Photoemission Experiments at SPring-8 Beamline BL25SU

COLLABORATORS

Photoemission

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Samples and bulk properties

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Theory

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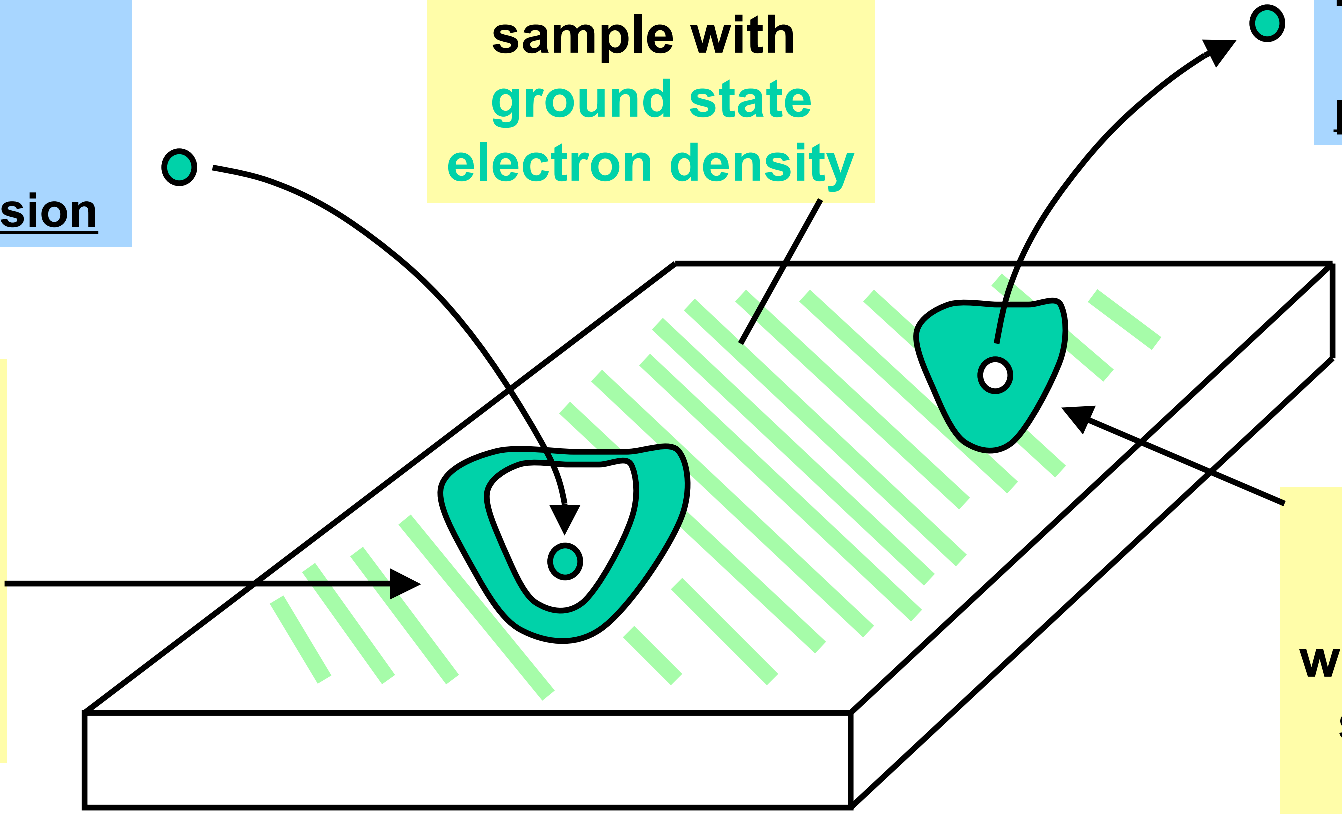
Supported at U-M by U.S. N

electron removal (and addition) to study single-particle behavior of many-body system

Spectroscopy of energy and momentum dependence of spectral weight

$$\rho\ (k,\omega) = \quad (1/\pi)\ \ \mathrm{Im}\ [1/\ (\omega - \varepsilon_k - \Sigma(k,\omega))]$$

of single particle Green's function



Insert e –
from ∞
<u>inverse</u>
<u>photoemission</u>

sample with
ground state
electron density

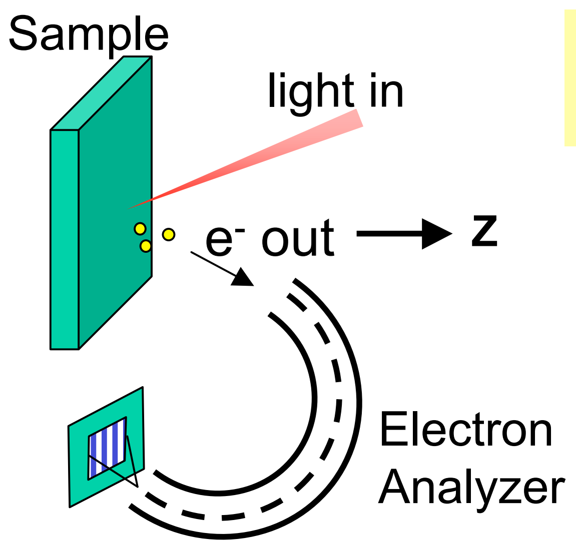
remove e –
<u>photoemiss</u>

added
electron
with
hole
screening
cloud

added
hole
with electro
screening
cloud

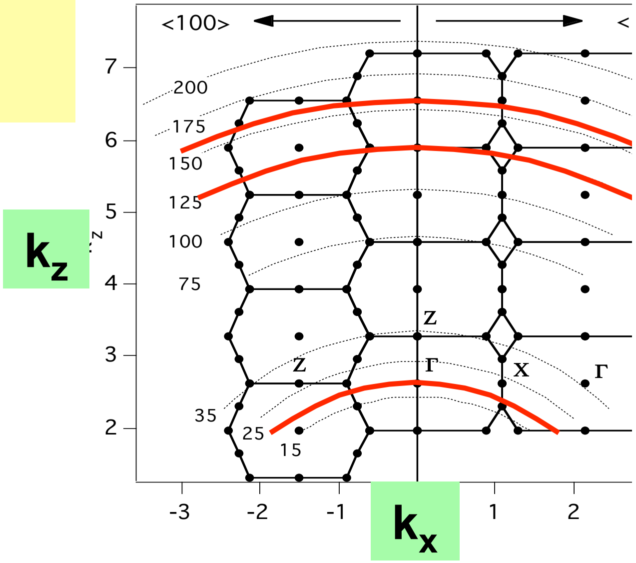
Both processes together give unbound hole/electron pair

Photoemission spectroscopy to measure $\rho\ (k,\omega)$ or k-summed $\rho\ (\omega)$

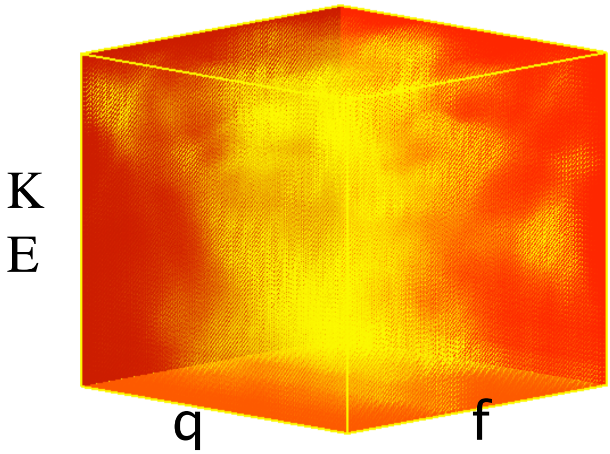


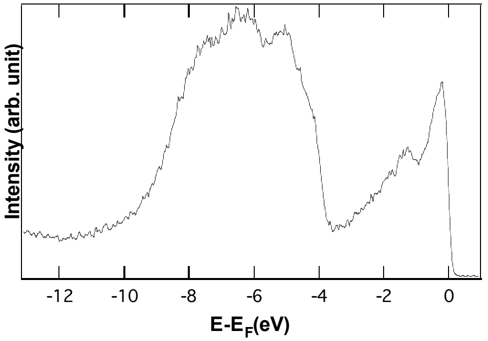
Angle variation moves on spherical k-space surfaces.

Vary photon energy to change k_z



Full electronic structure
@ fixed photon energy
—3D data set—

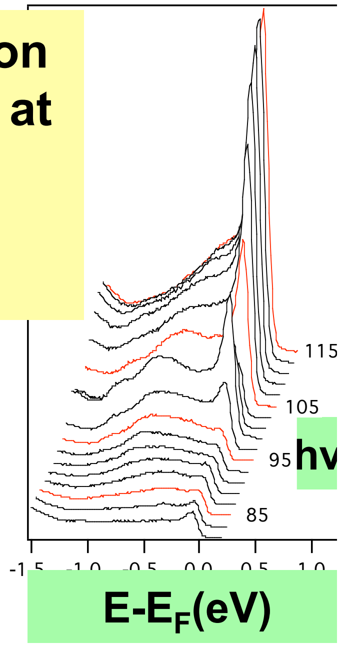




Angle integrated
Or k-summed

Cross-section resonances at core level absorption edges

= RESPES

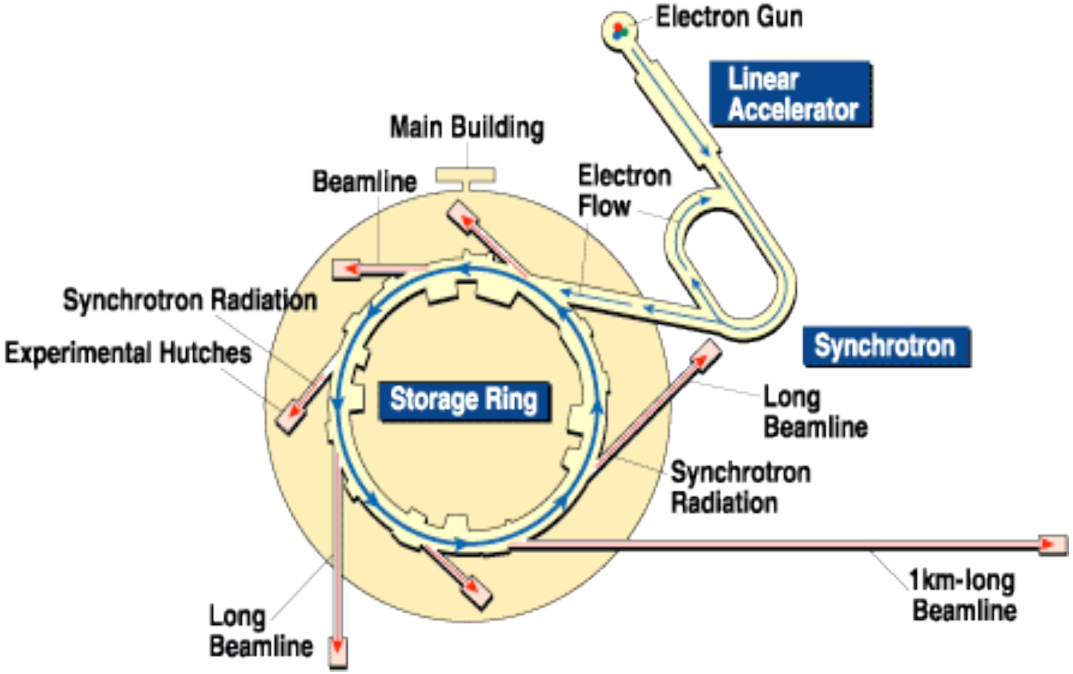


High photon energy—more bulk sensitive

SPring-8

3rd generation synchrotron in western Japan

- 1GeV / 140m long Linac
- 8GeV / 396m circumference boost ring
- 8GeV / 1436m circumference storage ring
- insertion devices : 4 x 30m, 34 x 6m
- 300eV ~ 300keV photon energy



