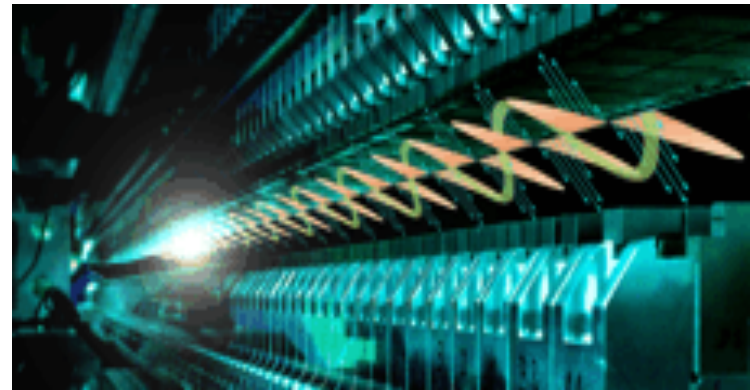
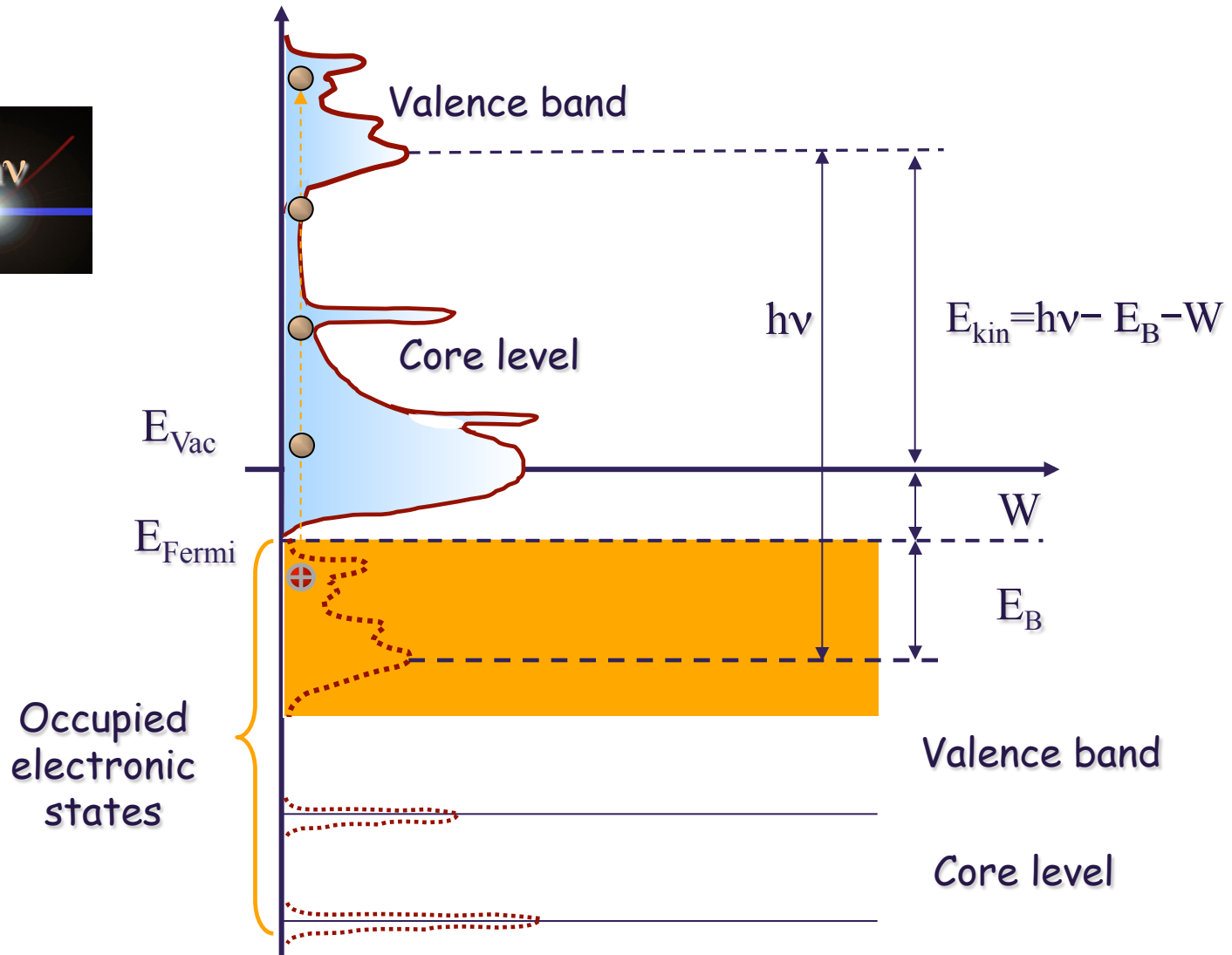
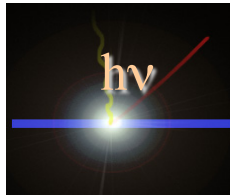
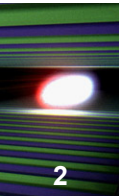


# *New Opportunities for PES of Condensed Matter Using FELs*

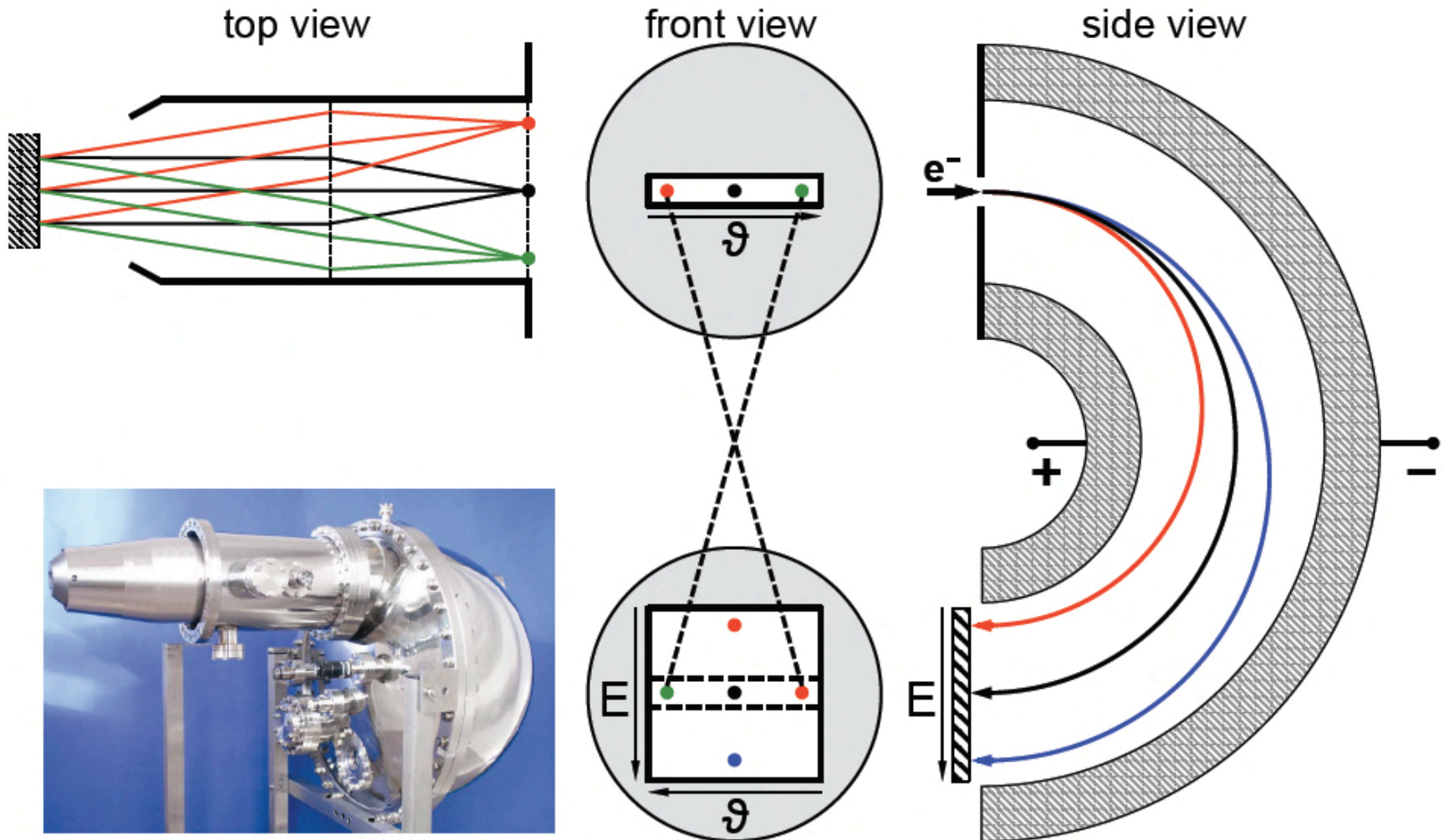
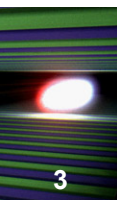
*S.L. Molodtsov  
European XFEL GmbH*



# Photoemission spectroscopy: Basics



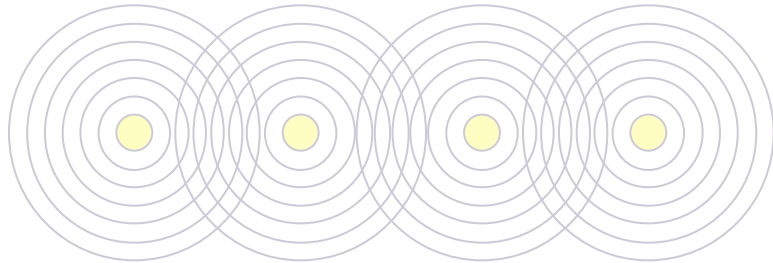
# Photoelectron analyzer



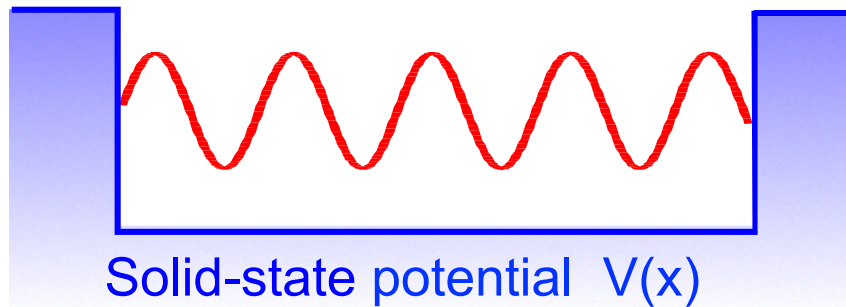
# Single-particle system

freie Elektronen :

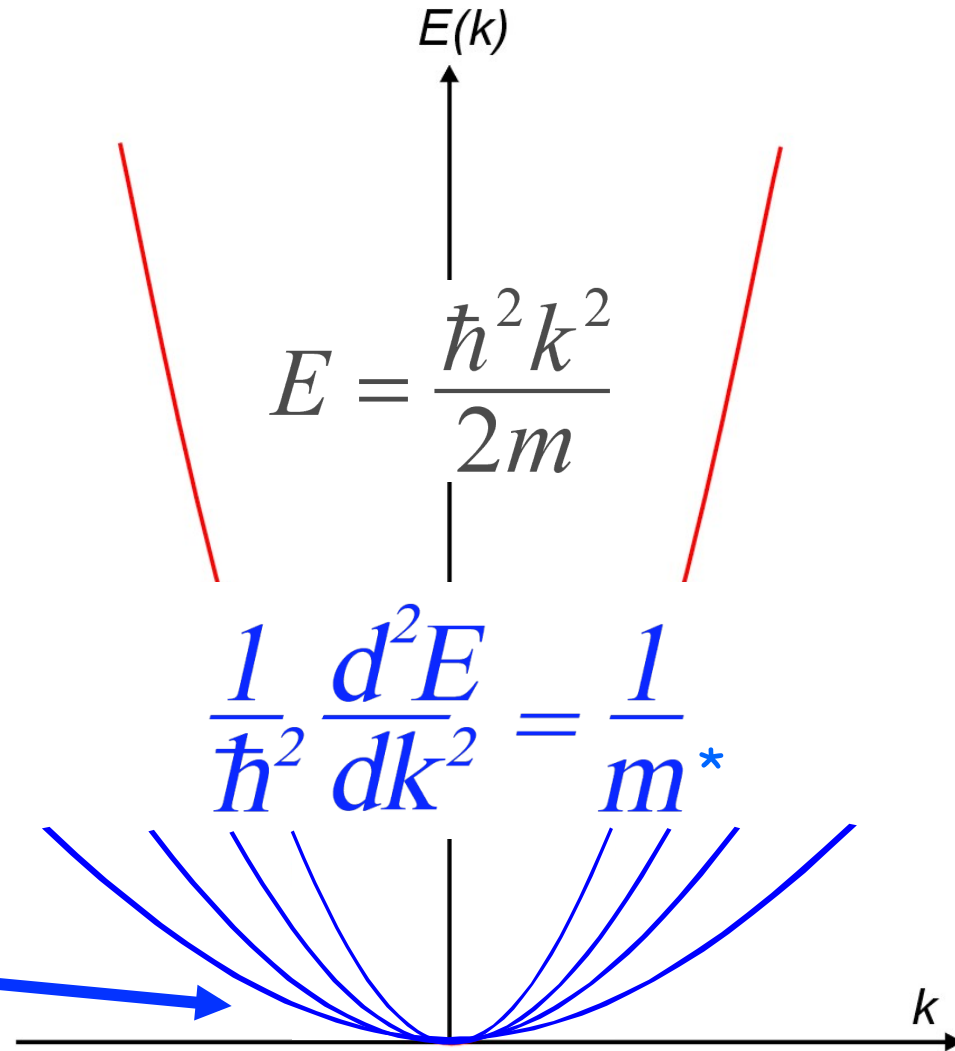
4



1 - dim. solid state:

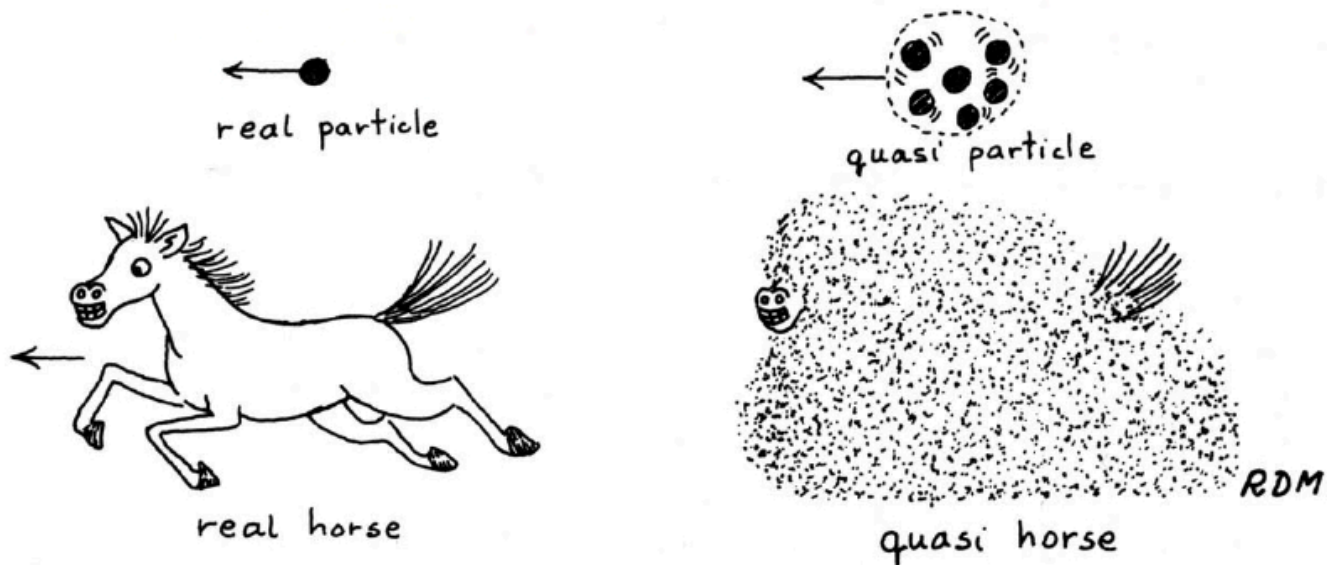
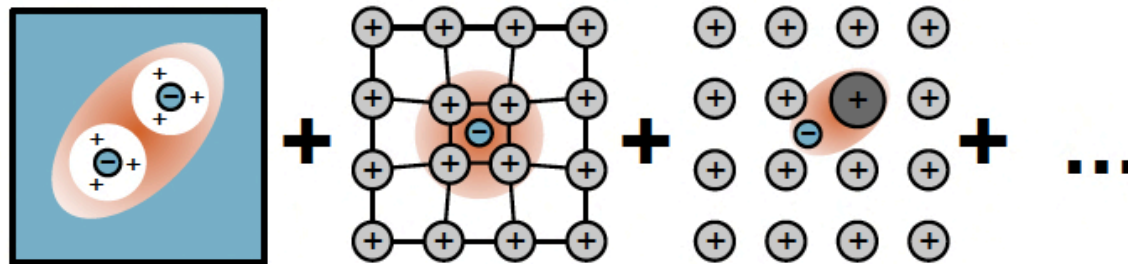


