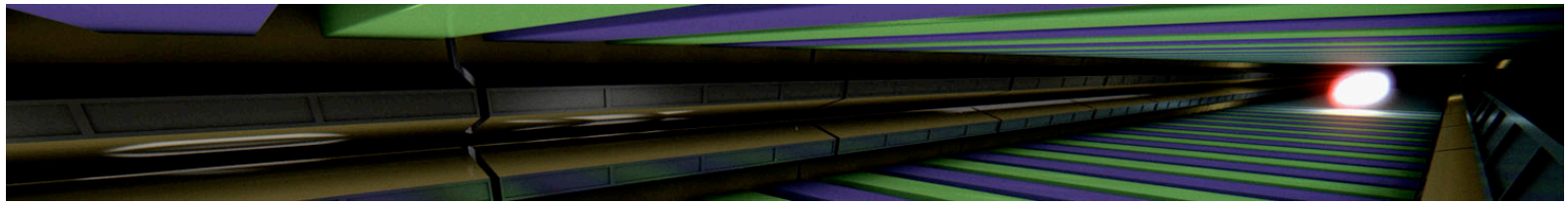
European XFEL



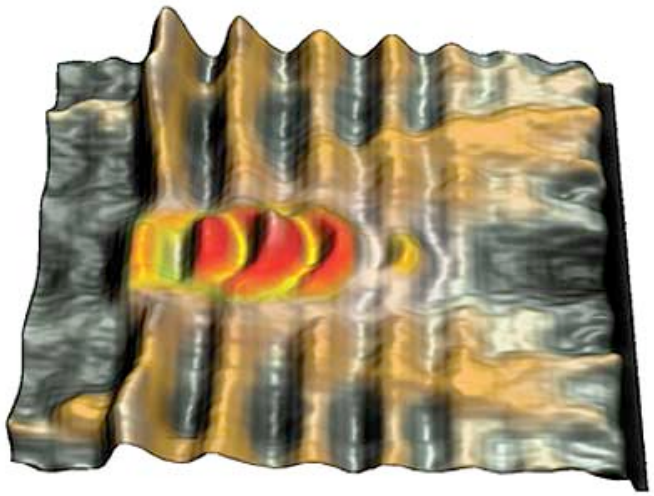
Spectroscopy of Correlated Materials: Challenge and FEL Potentialities

Serguei L. Molodtsov

European XFEL Project Team (EPT)

- heavy-fermion/Kondo 4*f* systems
- occupied electronic states of Yb & Eu based materials (ARPES & XPS)
- unoccupied electronic states, 2-particle response by RIXS
- fs lattice and electron dynamics by RIXS, RXS, XPS & ARPES

PRL Cover, Vol. 102, Iss. 2 (2009)

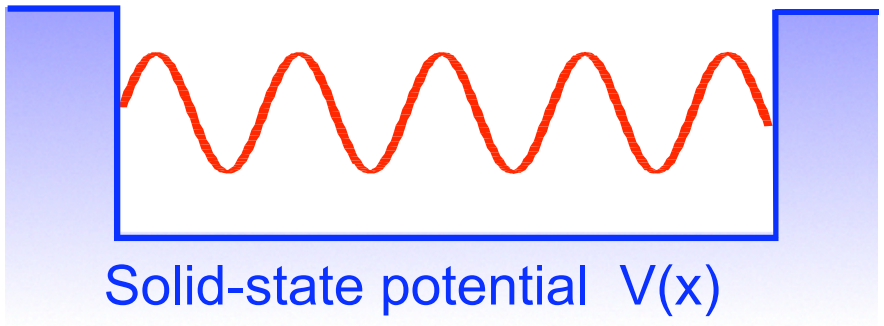


Photoemission from mixed-valent $EuNi_2P_2$

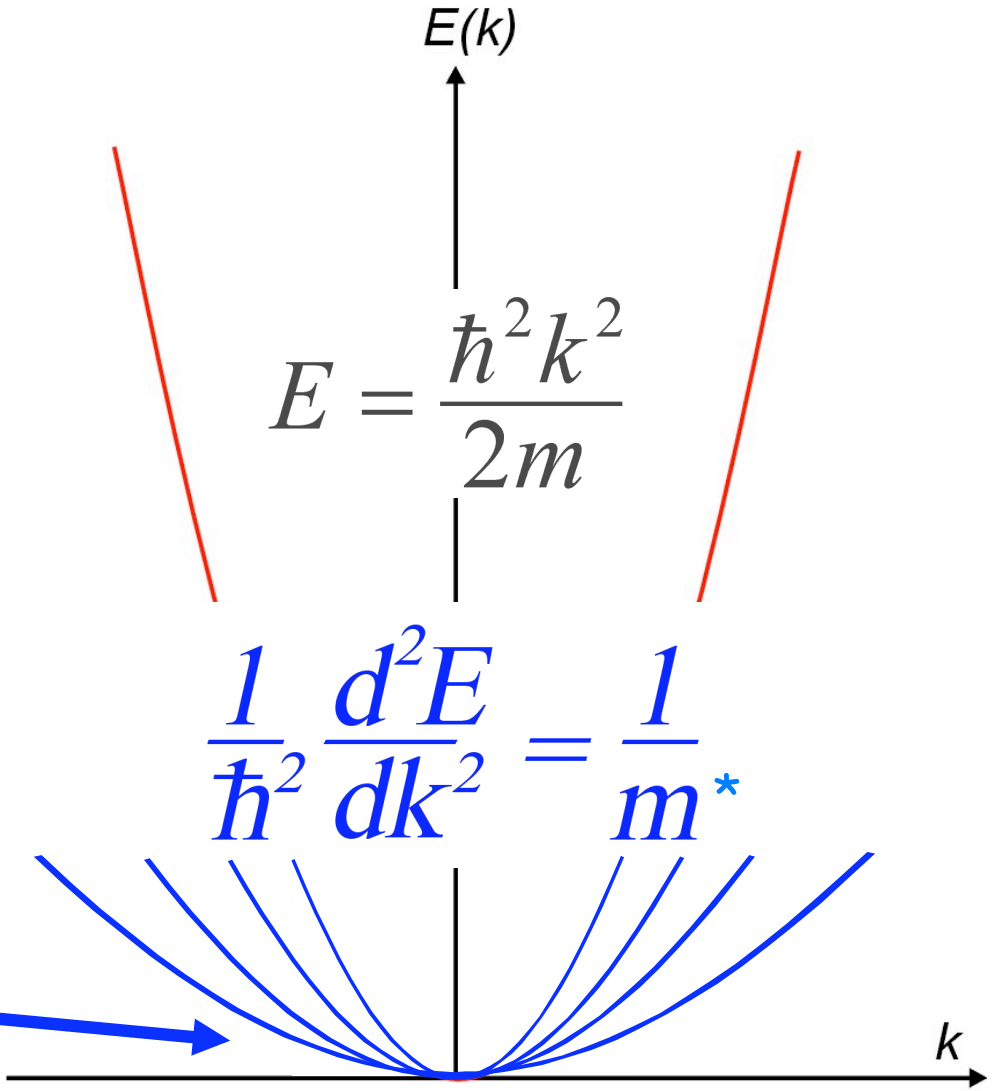
Danzenbächer *et al.*, PRL **102** (2009) 026403

Single-Particle System

1 - dim. solid state:



Heavy-fermion system



European XFEL

Non-Correlated Materials

solid state

↓

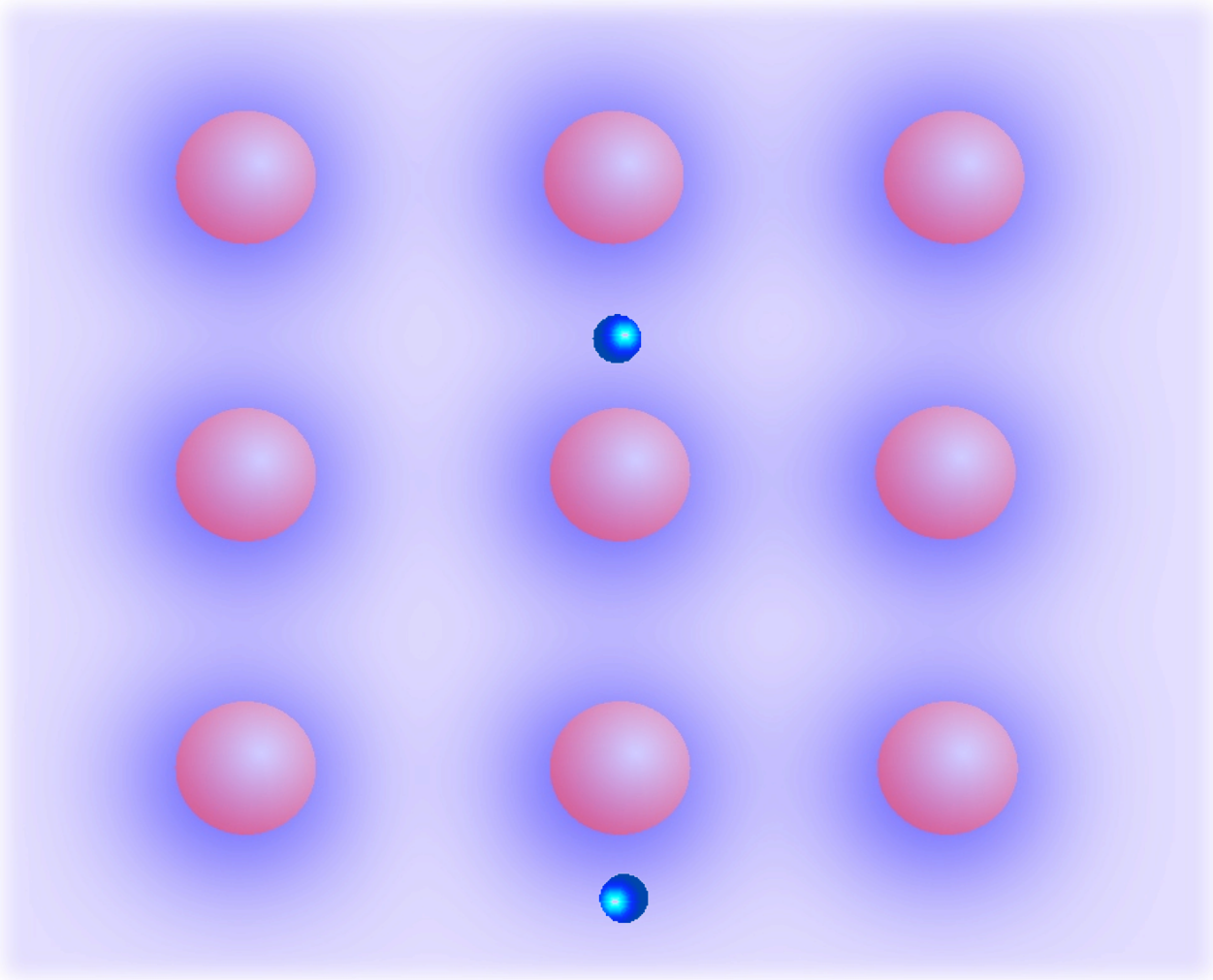
potential averaged
over all electrons

↓

single-particle
calculations,
LDA approach

Problem: ↓

negligence
of electron correlations

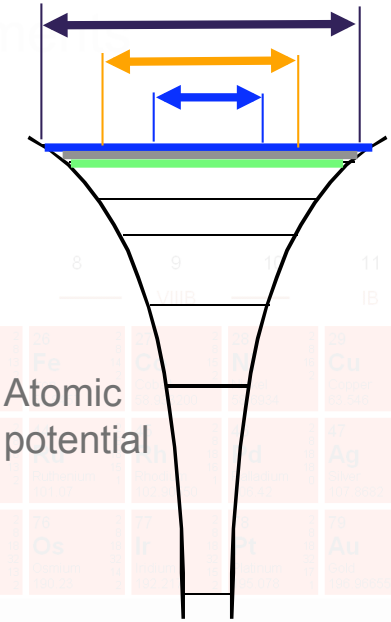


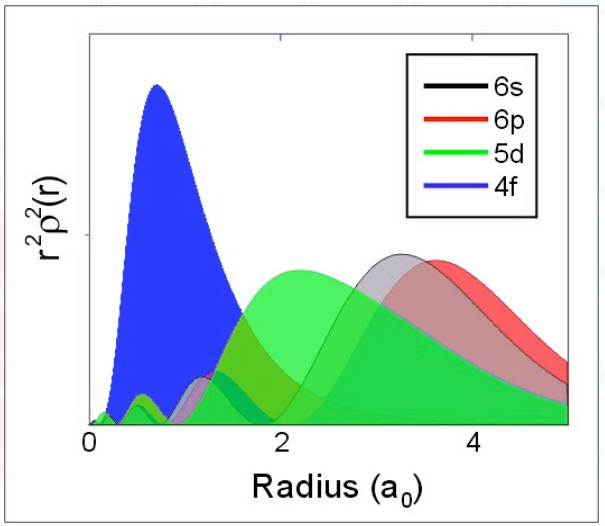
European XFEL

Correlated *f*-Materials

Electron configuration:

