Genuine Kondo resonance in rare earth compounds and metal-insulator transitions in the bulk of various V oxides studied by HAXPES

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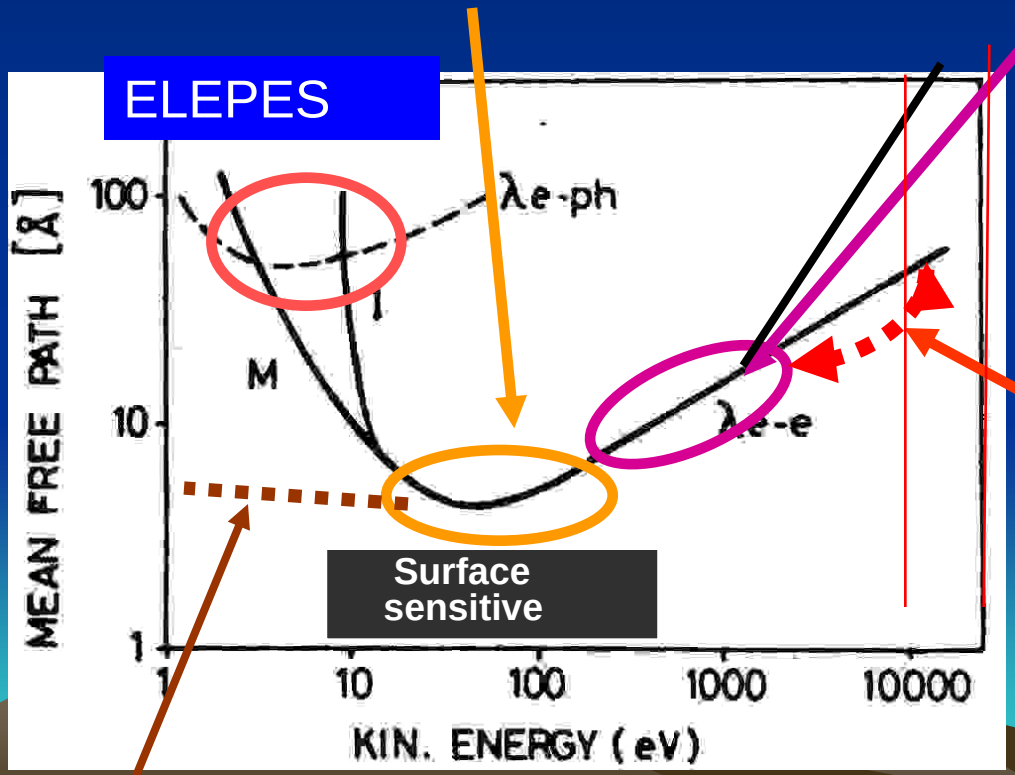
Inelastic mean free path (λ)

λ has a minimum in E_K=20～120eV

λ=3～5Å, which often covers 1 or 2 surface layers ⇒ surface sensitive

Bulk sensitive SXPES & SXARPES are possible above several hundred eV

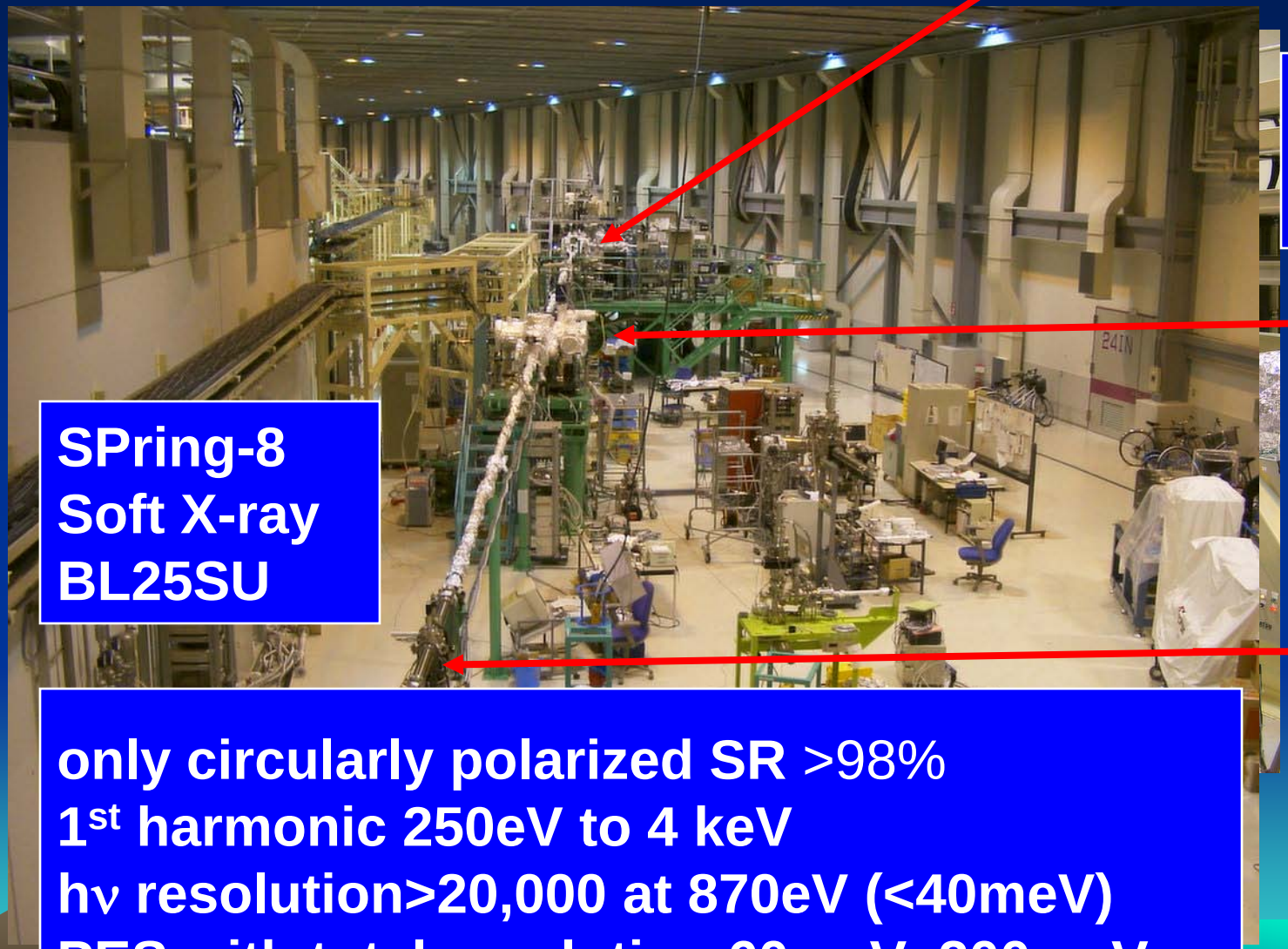


A few keV HAXPES is more bulk sensitive

λ does not necessarily increase in "some materials"

State of the art 3D Fermiology

SX-ARPES



Commissioned in 1999, still the world best

G

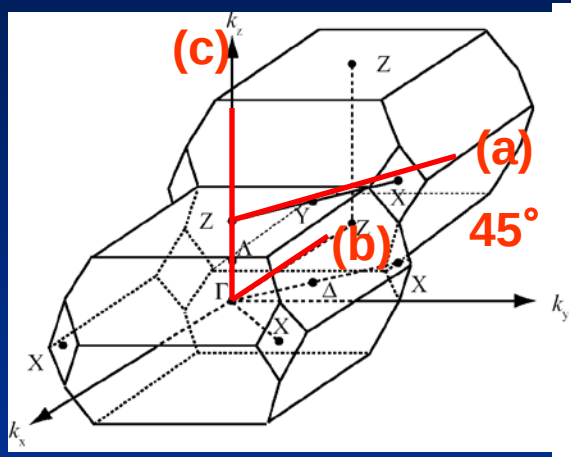
10m

entrance slit

SPring-8
Soft X-ray
BL25SU

only circularly polarized SR >98%
1st harmonic 250eV to 4 keV
hν resolution>20,000 at 870eV (<40meV)
PES with total resolution 60meV~200meV

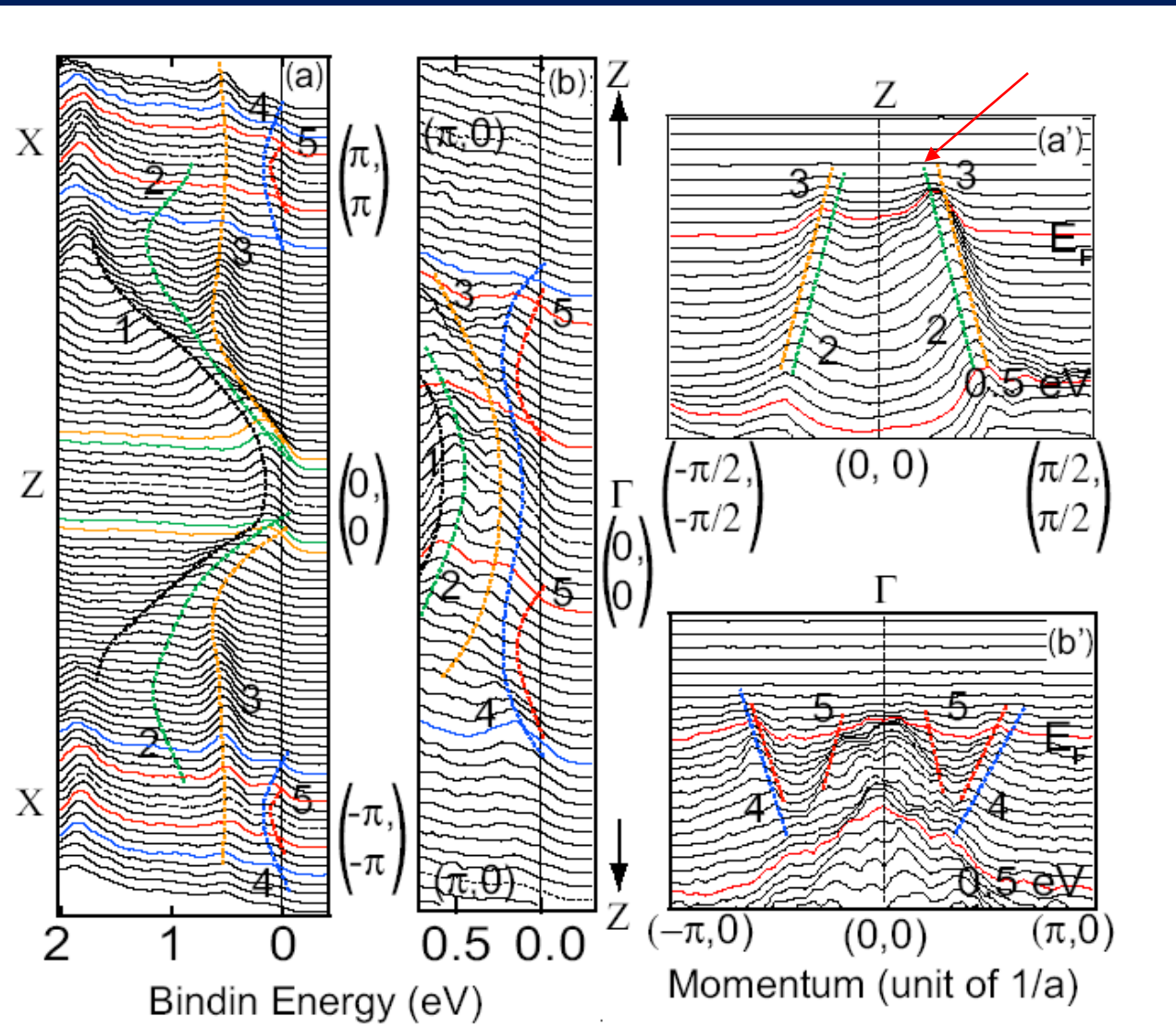
SX-ARPES of $CeRu_2Ge_2$ in the paramagnetic phase measured at ~20K (k_z are defined by hν)