Heavy-fermion system

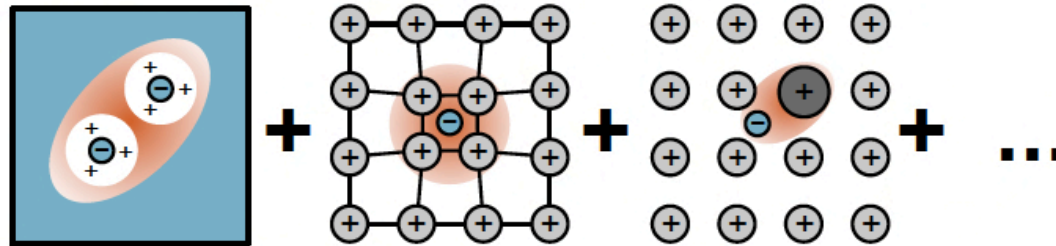




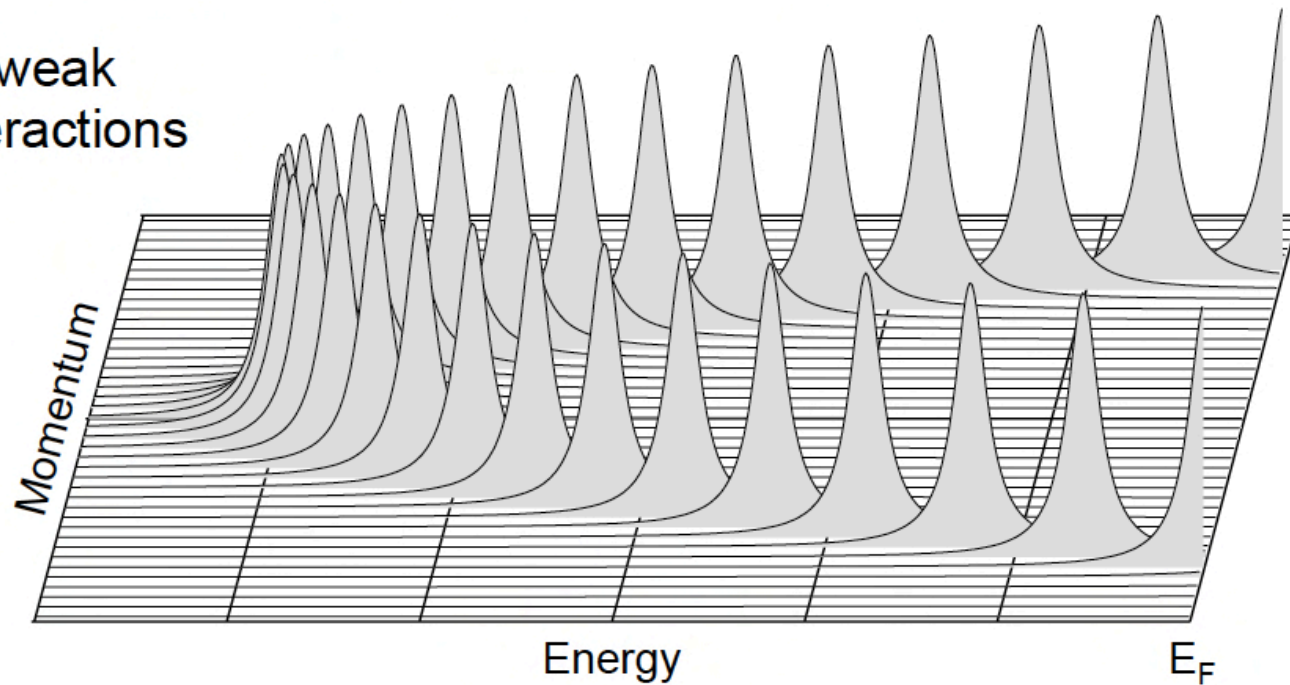
# Lead actor: The quasi-electron

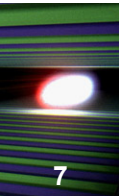


# Lead actor: The quasi-electron

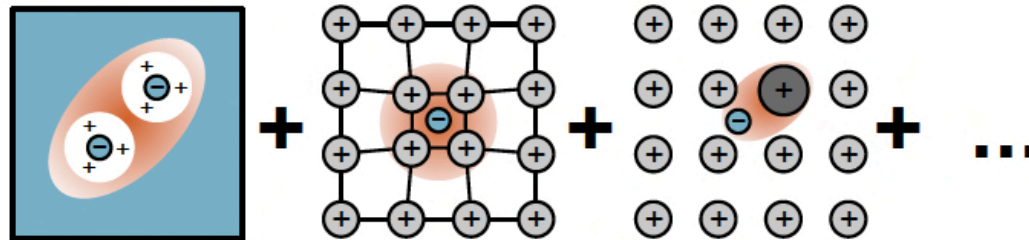


weak  
interactions

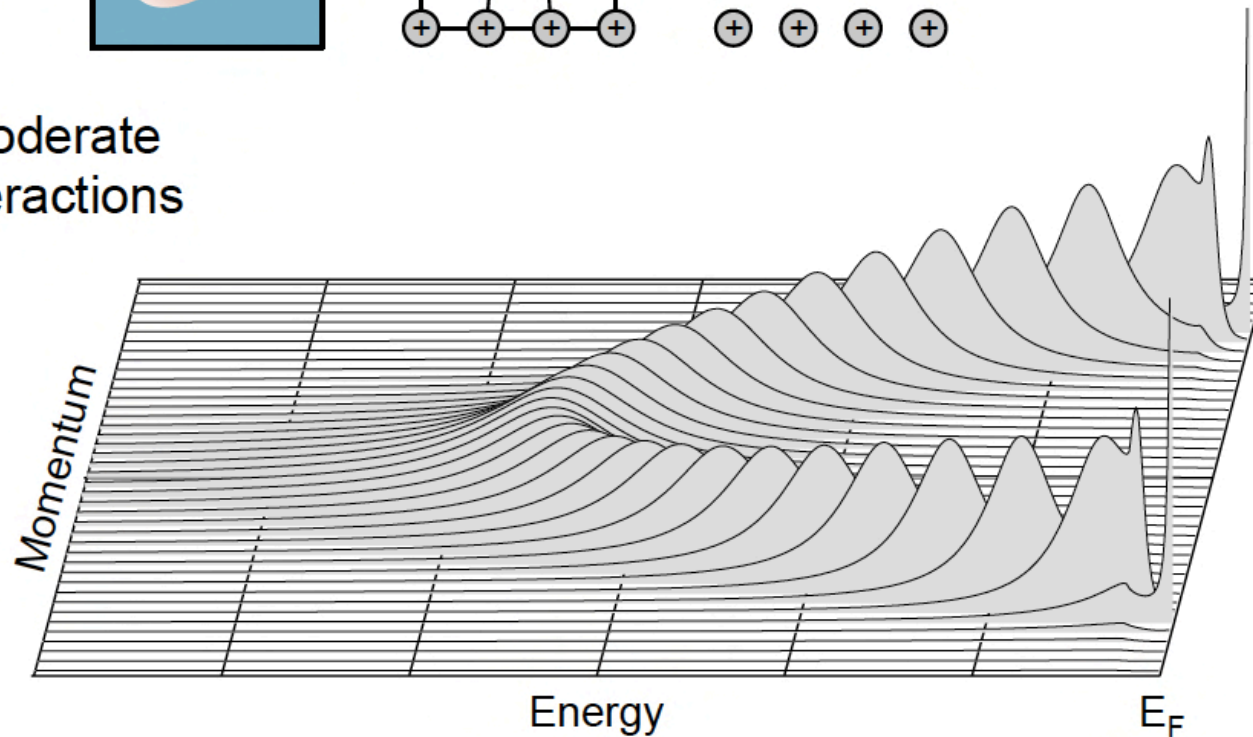




## Lead actor: The quasi-electron



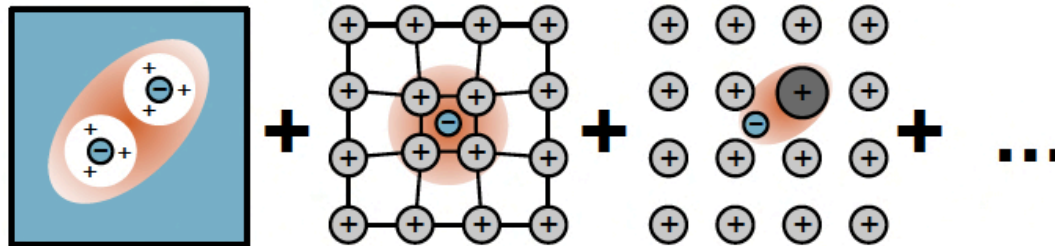
moderate  
interactions



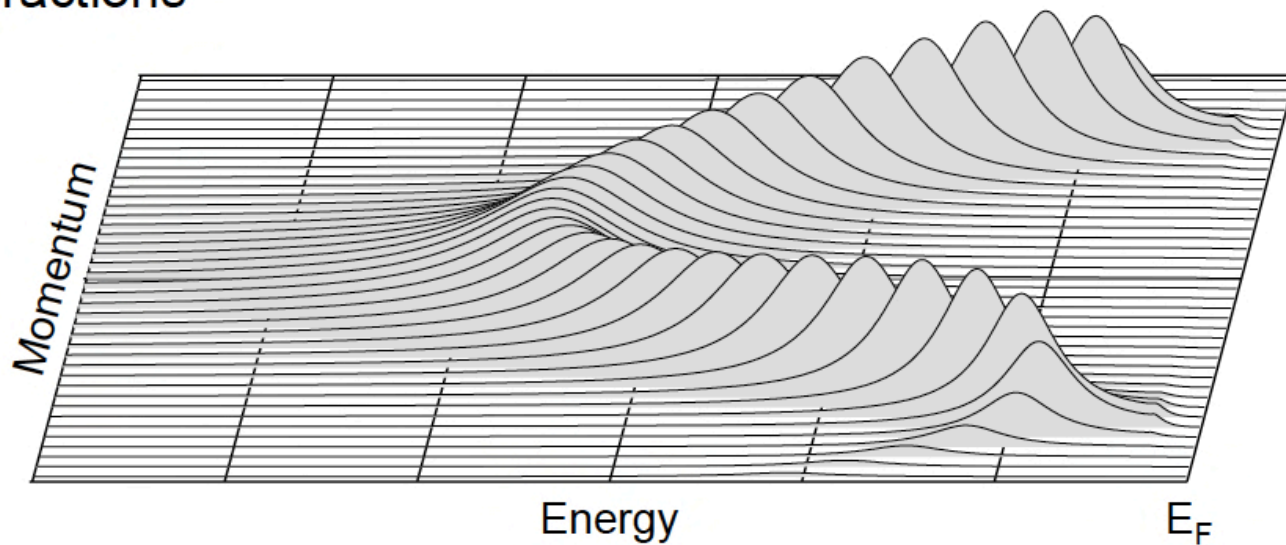
## Strong correlations

8

## Lead actor: The quasi-electron



strong  
interactions



# Nobel prize to X-ray spectroscopy work

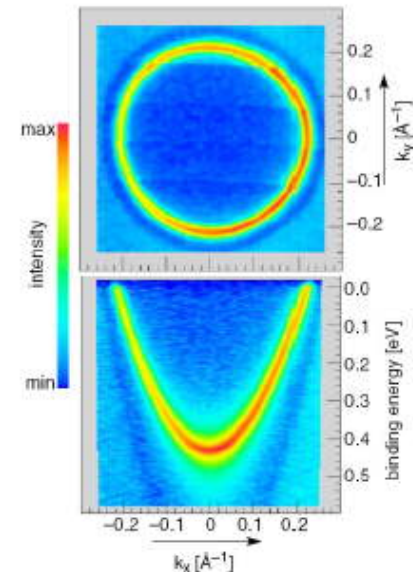
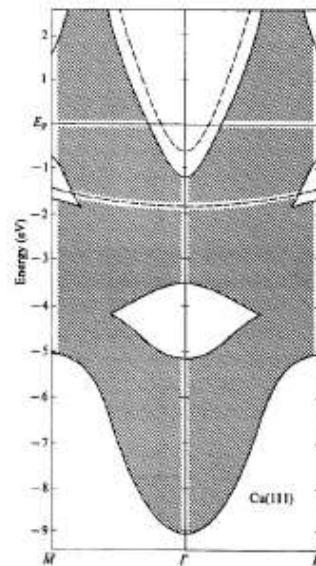
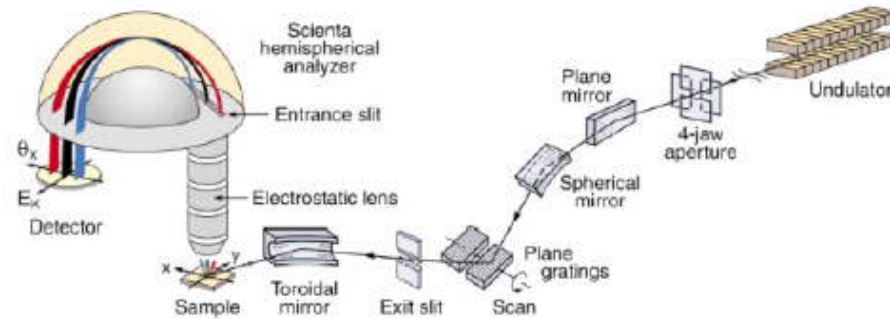
9



K. Siegbahn  
Nobelprize 1981

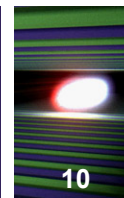
e.g. Cu-sp Shockley  
surface state

## Angle-resolved photoemission - ARPES



Taken from F. Reinert und S. H fner, New Journal of Physics 7, 97 (2005)





solid state



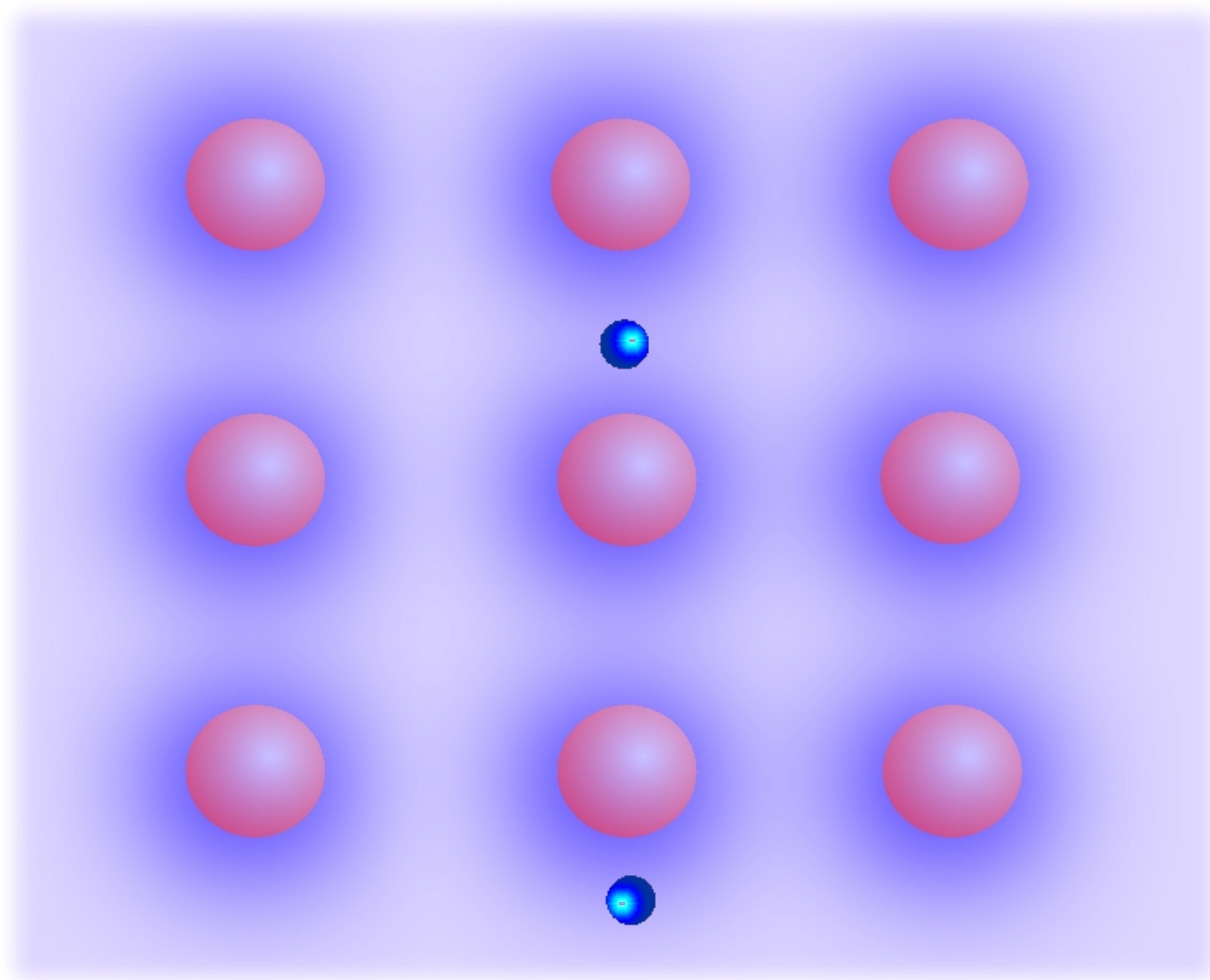
potential averaged  
over all electrons



single-particle  
calculations,  
LDA approach

**Problem:** ↓

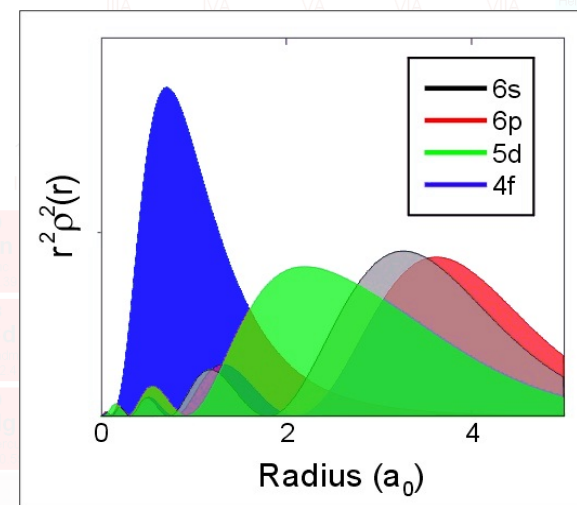
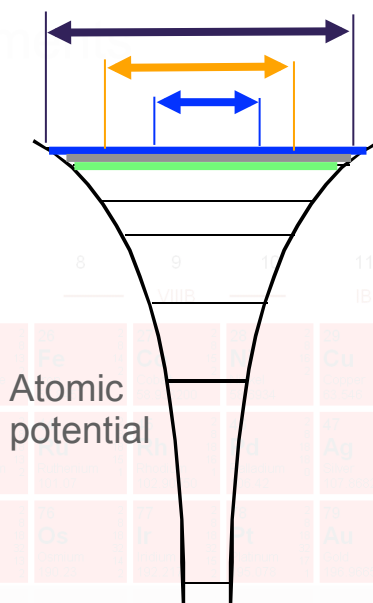
negligence  
of electron correlations





## Electron configuration:

1	2																	3	4	5	6																
1	H																	2	IIA																	2	
																		[Xe]		4f <sup>n</sup>		5d <sup>m</sup>		6s <sup>2</sup>													
3	Li																	4	Be																		
																		Lithium 6.941		Beryllium 9.012182																	
5	B																	6	C																		
																		Boron 10.811		Carbon 12.0107																	
7	N																	8	O																		
																		Nitrogen 14.00643		Oxygen 15.999																	
9	F																	10	Ne																		
																		Fluorine 18.998403		Neon 20.1797																	
11	Na																	12	Mg																		
																		Sodium 22.989770		Magnesium 24.3050																	
13	Al																	14	Si																		
																		Aluminum 26.981538		Silicon 28.0855																	
15	P																	16	S																		
																		Phosphorus 30.973762		Sulfur 32.06																	
17	Cl																	18	Ar																		
																		Chlorine 35.453		Argon 39.948																	
19	K																	20	Ca																		
																		Potassium 39.0983		Calcium 40.078																	
21	Sc																	22	Ti																		
																		Scandium 44.955912		Titanium 47.88																	
23	V																	24	Cr																		
																		Vanadium 50.9415		Chromium 51.9961																	
25	Mn																	26	Fe																		
																		Manganese 54.938045		Iron 55.845																	
27	Co																	28	Ni																		
																		Cobalt 58.933195		Nickel 58.6934																	
29	Cu																	30	Zn																		
																		Copper 63.546		Zinc 65.38																	
31	Ga																	32	Ge																		
																		Gallium 69.723		Germanium 72.64																	
33	As																	34	Se																		
																		Arsenic 74.9216		Selenium 78.96																	
35	Br																	36	Kr																		
																		Bromine 79.904		Krypton 83.80																	
37	Rb																	38	Sr																		
																		Rubidium 85.4678		Strontium 87.62																	
39	Y																	40	Zr																		
																		Yttrium 88.90584		Zirconium 91.224																	
41	Nb																	42	Mo																		
																		Niobium 92.90638		Molybdenum 95.94																	
43	Tc																	44	Ru																		
																		Technetium 98		Ruthenium 101.07																	
45	Rh																	46	Pd																		
																		Rhodium 102.9055		Palladium 106.36																	
47	Ag																	48	Cd																		
																		Silver 107.8682		Cadmium 112.411																	
49	In																	50	Hg																		
																		Indium 114.818		Mercury 200.59																	
51	Sb																	52	Te																		
																		Antimony 121.757		Tellurium 127.6																	
53	Bi																	54	Po																		
																		Bismuth 208.9804		Polonium 209																	
55	Cs																	56	Ba																		
																		Cesium 132.90545		Barium 137.327																	
57 to 71																	57 to 71																				
73	Tl																	74	Pb																		
																		Thallium 204.3833		Lead 207.2																	
75	Bi																	76	Po																		
																		Bismuth 208.9804		Polonium 209																	
77	Ir																	78	Pt																		
																		Iridium 223.0289		Platinum 231.036																	
79	Au																	80	Hg																		
																		Gold 196.96657		Mercury 200.59																	
81	Tl																	82	Pb																		
																		Thallium 204.3833		Lead 207.2																	
83	Bi																	84	Po																		
																		Bismuth 208.9804		Polonium 209																	
85	At																	86	Rn																		
																		Astatine 210		Radon 222																	
87 to 103																	87 to 103																				
105	Db																	106	Sg																		
																		Dubnium 261		Seaborgium 266																	
107	Bh																	108	Hs																		
																		Bohrium 264		Hassium 277																	
109	Me																	110	Dt																		
																		Mendelevium 258		Darmstadtium 289																	
111	Rg																	112	Cn																		
																		Rutherfordium 261		Copernicium 285																	



## Lanthanoids

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
138.9055	140.116	140.90765	144.24	(145)	150.36	151.964	157.25	158.92534	162.50	164.93032	167.26	168.93421	173.04	174.967
2	8	10	14	16	18	20	22	24	26	28	30	32	34	36

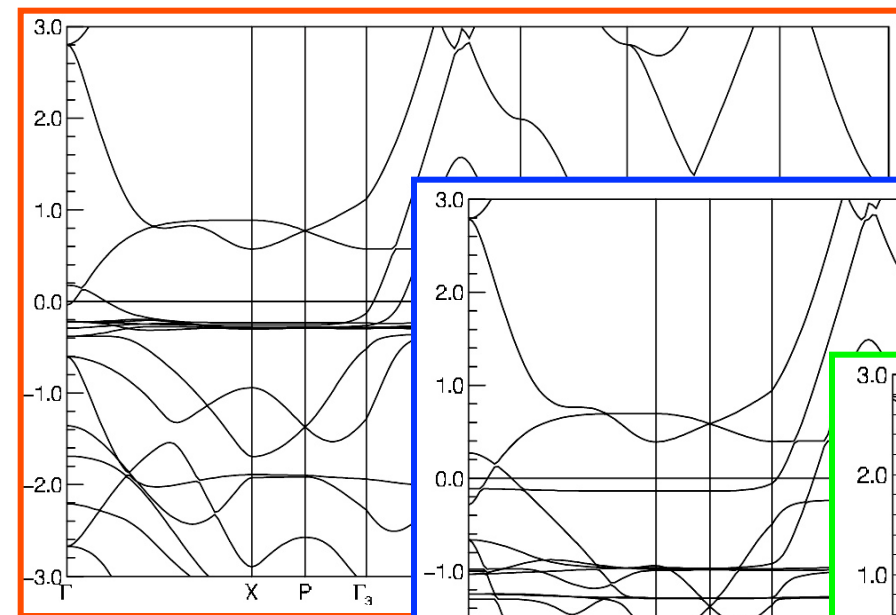
89	90	91	92	93	94	95	96	97
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium
(227)	232.0381	231.03588	238.0289	(237)	(244)	(243)	(247)	(247)
2	8	10	14	16	18	20	22	24

f - electrons

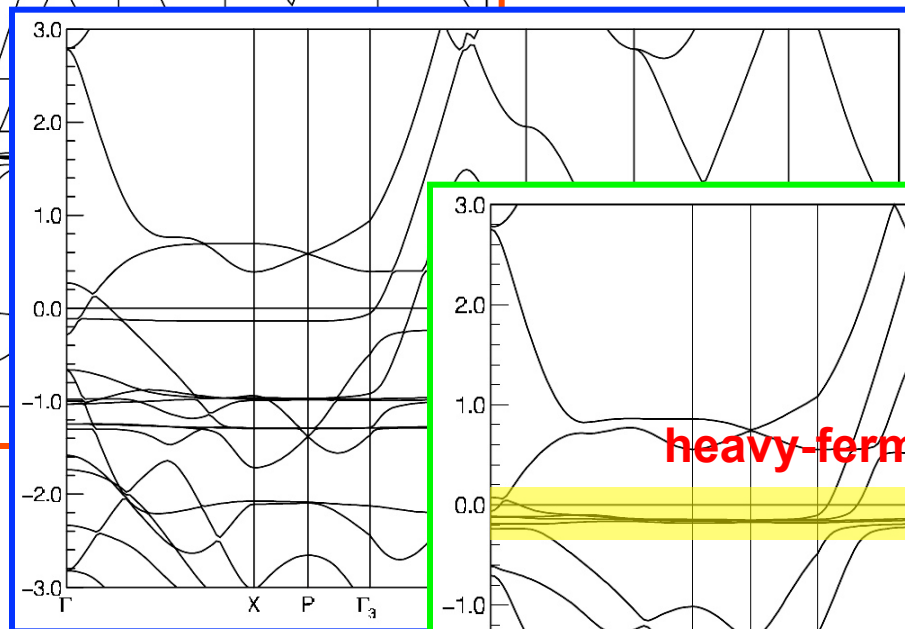
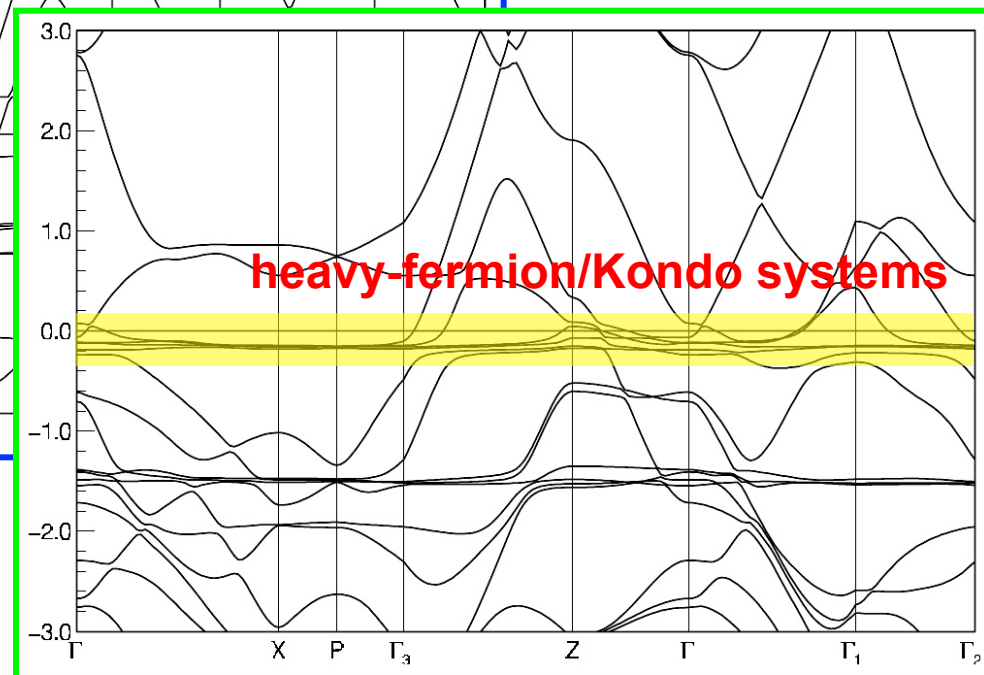
*f* - electrons