$$[Xe]\ 4f^{n}\ 5d^{m}\ 6s^{2}$$





Lanthanoide

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

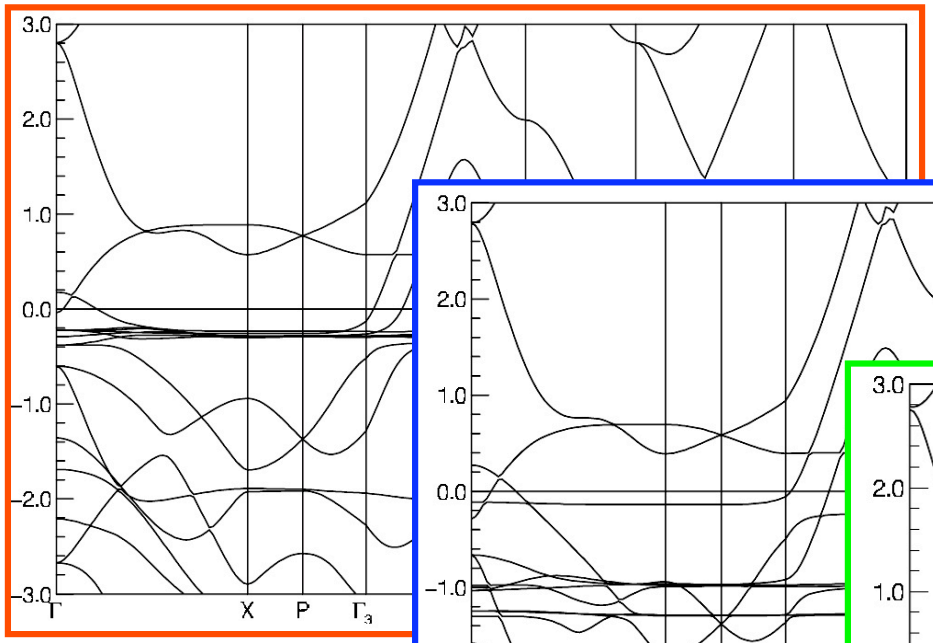
f - electrons

European XFEL

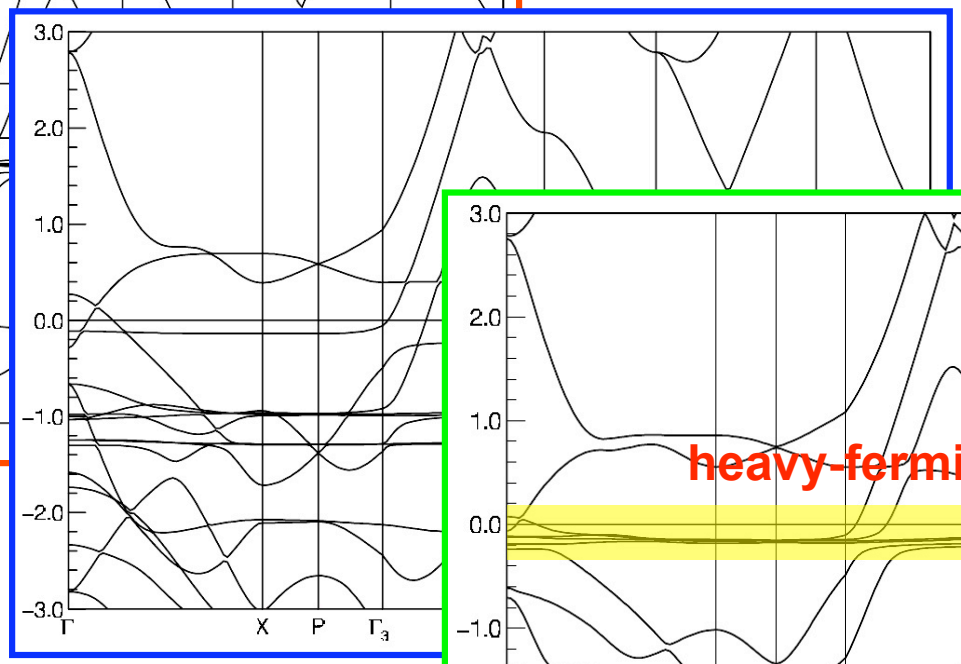
Correlated *f*-Materials

heavy-fermion compound

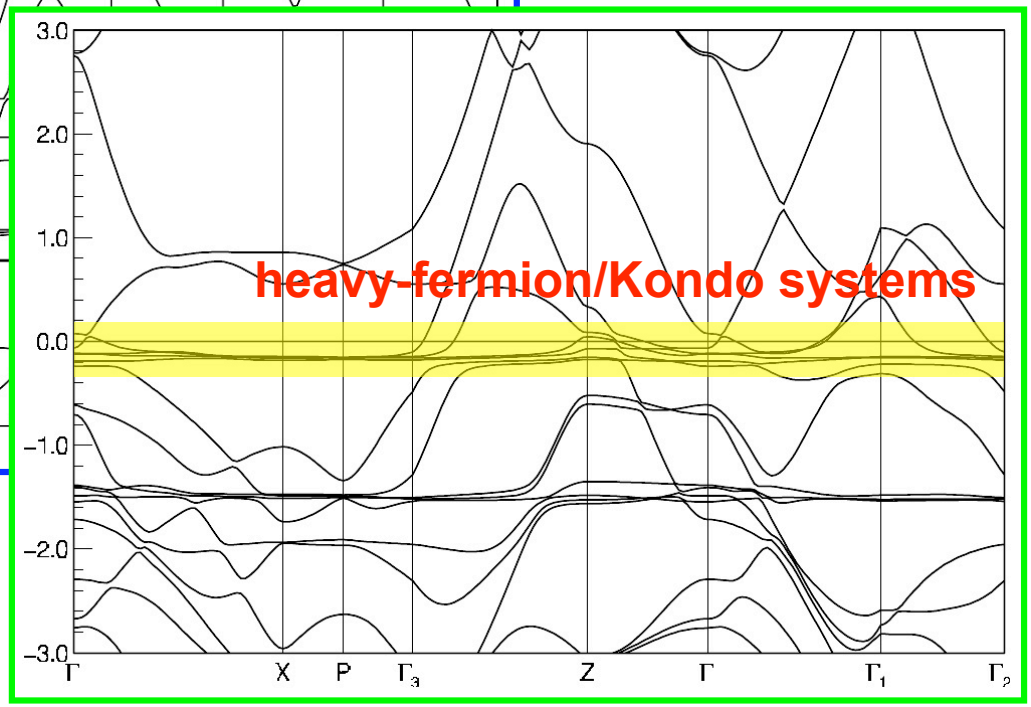
$YbRh_2Si_2$



LDA band structure



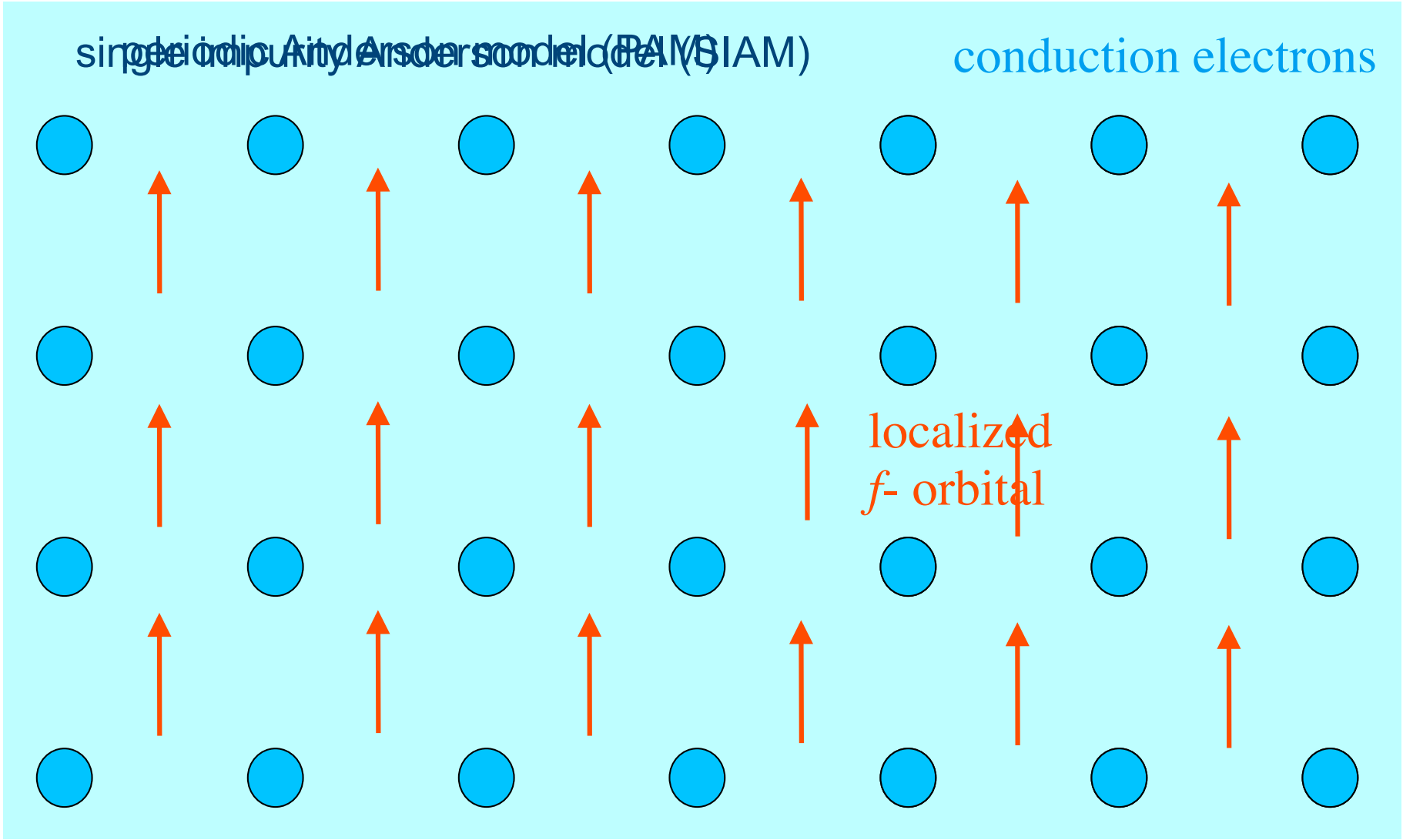
LDA + *U* approach band structure



fully relativistic band structure

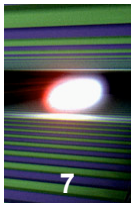
T. Jeong and W.E. Pickett,
J. Phys.: Condens. Matter **18** (2006) 6289

Correlated Anderson Models (SIAM vs. PAM)



European XFEL

Periodic Anderson Model (PAM)



Hamiltonian:

$$H = \sum_{\mathbf{k},\sigma} \varepsilon(\mathbf{k}) d^{+}_{\mathbf{k}\sigma} d_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\sigma} \varepsilon_f(\mathbf{k}) f^{+}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma}$$

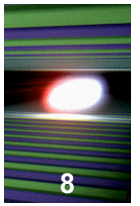
$$+ \frac{U_{ff}}{2} \sum_{i,\sigma} n^{f}_{i,\sigma} n^{f}_{i,-\sigma}$$

$$+ \sum_{\mathbf{k},\sigma} V_{\mathbf{k}}(\varepsilon) \left(d^{+}_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma} + f^{+}_{\mathbf{k}\sigma} d_{\mathbf{k}\sigma} \right)$$

- Kondo behavior is due to interplay between on-site correlation and electron hybridization (change of valence)
- Time scale of electron system response is of the order 1 - 100 fs (FEL)

European XFEL

Importance and Challenge



These materials are of high importance:

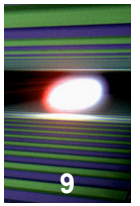
- anisotropy of transport properties
- anisotropy of magnetic properties
- switches from Kondo to magnetic behavior, particularly in the region of quantum critical points (QCP, e.g YbRh2Si2)

But extremely difficult to study:

- theoretical description is not straightforward
- experimental methods require high energy and momentum resolution to sample both occupied and unoccupied electronic states
- correlated 2-particle response across the (Kondo) gap is necessary
- electron/spin dynamics of Kondo-to-magnetic-state transition should be explored

European XFEL

Spectroscopy of Occupied Electronic States



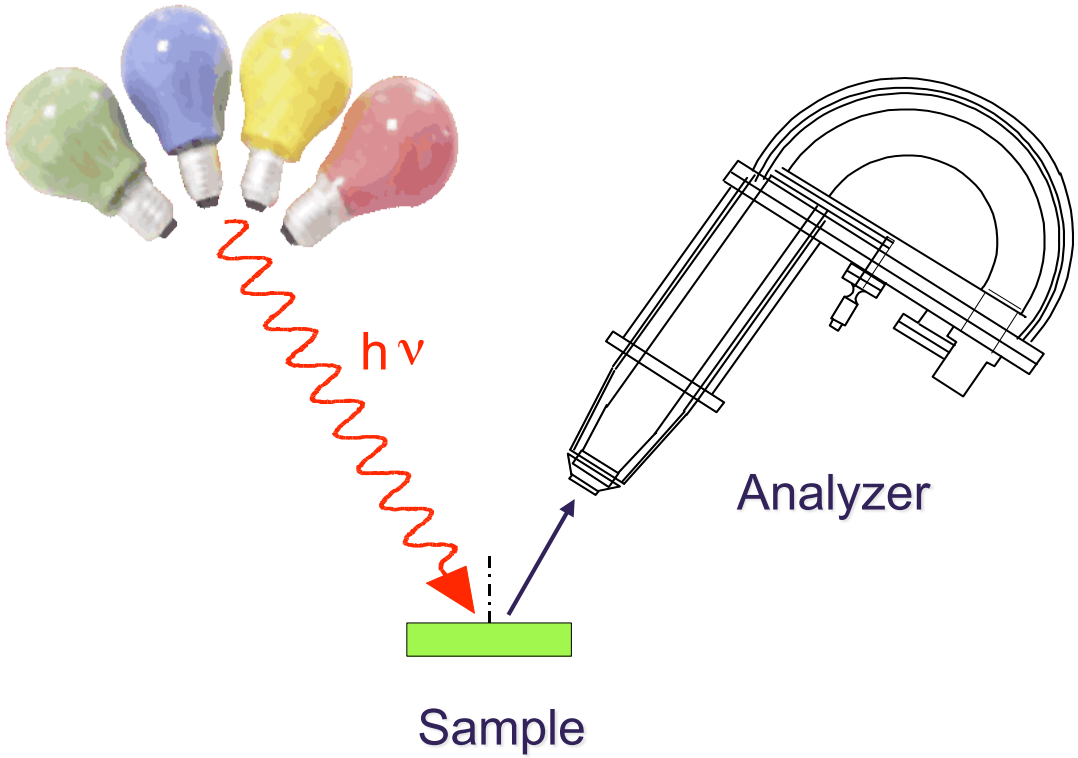
Electronic Structure of Occupied States

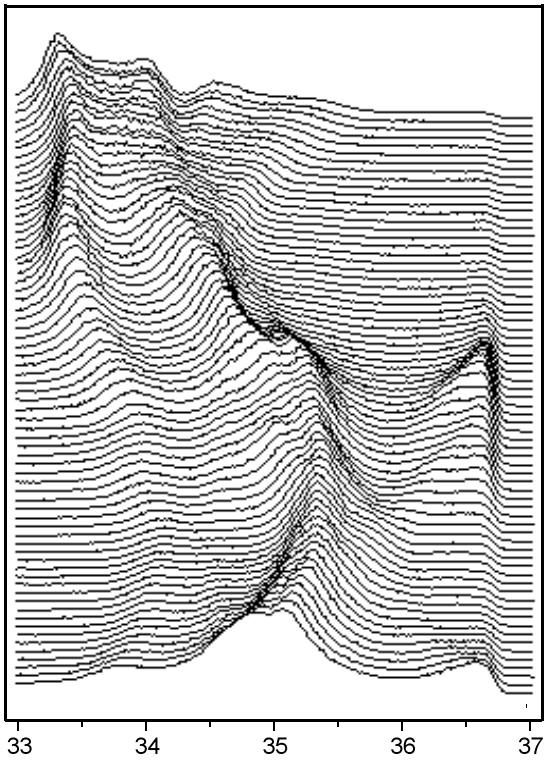
Angle-resolved photoemission spectroscopy (ARPES)

Core-level X-ray photoemission spectroscopy (XPS)

1-particle response

Angle-Resolved Photoemission Spectroscopy (ARPES)



