Bulk-sensitive x-ray spectroscopies on Yb Kondo systems

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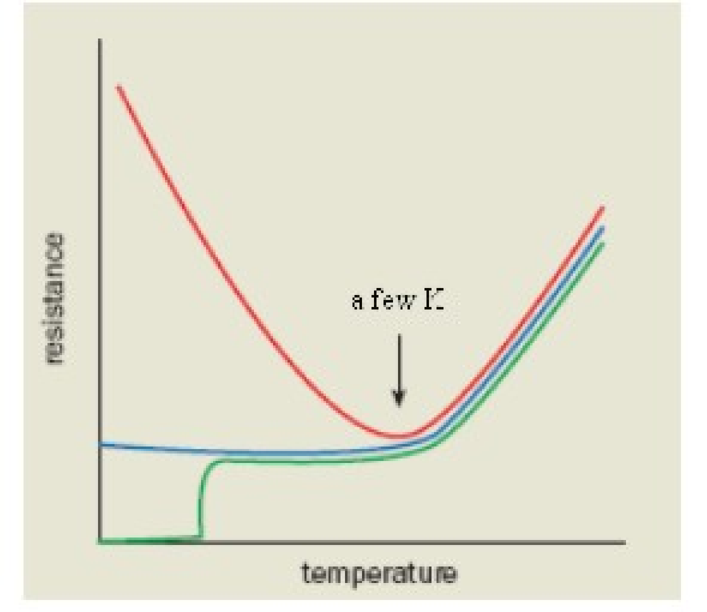
Corpes07 - Dresden

02/05/2007

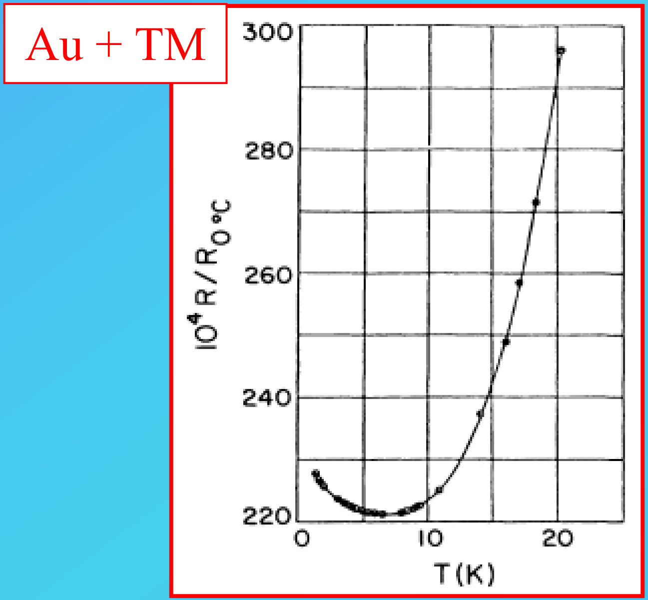
the Kondo effect



transition to a superconducting state (Pb, Al,…)

saturation of the resistance (Au, Cu,…)

increase of the resistance (Au, Cu + magnetic impurity)

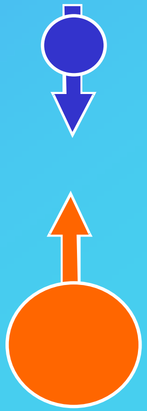


the magnetic impurity acts as a big scattering centre

W.J. de Haas *et al.* Physica **3**, 440 (1936)

J. Kondo, Prog. Theor. Phys. **32**, 37 (1964)

the Kondo effect



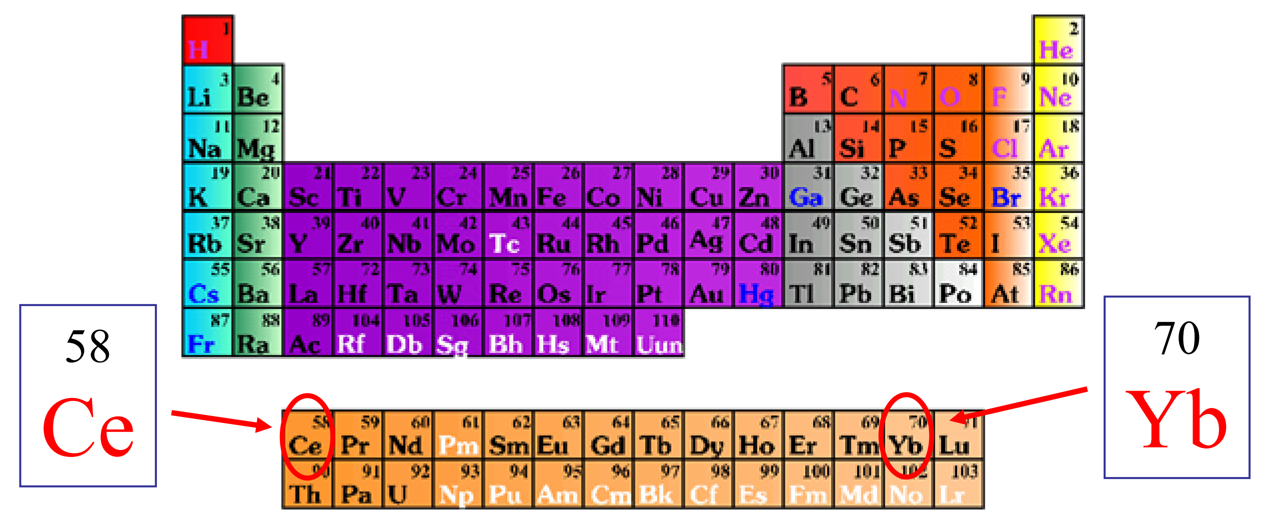
impurity spin

$$\boxed{\mathbf{H = - J\,(S \cdot s)}}$$

cond *e*⁻ spin density

negative exchange constant

Yb and Ce on the periodic table



Yb ground state : [Xe] $5d^0\ 6s^2\ 4f^{14}$ divalent

Ce ground state : [Xe] $5d^1\ 6s^2\ 4f^1$ trivalent

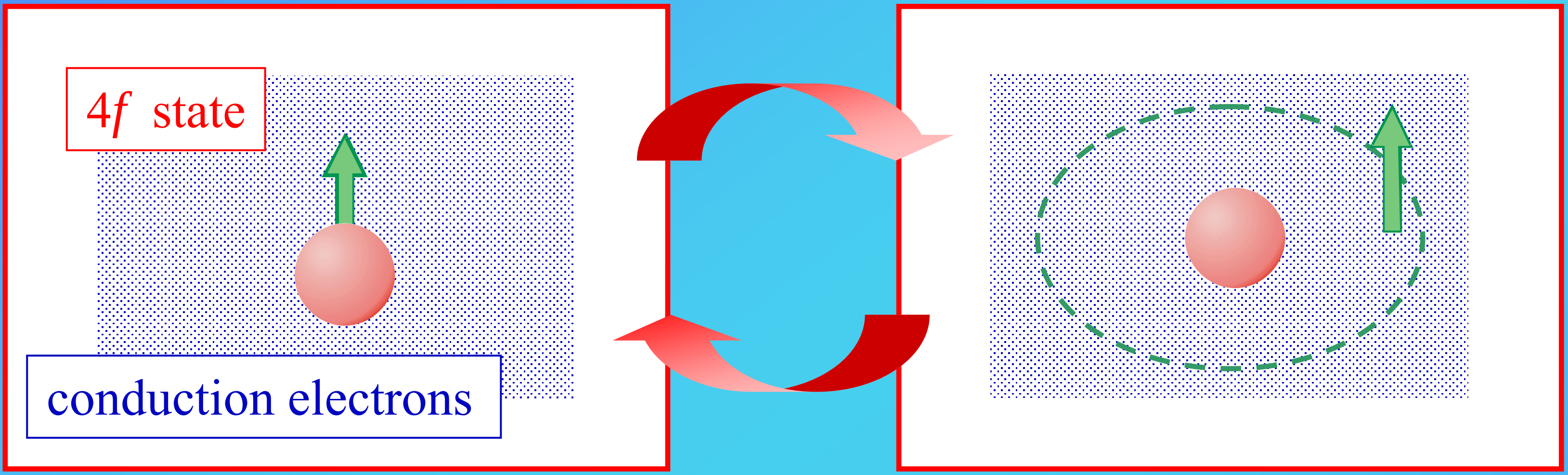
Yb: $4f^{13} – 4f^{14}$ electron-hole counterpart of **Ce** ($4f^1 – 4f^0$)

energetically close configurations

$4f^0$ - $4f^1$ energy separation in Ce compounds ≈ 2eV

$4f^{13}$ - $4f^{14}$ energy separation in Yb compounds ≈ some 100 meV

valence fluctuations



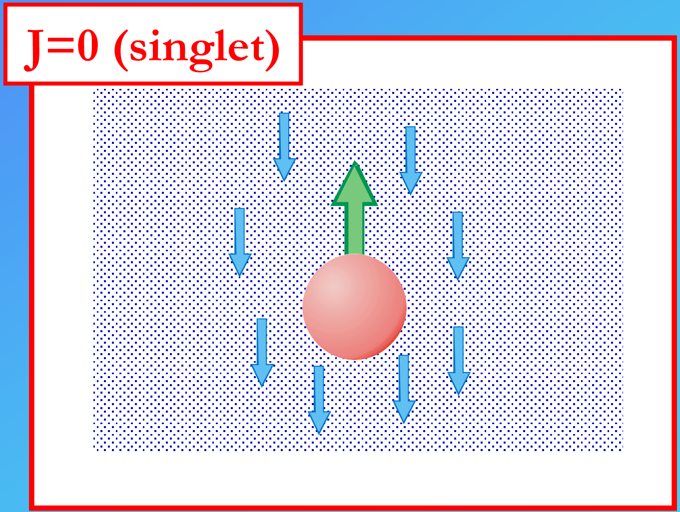
1 electron	$\mathrm{Ce}^{3+}\ (4f^{\,1})$	hybridization	$\mathrm{Ce}^{4+}\ (4f^{\,0})$	**0 electrons**
1 hole	$\mathrm{Yb}^{3+}\ (4f^{\,13})$	$\rightleftharpoons$	$\mathrm{Yb}^{2+}\ (4f^{\,14})$	**0 holes**

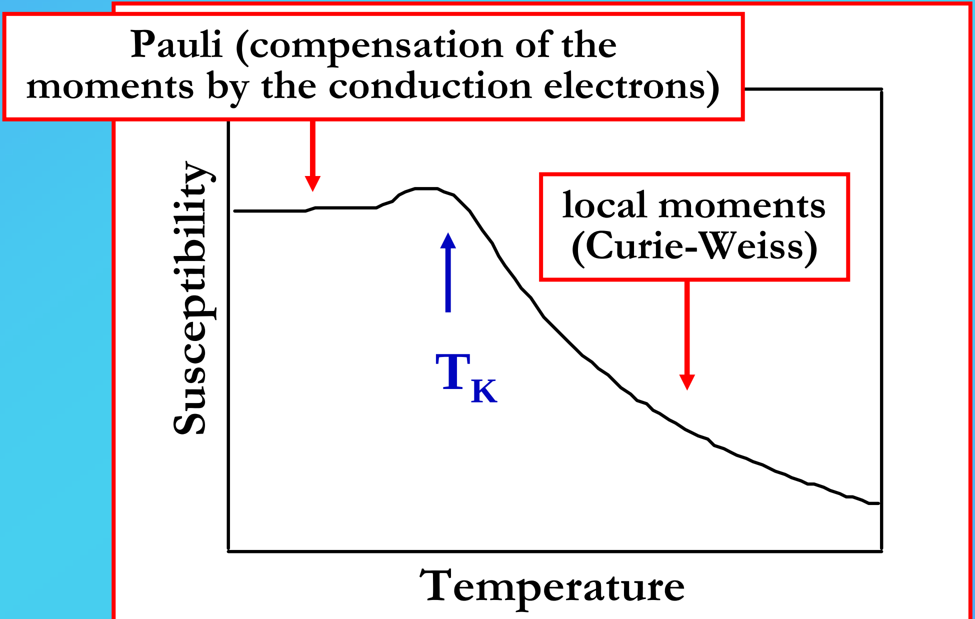
the lowest E configuration is 3+

$f^{\,1}$	Ce
h^{1}	Yb

the mixed ground state in Ce compounds

J=0 (singlet)

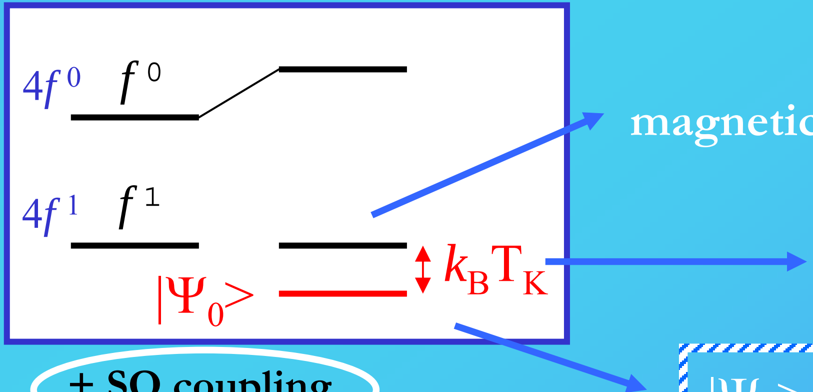



Pauli (compensation of the moments by the conduction electrons)

local moments (Curie-Weiss)