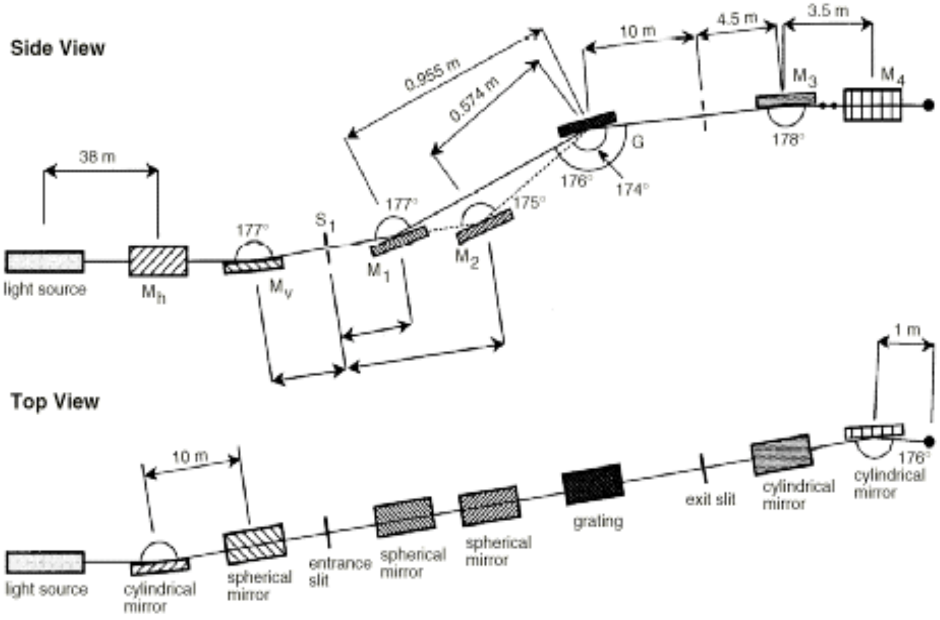
SPring-8 and APS similar

	Spring-8	APS
Operated by	JASRI	ANL
Supported by	JAERI & RINKEN	US DoE
Location	Harima Science Garden City	Argonne
Ring energy	8 GeV	7 GeV
Number of beamlines	62	68
Ring circumference	1436 m	1104 m

SPring-8 beamline BL25SU

Twin helical undualtor beamline

- undulator period : 120mm
- number of periods : 12 x 2
- tunable energy range : 300eV ~ 3keV
- brilliance : 1.89 ~ 7.85 x 10^{17} ph/s/mrad^2/mm^2/0.1% b.w.
- total power : < 1.67kW
- power density : < 3.0kW/mrad^2



Schematic View of Beamline

Resolving power

$E/\Delta E > 10000$

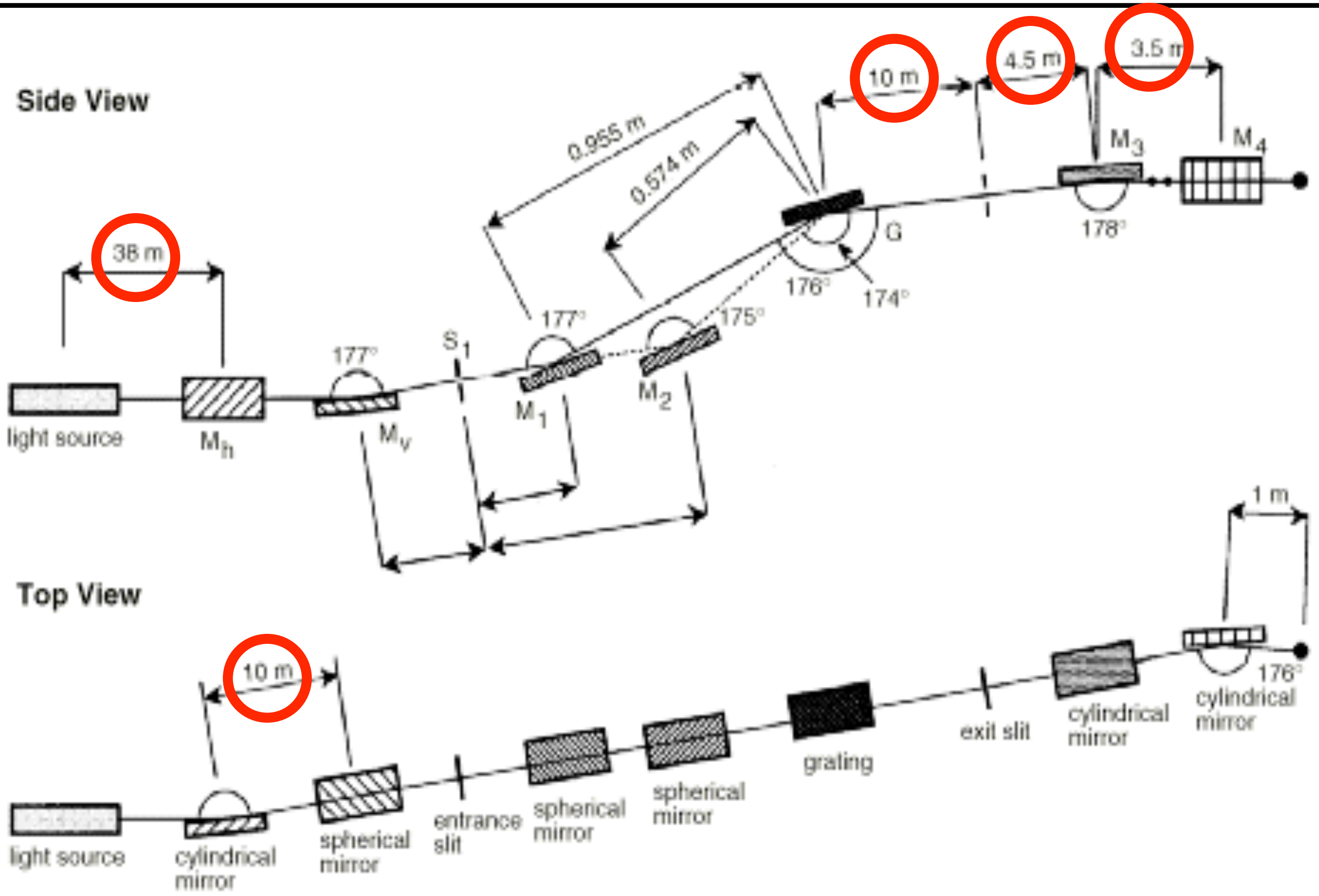
Photon flux

$> 10^{11}$ ph/s/0.2% b.w.

Beamsize

~ 0.1mm x 0.1mm

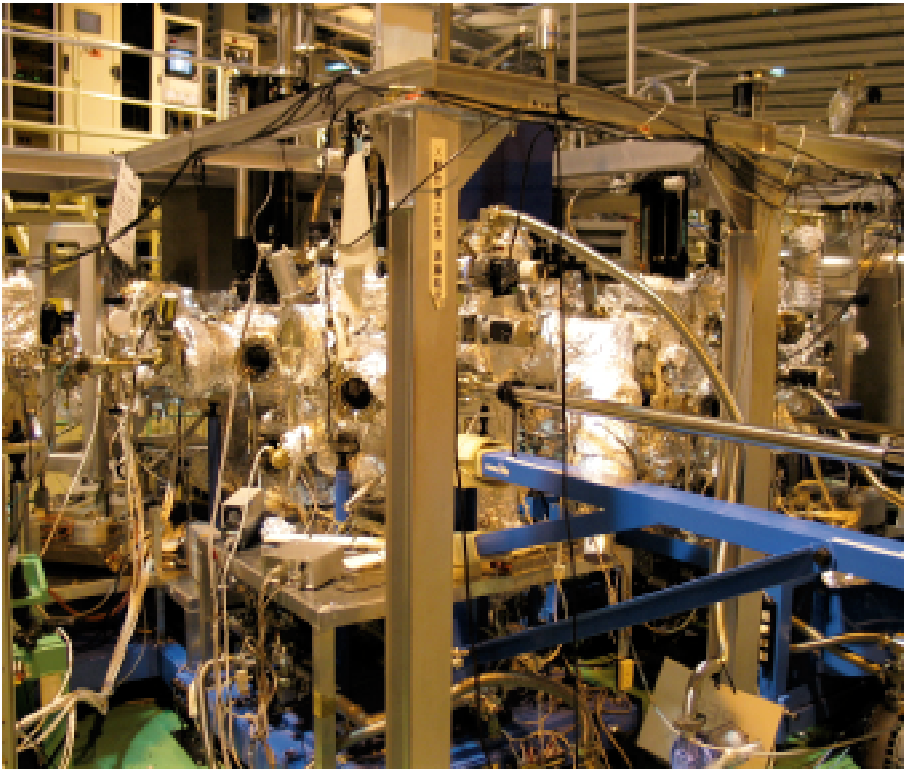
SPring-8 beamline BL25SU layout



Schematic View of Beamline

To get the resolution and small spot ---- this is a large beamline.

Photos: BL25SU beamline and endstation



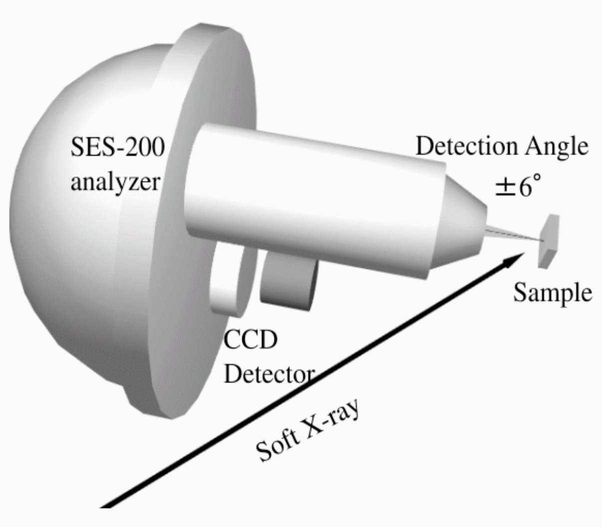
Looking down the beamline from the endstation

Looking at the ARPES endstation.