Correlated *f*-materials

12



LDA band structure

LDA + *U* approach  
band structure

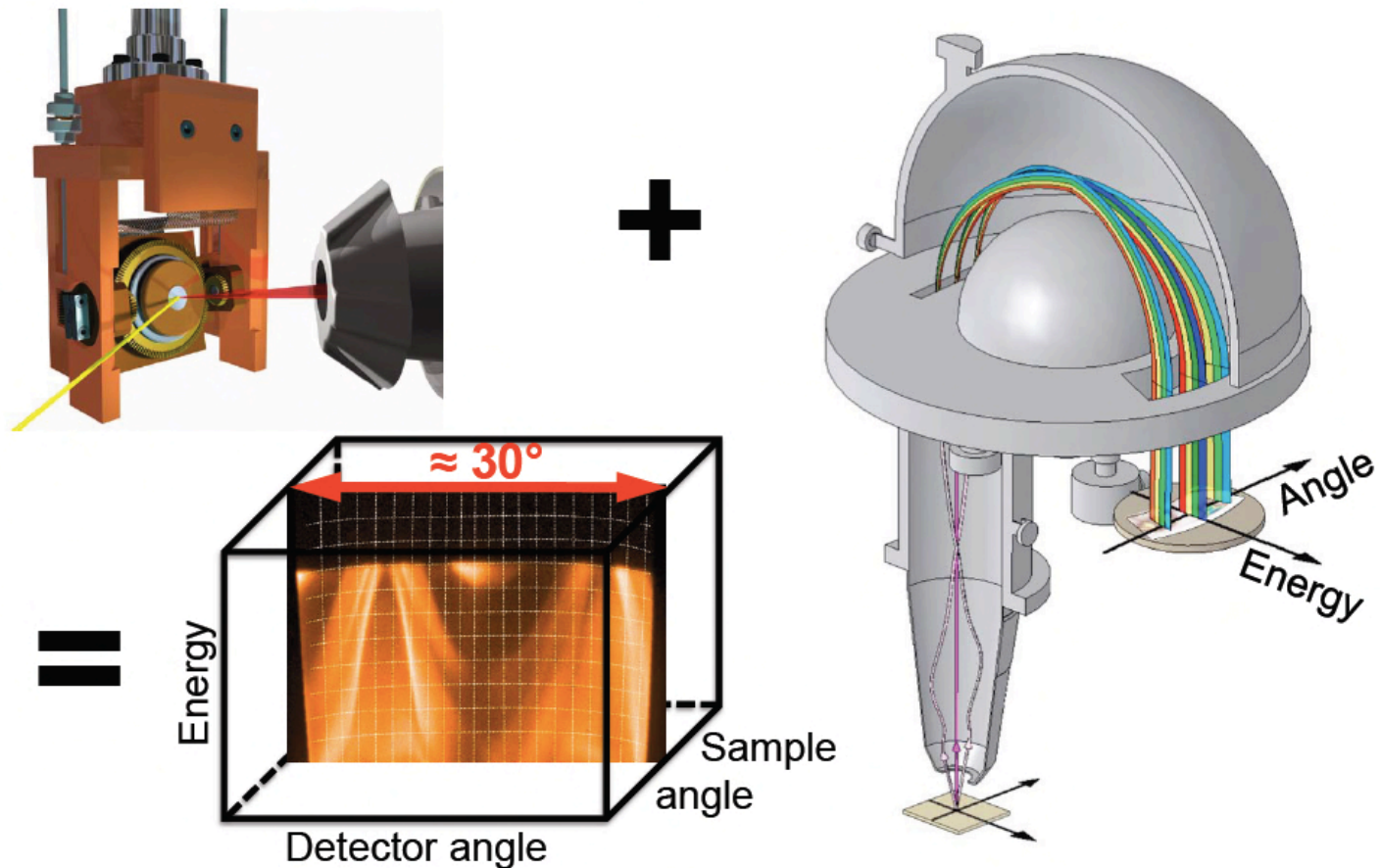
fully relativistic band structure

heavy-fermion compound

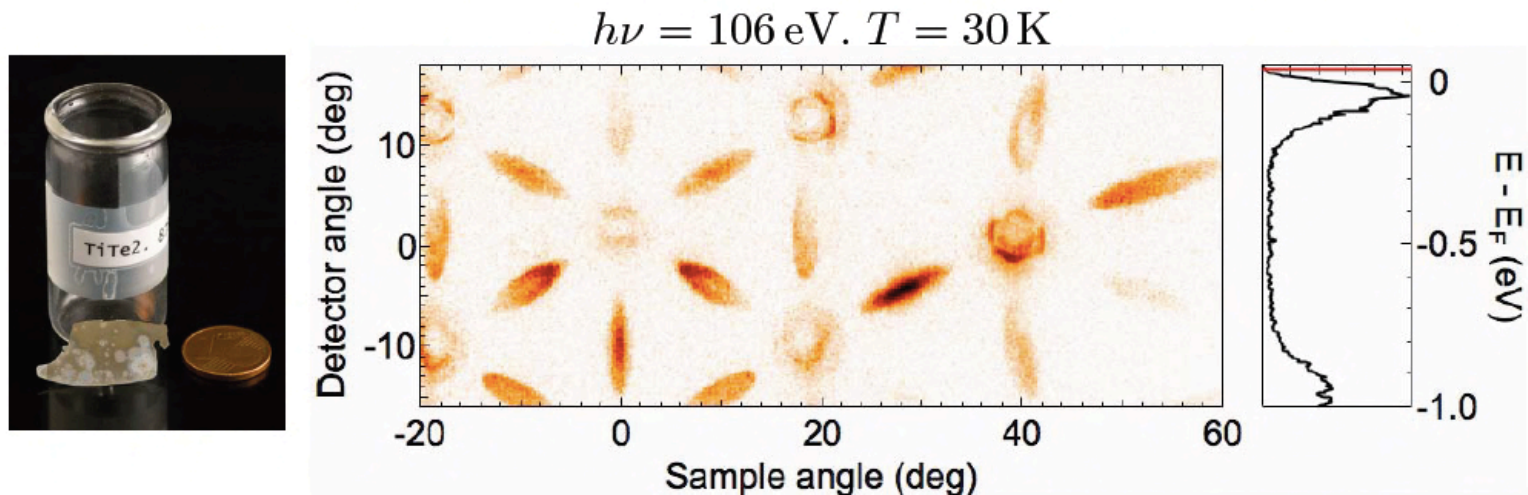
 $\text{YbRh}_2\text{Si}_2$ 

T. Jeong and W.E. Pickett,  
J. Phys.: Condens. Matter **18** (2006) 6289

# Angle-Resolved PhotoElectron Spectroscopy



# Band mapping (seeing is believing)

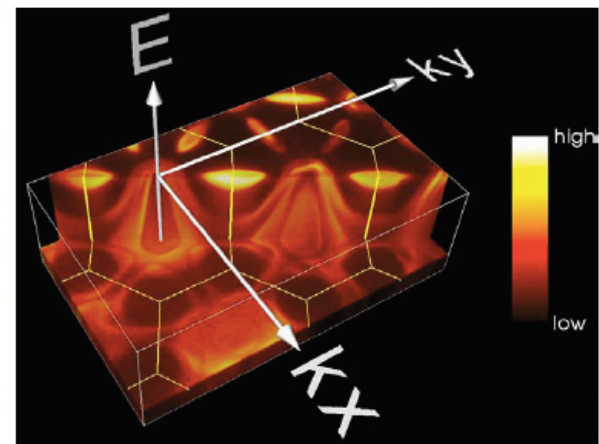


K. Rossnagel, et al. Uni Kiel

$$E - E_F = E_{\text{kin}} + W - h\nu$$

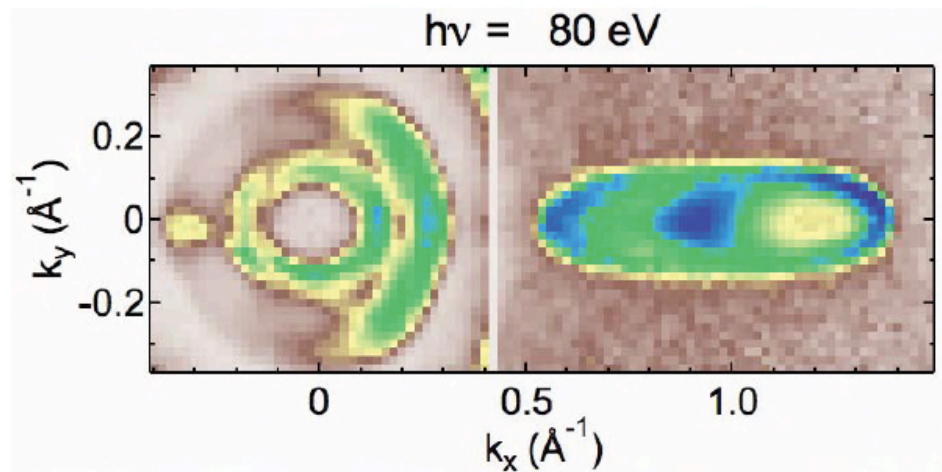
$$\begin{pmatrix} k_{\parallel x} \\ k_{\parallel y} \end{pmatrix} = \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}} \begin{pmatrix} \sin \Theta_D \\ \cos \Theta_D \sin \Phi_S \end{pmatrix}$$

Beamline 7, ALS, Berkeley





# Fermi surface tomography



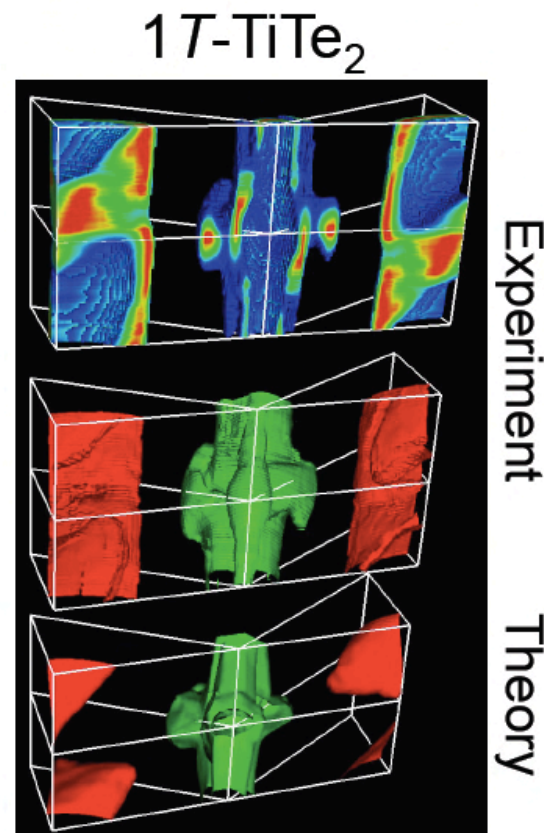
K. Rossnagel, et al. Uni Kiel

$$\mathbf{k}_{\parallel}^2 + k_{\perp}^2 = \frac{2m}{\hbar^2} (E_{\text{kin},F} + V_0)$$

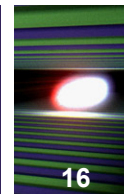
$$\mathbf{k}_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{\text{kin},F}} \begin{pmatrix} \sin \Theta_D \\ \cos \Theta_D \sin \Phi_S \end{pmatrix}$$

$$E_{\text{kin},F} = h\nu - W$$

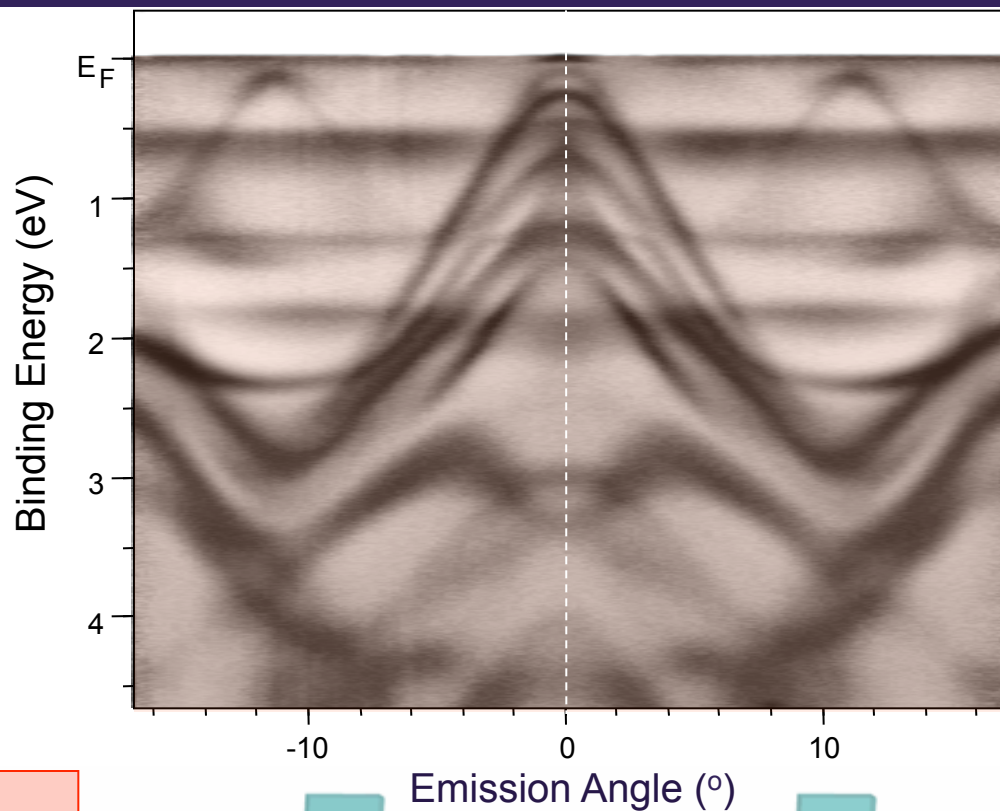
Beamline 7, ALS, Berkeley



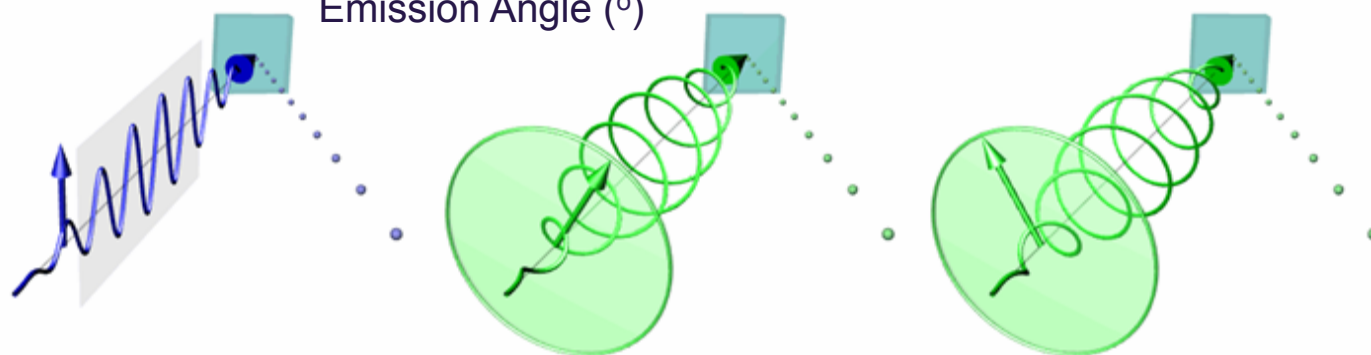
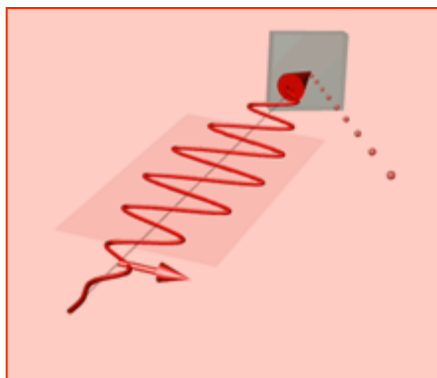
# Light-polarized ARPES on heavy-fermion $\text{YbRh}_2\text{Si}_2$ (S. Molodtsov, et al.)