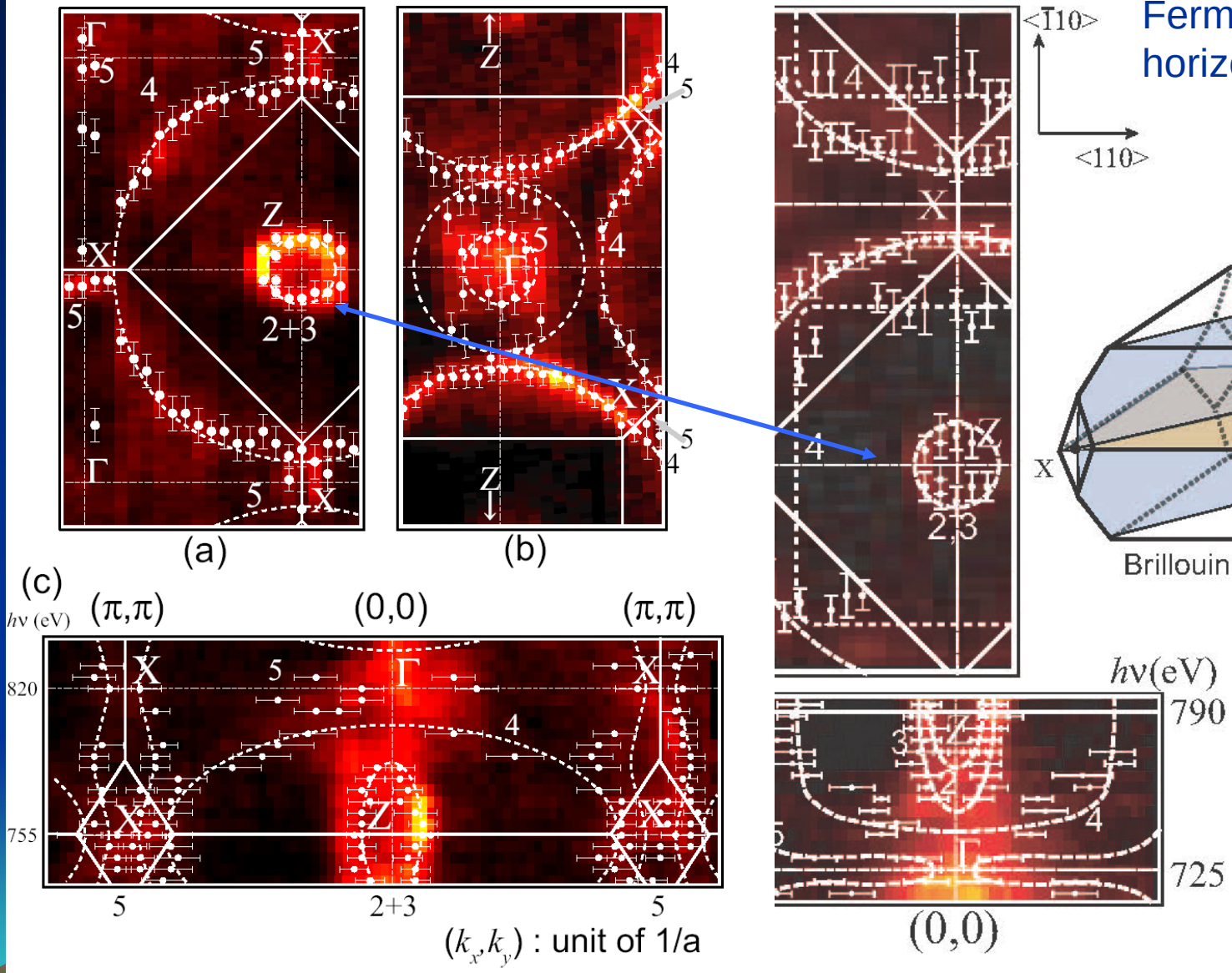


(a) 755 eV

(b) 820 eV

(c) 735~840 eV with 5 eV step





Fermi surfaces in two horizontal planes

FS in the vertical plane

$CeRu_2Ge_2$

$CeRu_2Si_2$

Genuine 3D bulk Fermi surfaces can be obtained

PRL 88, 036405 (2007)

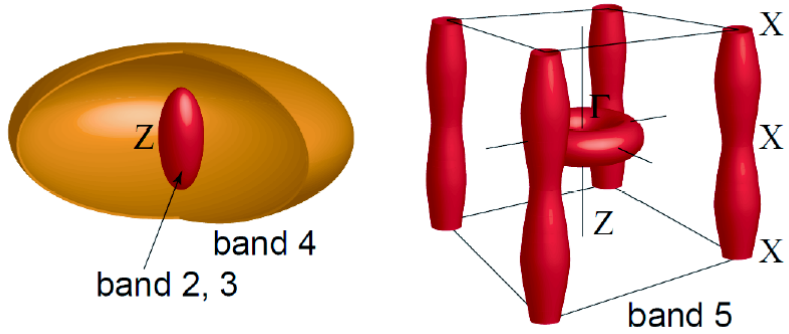
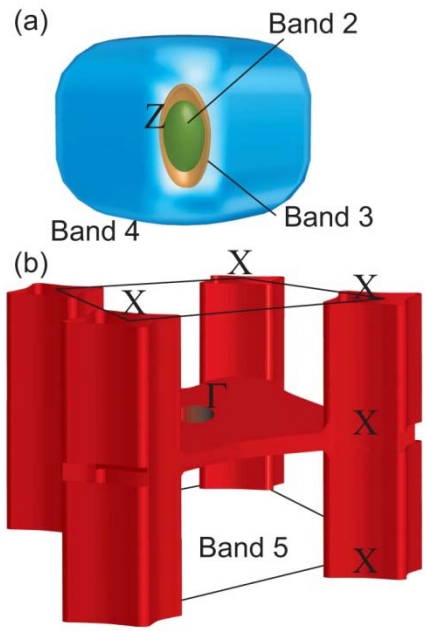


FIG. 4: (color online) The FS shape of each band imaged from Fig. 3. (left) Hole-like FSs centered at the Z point derived from the band 2, 3 and 4. (right) Electron-like FS centered at the Γ point from the band 5.

$CeRu_2Ge_2$

PRB 77,035188 (2008)



$CeRu_2Si_2$

Surface electronic structure is different from the bulk in high Tc cuprates

electron doped high T_c cuprate superconductor (HTCS): $Nd_{1.85}Ce_{0.15}CuO_4$ (NCCO)

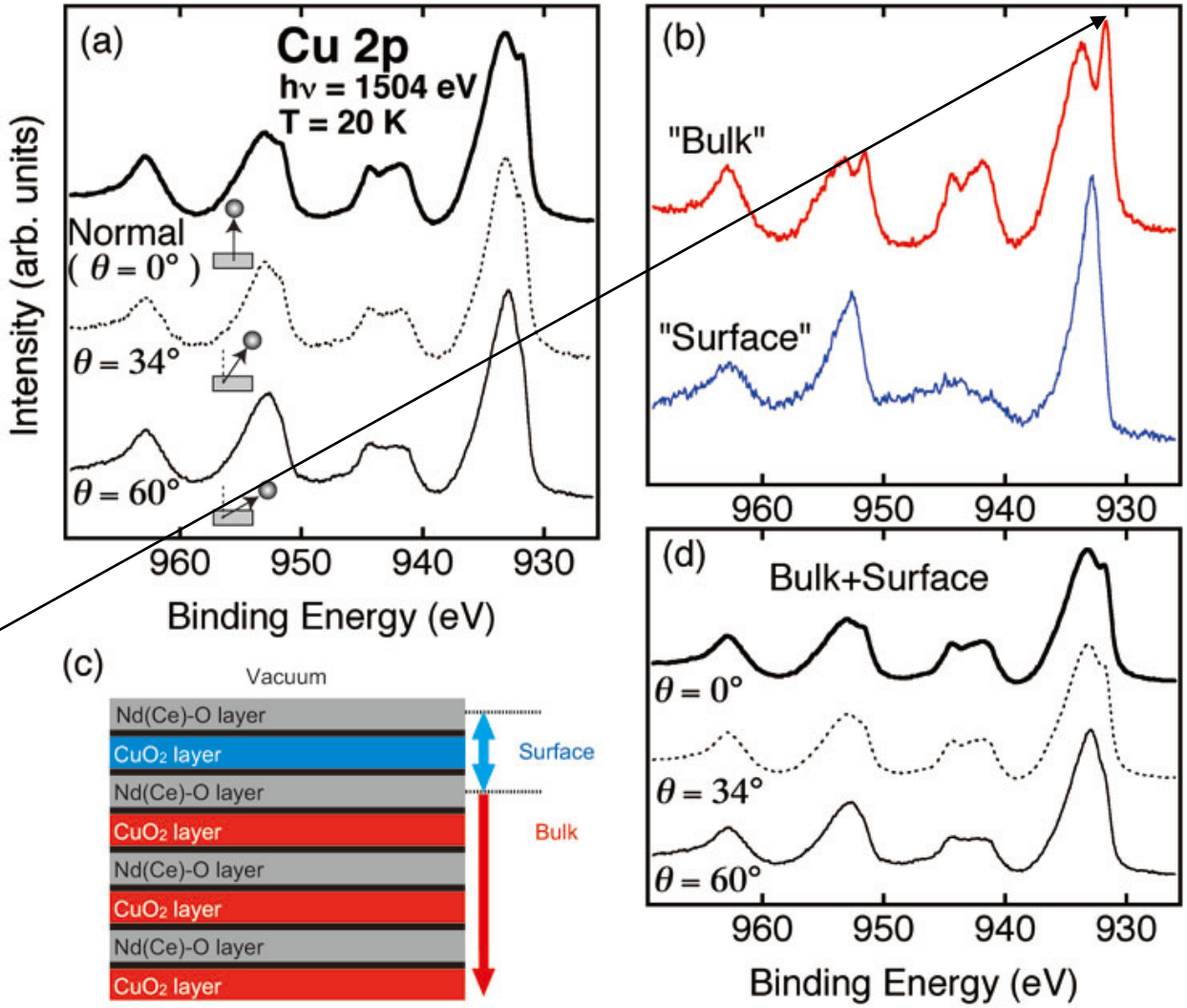
Cu 2p core
E_K~570 eV

Bulk: exp(-s/λcosθ)

s=6.0A

Surface sensitive for larger θ

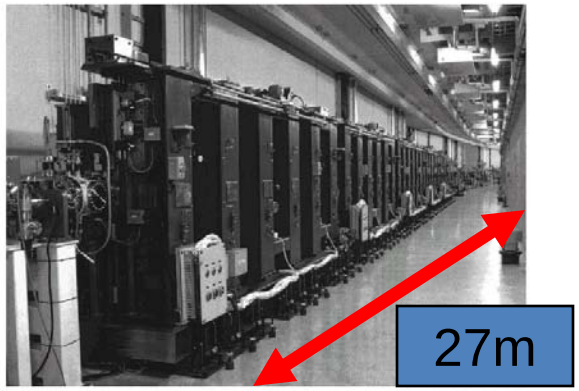
Sharp threshold peak is long-range metallic screening

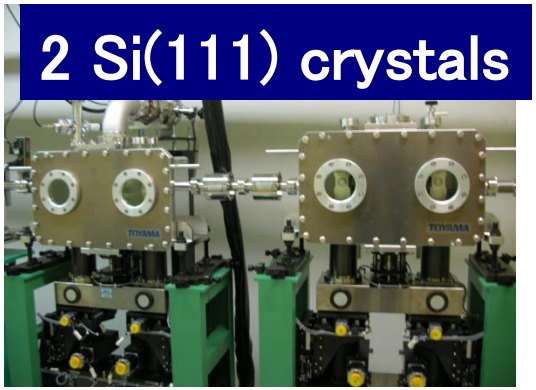


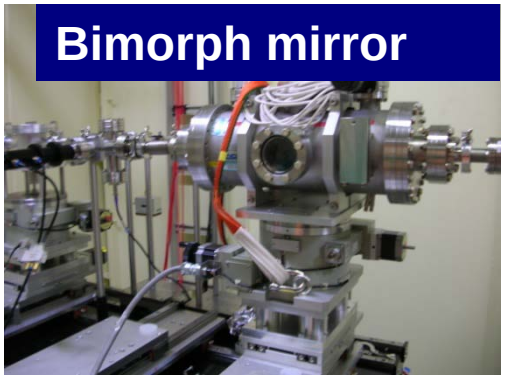
M,Tsunekawa, SS, New J. Phys. **10**, 073005 (2008)

HAX-PES BL19LXU of SPring-8 Rev.Sci.Instr.73, 1125 (2002)

Type	27-m In-vacuum undulator
Undulator period	32 mm
Number of periods	781
Tunable energy range	Fundamental: 7.2 ~18 keV 3rd harmonics: 22 ~ 54 keV
Brilliance	8 × 10^{20} photons/s/mrad^2/mm^2/0.1% b.w./100mA
Maximum flux at sample	2 × 10^{14} photons/s (with Si 111 monochromatic beam)





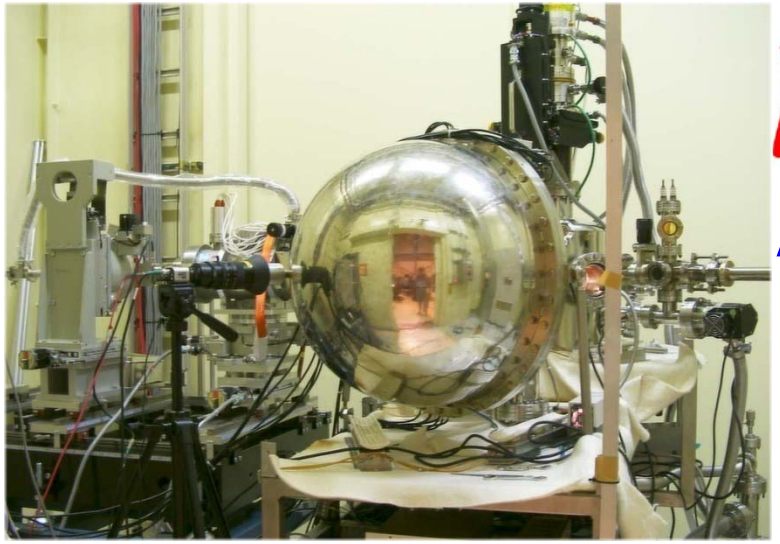


High resolution is realized by Si (444), (551), (555) channel cut crystals

Samples are cleaved or fractured at any temperature from 350~17 K in UHV < few times 10^{-8} Pa

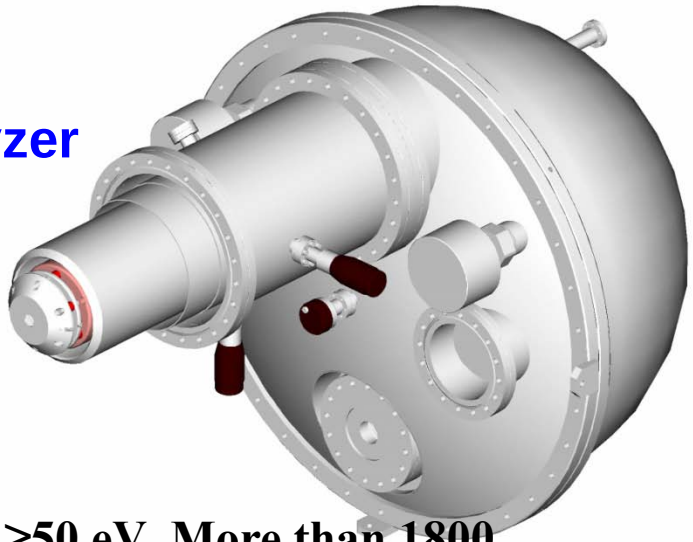
Closed cycle He cryostat

Surface degradation is negligible over days



MBS

A1-HE Analyzer



FWHM Resolving power Epass/ΔE at Epass ≥50 eV More than 1800
and 0.2mm straight slit Typ. 2000

