IXS sous pression dans les systèmes d'électrons *f*

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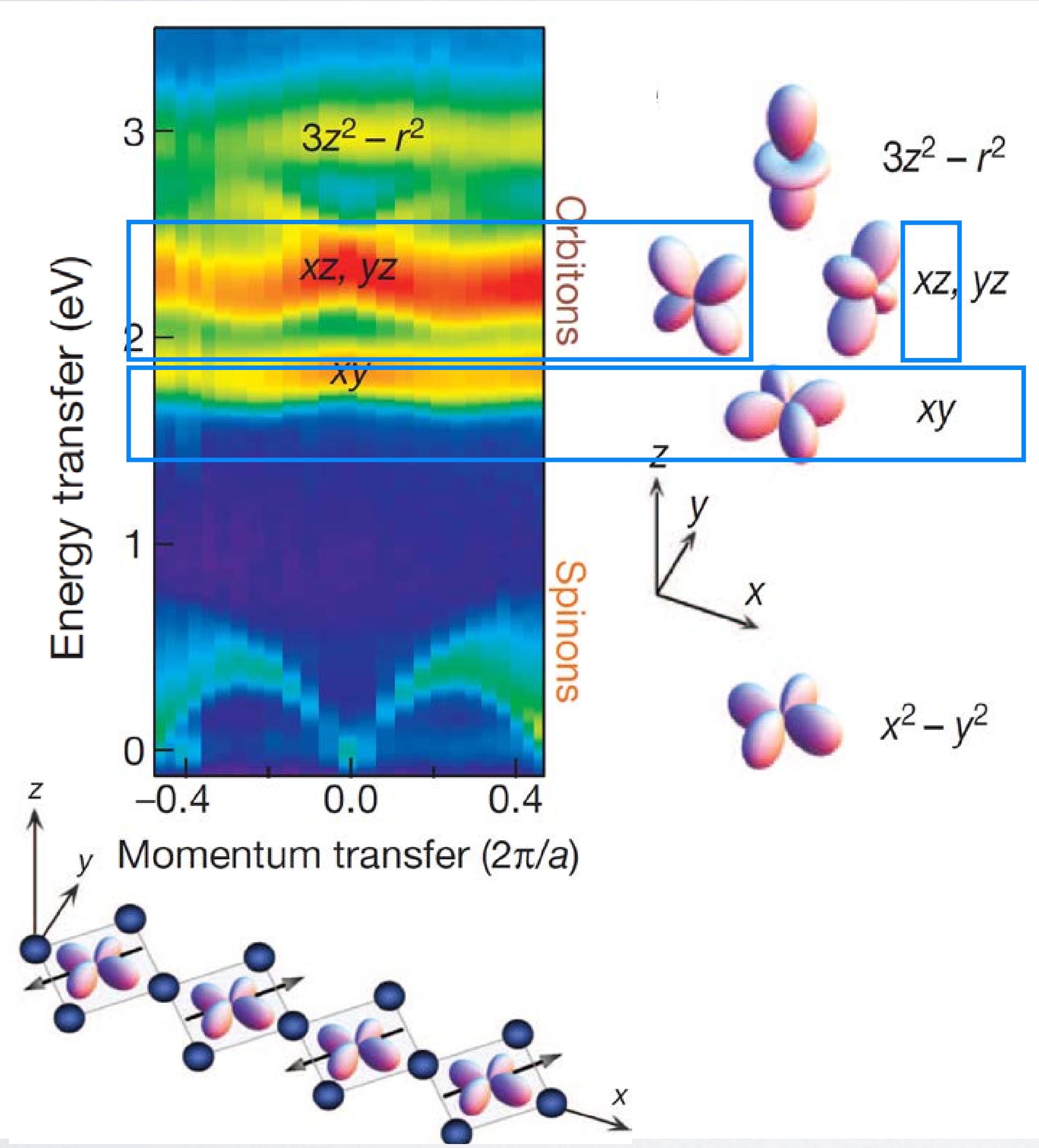
SOLEIL SYNCHROTRON

Groupe De Recherche
Matériaux et Interaction en COmpétition

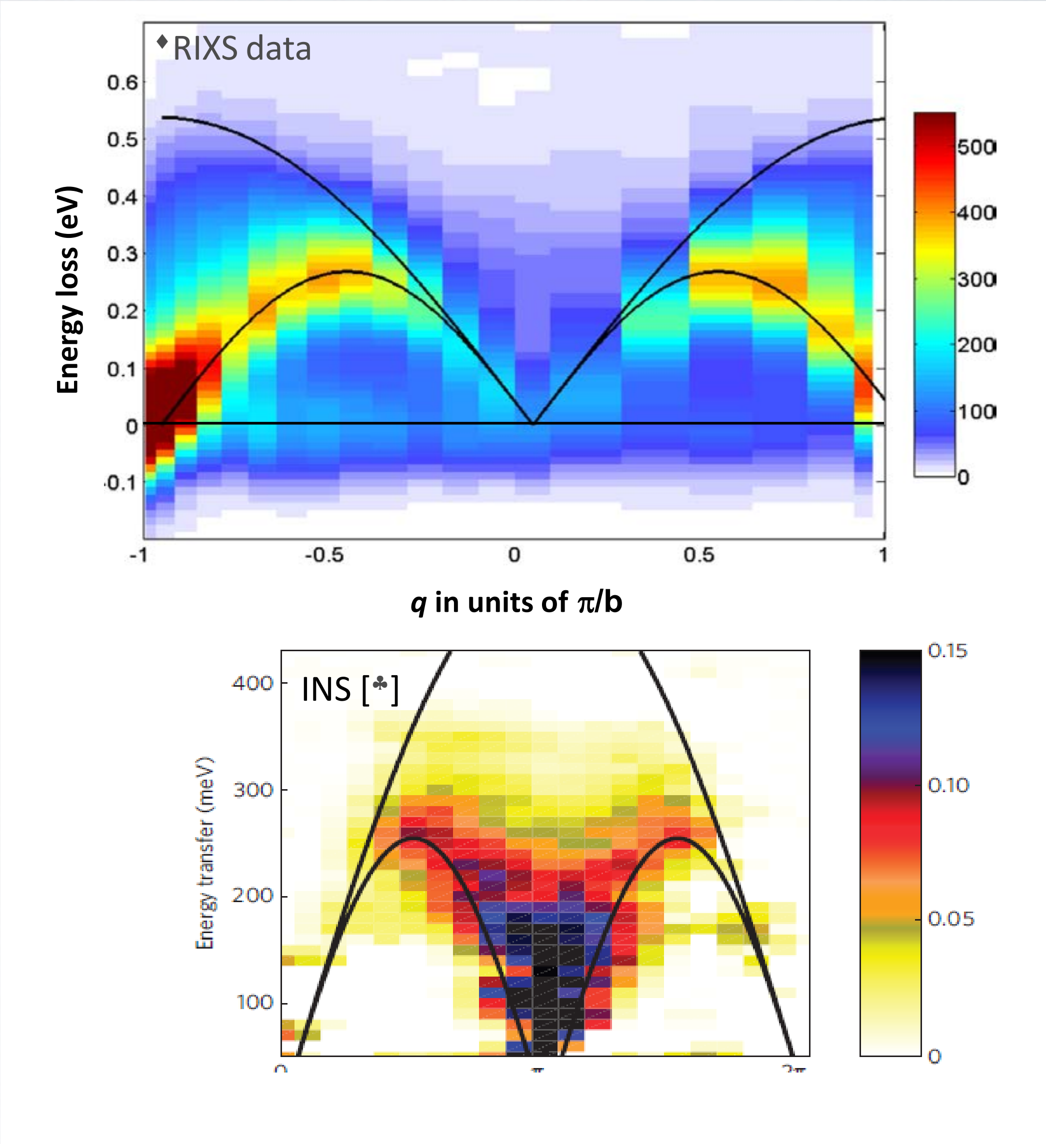
RIXS vs INS

Sr_2CuO_3



Schlappa et al., Nature (2012)

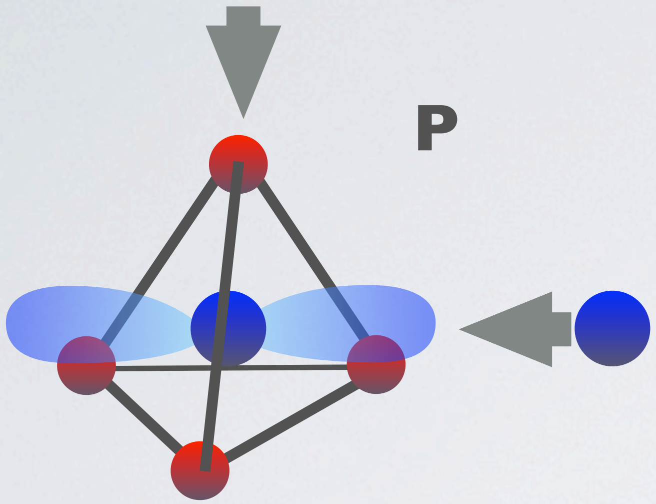
$CaCu_2O_3$



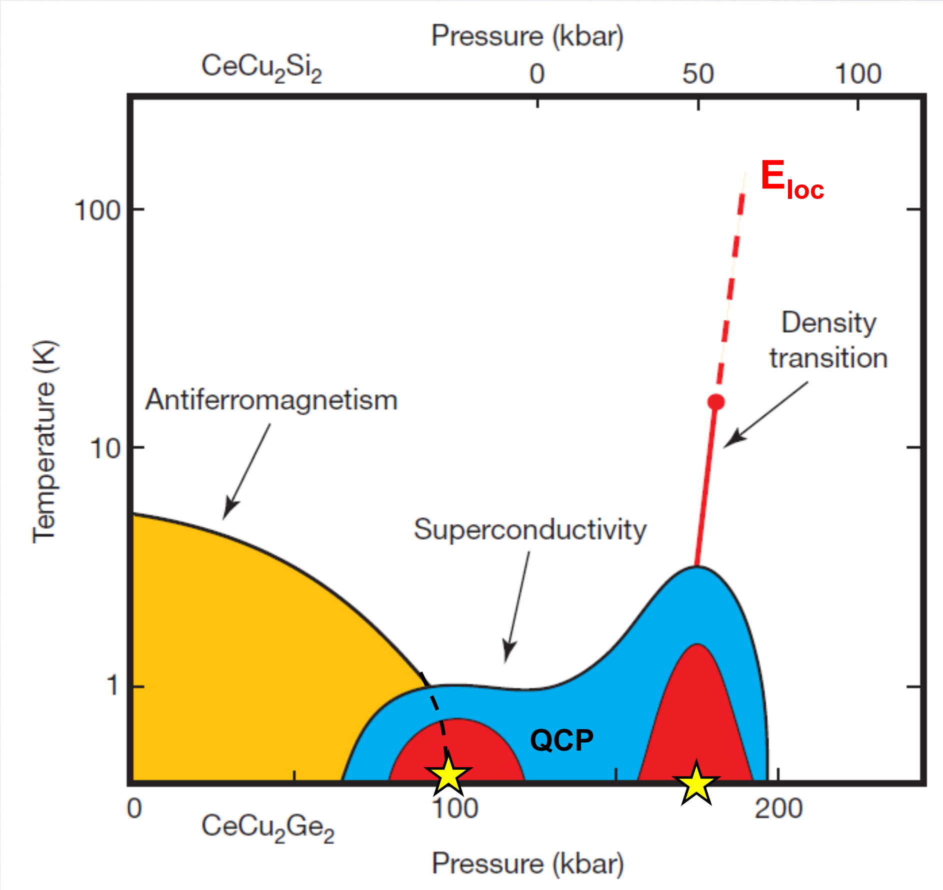
Bisognio et al., arXiv:1310.8346

small sample
magnetic and non magnetic excitations

Why pressure matters ?



