Mac

Workshop on frontier science using soft x-rays at the APS

SUMMARY

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A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Science overview

Two branches

- Angle resolved photoemission
- Scattering

Common theme: soft x-rays

Materials Sci.

Cond. mat. Physics

Chemistry

Biology

(not crystallography)

Office of Science
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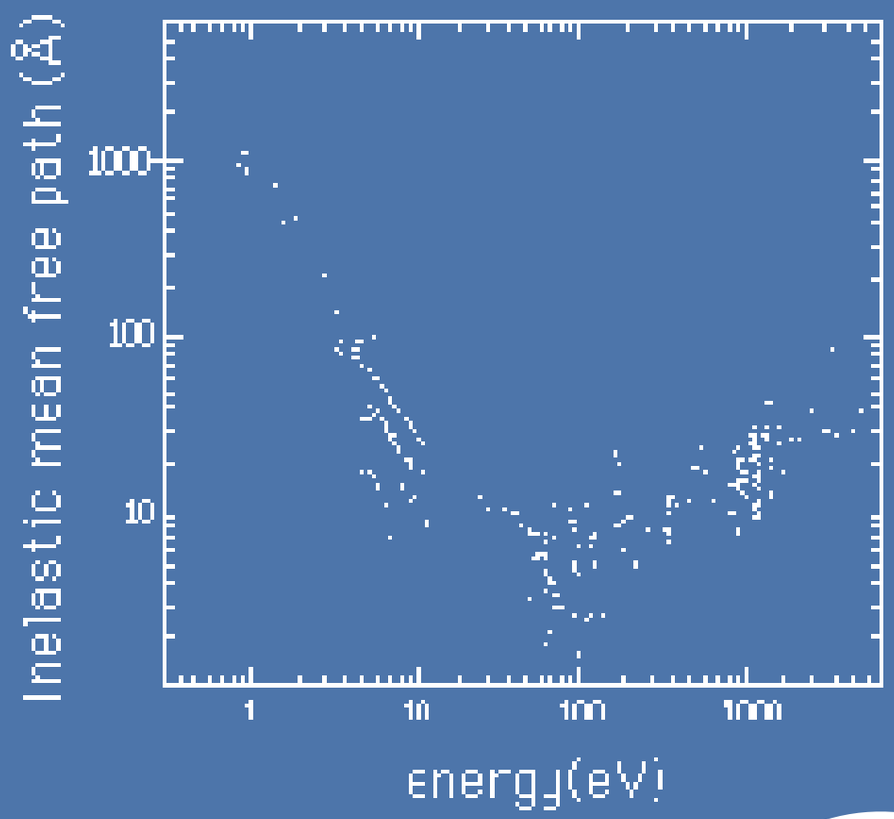
Angle resolved photoemission

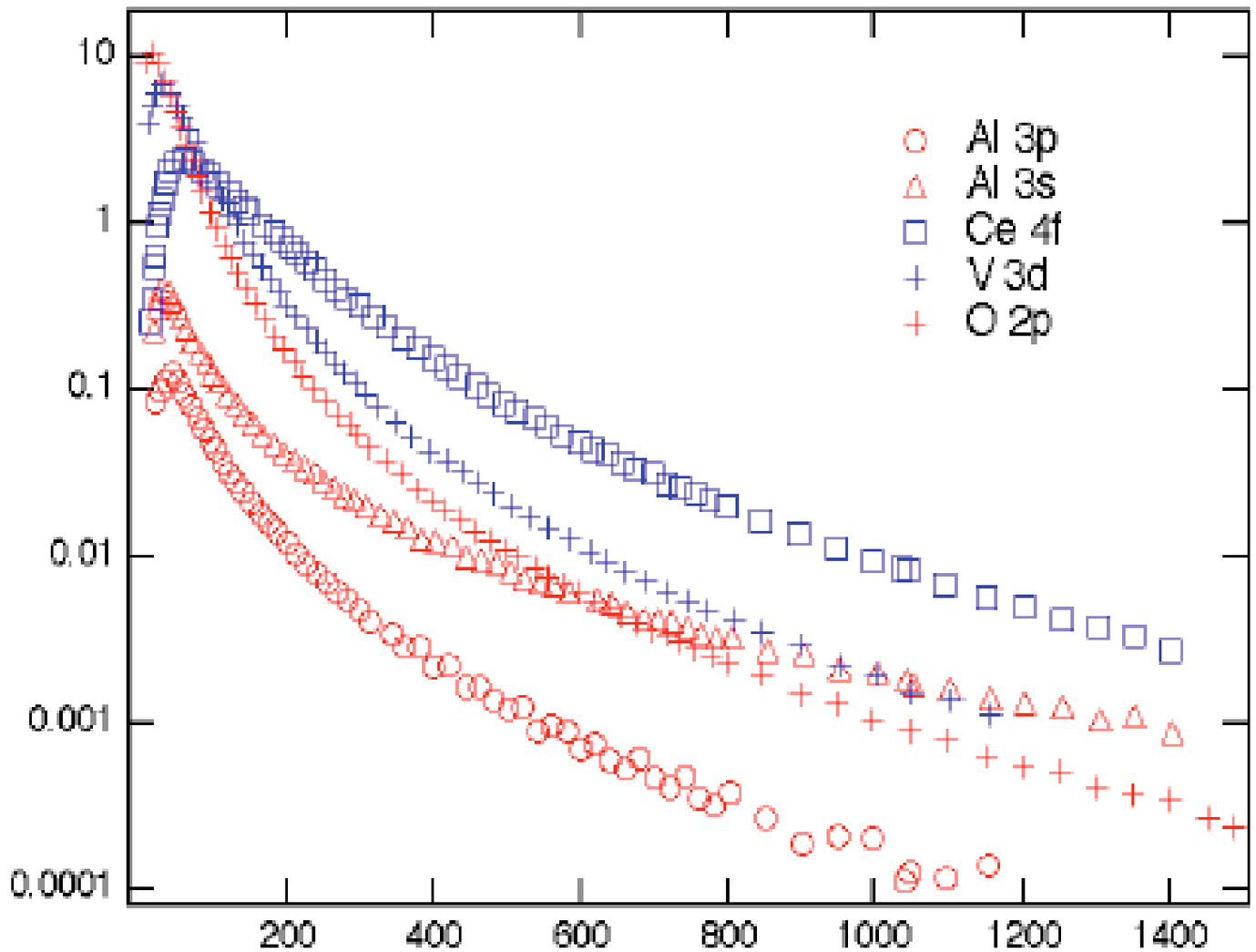
- Jim Allan, (U. of Michigan) Photoemission experiments at SPring8 Beamline BL25SU
- Marco Grioni (Ecole Polytechnique Lausanne) - Bulk electronic properties from high - and higher - energy spectroscopies
- Stephan Rosenkranz (ANL) - Orbital correlations in complex oxides
- Atsushi Fujimori (University of Tokyo) - Soft x-ray photoemission and magnetic circular dichroism of correlated systems and nano-materials
- Jim Tobin (LLNL) Using higher energy x-rays and spin detection to go after non-magnetic electron correlation, half-metallicferromagnetic behavior and magnetic ordering
- Michael Sing (Universitaet Augsburg) - Valence band studies on transition metal oxides by soft x-ray photoemission

Angle resolved photoemission

- ARPES probes the elementary excitations in solids
  - Thermal and electrical conductivities
  - optical properties...
- ARPES is surface-sensitive
  ⇒need high photon energy



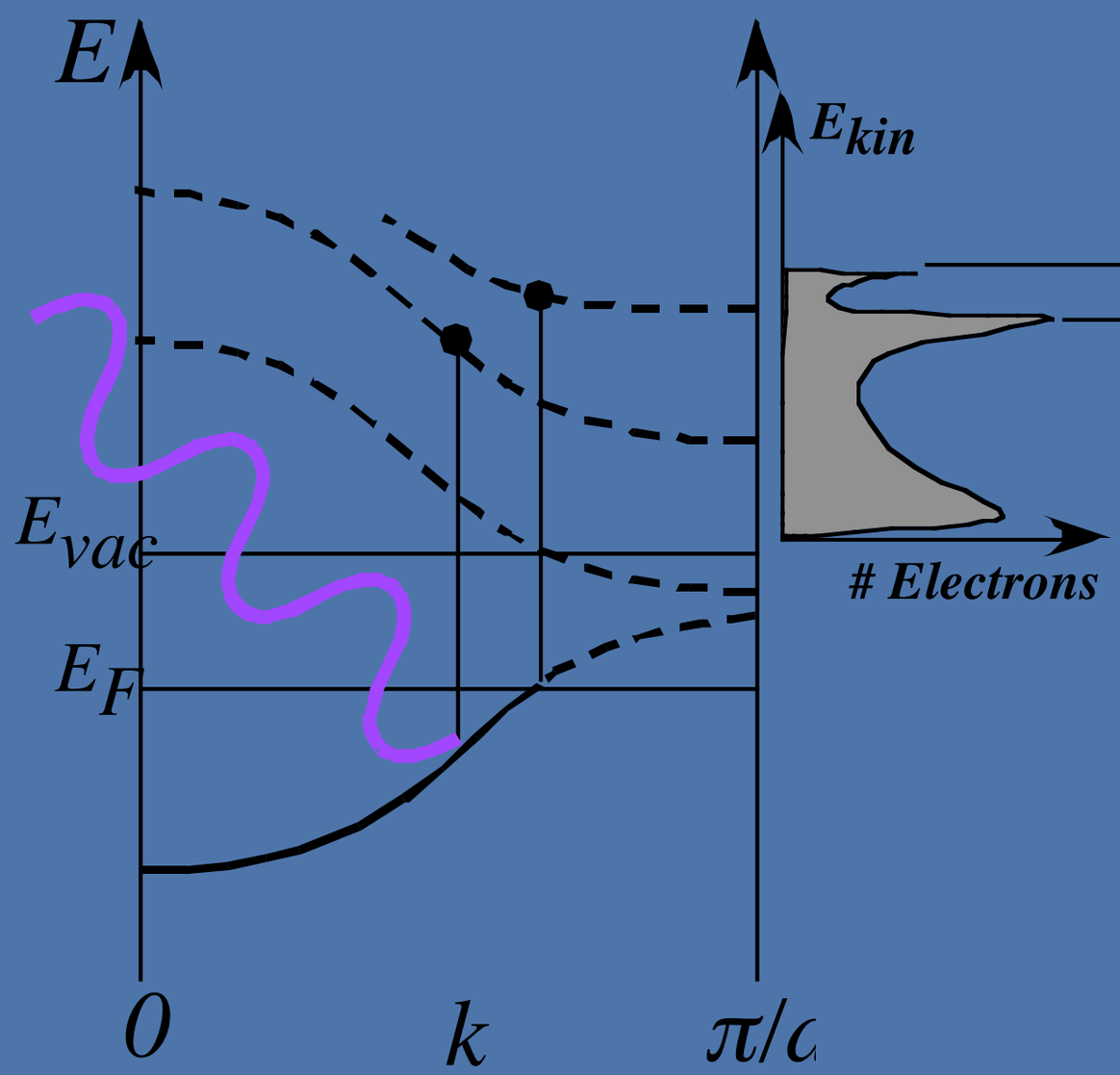
High hν photoemission cross-sections small

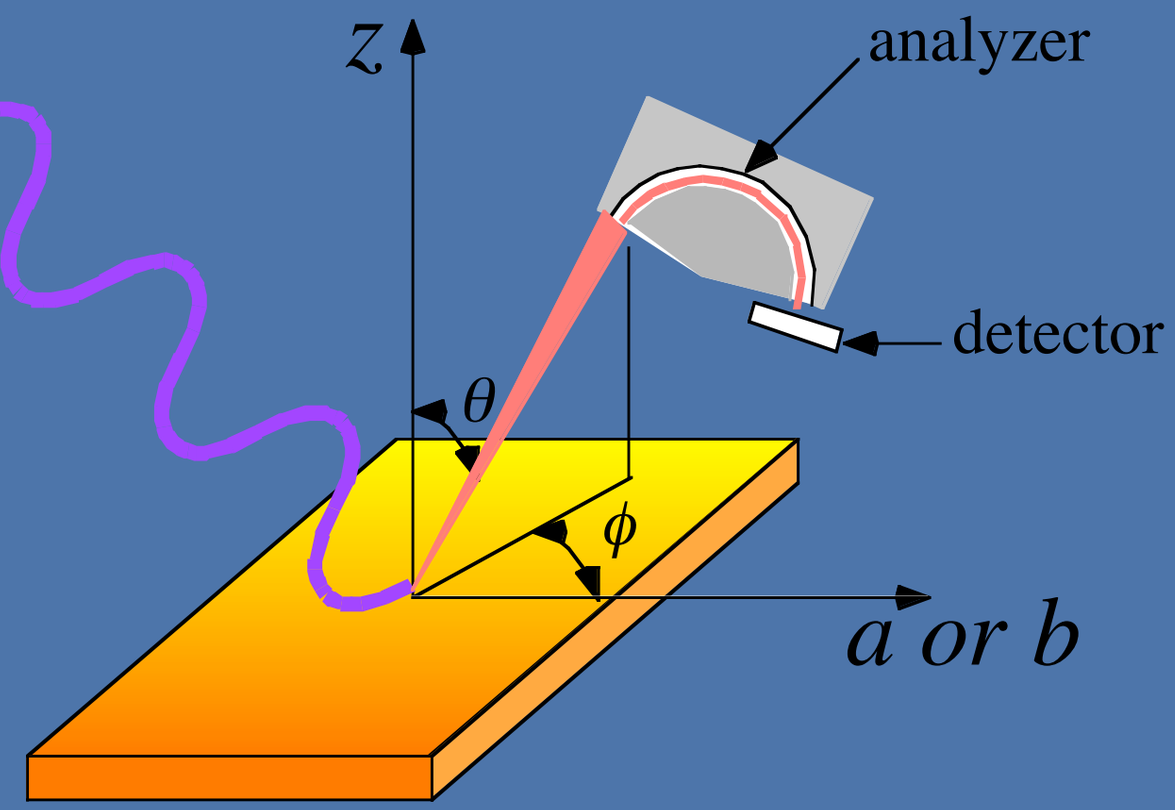


Cross-sections very small, especially for sp electrons
challenging to get good S/N ratio in data