Mode of lens

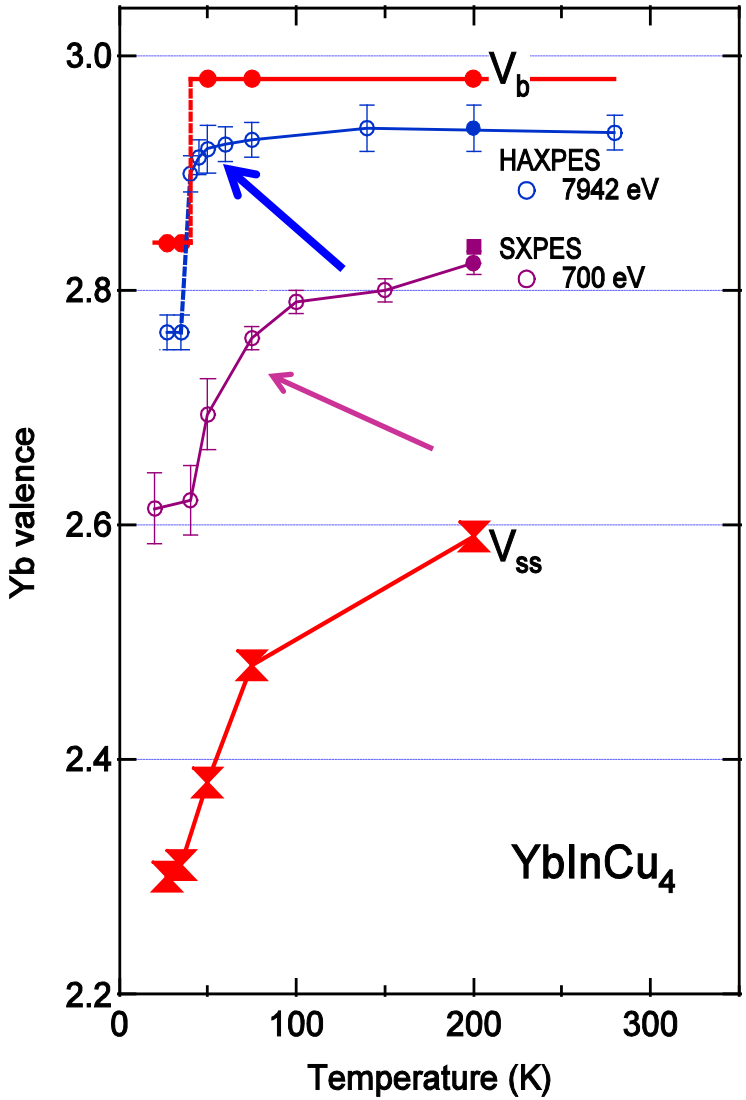
HE12: 20, 50, 100, 200, 500V (requires good light focussing)

Sample –Ana. distance is 55 mm, bakable ⇒ UHV

V_{retard}:14kV compatible, long term stability ±8mV at 8kV

1st order bulk valence transition is known in $YbInCu_4$ at ~42K

However, PES for E_K < few hundred eV cannot detect such a steep V_b change ⇐*This is because it probes the surface and the subsurface region (SXPES is not enough)*



6keV HAXPES was first done by Sato et al. PRL93, 246404 (2004). But still the valence change was not sharp enough.

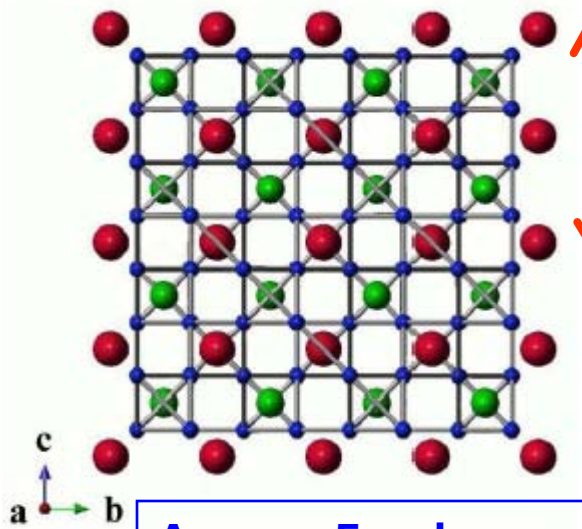
Our 8keV HAXPES gave larger Vb but the valance change is still not sharp enough⇔

Subsurface contribution is not negligible even at hν=8keV

Quantitative analysis is required

PES probes signals from the surface, subsurface and bulk
Their relative weights depend upon the inelastic mean free path λ

S.Tanuma et al., Surf. Interface Anal. 21, 165 (1993)



Lattice constant is 7 A

	valence	thickness	
Surface	(Vs)	s	1.5A
Subsurface	(Vss)	ss	6.5A
Bulk	(Vb)		

Among 5 unknown parameters V_s=2.0 assumed

Other 4 quantities are uniquely determined from more than 4 experiments

Relative spectral weight:

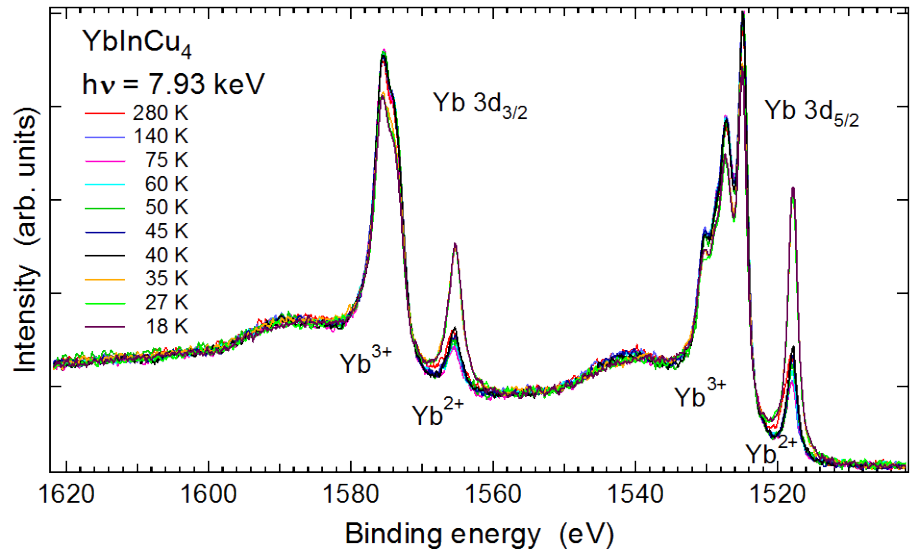
Bulk: $W_b = \exp(-(s+ss)/\lambda)$

Surface: $W_s = 1- \exp(-s/\lambda)$

Subsurface: $W_{ss} = \exp(-s/\lambda)- \exp(-(s+ss)/\lambda)$

Vss: temp.dependent
Vb=2.98(high)／2.84(low)

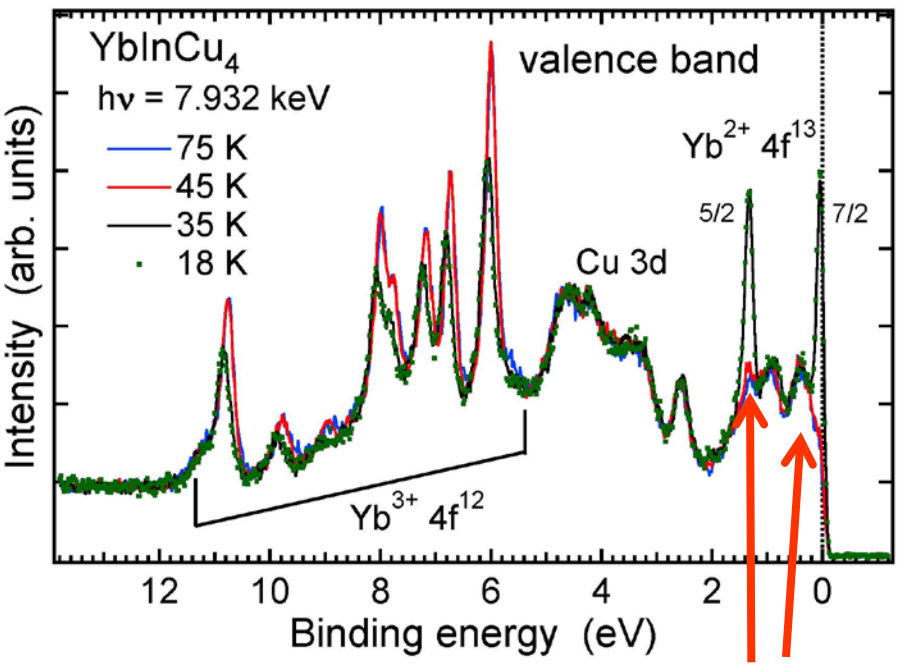
Clear 1st order Vb change confirmed



18
27
35K

above 40K

S.Suga et al.
J. Phys. Soc. Jpn. (2009)

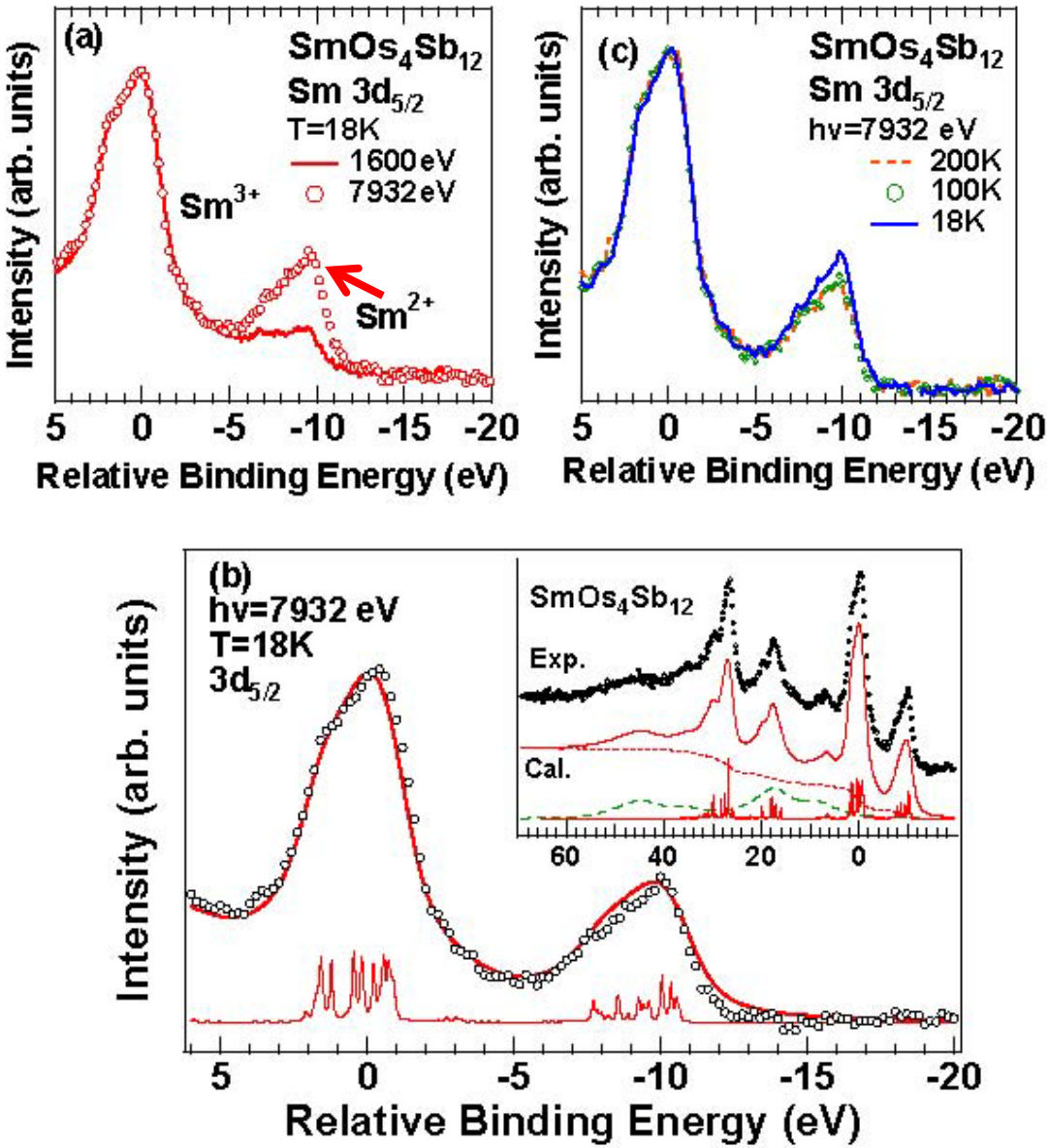


T<Tt: ε_f= –0.71eV, Δ=117meV, U_{ff}=8.1eV, T_K=400K

T>Tt: ε_f= –0.73eV, Δ=67meV, U_{ff}=8.25eV, T_K~0K

Subsurface is an intrinsic interface between the surface and bulk in many Yb compounds

Kondo resonance and its s-o partner in the subsurface are observed for T>T_K⇐ these are not the bulk Kondo resonance



$SmOs_4Sb_{12}$
γ~850mJ/mol·K^2
Tc~2 to 3 K (Ferromag.)