Beamline enters from left.

BL25SU - endstations

High resolution PES/ARPES



SES-200 electron analyzer

Excitation energy : 300 ~ 1500eV
Total energy resolution : 100meV at 1keV
Angular resolution : ~0.2º
Spot size : 0.1 x 0.1mm
Sample temperature : 20K ~ 300K

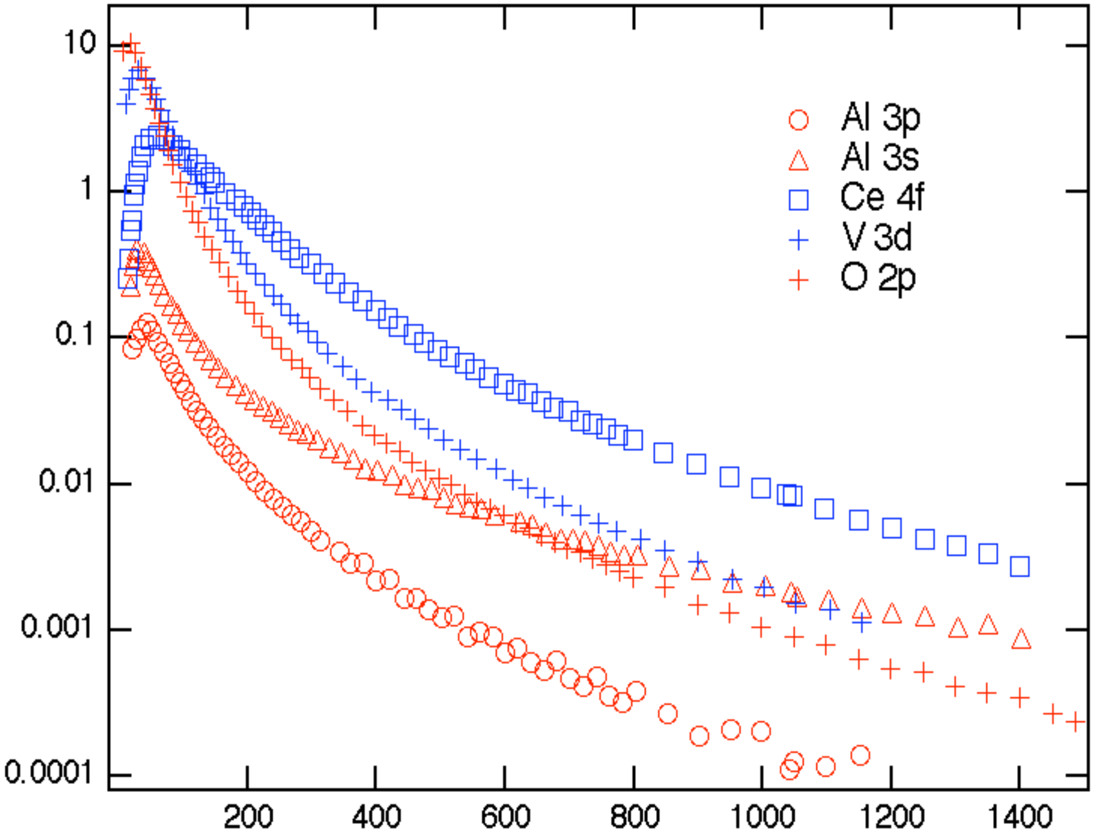
MCD

- XAS with total electron yield mode
- Either helicity of light or direction of magnetic field can be changed for each point in energy scan
- Magnetic Field ~ 1.4T
- Sample temperature : 45K ~ 300K

“2D PES”

- Display-type custom built analyz
- Energy resolution ~ 250meV
- Acceptance angle : ±60°
- Angular resolution : 0.6°

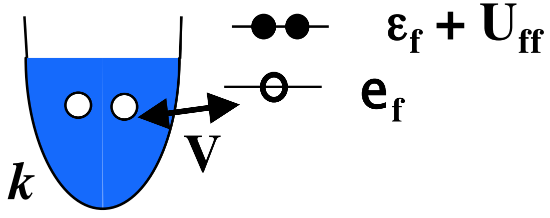
High hν photoemission cross-sections small



Cross-sections very small, especially for sp electrons challenging to get good S/N ratio in data

RESPES contrast very large because off-resonance signal so small

Anderson impurity model and emergent Kondo behavior



occupation n_f
near 1 for Ce^{3+}

N_f fold degenerate local orbital hybridized to conduction band

- Binding energy ε_f
- Hybridization $\Delta(\varepsilon) = \pi D(\varepsilon)$ V
- Local Coulomb Interaction U_f
- Spin orbit splitting Δ

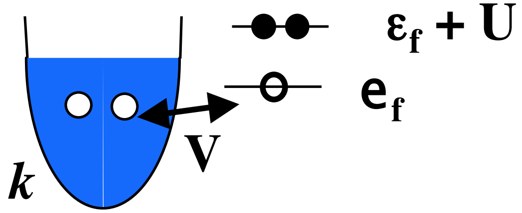
Low Energy Scale T_K:
$(U_{ff} \rightarrow \infty,\ f^0 \leftrightarrow f^1,\ \Delta_{LS}=0,\ )$

$$k_B T_K = E_F \exp(-1/J)$$

$$J = N_f \, \Delta / \pi \varepsilon_f$$

- Ground State Singlet
- Spin entropy quenched
  for $T \ll T_{Kondo}$

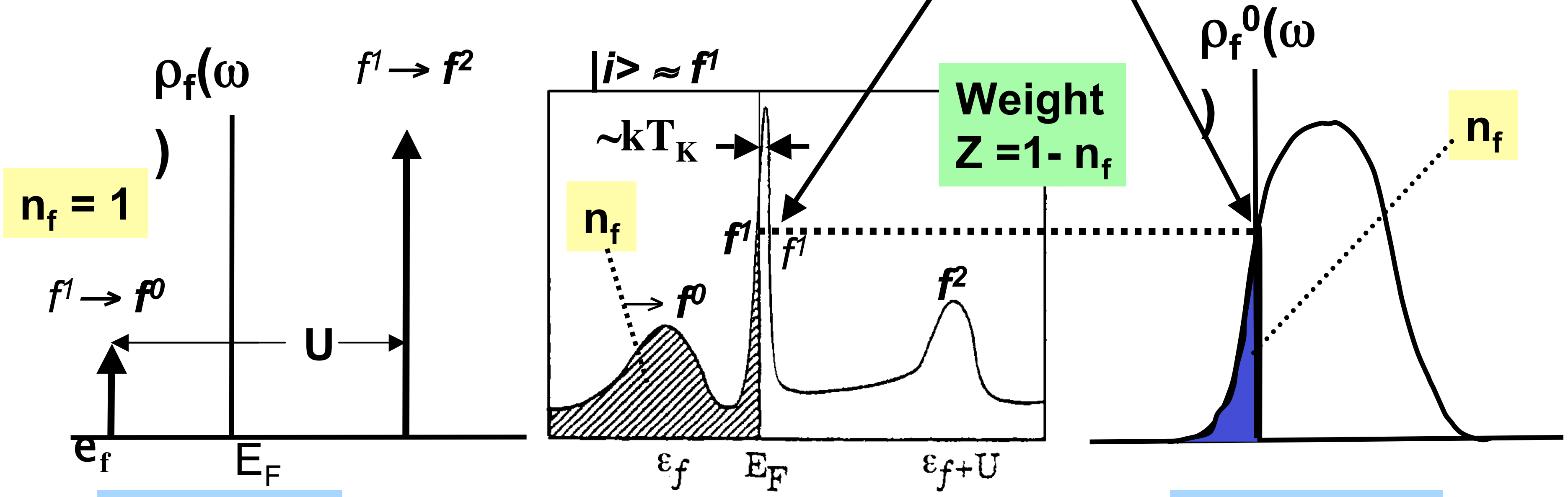
Quasi-particle of Anderson impurity model



Kondo / Suhl-Abrikosov resonance

a Fermi energy peak implied by Friedel Sum Rule (Langreth) for fixed n_f

$$\rho_f(\omega=E_F) = \rho_f^0(\omega=E_F)$$



V=0, U≠ 0
f^1 moment

U, V ≠ 0
no moment

U = 0, V ≠ 0
no moment

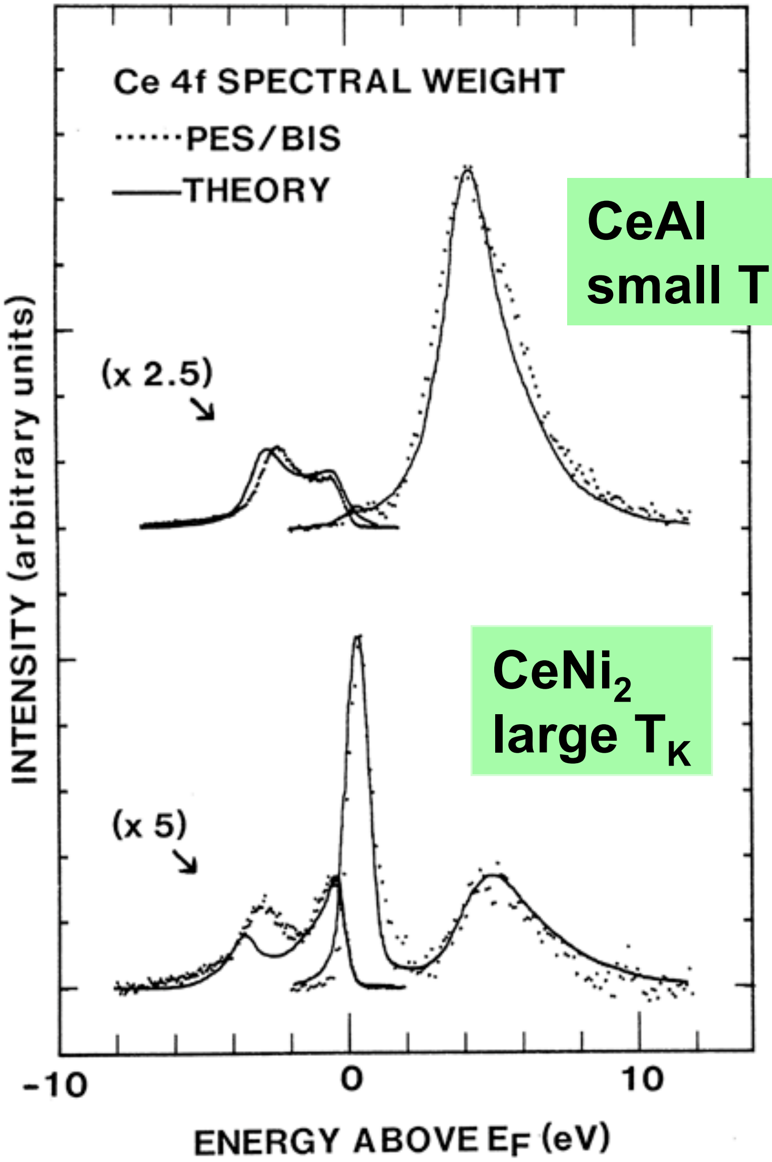
Fermi level peak in angle integrated Ce 4f spectra: early experiment and theory

Spectra from resonant photoemission

and x-ray inverse photoemission (Xerox PARC)

samples: (Maple, UCSD)

Allen et al PRB 1983



CeAl small T_K

$CeNi_2$ large T_K

Fig. from Allen et al Adv. in Physics 1985

Spectral theory: Gunnarsson & Schönhamme PRL 1983

basis for

Kondo Volume Collapse model for Ce α - γ transition
Allen & Martin PRL
Allen & Liu PRB ‘92

“Dense impurity ansatz” for Ce compounds

Use of impurity model for concentrated cerium materials?