$\chi(T) = C/T$ Curie law at high T

$\chi(T) =$ constant non-magnetic at low T



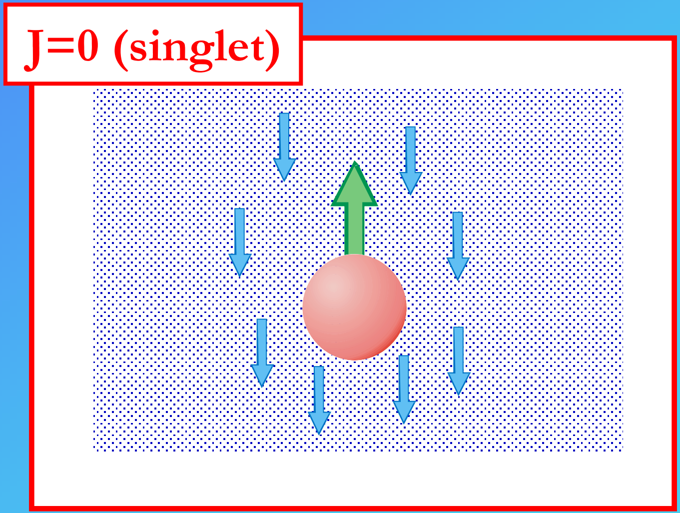
+ SO coupling

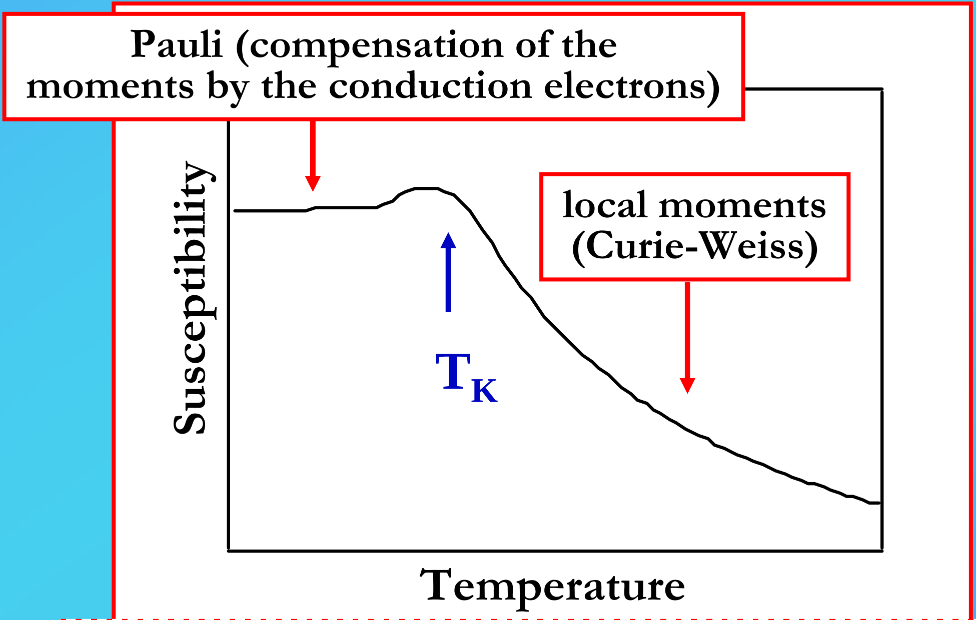
magnetic (3^+) states

$k_BT_K \approx 1$ - 2 eV

$|\Psi_0> = \alpha\, |f^1> + \beta\, |f^0>$ **SINGLET**

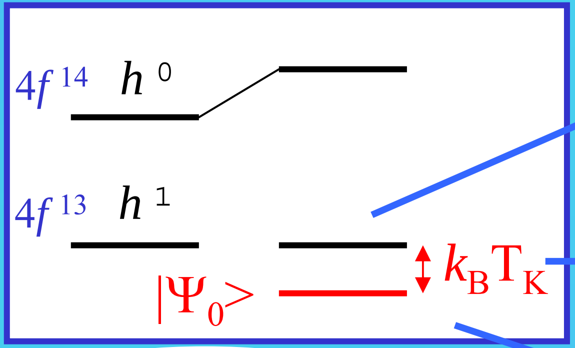
the mixed ground state in Yb compounds





$\chi(T) = C/T$ Curie law at high T

$\chi(T) =$ constant non-magnetic at low T



magnetic (3^+) states

$k_BT_K \approx 1 - 100$ meV

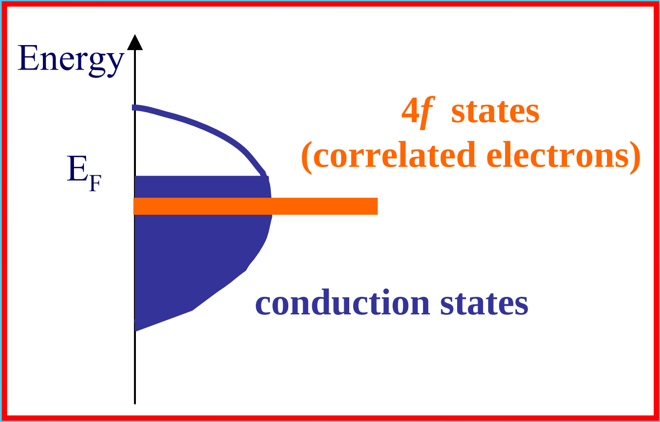
+ SO coupling

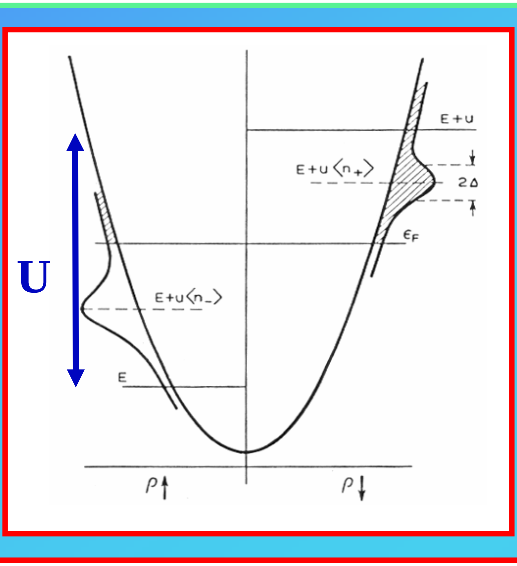
$|\Psi_0> = \alpha\,|h^1> + \beta\,|h^0>$ **SINGLET**

the Kondo effect and the Anderson impurity model

$$H_{AIM} = H_{band} + H_{impurity} + \boxed{H_{mix}}$$

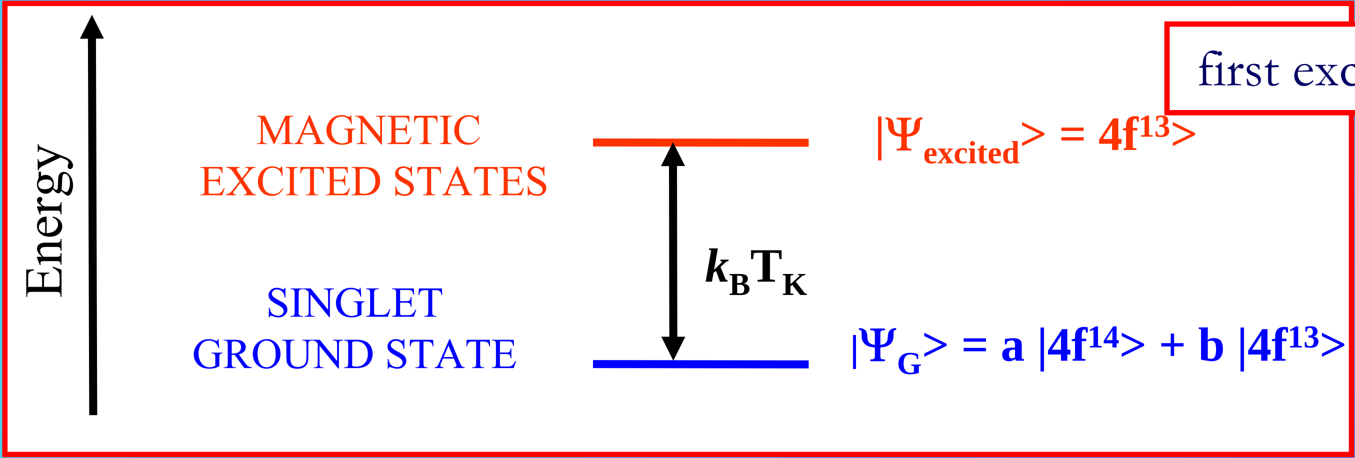
From this term a low energy scale $k_B T_k$ emerges





AIM more general than the Kondo Hamiltonian

P.W.Anderson, PR **124**, 41 (1961)



first excited state at $k_B T_K$

MAGNETIC EXCITED STATES

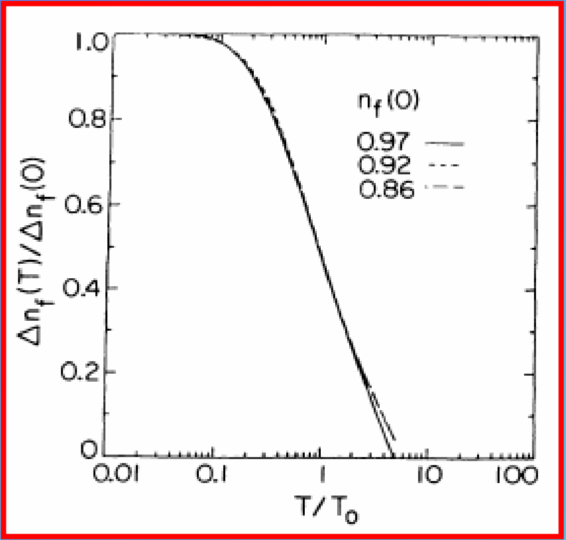
$|\Psi_{excited}\rangle = 4f^{13}\rangle$

SINGLET GROUND STATE

$|\Psi_G\rangle = a\,|4f^{14}\rangle + b\,|4f^{13}\rangle$

solving the AIM: the T/T_K scaling

4*f* occupation



Ce

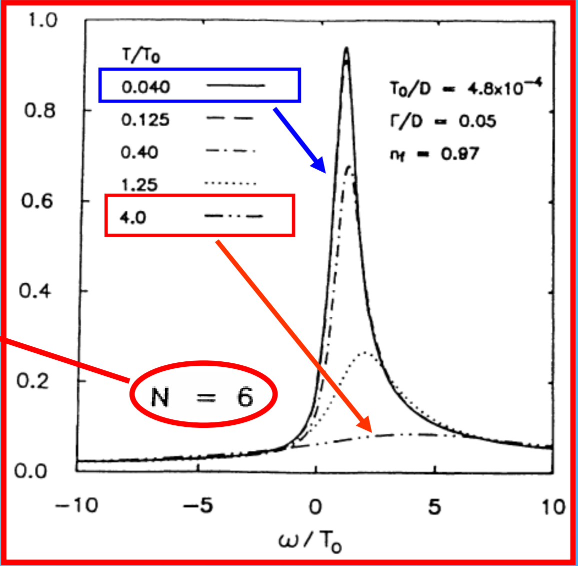
lowest E configuration

$f^1_{5/2} \rightarrow N=6$

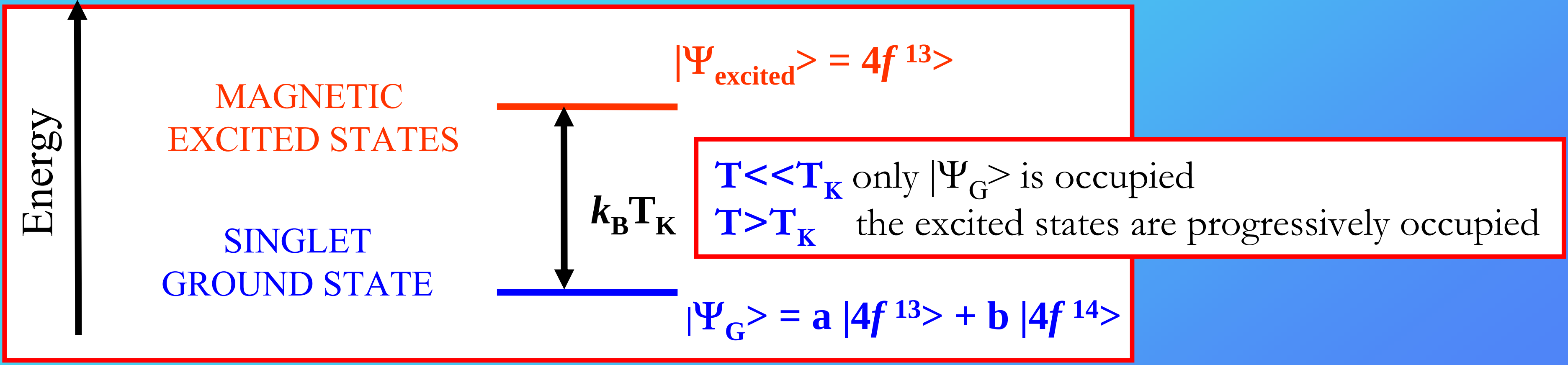
Yb

lowest E configuration

$h^1_{7/2} \rightarrow N=8$



thermal depopulation
of the singlet state



MAGNETIC EXCITED STATES

$|\Psi_{excited}\rangle = 4f^{13}\rangle$

$k_B T_K$

SINGLET GROUND STATE

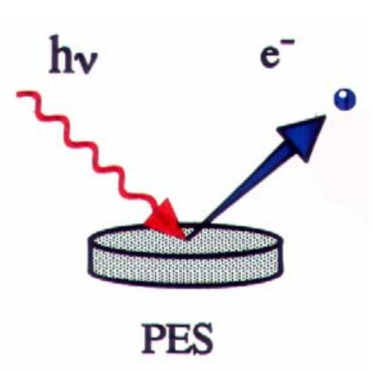
$|\Psi_G\rangle = a\,|4f^{13}\rangle + b\,|4f^{14}\rangle$

$T \ll T_K$ only $|\Psi_G\rangle$ is occupied

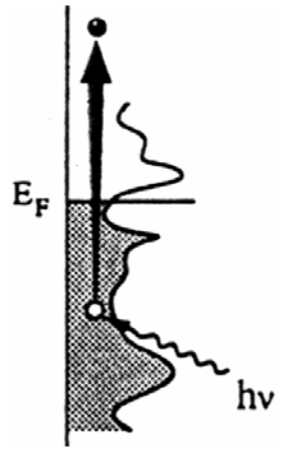
$T > T_K$ the excited states are progressively occupied

N.E.Bickers *et al.* PRB **36**, 2036 (1987)