16

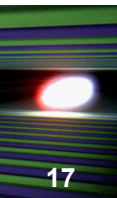


$\text{YbIr}_2\text{Si}_2$

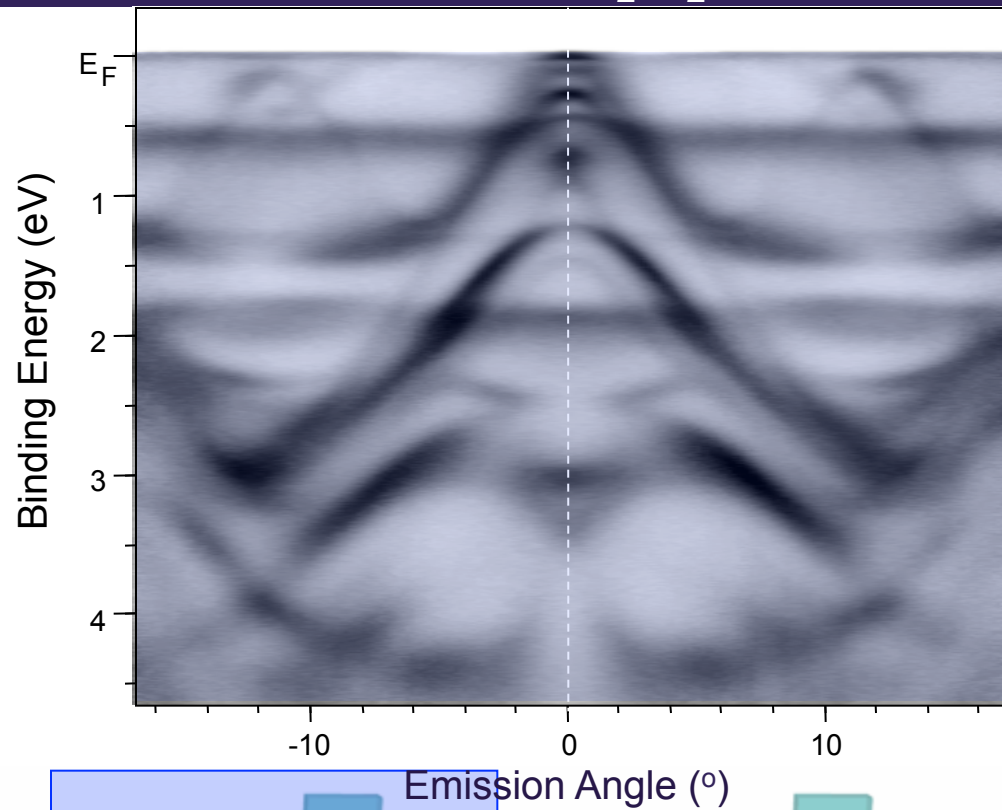




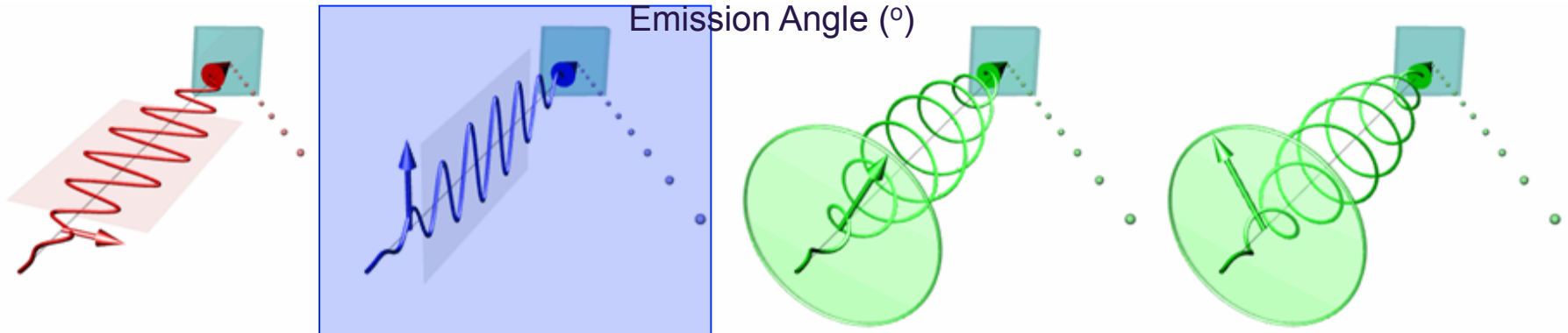
# Light-polarized ARPES ( $\text{YbRh}_2\text{Si}_2$ )



17

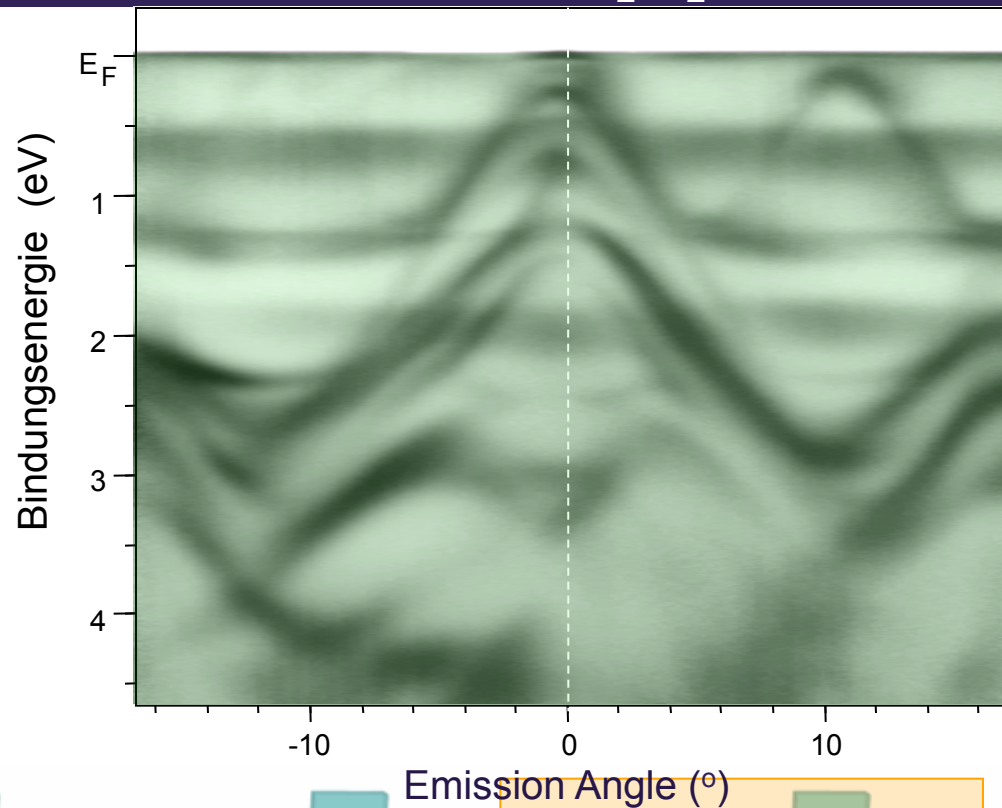


$\text{YbIr}_2\text{Si}_2$

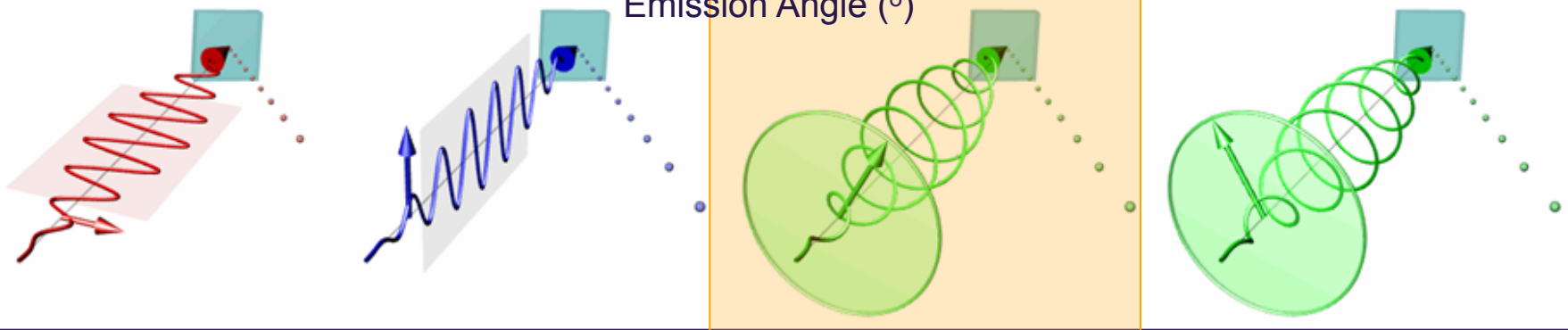


# Light-polarized ARPES ( $\text{YbRh}_2\text{Si}_2$ )

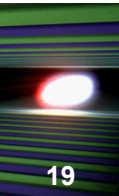
18



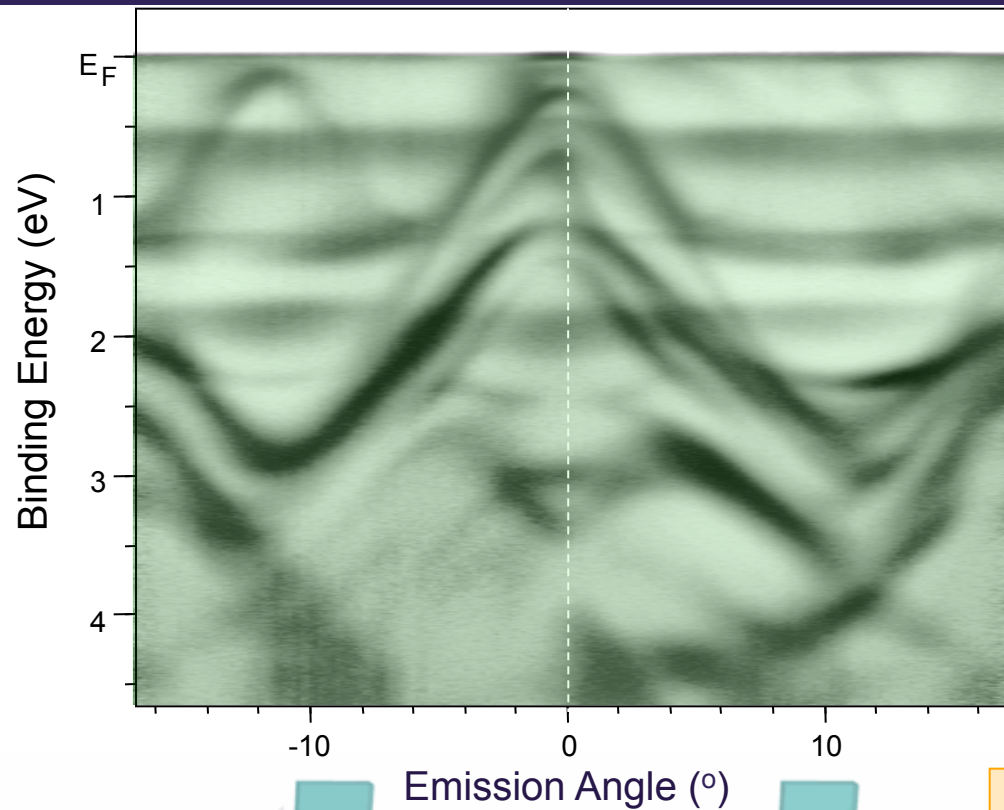
$\text{YbIr}_2\text{Si}_2$



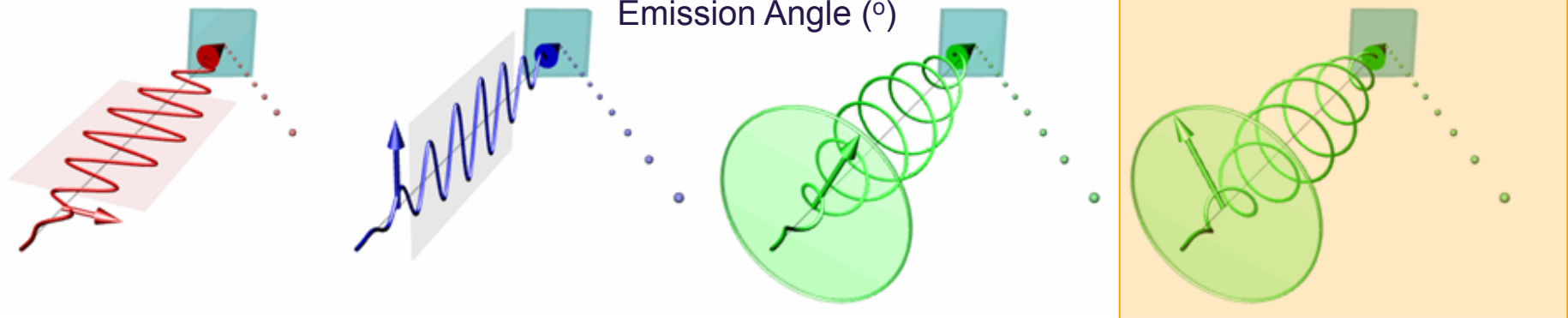
# Light-polarized ARPES ( $\text{YbRh}_2\text{Si}_2$ )



19

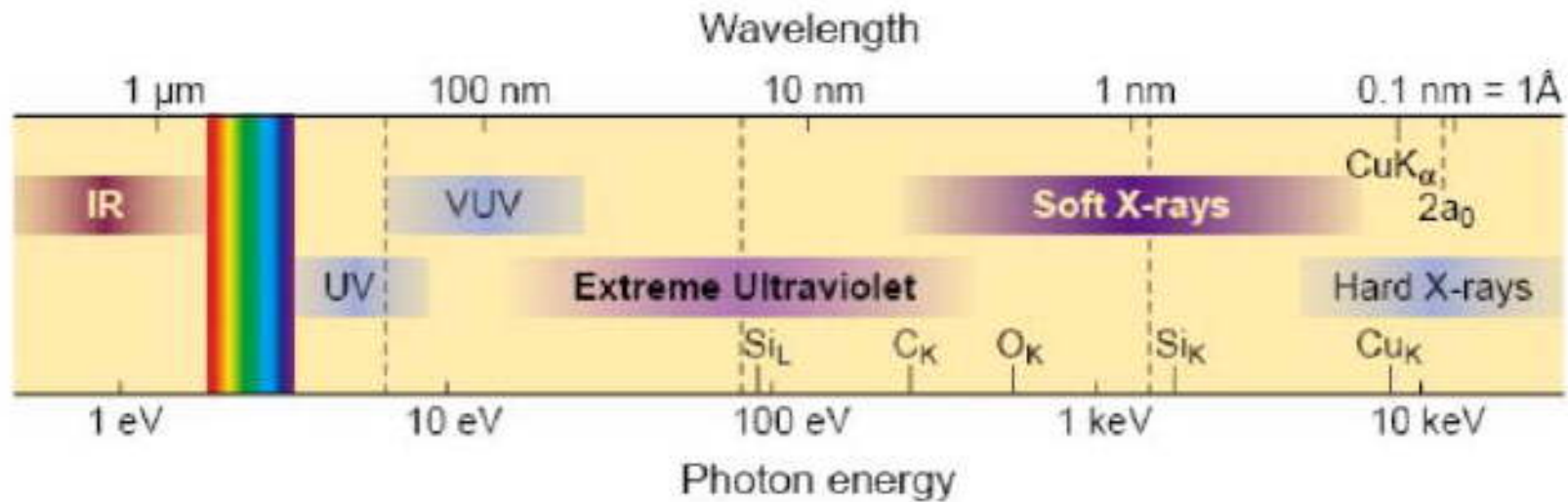


$\text{YbIr}_2\text{Si}_2$



# Spectral range and radiation sources

20



Exchange (He) lamps – VUV/Extreme Ultraviolet

Röntgen (Cu) tubes – Soft/Hard X-rays

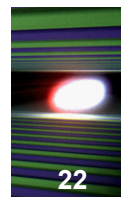
Disadvantages: (i) low intensity; (ii) discrete spectrum; (iii) no time structure