The modern view:

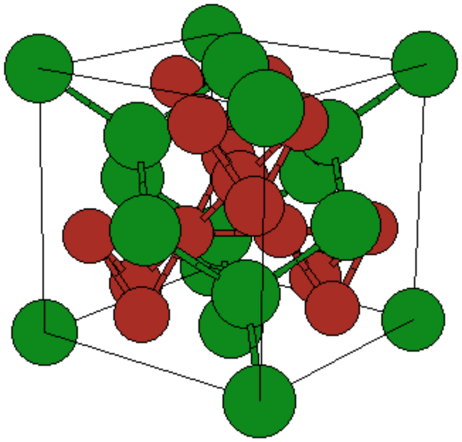
Impurity spectral function an ansatz
for local (k-summed) spectral function

I.e. $\rho_{LOC}(\omega) \equiv \Sigma_k \rho(k,\omega) \approx \rho_{IMP}(\varepsilon)$

Impurity model ⇔ local properties

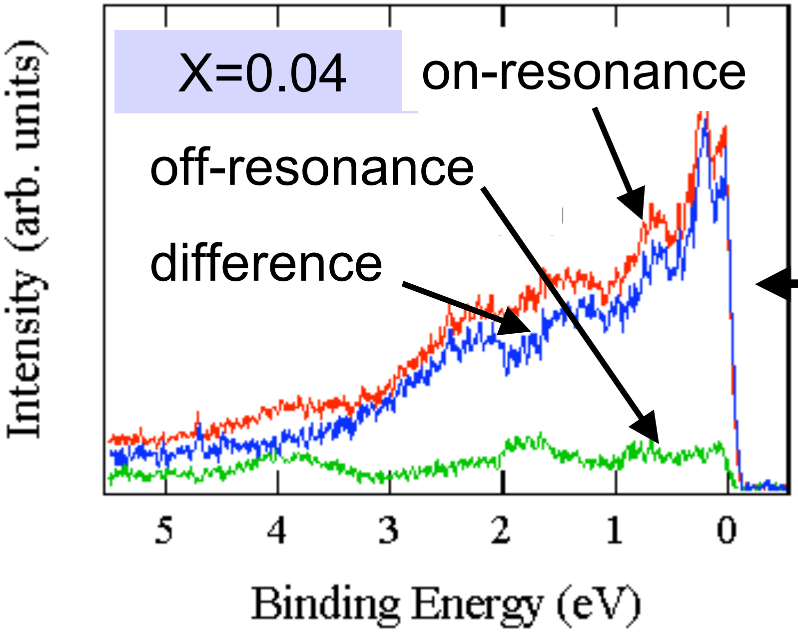
Angle resolved studies of $\rho(k,\omega)$ in progress but very difficult
---- subject of another talk
(e.g. Denlinger et al, JESRP 117, 8 (2001))

RESPES of $La_{1-x}Ce_xAl_2$ at Ce 3d edge: dilution study test dense impurity ansatz for $\rho_{LOC}(\omega)$



- Cubic Laves structure--four Ce nearest neighb
- For $x = 0.04$, probability of isolated Ce impurity $(1-0.04)^4 = 0.85$ ⇒ dominates spectrum

- Probability for an isolated Ce-ion pair = $4\times(0.96)^3\times0.04\times(0.96)^3 = 0.125$ ⇒ almost negligible in spectrum



Beamline 25SU

SPring

Photon energy--- 882 eV

- **Bulk sensitive**
- **Measure very dilute sample with good S/N from Ce 4f cross-section resonance at Ce 3d edge**

Energy resolution 100 meV

Temperature 20K

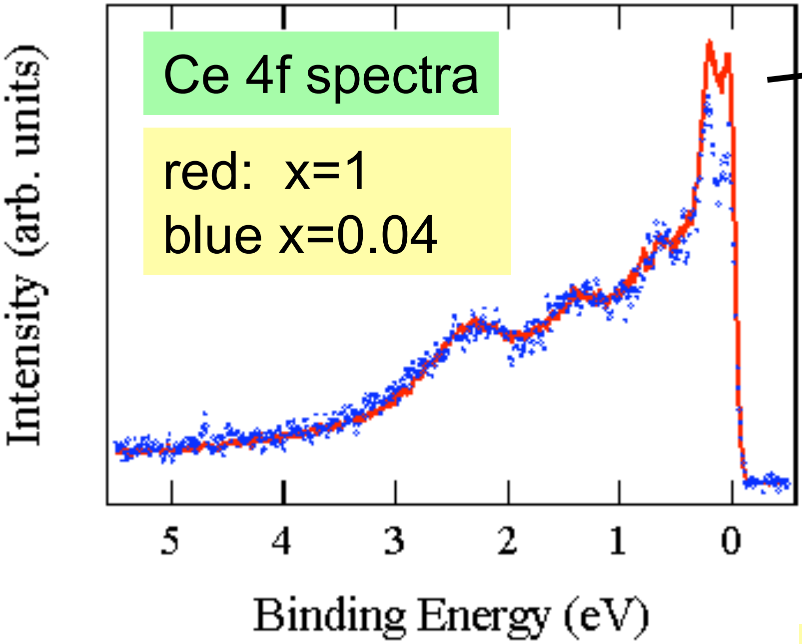
Fractured polycrystal. samples (UCSD

Angle integrated Ce 4f spectrum $\approx$ x-independent in $(La_{1-x}Ce_x)Al_2$

H.-D. Kim et al
Physica B, 2002

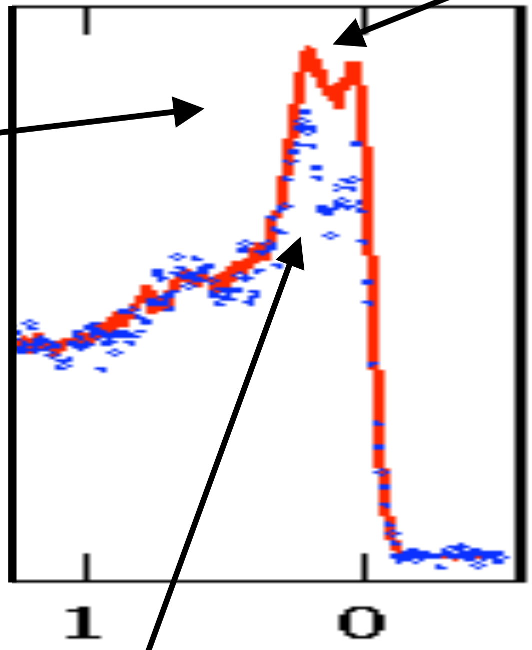
SPring-8

Volume expansion with dilution
$\Rightarrow$ T_K decreases with dilution known:
5K (x=1) → 0.5K (x=0.04)
$\Rightarrow$ small change in spectrum near E_F



Ce 4f spectra

red: x=1
blue x=0.04

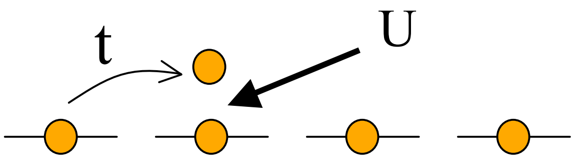


Large T_K materials at BL25SU ----
R.-J. Jung et al, PRL 91, 157601

Spin-orbit sideband (hi res studies of resonance pioneered by Baer et al '85)

Hubbard model and Mott-Hubbard insulators

one band Hubbard model



1 orbital and 1 e$^-$ per site

t – “hopping” gives site charge fluctuations and band width
U – local Coulomb repulsion suppress site fluctuations
→ equal # e$^-$/site

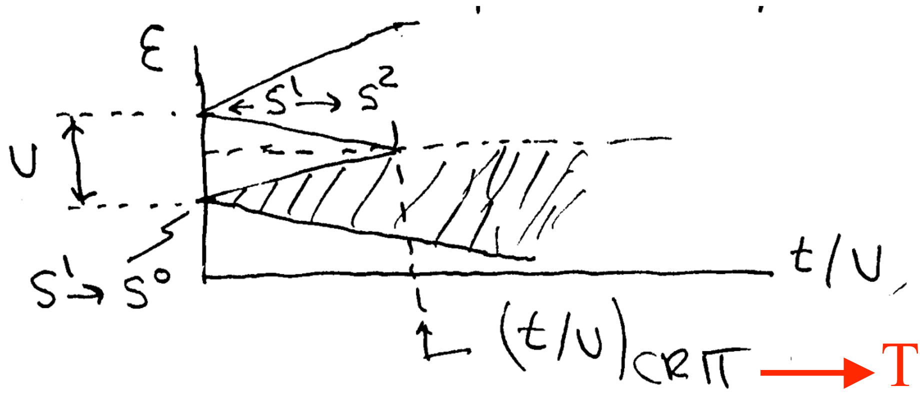
if t/U small
⇒ Mott-Hubbard INSULATOR

residual antiferromagnetic coupling $J_{AF} \sim t^2/U$
but magnetic ordering not essential for insulator

many Mott-Hubbard insulators exist in nature

Mott insulator to metal transition
the early thinking

Mott idea: increase t/U, lose gap
get insulator to metal transition



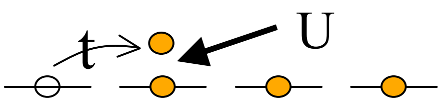
→ Transition

Also from Mott:

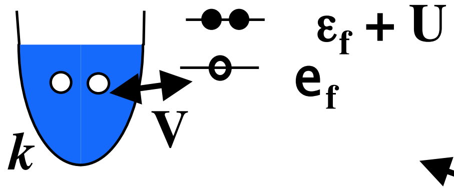
self consistent screening to reduce U in metal state
(beyond Hubbard model, long range Coulomb)