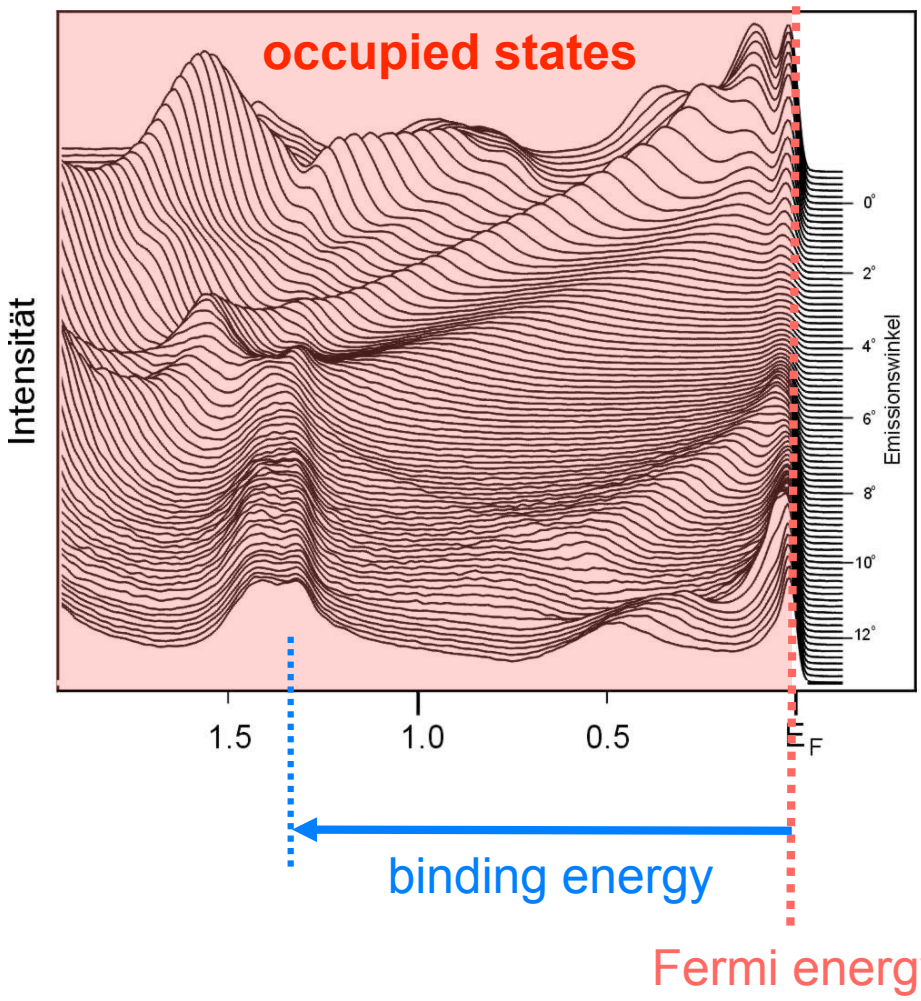


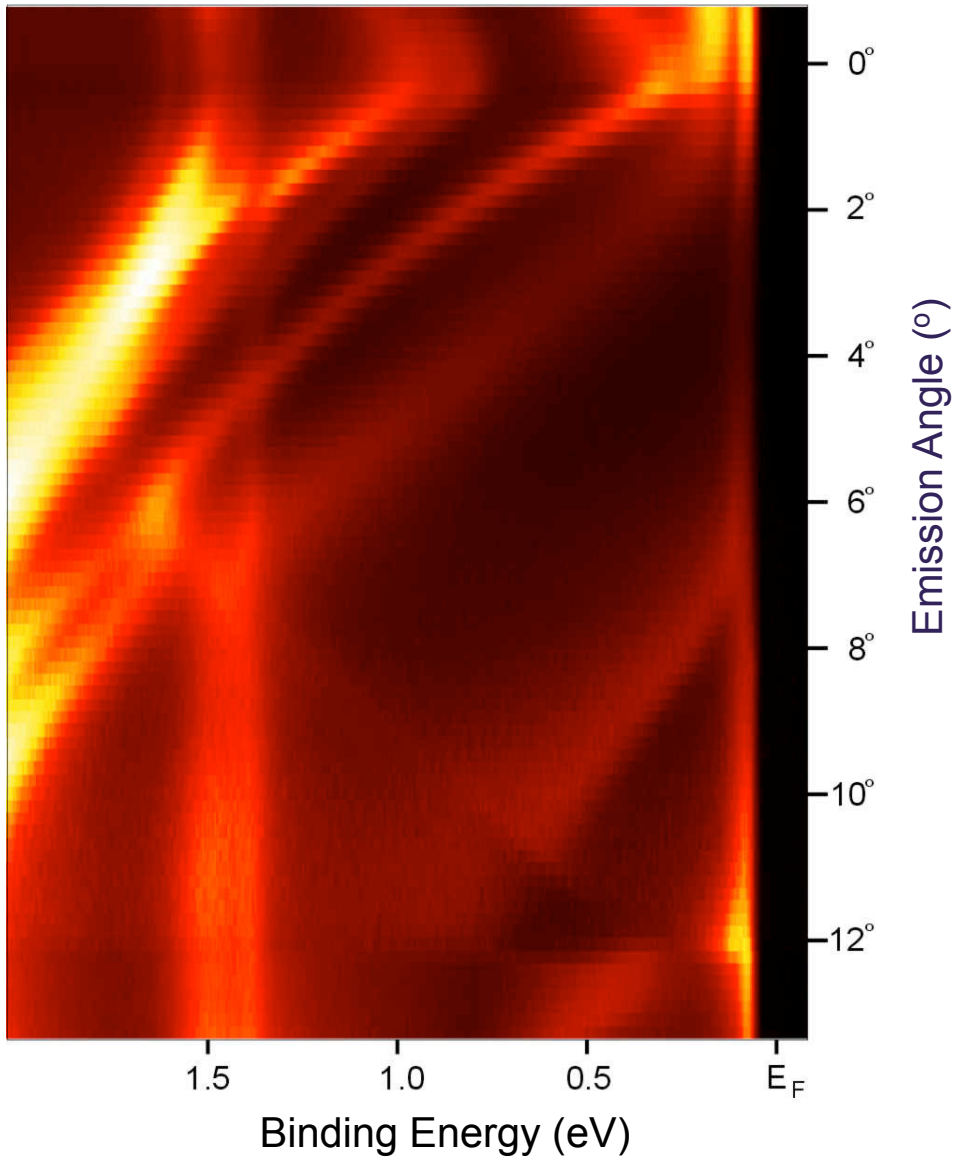
ARPES

European XFEL

Angle-Resolved Photoemission Spectroscopy

Example: $YbRh_2Si_2$

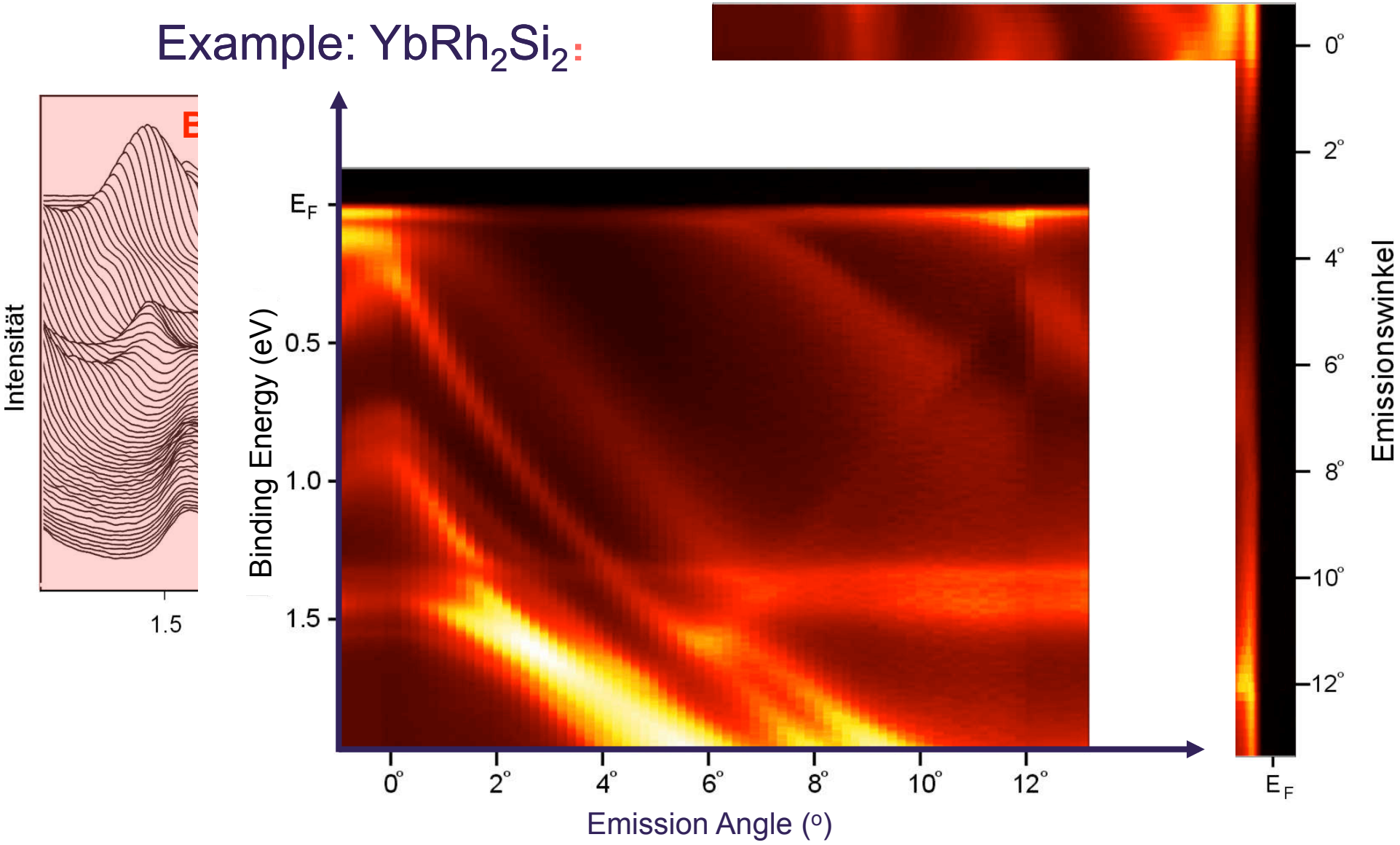




European XFEL

Angle-Resolved Photoemission Spectroscopy

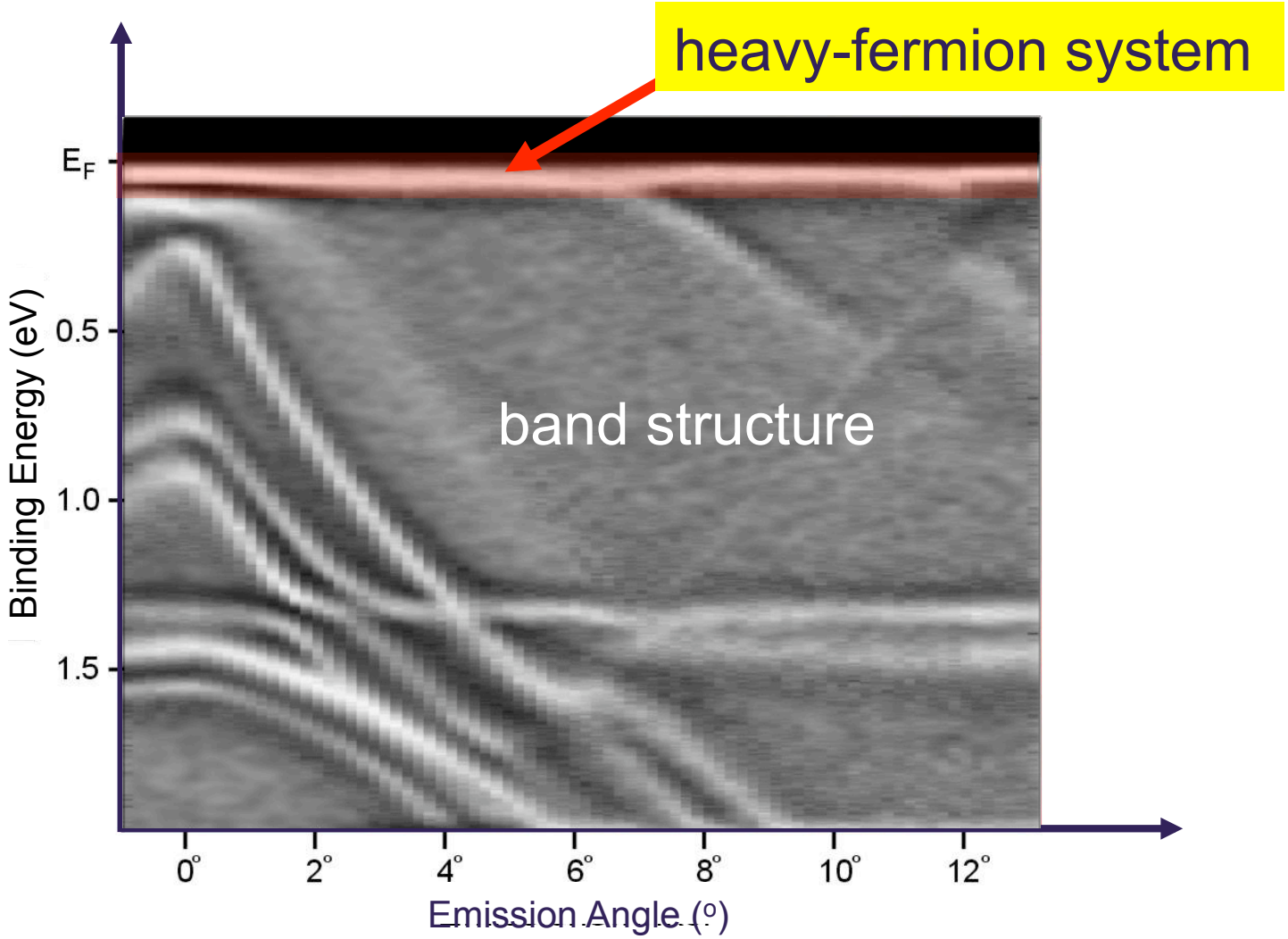
Example: $YbRh_2Si_2$:



European XFEL

Angle-Resolved Photoemission Spectroscopy

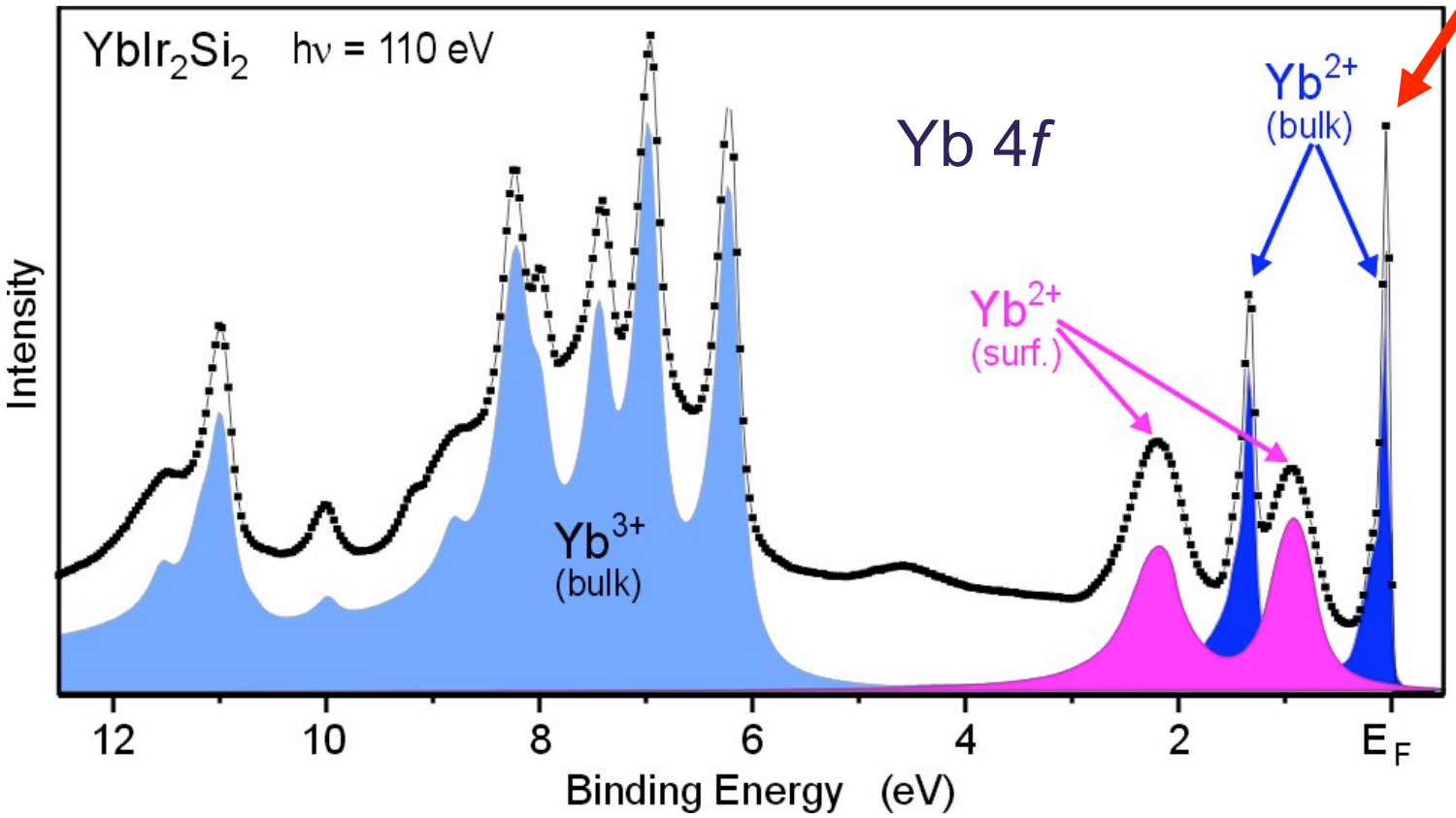
Example: $YbRh_2Si_2$



Core-level Photoemission Spectroscopy (XPS)

Example: $YbIr_2Si_2$

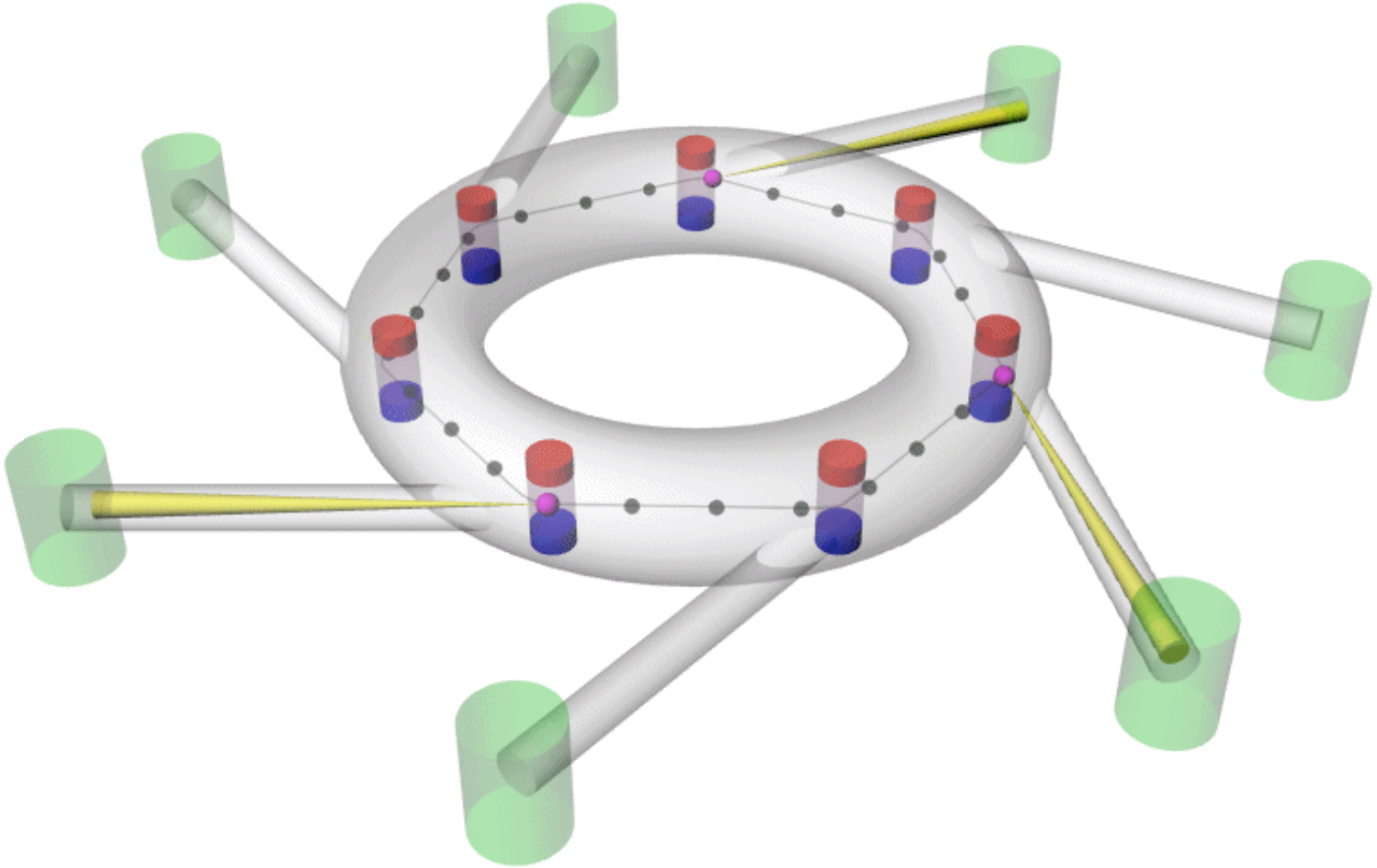
Kondo system



mean valence ~2.9

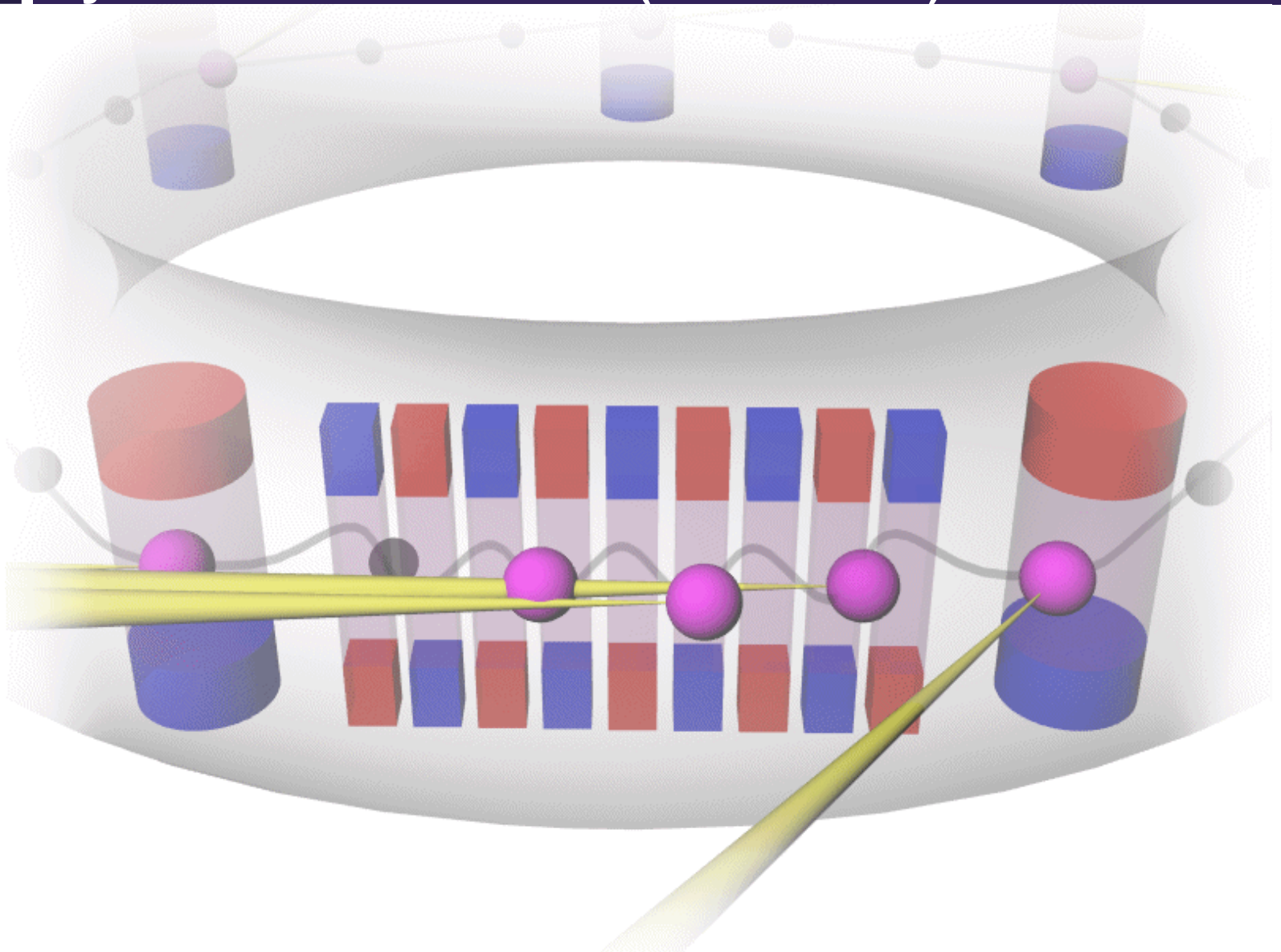
European XFEL

Synchrotron Radiation (dipoles)