Non disorder parameter
Delocalization
Metal Insulator Transition
Crystal Electric Field
Magnetic collapse
Valence change
Orbital occupation
Structural transition
Anisotropy
Superconductivity



➡New methods of investigation

Outline

- *f*-electron delocalization
- Catching up *f*-electrons
- Perspectives at SOLEIL

Outline

- *f*-electron delocalization : IXS / Ce / $CeCu_2Si_2$
- Catching up *f*-electrons
- Perspectives at SOLEIL

Mixed-valent state

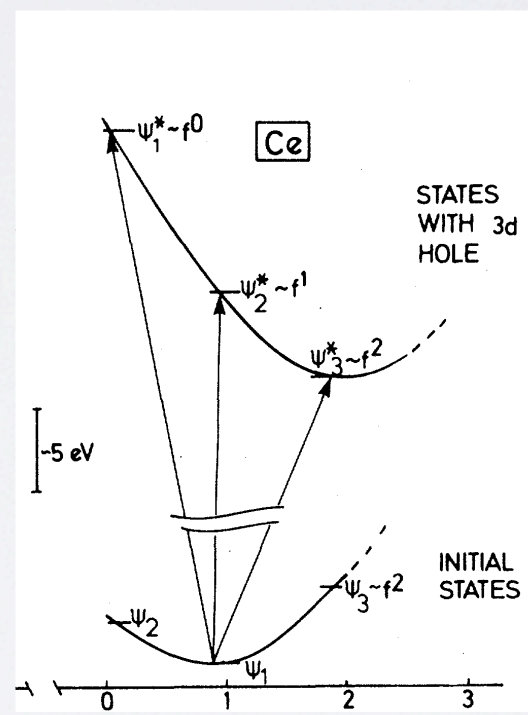
Mixed valence defined as a quantum **supersposition** of *f*-states

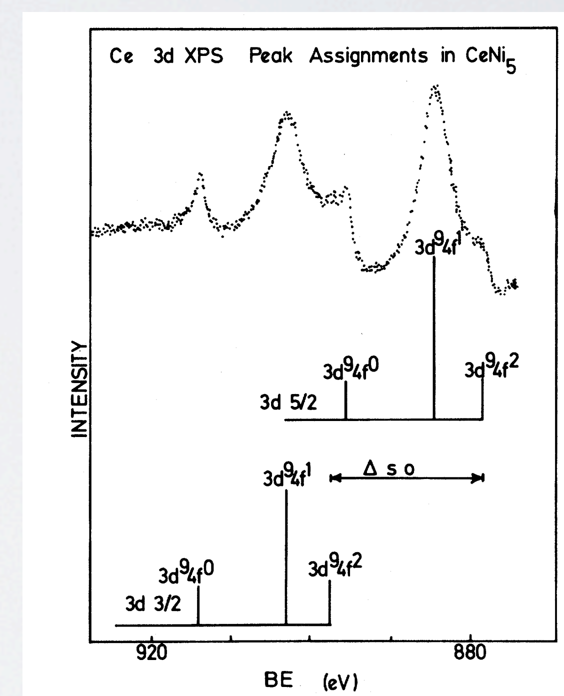
$$|g\rangle = c_0|4f^0\rangle + c_1|4f^1\rangle + c_2|4f^2\rangle$$

lifting in presence of a core-hole;

$$|f\rangle \longrightarrow \begin{cases} |\underline{c}4f^0\rangle \\ |\underline{c}4f^1\underline{v}\rangle \\ |\underline{c}4f^2\underline{v}^2\rangle \end{cases}$$

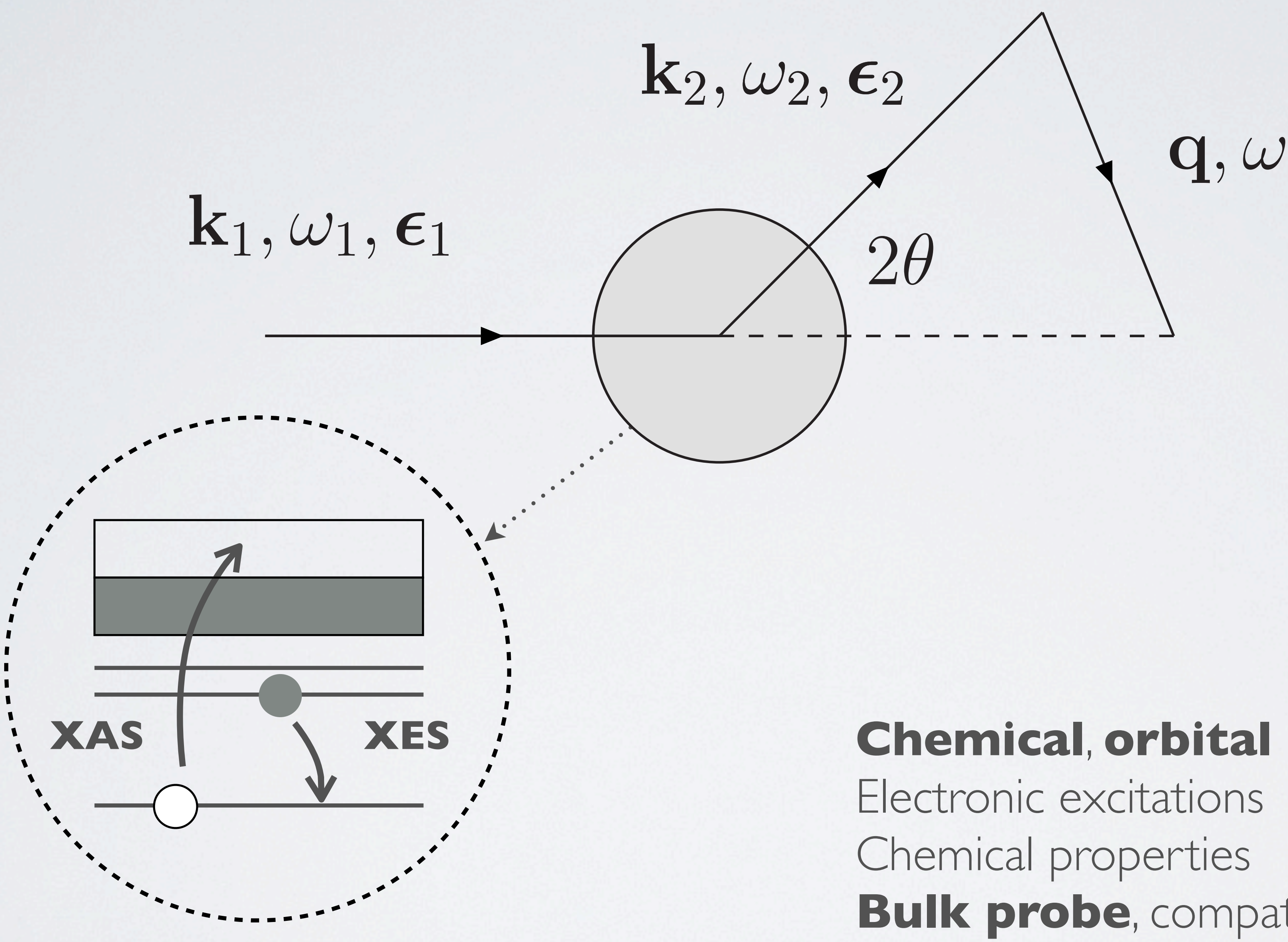
this is the case in core-hole spectroscopy (XAS, XPS)





*Fuggle, Gunnarson et al., PRB **27** (1983), 7330.*

IXS/RIXS process



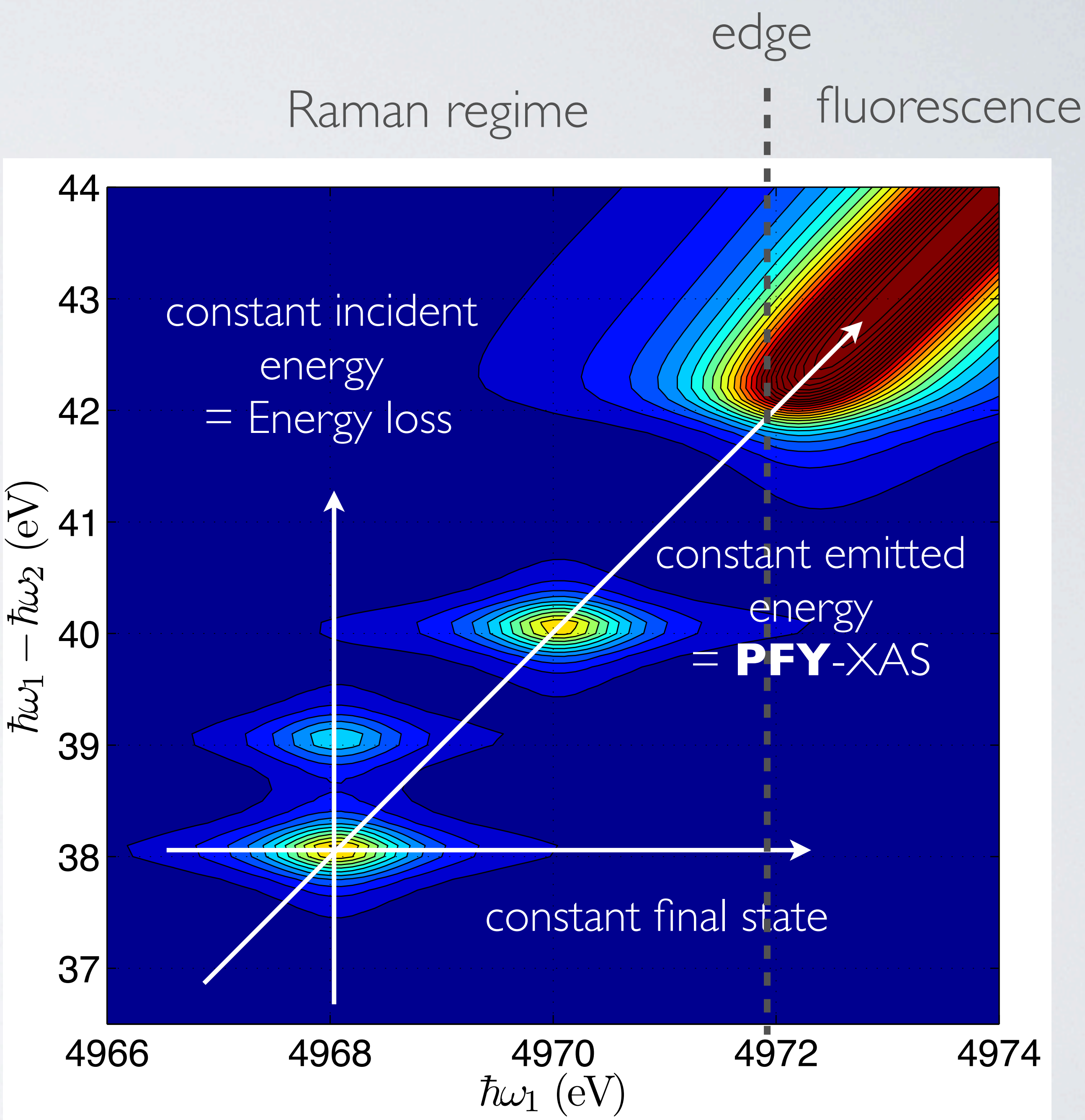
Chemical, **orbital selectivity**
Electronic excitations
Chemical properties
Bulk probe, compatible with high pressure sample environment

RIXS cross section

Kramers-Heisenberg
formula

XES ⊗ XAS

$$\frac{d^2\sigma}{d\omega_1 d\omega_2} = \sum_f \left| \sum_n \frac{\langle f|T_2|\rangle\langle n|T_1|g\rangle}{E_g - E_n + \hbar\omega_1 - i\frac{\Gamma_n}{2}} \right|^2 \times \frac{\Gamma_f/2\pi}{(E_g - E_f + \hbar\omega_1 - \hbar\omega_2)^2 + \frac{\Gamma_f^2}{4}}$$



JPR et al. RMP 82, 2010

Getting sharp

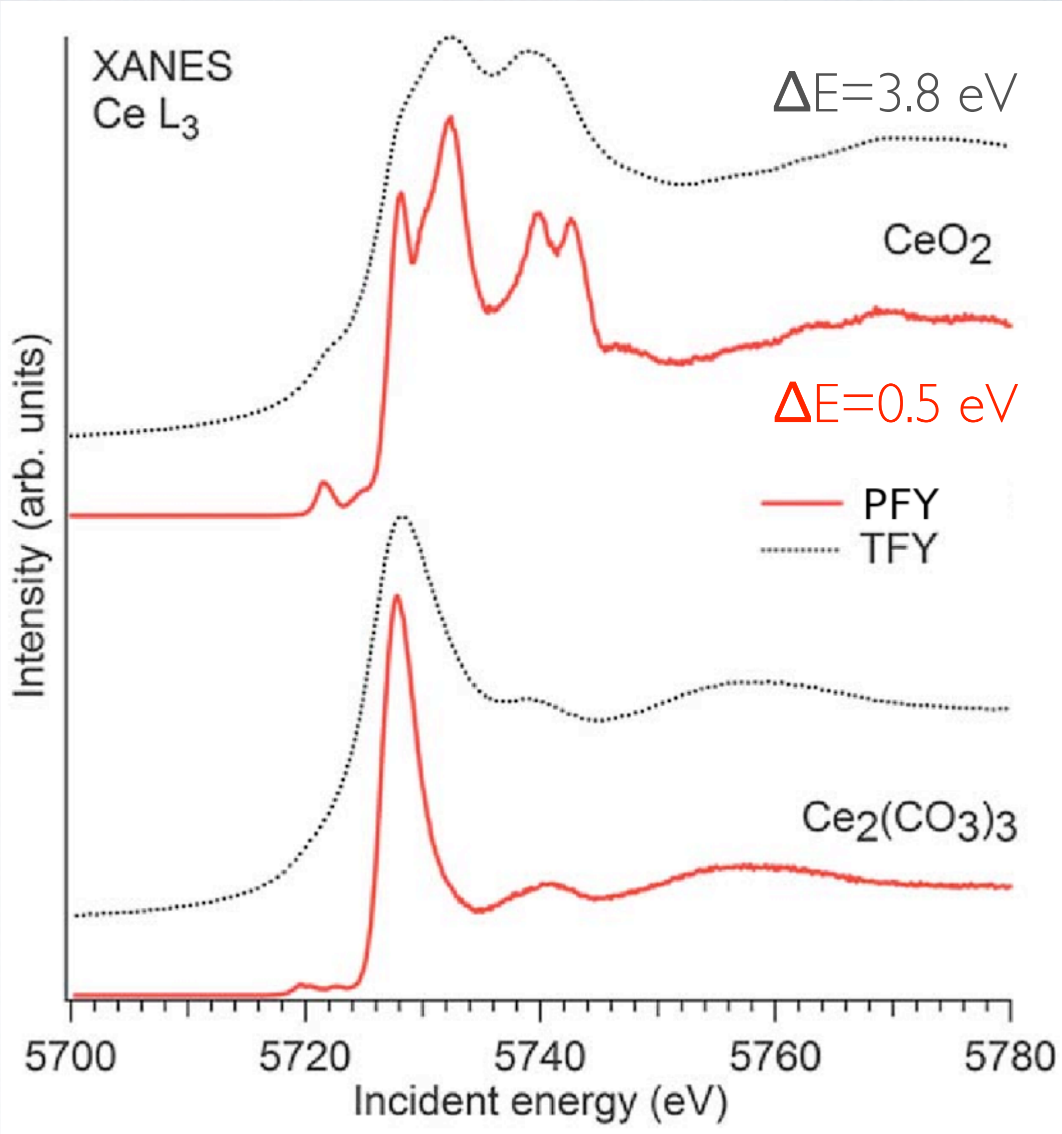
ID26 (ESRF)

sharpening effects :

$$\frac{d^2\sigma}{d\omega_1 d\omega_2} = \sum_f \left| \sum_n \frac{\langle f|T_2|\rangle\langle n|T_1|g\rangle}{E_g - E_n + \hbar\omega_1 - i\frac{\Gamma_n}{2}} \right|^2 \times$$

$$\frac{\Gamma_f/2\pi}{(E_g - E_f + \hbar\omega_1 - \hbar\omega_2)^2 + \frac{\Gamma_f^2}{4}}$$