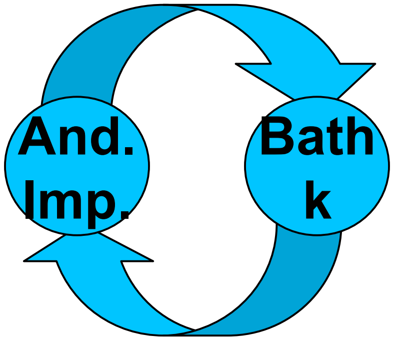
Mixing of Kondo and Mott-Hubbard Physics: Dynamic Mean Field Theory

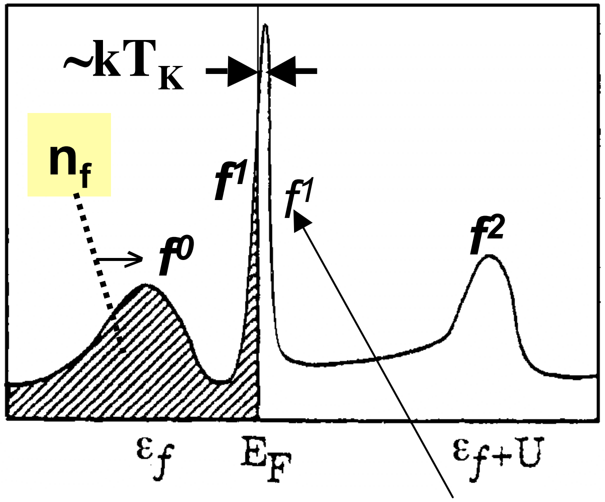
DMFT exact as dimension →∞
lattice ⇔ a self-consistent Anderson impurity
finds $\Sigma(k,\omega) = \Sigma(\omega)$



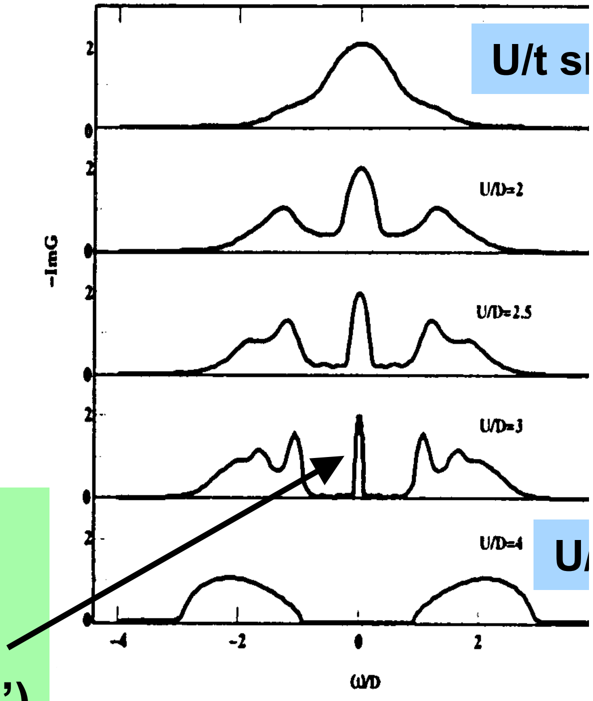
1-band Hubbard for Mott transition







Kondo physics—spin singlet & Suhl-Abrikosov/Kondo resonance

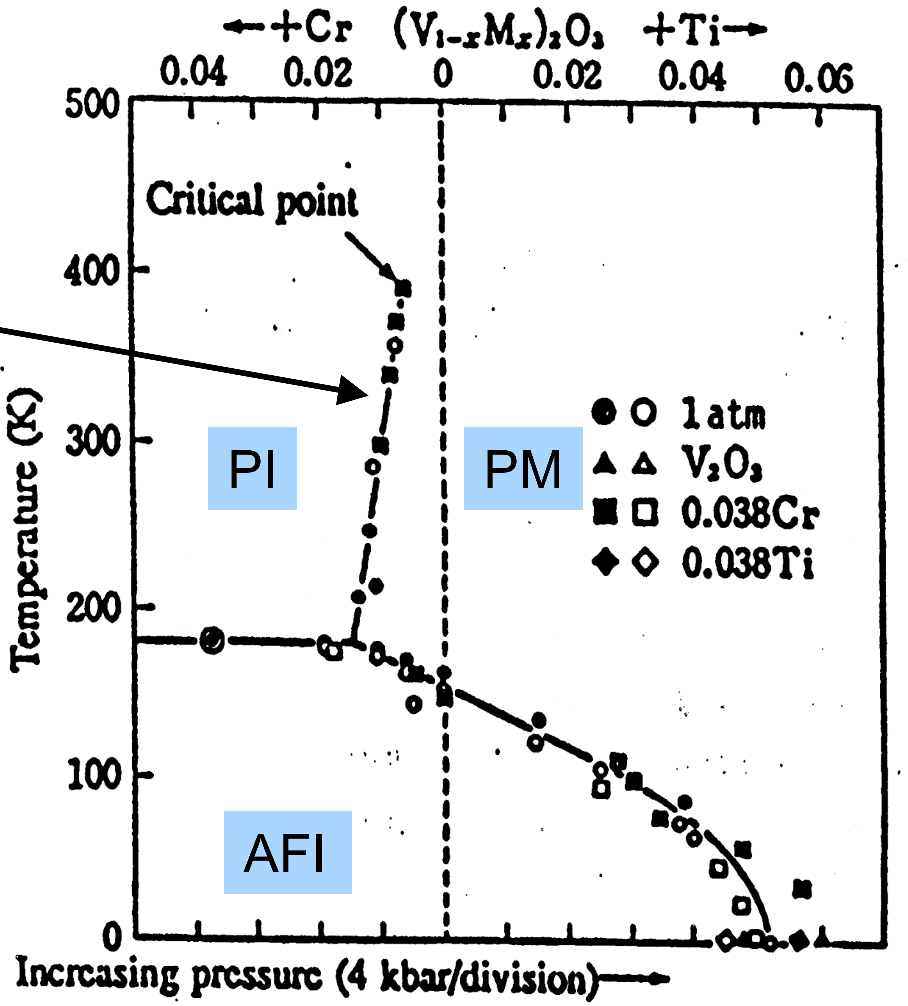


quasi-particle peak growing in gap as U/t decreases (“bootstrap Kondo”)

Paradigm example: $(V_{1-x}M_x)_2O_3$ (M=Cr, Ti)

McWhan, Rice et al.
PRL ’69, PRB ‘73

PI ⇔ PM
interpreted
as Mott transition of
1-band
Hubbard model



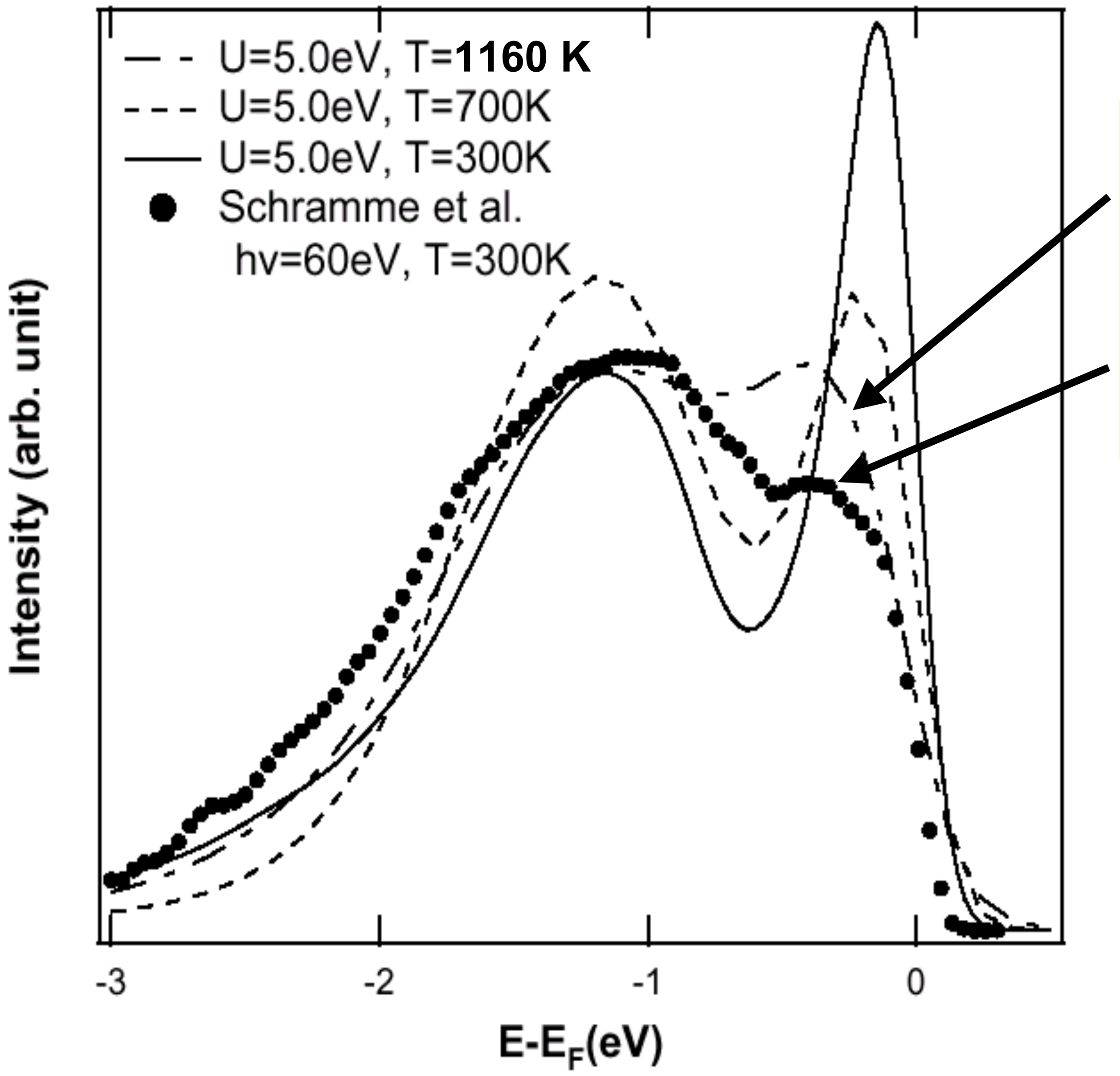
$2e^-$/ V^{3+} ion
3 orbitals/io
4 ions/cell

more
complex
than
1-band
Hubbard

Importance of realism: Ezhov et al, PRL ’99, Park et al, PRB ’00

⇒ Motivation for LDA + DMFT calculations (Held et al, PRL ’01)