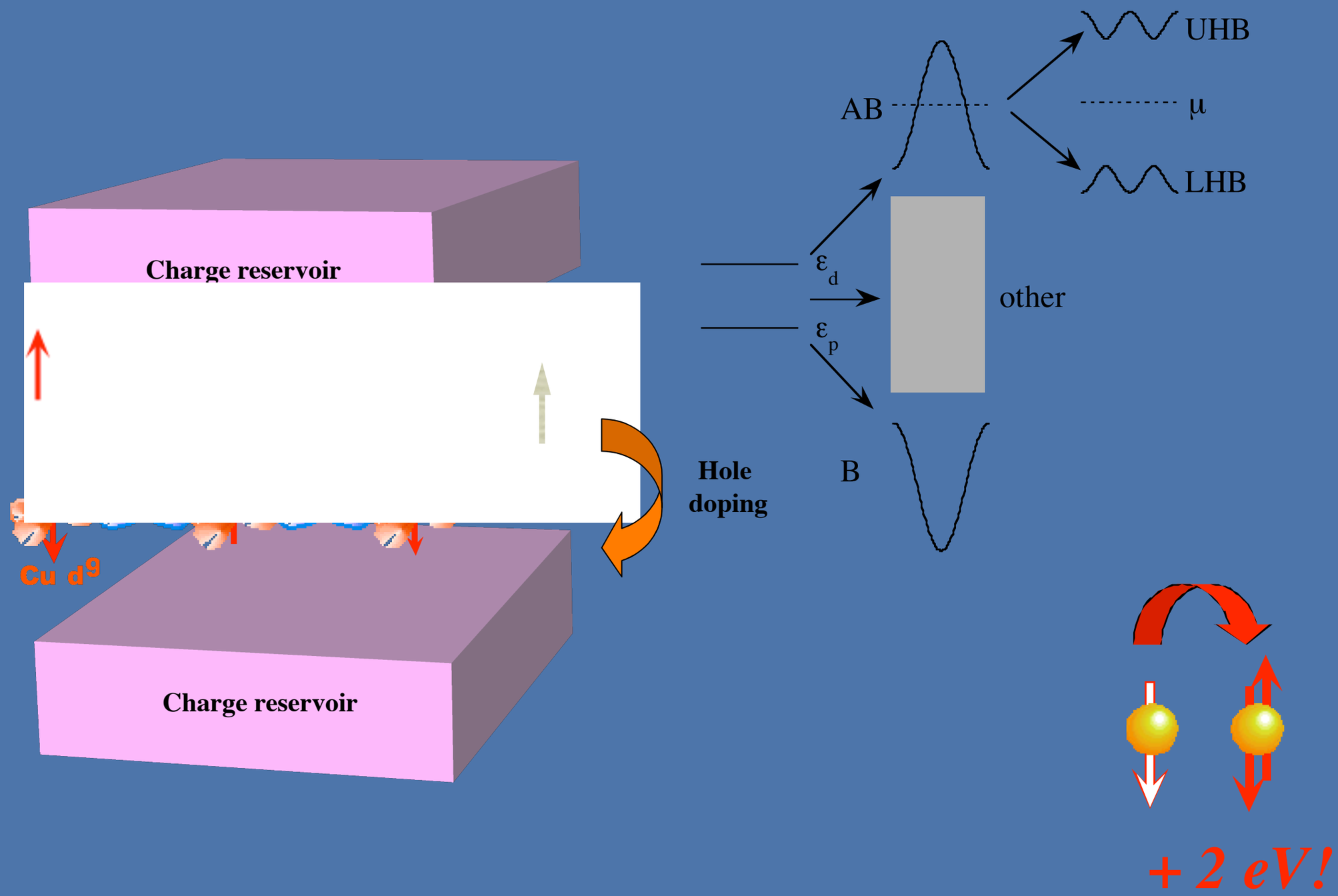
RESPES contrast very large
because off-resonance signal so small

Angle resolved photoemission



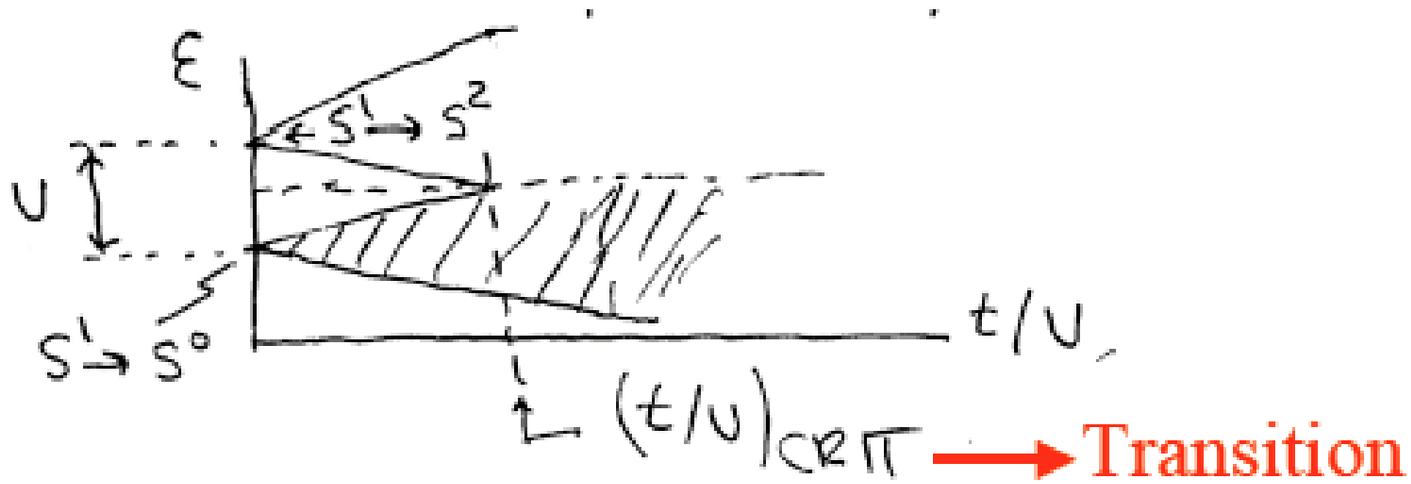


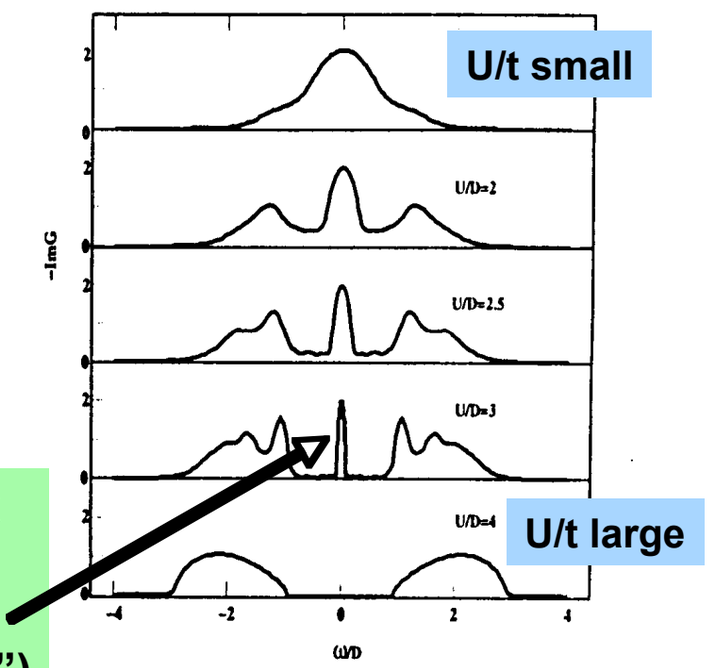
$$\vec{k}^{f}_{//} = \vec{k}^{i}_{//} = \sqrt{\frac{2mE}{\hbar^2}} sin\theta$$


Charge reservoir
Cu d9
Charge reservoir
Hole doping
AB
B
UHB
μ
LHB
εd
εp
other
+ 2 eV!

Mott insulator to metal transition
the early thinking

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





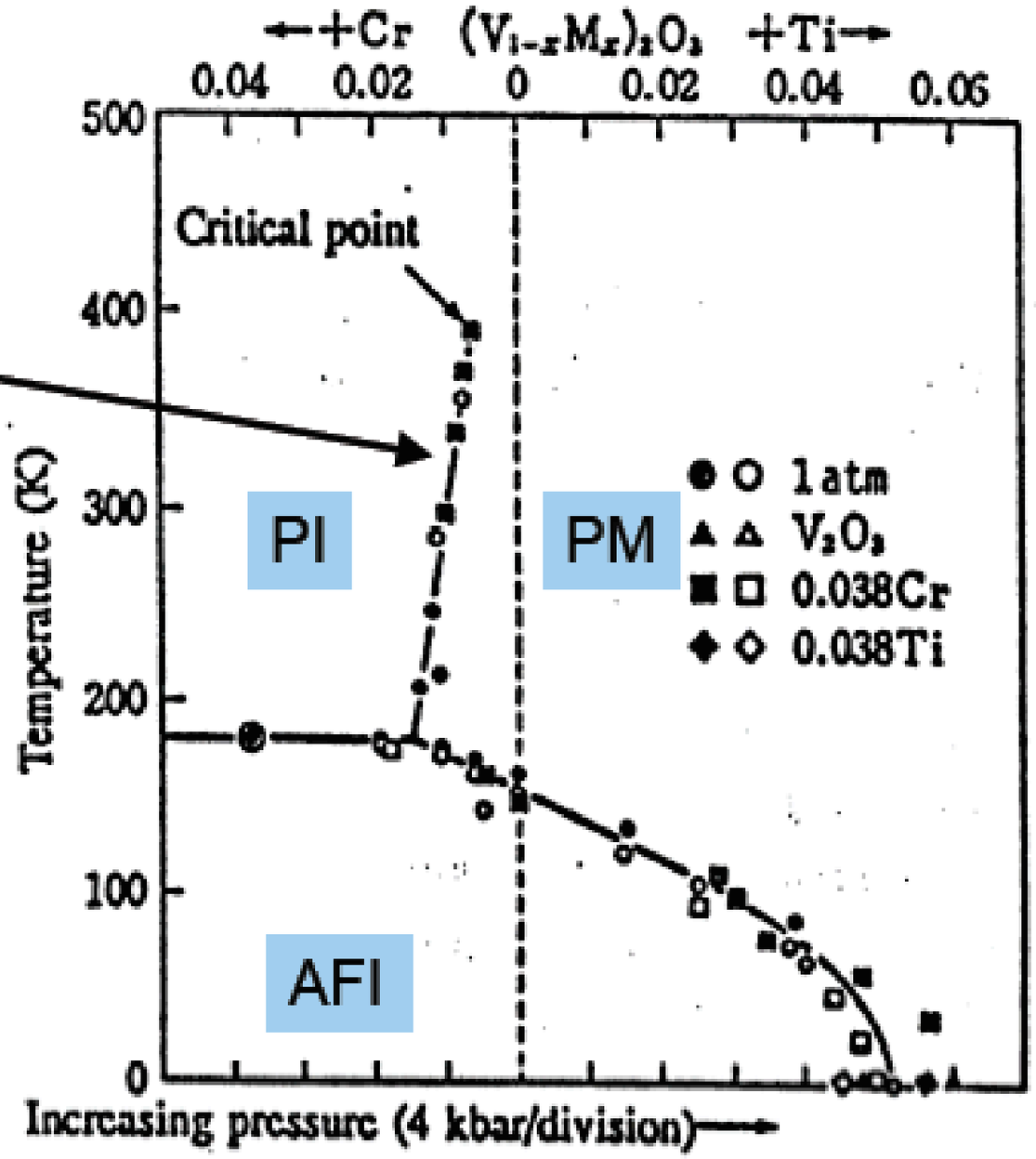
quasi-particle peak
growing in gap
as U/t decreases
("bootstrap Kondo")

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

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



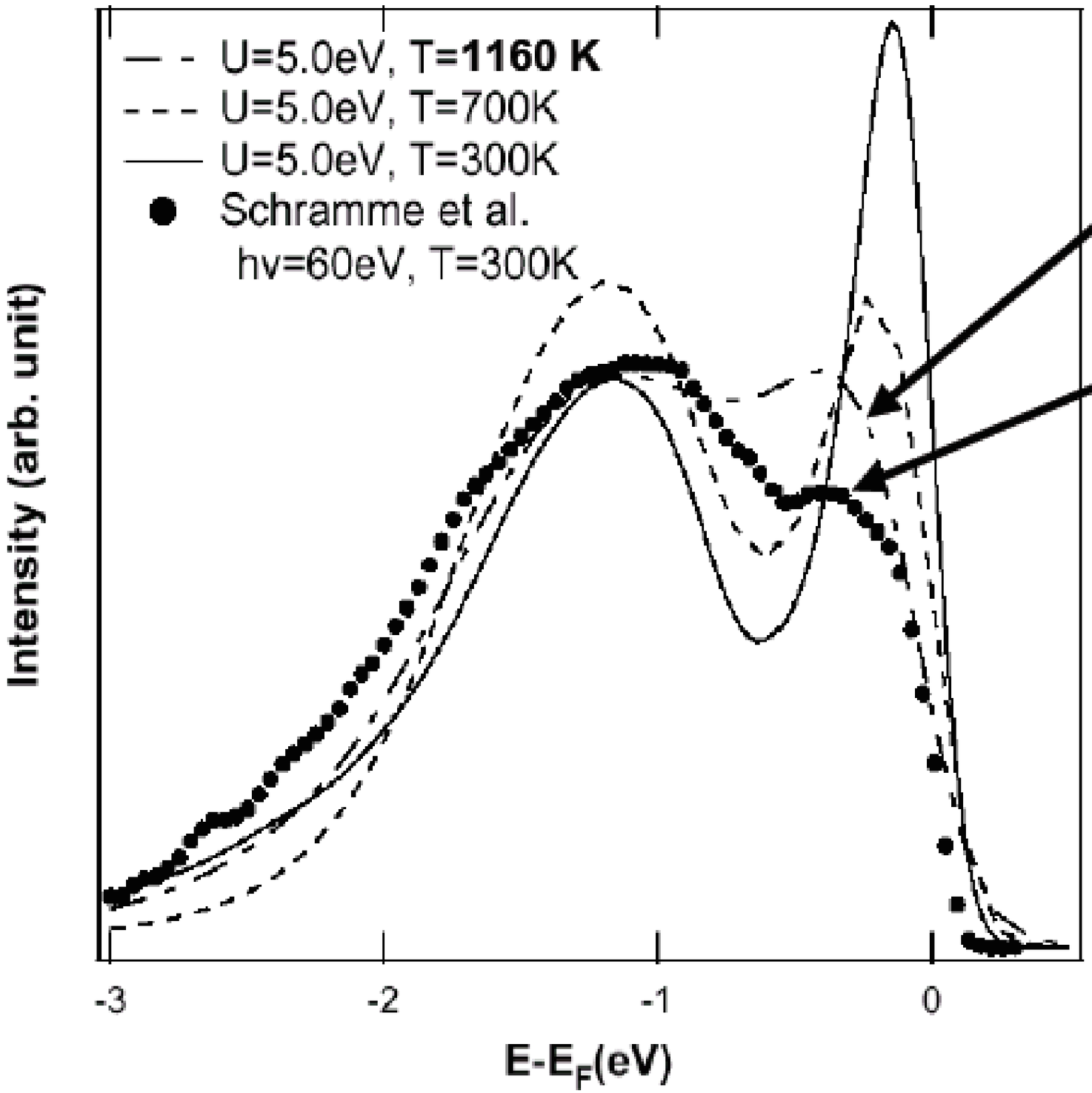
2e⁻/ V^{3+} ion
3 orbitals/ic
4 ions/cell