Sm^{2+} is rich in the bulk and the valence mixing is really taking place in the bulk.

In addition, the Sm^{2+} 3d component is found to increase at lower T below the predicted Kondo temperature (~20 K), strongly suggesting that the valence mixing and heavy Fermion behavior coexist in this material

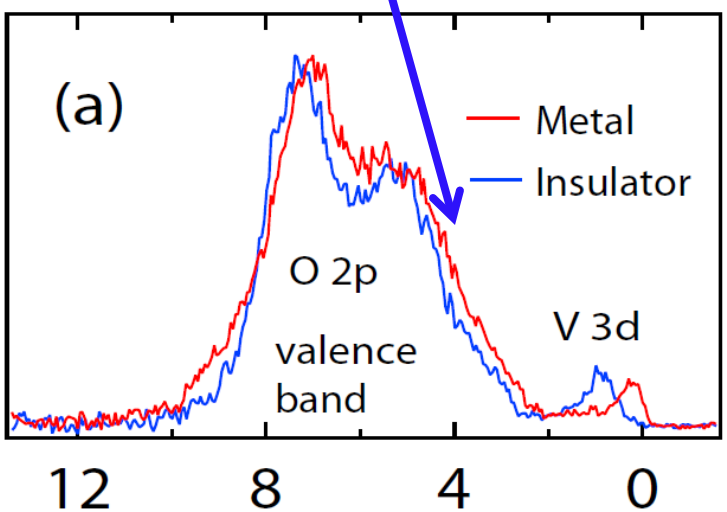
Yamasaki , A.S., SS et al., PRL 98, 156402 (2007)

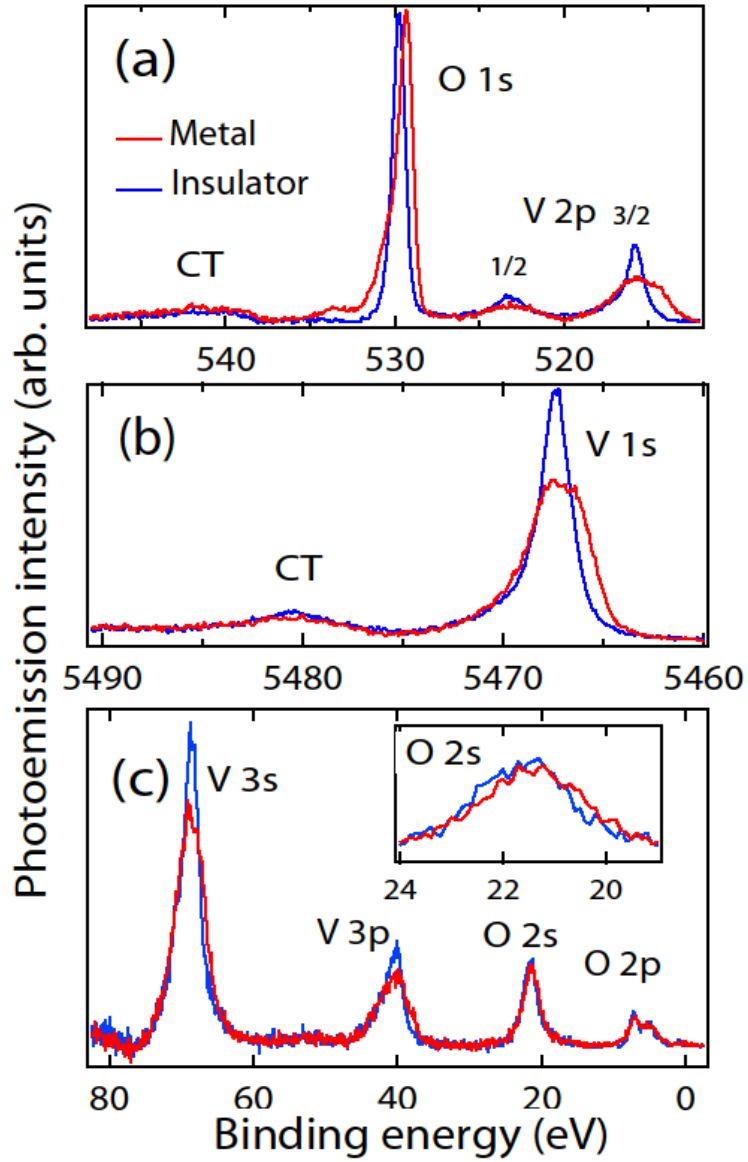
Metal-insulator transition in VO_2

8keV HAXPES on fractured surface of bulk with Tv=340K
All O 1s, V 2p, V1s, V 3s, V 3p, O 2s showed changes on MIT

MIT changes of O 2p band is much more prominent than

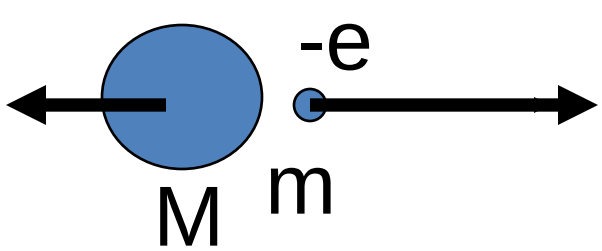
HAXPES on a thin film (10nm) with Tv~292K Eguchi et al. PR B**78**,075115 (2008)





We measured HAXPES of many RE & TM compounds at 8keV: Is recoil effect essential in HAXPES?

$E_R \sim E_K \times m/M$

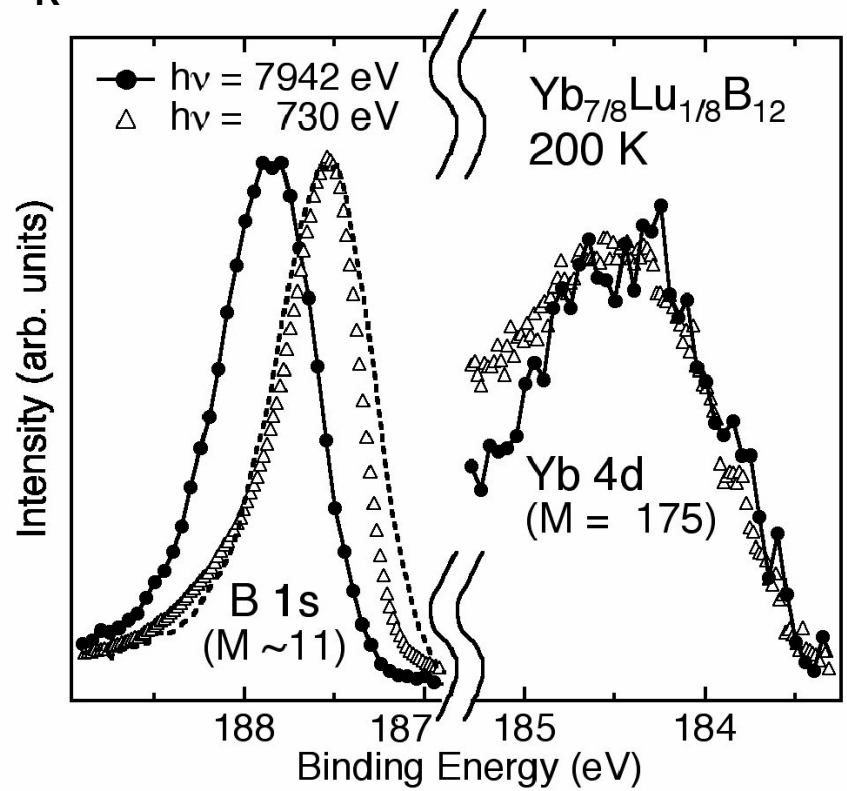


Single nucleus (ion) recoil on photoelectron emission

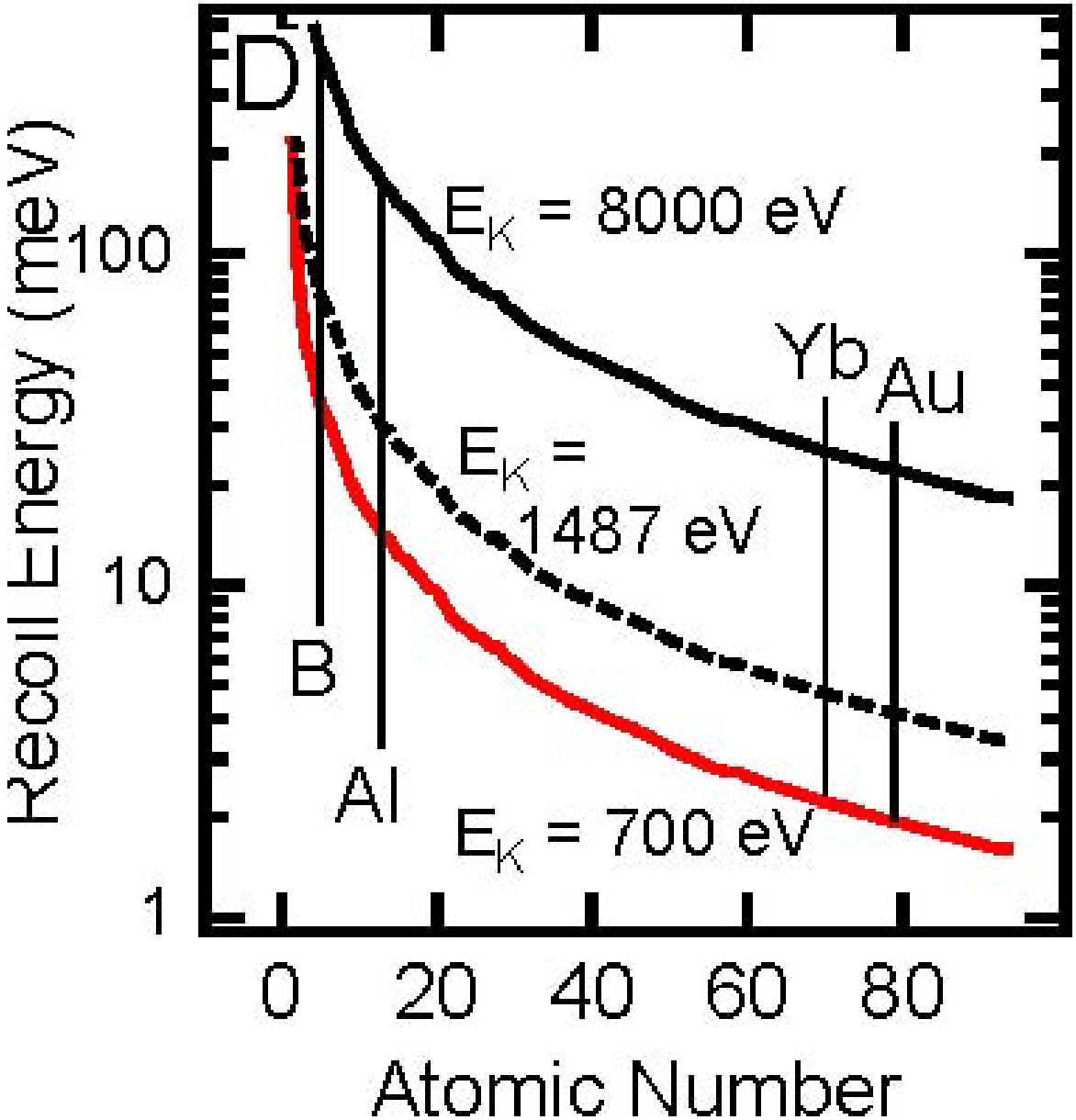
E_R is then transferred to phonons in solids