T-dependent LDA +DMFT(QMC) theory compared to PM phase low hν photoemission for V_2O_3



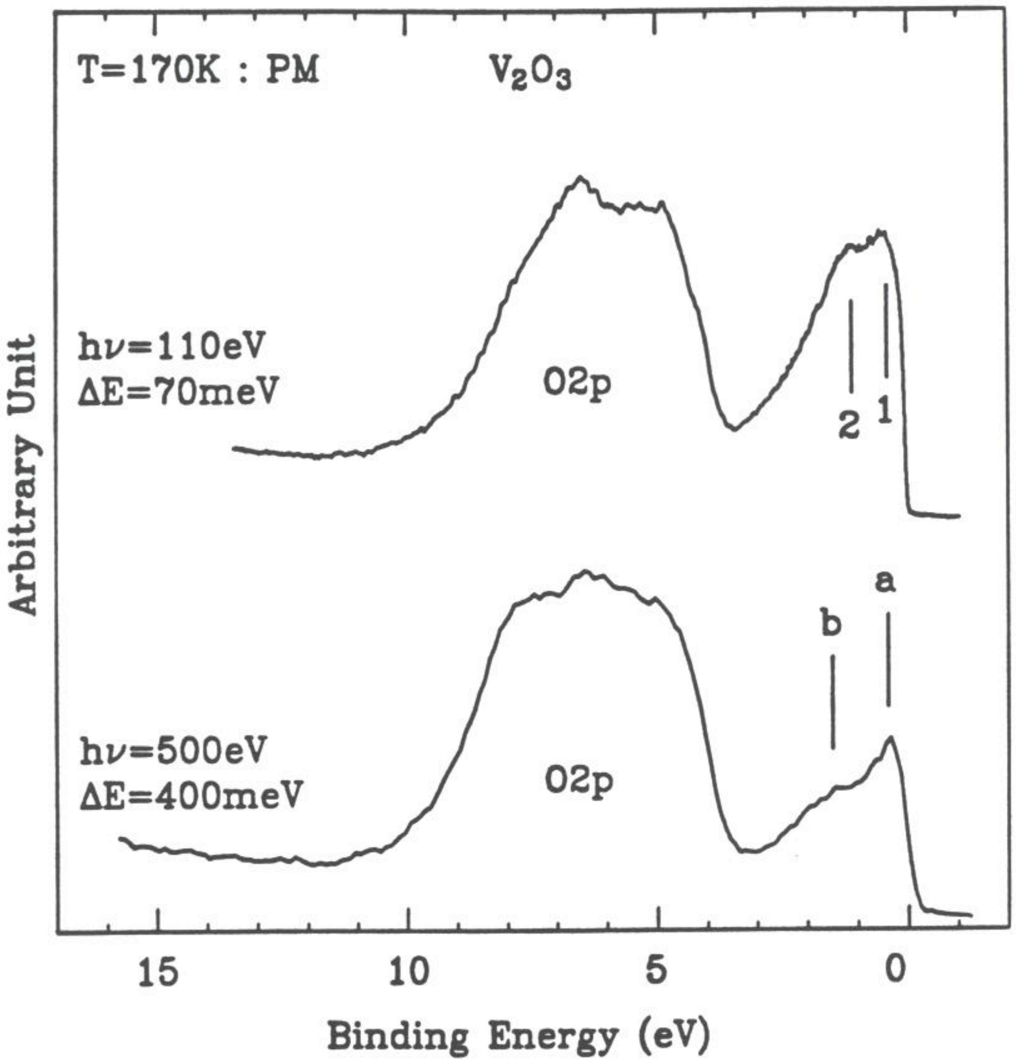
LDA + DMFT (QMC) at 1160K

compared favorably to 300K 60 eV data (Held et al, PRL ‘01)

But theory peak sharpens up with decreasing T

Shows large disagreement with data for same T.

Early evidence of bulk/surface difference for V_2O_3



J.-H. Park thesis
NSLS "dragon" beamlin
(Univ. of Michigan 1994)

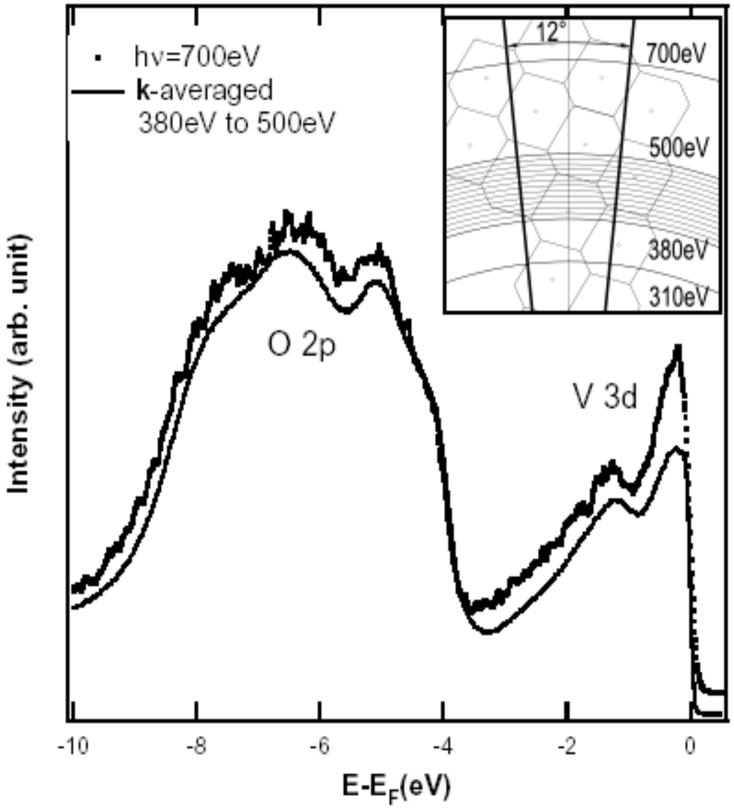
Systematic reduction of near E_F peak in metallic phase for low photon energy relative to high photon energy

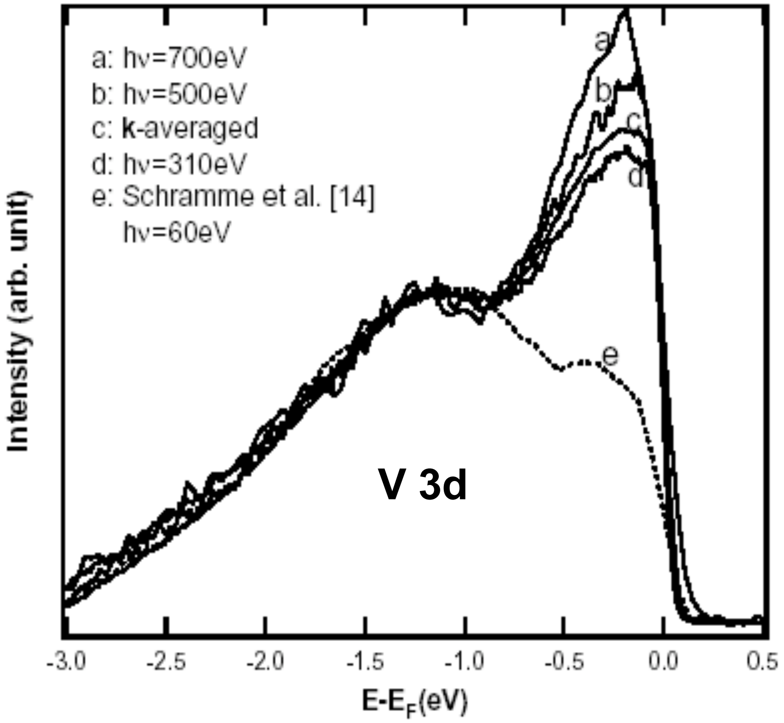
implies surface effect

but resolution not good at high photon energy at that time.

High resolution possible at SPring-8
→ newly observed E_F peak for V_2O_3

New results achieved with high photon energy and small (approx 100 mm diameter) photon spot.





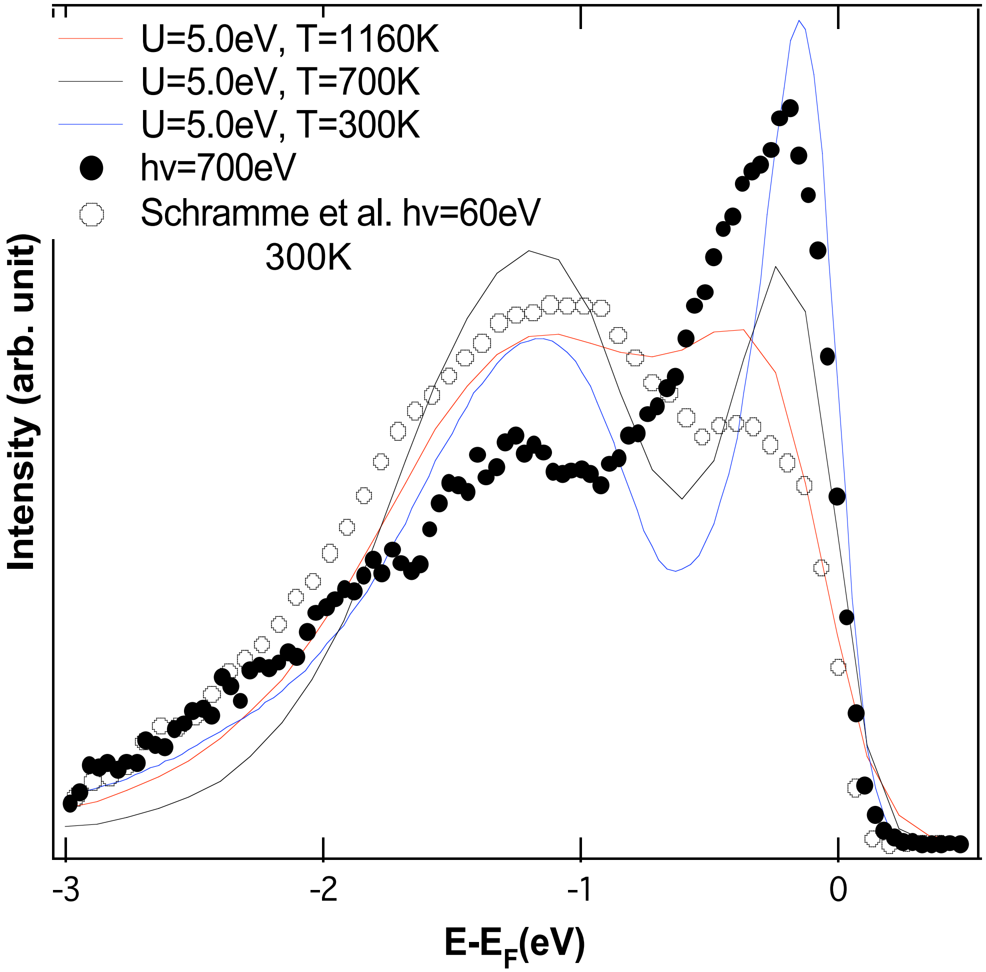
SPring8 collaboration with S. Suga et al.
Early small spot work at ALS with J. D. Denlinger important!