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

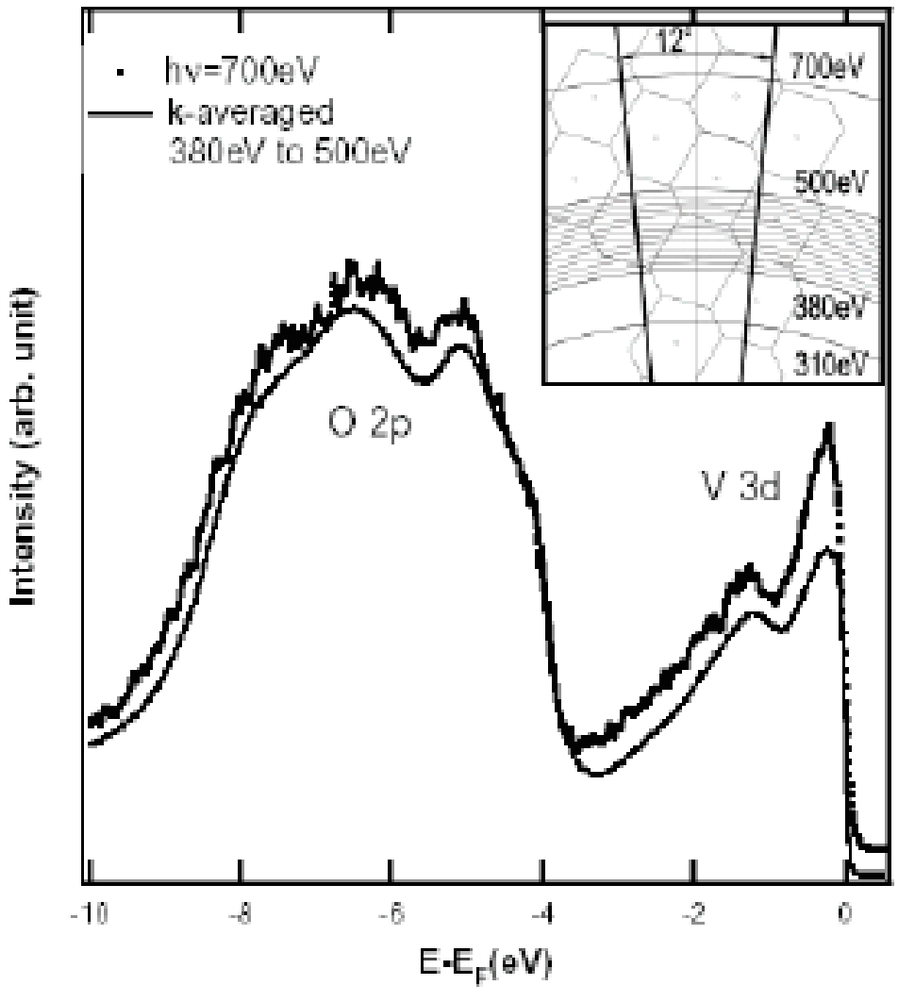
compared favorably to 300K 60 eV data (Held et al, PRL '01)

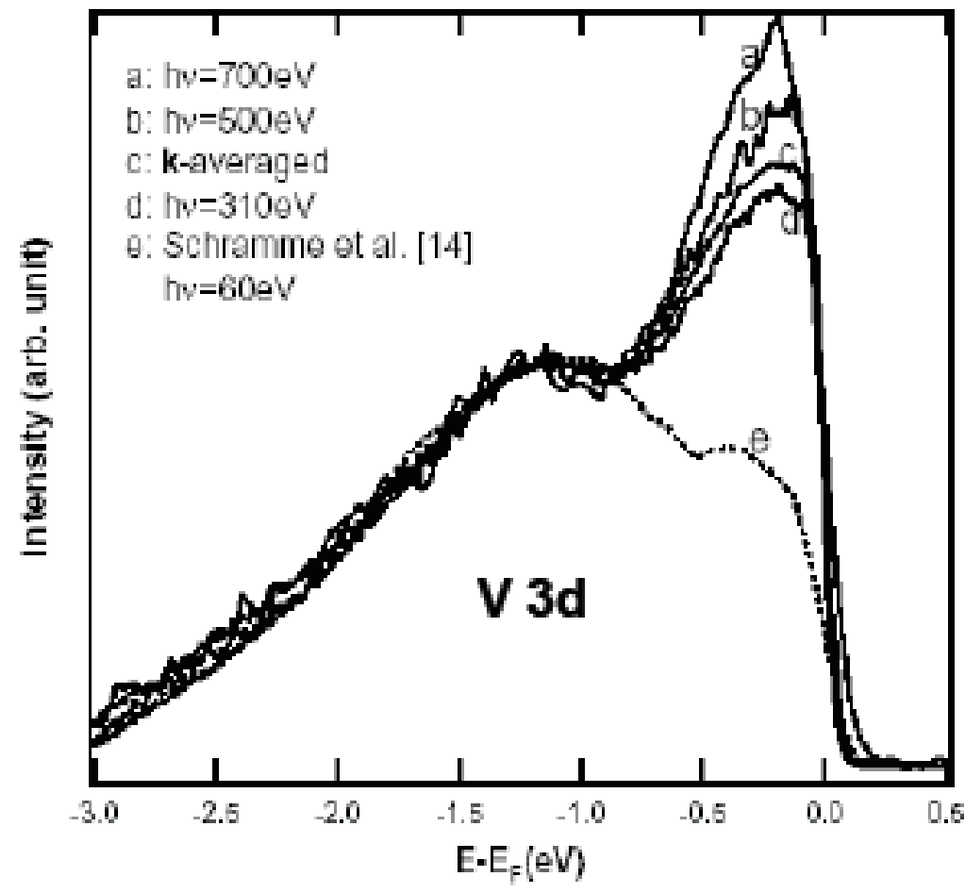
But theory peak sharpens up with decreasing T

Shows large disagreement with data for same T.

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.





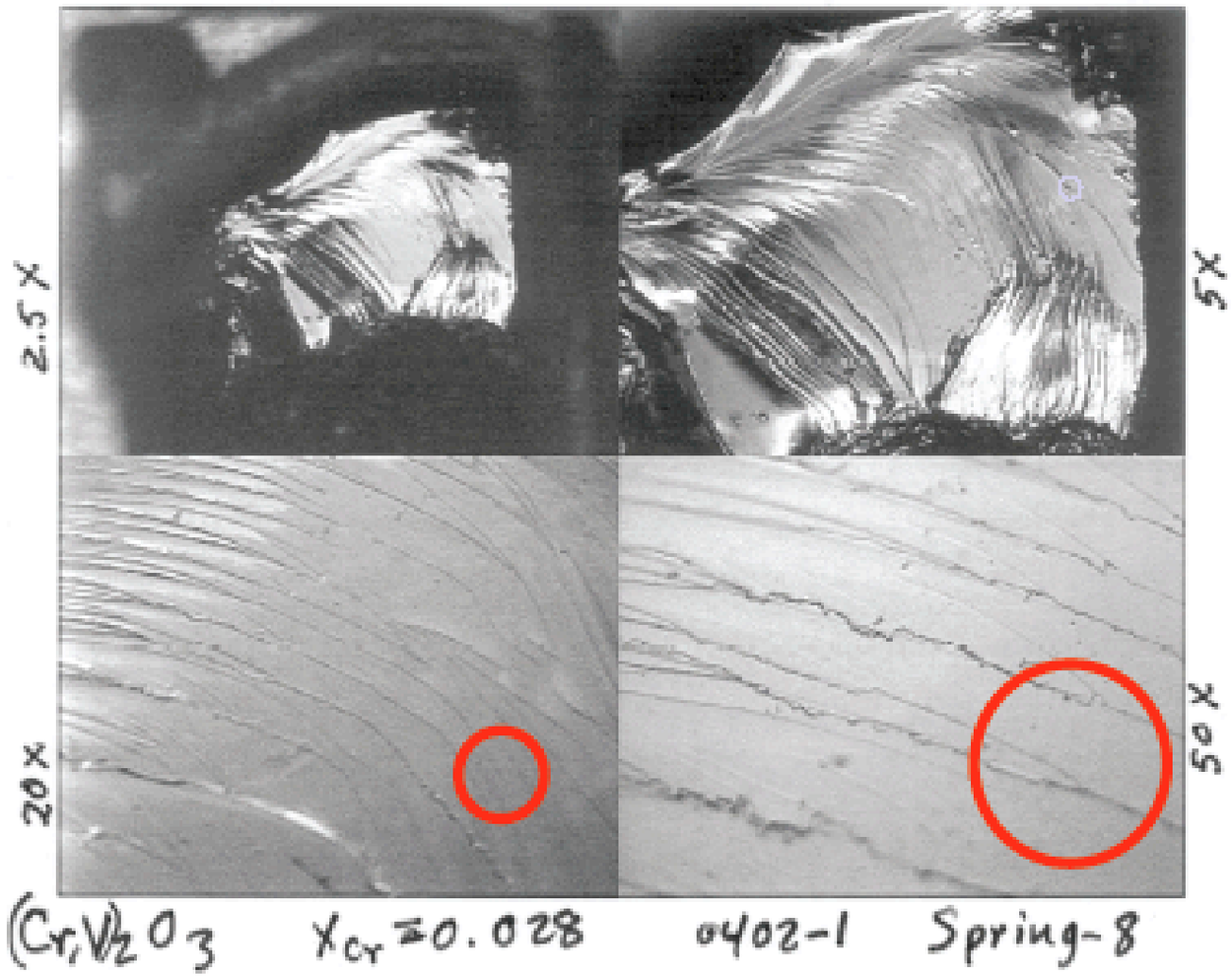
SPring8 collaboration with S. Suga et al.
Early small spot work at ALS with J. D. Denlinger important!

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

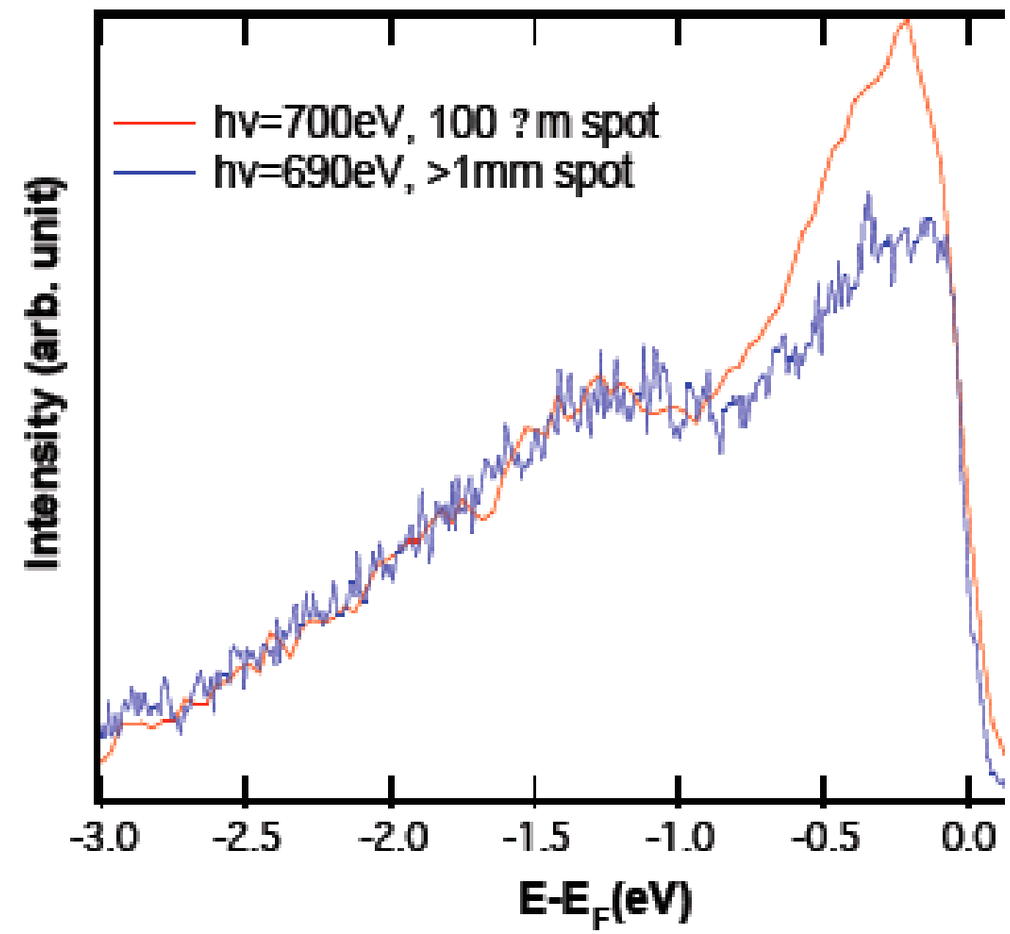
S.-K. Mo et al, PRL 90, 186403 (2003)

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

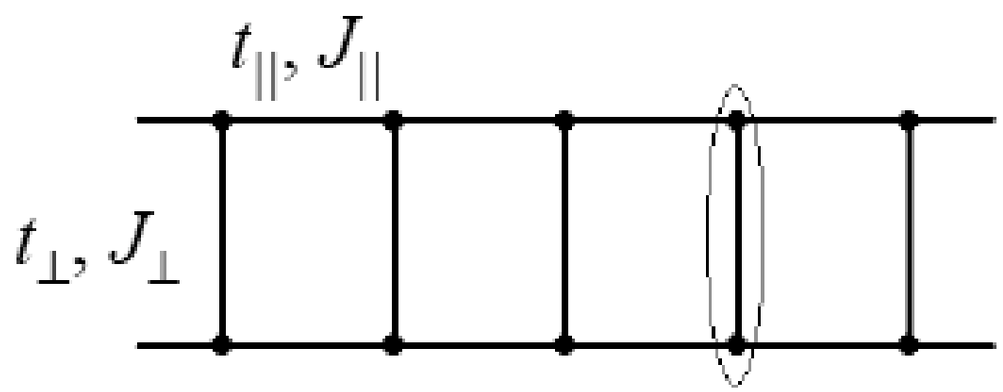
Difference for 300 eV to 500 eV range even larger

Soft X-ray scattering

- Many collective phenomena at longer wavelenghts
  - Spin ordering, magnons
  - Polarons, bi-polarons, etc.
  - Biological structures
- Weak phenomena⇒need resonant scattering from LOW-lying energy levels which participate in phenomena.