E_R is transferred to center-of-mass recoil, vibration & rotation in molecules

Yes, for some light element.
E_R~300meV for B 1s at ~8keV



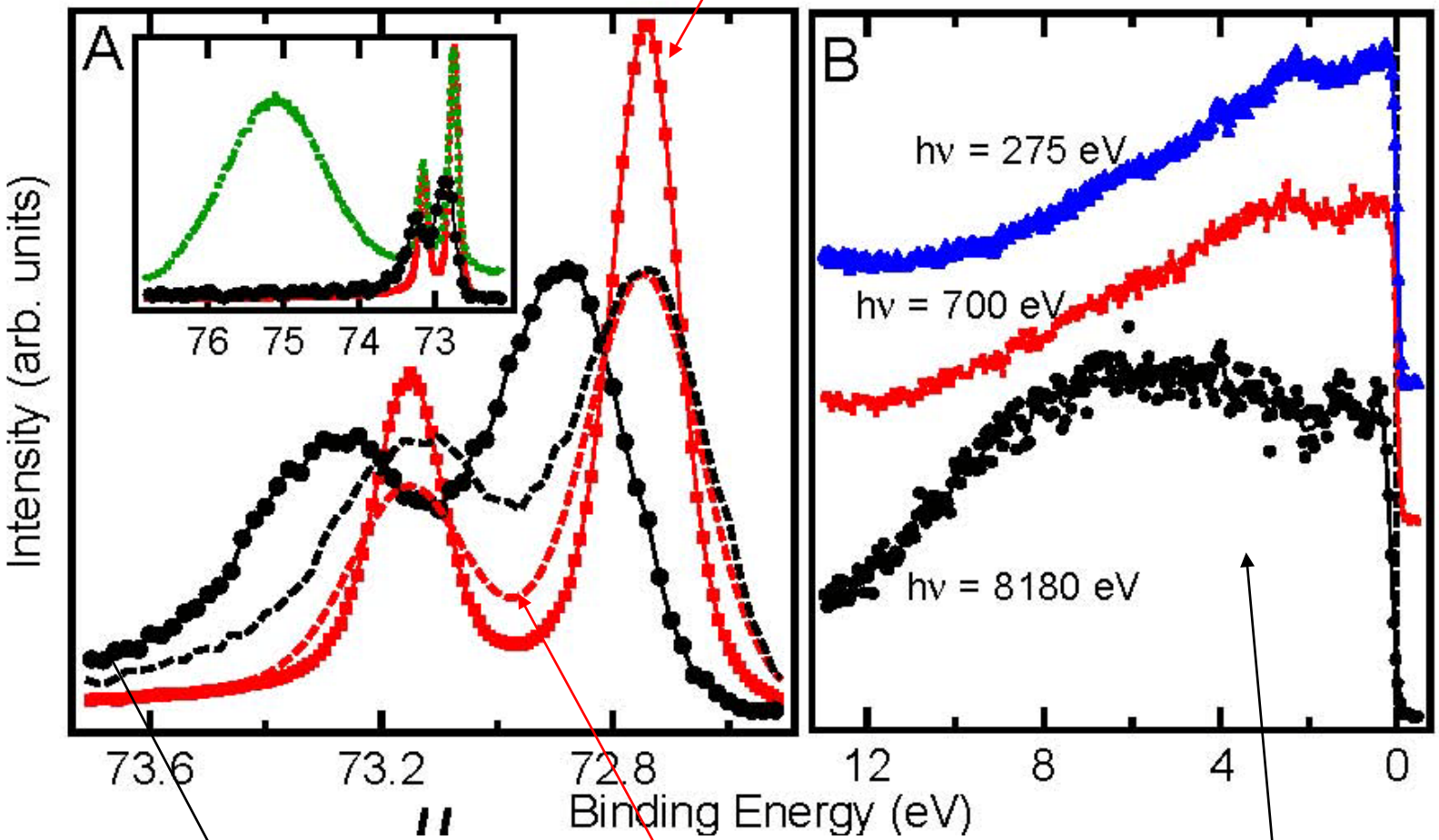
S.Suga, Appl. Phys. A**92**, 479 (2008)
S.Suga and A .Sekiyama, Euro. Phys. J. **169**, 227 (2009)



Single nucleus recoil effects

If once recoil takes place, the HAXPES resolution will be limited by this effect & HAX-ARPES becomes disturbed

Al 2p core-level



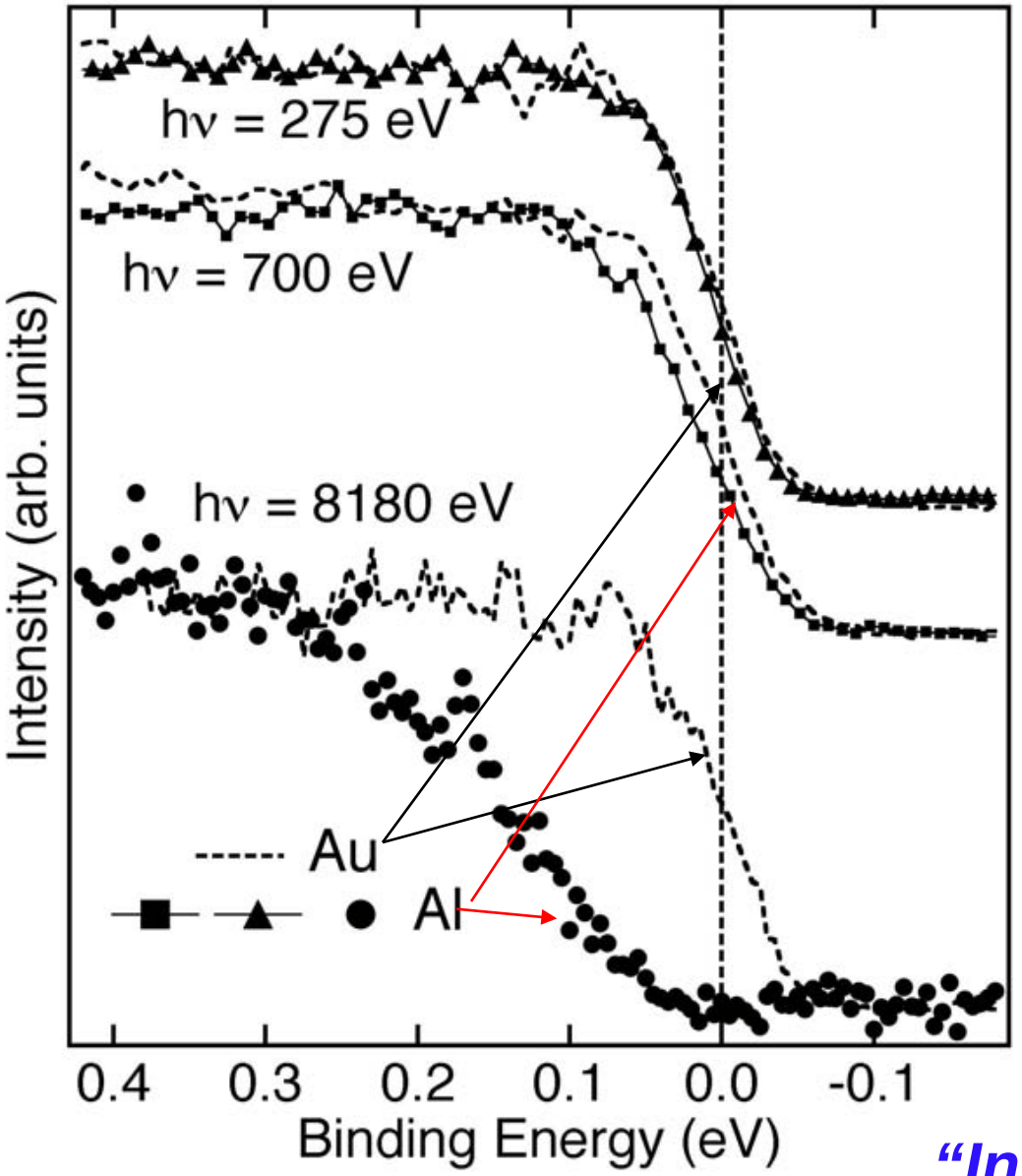
hν=700 eV(ΔE_K~90meV)

hν=8180 eV(200 meV)

hν=700 eV(ΔE_K~200meV)

Valence band

Recoil shift ~140 meV



VB wave function is extended over the whole crystal

The mass to accept the photoelectron momentum is extremely large

So no recoil effects were expected for VB in solids

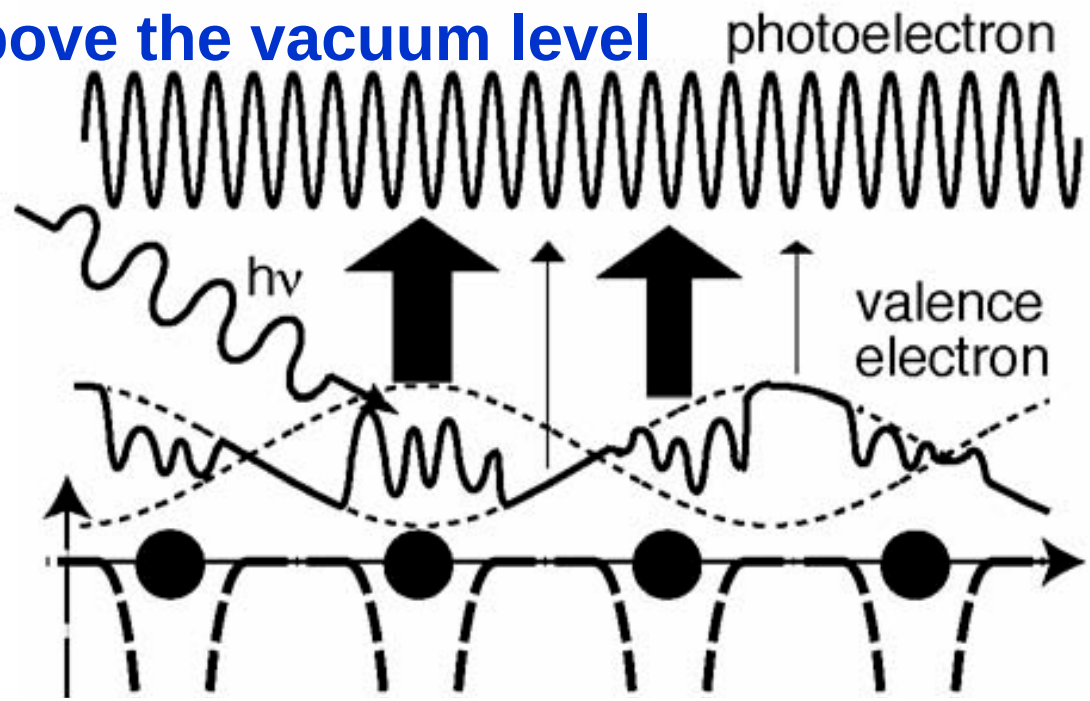
However,

Clear recoil effects ~150 meV are observed for the Al valence band

Jan.2007 Patent in Japan
特願2007-005230

"Instrument for Surface Atom Visualization"
A.Sekiyama & S.Suga

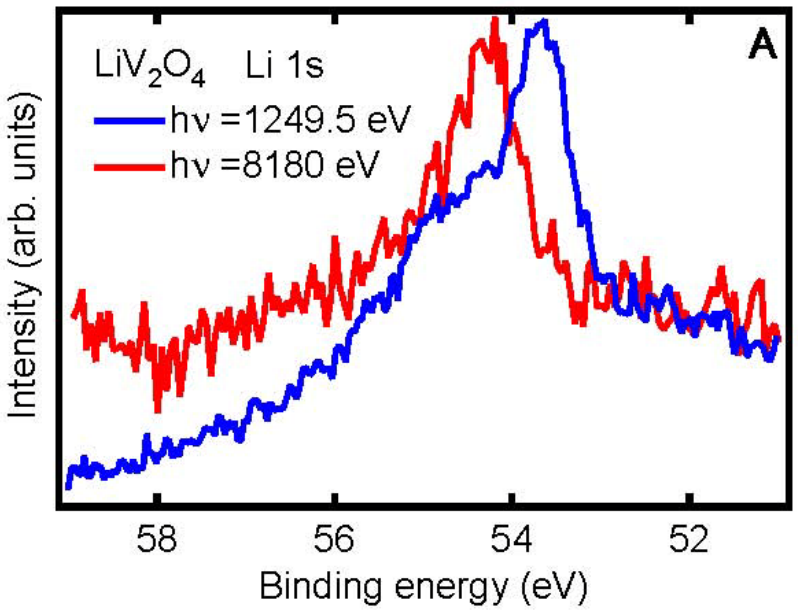
There is no doubt on the rapid spatial–oscillation of the high energy electron wave functions with the energy of several keV above the vacuum level

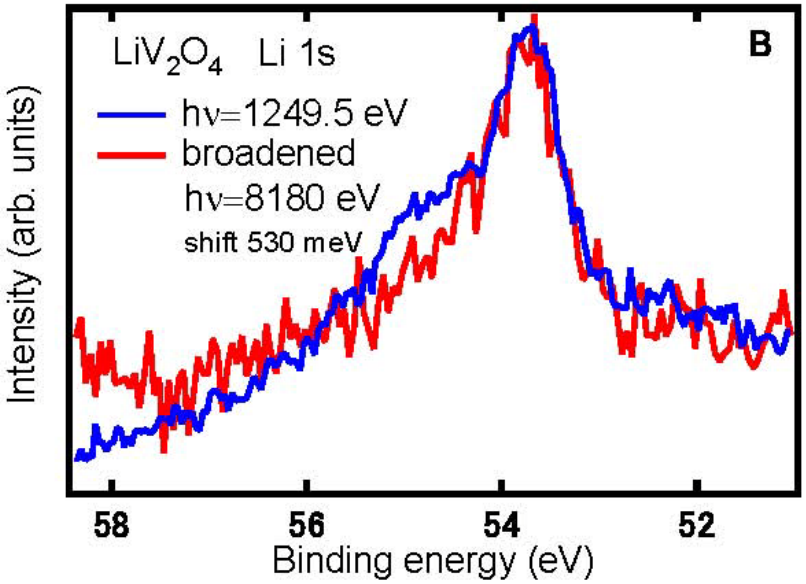


Valence-electron wave function is smoothly oscillating in the region away from the ions or nuclei. However, the spatial-oscillation becomes very rapid in the vicinity of the nucleus providing electrons to the valence-band due to the core electron potential. **a linear combination of Wannier functions centered at such nucleus site with proper relative weights (or significant expansion coefficients**