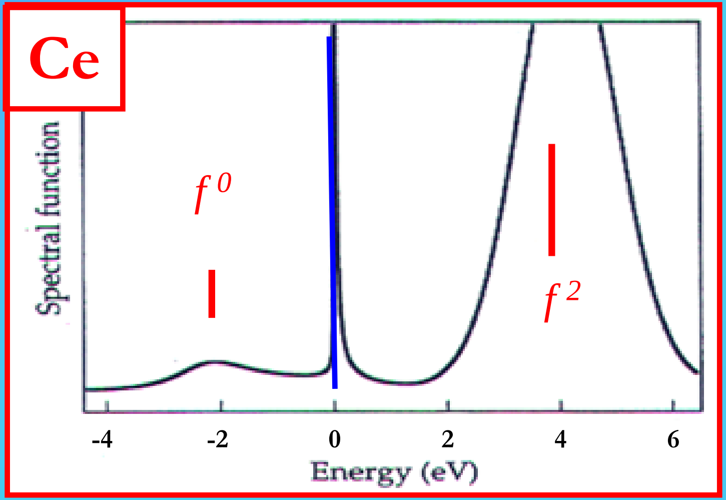
4*f* electrons in Ce and Yb



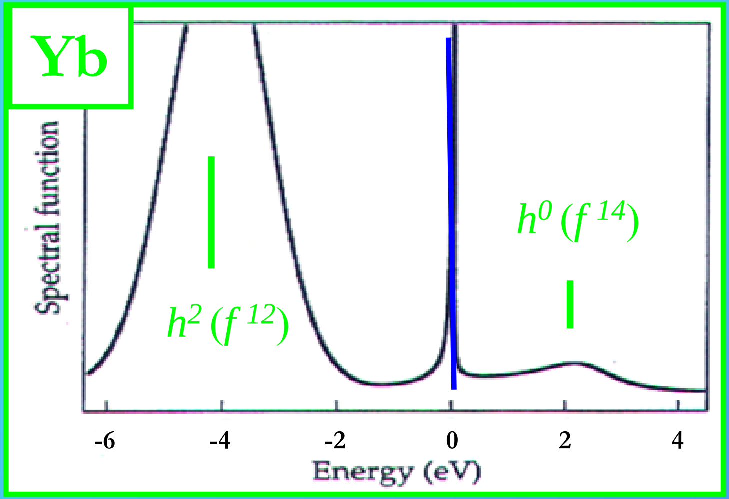
photoemission



occupied DOS

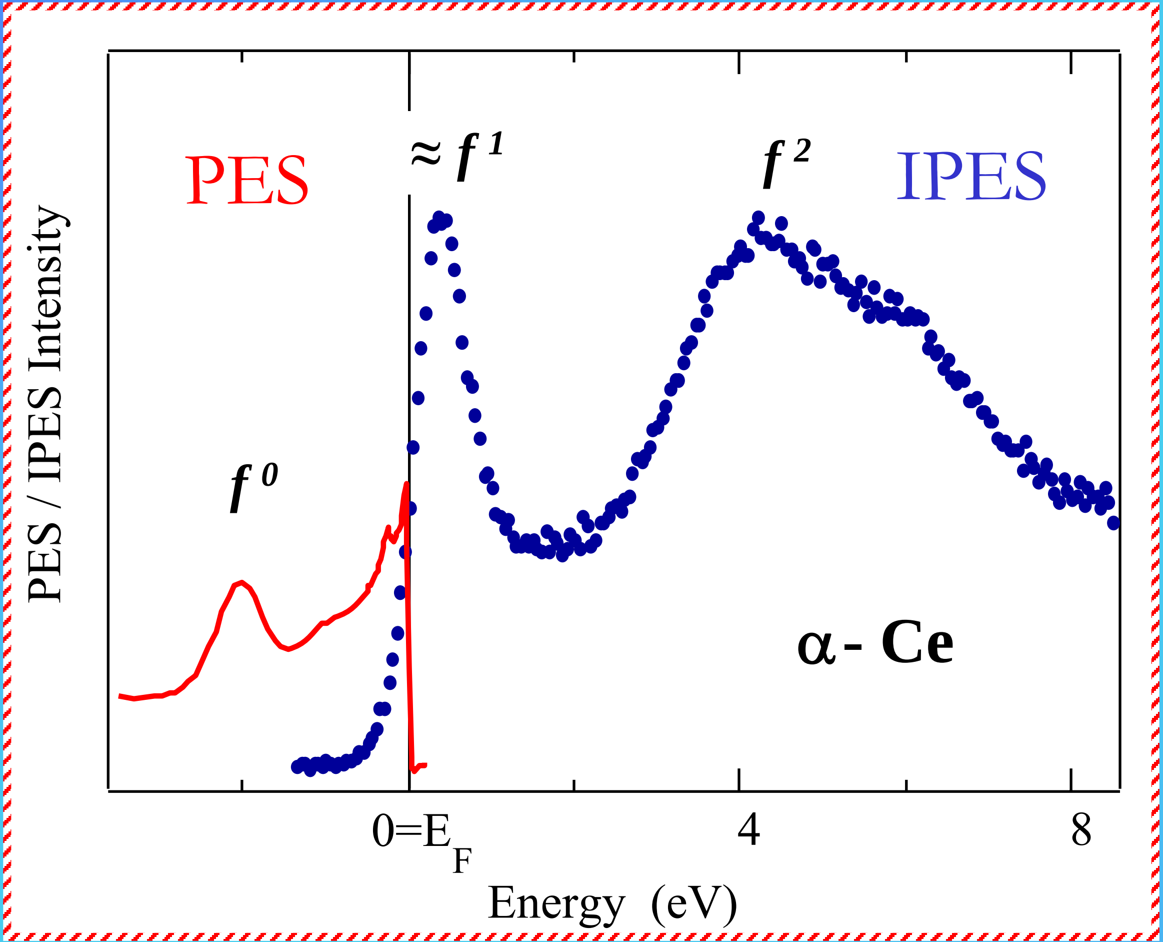


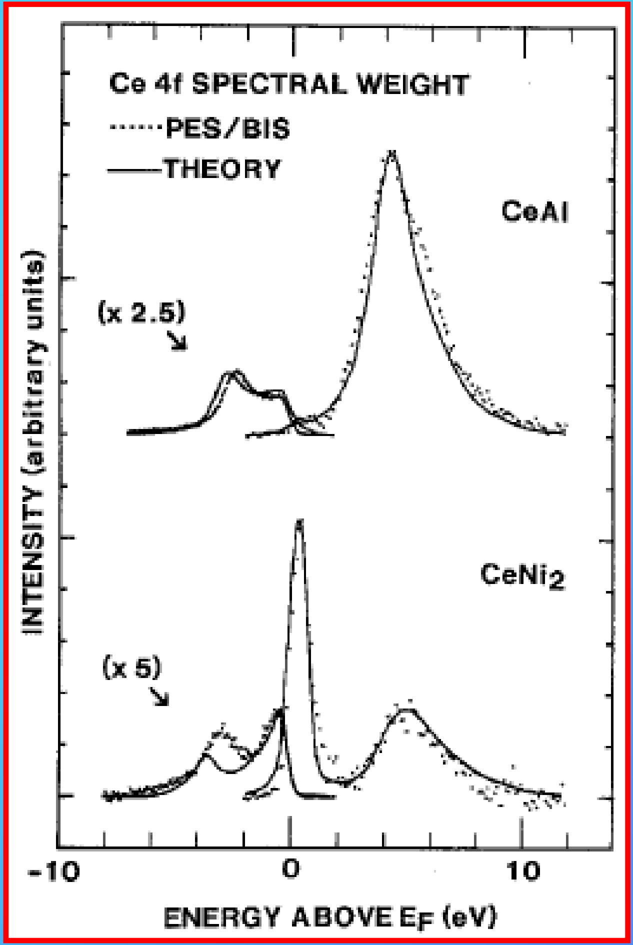
DOS of the KR mainly in the unoccupied states



DOS of the KR mainly in the occupied states

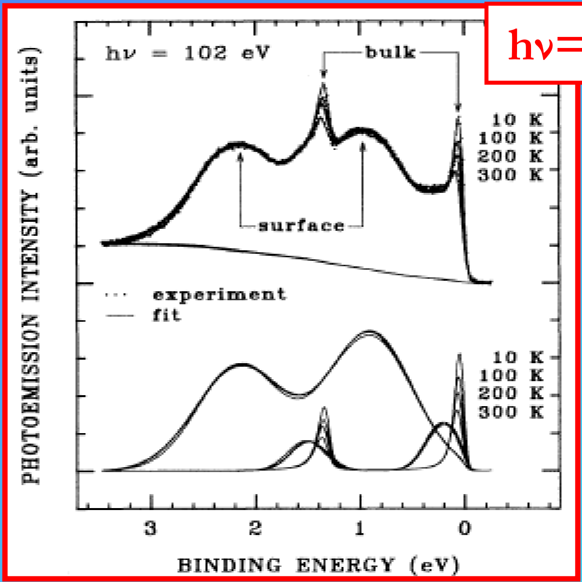
spectroscopies for Kondo systems





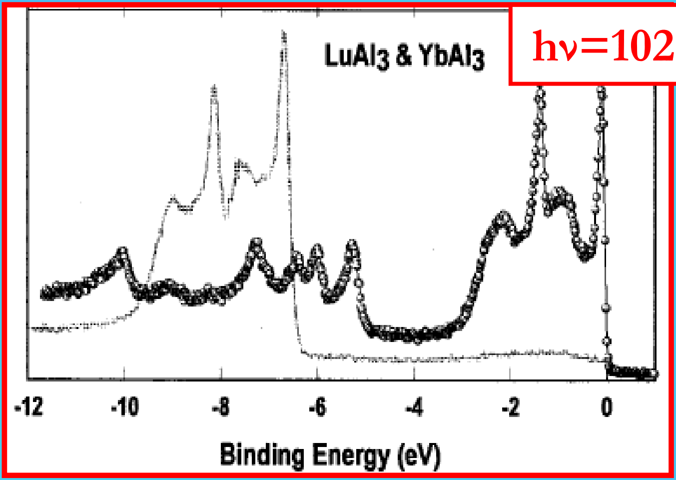
J.W.Allen *et al.* Adv. in Phys. **35**, 275 (1986)

probing the Kondo scale with photoemission



hν=102 eV

L.H.Tjeng *et al.* PRL **71**, 1419 (1993)



hν=102 eV

J.J.Joyce *et al.* PRB **54**, 17515 (1996)

$YbAl_3$

$T_K \approx 400K$

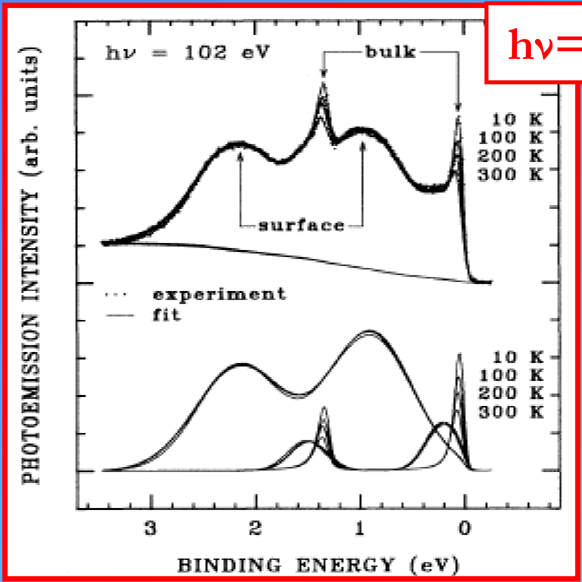
"nearly" heavy fermion

to complicate the issue:

surface contributions

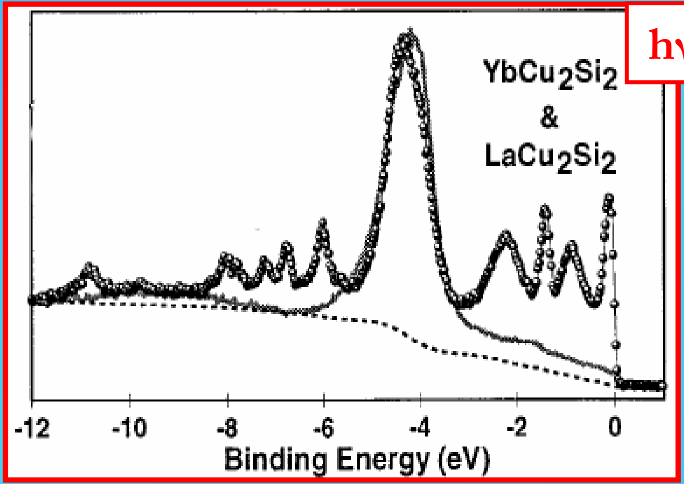
non-*f* contributions

probing the Kondo scale with photoemission



hν=102 eV

L.H.Tjeng *et al.* PRL **71**, 1419 (1993)



hν=120 eV

J.J.Joyce *et al.* PRB **54**, 17515 (1996)

$YbAl_3$

$T_K \approx 400K$

"nearly" heavy fermion

$YbCu_2Si_2$

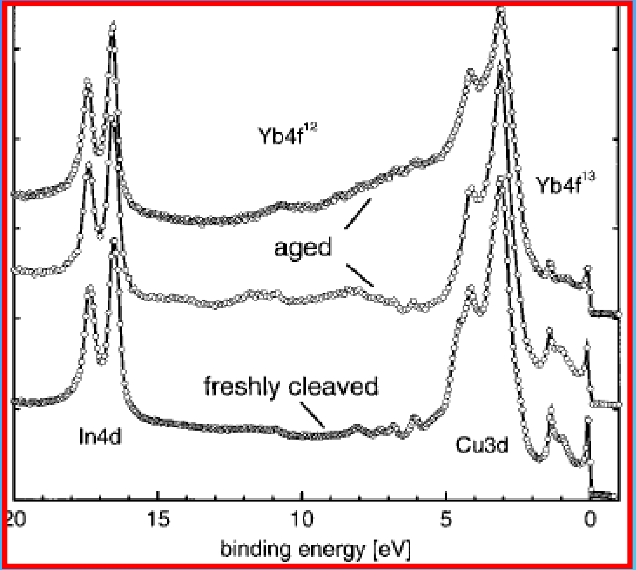
$T_K \approx$ 40-60K

to complicate the issue:

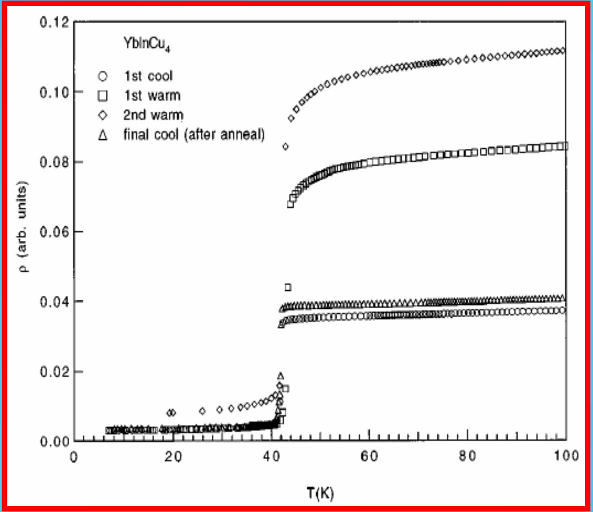
surface contributions

non-*f* contributions

probing the Kondo scale with photoemission



F.Reinert *et al.* PRB **58**, 12808 (1998)