Monotonic increase of peak with increasing hν ⇒
Probe depth increase outweighs k_z dependence

S.-K. Mo et al, PRL 90, 186403 (2003)

Comparison of data to LDA+DMFT PM phase theor

S.-K. Mo et al, PRL 90, 186403 (2003)

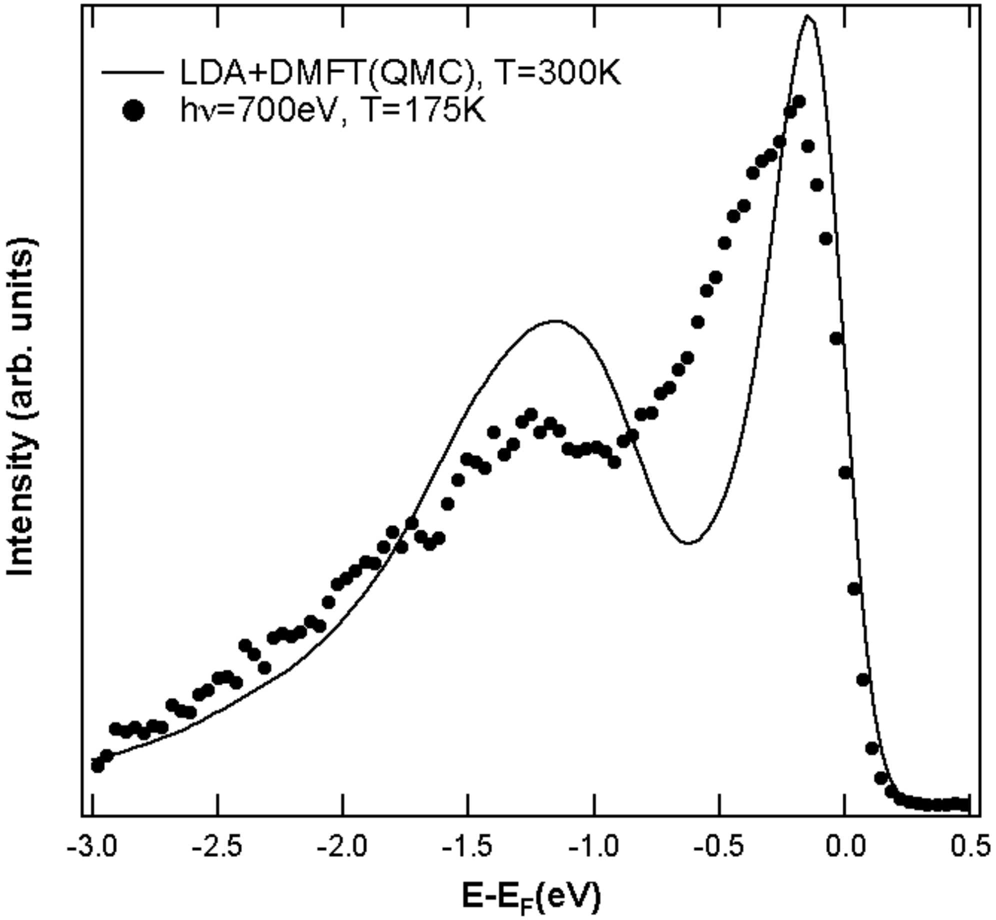


Qualitative agreement on presence of prominent E_F peak in spectrum

Previous "agreement" of 1160 K theory and 300K data at 60 eV now seen as fortuitous due to peak suppression from high T in theory and surface effect in data.

Compare V_2O_3 PM phase spectrum to LDA + DMFT (t-orbitals, U=5.0 eV, 300K)

S.-K. Mo et al, PRL 90, 186403 (2003)

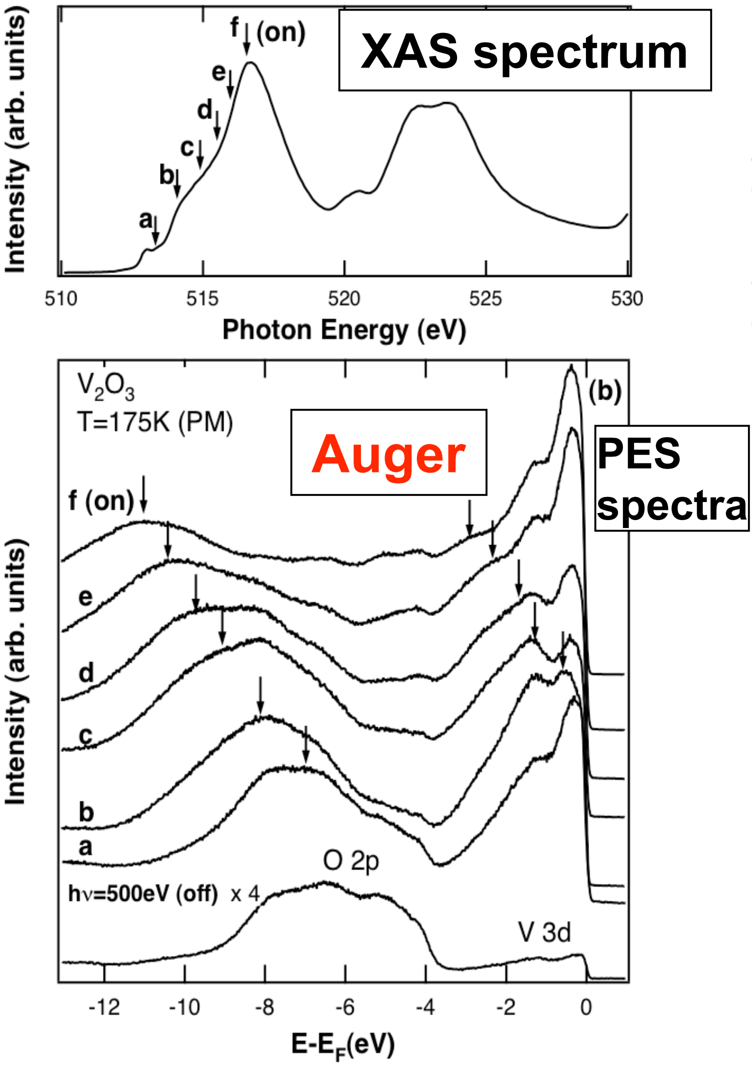


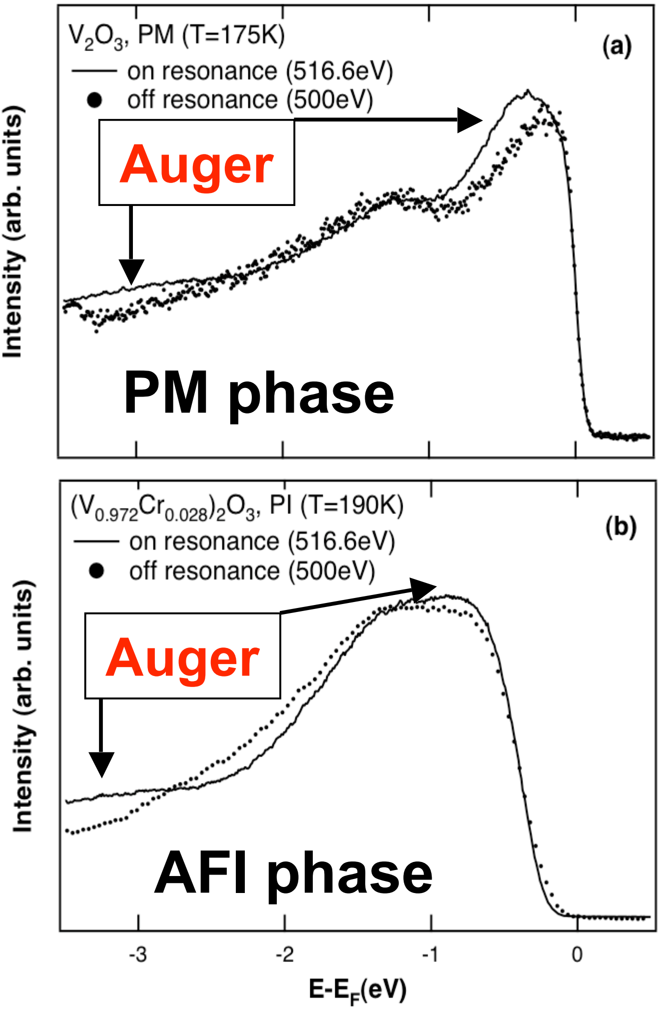
Qualitative agreement on presence of prominent E_F peak in spectrum

But experimental peak width larger than theory width, roughly by factor of 2

And experimental peak weight larger than theory weight

Didn't do RESPES at V 2p→3d edge (near 500 eV) to avoid Auger contribution





peak below E_F
in PM phase
Is an artifact

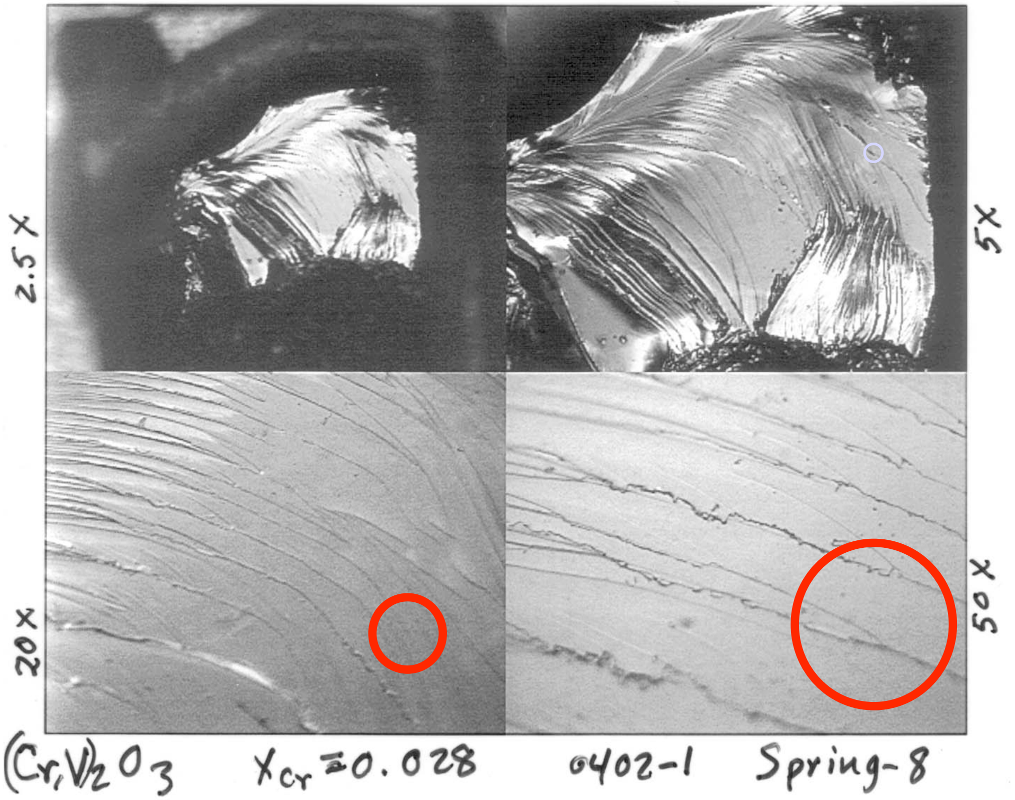
effect in AFI
phase smaller
but still visible