Recoil on core photoemission in LiV_2O_4

Fig.1





LIV_2O_4 is a heavy Fermion material

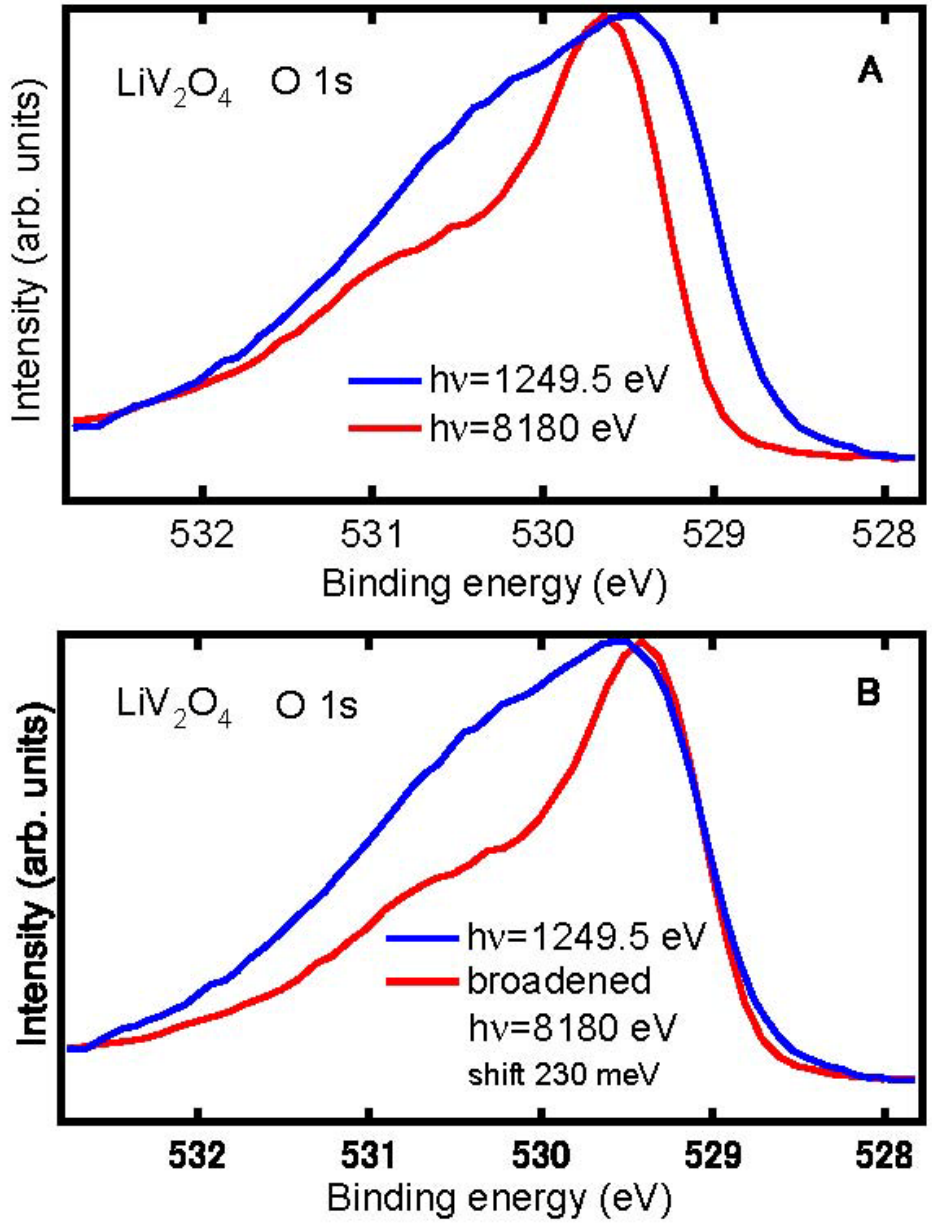
Li 1s core-level photoemission shows a clear recoil shift between

hν=1249.5 and 8180 eV at 20 K

ΔE_K is 215↔207 meV

Threshold shift is ~530 meV

Fig.2

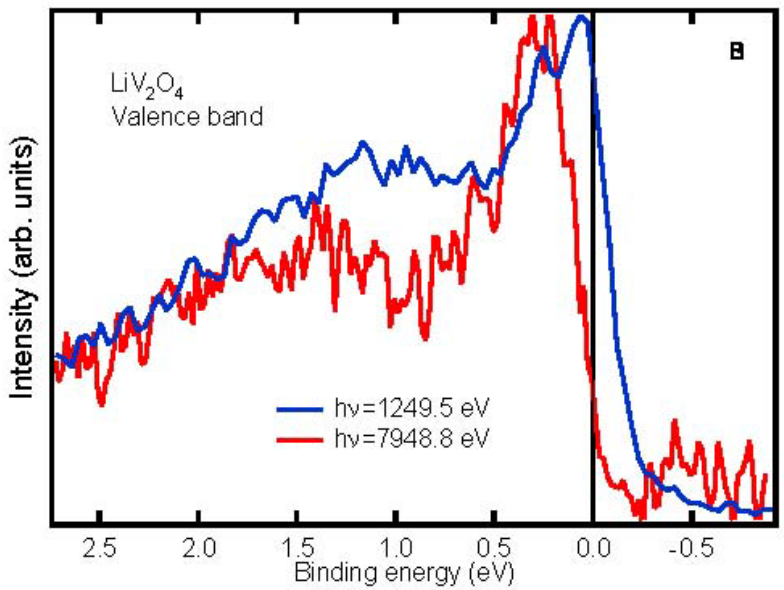


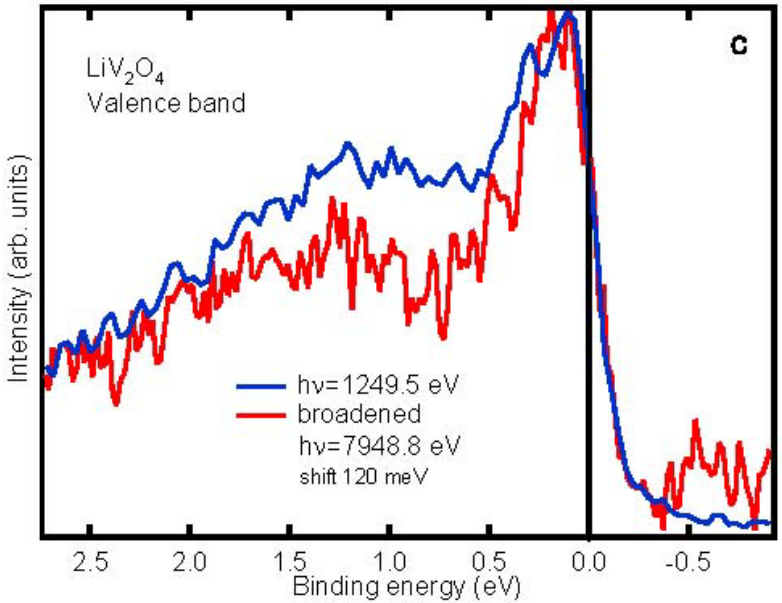
O 1s spectra has rather different shape between 1249.5 and 8180 eV(surface layer)

ΔE_K is 215↔207 meV

Low E_B threshold well overlaps for the shift of 230 meV

Clear recoil for O 1s





In LiV_2O_4, a clear shift of 120 meV is observed for VB

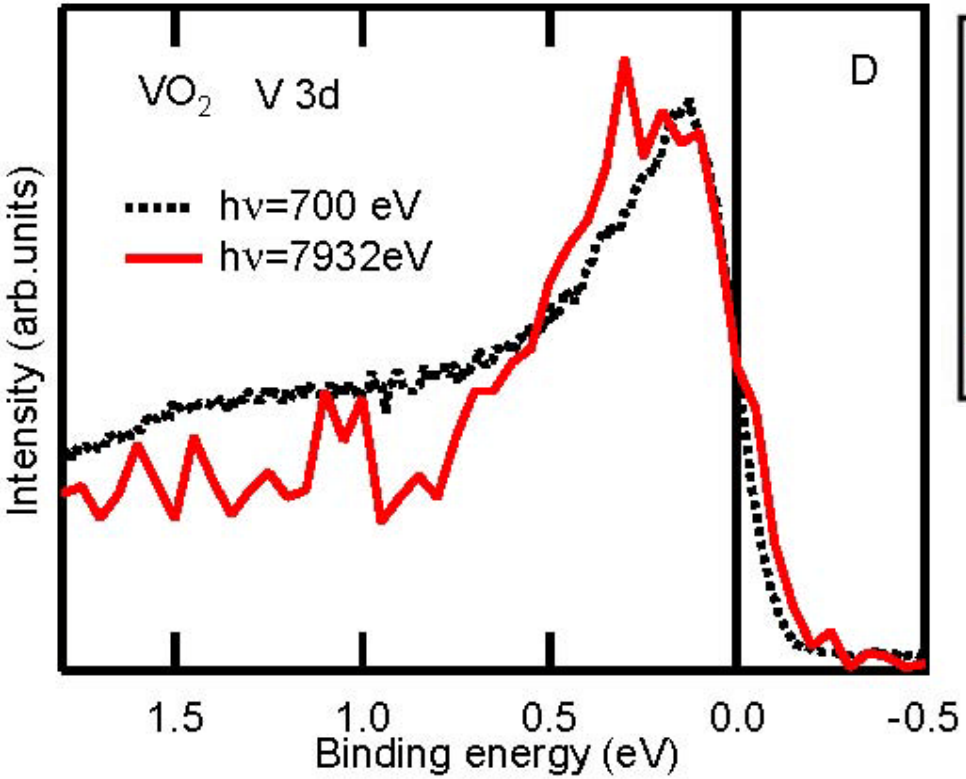
This value is larger than the predicted single nucleus recoil of

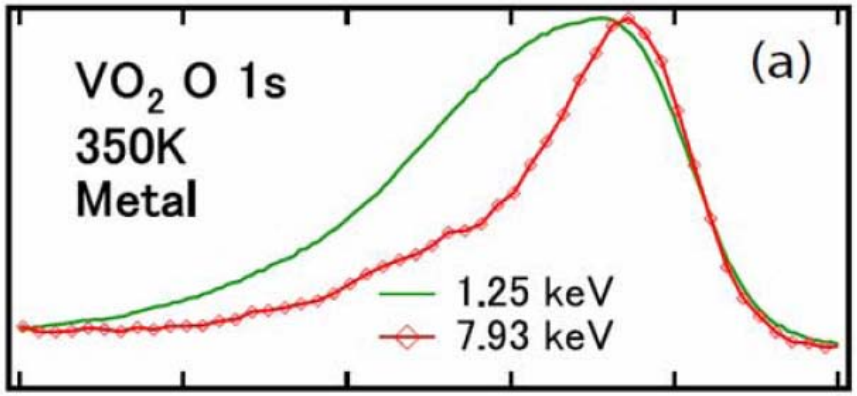
540 meV for Li 2s

230 meV for O 2p

70 meV for V 3d

Weighted sum of the recoil shift for the VB composed of V3d, O2p and Li2s is observed, because the VB is described by a linear combination of the Wannier function centered at V, O and Li sites.

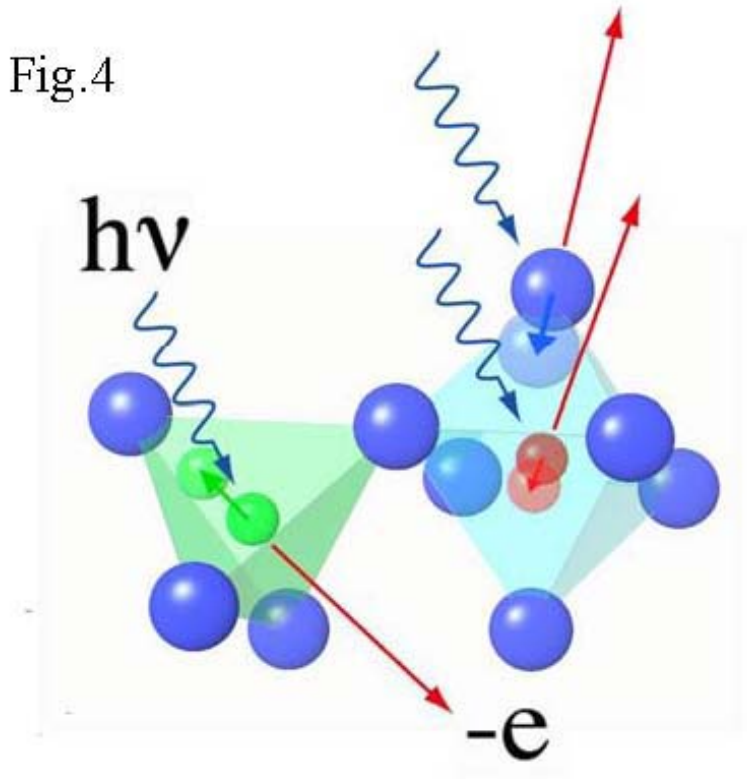


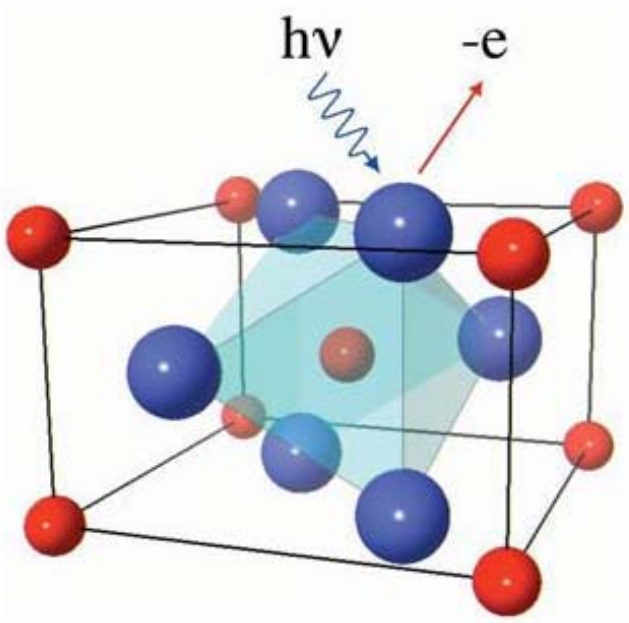


However, no recoil shift in the case of metallic VO_2 with the equivalent VO_6 octahedron. No recoil for all core states. Why?

Recoil effects were observed for all core and VB in LiV_2O_4

Recoil effects are negligible in VO_2 single crystal even in the metallic phase at 350K





Tetrahedron & octahedron

Distorted octahedron: rutile

Table S3 Inter-atomic distances in A.