J.L.Sarrao *et al.* PRB **54**, 12207 (1996)

YbInCu$_4$

$T_v = 42K$

first order transition

0.5% volume collapse at T>Tv

$T_K \approx 20K \quad T>T_v$

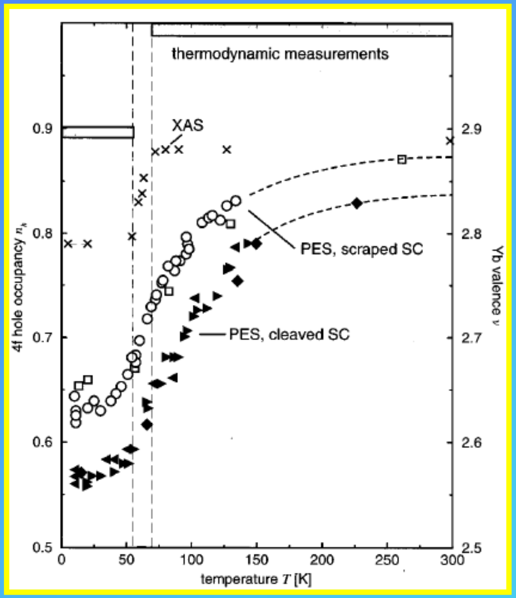
$T_K \approx 400K \quad T<T_v$

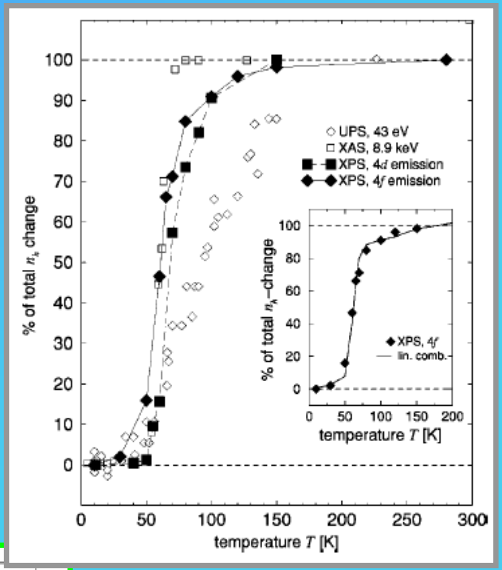
to complicate the issue:

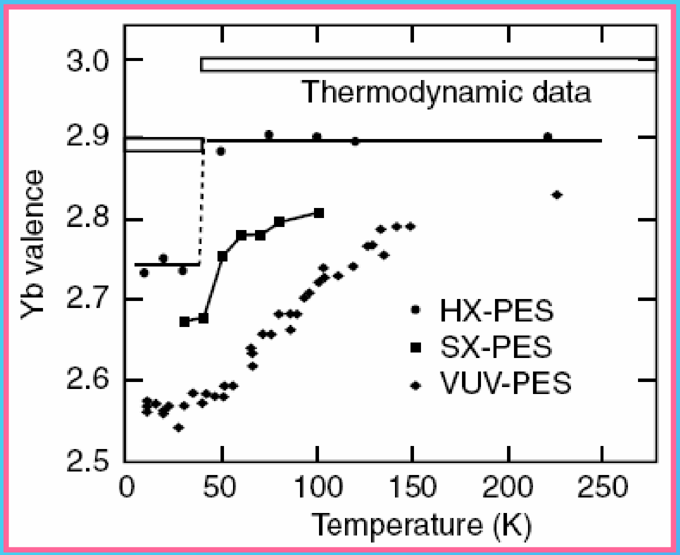
rapid oxidation

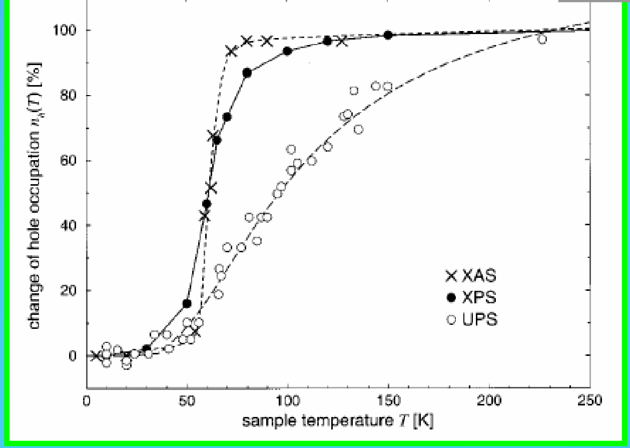
temperature cycling

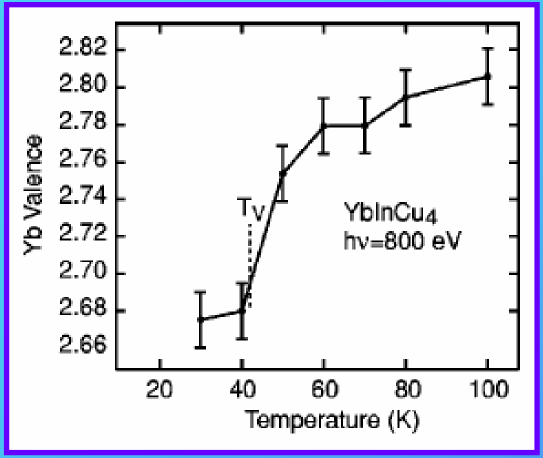
probing the Kondo scale with photoemission?!?

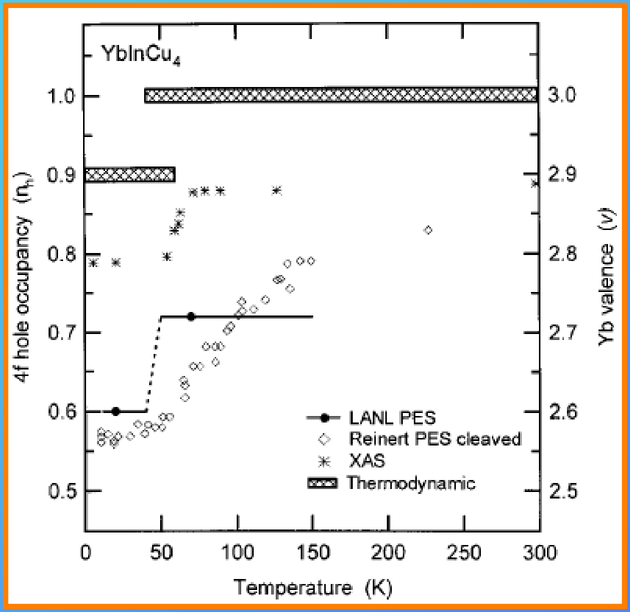




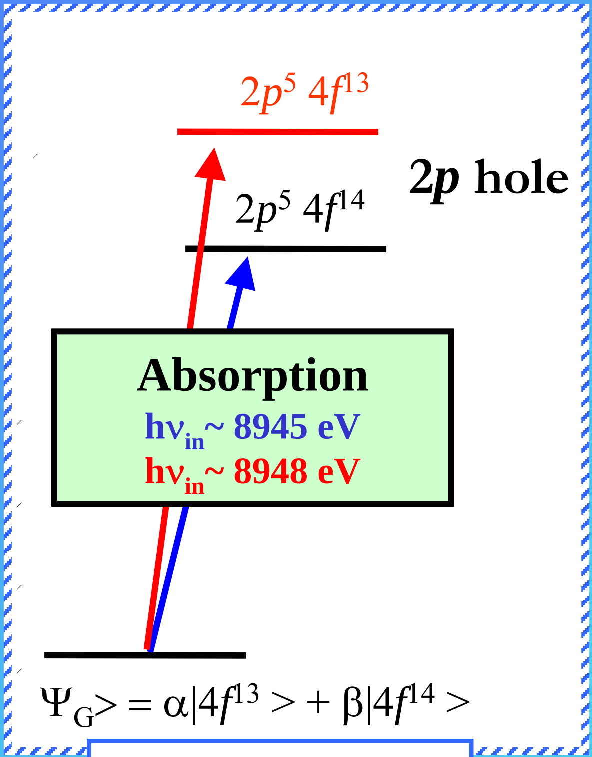








Why not trying something else? PFY-XAS



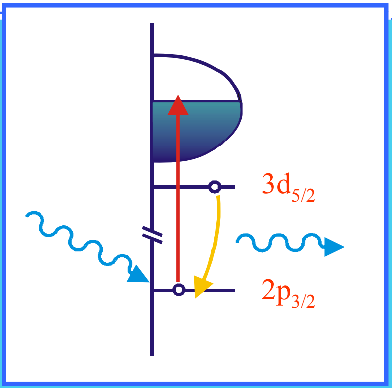
Absorption

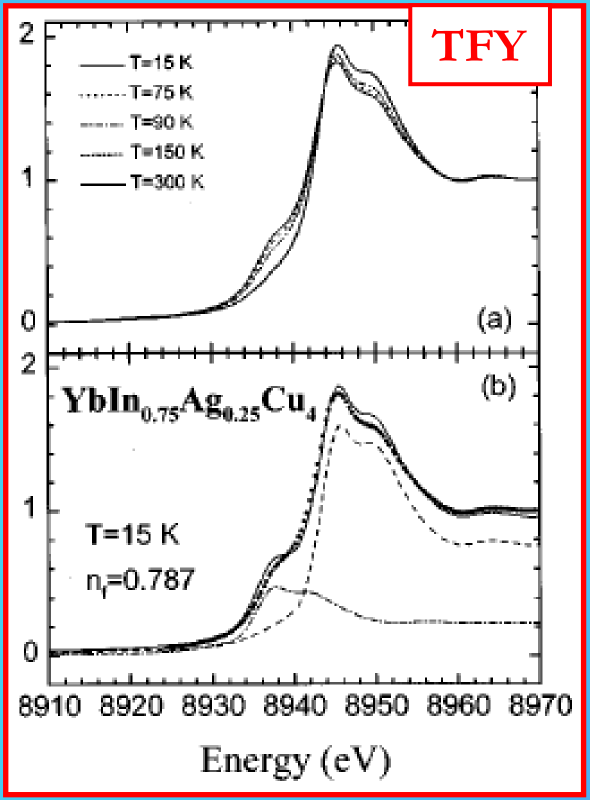
$h\nu_{in}$ ~ 8945 eV

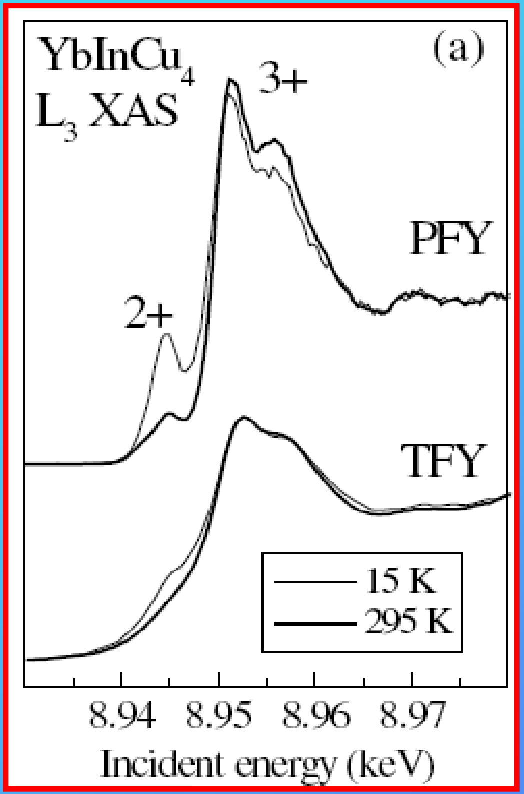
$h\nu_{in}$ ~ 8948 eV

$\Psi_G> = \alpha|4f^{13}> + \beta|4f^{14}>$

PFY: we record only the $2p^5 3d^{10} \rightarrow 2p^6 3d^9$ fluorescence





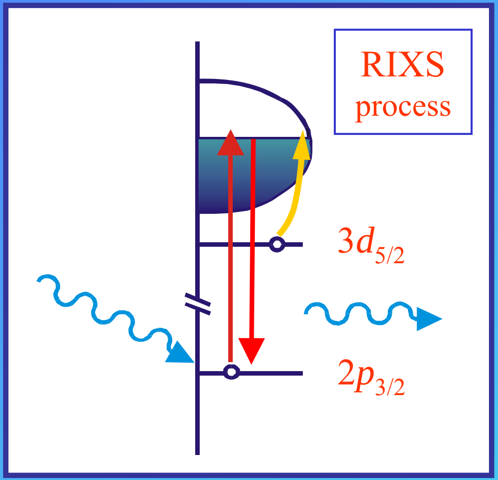


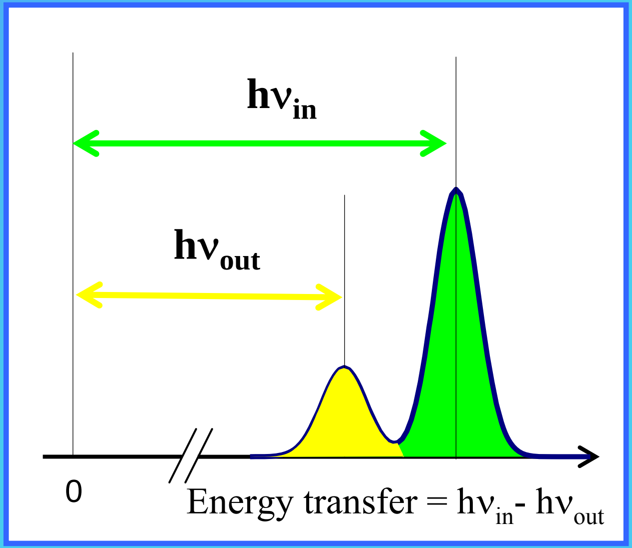
A.L.Cornelius *et al.* PRB **56**, 7993 (1997) C.Dallera *et al.* PRL **88**, 196402 (2002)