Spin ladders

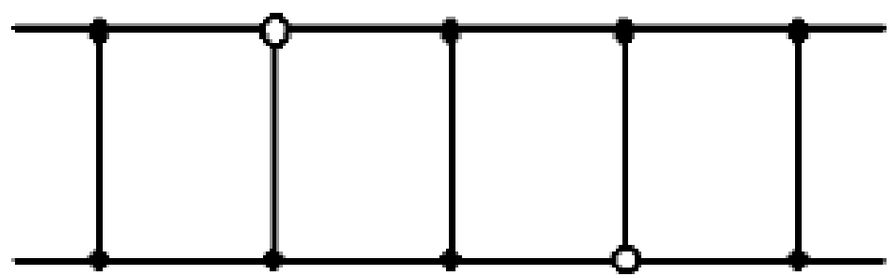
E. Dagotto, J. Riera, and D. Scalapino, *Phys. Rev. B*, **45**, 5744 (1992)
E. Dagotto and T. M. Rice, *Science*, **271**, 618 (1996)



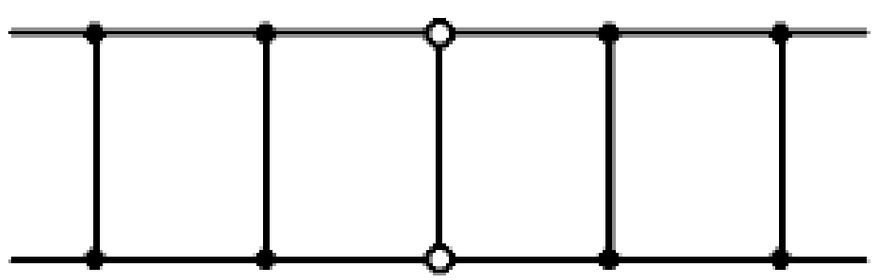
- Spin liquid (exponential decay in correlation)

$$J_{\perp} >> J_{||}$$

- Singlets across the rungs



- Doped hole breaks a singlet (costs $\sim J_{\perp}$)

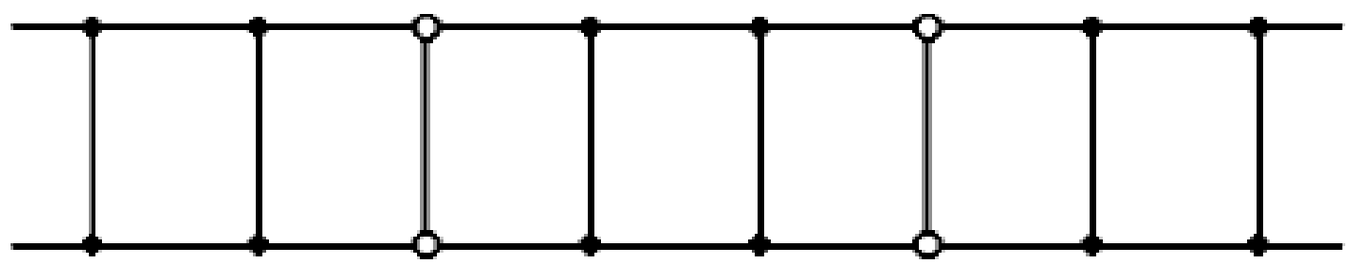


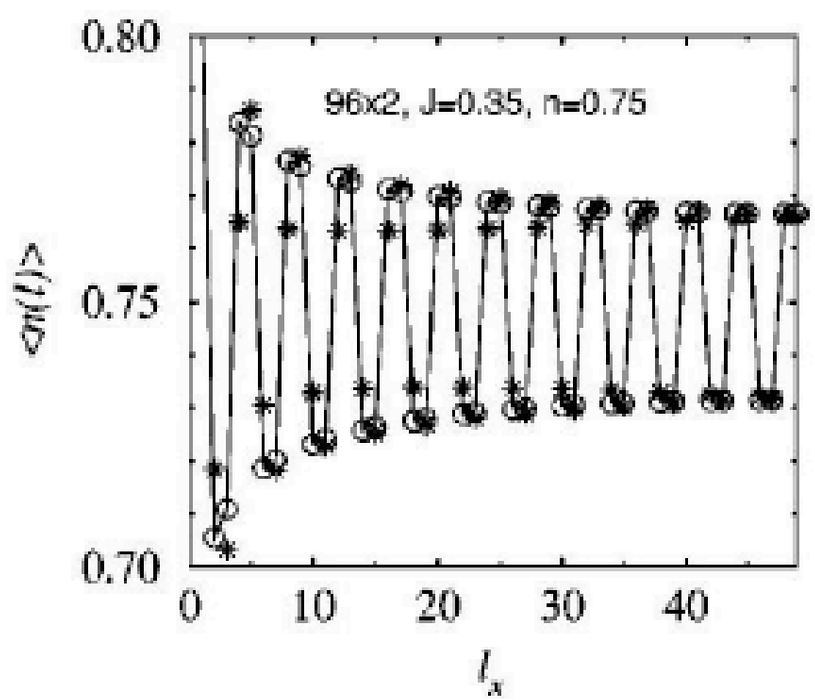
- Holes bind into pairs
- Superconductivity without phonons,
  D~ d_{x2-y2} [M. Sigrist, *PRB*, **49**, 12058 (1994)]

Spin ladders

E. Dagotto, J. Riera, and D. Scalapino, *Phys. Rev. B*, **45**, 5744 (1992)
S. White, I. Affleck, and D. Scalapino, *Phys. Rev. B*, **65**, 165122 (2002)
S. Carr, A. Tsvelik, *Phys. Rev. B*, **65**, 195121 (2002)

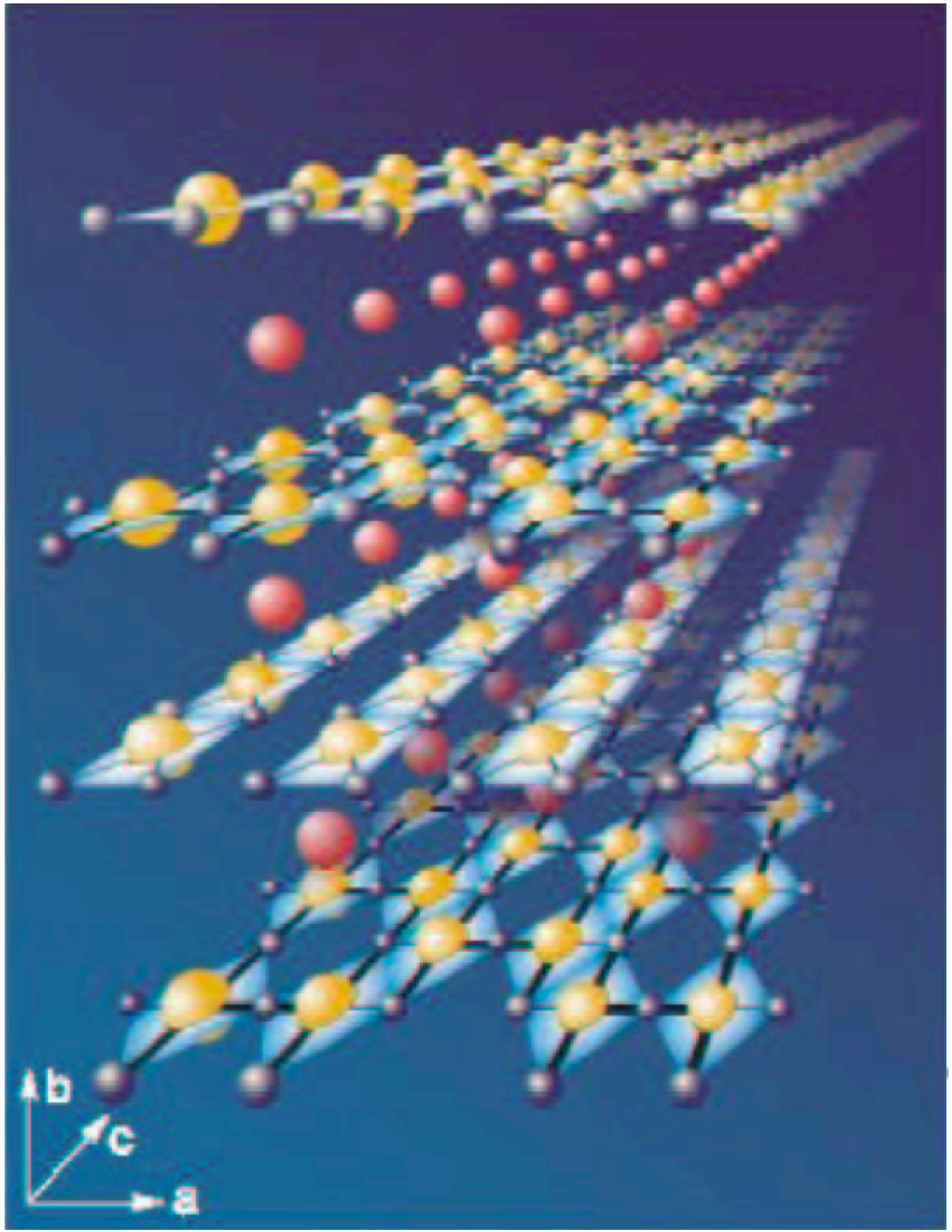
Superconductivity not automatic – models also reveal a "charge density wave"

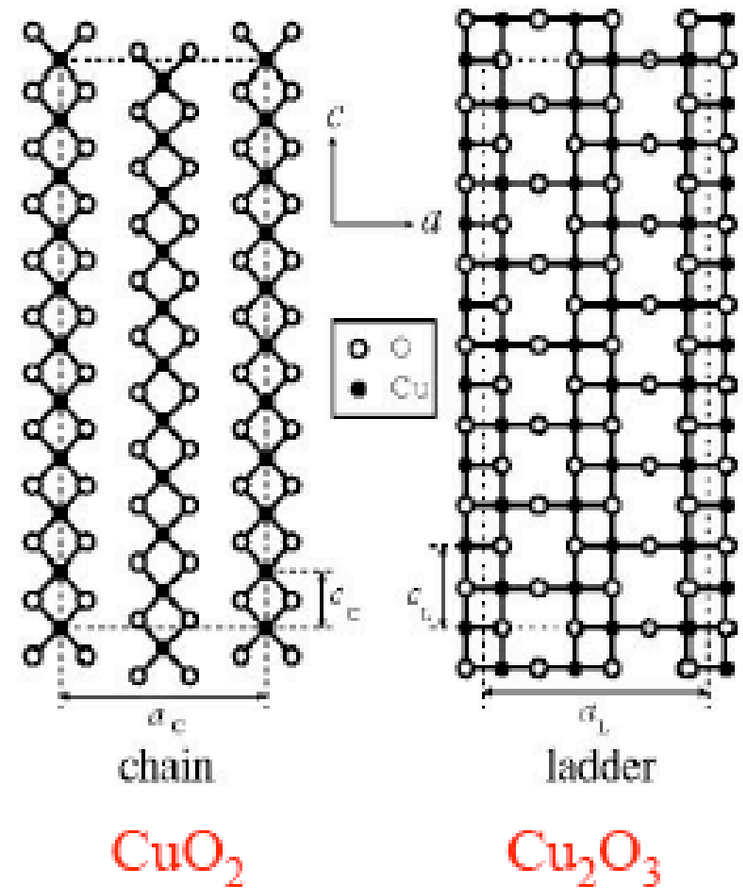




- holes "crystallize", drive system insulating
- Particularly stable for d rational (commensurate)
- Almost a CDW: power law correlations $1/|n-n'|^{K+r}$. Friedel oscillations easily induced.
- Reminiscent of ordered stripes vs. SC in perovskite cuprates
- *Not high T_c, but worthy of study in its own right*

$Sr_{14-x}Ca_xCu_{24}O_{41}$





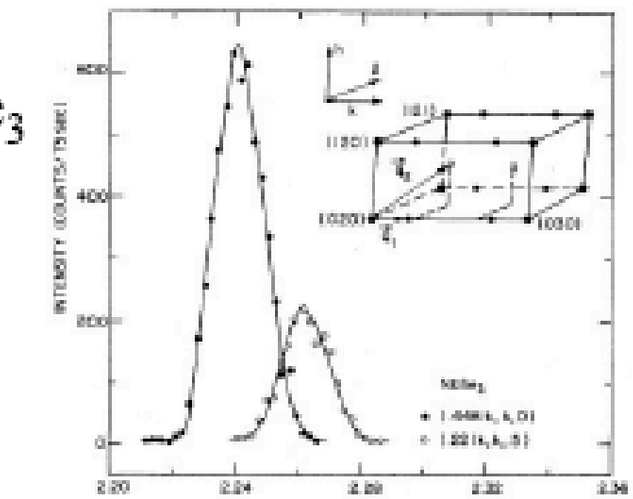
- $x = 13.6 \Rightarrow$ superconductivity $T_c = 12$ K at P = 3 GPa [2]
- $x = 0 \Rightarrow$ insulating with a CDW [3]
- $m^* \sim 50$ ($10^3 - 10^4$ more typical) [4]
- Exhibits characteristics of *both* phases predicted by Dagotto (1992)

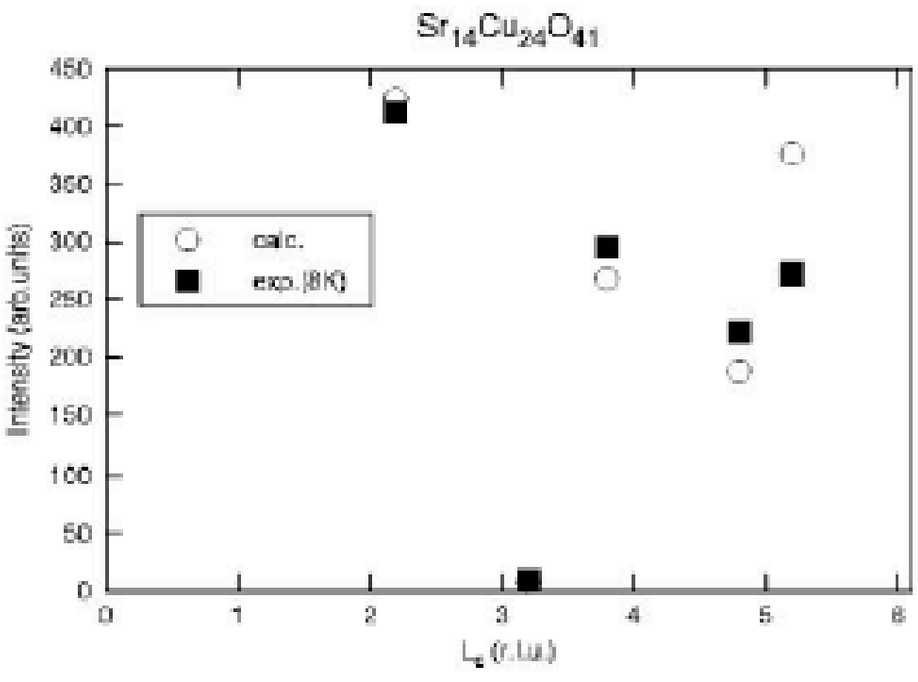
Study with x-ray scattering?