LiV_2O_4

	V-O	V-V	O-O	Li-O
T_{room}	1.971	2.915	2.649 2.921	1.949
20 K	1.969	2.909	2.649 2.914	1.940

Inter-atomic distances are shorter in VO_2 Then momentum is shared by many nuclei in VO_2

VO_2

	V-O	V-V	O-O
350 K	1.921 1.933	2.851 3.522 4.555	2.575 2.725 2.851

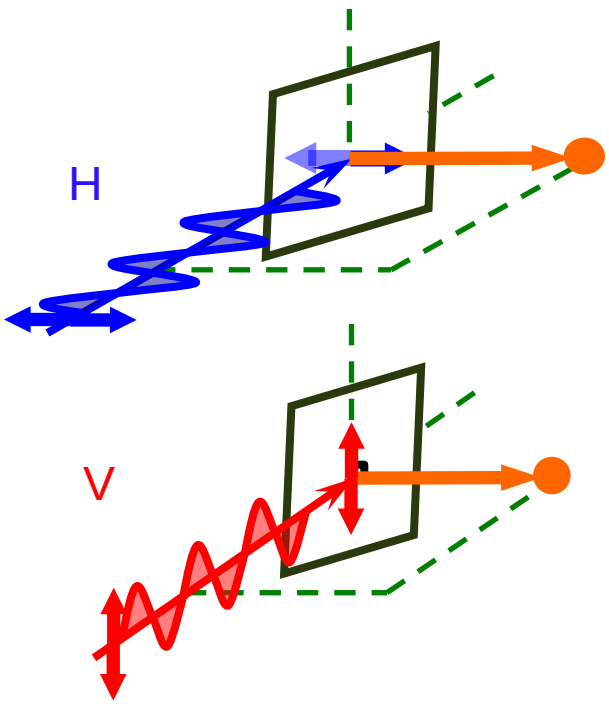
Single nucleus recoil does not take place in VO_2

Theoretical work is expected for theoreticians

Though HAX-ARPES is expected to be a powerful method for 3D Fermiology, the possible recoil effects should be seriously considered in the real application.

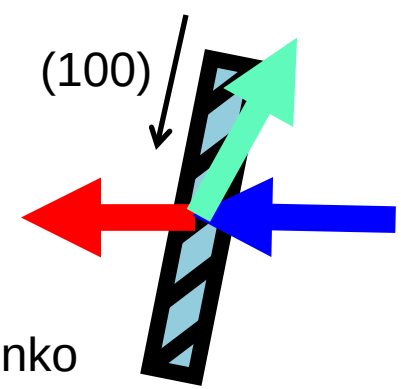
The resolution realized by the X-ray optics and electron optics can be down to 30 to 10meV or even better than 1meV in the near future. The possible recoil effects may deteriolate it if once the recoil takes place.

Polarization controlled HAXPES

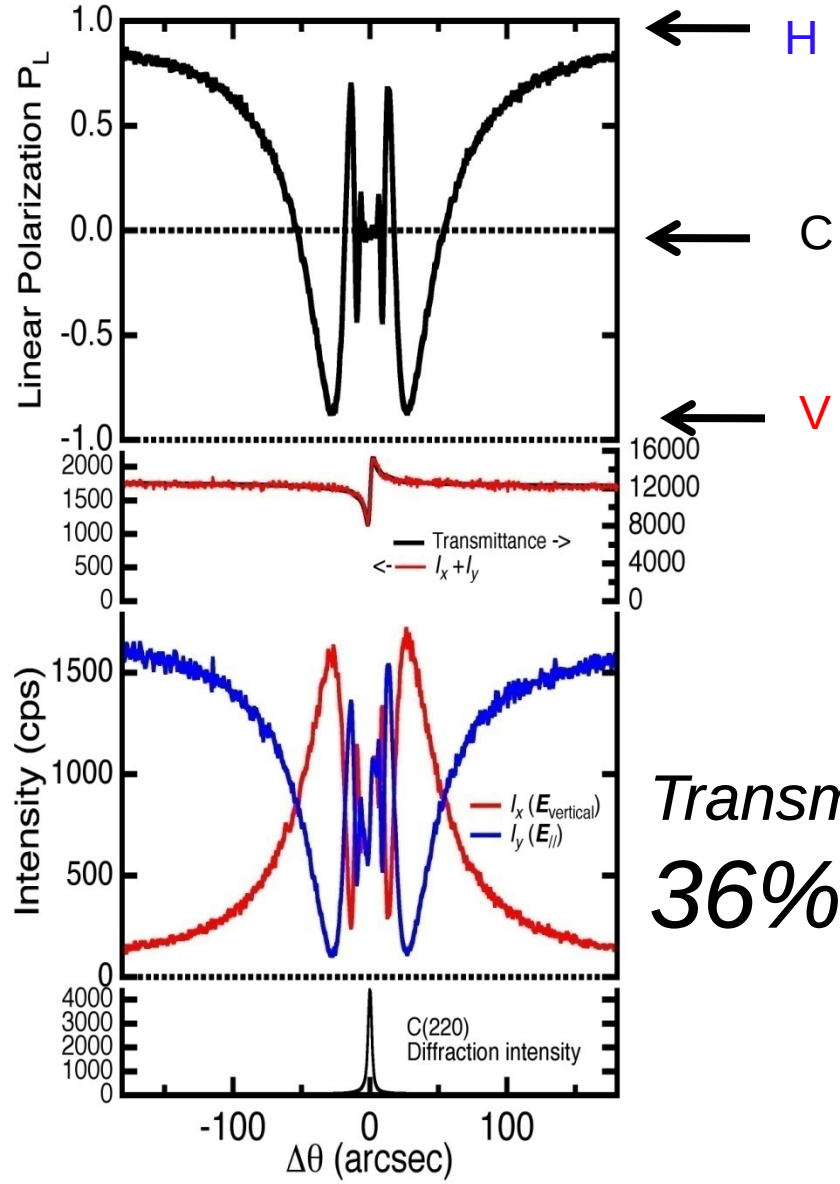


Polarizer:Diamond (220) surface

C(220)reflection
2θ~76˚
at λ ~1.54Å
(hν ~7938 eV)

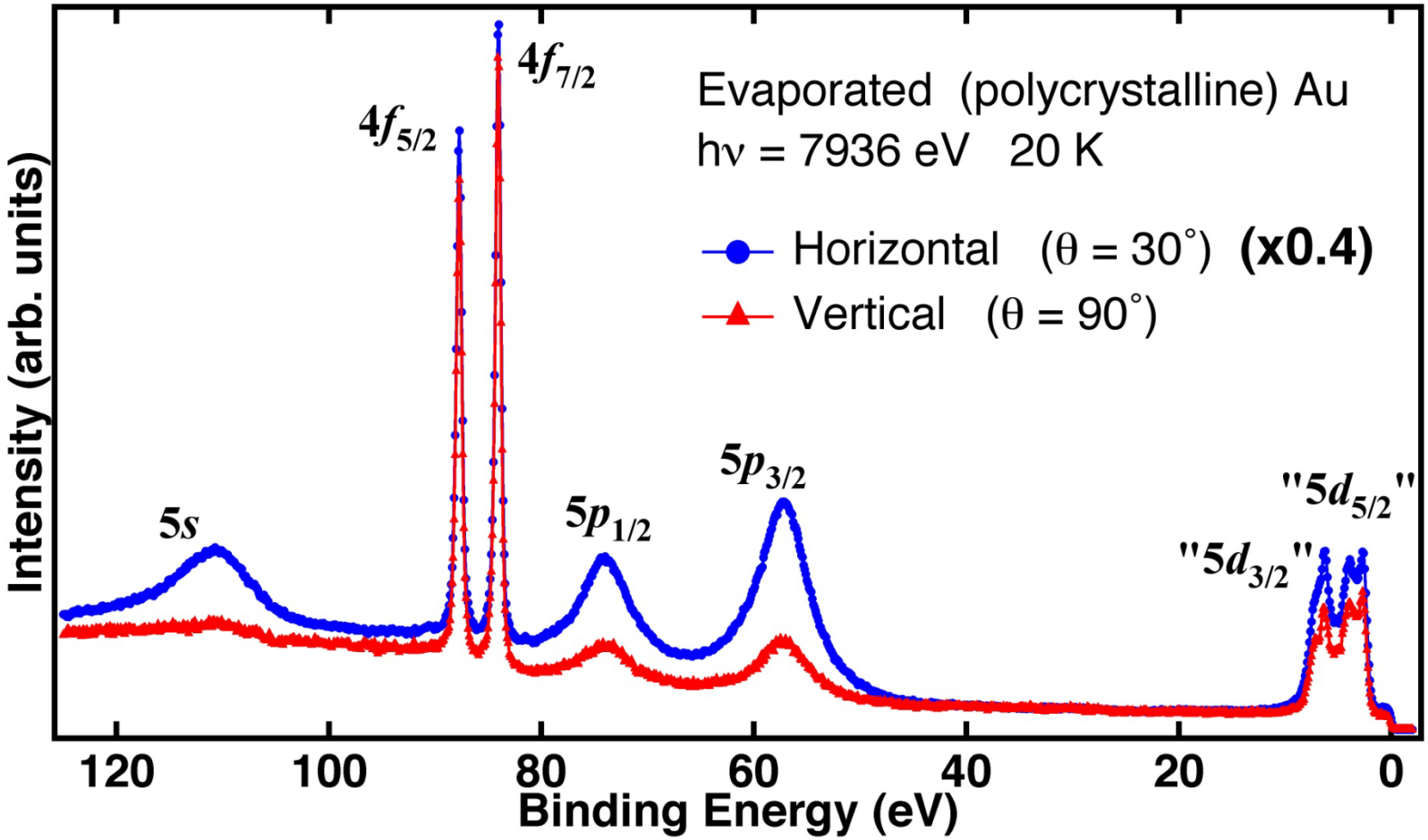


Sumitomo Denko
0.7mm^t 20,000 $



Transmittance

36%



Linear polarization controlled HAXPES is often quite useful for identification of the s states

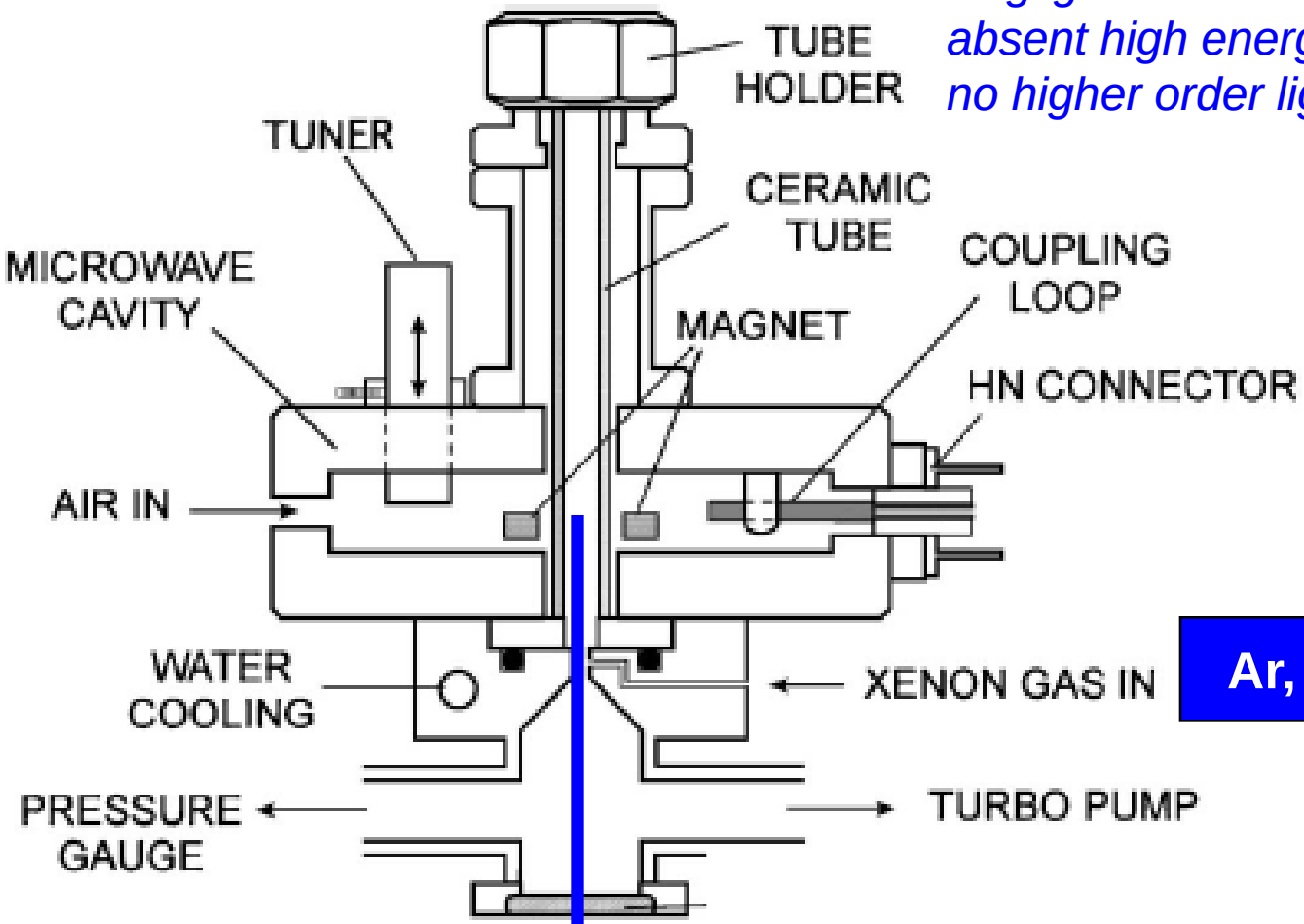
It can be also used for measurement of circular dichroism *A.Sekiyama et al. in press.*

Ultra-high resolution ELEPES is developed

ELEPES (extremely low energy PES)

- PES in 20-130 eV E_K is surface sensitive
- SXPES in several hundred eV E_K is more bulk sensitive
- Still, bulk and surface spectral weights are often comparable
- Bulk weight > 90% is realized for E_K>6 keV: HAXPES:
- resolution ~ 50meV⇐recoil?
- Depending upon materials, ELEPES is also bulk sensitive
- So far laser with $h\nu \sim 7$ eV has been mostly employed
- Such a laser is very expensive, requires a high skill for operation, still in most cases only 1 $h\nu$ was available
- High repetition or quasi CW is required to be space-charge free
- Therefore one cannot use the full power
- Such a resolution ≤1meV is possible now by inexpensive non-laser CW new light source in your lab.
- One can save a lot of time & money in your life.
- SR-ELEPES is useful, but one must stay SR facility apart from your family and/or your lovely kids, not always useful for urgent case

Negligible Doppler broadening
Negligible self absorption
absent high energy component
no higher order light



Ar, Kr, Xe

FIG. 1. Schematic diagram of Xe discharge lamp.