**Revolution with synchrotron radiation !!!**

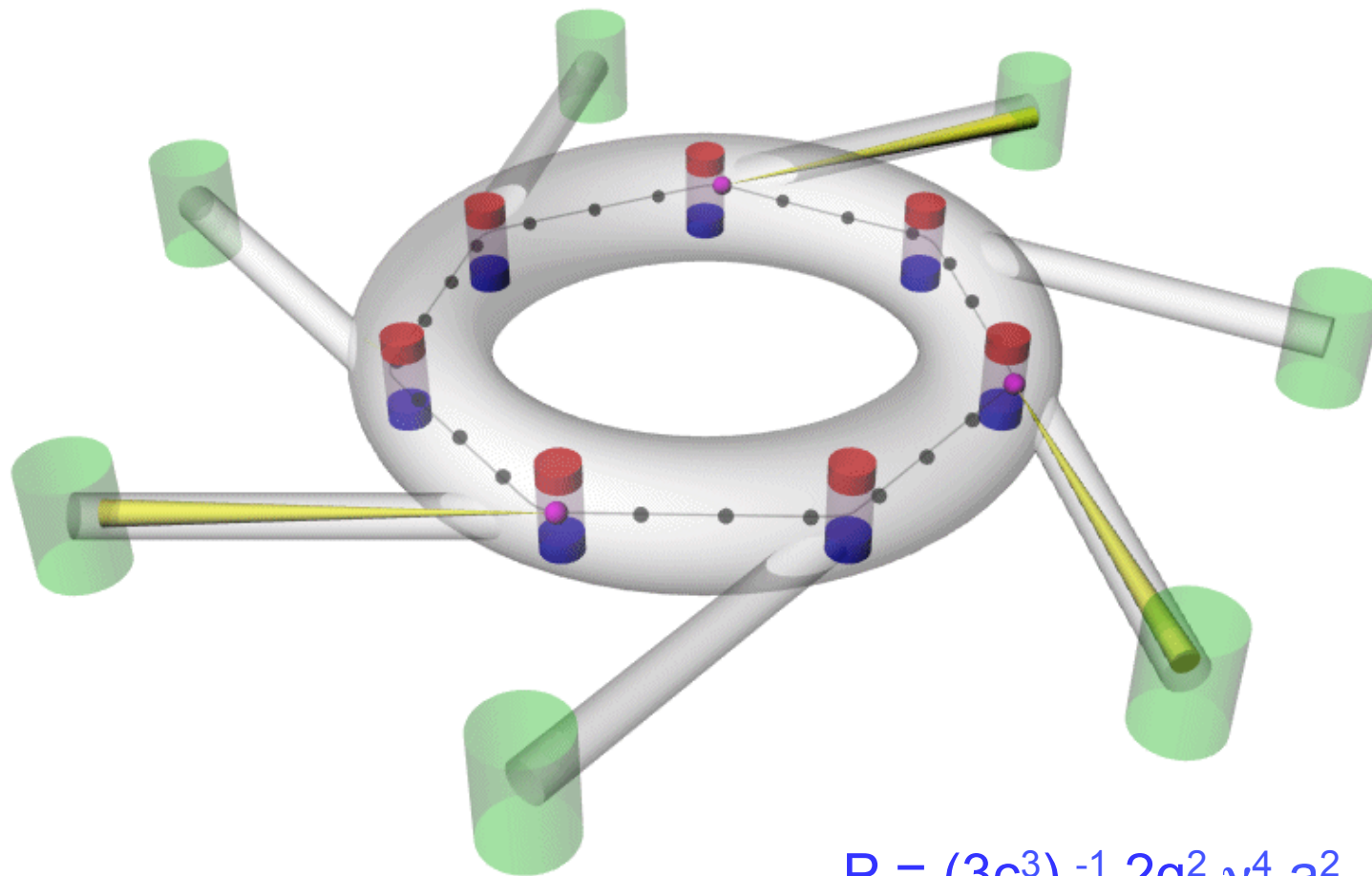
# Synchrotron Radiation

## *Synchrotrons/Storage Rings*

# Synchrotron Radiation (dipoles)



22

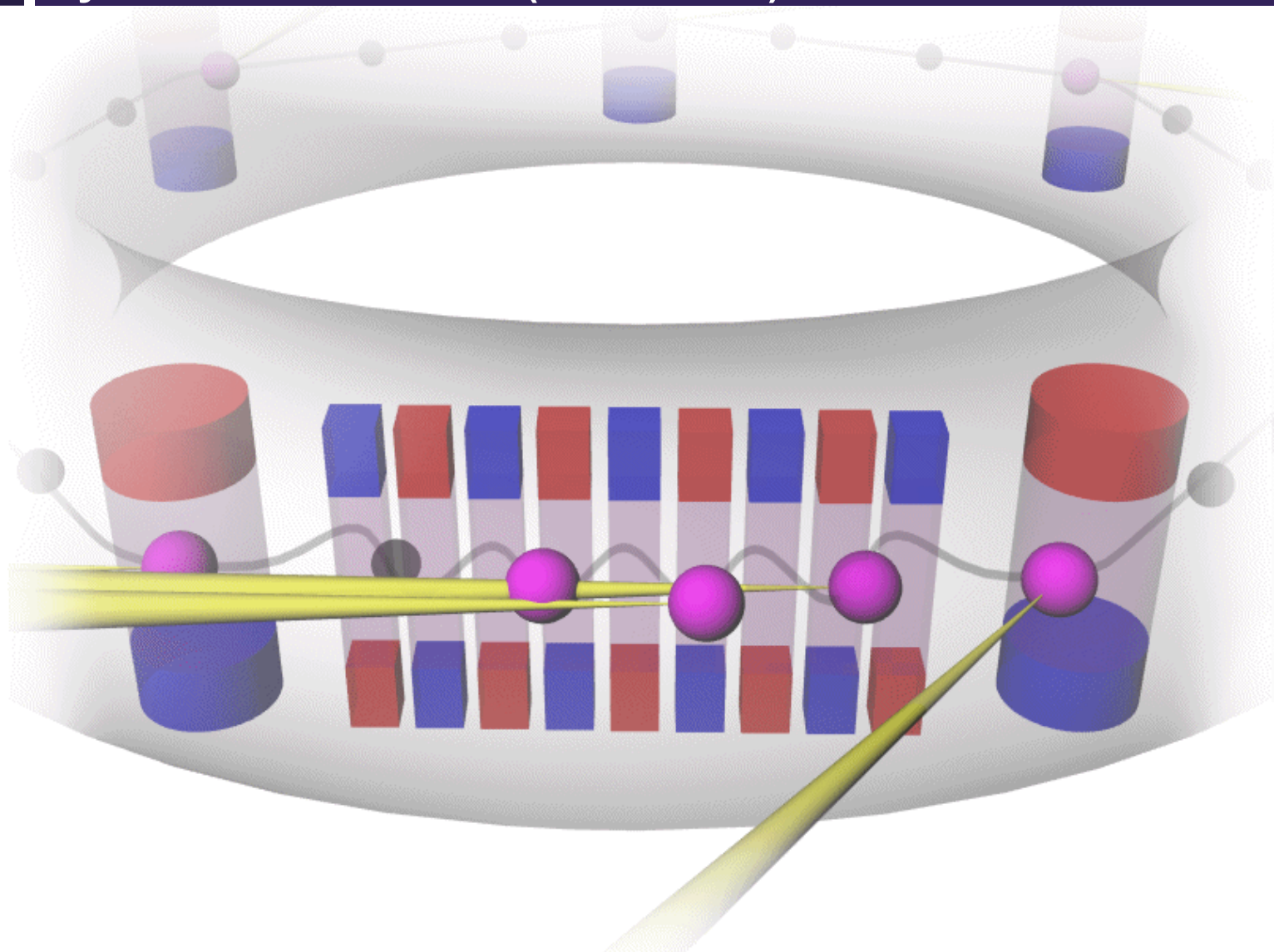


$$P = (3c^3)^{-1} 2q^2 \gamma^4 a^2$$

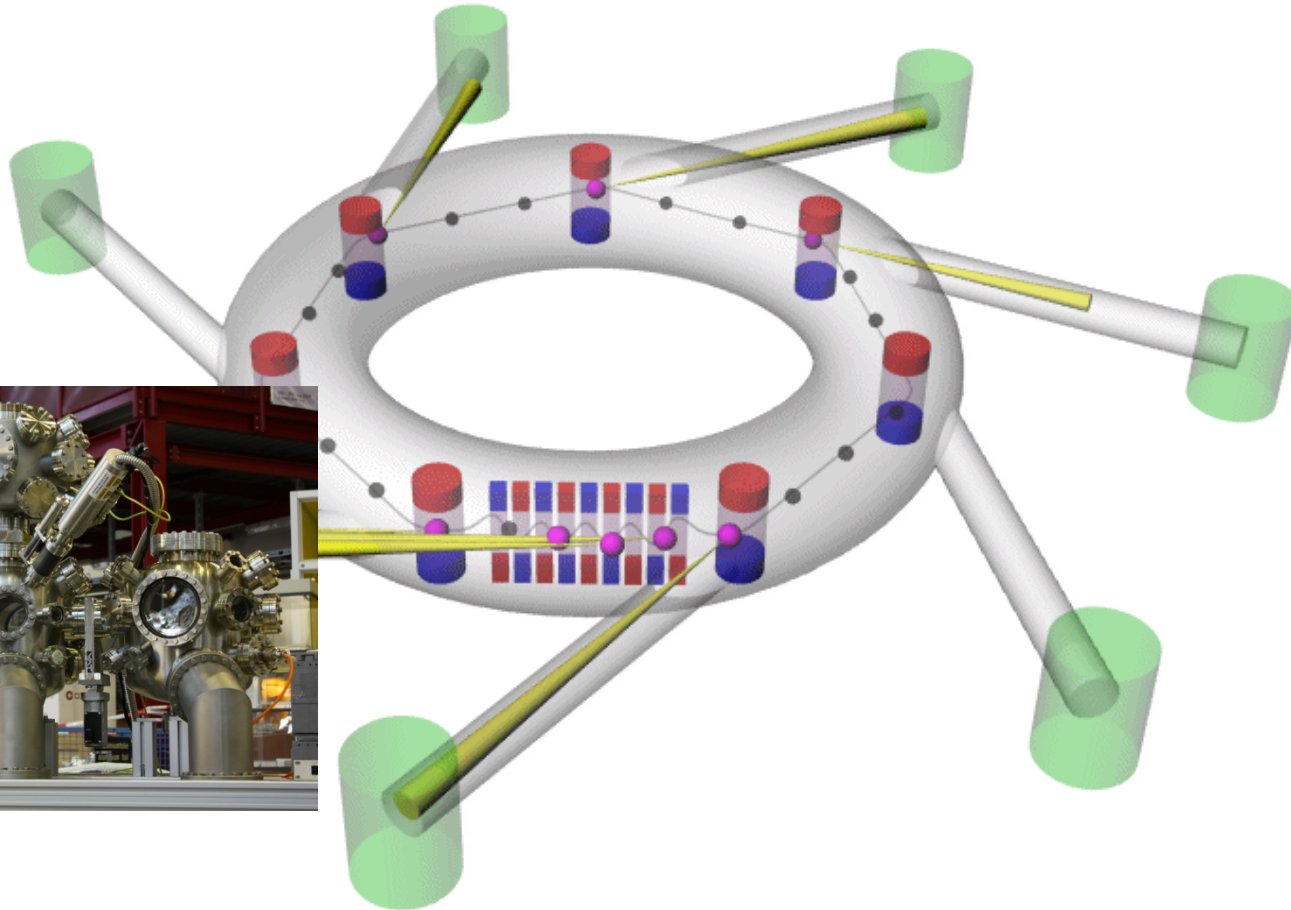
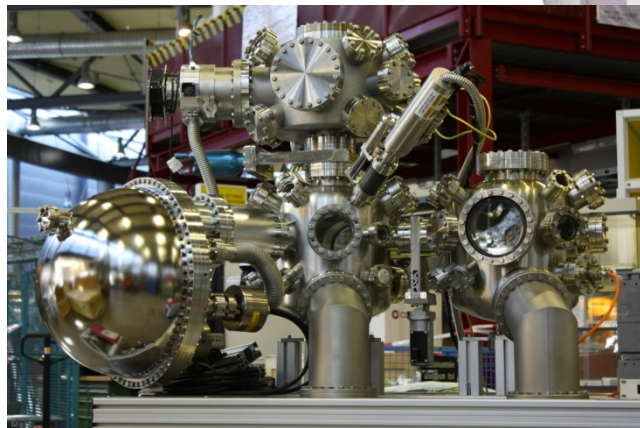
$P$  – radiated power;  $c$  – light velocity;  $q$  – particle charge;  $a$  – acceleration;  $\gamma$  - normalized energy



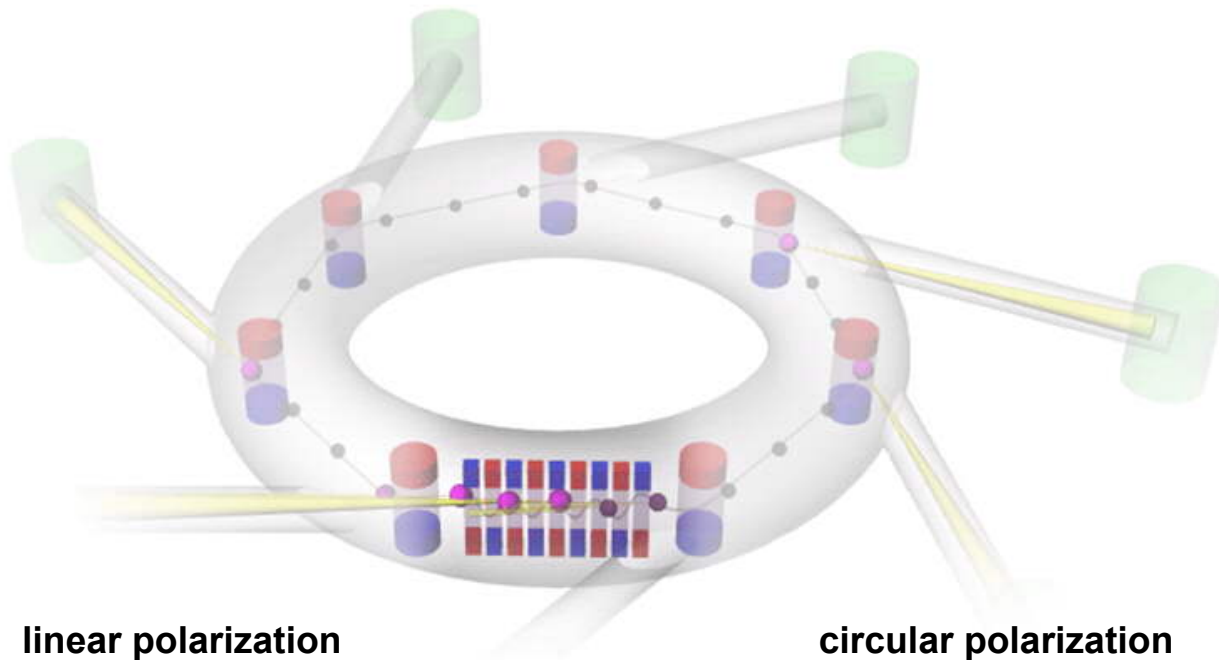
# Synchrotron radiation (undulators)



# Synchrotron radiation (sources + exp. stations)

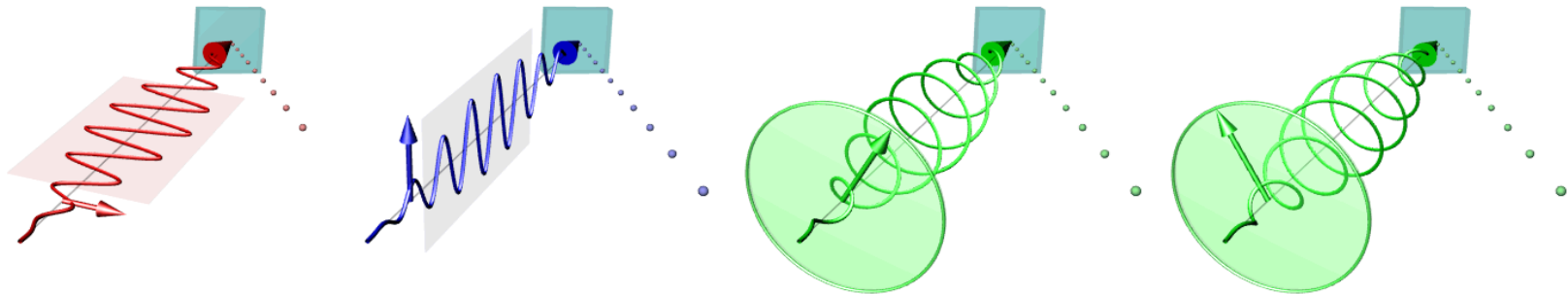


# Synchrotron Radiation (light polarization)

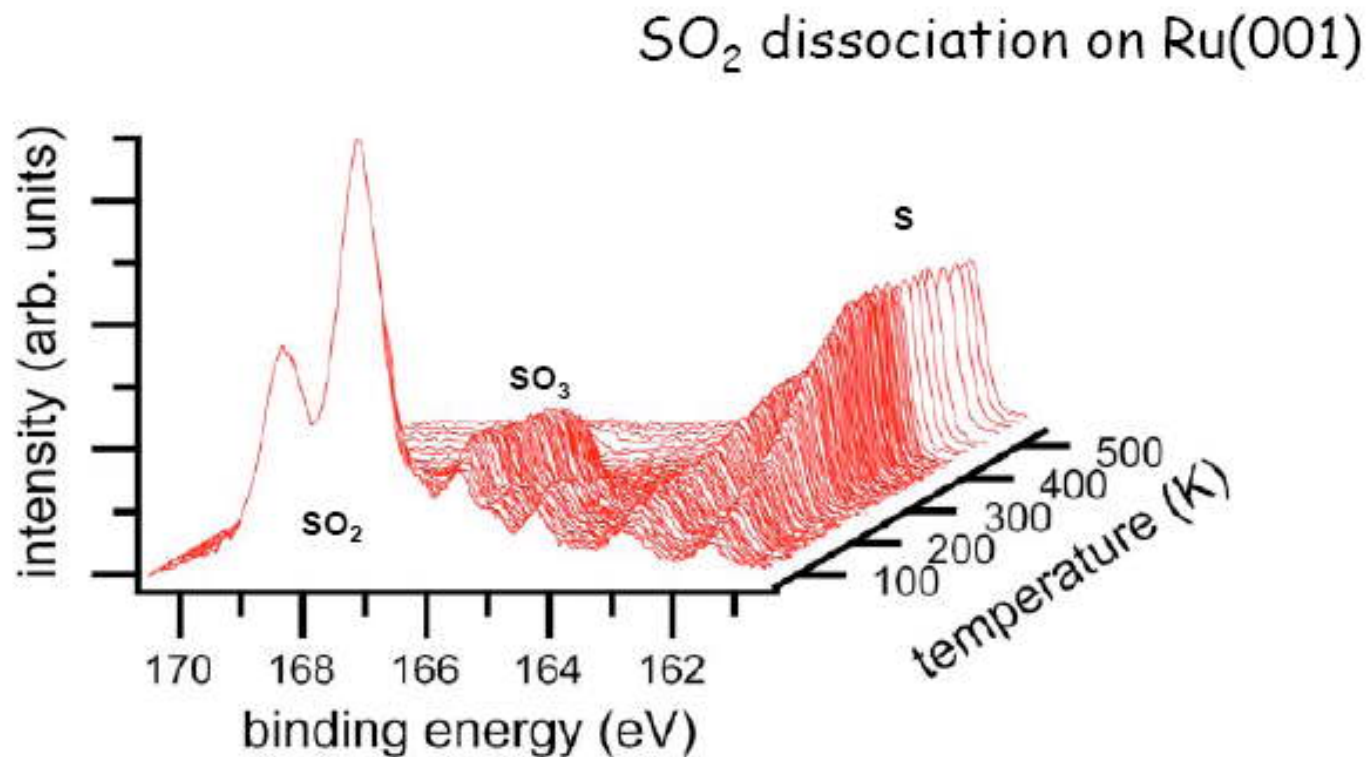
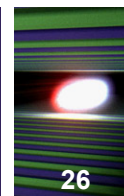


**linear polarization**

**circular polarization**



# Spectroscopic toolbox: X-ray photoelectron spectroscopy, ESCA

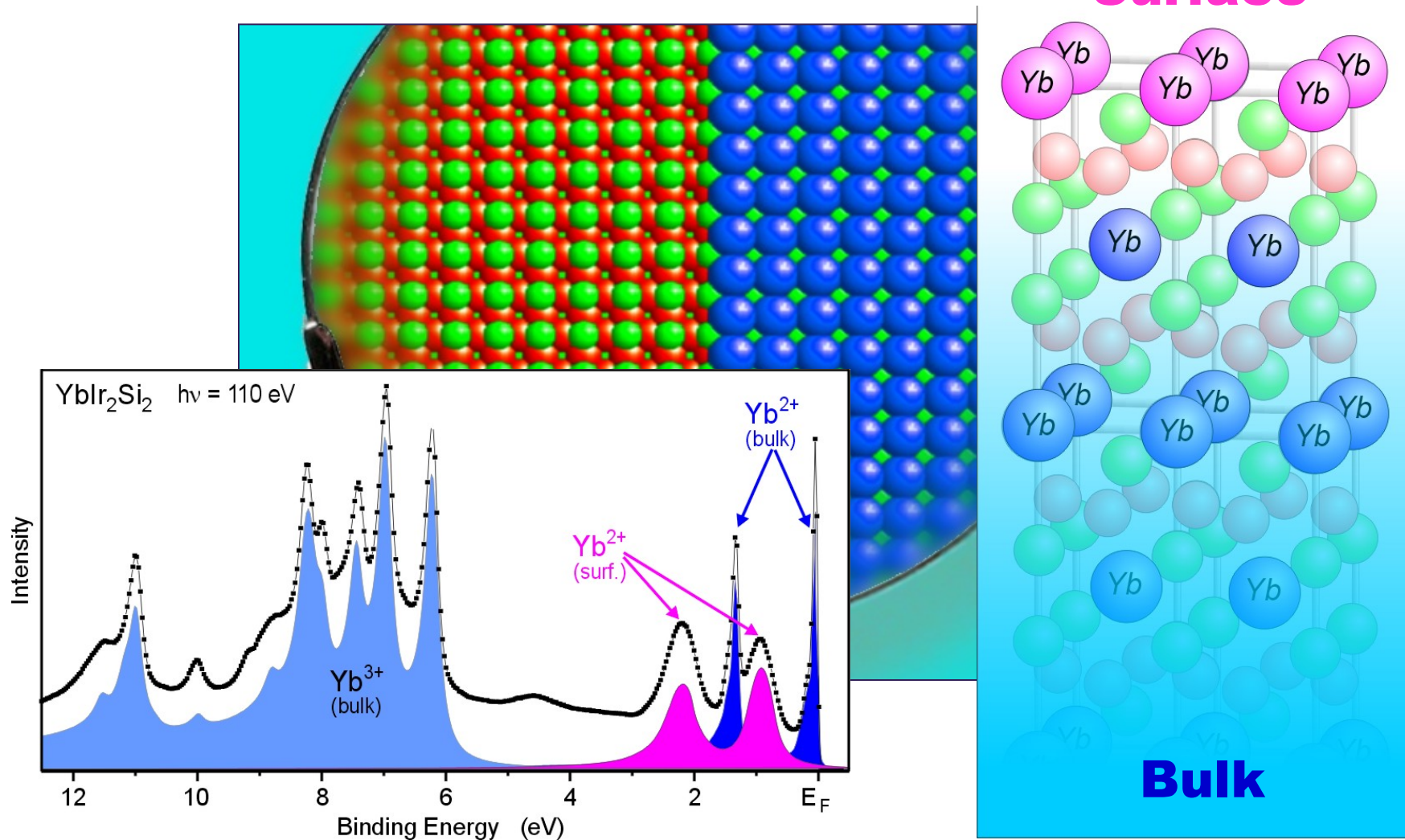


F. Hennies et al., J.Chem.Phys. 127, 154709 (2007)

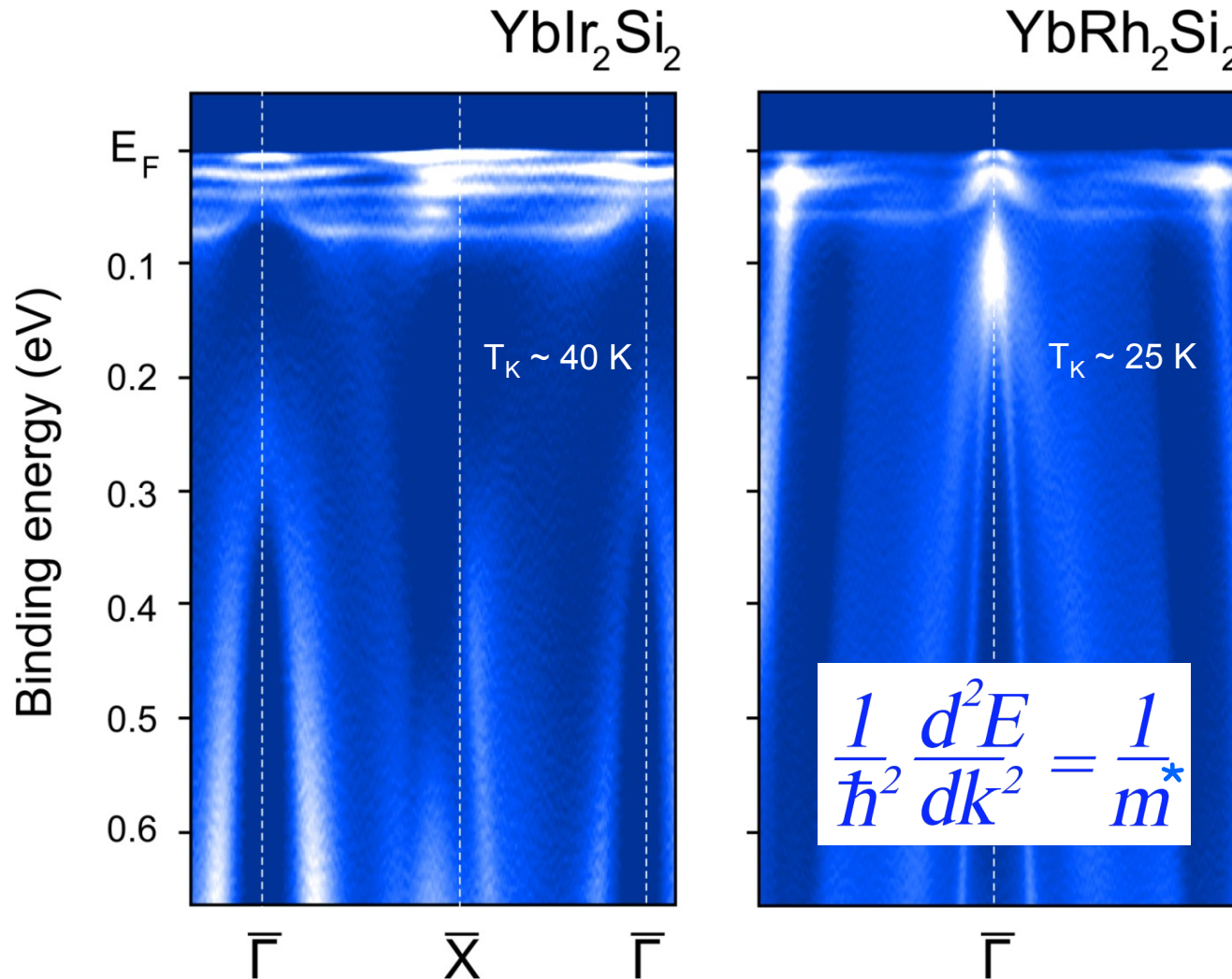


# Characterization of cleaved samples: $\text{YbRh}_2\text{Si}_2$ (S. Molodtsov, et al.)

27

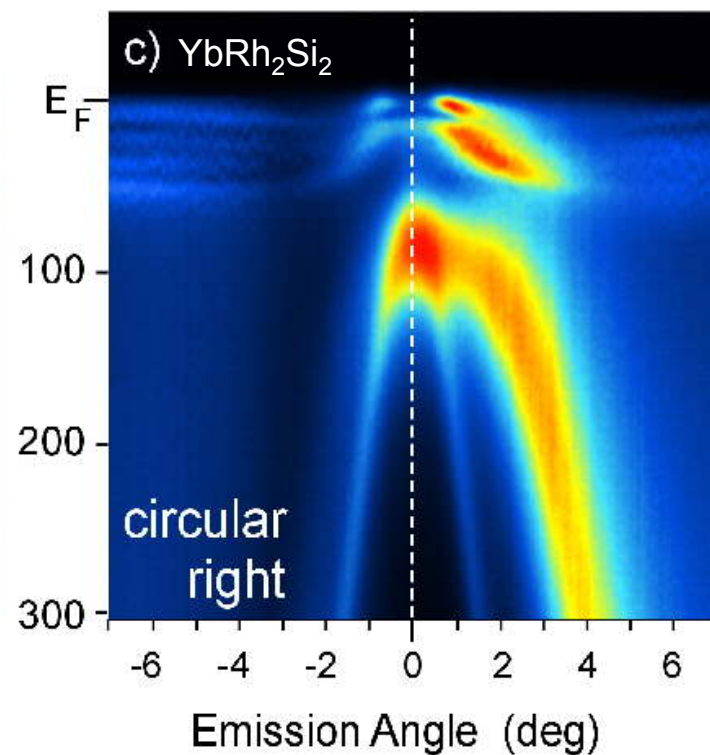
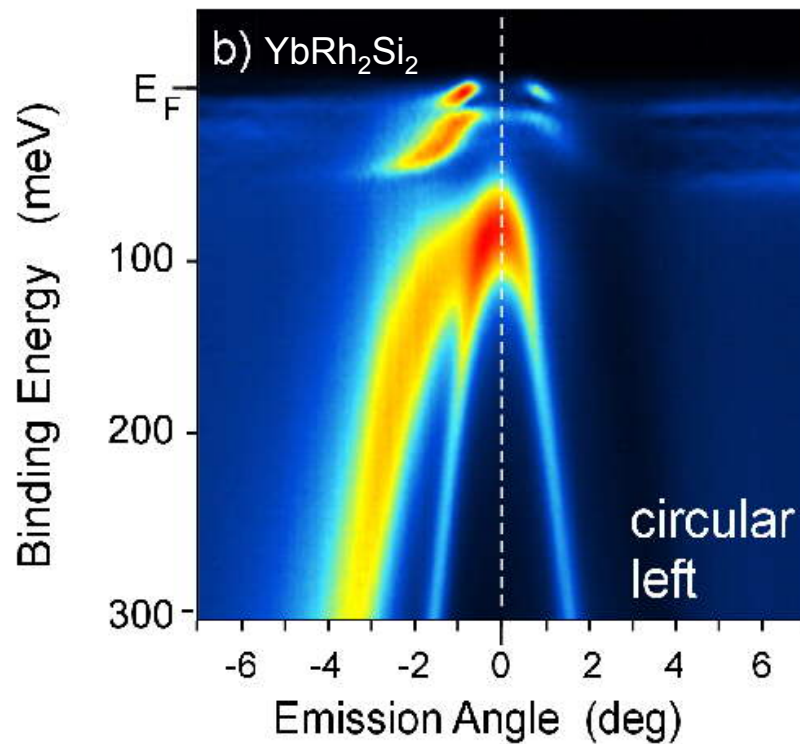