1. modulation wavelength (commensurate?)
2. coherence length
3. form factor (sinusoidal?)
4. D(T) (mean field or no?)

R. M. Fleming, D. E. Moncton, and D. B. McWhan, *Phys. Rev. B*, **18**, 5560 (1978)

$NbSe_3$





T. Fukuda, *PRB*, **66**, 12104 (2002)

[refinement of study by D. E. Cox, *PRB*, **57**, 10750 (1998)]

L_c	L	(l,m)
1.5	15	(-2,5)
2.2	22	(-2,6)
3.2	32	(-1,6)
3.8	38	(1,4)
4.8	48	(2,4)
5.2	52	(1,6)

S. van Smaalen, *PRB*, **67**, 26101 (2003)

Conclusion: no obvious evidence for a CDW in $Sr_{14}Cu_{24}O_{41}$

Two types of CDWs

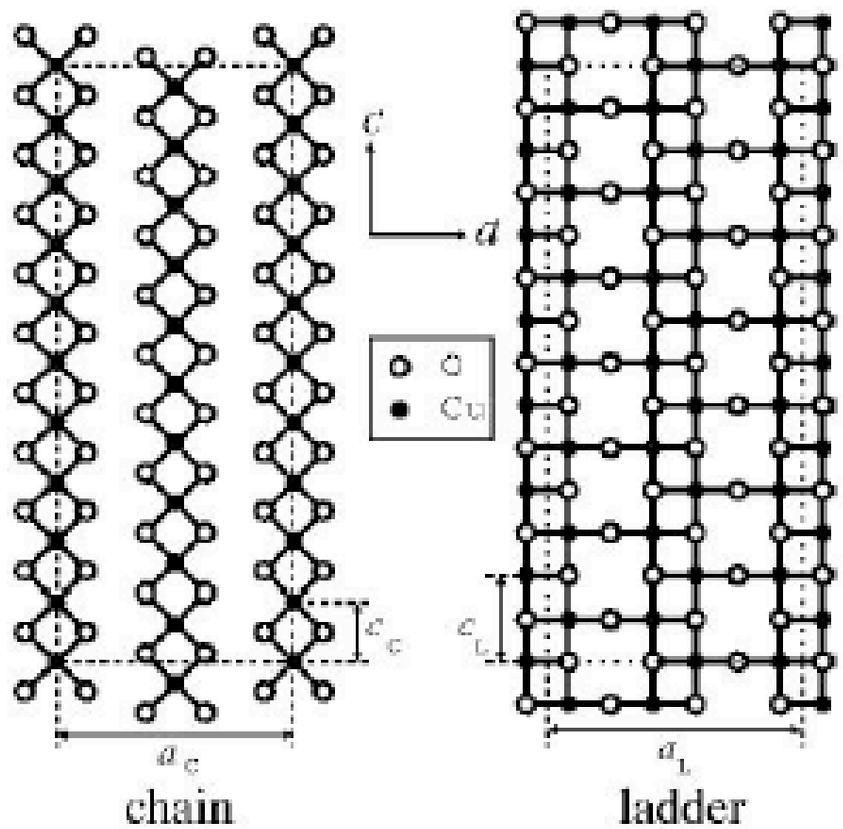
	Peierls CDW	***Wigner crystal*** [E. Wigner, *Phys. Rev.*, **46**, 1002 (1934)]
Examples	$NbSe_3$, $K_{0.3}MoO_3$	^{3}He surface, 2DEG, (Mott state!)
Mechanism	H_{ep}	Coulomb
Effective mass	$\sim 10^3 - 10^4$	???
Charge modulation	$\sim Z = 10^1 - 10^2$	$\sim U \cdot \mathsf{r}(E_F) \sim 10^{-2}$
Cross section	$\sim Z^2 \sim 10^2 - 10^4$	$\sim 10^{-4}$
Bottom line	Easy to measure	Hard to measure

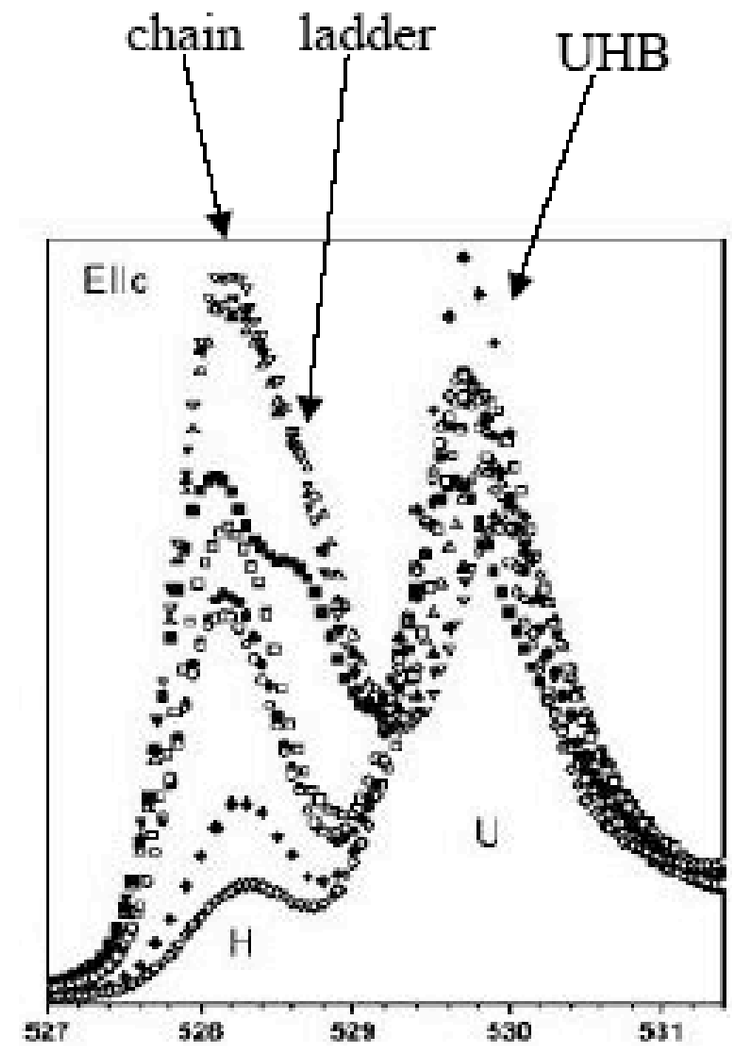
Scattering from Wigner crystal *nominally* weaker by $\sim 10^{-6}$

Hole crystal predicted by Dagotto et. al. is Wigner, not Pieierls.

Could a Wigner crystal (many-body CDW) be responsible for the transport properties of $Sr_{14}Cu_{24}O_{41}$?

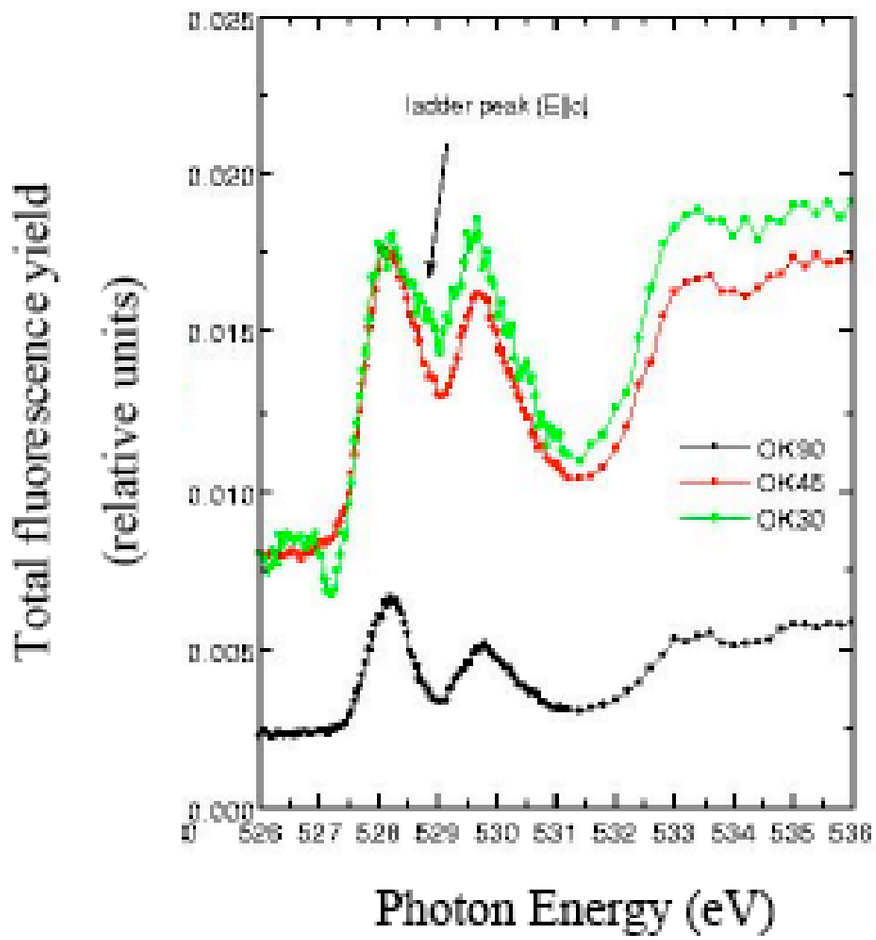
Edge structure in $Sr_{14}Cu_{24}O_{41}$

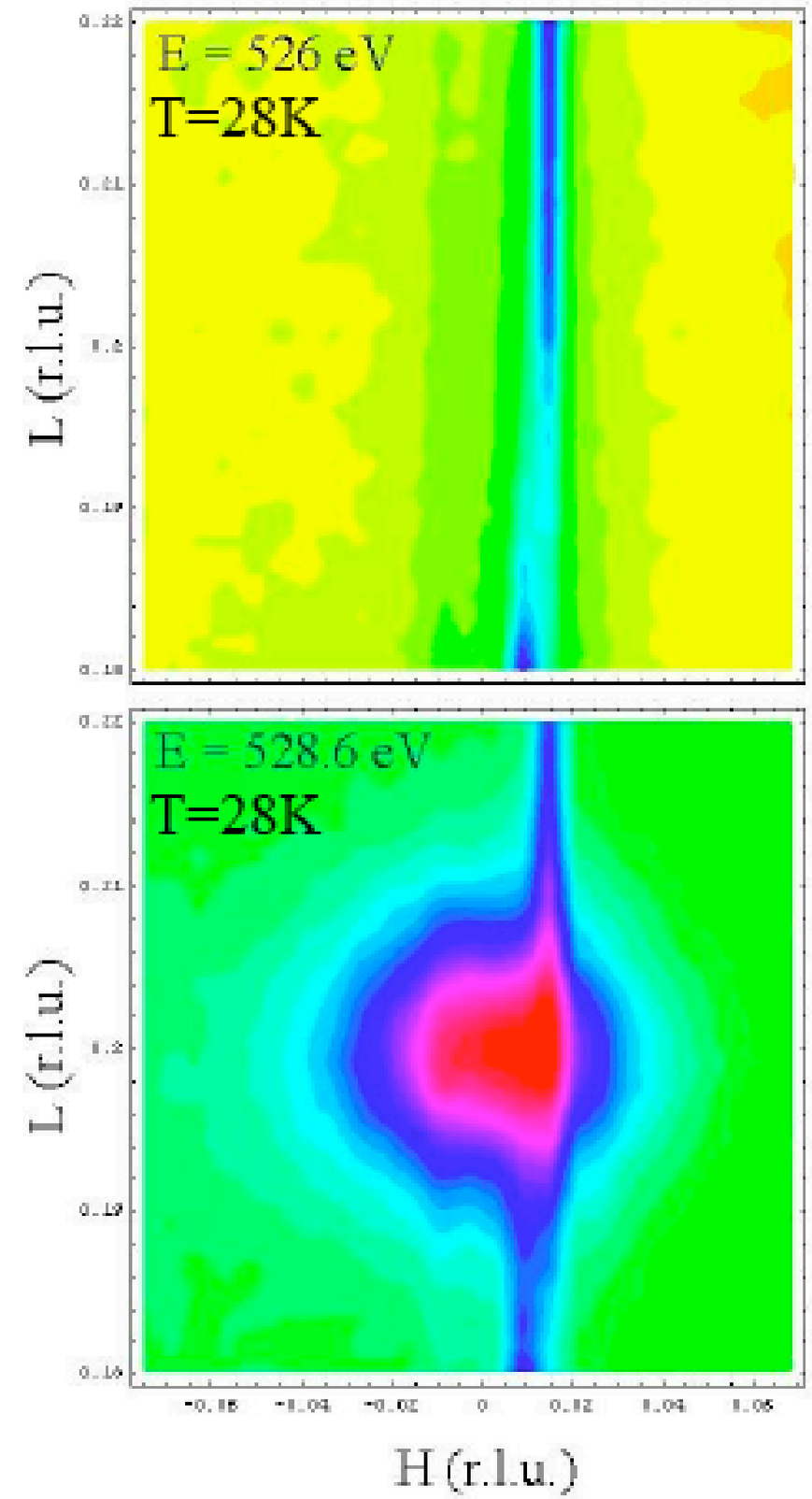




N. Nücker, et. al., *PRB*, **62**, 14384 (2000)

Valence modulation in $Sr_{14}Cu_{24}O_{41}$



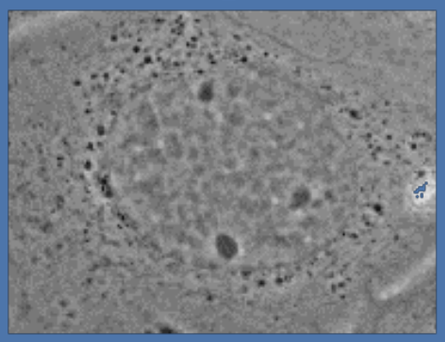


- $L = 0.200 \pm 0.009$ r. l. u. $\Rightarrow$ l $= 5.00 \pm 0.24\ c_L$.
- *Does not index to 27.3 Å unit cell.*
- $x_c = 255$ Å, $x_a = 274$ Å
- No measurable off-resonant signal $\Rightarrow$ purely electronic phenomenon