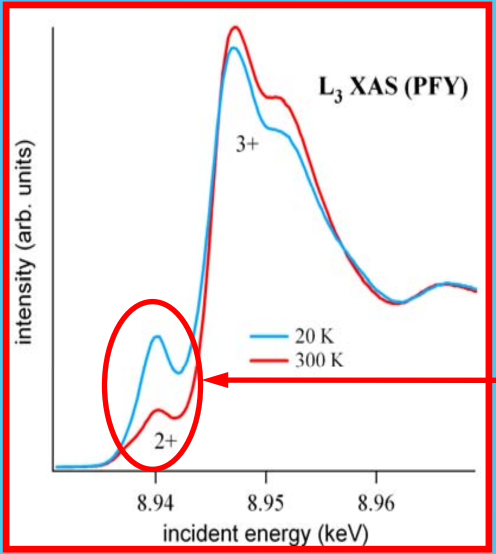
increased bulk sensitivity ☺

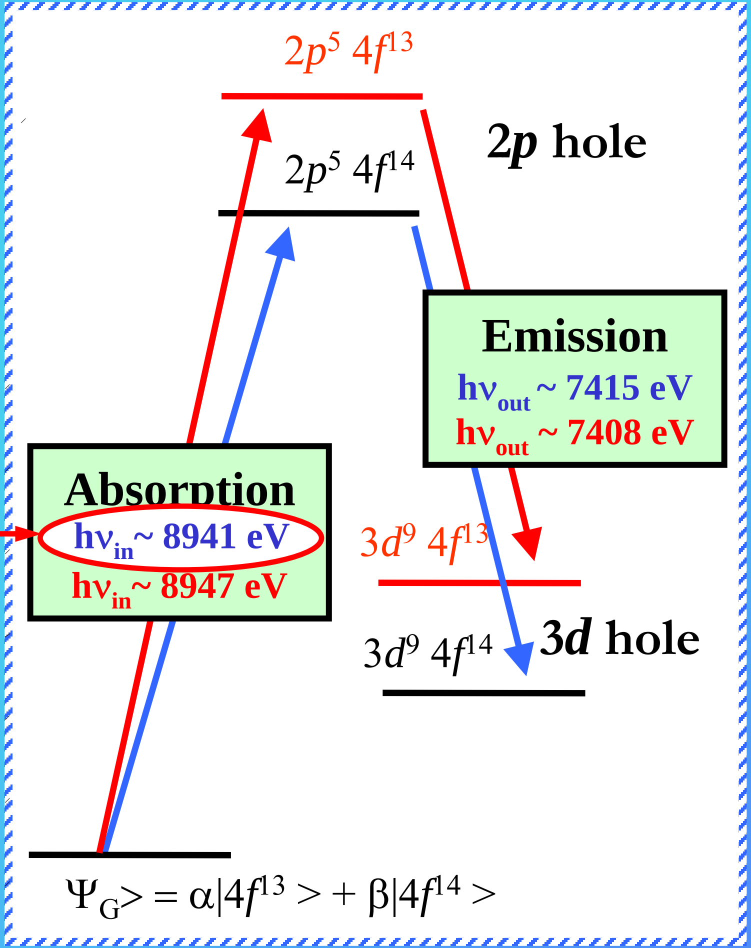
the analysis assumes two replicas of the same lineshape ☹

even better…RIXS



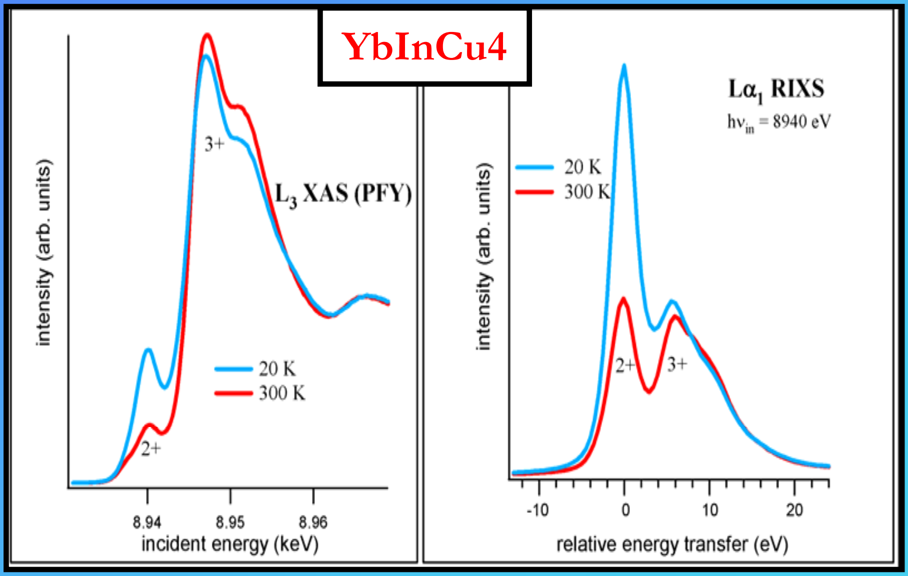


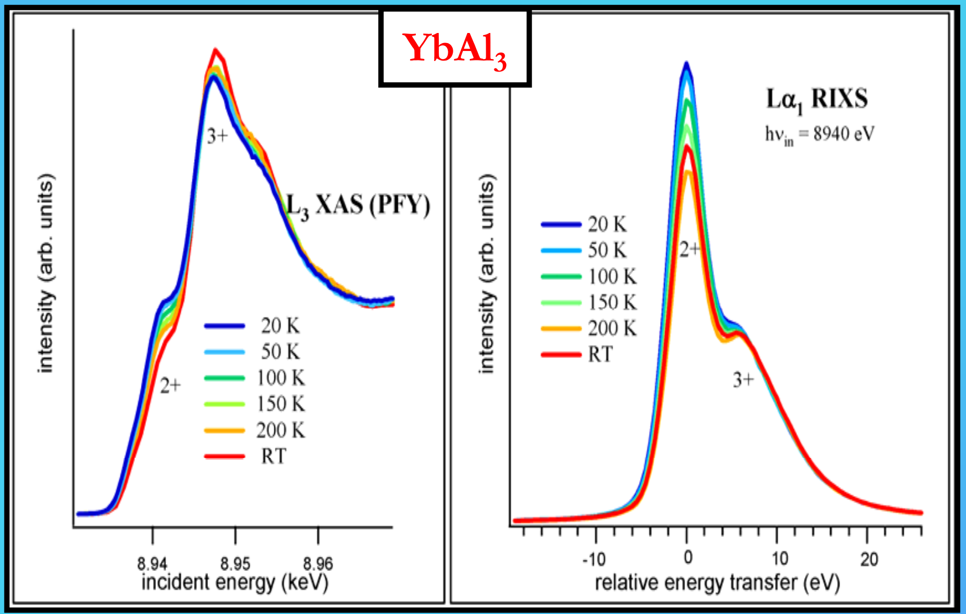


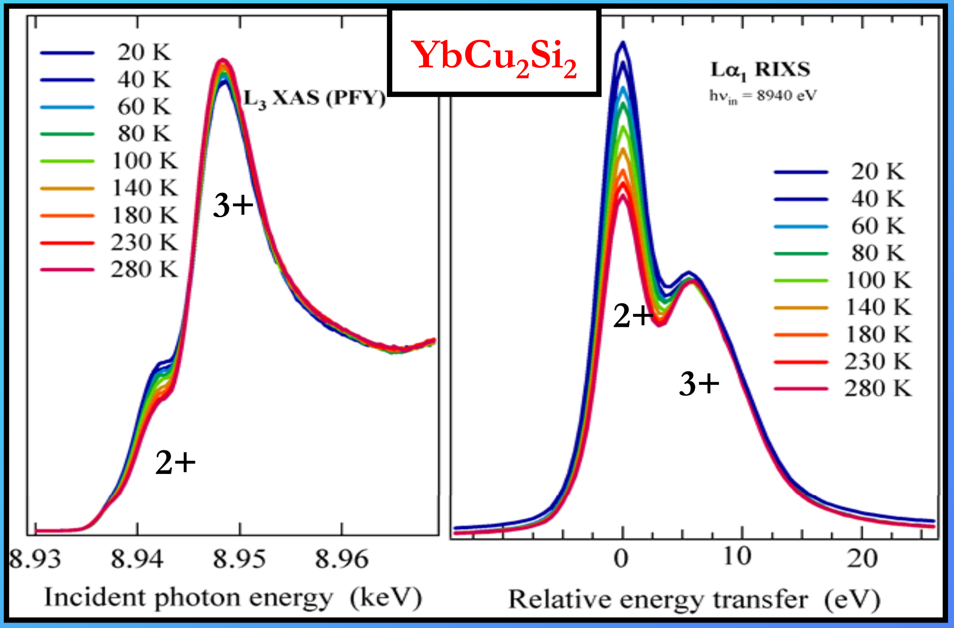


the weaker 2+ channel is resonantly enhanced

probing the Kondo scale with RIXS







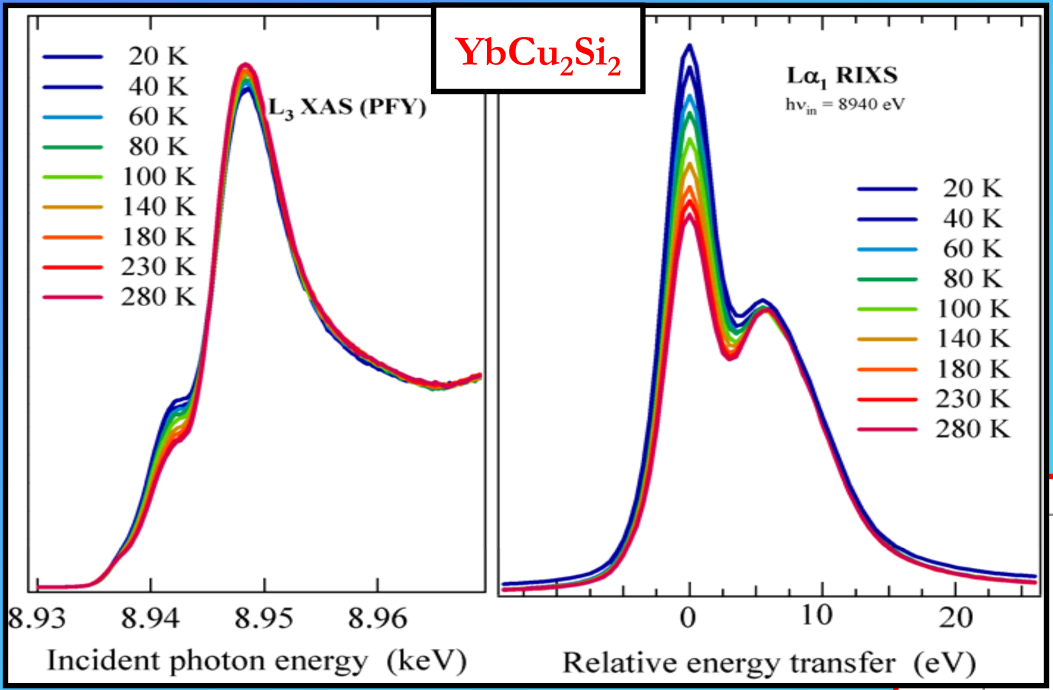
$$n_h = \frac{I_{3+}}{I_{3+}+I_{2+}} = \frac{I_{3+}}{I}$$

$$\rightarrow \quad \frac{\left(\frac{dI_{3+}}{I_{3+}}\right)}{dn_h} = \frac{I}{I_{3+}} \qquad \frac{\left(\frac{dI_{2+}}{I_{2+}}\right)}{dn_h} = -\frac{I}{I_{3+}}\left(\frac{I}{I_{2+}}\right)$$

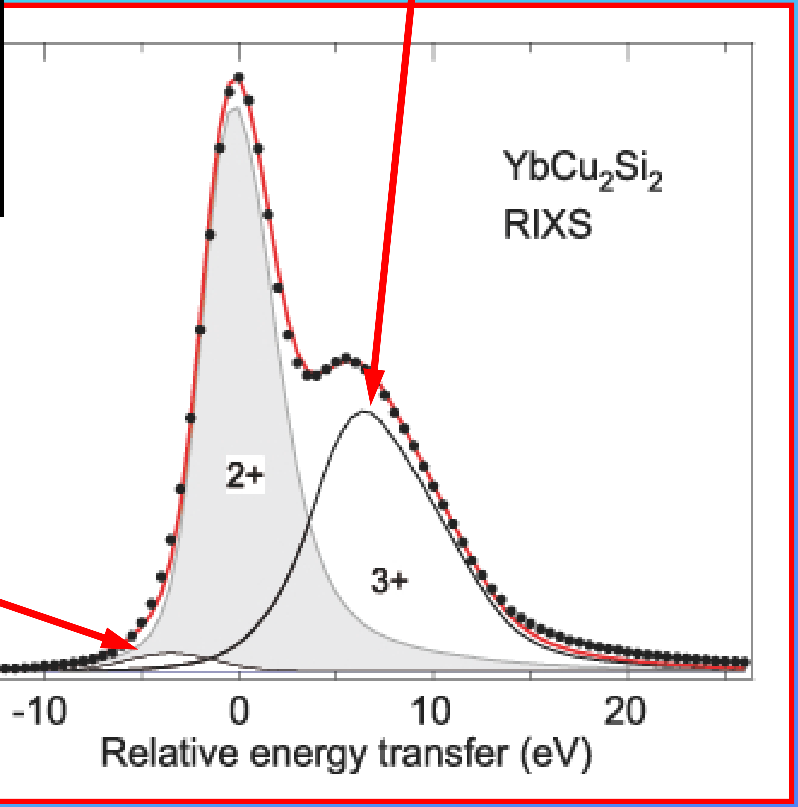
the minority component is the more affected by valence changes