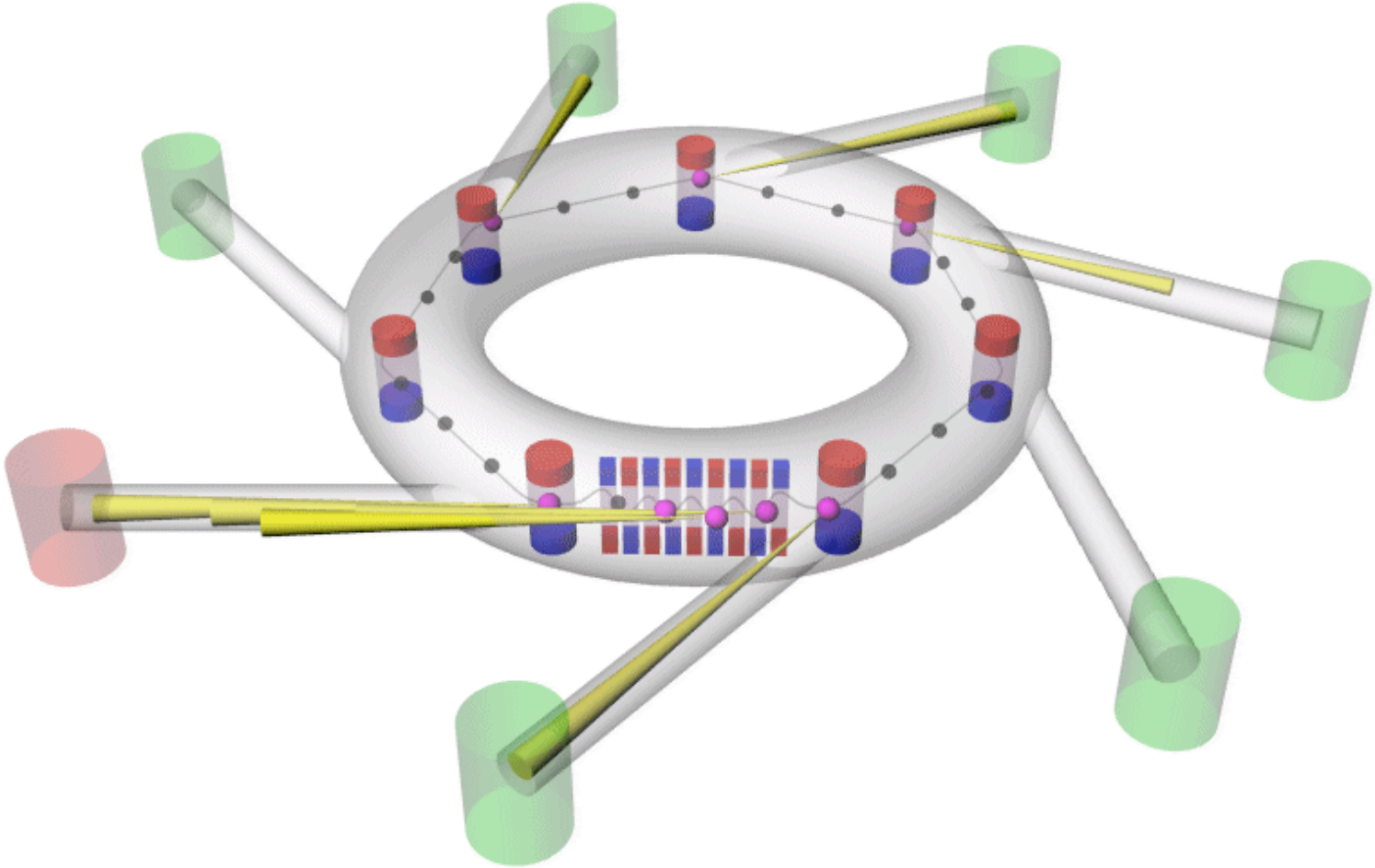
European XFEL

Synchrotron Radiation (undulators)



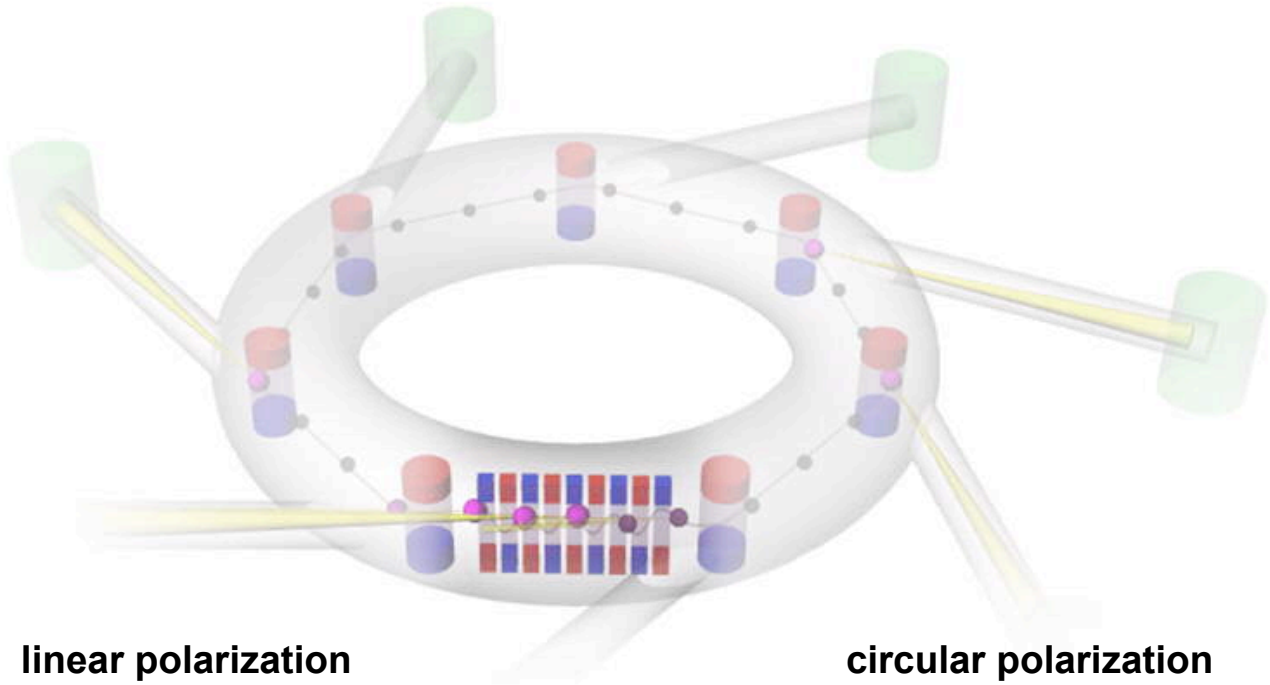
European XFEL

Synchrotron Radiation (sources + exp. stations)

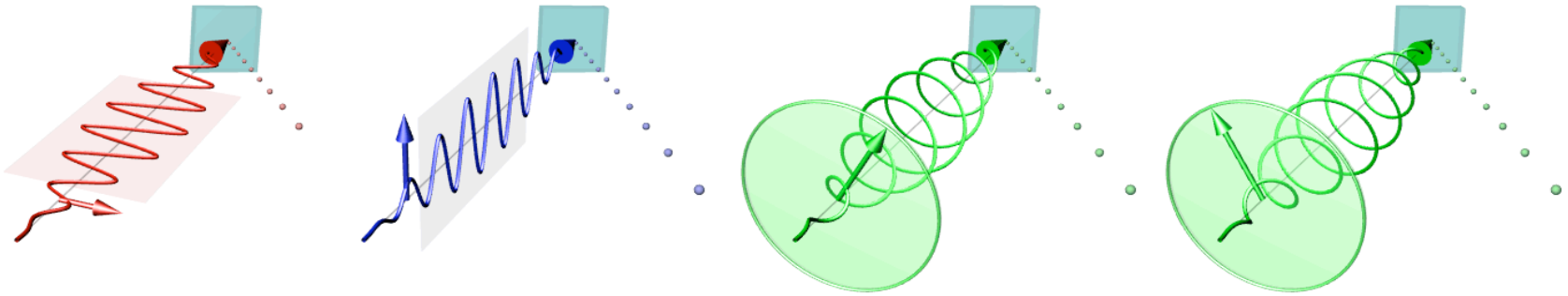


European XFEL

Synchrotron Radiation (light polarization)

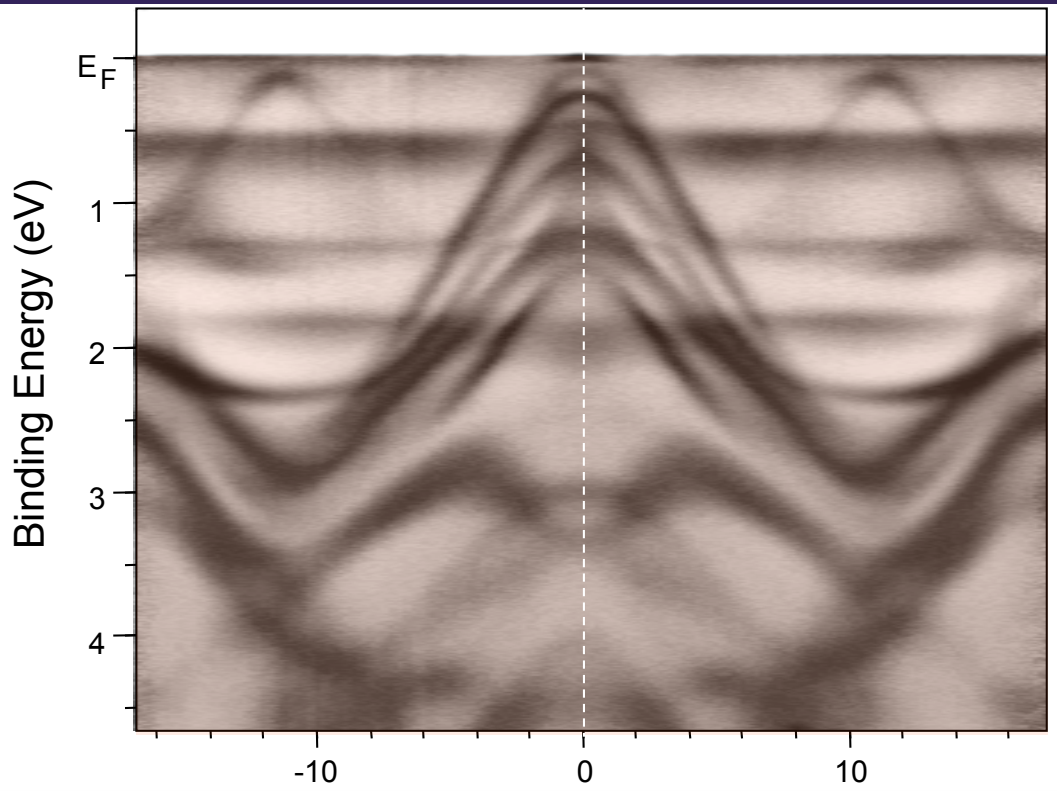


linear polarization **circular polarization**

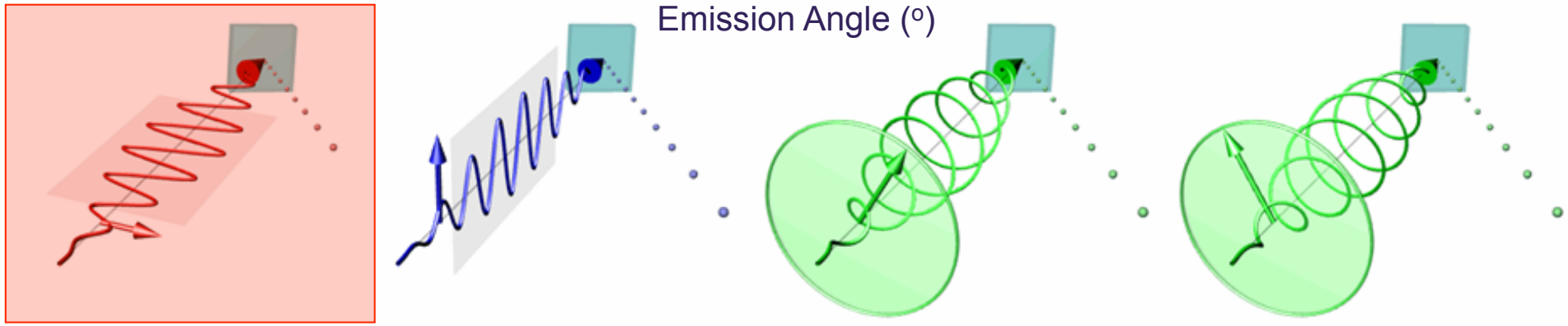


European XFEL

Light-polarized ARPES ($YbRh_2Si_2$)

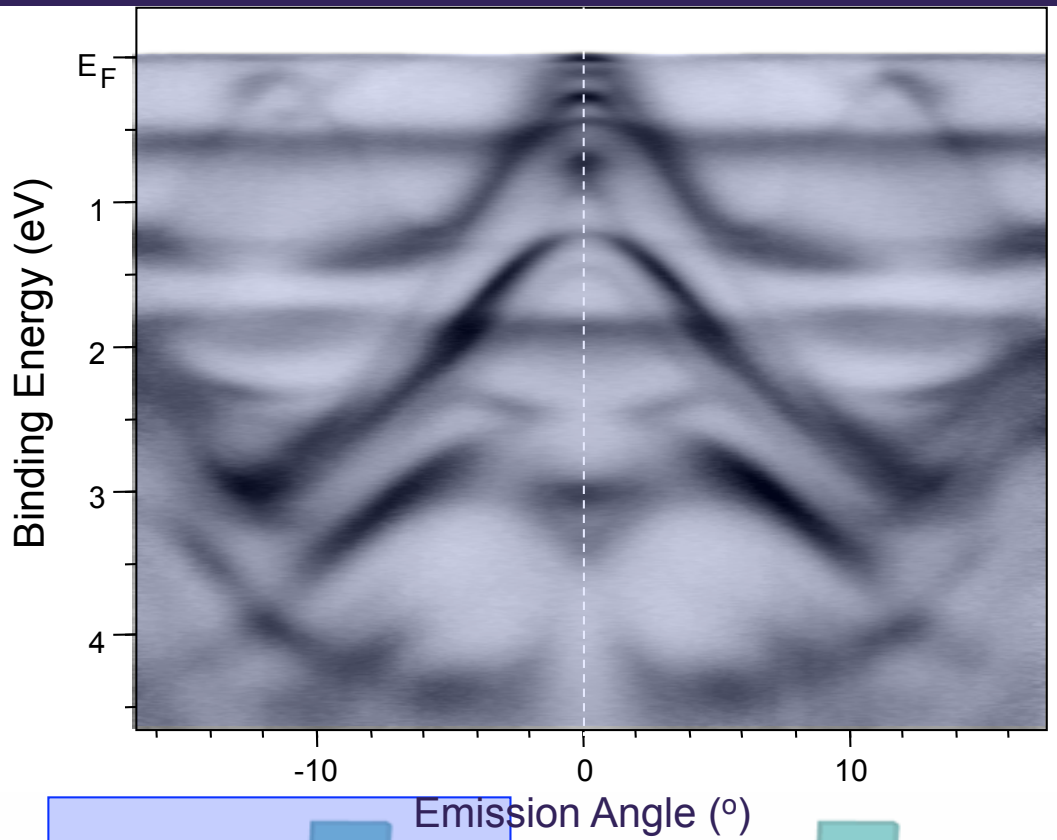


$YbIr_2Si_2$

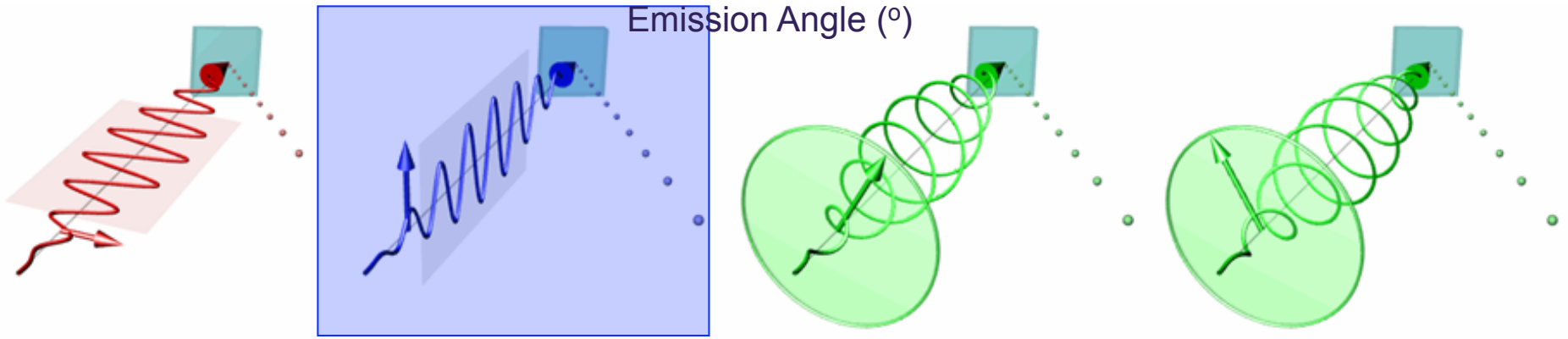


European XFEL

Light-polarized ARPES ($YbRh_2Si_2$)