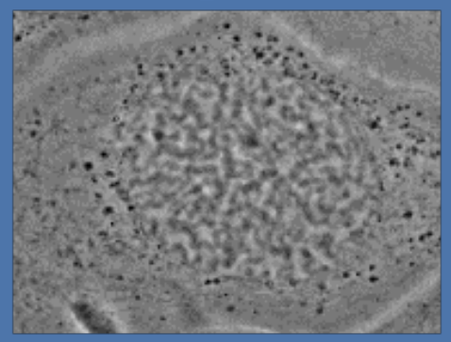
John Marko (UIC) X-ray study of mitotic chromosome structure

Cell division

Interphase



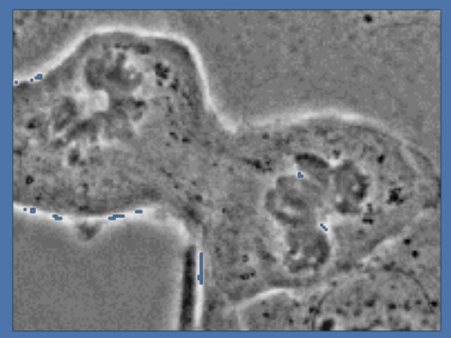
Prophase



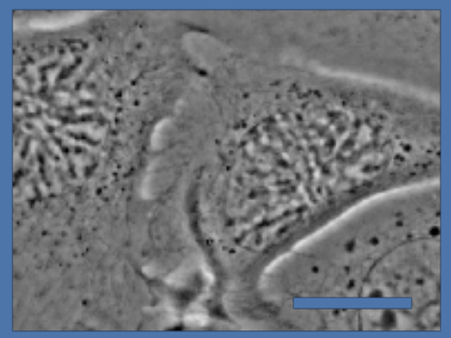
Metaphase

Anaphase

Telophase

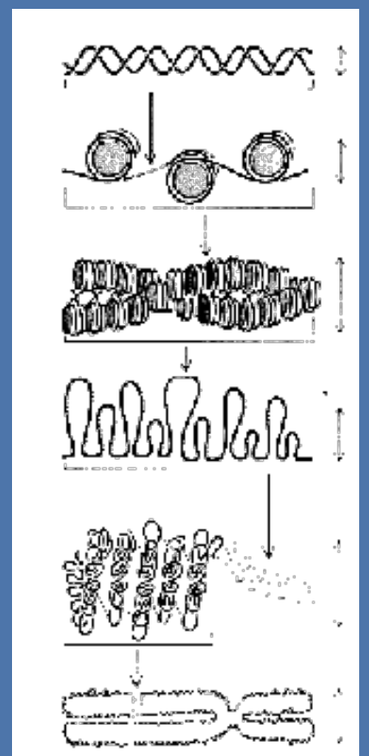


Two daughter cells

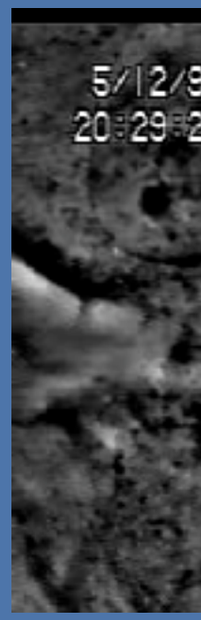


Chromosome hierarchy

Bar: 20 μm



2 nm	DNA double helix
11 nm	DNA wrapped around proteins
30 nm	Chromatin Fiber
300 nm	Loop Folding
700 nm	Helical Folding
1400nm	Metaphase Chromosome

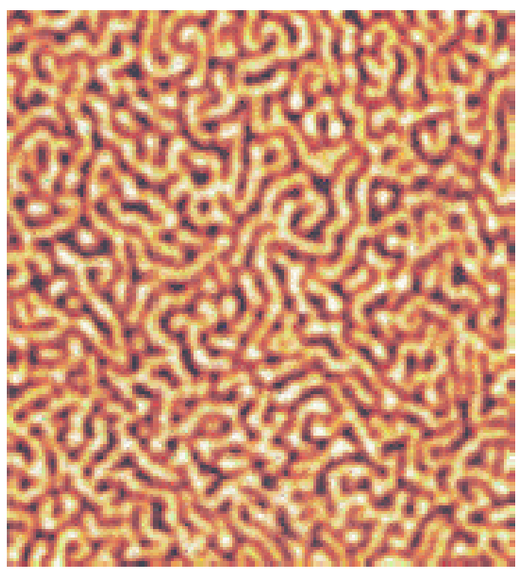


Coherent imaging, others

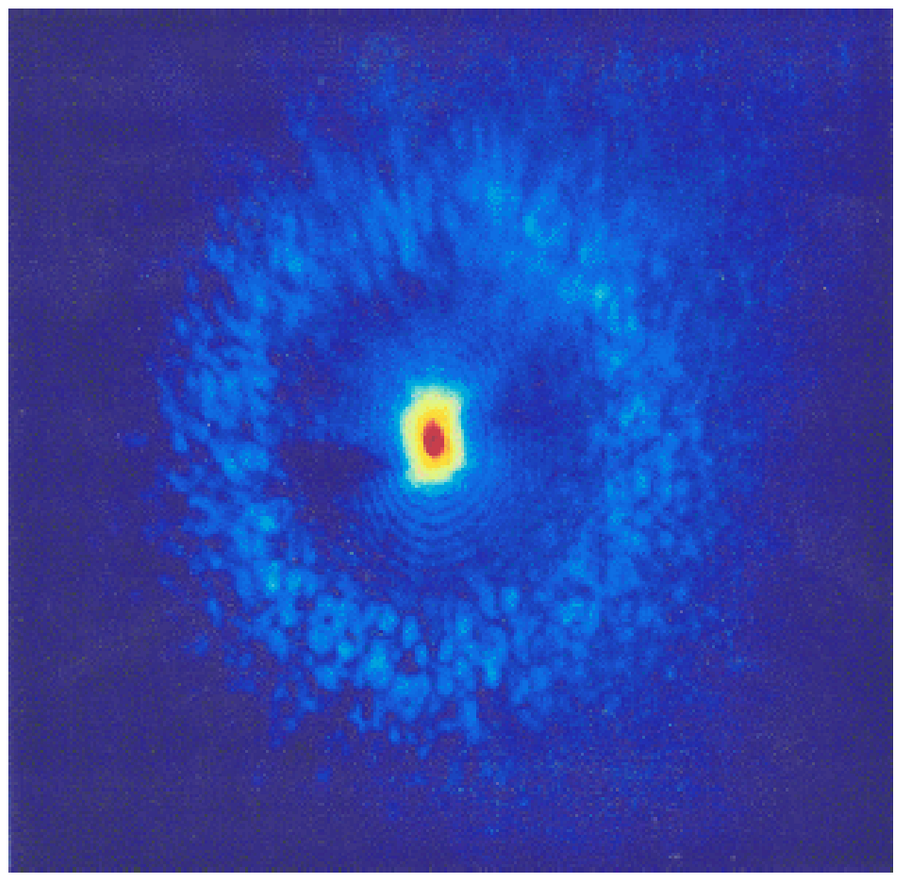
- John Freeland, David Patterson (APS) 2-ID-B, 4-ID-C
- Steve Kevan (University of Oregon) - Coherent soft x-ray magnetic scattering
- Pupa de Stasio (UW)(University of Wisconsin) - Spectromicroscopy of cells, tissues and minerals at the 10-100 nanometer scale
- Uwe Weierstall (Arizona State University) - Coherent x-ray diffractive imaging at the Advanced Light Source

Coherent Soft X-ray Scattering

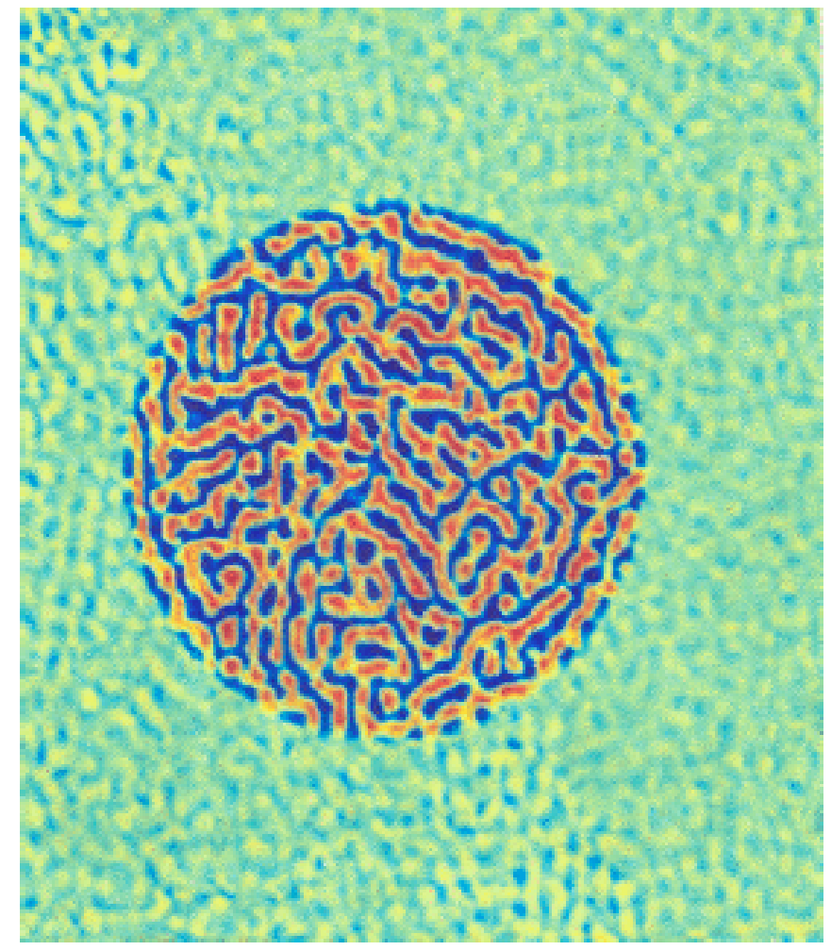
Magnetic "Worm" Domains



X-ray Speckle Pattern



Domain Reconstruction



Example of a New Collaboration:

- oxide thin films, correlated electrons, nanomagnetism, electron spectroscopy
- UBC, SFU, FZ – Juelich, IBM Almaden, Stanford University, BESSY

Primary Brain Neoplasia: Incidence

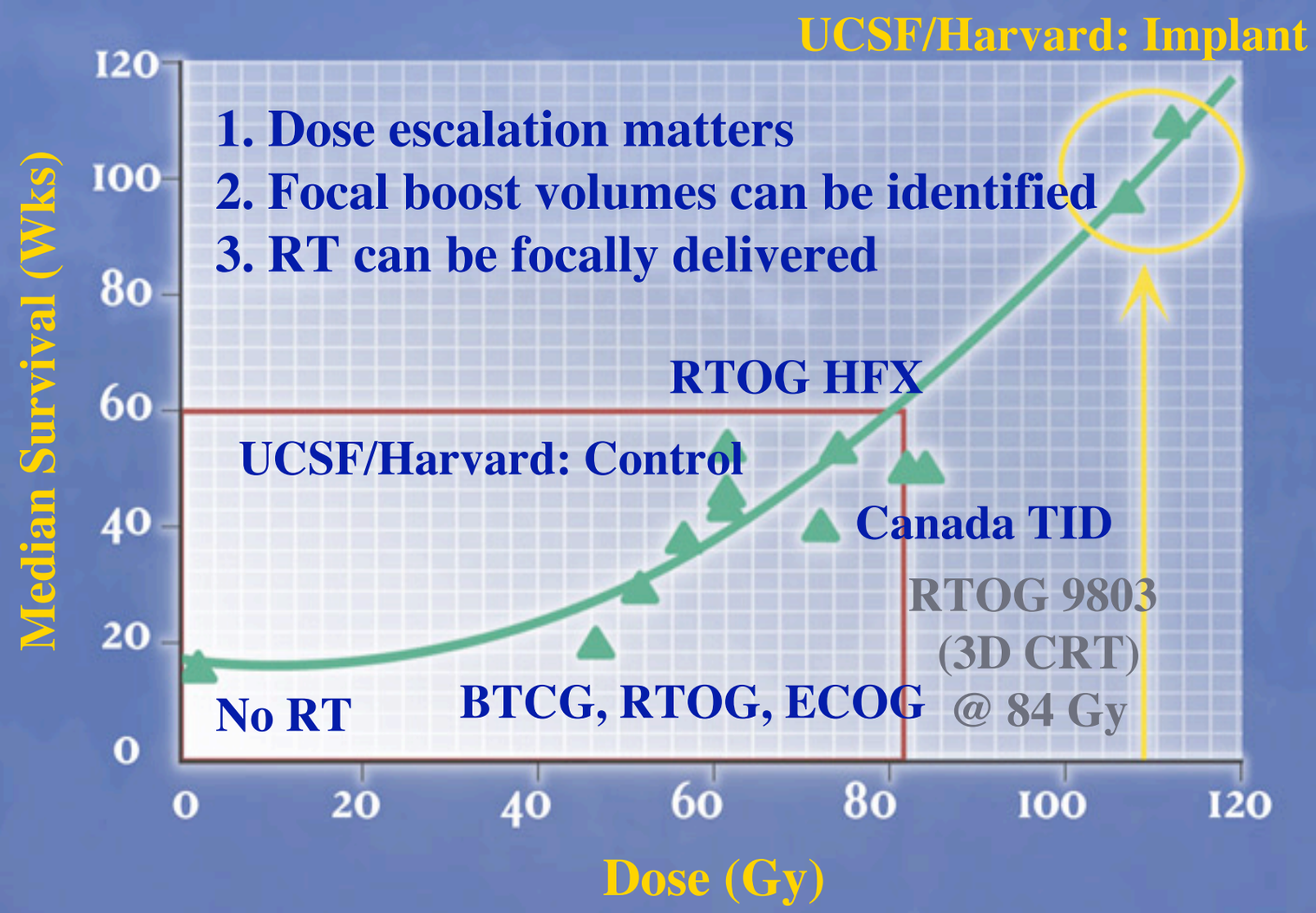
- 16,500 new cases predicted[1]
- 13,000 deaths/year[1]
- 1.4% of all cancers and 2.4% of all cancer deaths[2]
- 20%–25% of pediatric cancers[2,3]
- 60% are malignant glioma[3]

1. Greenlee RT et al. *CA Cancer J Clin*. 2000;50:7-33.
2. http://www.cancer.org/. Accessed June 2000.
3. Chamberlain MC, Kormanik PA. *West J Med*. 1998;168:114-120.