L.Moreschini *et al.* PRB **75**, 35113 (2007)

probing the Kondo scale with RIXS



3+ component evaluated far from the resonance

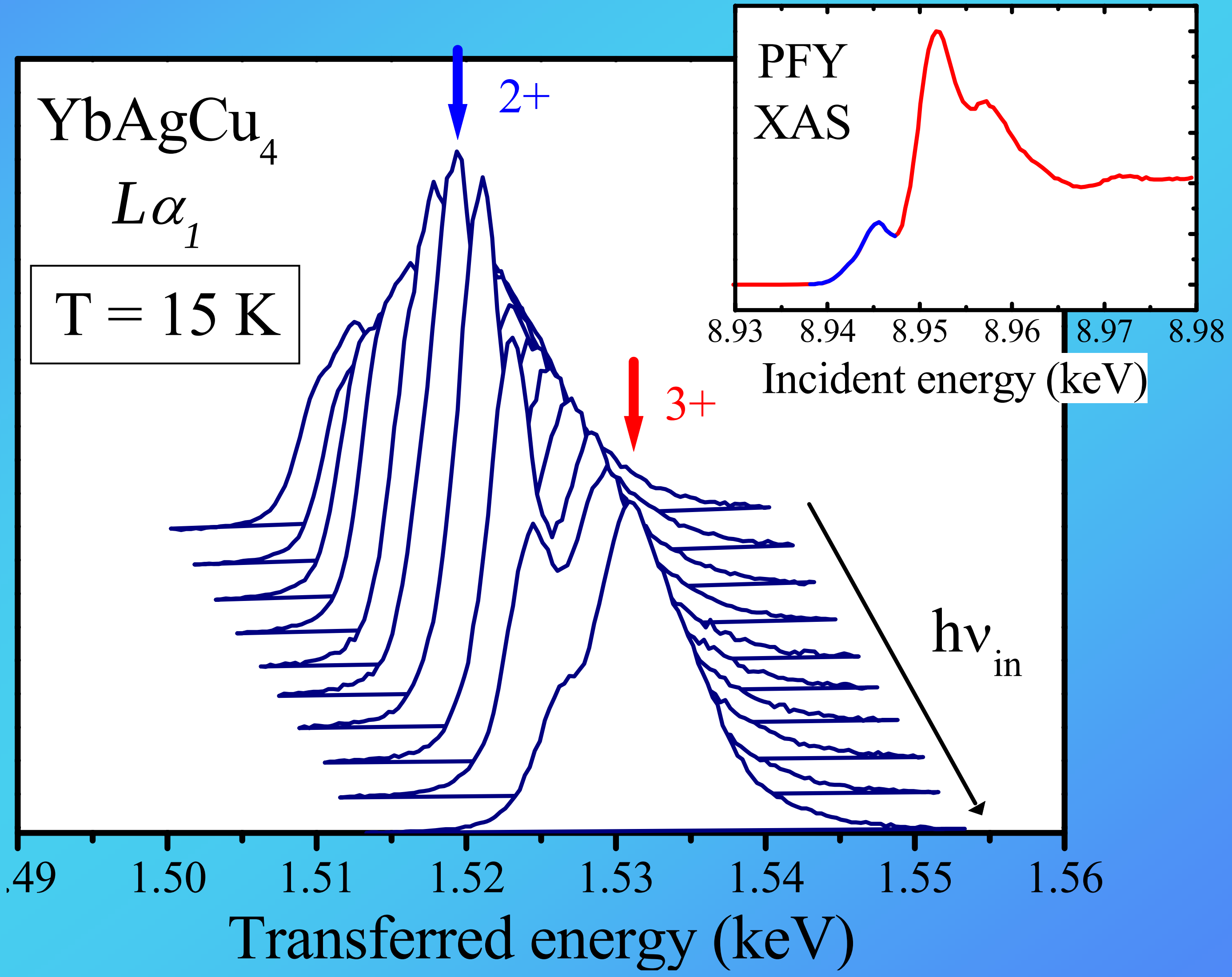


quadrupole
$2p^6\,4f^{13} \rightarrow 2p^5\,4f^{14}$
transition

L.Moreschini *et al.* PRB **75**, 35113 (2007)

RIXS on $YbAgCu_4$

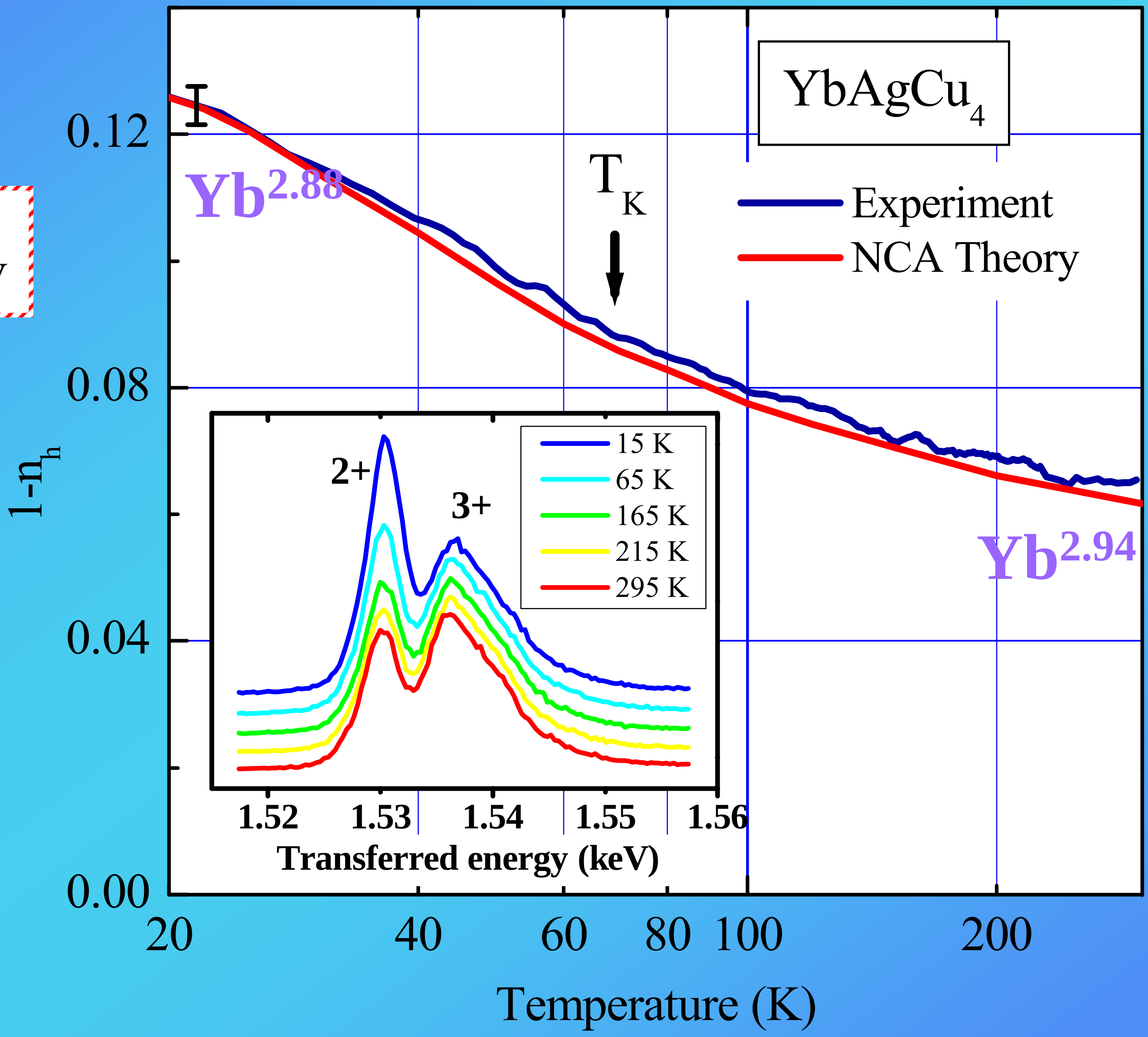
$T_k = 70$ K
$k_B T_K \approx 7$ meV



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

RIXS on $YbAgCu_4$

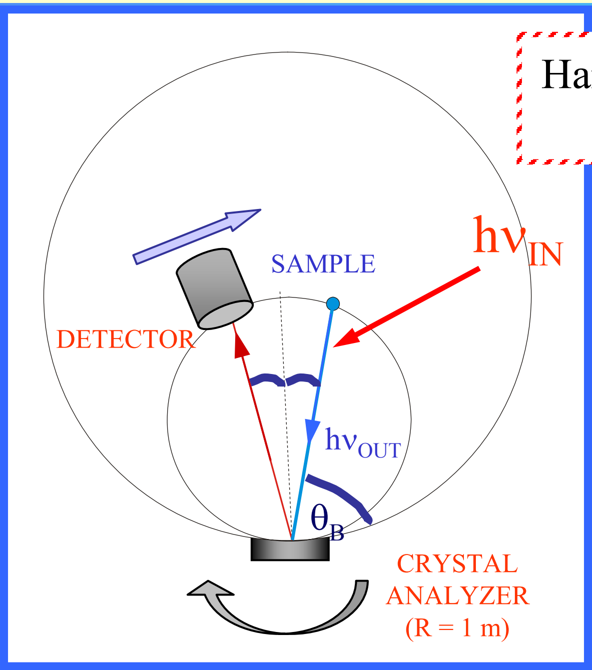
$T_k = 70$ K
$k_B T_K \approx 7$ meV



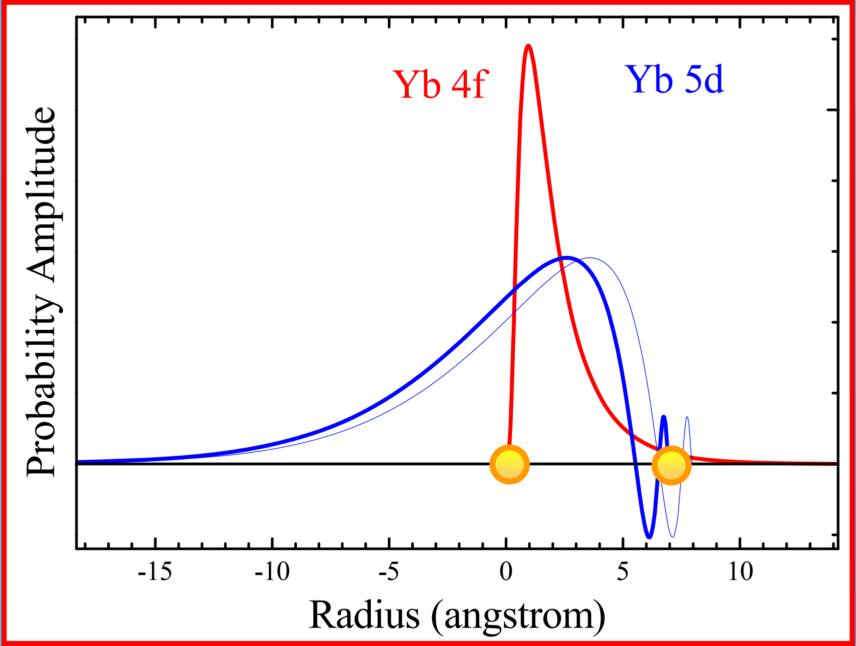
C. Dallera et al. PRL **88**, 196403 (2002)

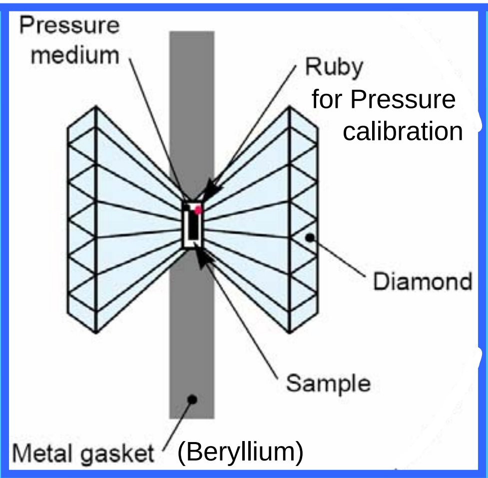
RIXS measurements under pressure

Si spherical crystal analyzer (Rowland geometry)
ESRF ID26



Hard x-ray range
(> 2 keV)