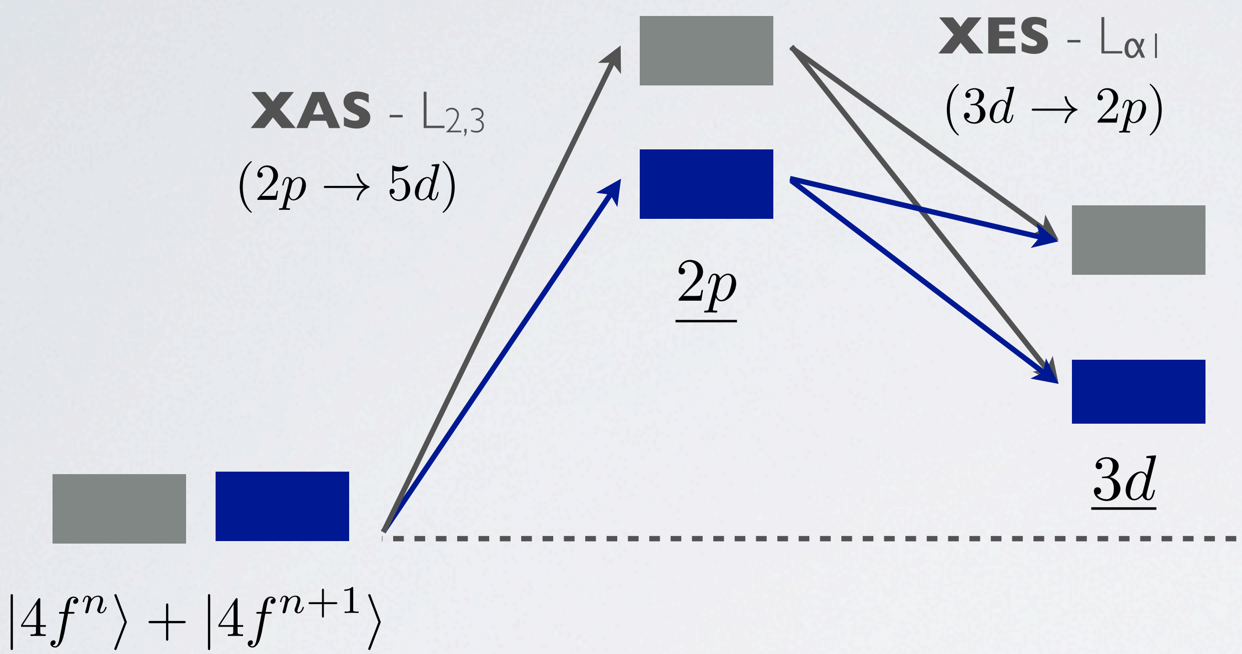
$$\boxed{\Gamma_{RIXS} = \sqrt{1/\Gamma_n^2 + 1/\Gamma_f^2}^{\,-1} \sim \Gamma_f \qquad (\Gamma_f \ll \Gamma_n)}$$



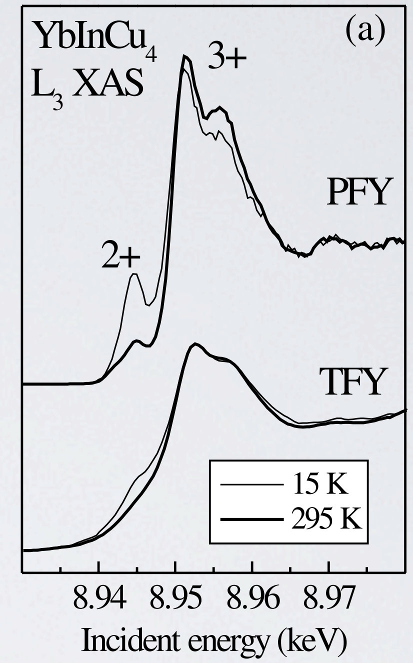
Kvashnina et al., J. Anal. At. Spec. ***26*** *(2011), 1265*

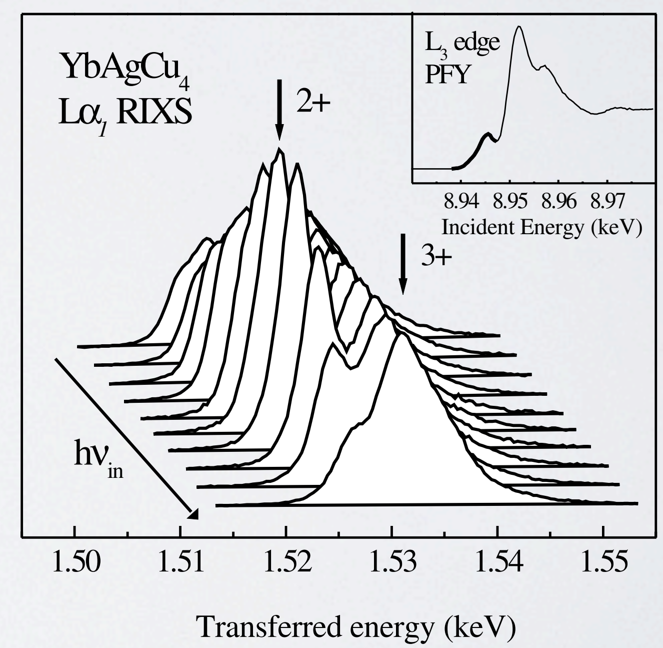
Looking for valence change

2*p*3*d*-RIXS :



splitting of mixed *f* states
resonance & **sharpening** effect
accurate determination of valence state





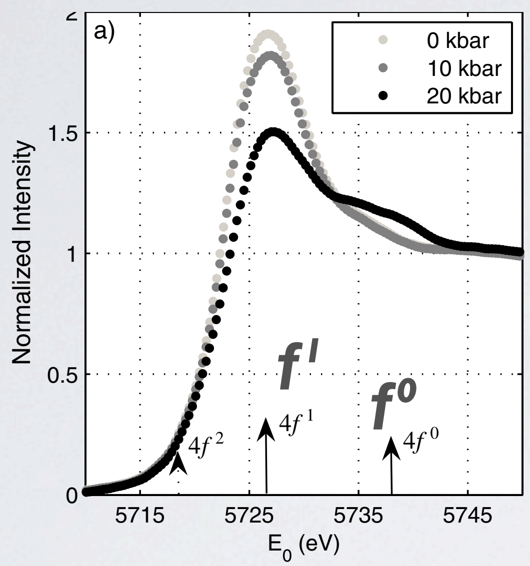
*C. Dallera, JPR et al., PRL **88** (2002), 196403.*

2p3d RIXS in Ce

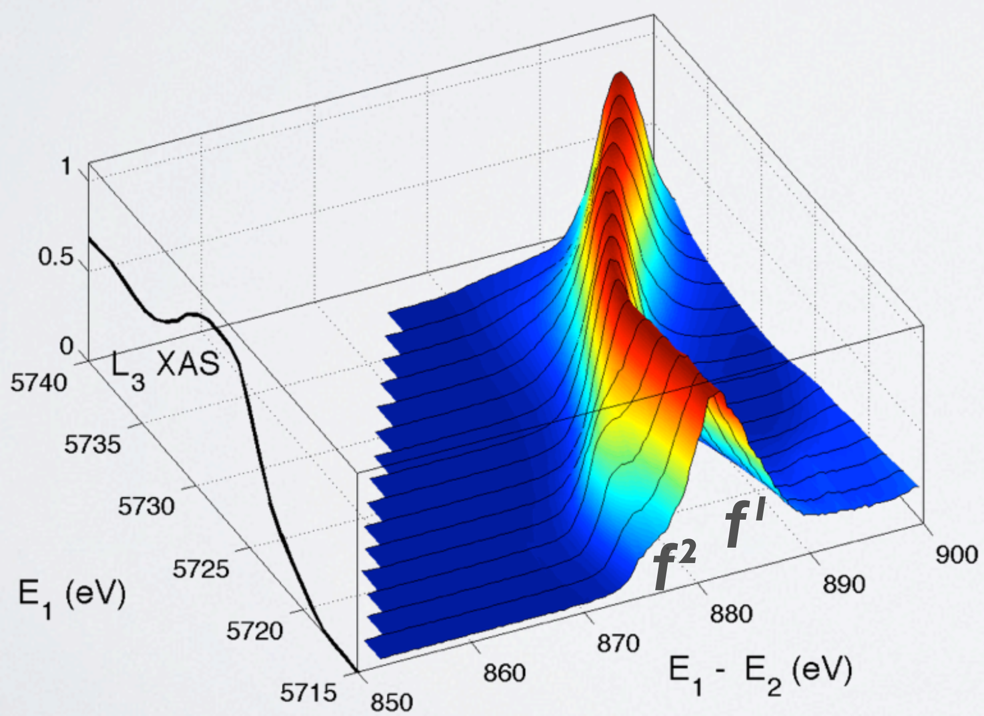
ID12 (ESRF)

Th-doped Ce, and pure Ce

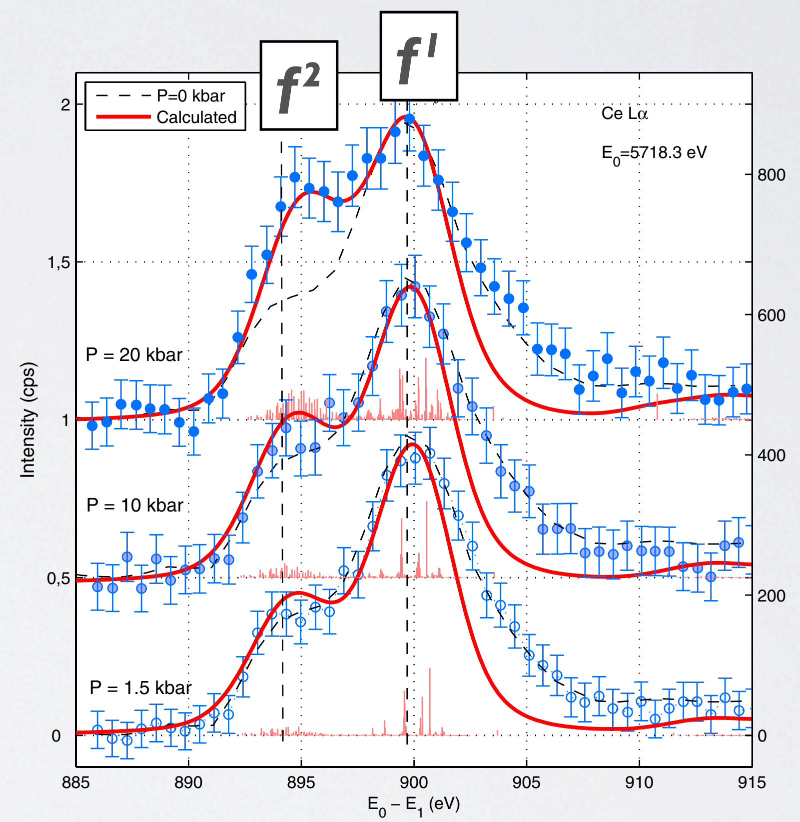
XAS

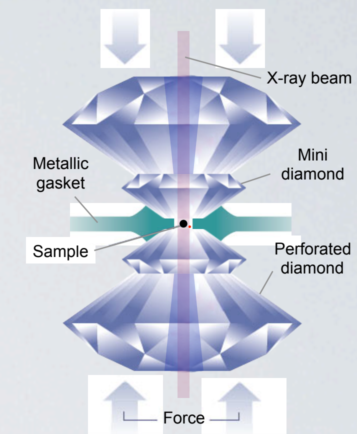


RXES



Pressure dependance





diamond anvil cell

JPR et al., Phys. Rev. Lett. ***93*** *(2004), 067402.*
and Phys. Rev. Lett. ***96*** *(2006), 237403.*