S.-K. Mo
Physica E
in press

Giving up RESPES <u>hard</u> because of small off-resonance cross-section
but helped by small photon spot
well matched to sample area probed by analyzer

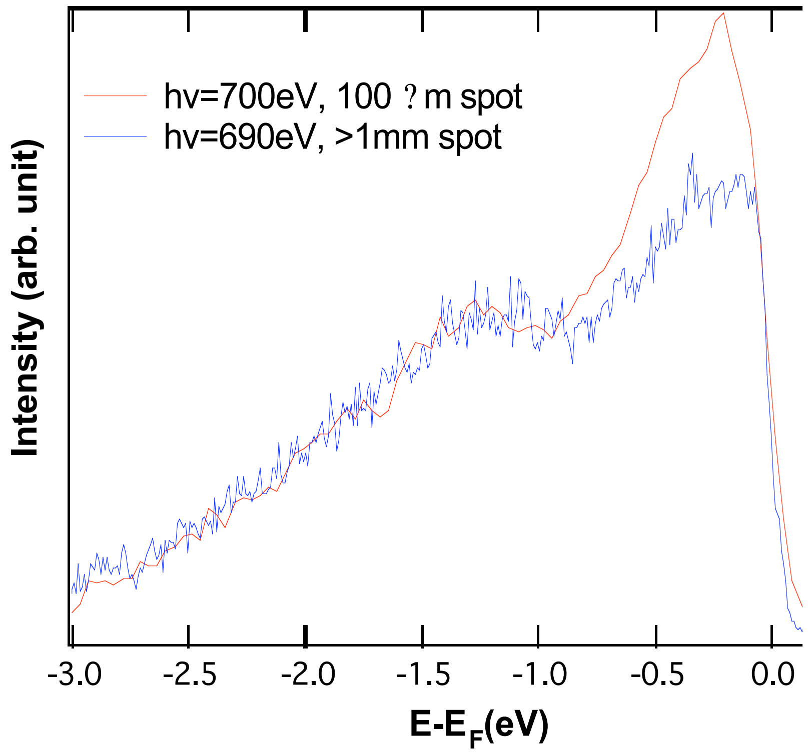
Small spot essential for large E_F peak !

Optical micrograph—J.D. Denlinger



○ = 100 µm spot size

With small spot can select probing point to <u>avoid steps and edges as much as possible</u>



E_F peak much reduced with larger spot

Difference for 300 eV to 500 eV range even larger

Why steps and edges matter

Reduced coordination the basic origin of bulk/surface difference

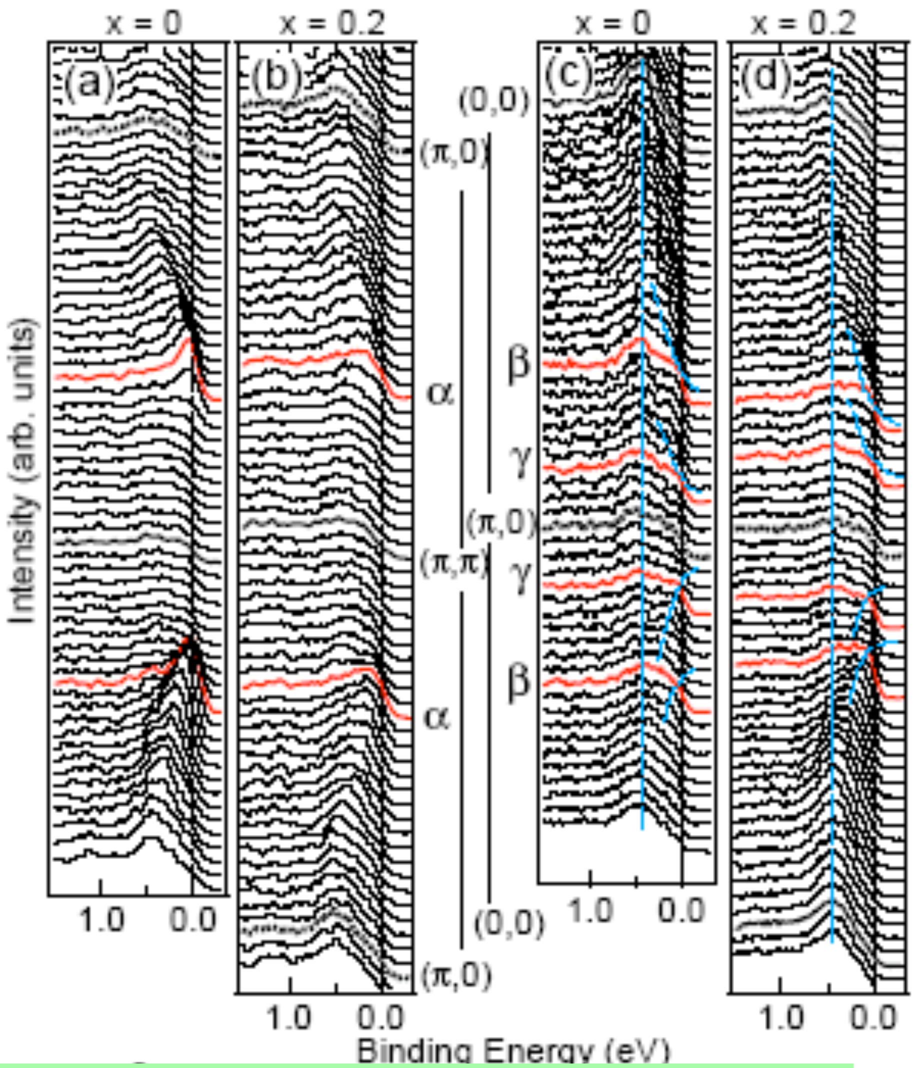
- **Reduces bandwidth on surface**
  ⇒ reduced t/U

- **Surface cohesive energy less than bulk**
  ⇒ surface binding energy |E| of local orbital increased
  B. Johansson, PRB 19, 6615 (1979)
  and so ….
  |E(corner atom)| > |E (edge atom)| > |E(smooth surface)|

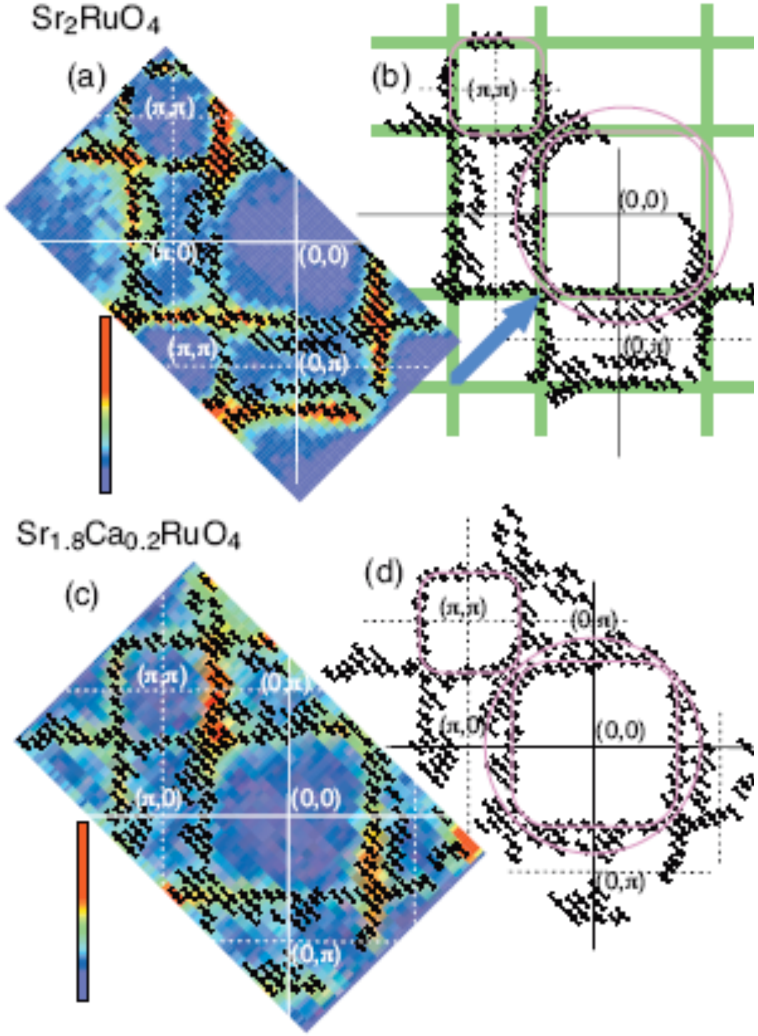
Experimental Verification by M. Domke et al, PRL 56, 1287 (198

Smooth Tm metal surfaces: shifted surface trivalent peaks
Rough Tm metal surfaces: also show trivalent peaks

ARPES is possible! Example: Sr$_{2-x}$Ca$_x$RuO$_4$ (x=0, 0.2)
Sekiyama et al, cond-mat/0402614



EDC's for various directions in Brillouin zone



Fermi surface maps: (b) and (d) are schematic comparisons to theory

Practical information from our experience

Time for the data-taking

Angle integrated spectrum

on resonance : 2 ~ 3 min

off resonance : 30 ~ 40 min

Angle resolved spectrum

on resonance : 30 ~ 40 min

off resonance : > 6 hrs

Data-taking time is increased compared to typical low energy photoemission:

i) lower photon flux (~ 10^{11}) compared to low E beamlines, for example,
Port 071 at SRC (6 x 10^{12} @ 50eV) or
Beamline 5-2 at SSRL (3 x 10^{12} @ 20eV)

ii) photoemission cross-sections are low at the higher photon energies

Conclusion

High photon energy high resolution
photoemision studies on SPring-8 BL25SU
challenging to get good S/N and small spot essentia

Nonetheless has given
new results on important correlated electron problem

- Anderson “dense impurity ansatz” in Ce systems
  good for angle integrated 4f spectra

- Metal-insulator transition in V_2O_3
  DMFT “Kondo peak” in PM phase

No comparable capability now in the United States!