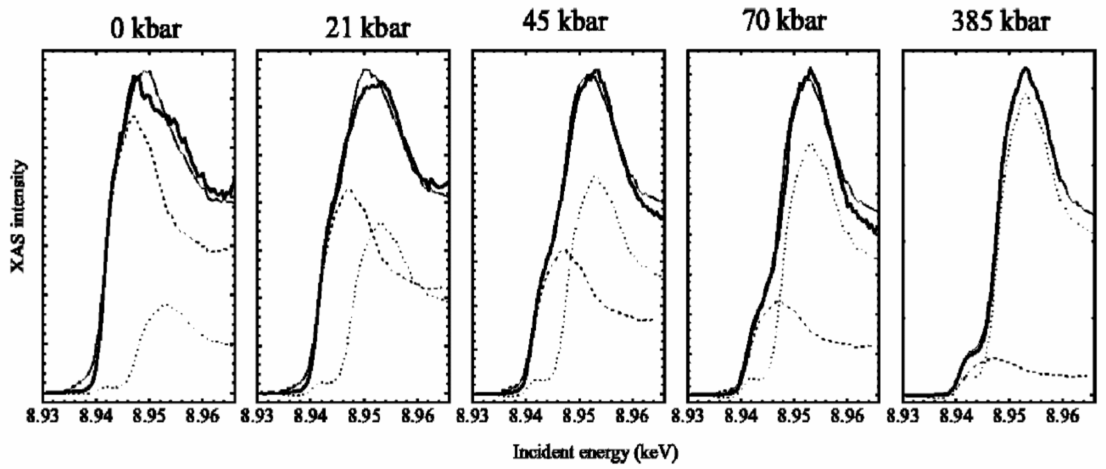
the trivalent Yb ion is smaller

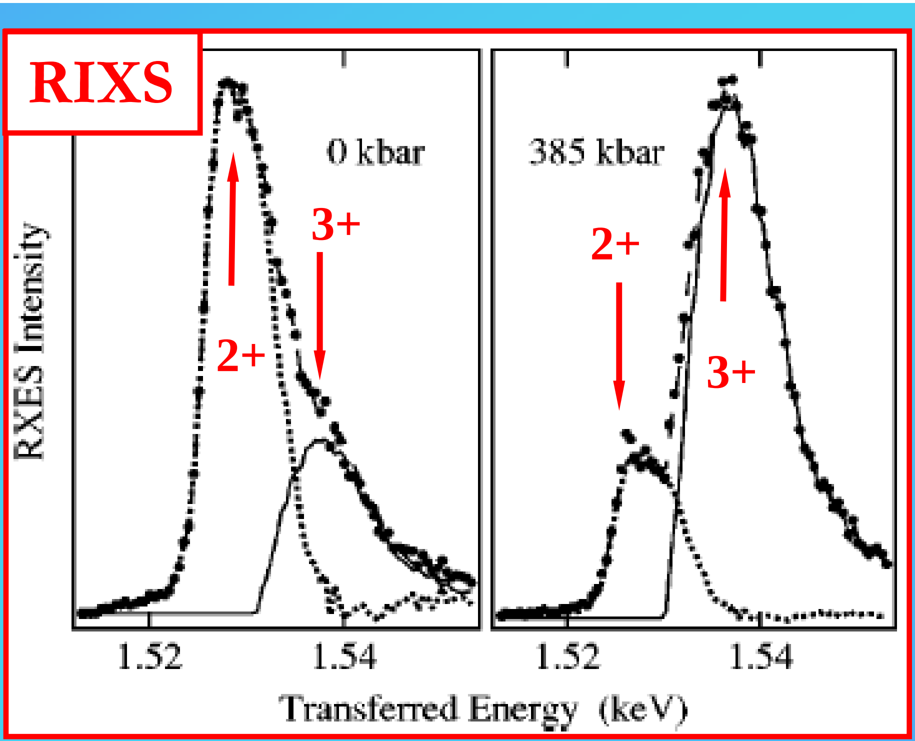
→ favoured at high pressure

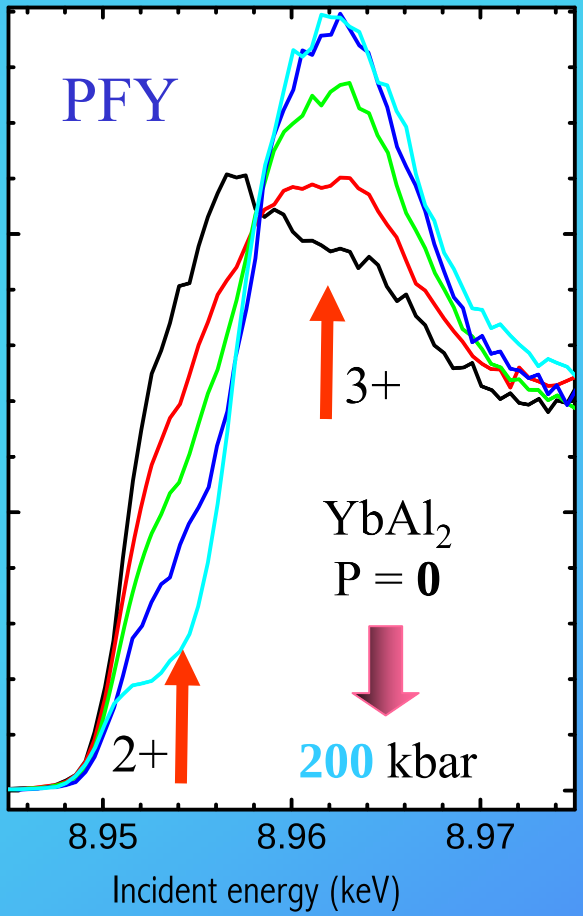
compression: bigger overlap

→ the *4f* electrons spill into the *5d* orbitals → stronger bonding

RIXS on $YbAl_2$ under pressure





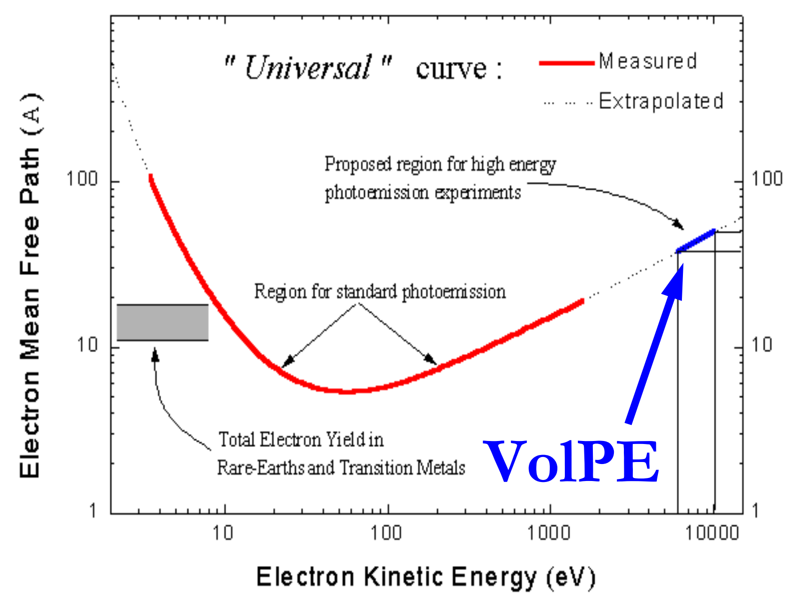


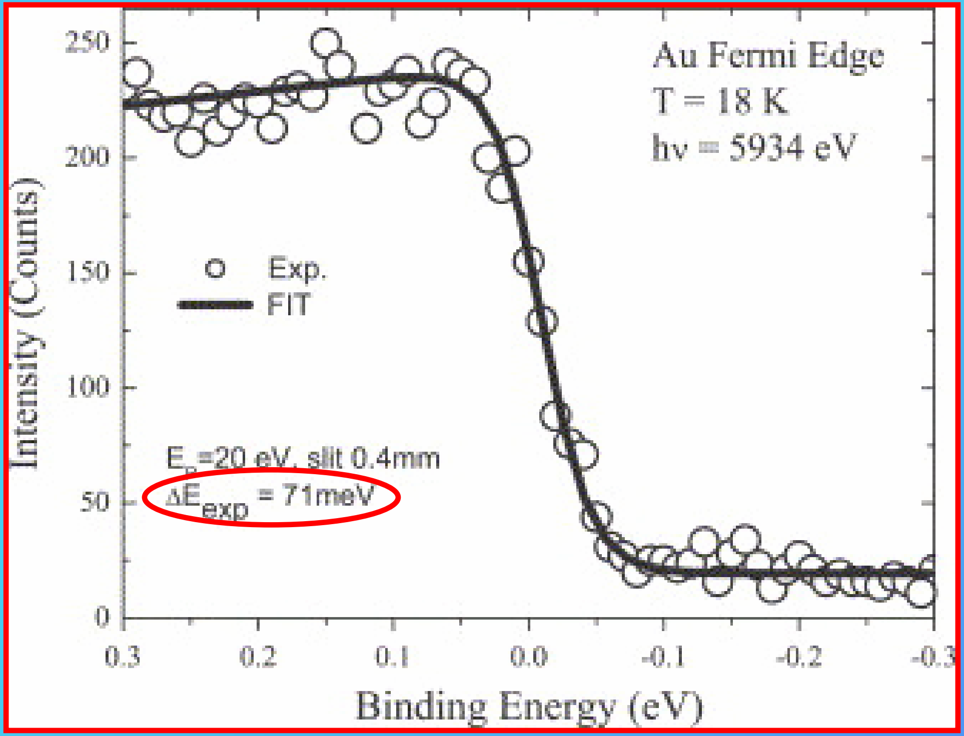
valence

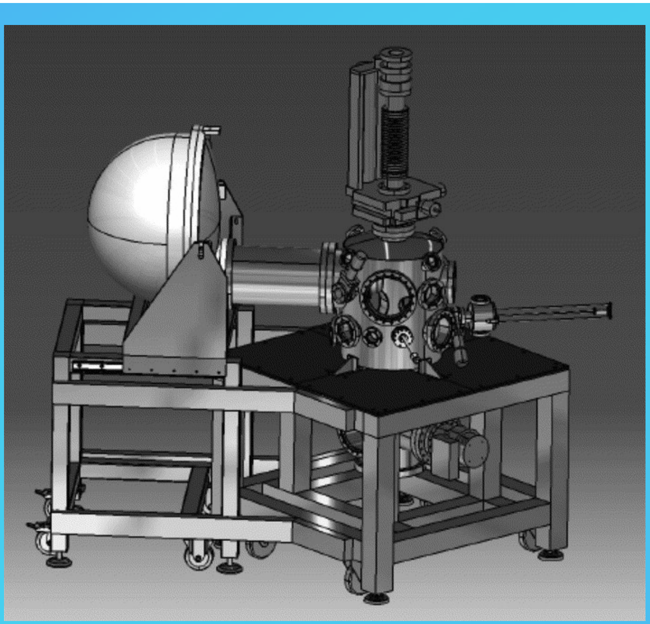
$$v = 2 + n_h = 2 + \frac{I_{3+}}{I_{3+} + I_{2+}}$$

C. Dallera *et al.* PRB **68**, 245114 (2003)

HAXPES - bulk sensitive photoemission

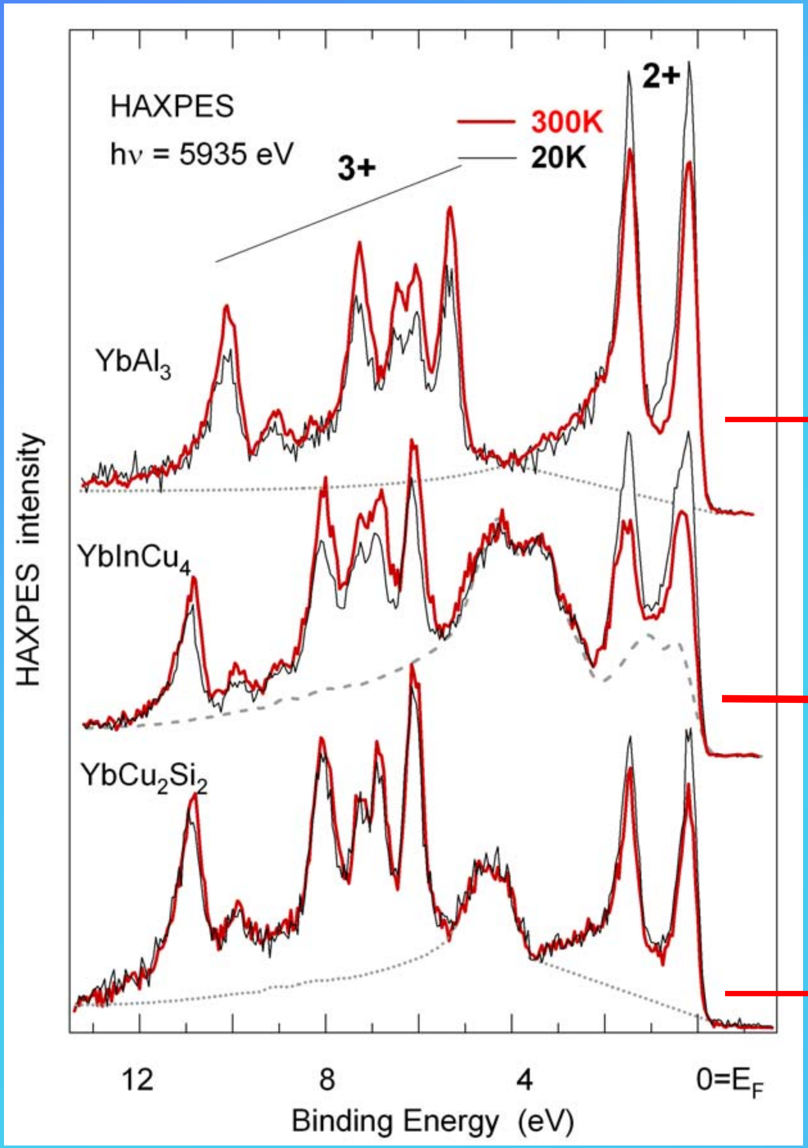






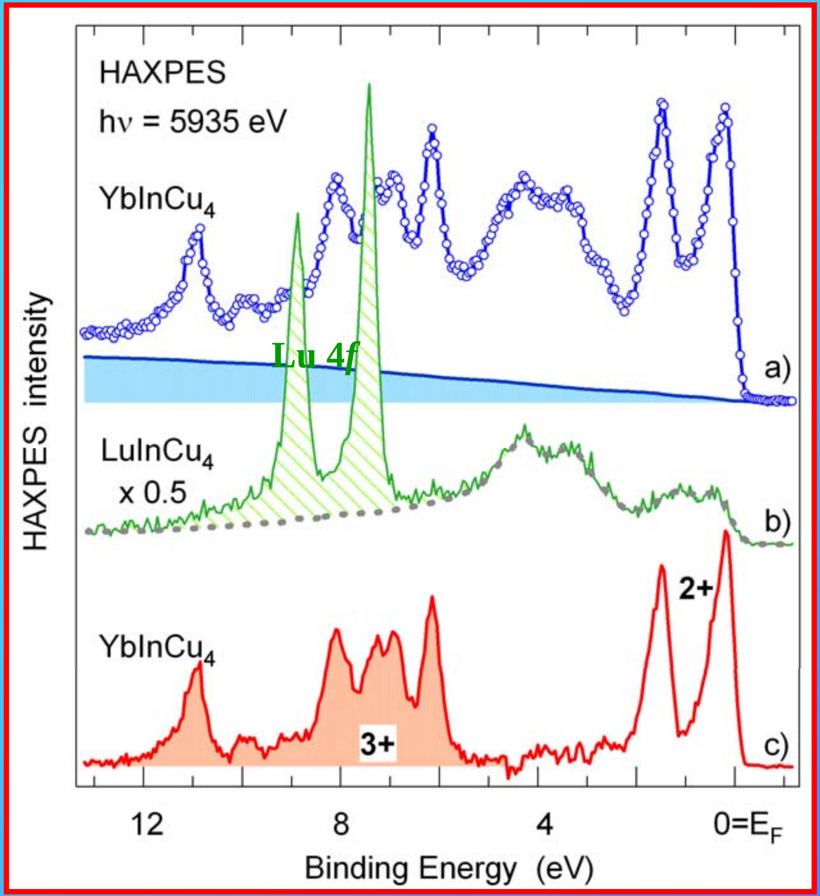
G. Panaccione *et al.* Nucl. Instr. and Meth. **547**, 56 (2005)