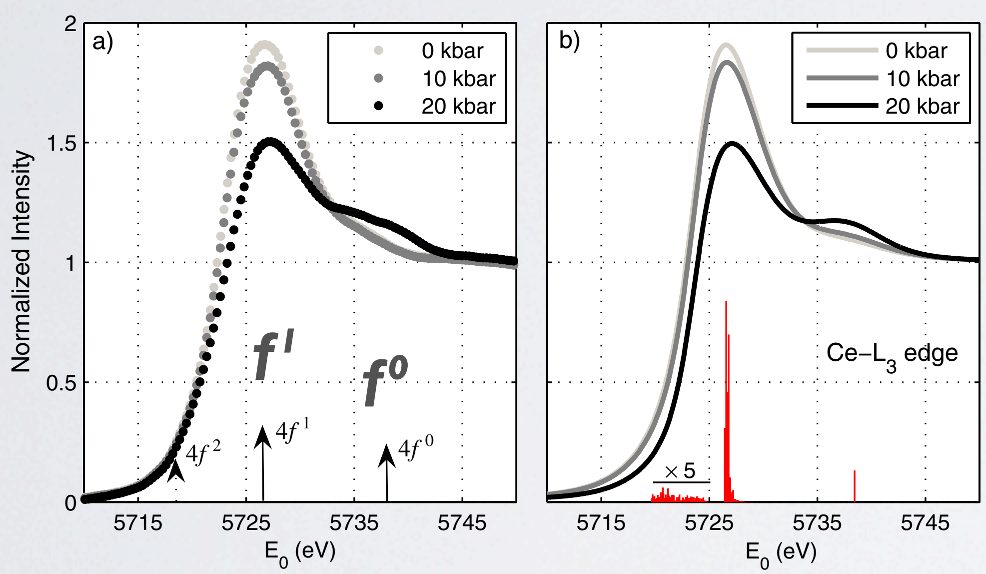
2p3d RIXS in Ce

Complete **characterization of the f-states** through the transition

Combination of XAS + RXES + **AIM calculations**

Valence increase at high pressure :

Exp. **Calc.**



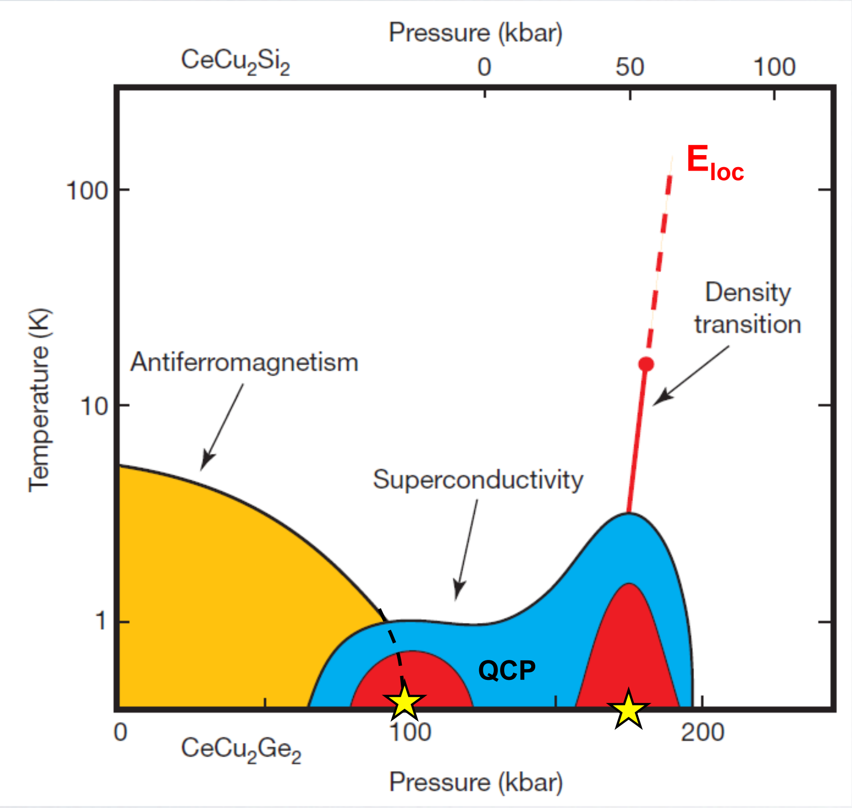
hybridization **f-states**

Phase	P (kbar)	V (eV)	$4f^0$ (%)	$4f^1$ (%)	$4f^2$ (%)	n_f	T_K (K)
Ce (γ)	0	0.31	5.1	92.5	2.4	0.97	70±10
-	10	0.34	7.7	89.6	2.7	0.95	200±50
Ce (α)	20	0.43	21.9	74.7	3.4	0.81	1700±200

JPR et al., Phys. Rev. Lett. ***93*** *(2004), 067402.*
and Phys. Rev. Lett. ***96*** *(2006), 237403.*

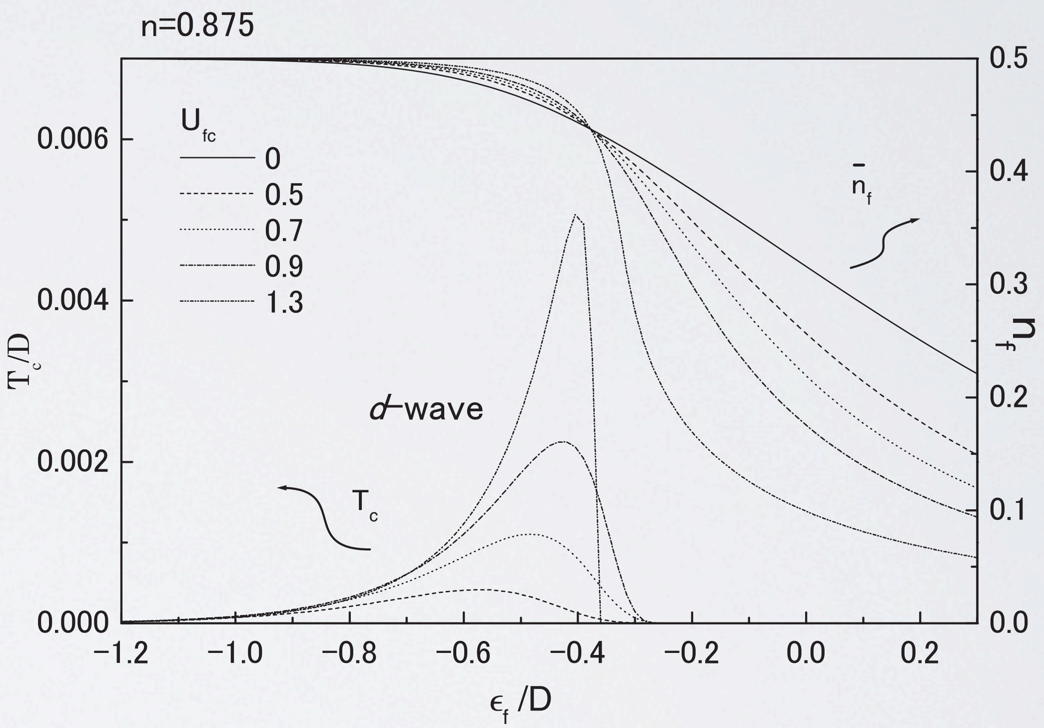
Superconductivity in $CeCu_2Si_2$

Two-dome superconducting phases near QCPs



Yuan et al., Science (2003)

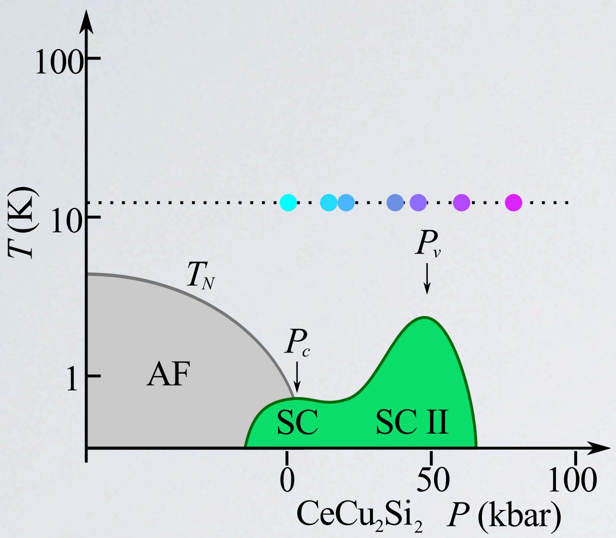
Superconductivity induced **by valence fluctuations** ?



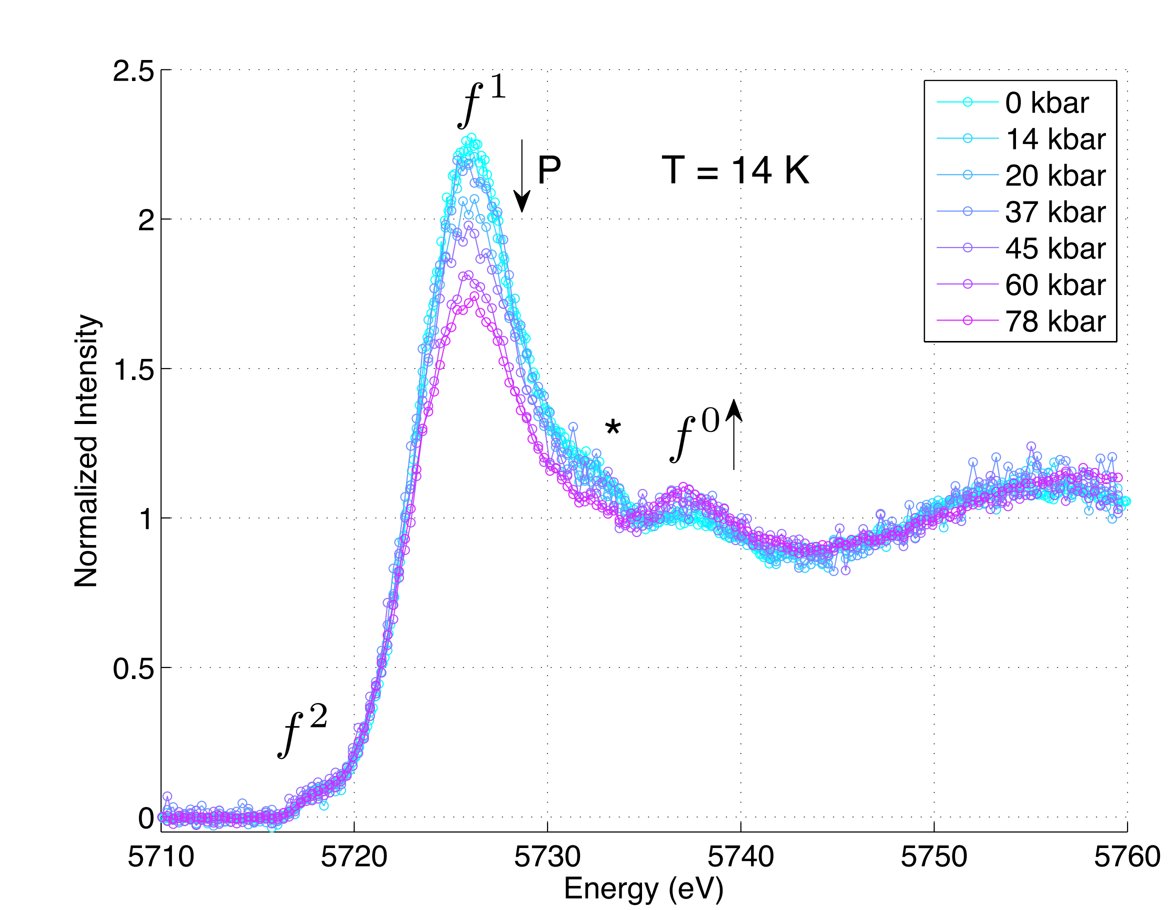
Onishi and Miyake, J. Phys. Soc. Jap. ***69*** *(2000) ;*
Holmes et al., J. Phys. Soc. Jap. ***76*** *(2007)*

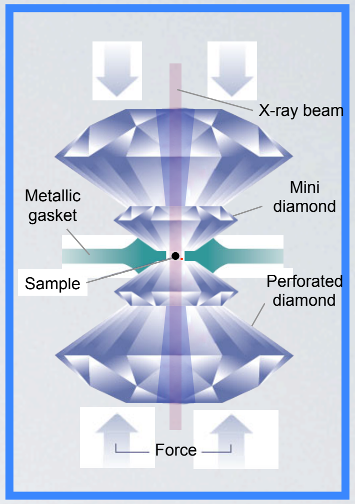
Looking for valence change

ID26 (ESRF)



Ce L_3 edge, PFY-XAS





diamond anvil cell

He cryostat

JPR et al., PRL ***106****, 186405 (2011)*

Calculations in the AIM

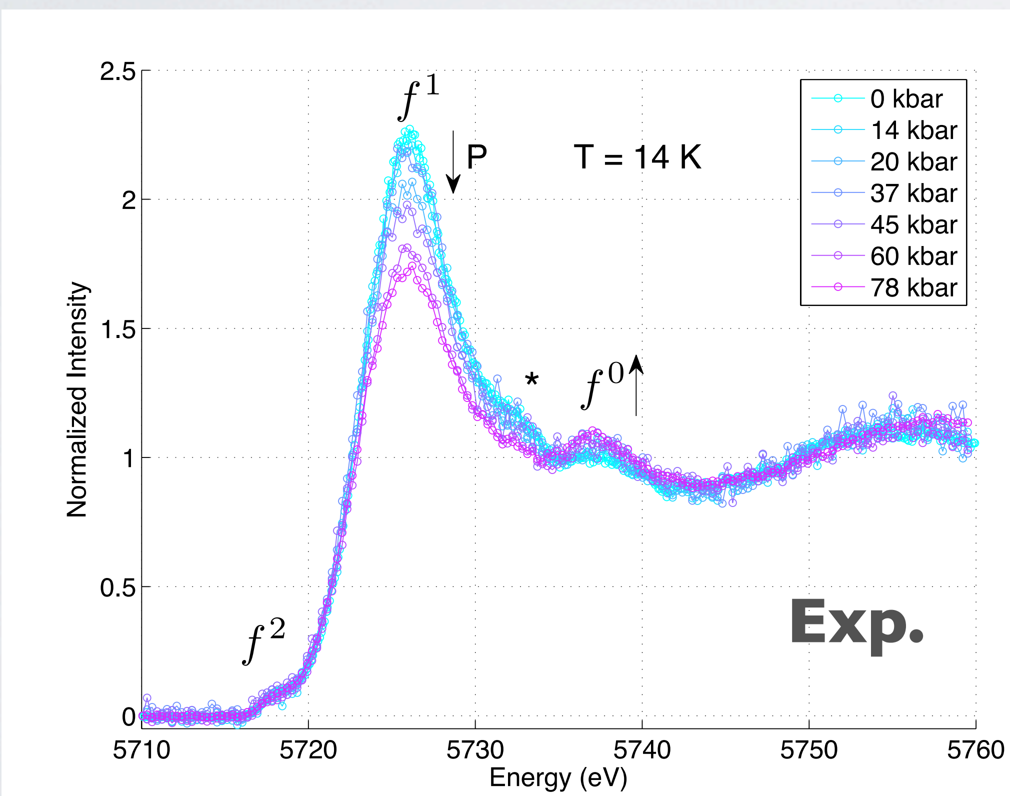
Simulation of Ce L_3 in $CeCu_2Si_2$ in Anderson impurity model :