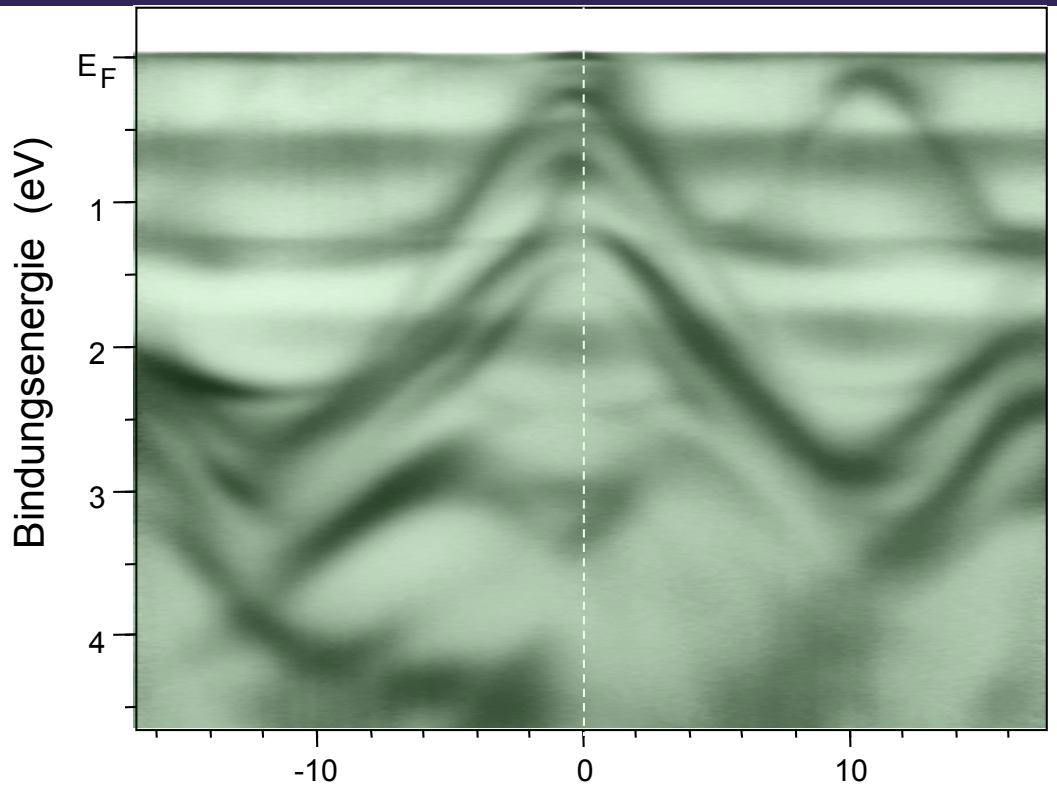


$YbIr_2Si_2$

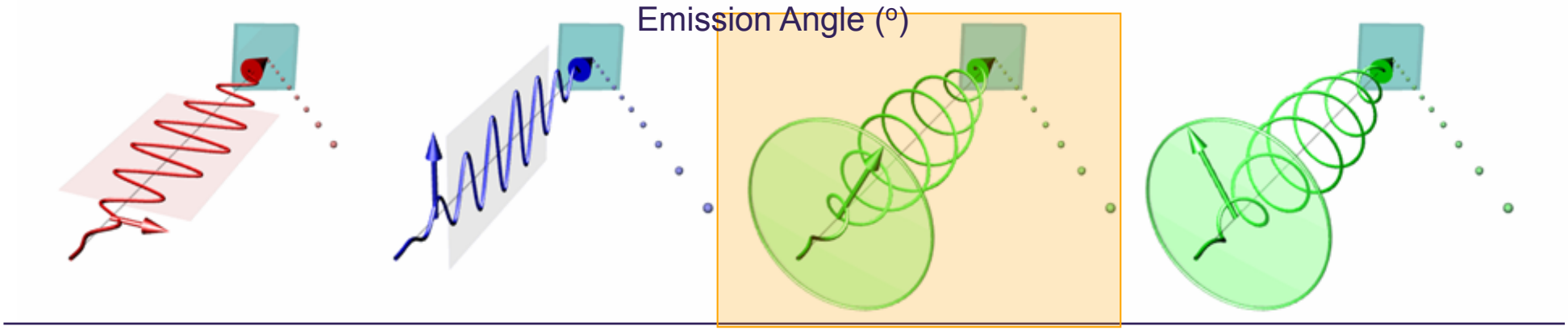


European XFEL

Light-polarized ARPES ($YbRh_2Si_2$)

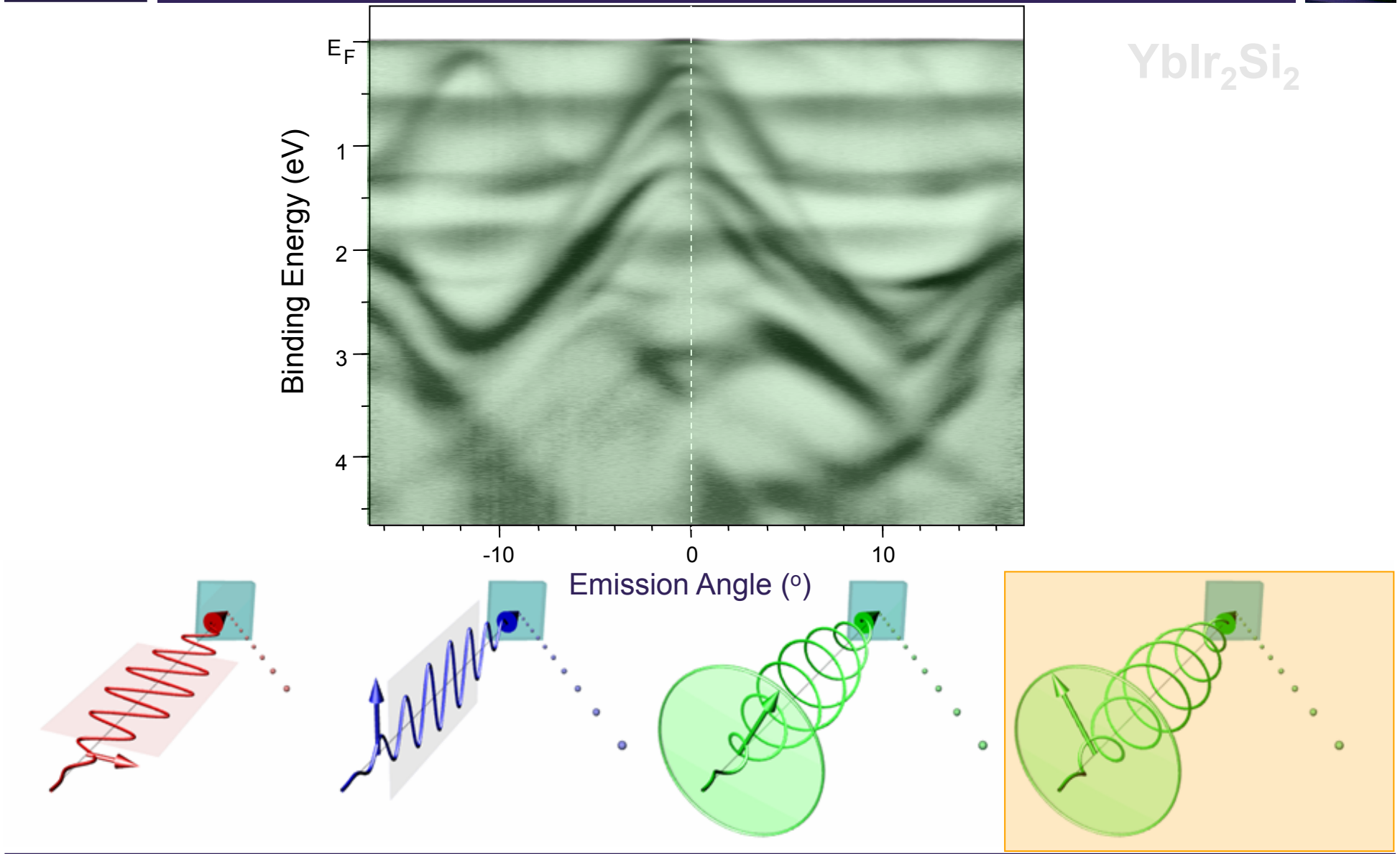


$YbIr_2Si_2$



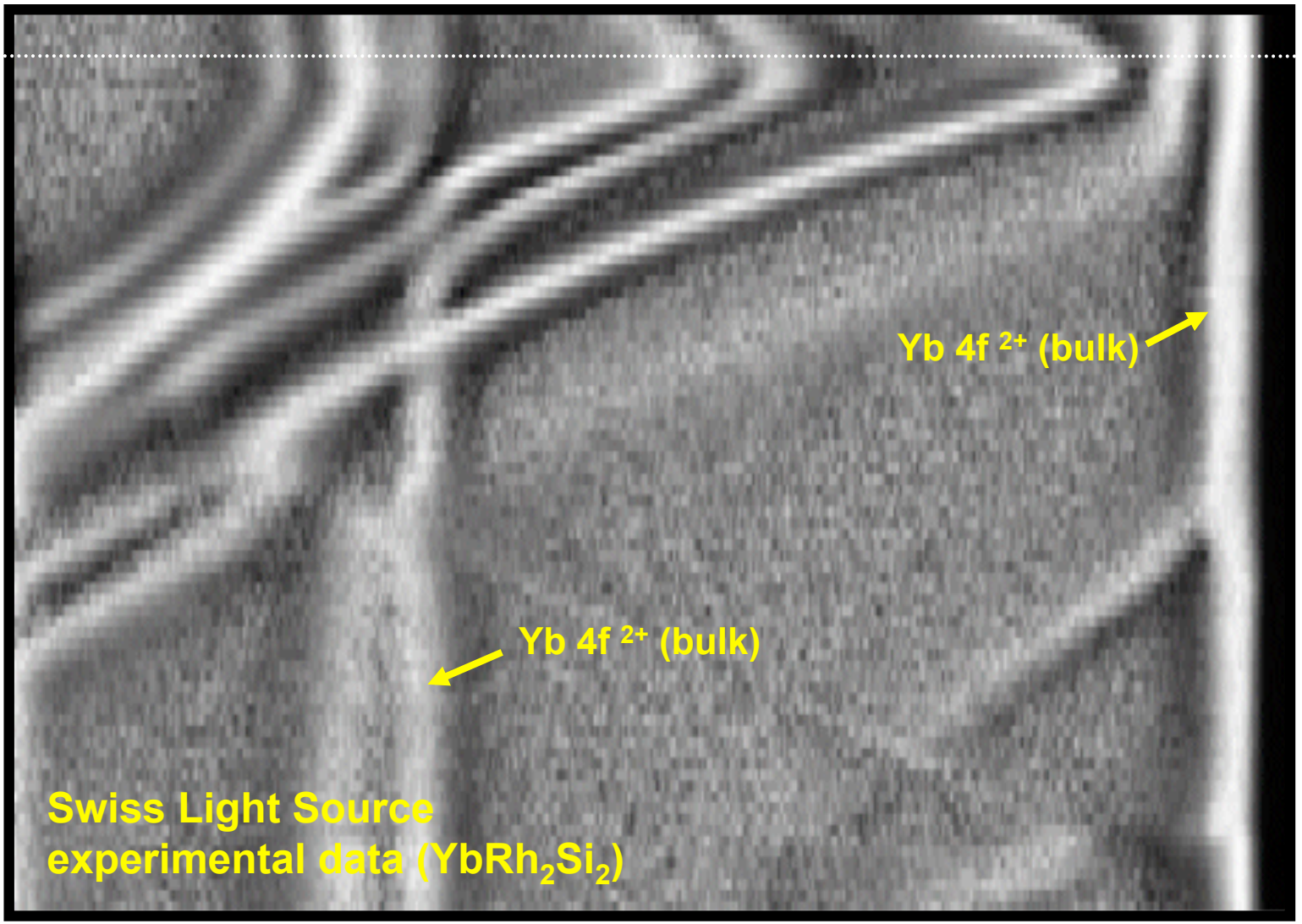
European XFEL

Light-polarized ARPES ($YbRh_2Si_2$)



European XFEL

Bands Mapping Across the Brillouin Zone



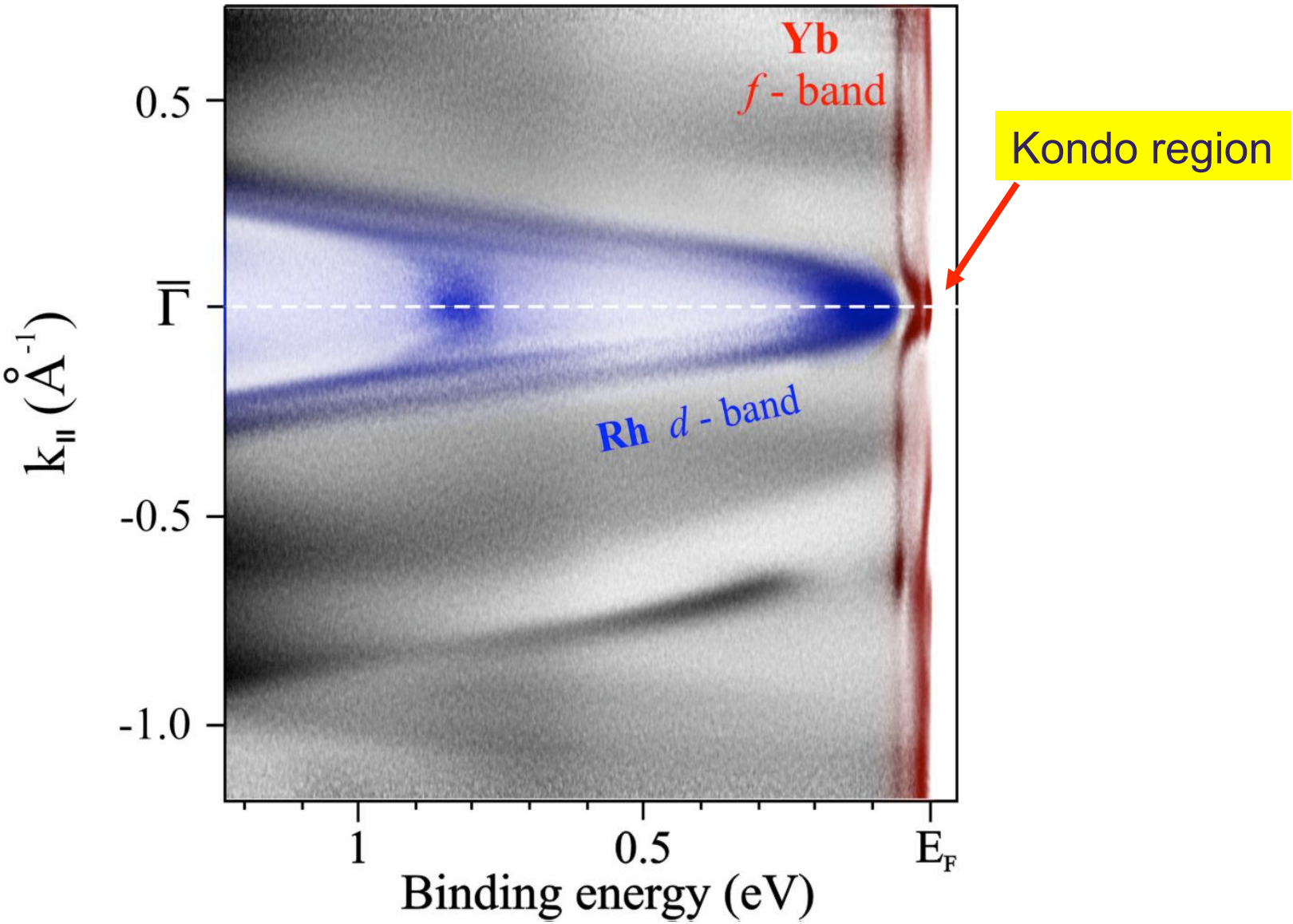
k

Energy

E_F

European XFEL

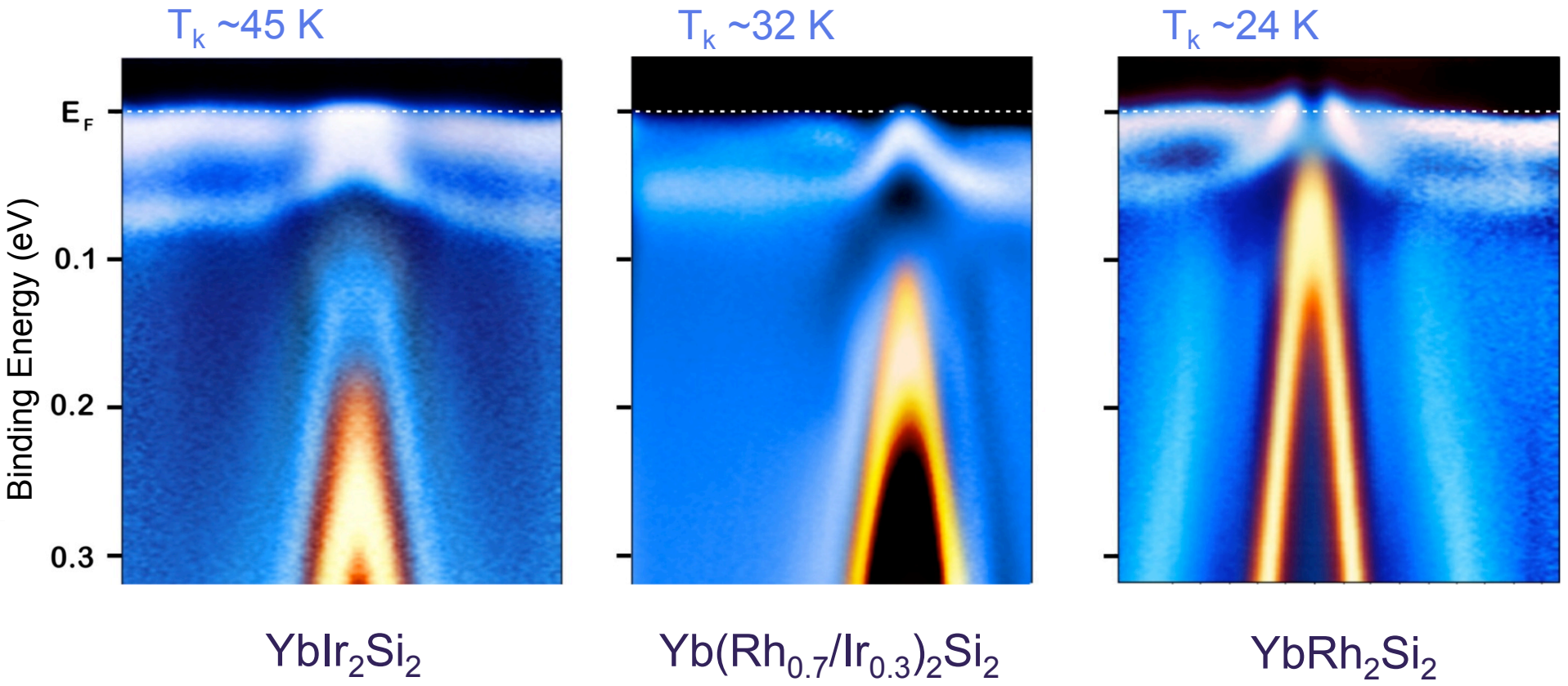
Ultra-High Resolution ARPES ($YbRh_2Si_2$)