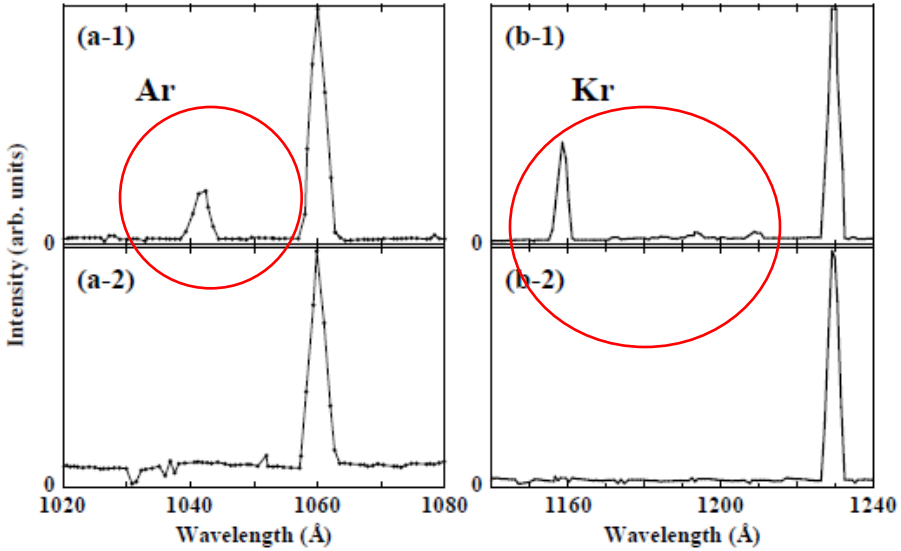
Heated LiF, CaF_2, sapphire 1mm^t

LiF UHV widow 1mm^t

Urbach tail of exciton absorption can completely suppress the high energy components

Heated LiF

Ar:10.1eV



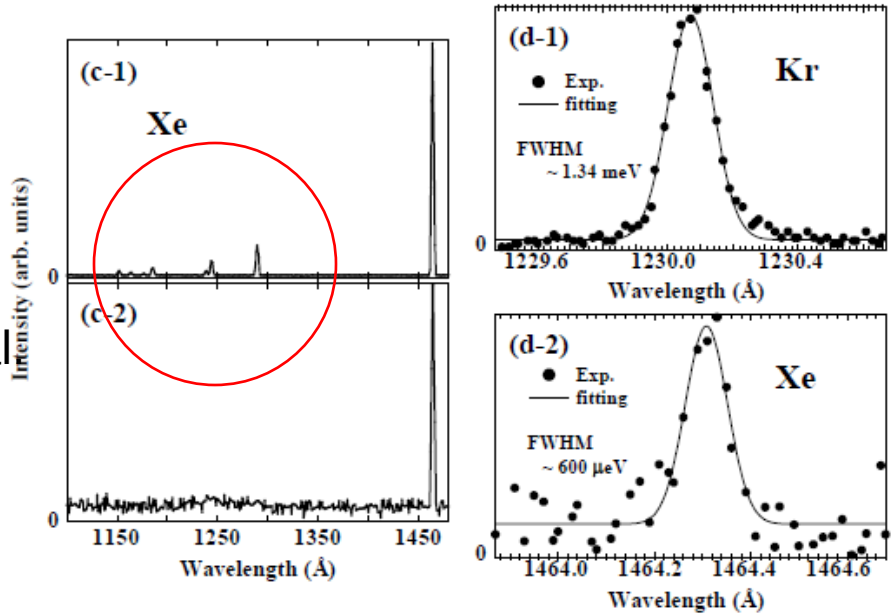
CaF_2

Kr:9.7eV

High energy components are fully suppressed

Sapphire

Xe:8.4eV



Resolution < 500μeV

Natural width is better than this.
The above value & statistics is induced by the limited resolution of a very poor monochromator

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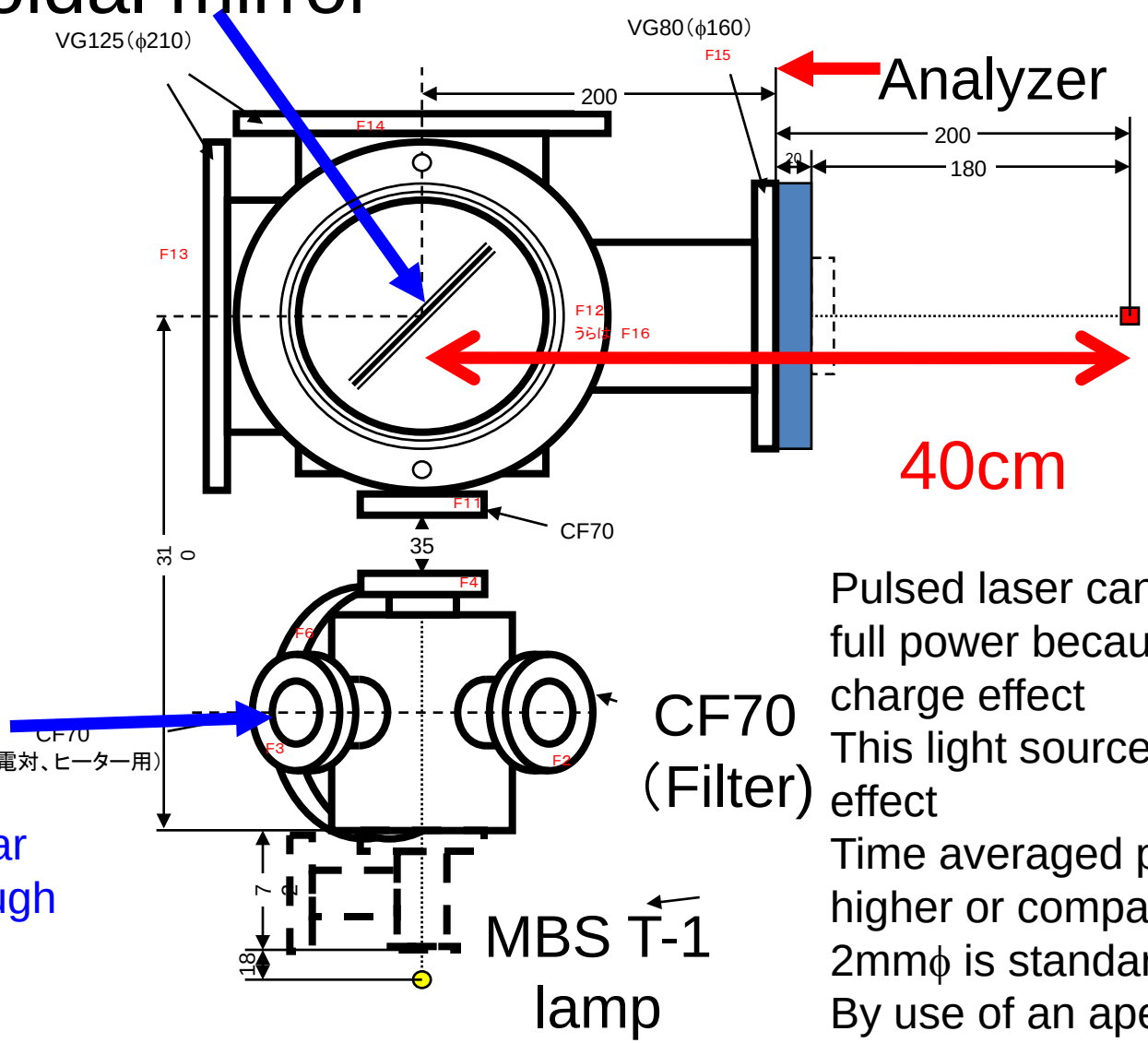
Jpn.J.Appl.Phys.
47, 2265 (2008)

toroidal mirror



Filter

LiF

CaF_2

Sapphire

on a linear feedthrough

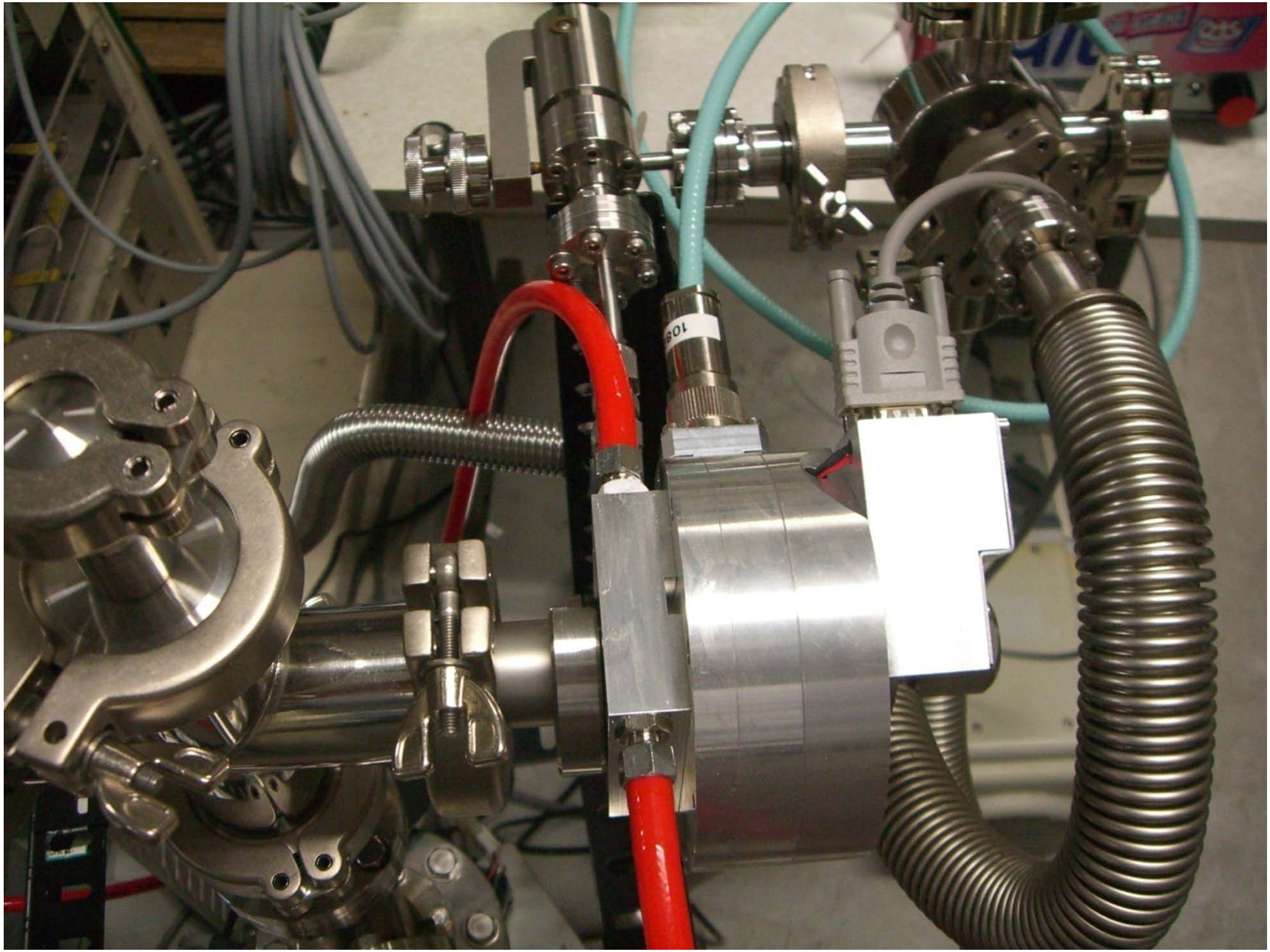
Pulsed laser cannot be used at full power because of the space charge effect

This light source is CW, no such effect

Time averaged photon flux is higher or comparable to laser.

2mmϕ is standard

By use of an aperture, 0.14 mmϕ is realized in my lab



10cm

Summary & Outlook

1. SX-ARPES is required to do 3D bulk Fermiology
2. High resolution HAXPES is necessary to probe genuine bulk electronic structures of strongly correlated electron systems
3. Combination of SX-PES and HAXPES is very powerful to resolve bulk, sub-surface (interface) and surface electronic structures
4. Recoil effects sometimes distort the VB spectral shapes. Therefore careful analysis will be required in HAX-ARPES
5. Ultrahigh resolution ELEPES is feasible in lab

   Combination of ELEPES, SXPES and HAXPES including their ARPES is the way how I go on.
6. Time resolved lab PES in 20-100 eV with <100fs is now possible in lab. even without FEL. One can develop new technique for XFEL in lab.

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