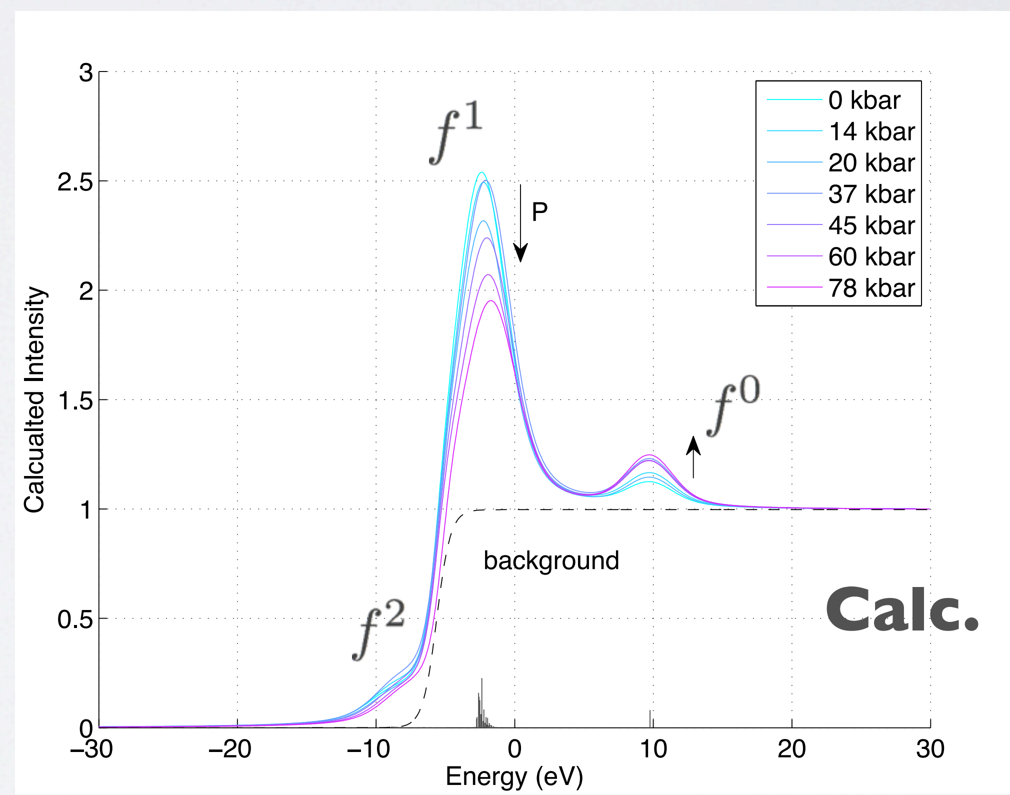
Parameters

U_{ff}=6.0 eV
$U_{fc}(2p)$ = $U_{fc}(2p)$ =10.4 eV

$\epsilon_f, f^0, f^1, f^2, V, W$

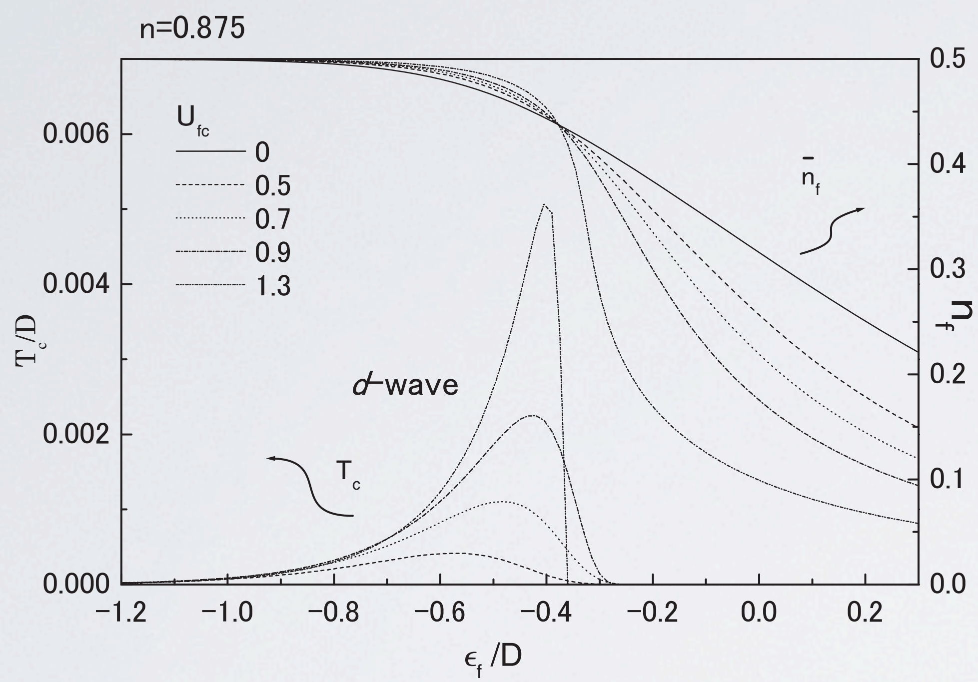
T=14 K

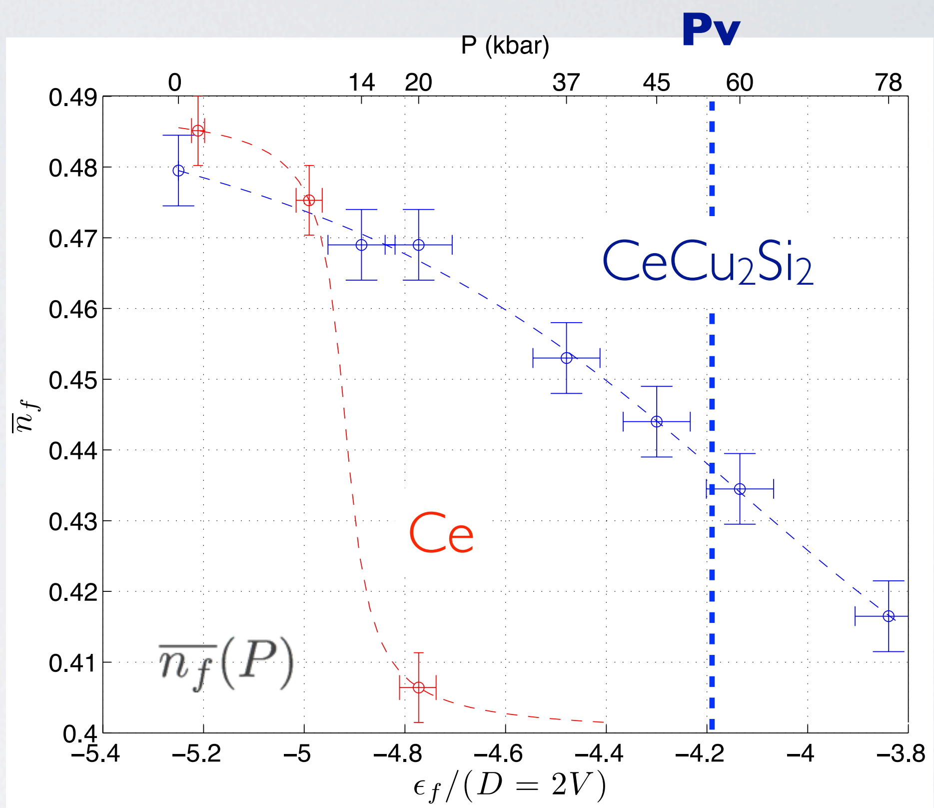




*JPR et al., PRL **106**, 186405 (2011)*

Calculations in the AIM





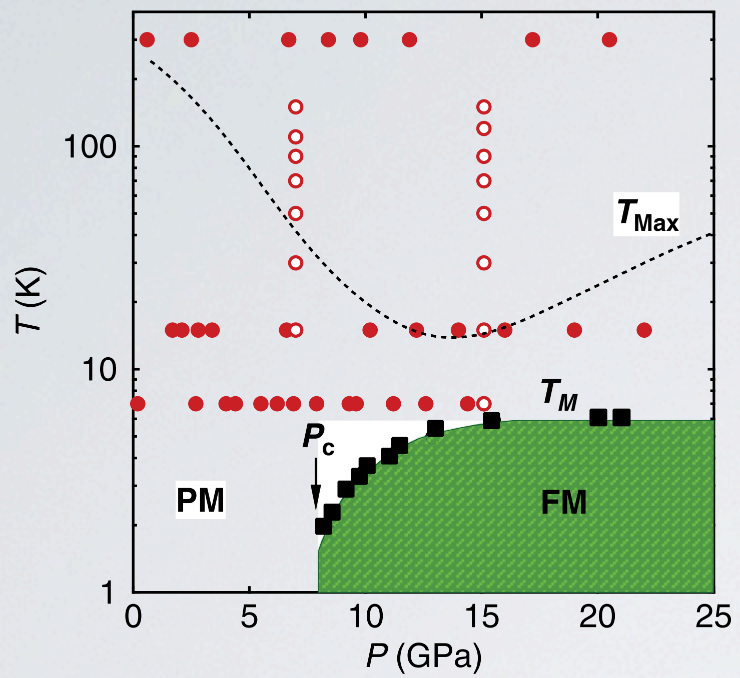
Continuous variation of n_f through P_v (at T=14 K) in agreement with valence fluctuation model providing **$T_{critical}$** ~ **0 K**

Evidence of a new pairing mechanism

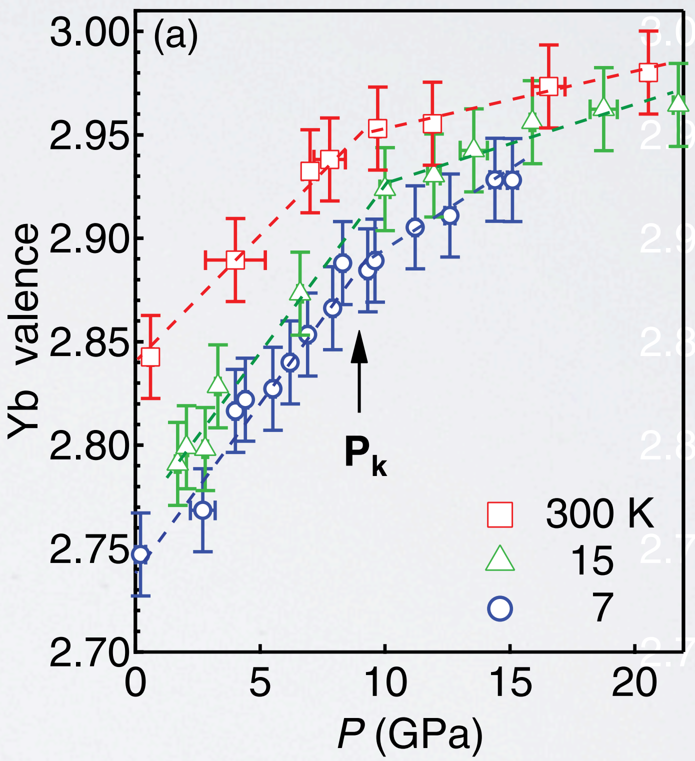
JPR et al., PRL ***106****, 186405 (2011)*

ID16 (ESRF)

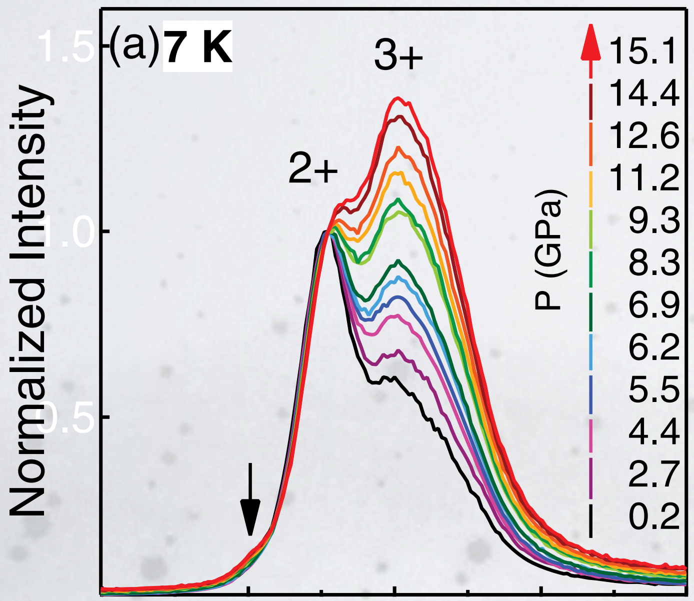
Hole-equivalent : $YbCu_2Si_2$



Kink at P_K is related to **magnetic order** (crossover from intermediate valence and Kondo regime). Unlike $CeCu_2Si_2$, **no superconductivity** is found