European XFEL

Tuning of Kondo Behavior by Rh/Ir Substitution

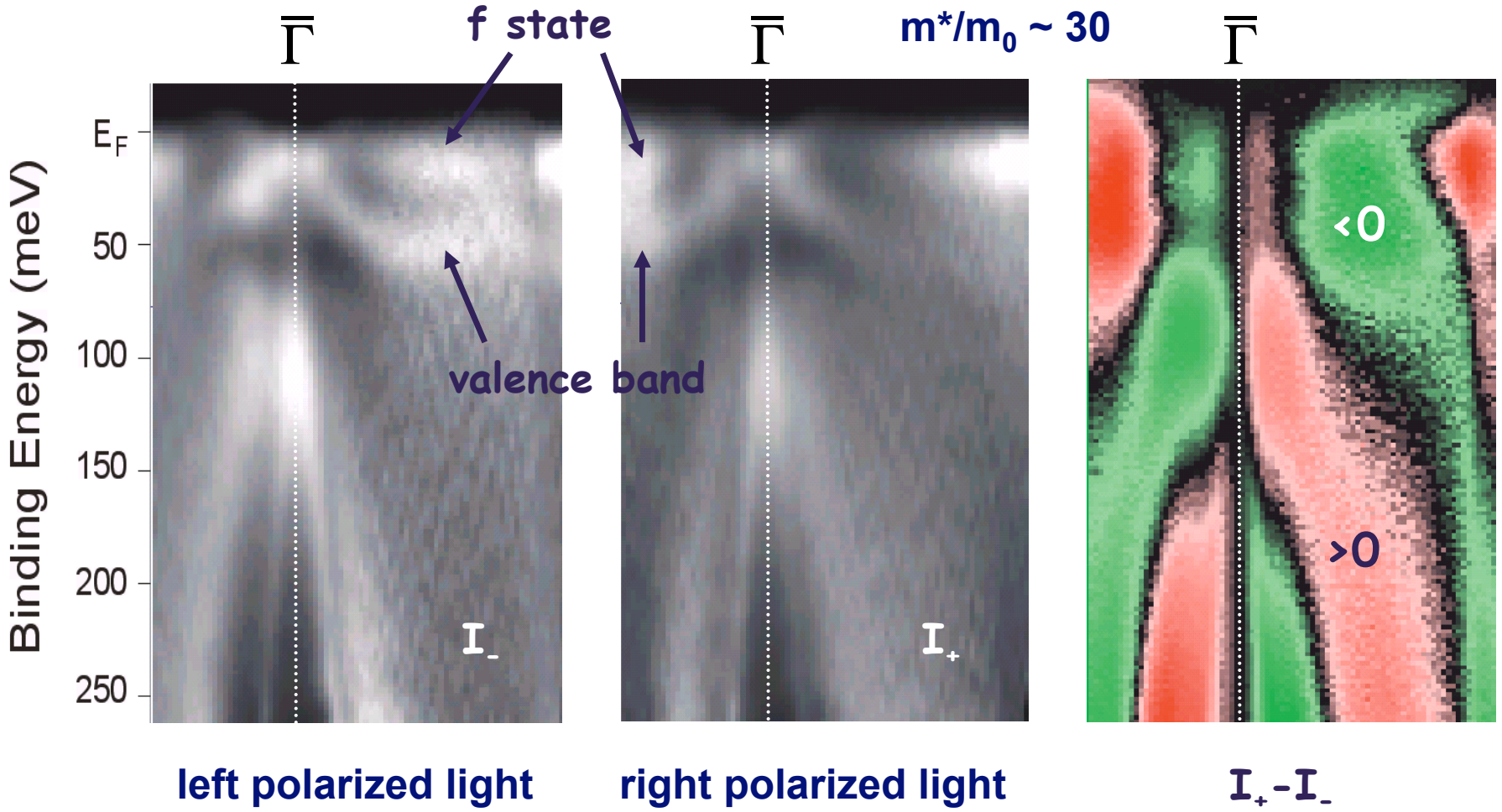
Kondo temperature T_k depends on valence-band position



Problem: ARPES is not able to sample unoccupied states

European XFEL

Circular Dichroism at E_F ($YbRh_2Si_2$)

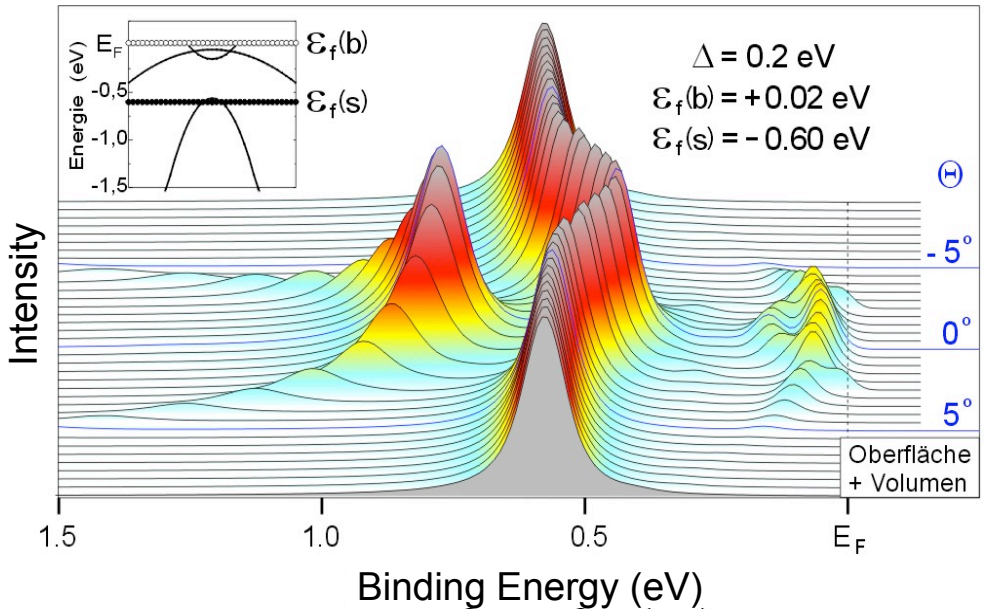


Valence band & *f* state reveal same symmetry and do not cross each other

European XFEL

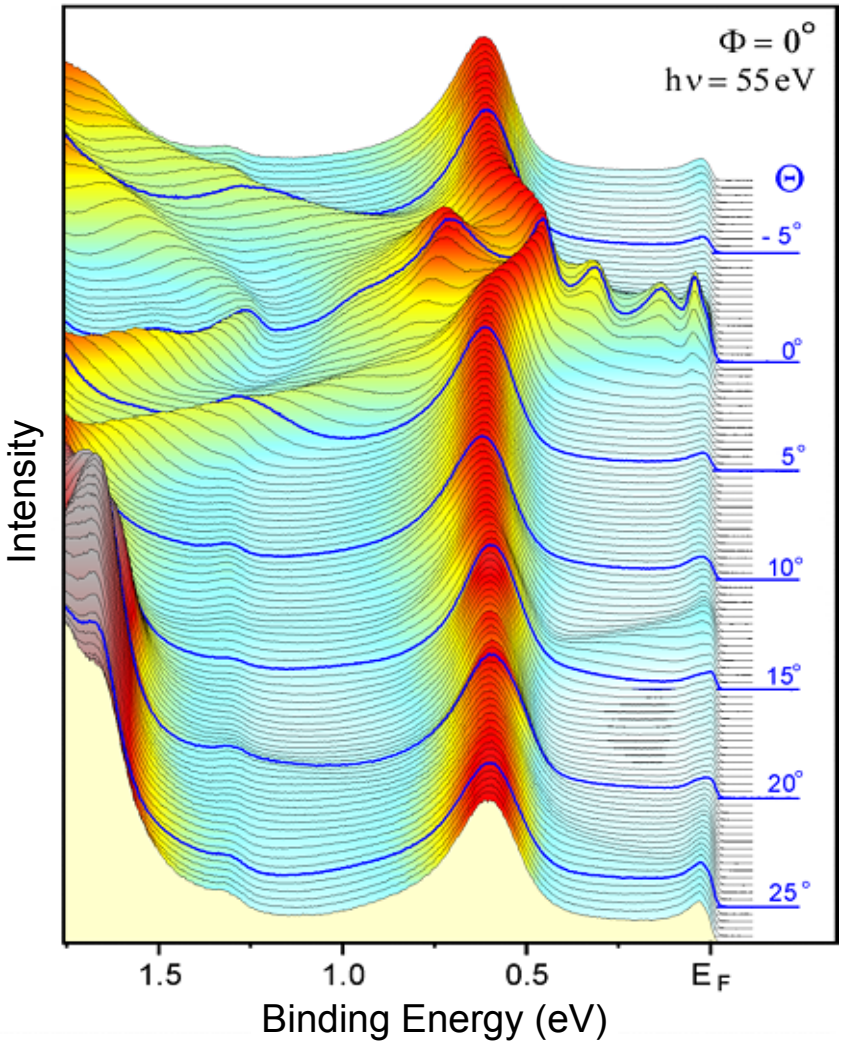
Theoretical PAM Simulations

Theory:



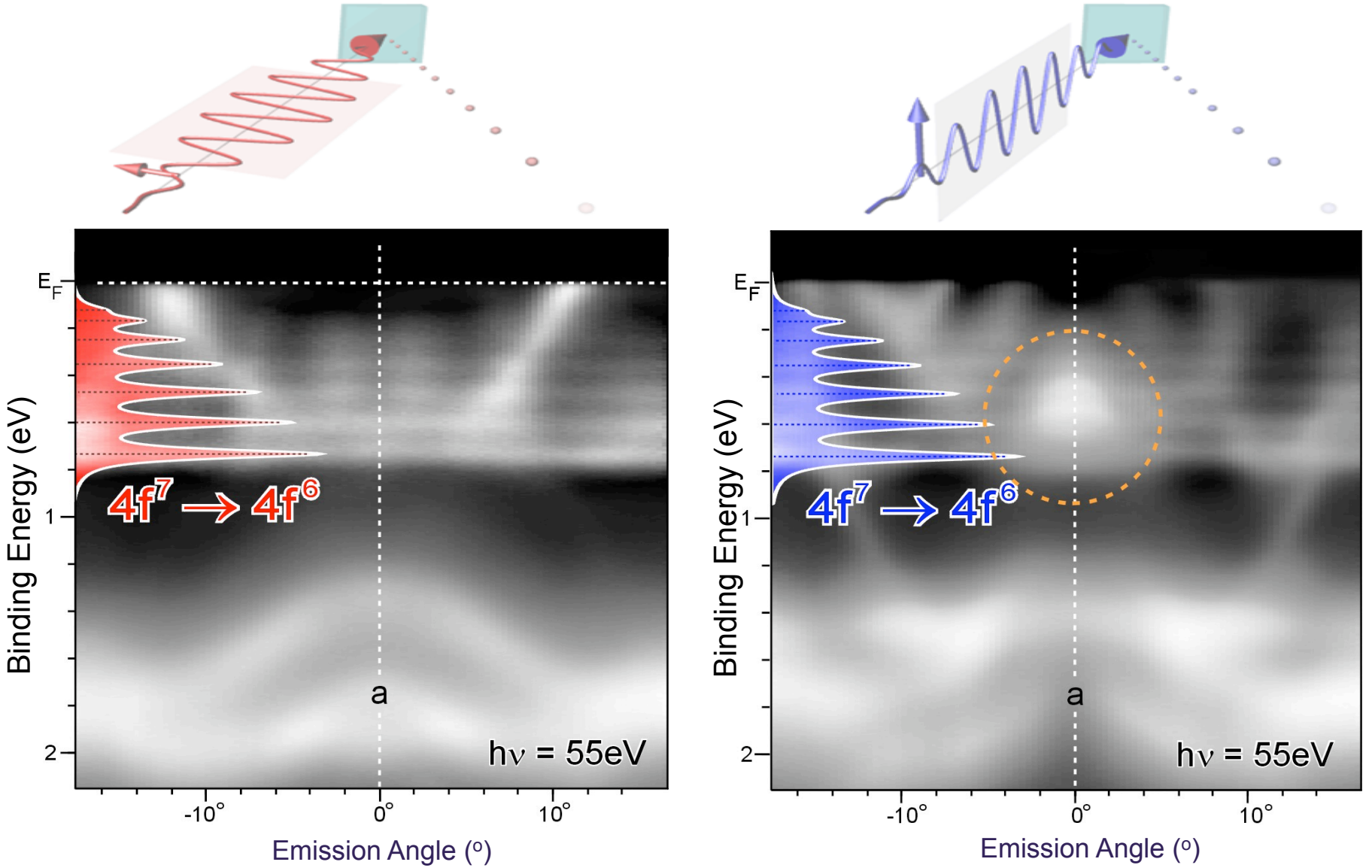
- good agreement between theory and experiment
- *k* - dependent variation of hybridization

Experiment:



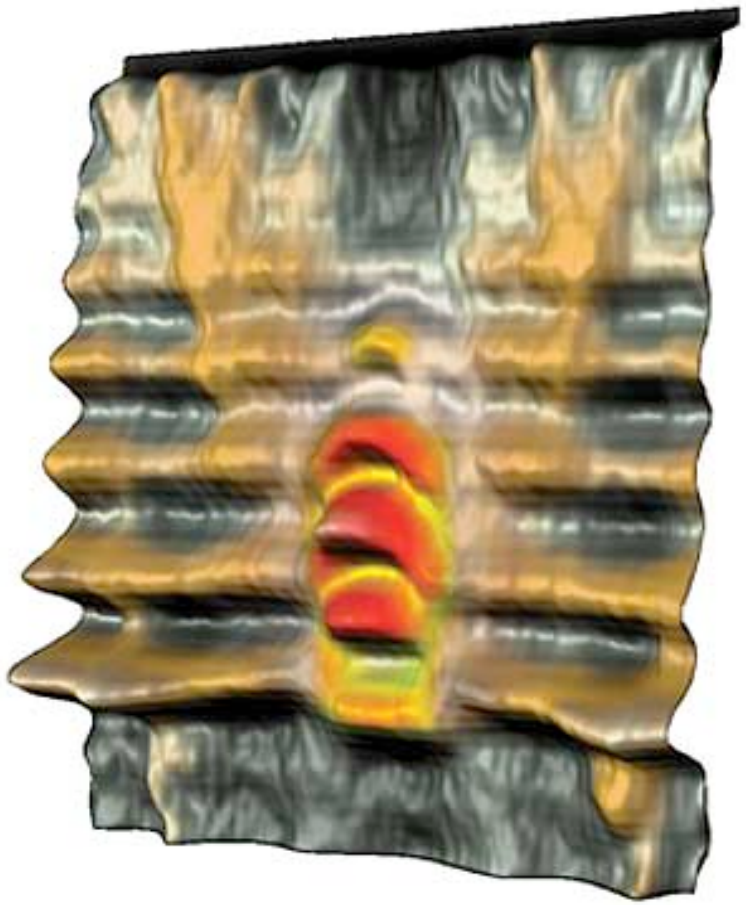
European XFEL

ARPES on $EuNi_2P_2$ (mixed-valent)

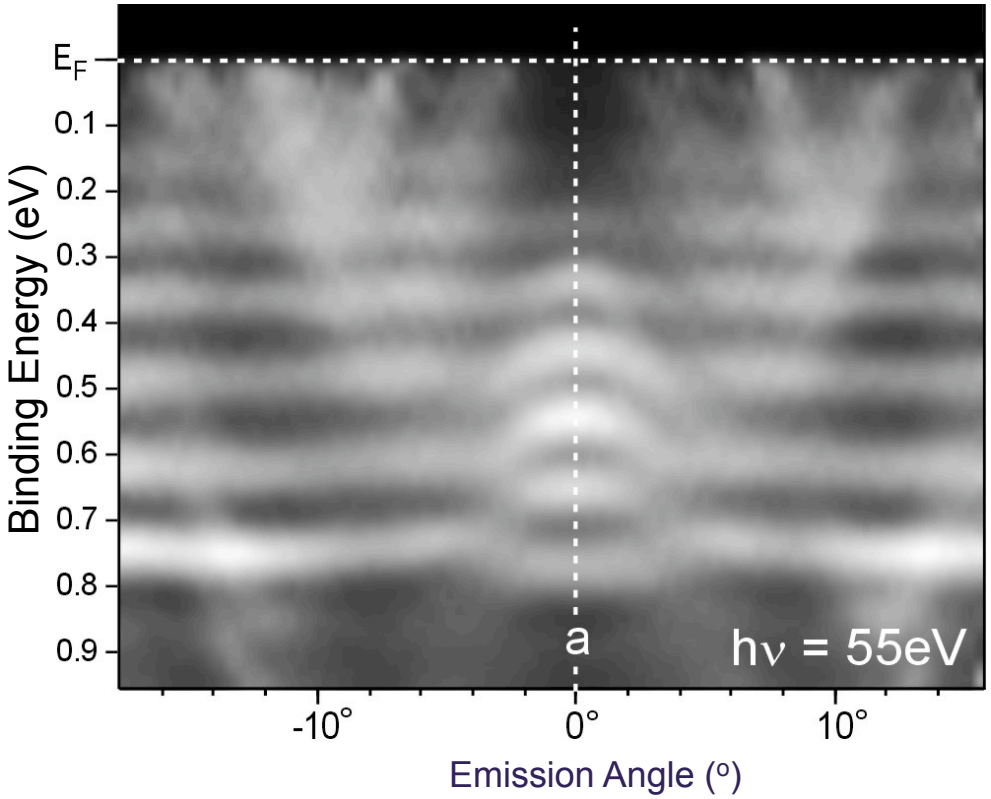


European XFEL

ARPES on $EuNi_2P_2$



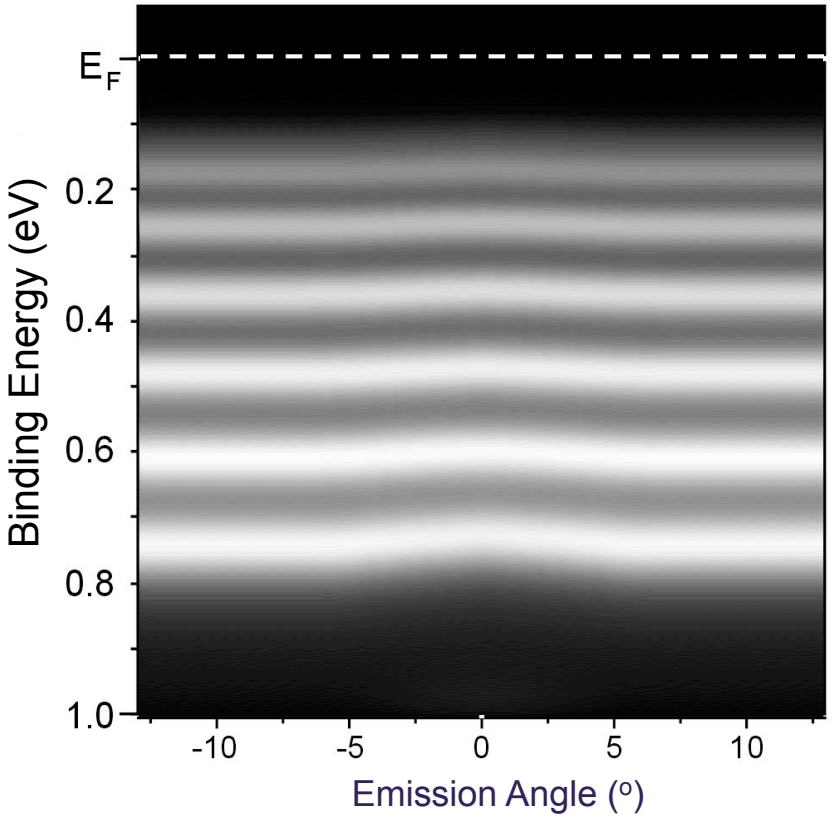
Experiment:



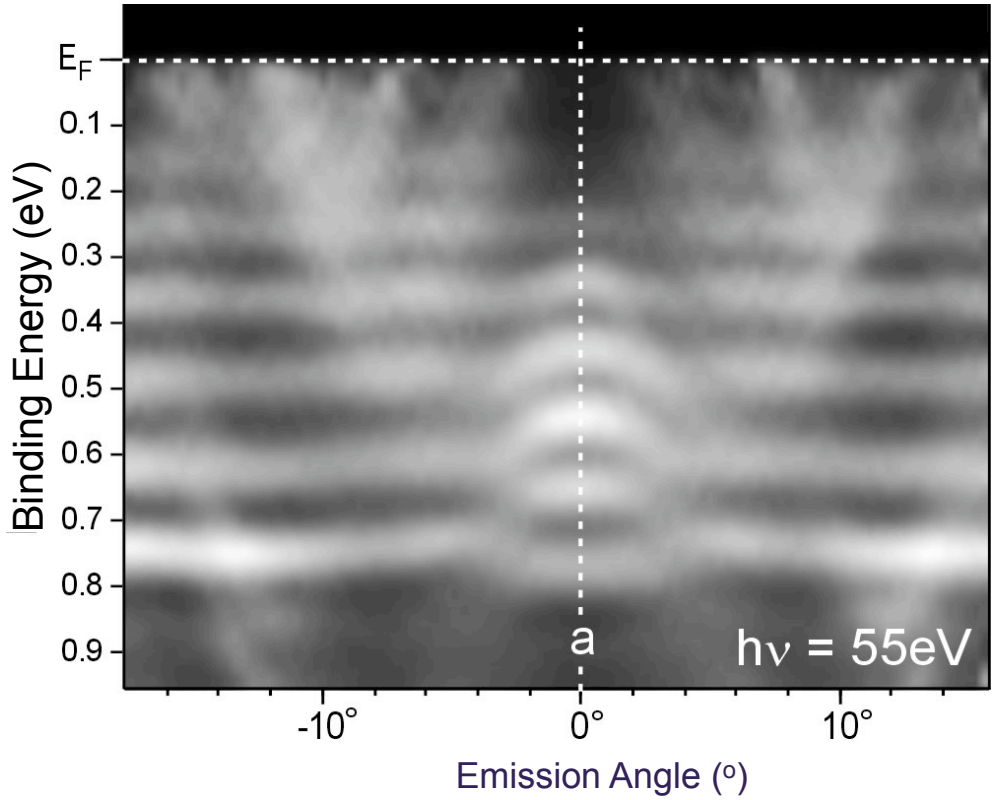
European XFEL

ARPES on $EuNi_2P_2$

Theory:



Experiment:

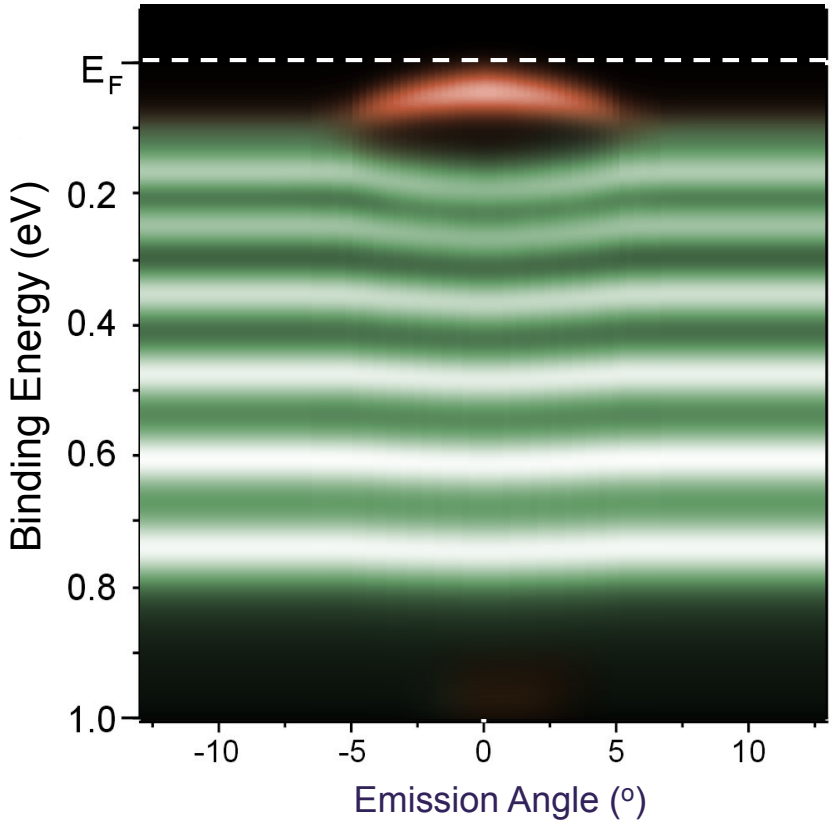


DESY HELMHOLTZ ASSOCIATION

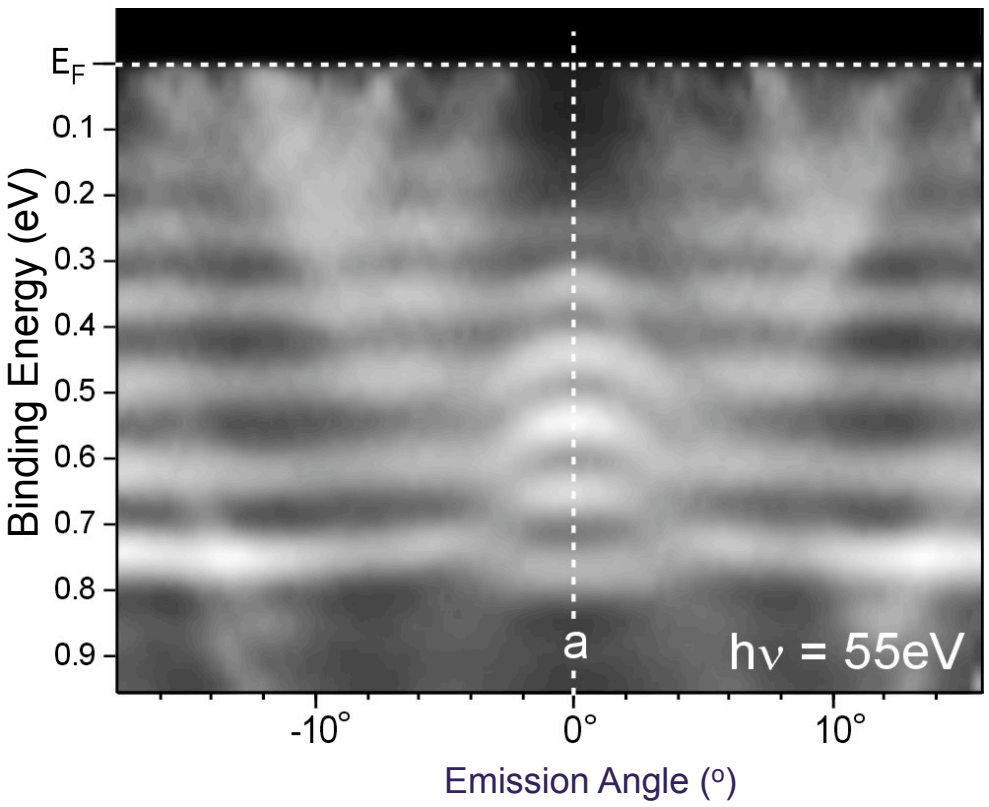
European XFEL

ARPES on $EuNi_2P_2$

Theory:



Experiment:



Heavy-fermion/Kondo behavior may be expected also in Eu systems

DESY HELMHOLTZ ASSOCIATION

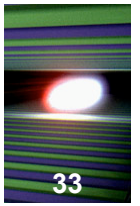
Conclusions from ARPES

ARPES Outcome:

- *f-d* hybridization reveals high anisotropy in reciprocal space
- momentum dependence of the *f-d* hybridization:
  - may lead to anisotropy of correlation phenomena including Kondo behavior;
  - should be considered for understanding of magnetic properties in compounds with RE metals

European XFEL

Cooperators & Publications



Studies were performed by:

Dresden University:	**D. Vyalikh, S. Danzenbächer, Yu. Kucherenko, K. Kummer, M. Holder, S. Molodtsov, C. Laubschat**
Stanford University:	**X.J. Zhou, W.L. Yang, N. Mannella, Z.-X. Shen**
Colorado University:	**D. Dessau**
Advanced Light Source:	**Z. Hussain, A. Fedorov**
Swiss Light Source:	**M. Shi and L. Patthey**
BESSY:	**R. Follath**
MPI CPfS Dresden:	**C. Krellner, Z. Hossain, N. Carocca, C. Geibel**
MPI PKS Dresden:	**A. Yaresko**

and published in:

Hayn *et al.*, **PRB 64** (2001) 115106; Danzenbächer *et al.*, **PRB 72** (2005) 033104; Vyalikh *et al.*, **PRL 96** (2006) 026404; Danzenbächer *et al.*, **PRL 96** (2006) 106402; Danzenbächer *et al.*, **PRB 75** (2007) 045109; Vyalikh *et al.*, **PRL 100** (2008) 056402; Danzenbächer *et al.*, **PRL 102** (2009) 026403

DESY HELMHOLTZ ASSOCIATION

Electronic Structure of Unoccupied States

Resonant inelastic X-ray scattering (RIXS)

2-particle response

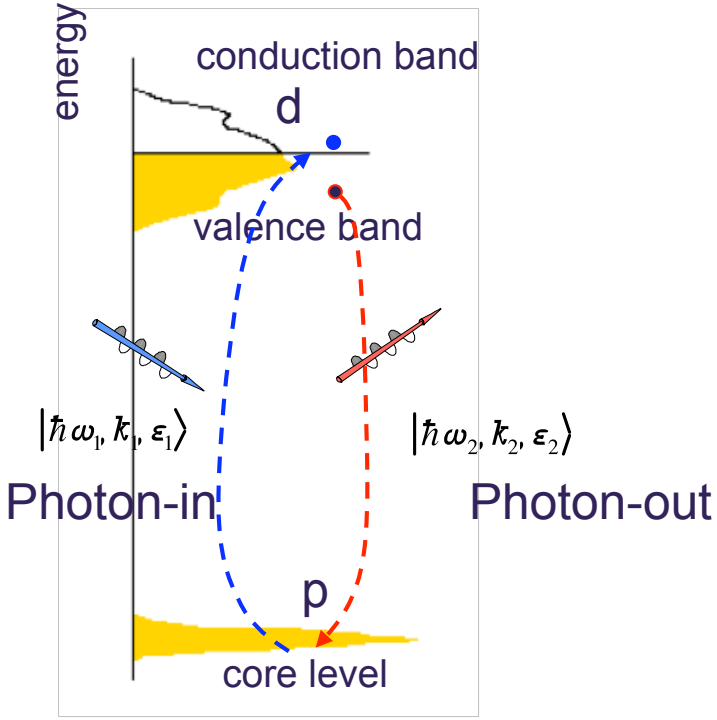
European XFEL

Basics and Advantages of RIXS

Energy loss: $\omega=\omega_2-\omega_1$

Momentum transfer: $q=k_2-k_1$

Resonance: $\omega_1 \sim \omega_{edge}$



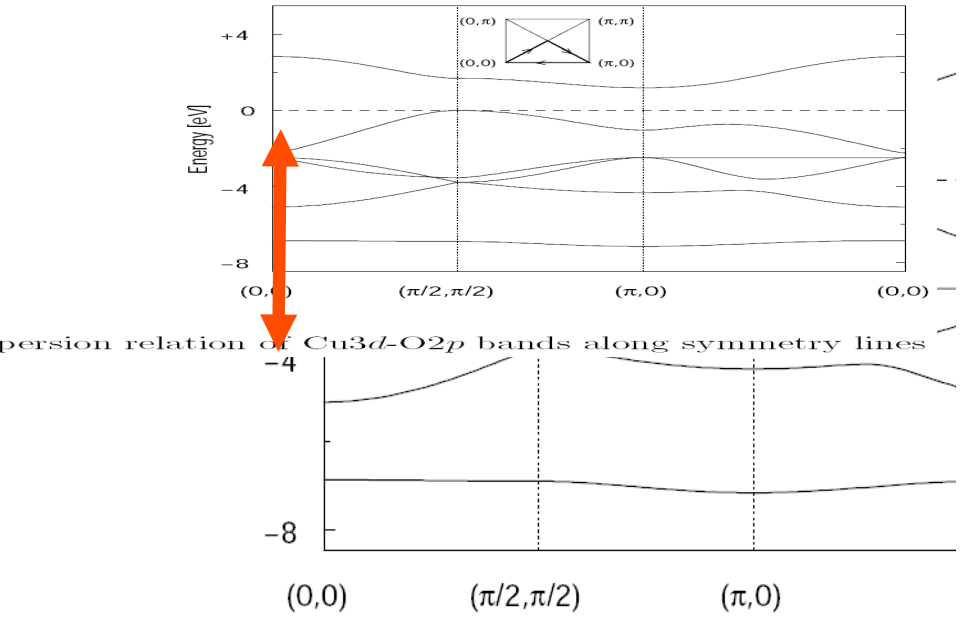
Features:

- study of element-specific electron correlations, 2-particle response
- finite momentum (**q**) transfer allows one to study indirect correlation gaps (Mott, Kondo, CDW, SDW, superconducting)
- study of optically forbidden (e.g. **d**-**d**) excitations
- can be applied in the presence of magnetic/ electric fields (space charge is not important, FEL application)
- energy resolution is not limited by the core-hole lifetime, k_BT resolution can be achieved
- magnetic properties (e.g. spin state) can be studied applying polarized radiation

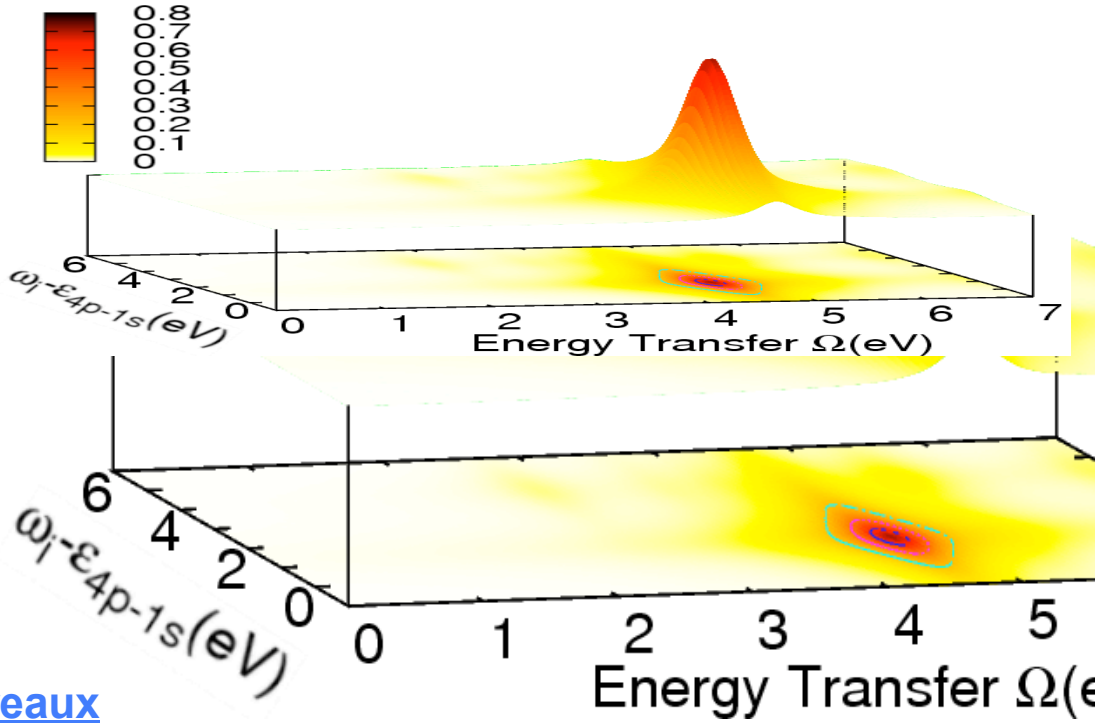
European XFEL

RIXS on Cuprates

$k_{in}=(0,0)$, $k_{out}=(0,0)$



Cu *K*-edge RIXS spectrum
(neglecting polarization, 4p)