## Crystal-field split f-states in Kondo systems

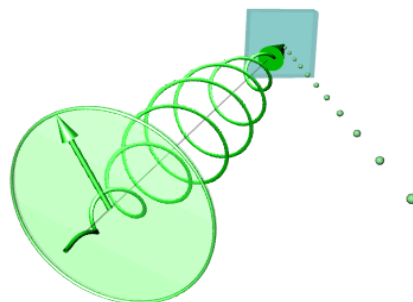


- effective mass mapping (transport phenomena)
- crystal field-split 4f states probing (magnetic properties)
- strength of electron states correlation (Kondo behavior)

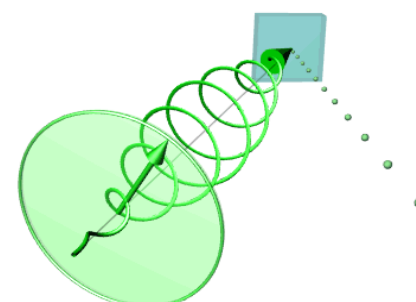


Symmetry of f-states in  $\text{YbRh}_2\text{Si}_2$ 

circular left

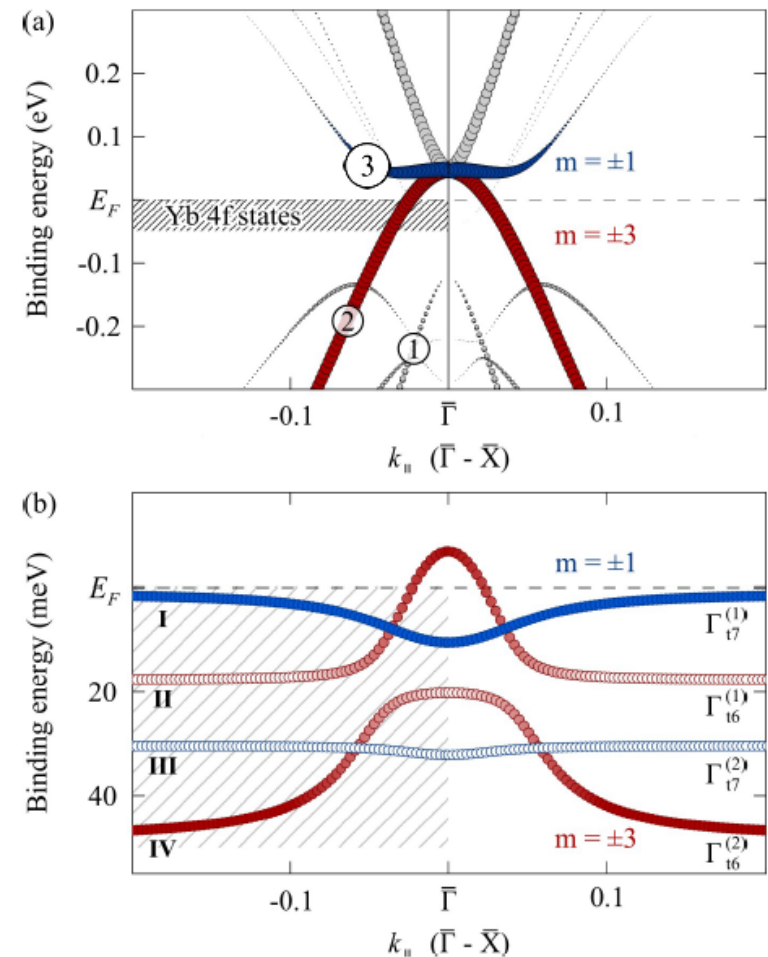
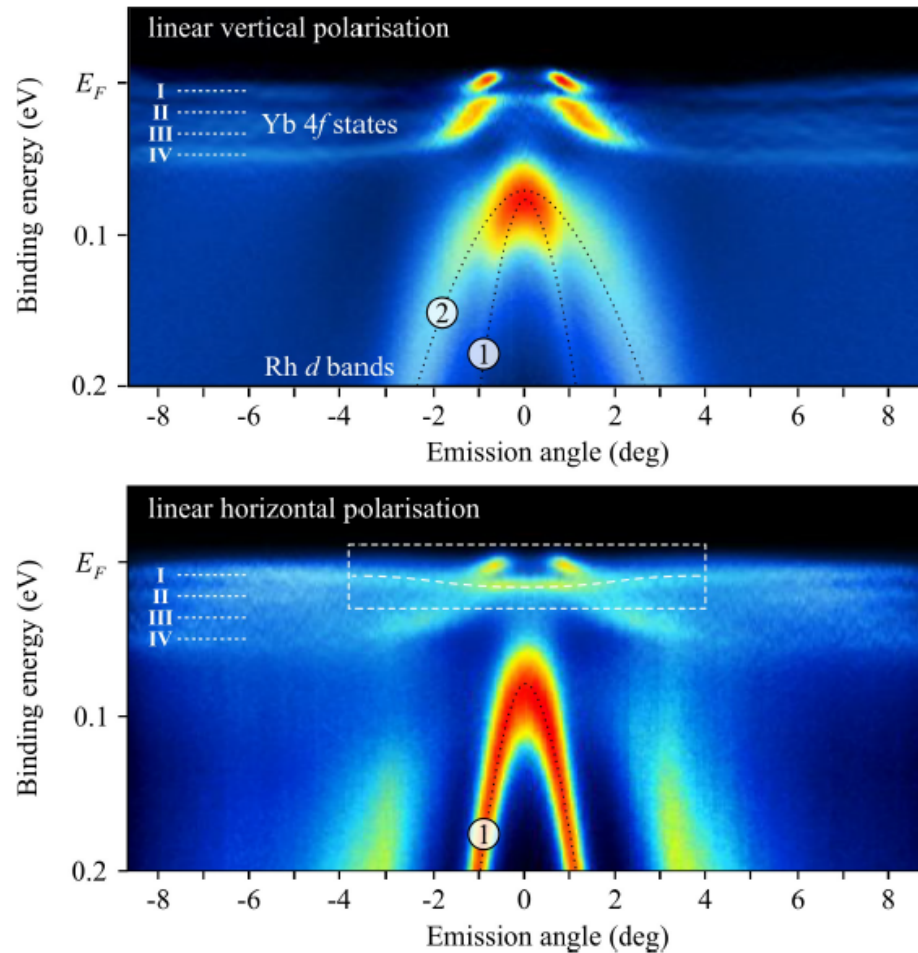


circular right



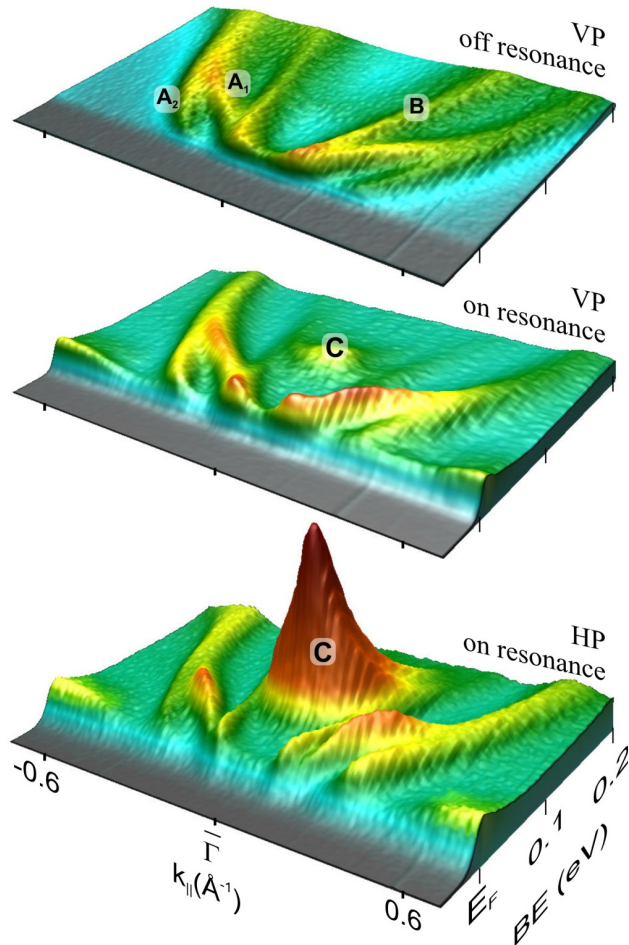
# Heavy-fermion behavior in $\text{YbRh}_2\text{Si}_2$

30

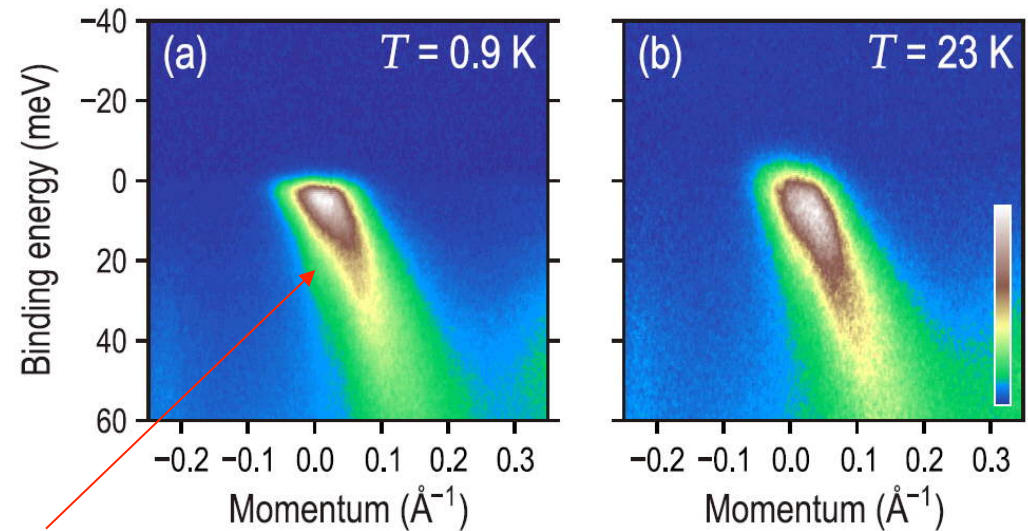


Dispersion of the 4f states around  $\Gamma$  where they hybridize to Rh d bands: Experiment & theory

## CeFePO

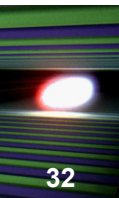


## LiFeAs



kink below  $T_c$

- which band is responsible for superconductivity?
- how large is superconducting gap?
- how strong is electron pairing (kink energy)?

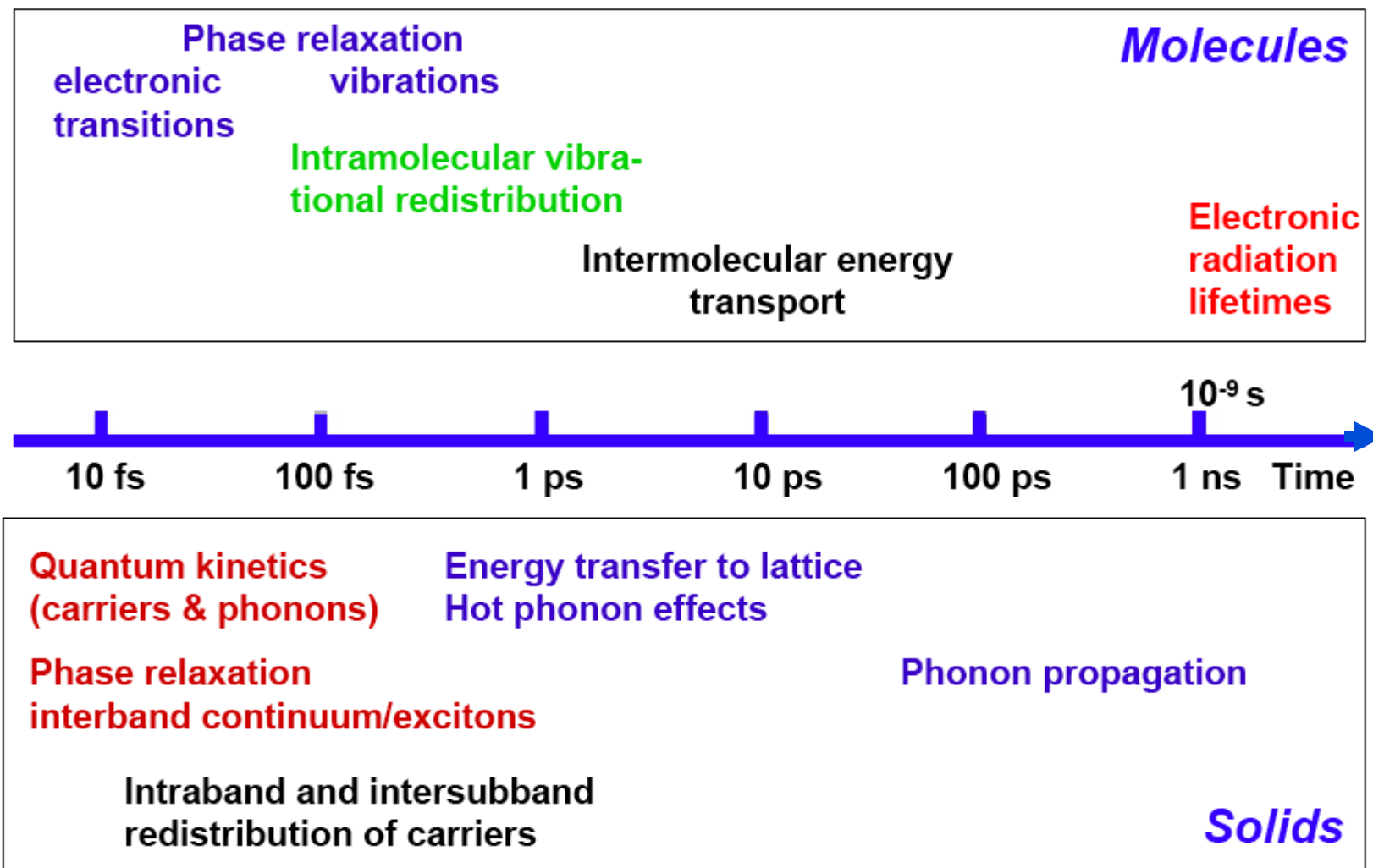


# What is missing?

**Electron system dynamics  
that is of the time scale order  
 $< 0.1$  ps**

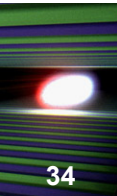
**Probing dynamics one can decide, e.g. in favor of spin  
or phonon mediated mechanism of electron pairing both  
in superconducting and Kondo systems**

# Time scales for dynamics



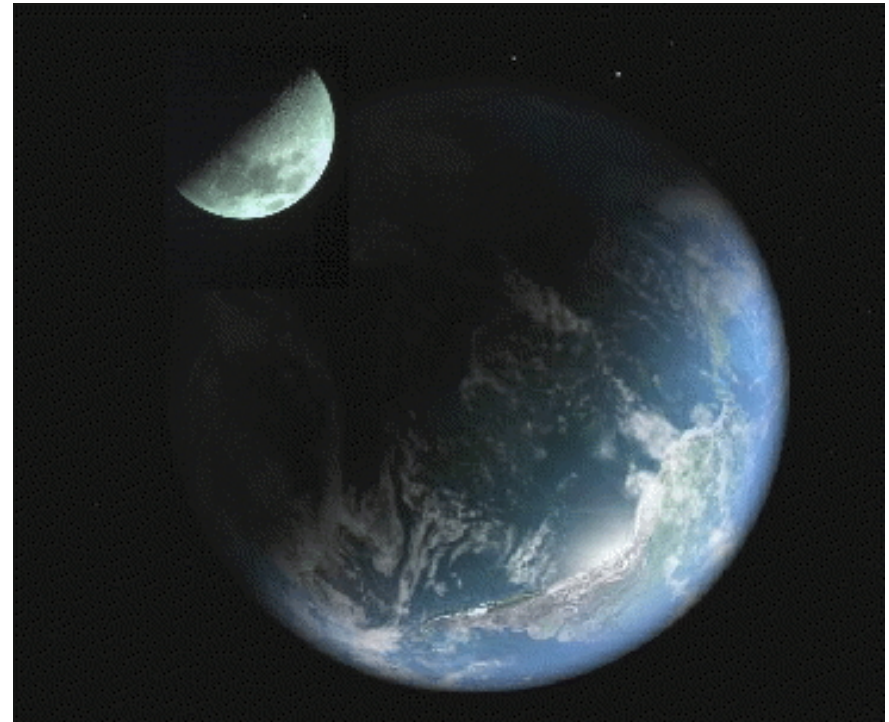


# What is a picosecond?



In 1 s light travels 300 000 km

Distance between earth and moon is 384 000 km

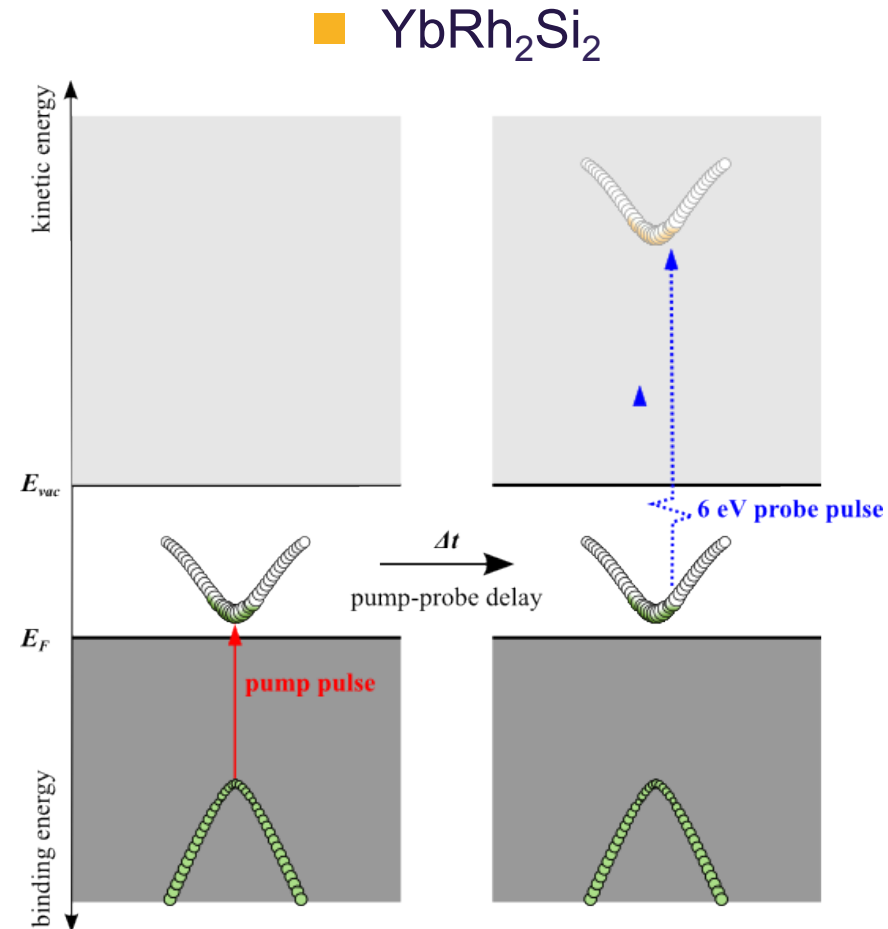
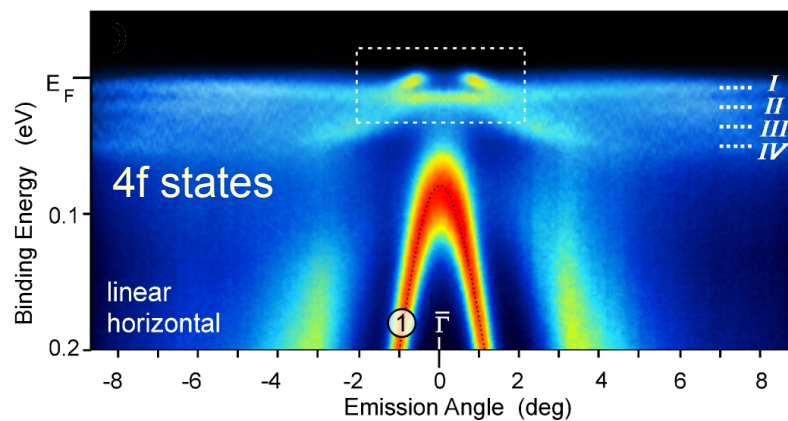
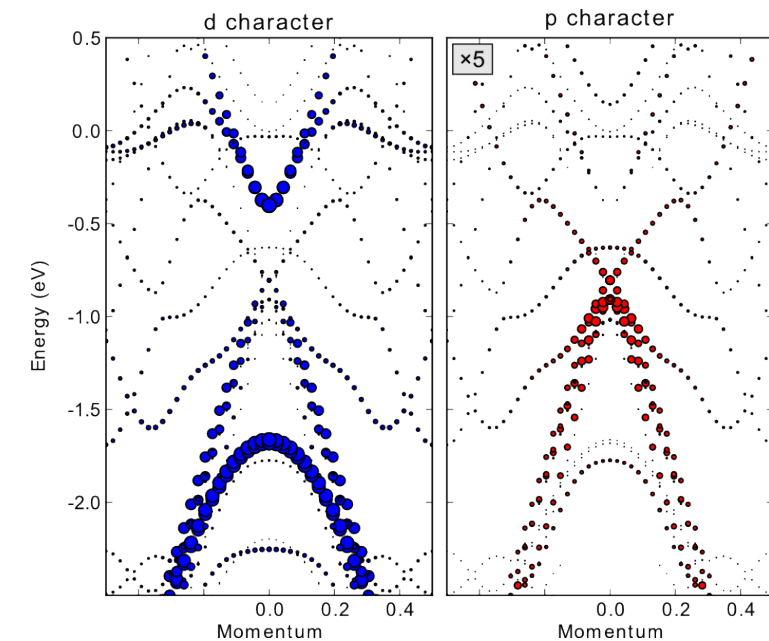