RXES, $L_{\alpha 1}$ line

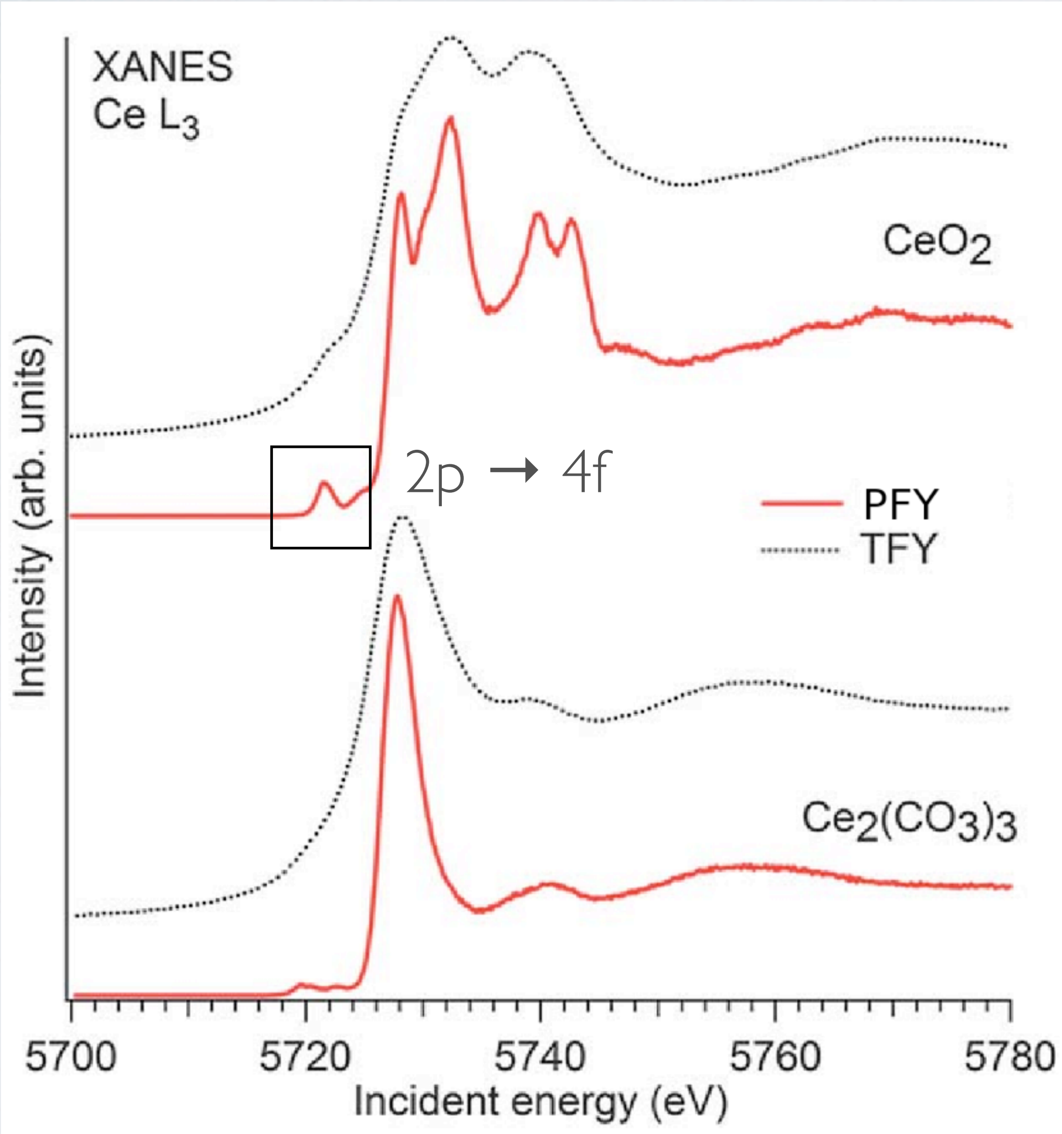


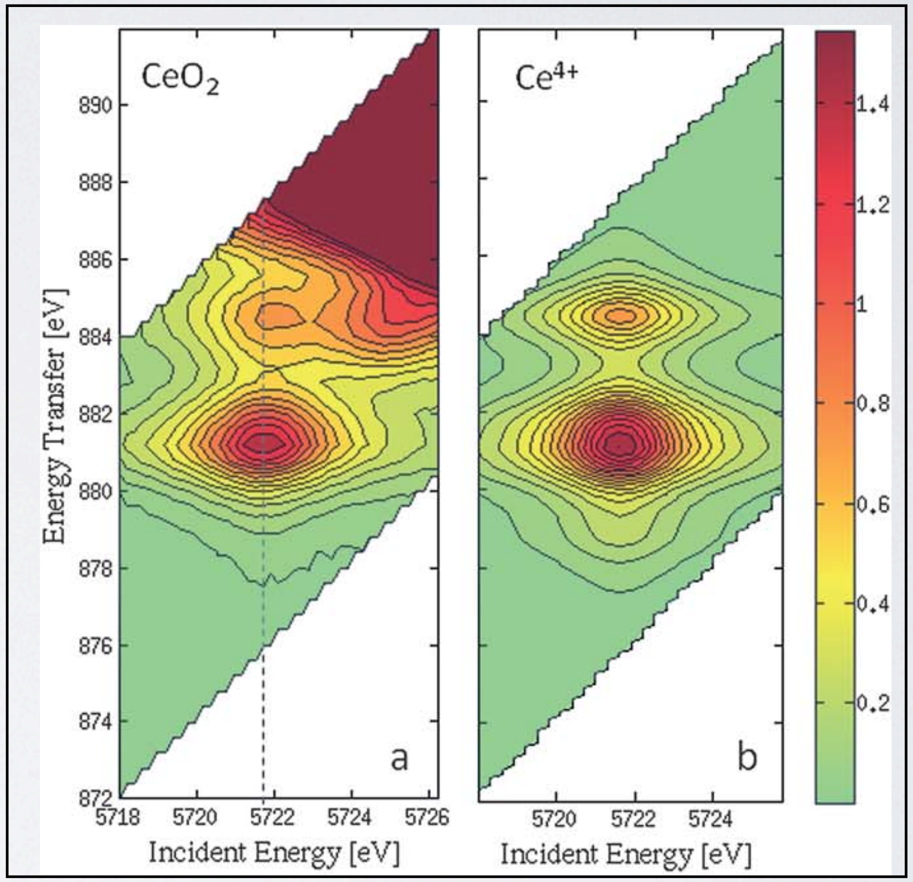
*A. Fernandez, JPR et al., PRB, **86**, 125104 (2012)*

Outline

- *f*-electron delocalization
- Catching up *f*-electrons : X-ray Raman Scattering
- Perspectives at SOLEIL

Probing the *f* electrons





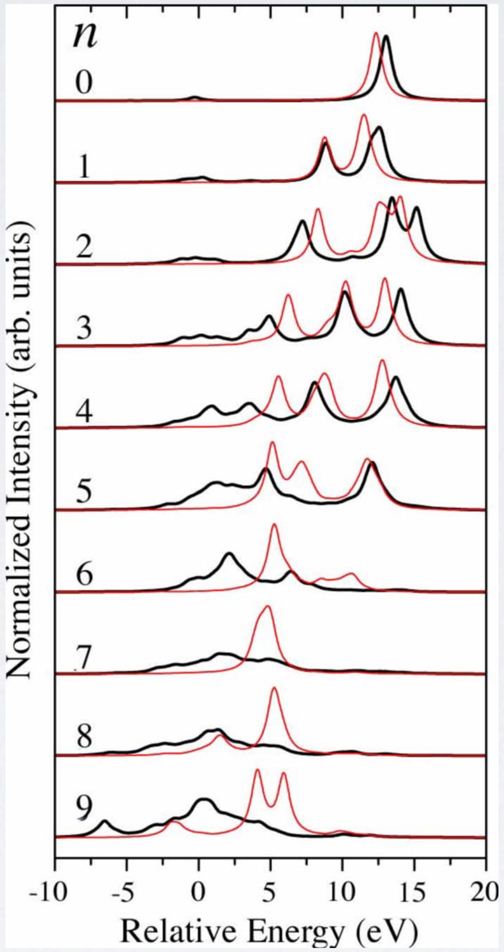
Kvashnina et al., J. Anal. At. Spec. ***26*** *(2011), 1265*

