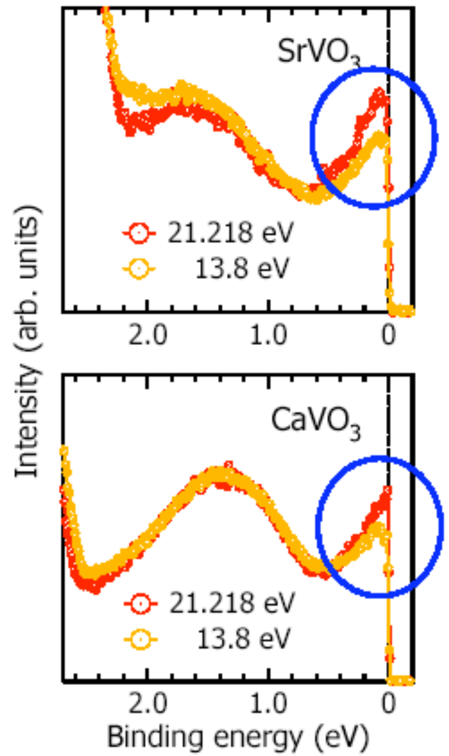


Surface

Bulk

Surface

Bulk



Surface

Bulk

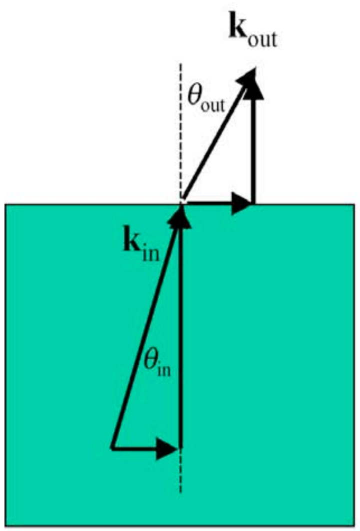
Contrary to the SX spectra, coherent peaks become weaker

What happens?

Other problems:

- Magnetic fields must be screened very well

- The total reflection angle for bulk state emission can be reached



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\|} = k_{in,\|} \equiv k_\|$$

"Snell's Law"

$$k_\| = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$

- Large Brillouin zones cannot be mapped completely