In 1 ps light travels 0,3 mm



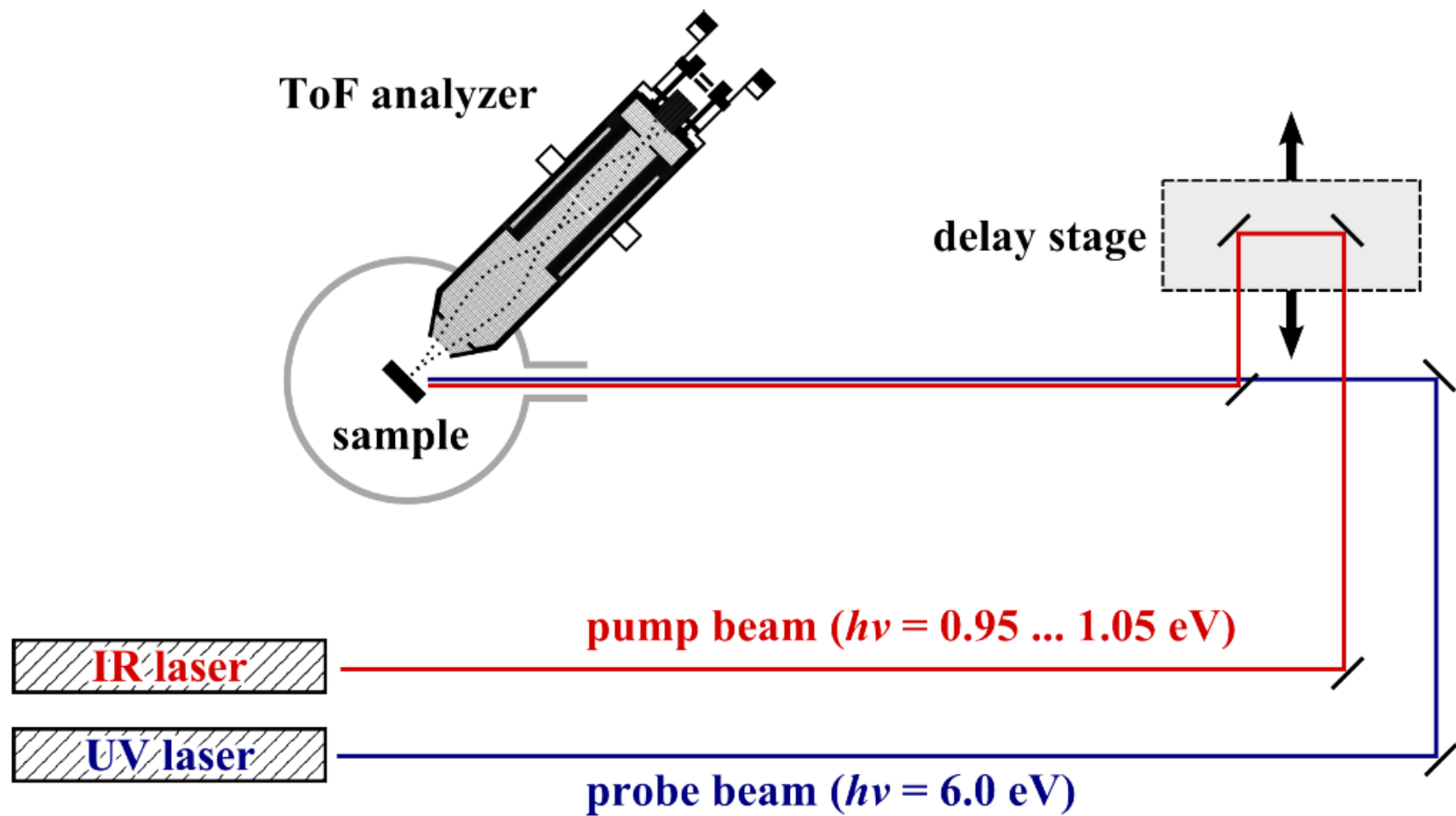
# Pump-probe experiment (K. Kummer, et al.)

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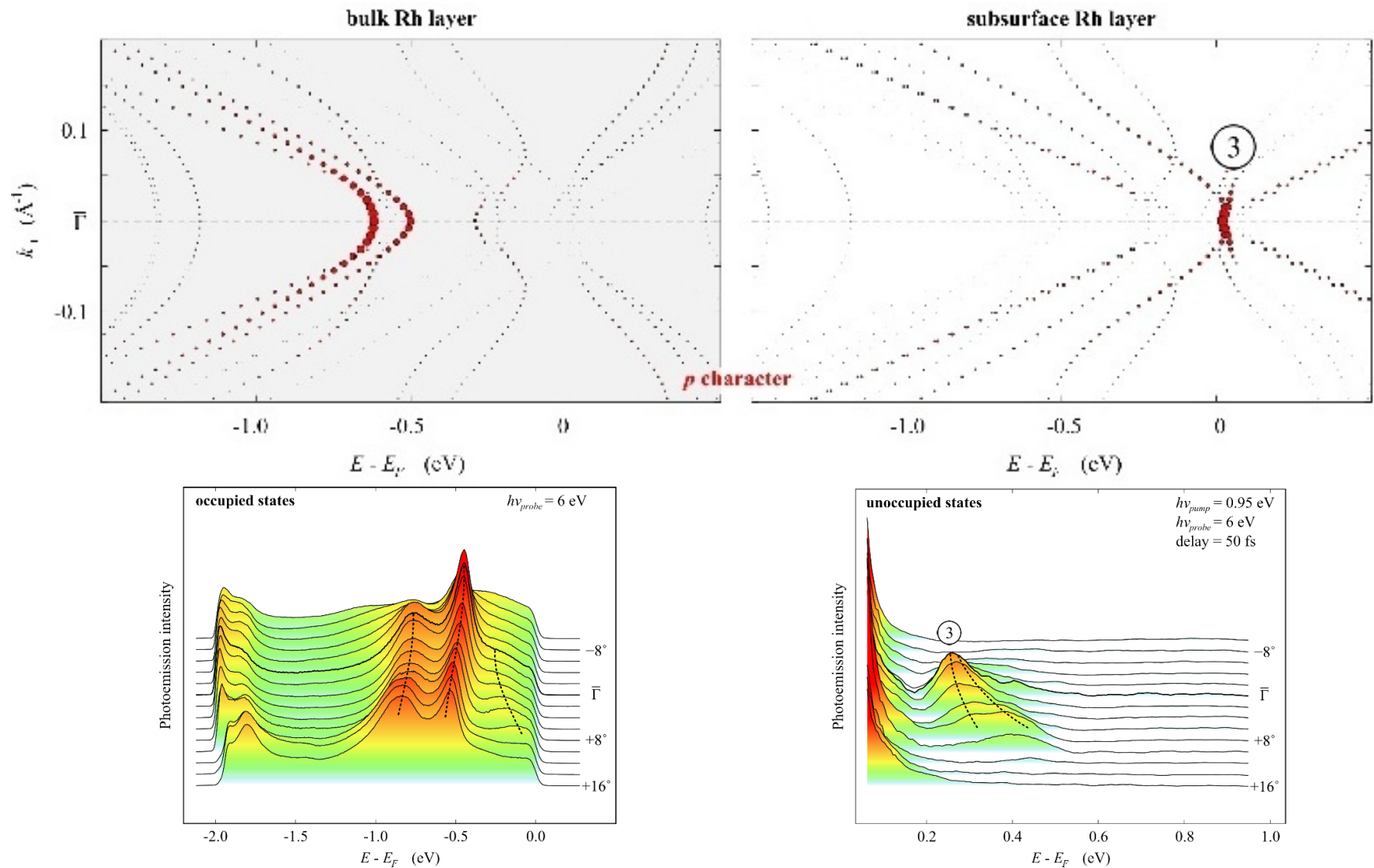


ARPES with MHz optical lasers

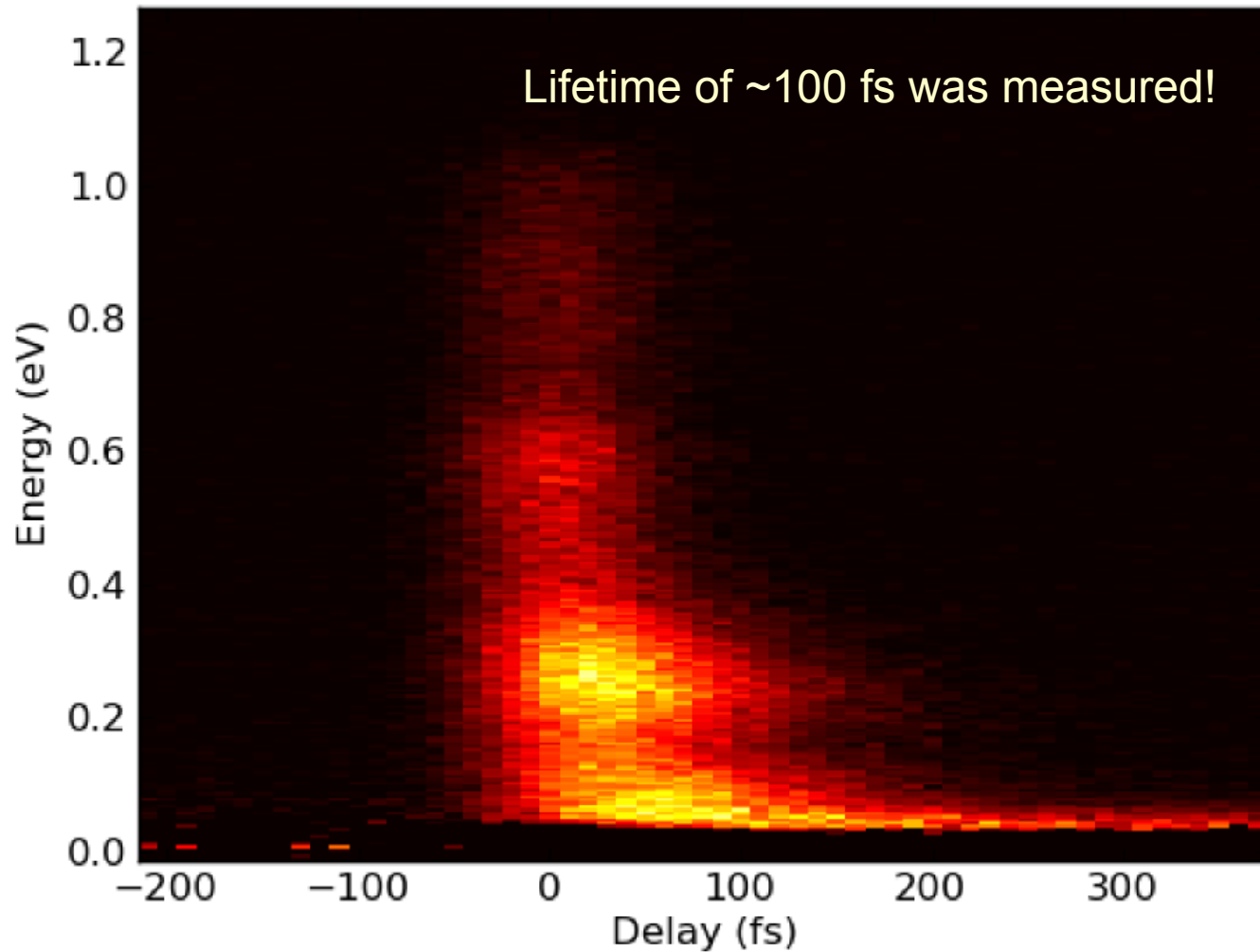
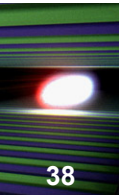
## Experimental setup



# YbRh<sub>2</sub>Si<sub>2</sub>: Projected *p*-character band structure

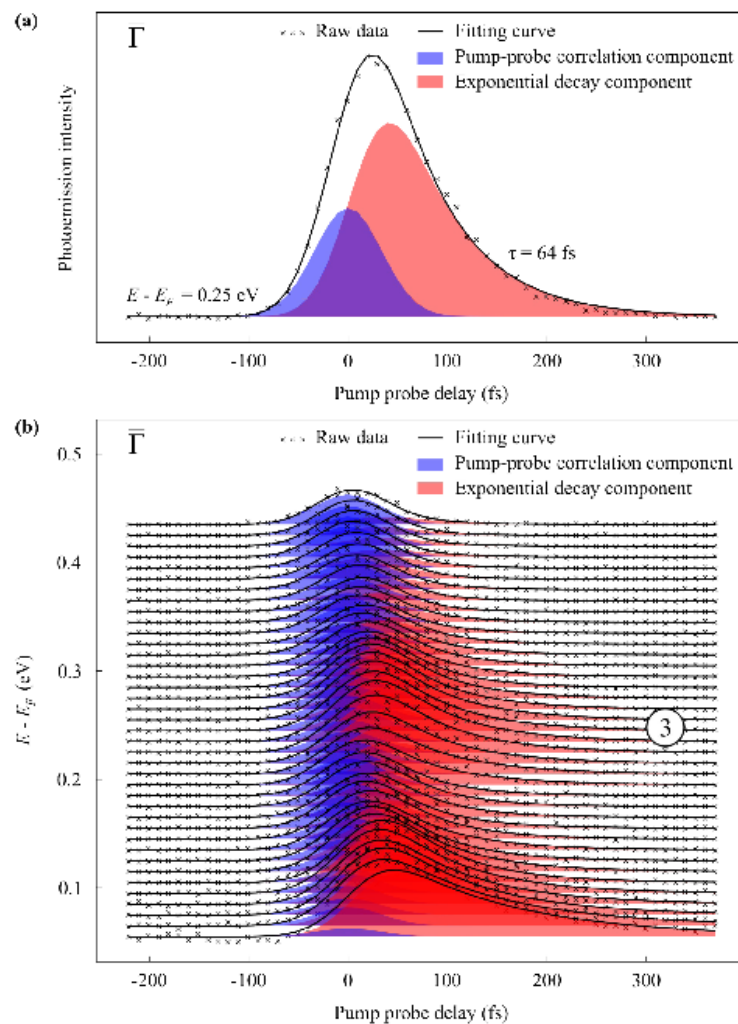
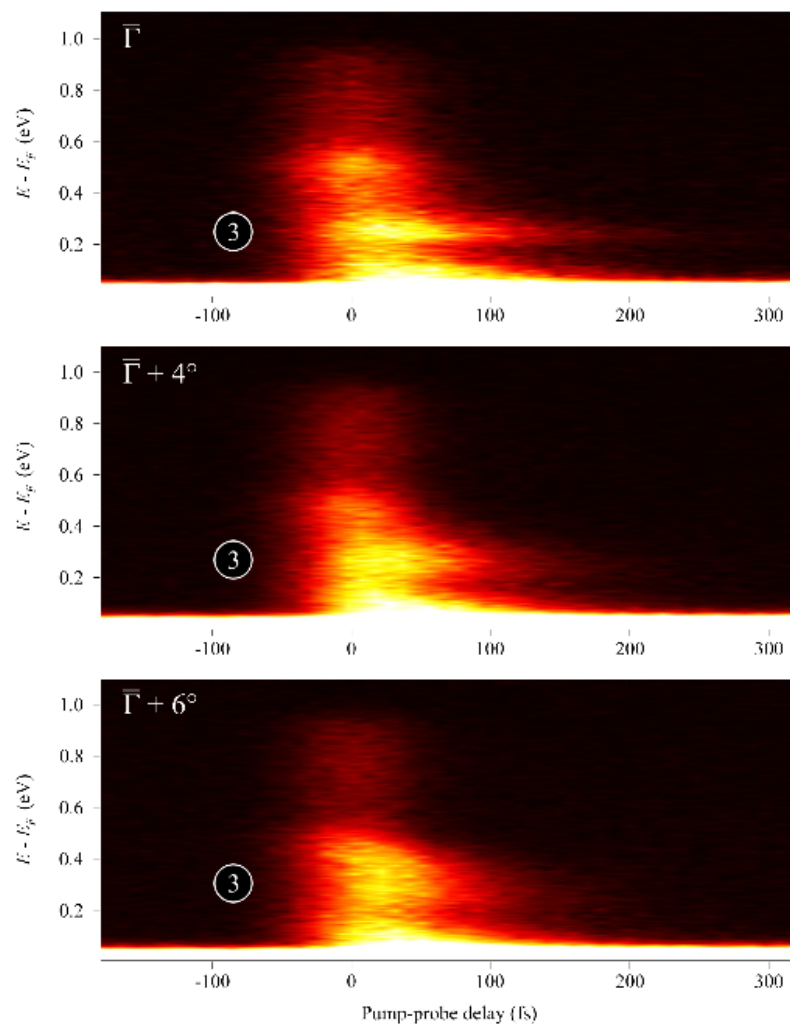


# Proof of principle pump-probe experiment



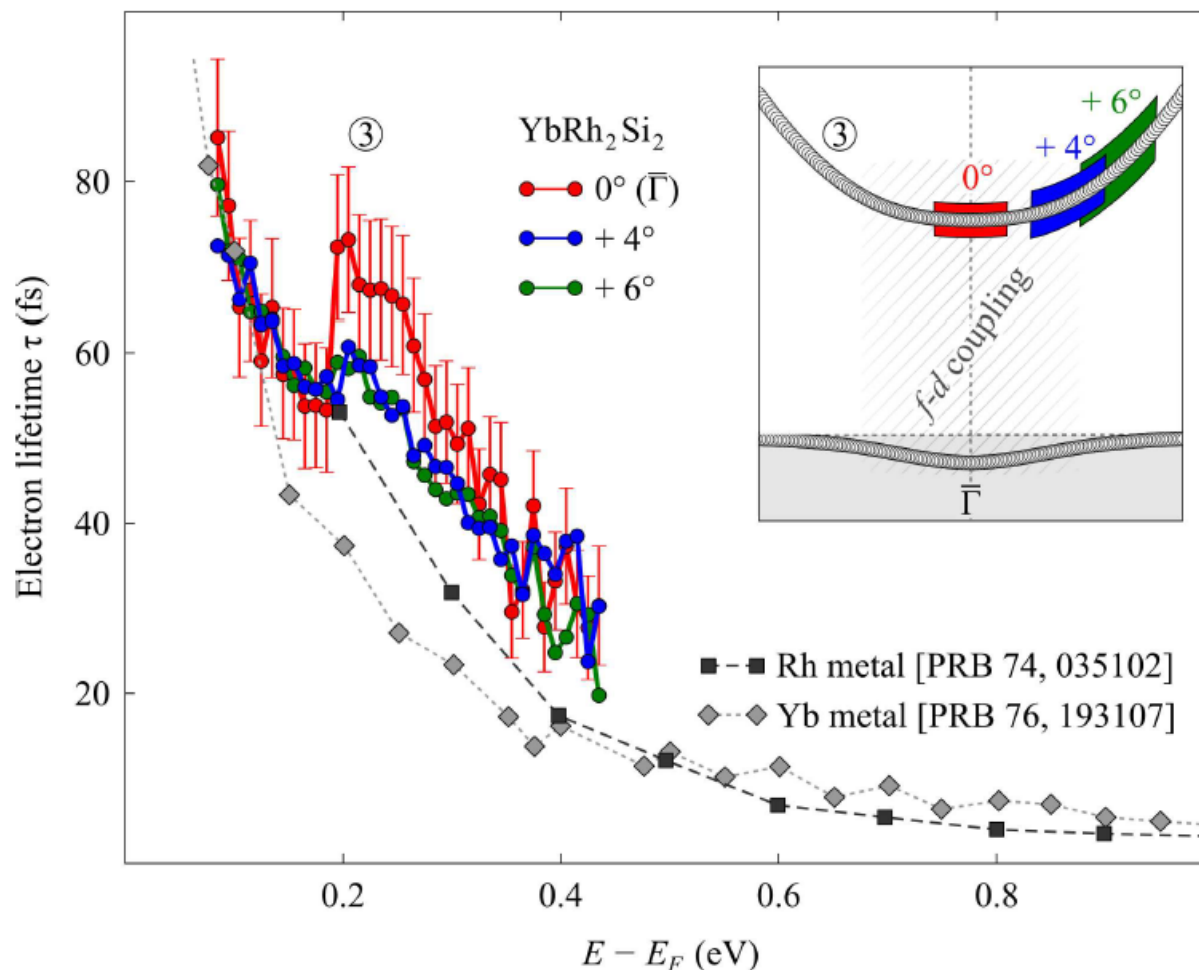
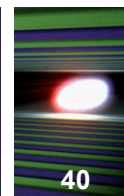
# Angle-resolved pump-probe experiments

39



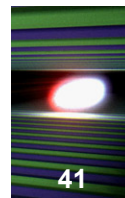
Pump-probe delay maps of the photoemission intensity above  $E_F$  and results of fit analysis

## Lifetime of electrons above Fermi energy



Jump in electron lifetime around  $\Gamma$  points at deviation from Fermi liquid theory and can be related to strength of correlation between  $d$  and  $f$  electrons. Effect depends on energy gap between  $d$  and  $f$  states.