Probing the *f* electrons

$N_{4,5}$ or **$O_{4,5}$** edges
(4d, 5*d* → f) probe directly the f electrons

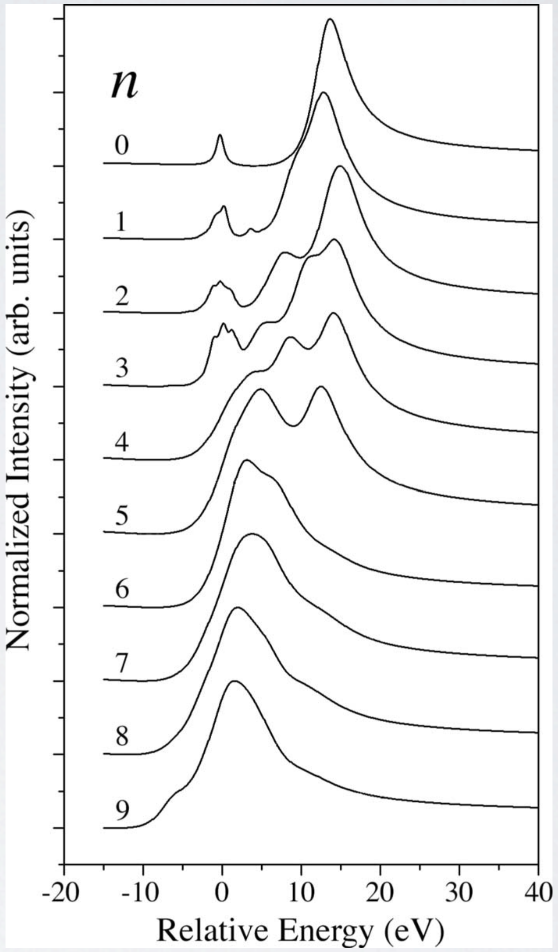
Hard x-ray wanted for HP studies

$O_{4,5}$ edges



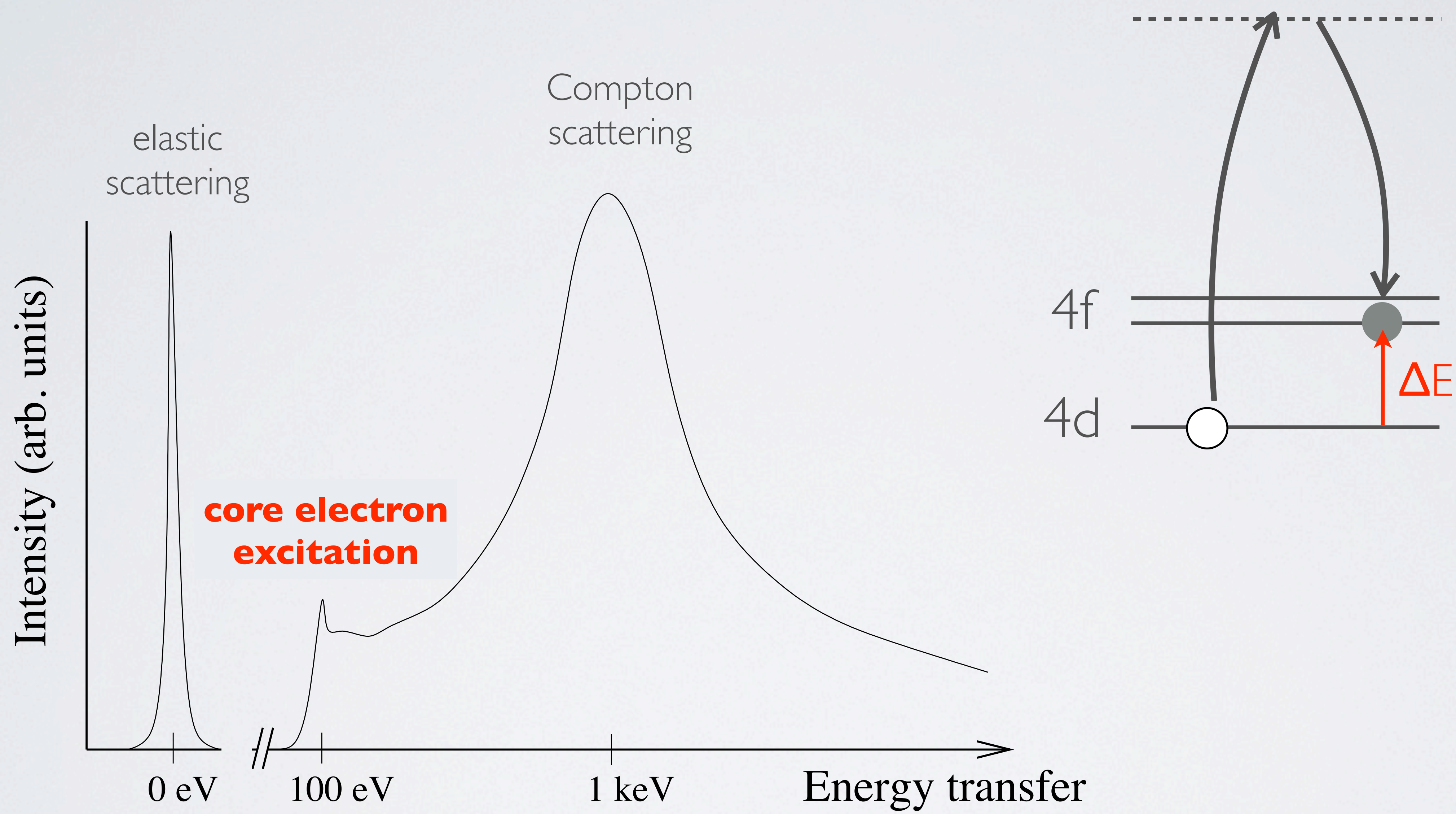
+Fano

giant dipolar resonance



*Moore and van der Laan RMP **81** (2009), 298.*

X-ray Raman scattering



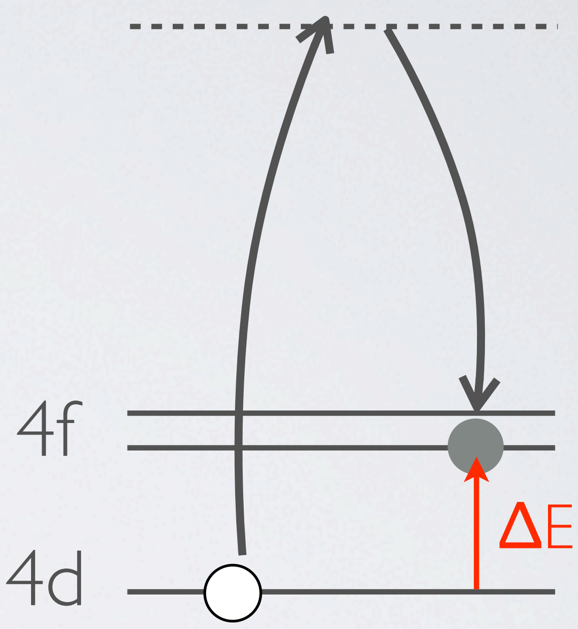
X-ray Raman scattering

Core transitions with high energy photons (similar to EELS for electrons) using the transition operator :

$$S(\mathbf{q},\omega) = \sum_f \left| \langle f | \sum_j e^{i\mathbf{q}\cdot\mathbf{r}} | g \rangle \right|^2 \delta(E_g - E_f + \hbar\omega)$$

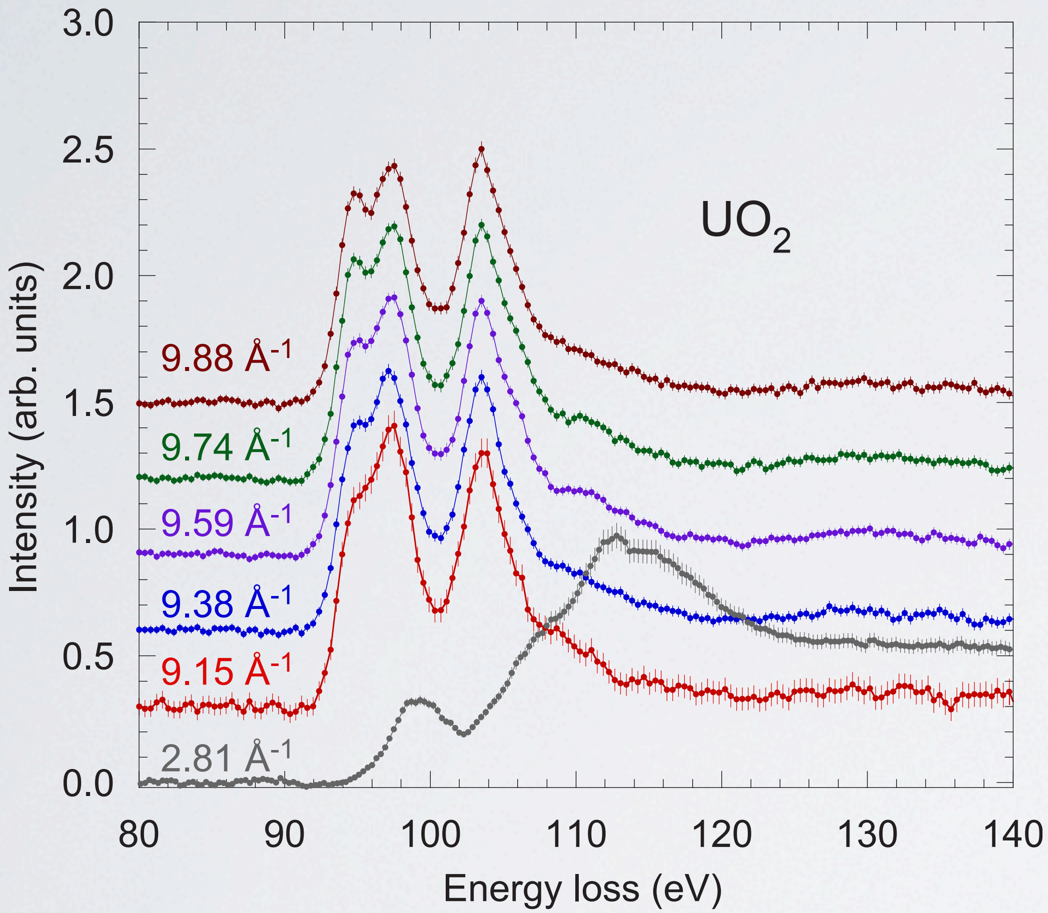
q plays the role of **ε** in soft XAS. But **non dipolar terms** arise at high q :

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 1 + i\mathbf{q}\cdot\mathbf{r} + (i\mathbf{q}\cdot\mathbf{r})^2/2 + \ldots$$



XRS in 5*f* electrons

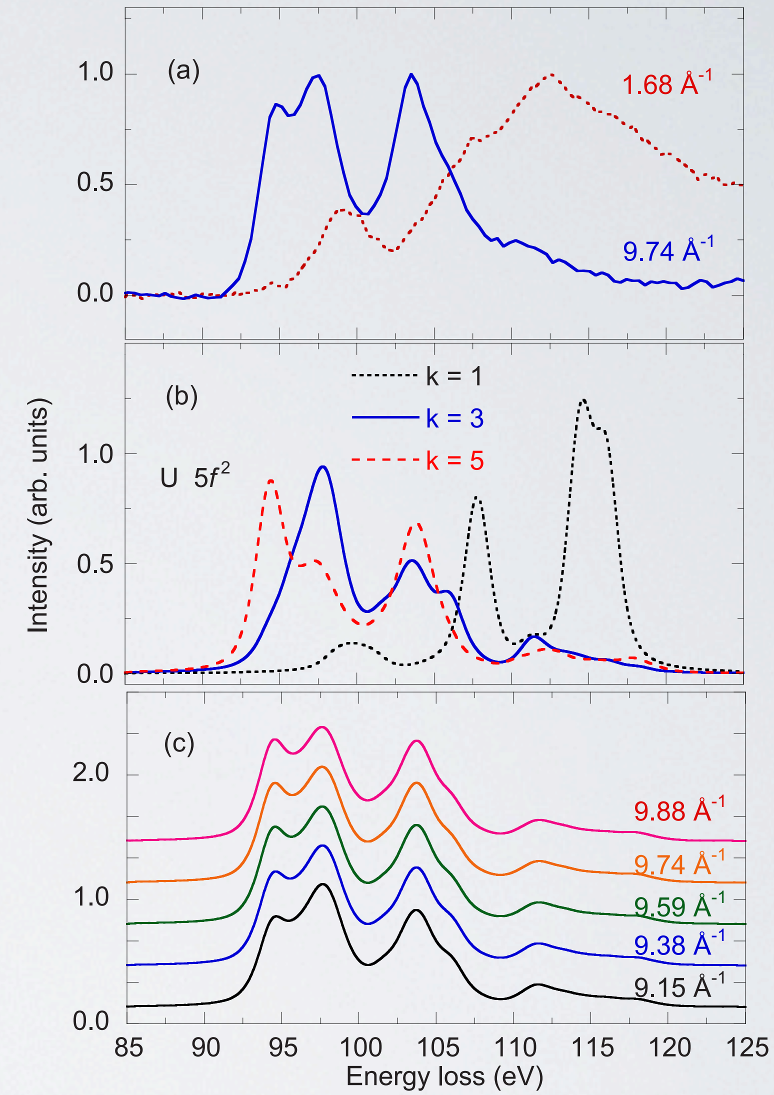
U, $O_{4,5}$ edges (5d → 5f)   E=9.6 keV



(high q)

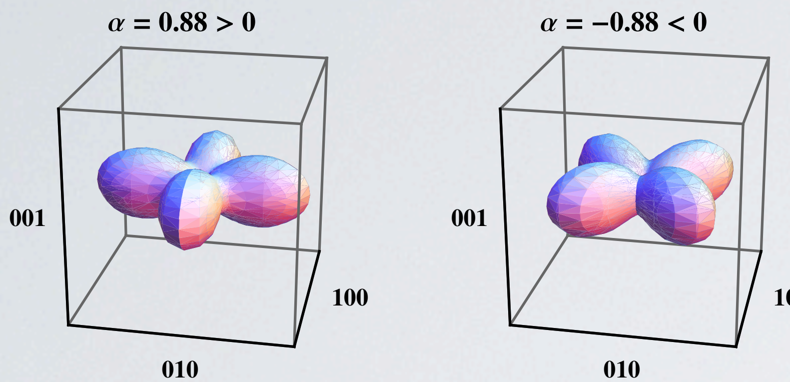
«giant resonance»
(low q)

*Caciuffo et al., PRB **81**, 195104 (2010)*

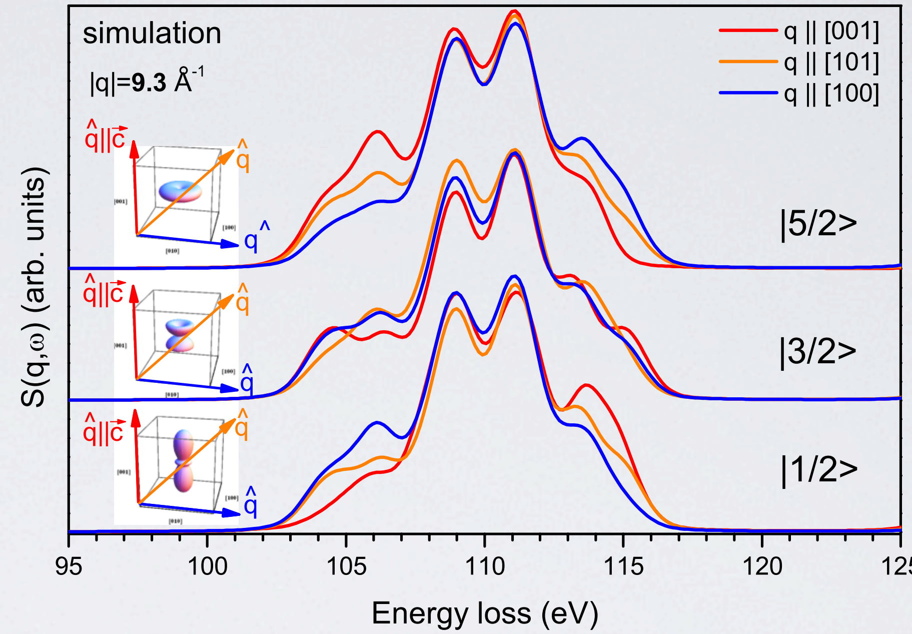


high-rank
multipolar transitions

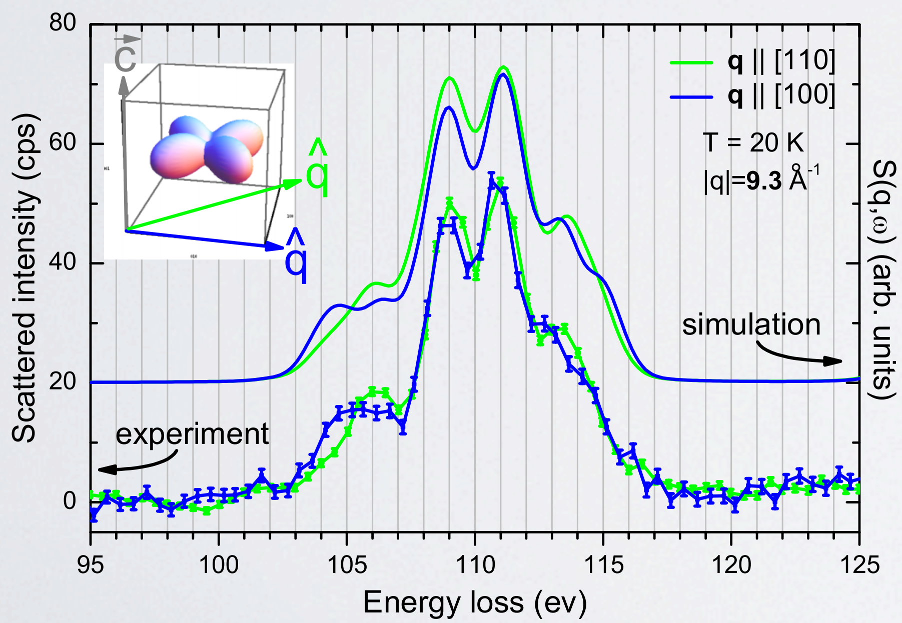
Ground state orbital occupation



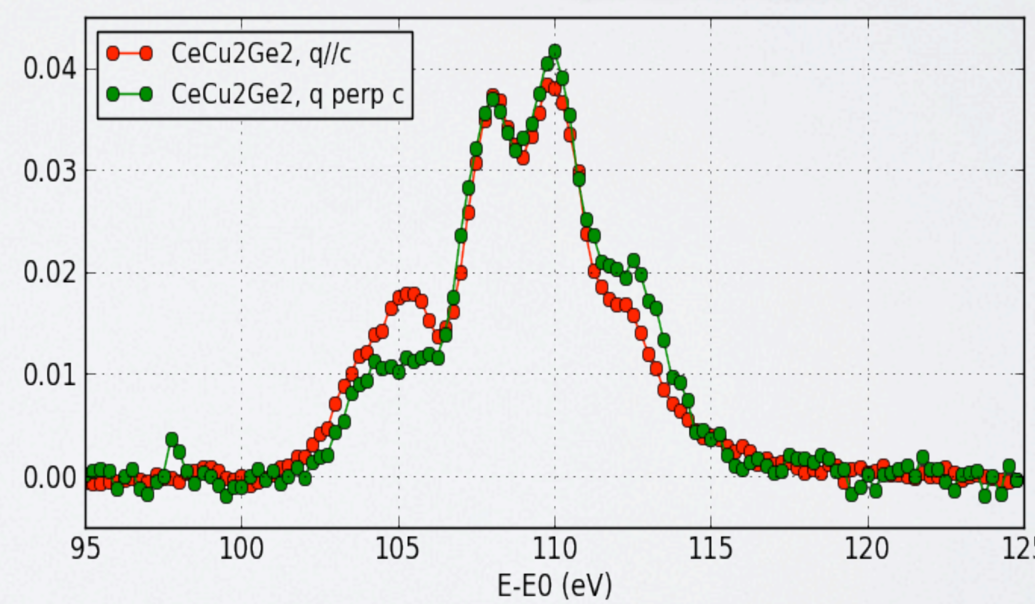
$\Gamma_7 = |0.88|\,|\pm5/2\rangle + 0.47\,|\mp3/2\rangle$