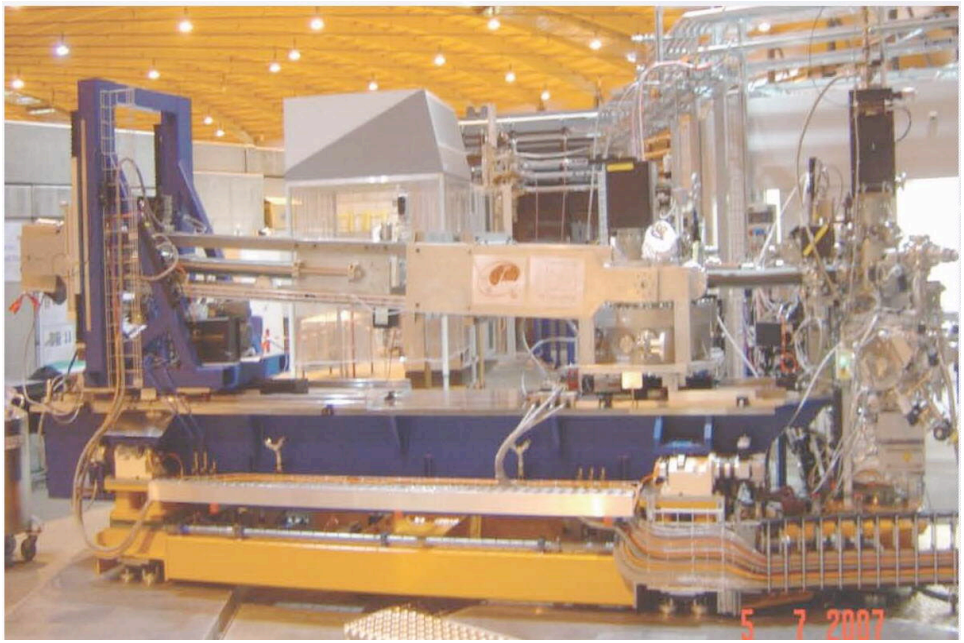
Theory: Tom Devereaux

Note: structure of occupied states (ARPES) should be known

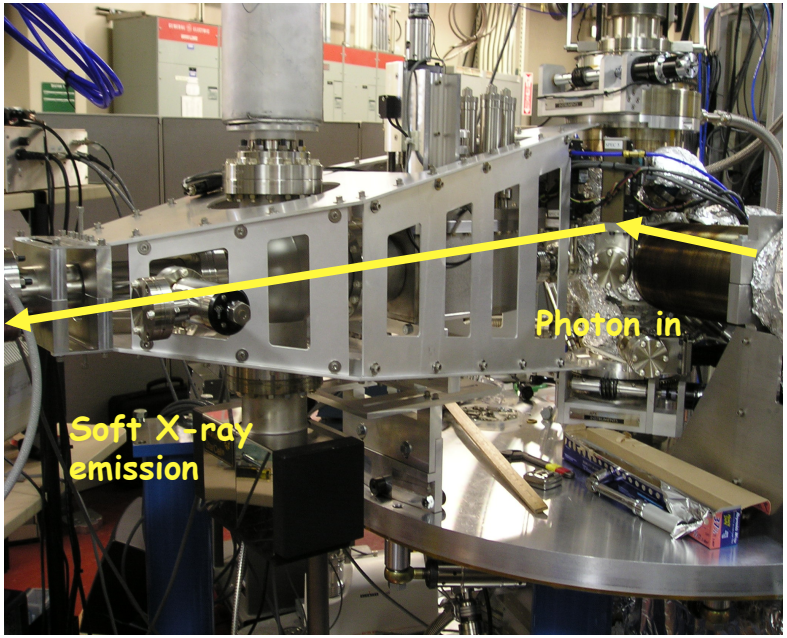
European XFEL

RIXS Instruments

SLS (Villigen)



ALS (Berkeley)



"Soft X-ray RIXS … " by M. Grioni

"Scientific opportunities …" by Z. Hussain

DESY HELMHOLTZ ASSOCIATION

Electronic Structure and Femtosecond Dynamics (FEL and Laser Applications)

Resonant (elastic) X-ray scattering (RXS)

Resonant inelastic X-ray scattering (RIXS)

Core-level X-ray photoemission spectroscopy (XPS)

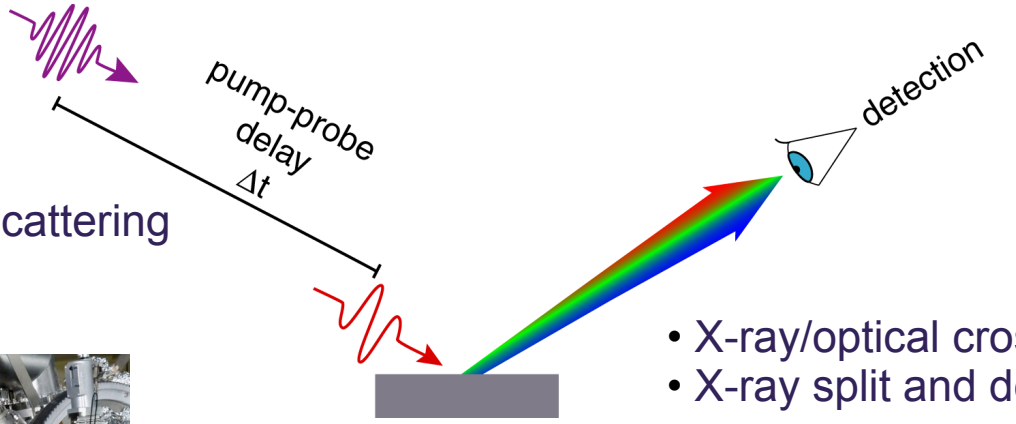
Angle-resolved photoemission spectroscopy (ARPES)

European XFEL

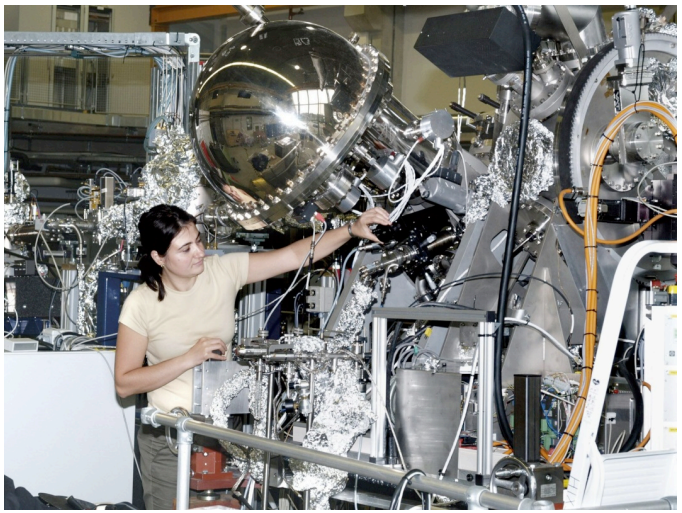
Experiments at FLASH (RIXS, RXS, XPS)

Femtosecond dynamics & Snapshots of non-reversible dynamic

electronic structure ↔ local chemical state ↔ nanometer order

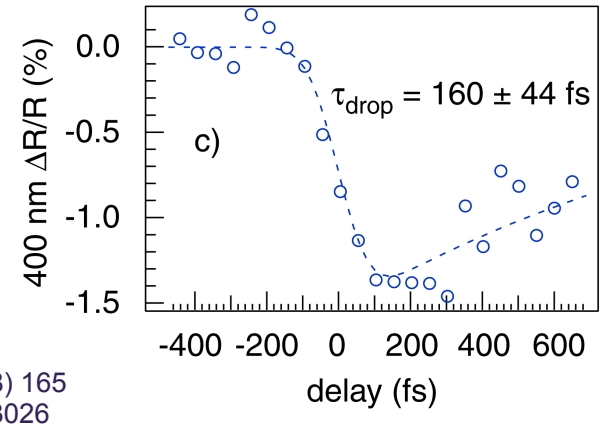


- Resonant inelastic X-ray scattering
- Electron spectroscopy
- resonant X-ray scattering



"Soft X-ray RIXS … " by A. Föhlisch

- X-ray/optical cross-correlation,
- X-ray split and delay



Nature Photonics **2** (2008) 165
N. J. Phys. **10** (2008) 033026

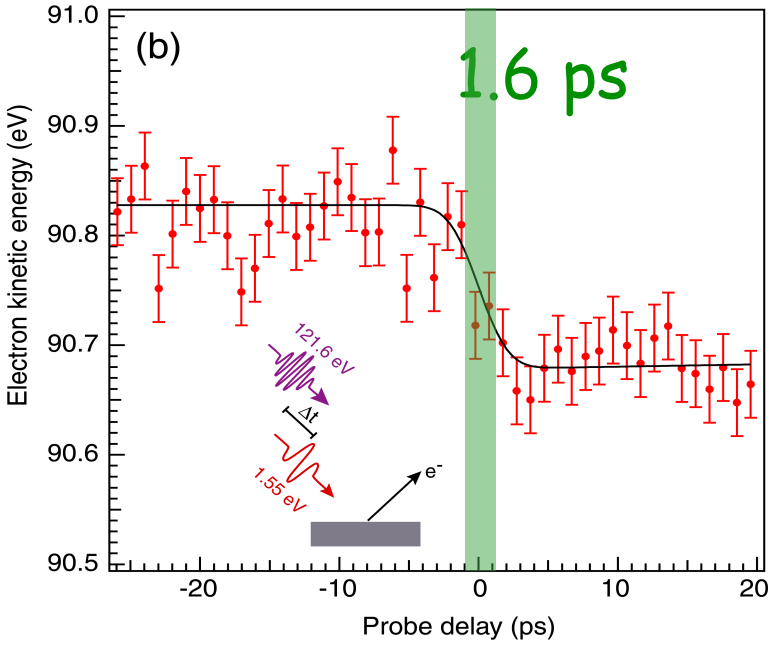
fs X-ray/optical cross-correlator

DESY HELMHOLTZ ASSOCIATION

European XFEL

Experiments at FLASH (RIXS, RXS, XPS)

Non-equilibrium dynamics from femtosecond soft X-ray spectroscopy in combination with femtosecond resonant X-ray scattering



fs XPS at Ge 3*d* core level,
surface photovoltage shift in n:Ge

Femtosecond electron spectroscopy for chemical analysis (XPS) and RIXS for surface and solution chemistry and phase transitions.

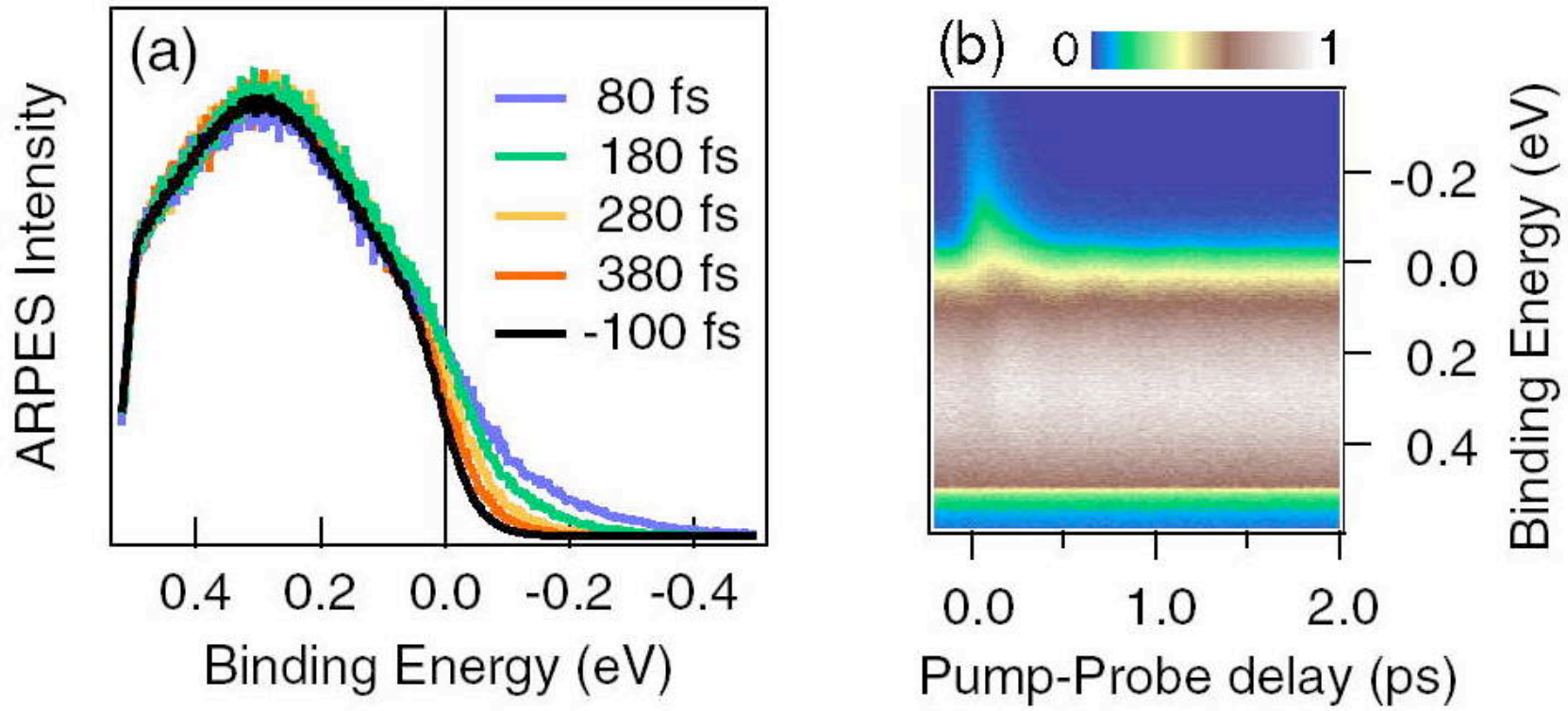
"Soft X-ray RIXS … " by A. Föhlisch

DESY HELMHOLTZ ASSOCIATION

European XFEL

Experiments with Lasers (ARPES)

Electronic structure of 1*T*-TaS_2 at a temperature above MI transition



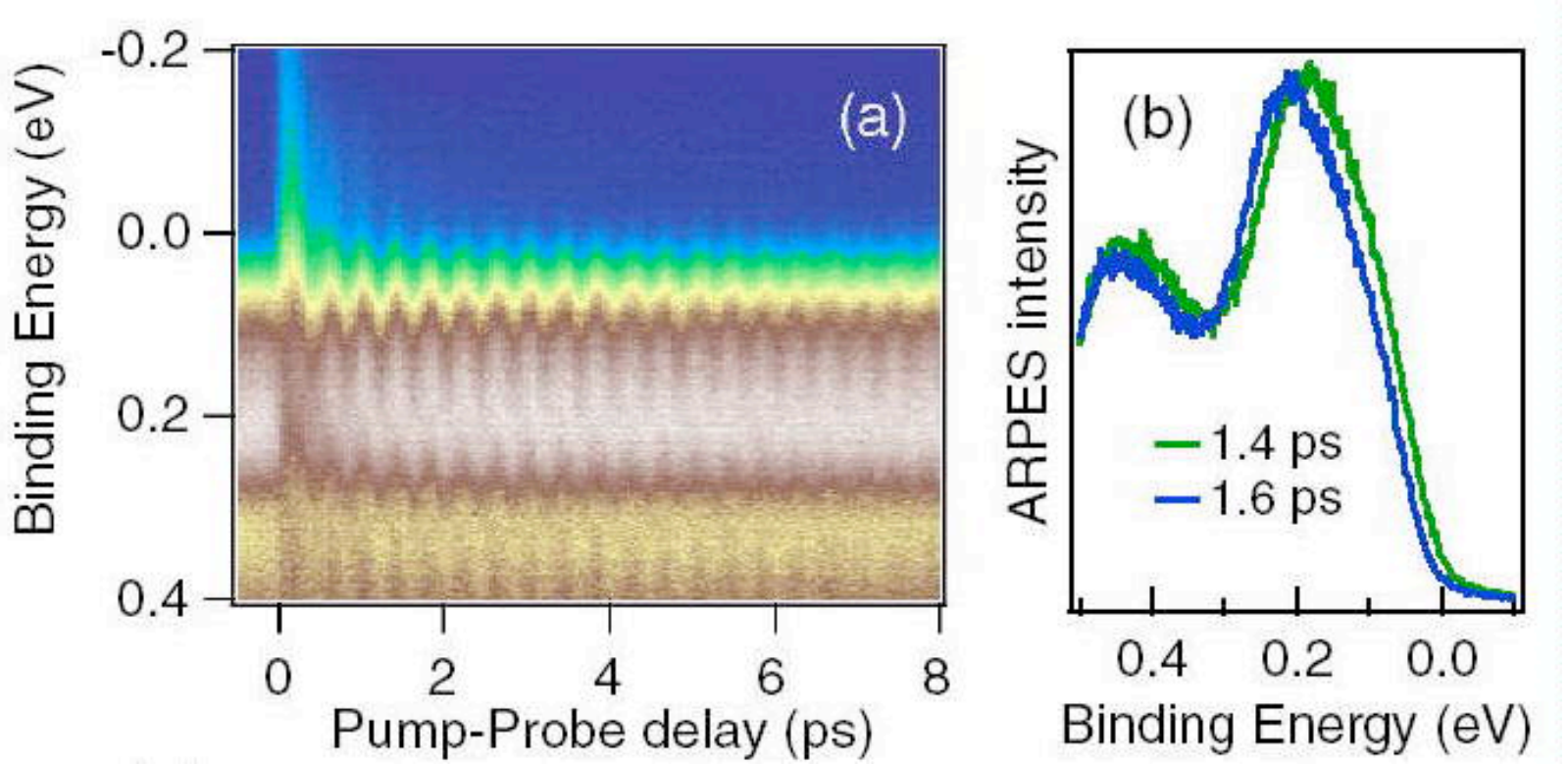
pump-probe experiments, relaxation of "hot" electrons

Perfetti *et al.*, PRL **97** (2006) 067402

European XFEL

Experiments with Lasers (ARPES)

Electronic structure of 1*T*-TaS_2 at a temperature below MI transition



pump-probe experiments,
charge density (CDW) oscillations

Perfetti *et al.*, PRL **97** (2006) 067402

European XFEL

f-Correlated Materials at European XFEL

RIXS:

- at the 3*d*- 4*f* threshold (700 eV - 1500 eV)
- data on unoccupied heavy-fermion electronic states, Kondo resonance above E_F
- study of electron correlations, 2-particle response, gaps around E_F
- magnetic properties (e.g. spin state) applying polarized radiation
- non-equilibrium fs dynamics of *f* and itinerant electron interactions, Kondo-state relaxation and magnetic – non-magnetic transitions

RXS:

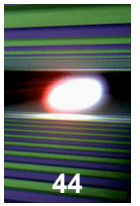
- non-equilibrium fs lattice dynamics
- correlation with dynamics of electron system and chemical properties

XPS:

- study of electron-system relaxations, 1-particle response, valence determination
- fs dynamics of electron correlations and chemical properties
- magnetic properties applying polarized radiation

European XFEL

Clip Board – copy and paste



Headline

- first level
  - second level
    - → third level

Headline

Texttext texttext texttext texttext texttext texttext

Keyword

1. Keyword
2. Keyword

- keyword
- keyword

Result headline

- result text
- result text

Result headline

Result text, result text, result text

Result headline

- result text
- result text
- result text