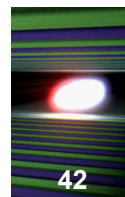




# But is it really time scale of Kondo (*f-d*) interaction?

**Cross sections of *d* and *f* electron  
excitations are extremely low at optical  
laser energies**

**Go to  $h\nu$  close (high harmonic generation, HHG)  
or above (XFEL) 100 eV!**

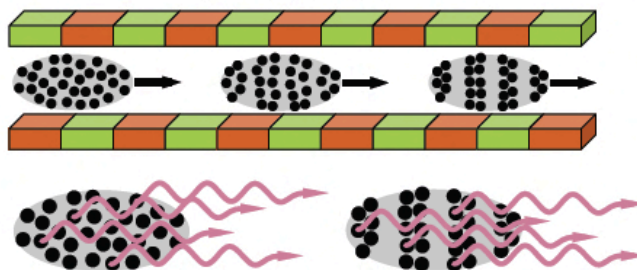


Sync. Rad. News 25:5, 12 (2012)

## Strobe lights: FEL versus HHG



### FEL (FLASH)

 $L = 27 \text{ m}$ 

$$h\nu \approx 25 - 300 \text{ eV}$$

(fundamental)

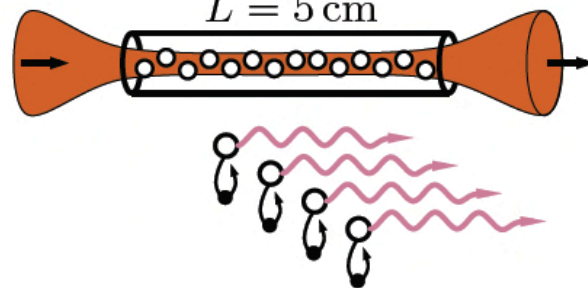
$$I \approx 10^{10} \text{ photons/s}$$

(space-charge  
& rep-rate limited)

$$\tau > 10 \text{ fs}$$



### HHG

 $L = 5 \text{ cm}$ 

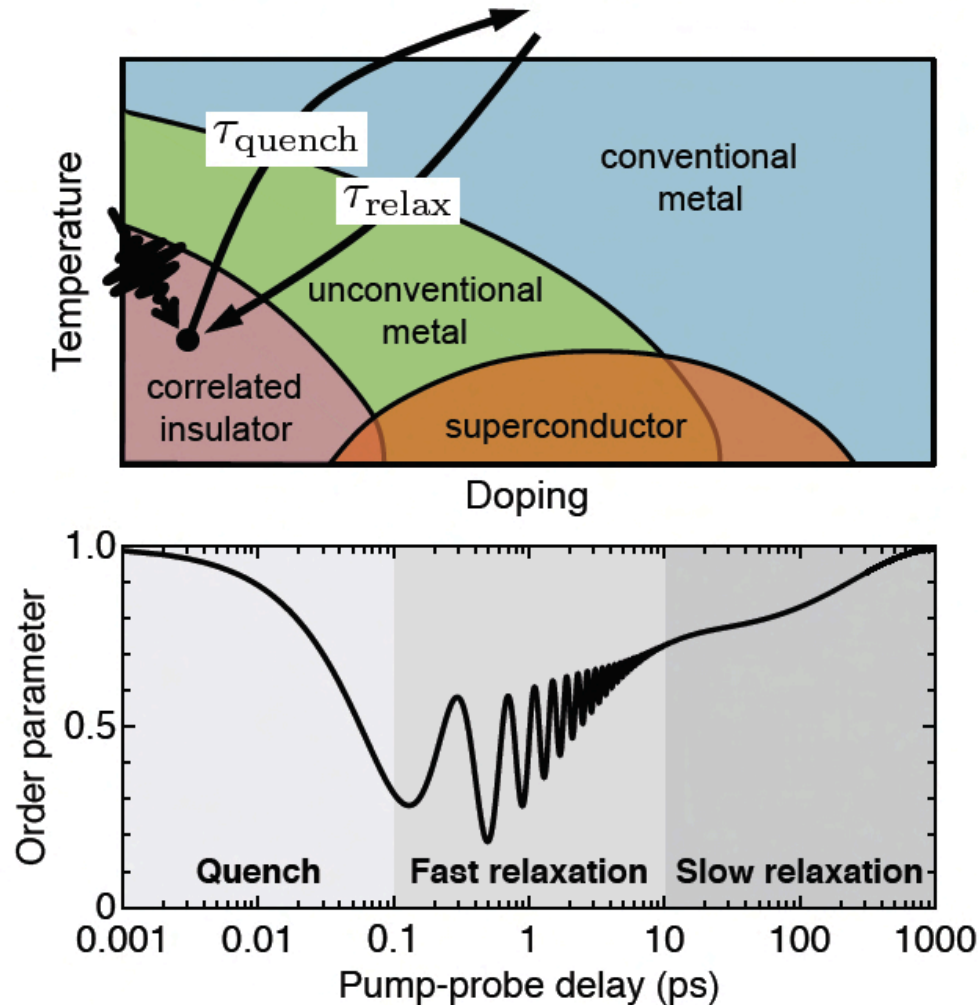
$$h\nu < 100 \text{ eV}$$

(practically)

$$I \approx 10^{10} \text{ photons/s}$$

$$\tau \leq 10 \text{ fs}$$

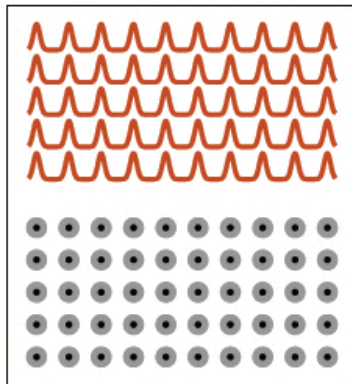
# Nature of condensed matter phases



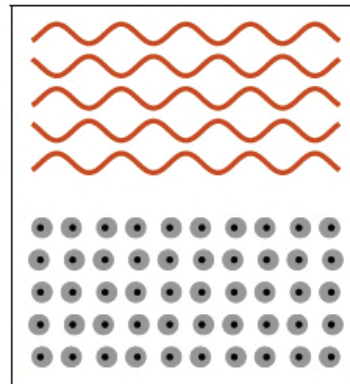
## Time scale of different interactions

# Time-domain classification (learning by destroying)

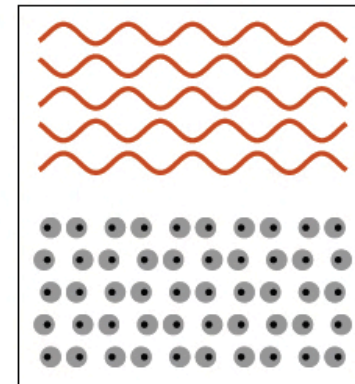
Mott insulator



Excitonic insulator



Peierls insulator

pump pulse  
excitation

$$\tau = \mathcal{O}\left(\frac{h}{t_{\text{hop}}}\right)$$

electron  
hopping

$$\tau = \mathcal{O}\left(\frac{2\pi}{\omega_{\text{plas}}}\right)$$

screening

$$\tau = \mathcal{O}\left(\frac{\pi}{\omega_{\text{amp}}}\right)$$

lattice  
vibration

0 fs

1 fs

10 fs

100 fs

1000 fs

# What can be done with HHG sources?

45

Nature **471**, 490 (2011)

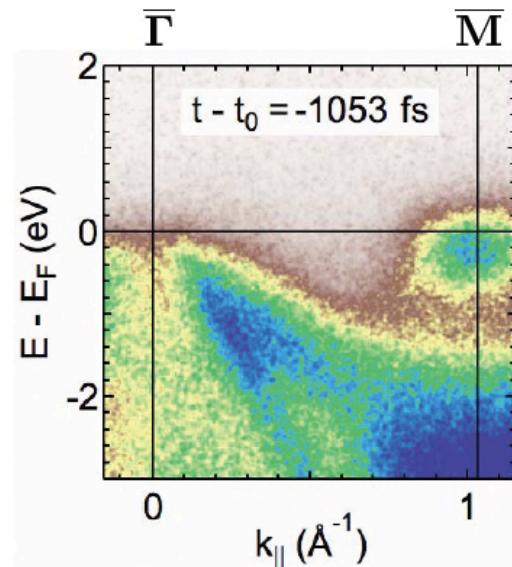
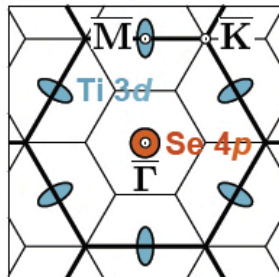
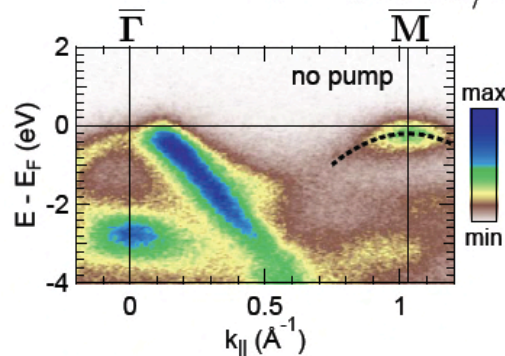
## trARPES using HHG

$$T = 125 \text{ K}$$

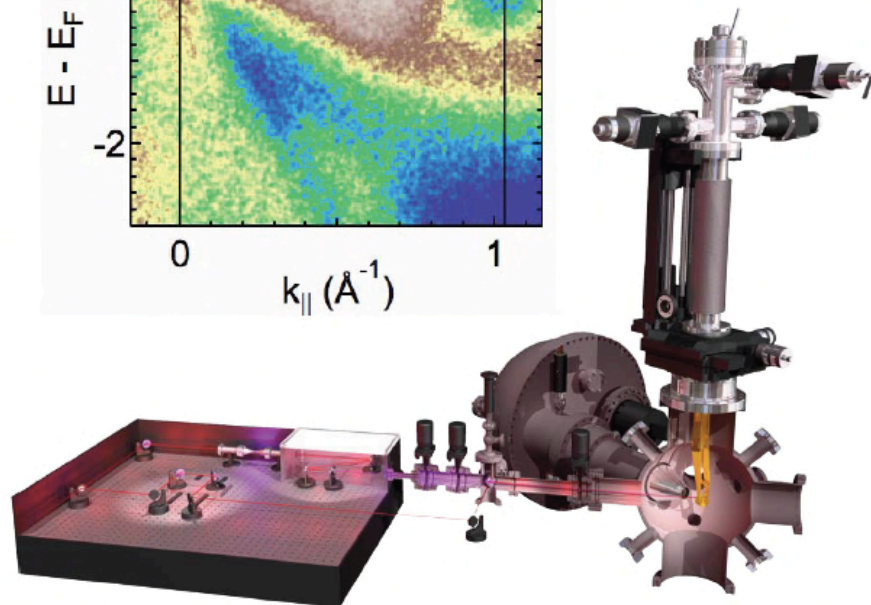
$$h\nu_{\text{pump}} = 1.57 \text{ eV. } h\nu_{\text{probe}} = 43 \text{ eV}$$

$$\Delta E \approx 400 \text{ meV. } \Delta t \approx 30 \text{ fs}$$

$$F = 1.75 \text{ mJ/cm}^2$$

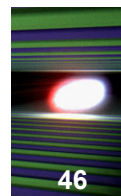


HHG setup  
Bauer group, Kiel

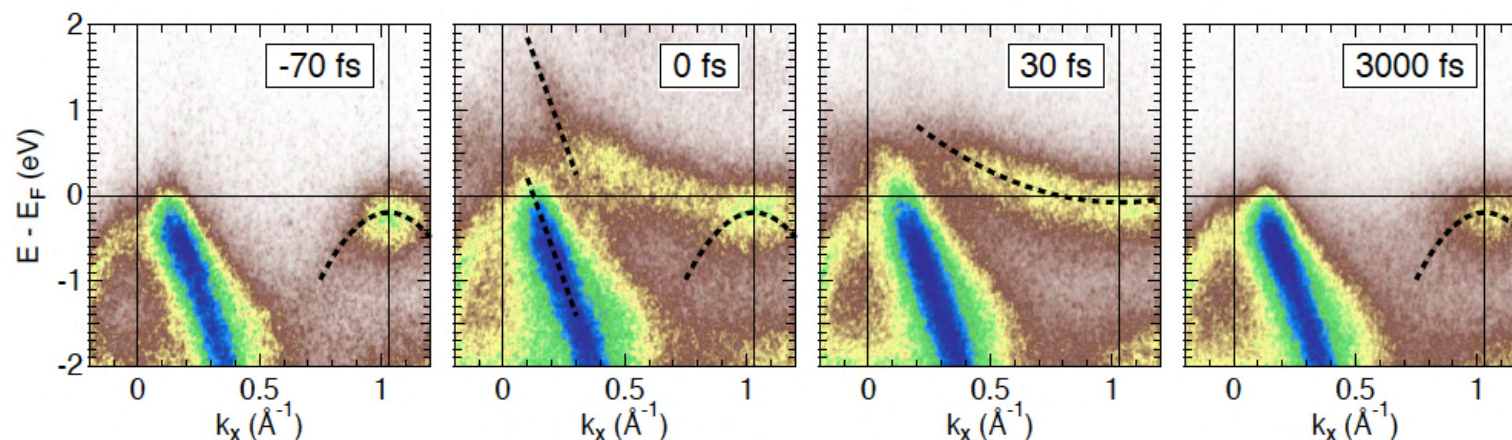




## What can be done with HHG sources?

Nature **471**, 490 (2011)

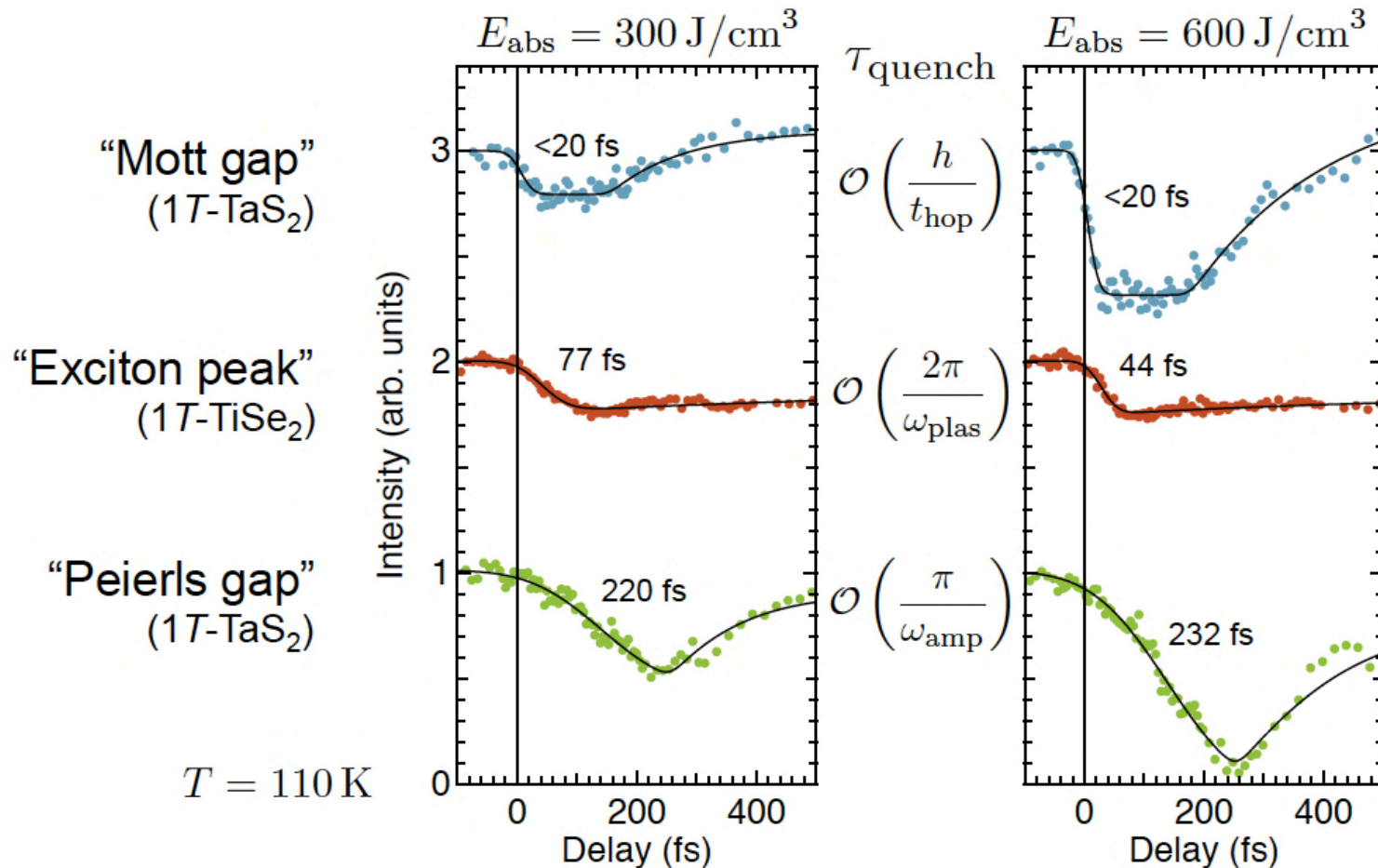
## Snapshots

instantaneous  
metallizationultrafast  
CDW quenchingpicosecond  
CDW recovery*s*-polarized probe

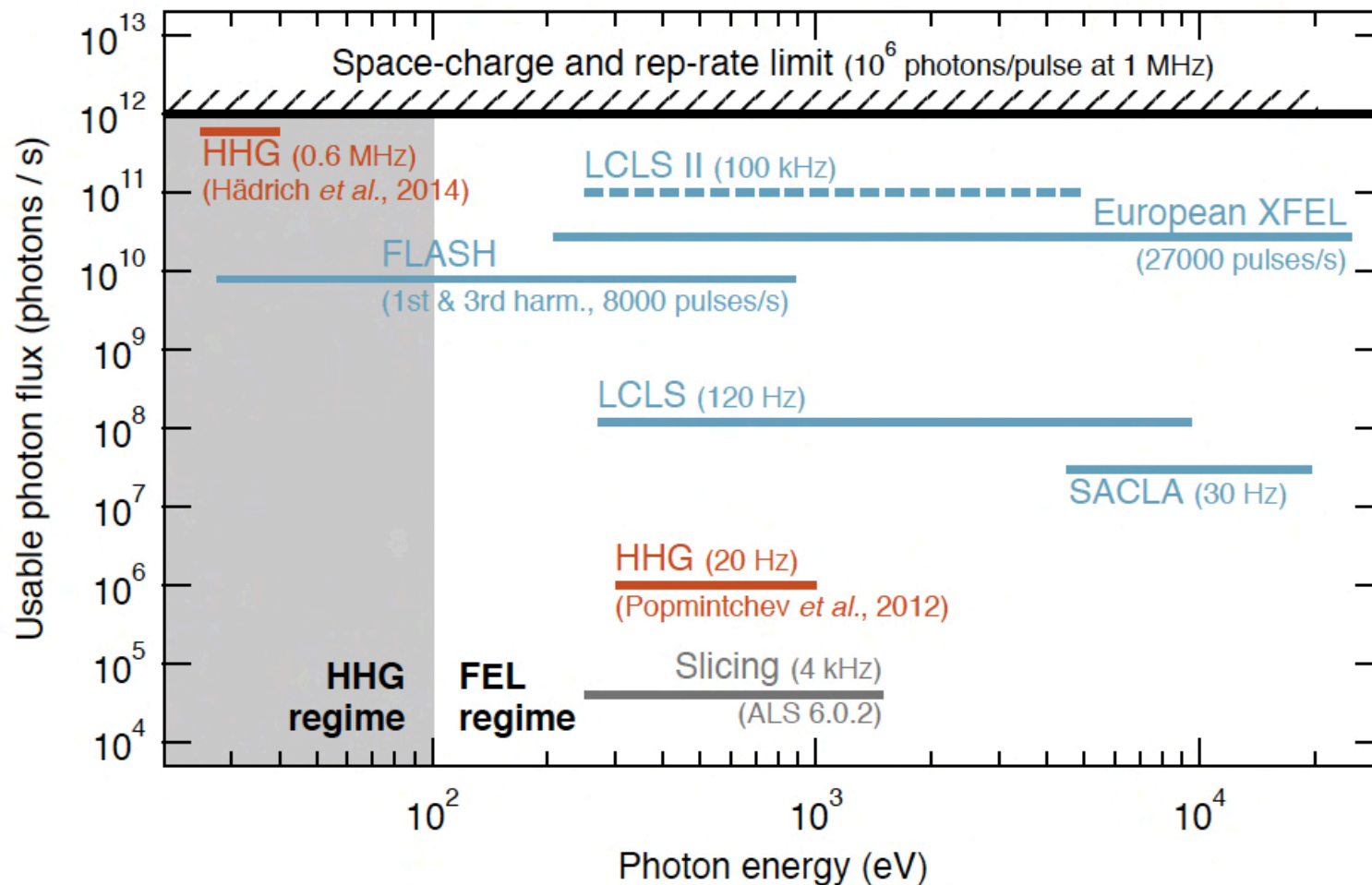
$$F_{\text{abs}} = 5 \text{ mJ/cm}^2$$

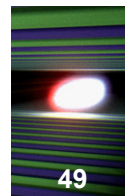
Nature Commun. 3, 1069 (2012)

# Hierarchy of quenching times



# FEL photoemission

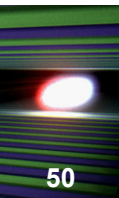




## Problem to be solved:

Please outline core-level PES spectra (intensity versus kinetic energy of electrons relative to the Fermi level) of an elemental sample that is characterized by electron-energy levels:

3p – 18.3 eV (binding energy); 3s – 34.8 eV; 2p – 297.3 eV and 294.6 eV; 2s – 378.6 eV that are excited by radiation with wavelength 8.26 and 3.13 nm. Which element builds this sample?



**Thank you for your attention  
and  
see you again today**