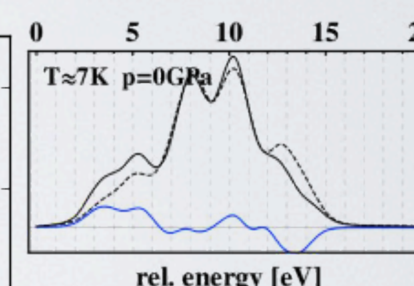


$CeCu_2Si_2$ ID20, ESRF



$CeCu_2Ge_2$ GALAXIES





L. Pourovskii, et al.

*Willers et al. PRL **109** (2012), 046401.*

Outline

- *f*-electron delocalization
- Catching up *f*-electrons
- Perspectives at SOLEIL : GALAXIES beamline

SOLEIL Synchrotron

26 beamlines

2.75 GeV
354 m
3.74 nm.rad
400 mA

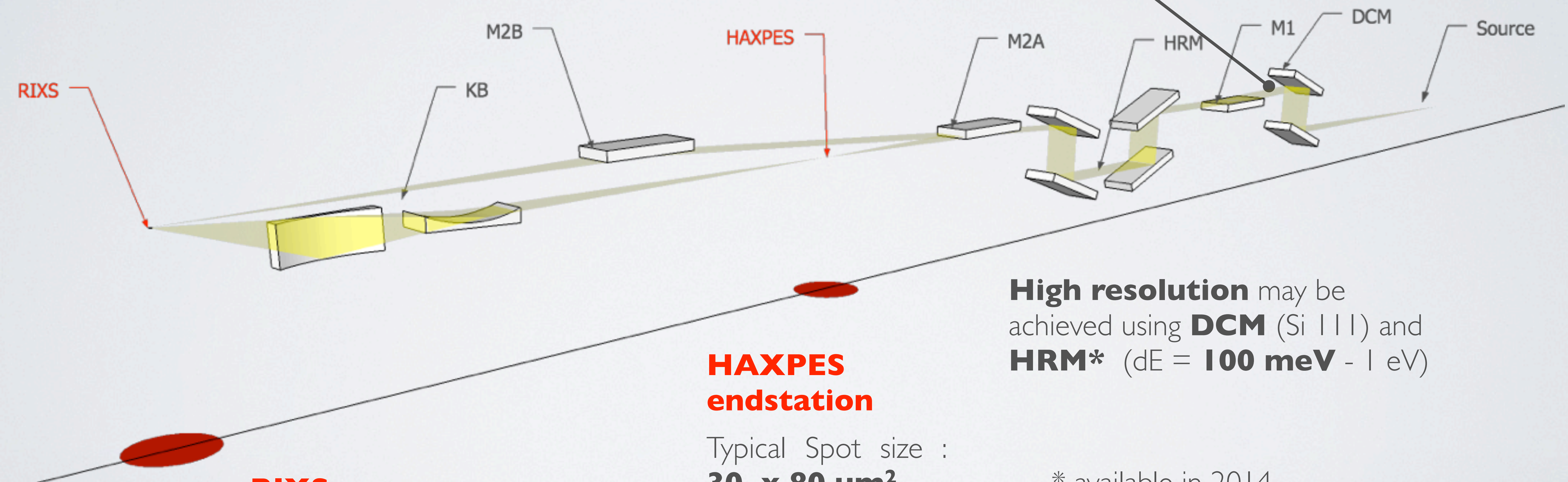
GALAXIES Beamline Layout

Open to users
May 2013

The GALAXIES beamline is dedicated to **hard X-ray photoelectron spectroscopy** and **Inelastic X-ray Scattering**.

Diamond **phase retarder***

The **U20 in vacuum undulator** provides **high flux** in the **2.3 - 12 keV** energy range.



High resolution may be achieved using **DCM** (Si 111) and **HRM*** (dE = **100 meV** - 1 eV)

HAXPES endstation

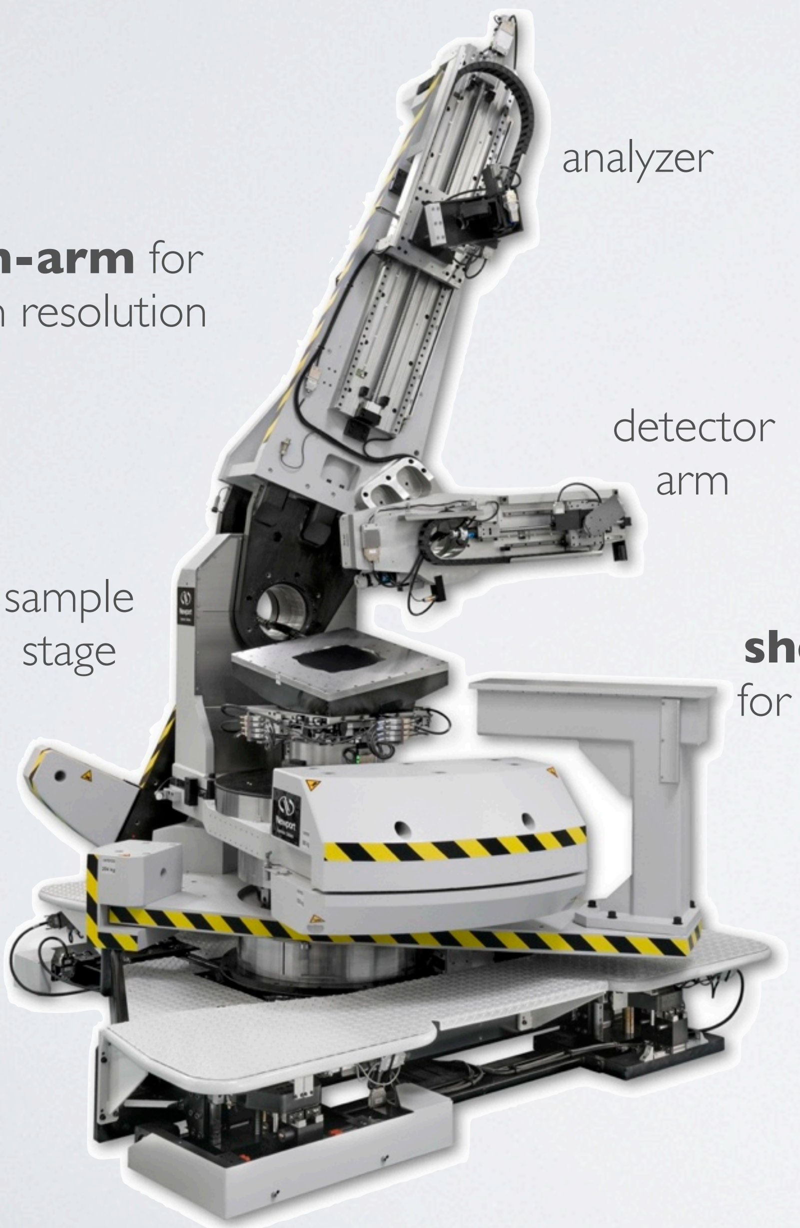
Typical Spot size : **30 x 80 µm²**

* available in 2014

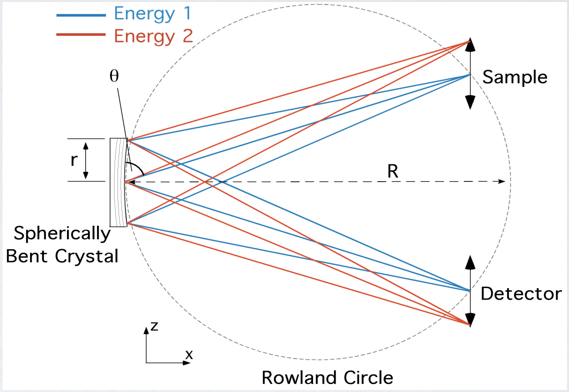
RIXS endstation

RIXS station

High resolution / High flux Spectrometer



Rowland circle geometry (0.5-2m)



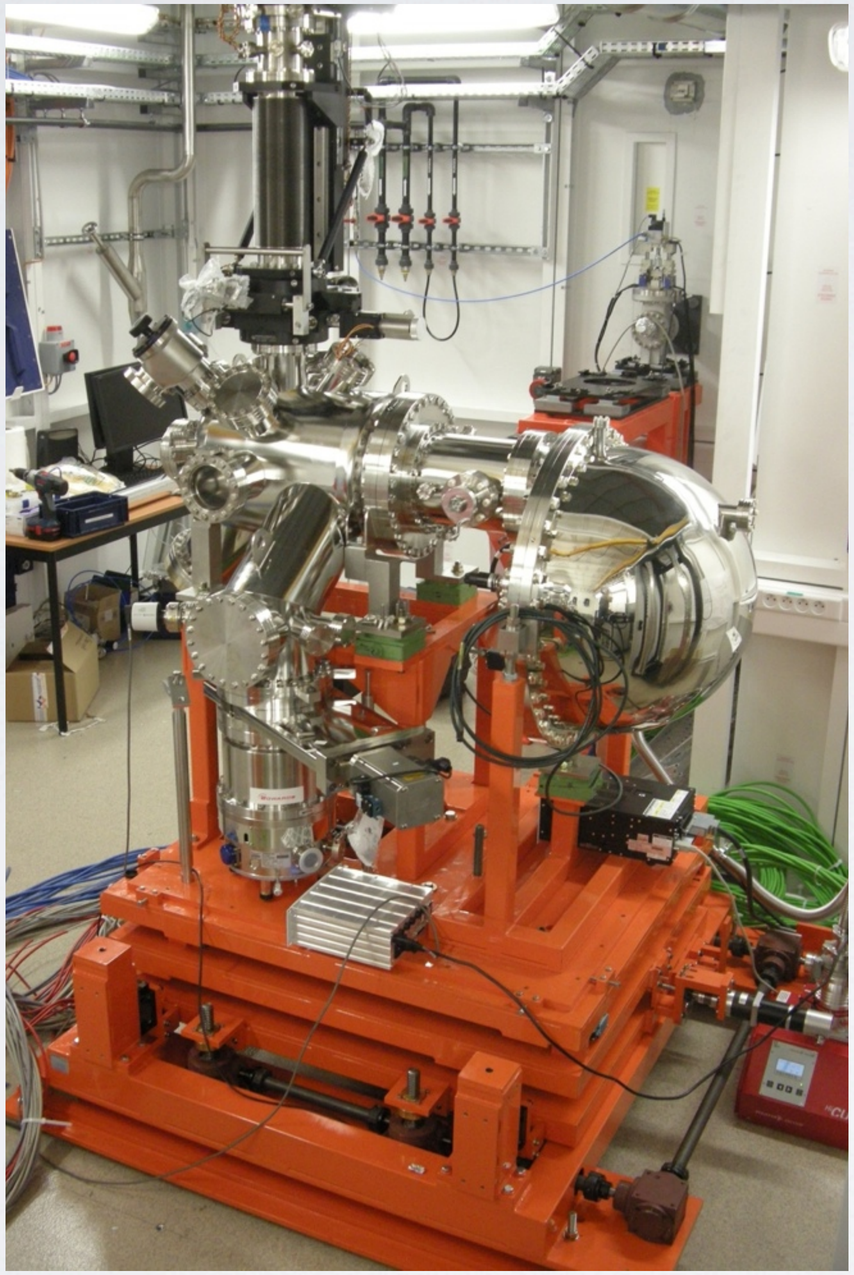
1 + 4-analyzer setup

HAXPES station

Thermionics 4-axis fully
motorized, manipulator
Closed-cycle 15K cryostat
In-situ bias

Preparation chamber

load lock
chamber
Ion gun, LEED,
heating element



SCIENTA EW4000
Ec < 12 keV , **wide angular lens +/- 30°**

motorized frame

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