Gliomas: Median Survival

Tumor Type	MS (mo)
Low Grade Oligodendroglioma	~120
Low Grade Astrocytoma	~60
Anaplastic Oligodendroglioma	~60
Anaplastic Astrocytoma	~36
Glioblastoma Multiforme	**< 12**

GBM: Dose Escalation



Gadolinium Neutron Capture Therapy

Why Gd?

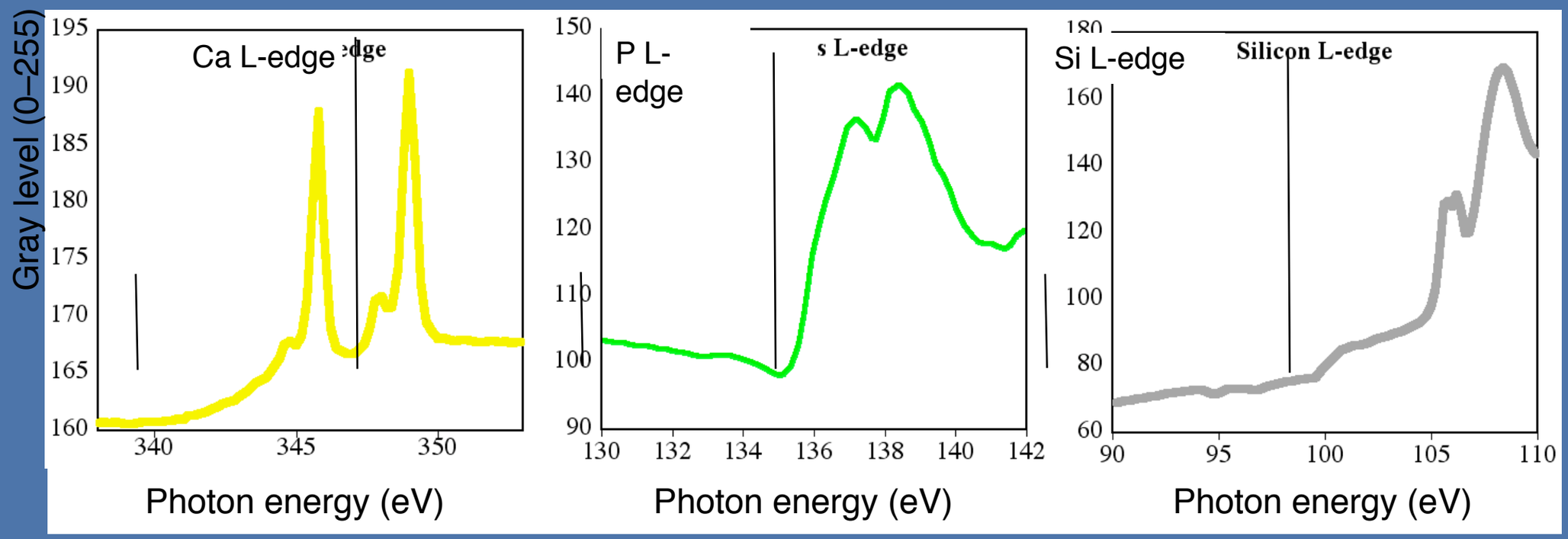
❶ Thermal neutron cross section for Gd is 254,000 barn

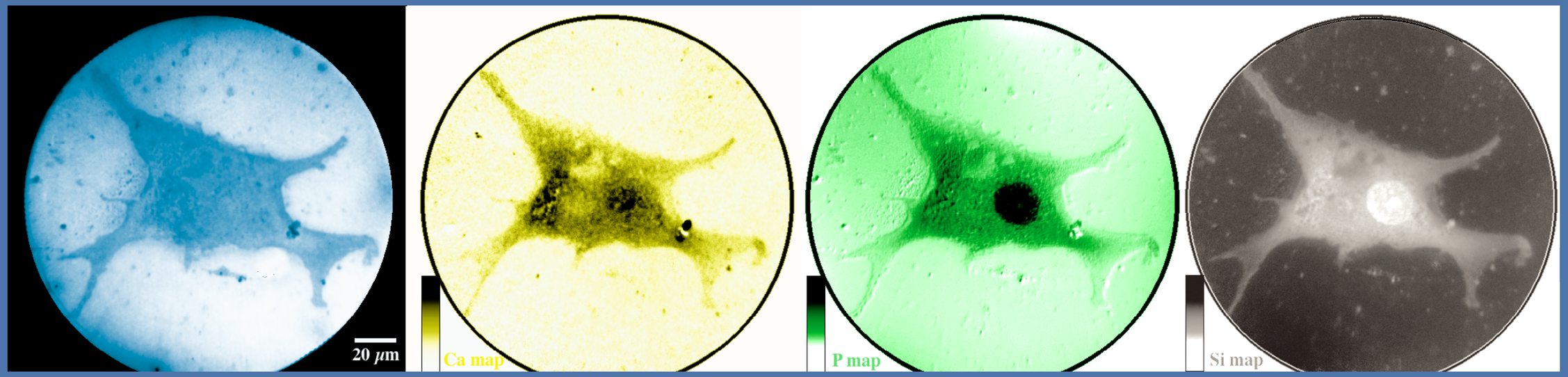
for ^{16}O is 0.00019 barn
for ^{12}C is 0.0035 barn
for ^{1}H is 0.333 barn
for ^{14}N is 1.83 barn

❷ Selective tumor uptake (MRI)

(for ^{10}B is 3,840 barn)

Gadolinium Neutron Capture Therapy Microchemistry of Glioblastoma cells *in vitro*



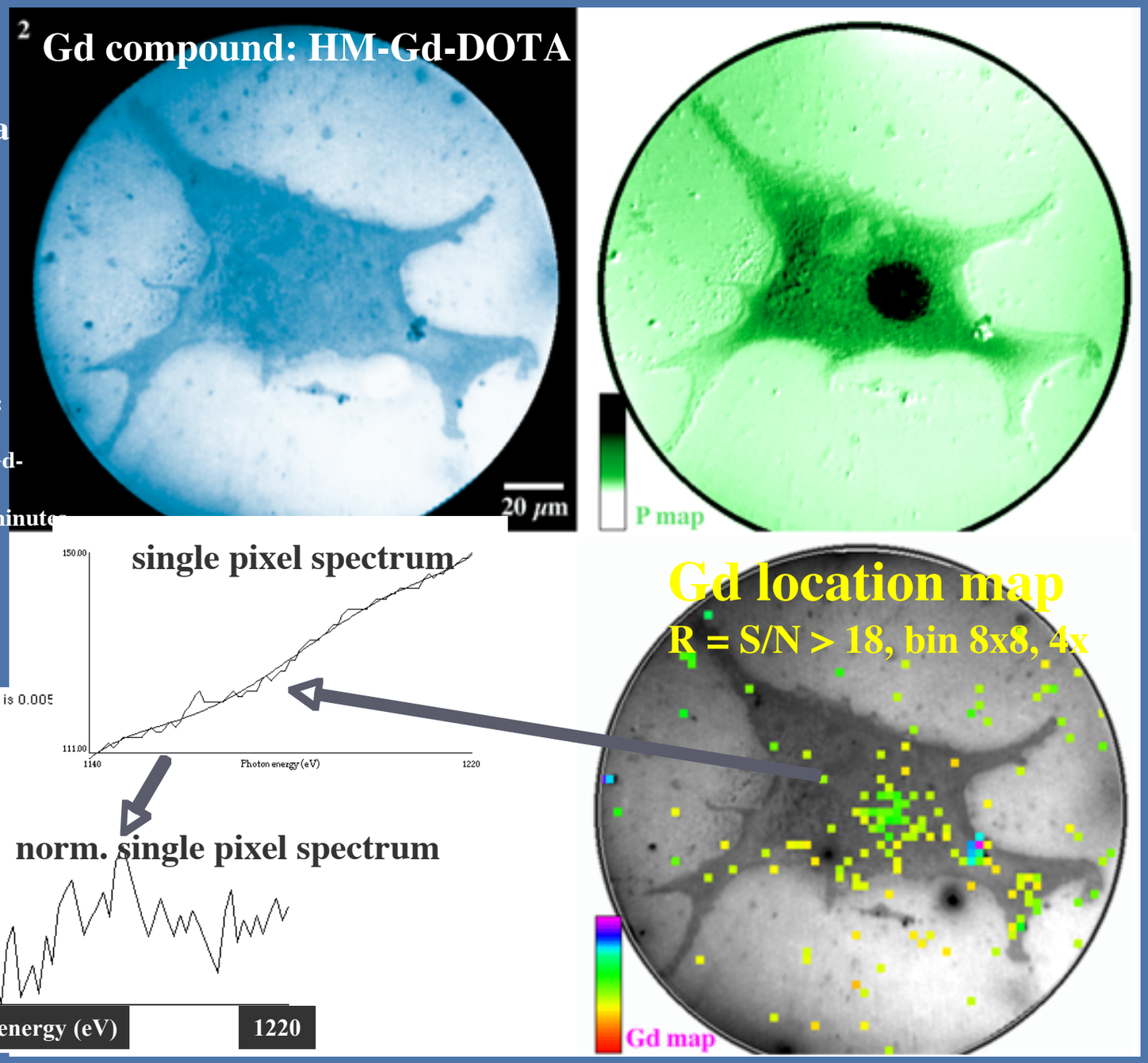


Cancer Research 61, 4272–4277, 2001

GDNCT

Gd in Glioblastoma cells *in vitro*

M059K Cell Preparation :
- Culture on Si wafer
- Exposed to 100 μM HM-Gd-DOTA 24 hrs
- Sputter with Ar 3kV 10 minutes
- Ash in UV/O_3 144 hrs



Reminder

$$\frac{\lambda}{1\text{Å}} = \frac{E}{12000\ \text{eV}}$$

3*d* Transition Metal Compounds

$L_{2,3}$ edge $2p \rightarrow 3d$

500 eV → 900 eV

20 Å → 12 Å

Rare Earth's (4*f* compounds)

$M_{4,5}$ edge $3d \rightarrow 4f$

800 eV → 1800 eV

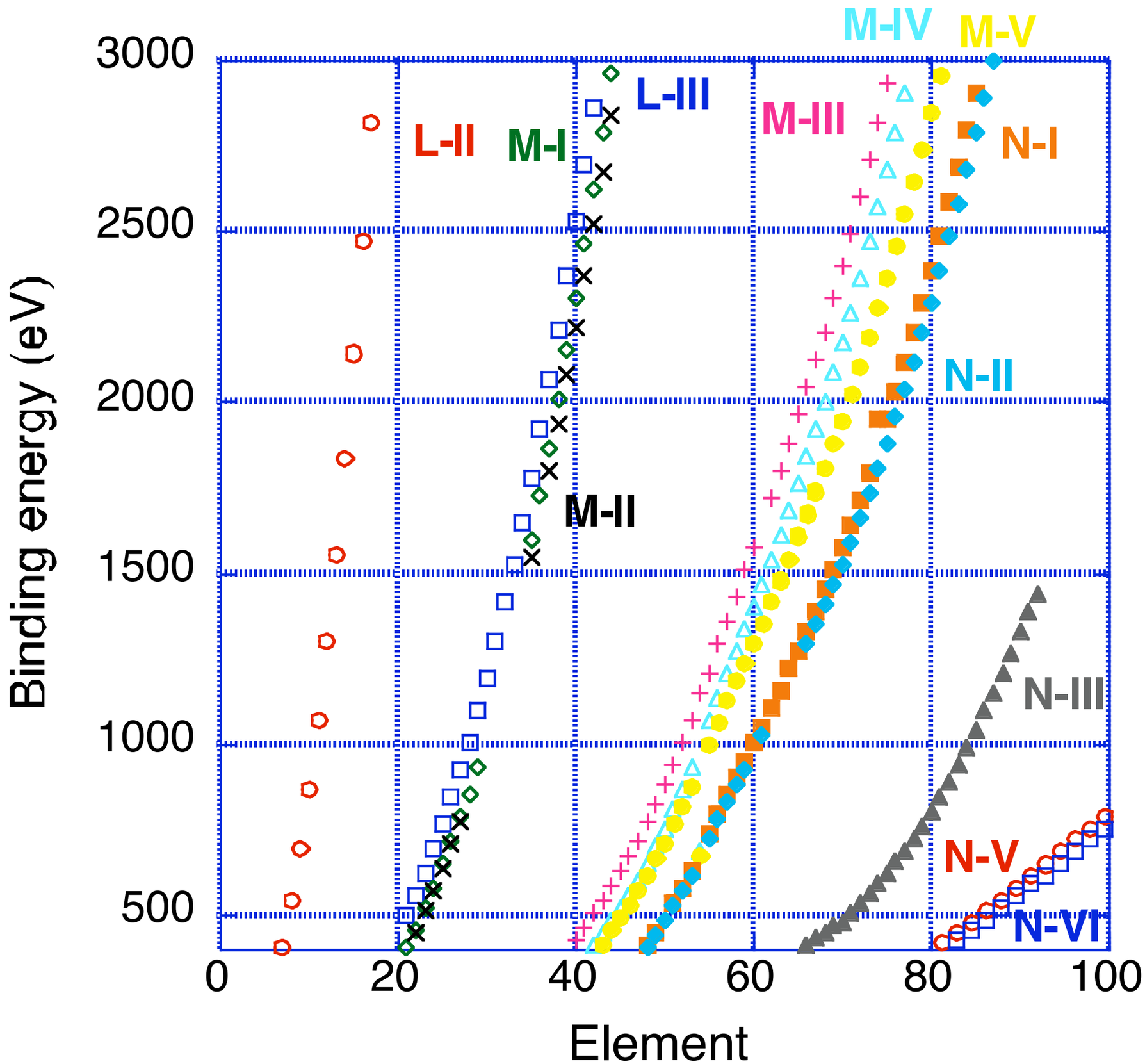
12 Å → 8 Å

C_{1s} - 280 eV → 40 Å

N_{1s} - 390 eV → 35 Å

O_{1s} - 530 eV → 25 Å

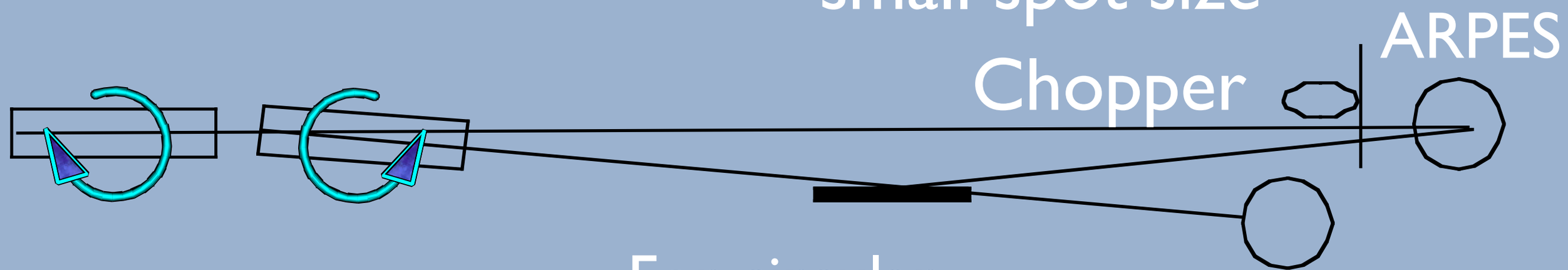
S_{1s} - 3000 eV → 4 Å


M-IV
M-V
L-III
M-III
L-II
M-I
N-I
N-II
M-II
N-III
N-V
N-VI
3000
2500
2000
1500
1000
500
0
20
40
60
80
100
Binding energy (eV)
Element

Proposed beamline

Beamline:

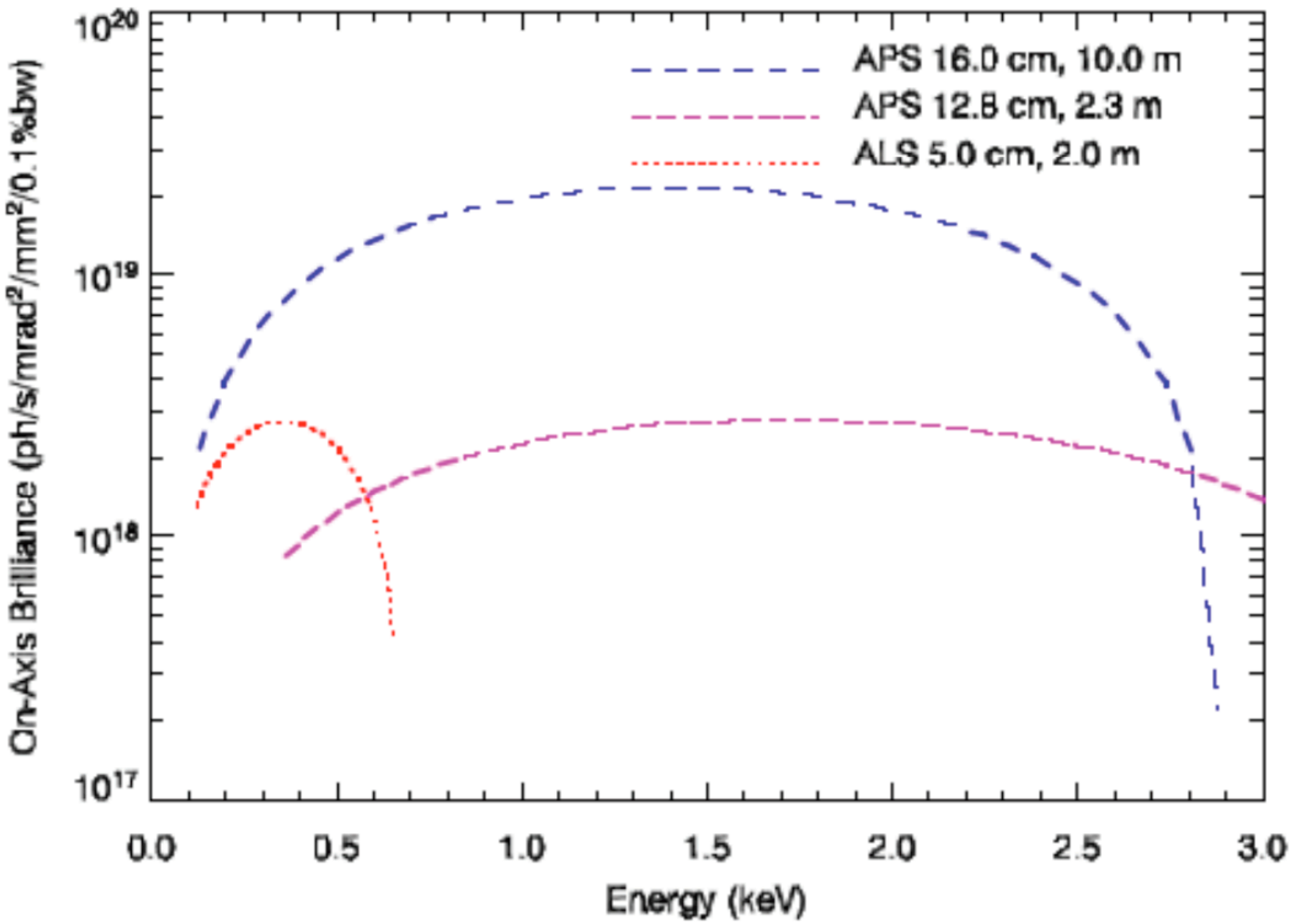
Vacuum UV
400-3000 eV
Very high resolution
small spot size



For circular
polarization exps
or low count rate,
both undulators combined

What can we do at the APS?

Brilliance Tuning Curves for Elliptically Polarized Devices



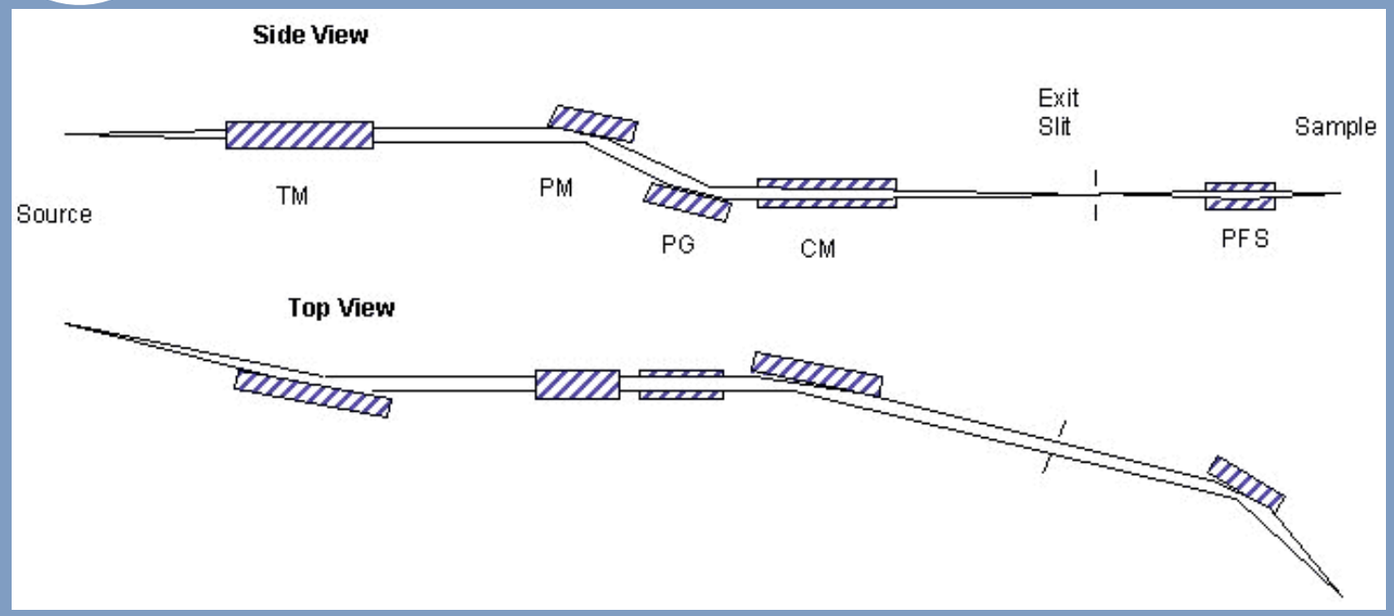
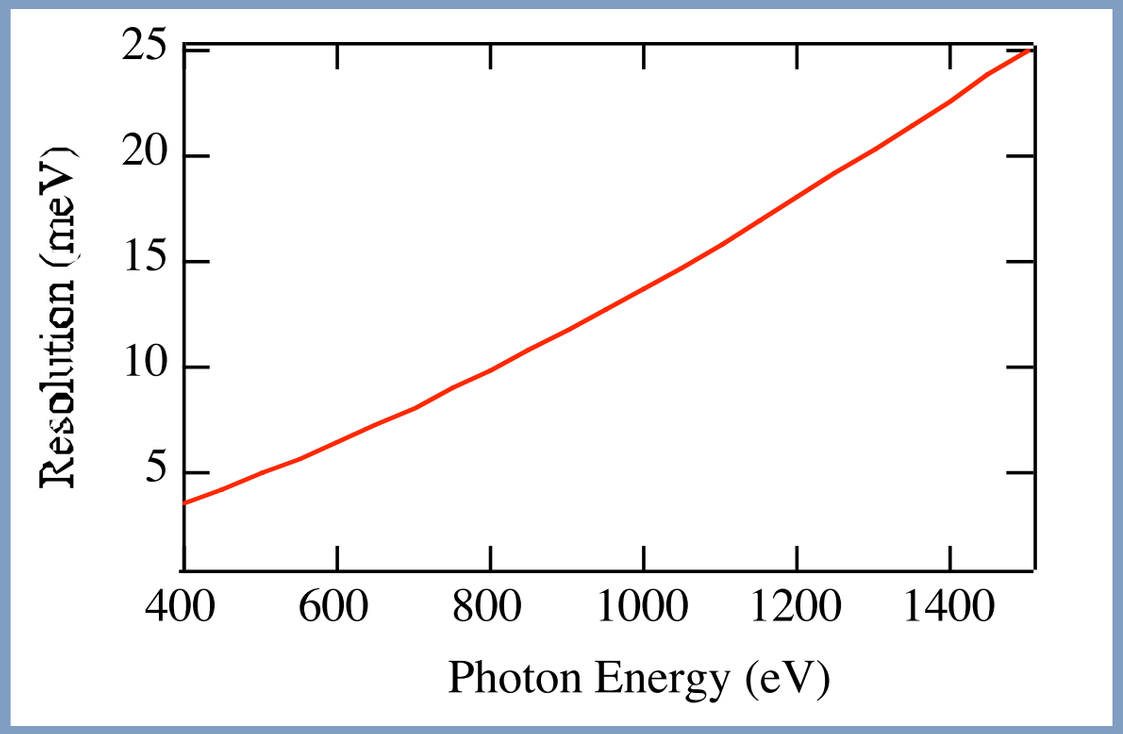
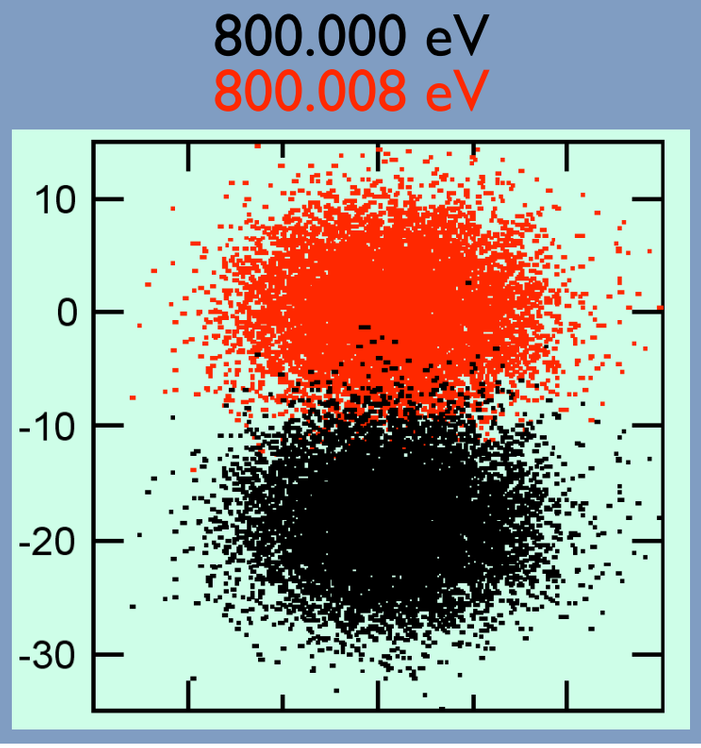
Advantages of high energy rin

- Low emittance
- High beam stability
- Large energy tunability

Superior performance

APS (7 GeV, 100 mA):10 m long straight section, =16.0 cm, N = 62
APS (7 GeV, 100 mA):5 m long straight section, =12.8 cm, N = 18 (current device)
ALS (1.9 GeV, 400 mA): 2 m long straight section, = 5.0 cm, N = 37

Proposed beamline. Design: R. Reininger



new design: only 4 mirrors VLS, exchange resolution for flux without slit change