valence band HAXPES



valence

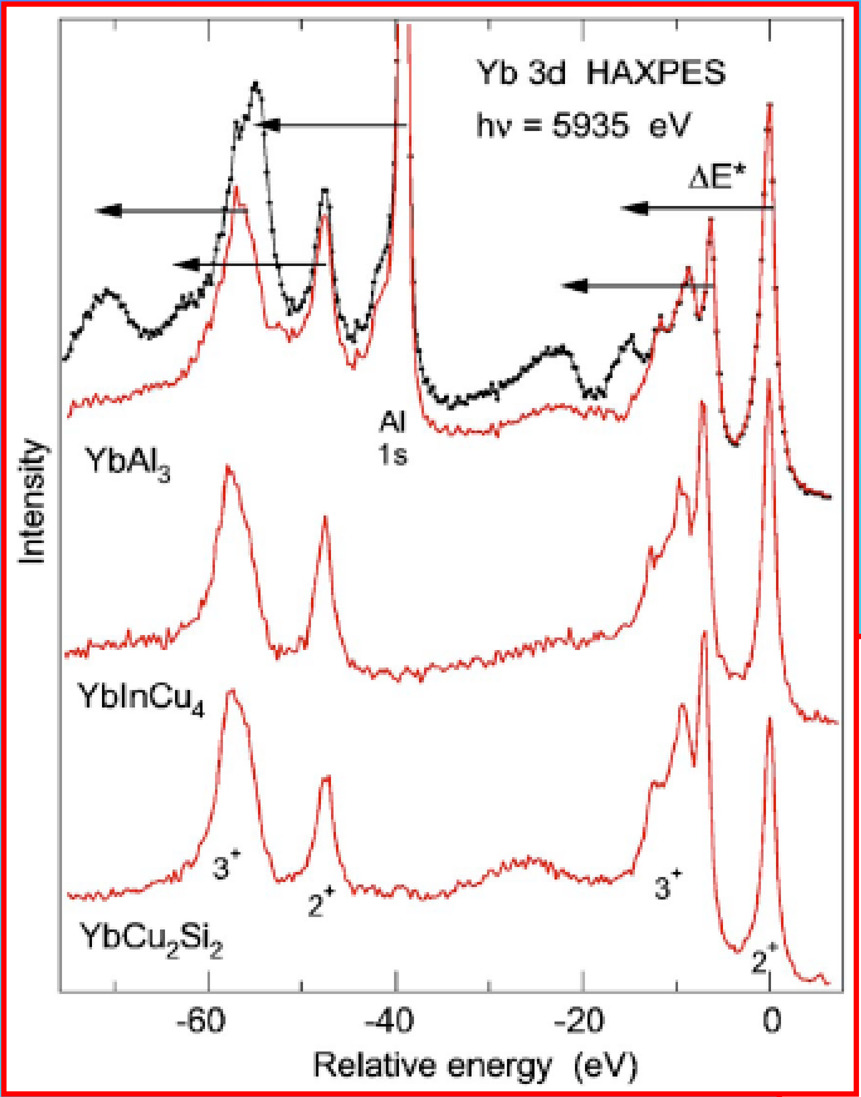
$$v = 2 + n_h = 2 + \frac{14 I_{3+}}{14 I_{3+} + 13 I_{2+}}$$

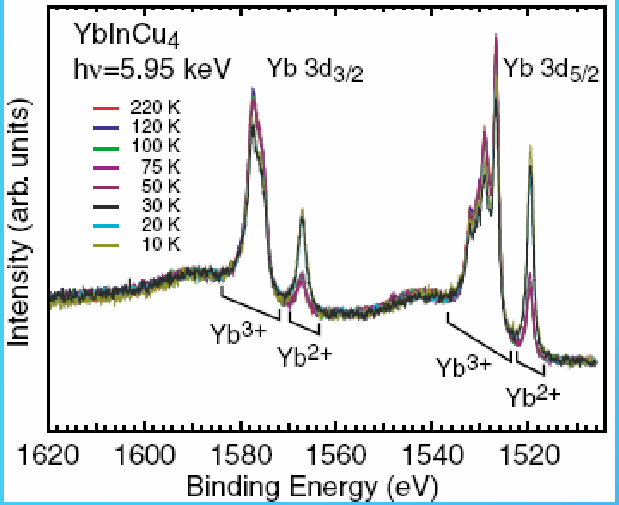


extrapolated

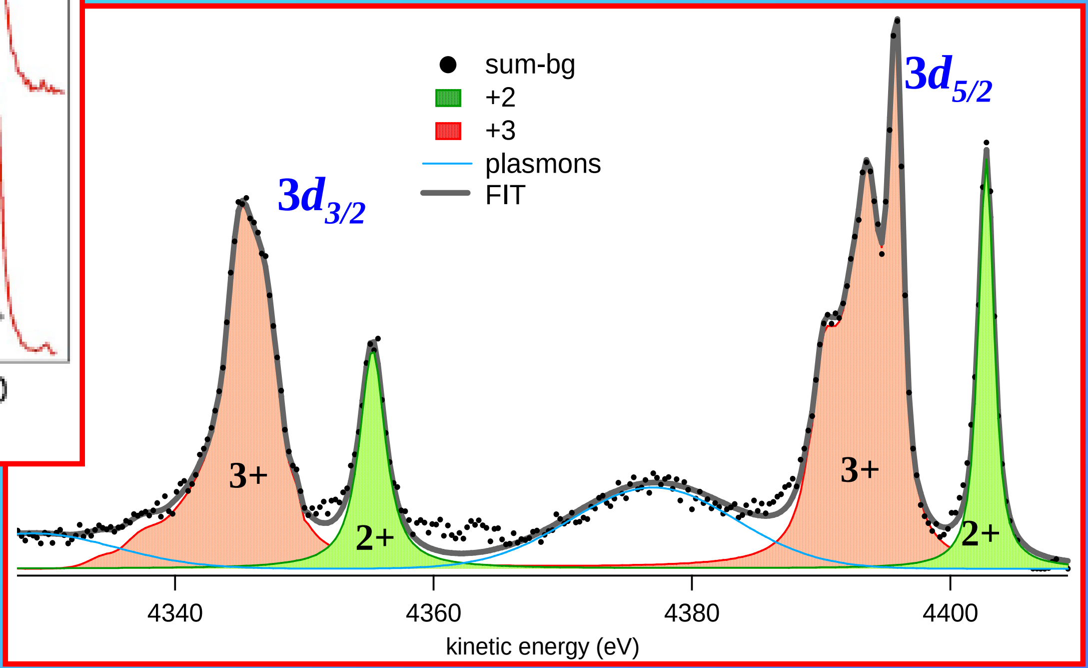
L.Moreschini *et al.* PRB **75**, 35113 (2007)

core levels HAXPES - another way around



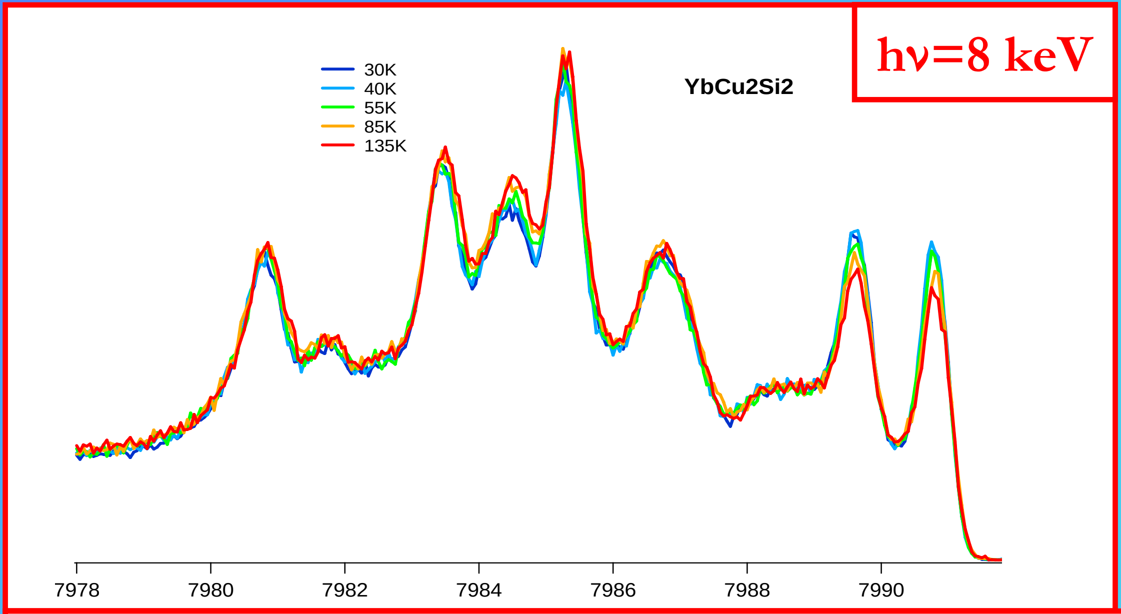


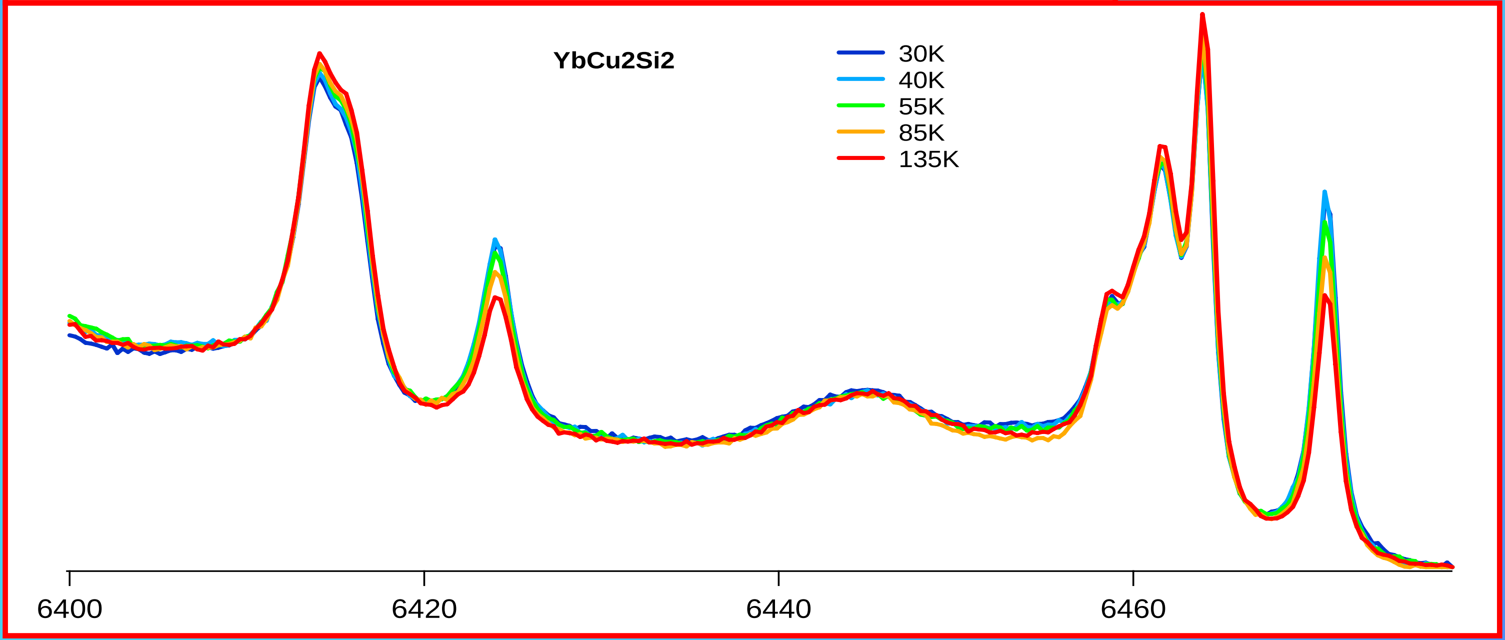
H. Sato *et al.* PRL **93**, 246404 (2004)



$$v = 2 + n_h = 2 + \frac{I_{3+}}{I_{3+} + I_{2+}}$$

recent HAXPES - looking for high count rate

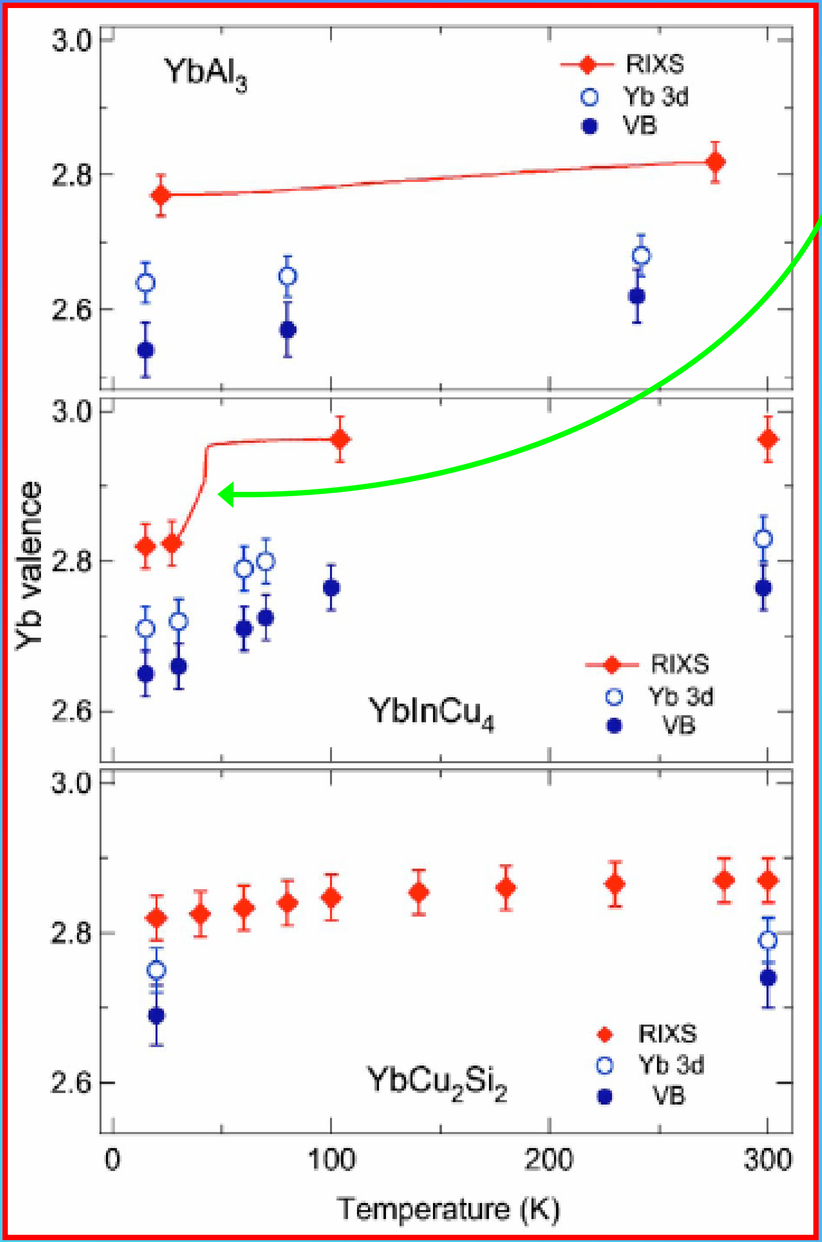




intensity ↑
resolution ↓

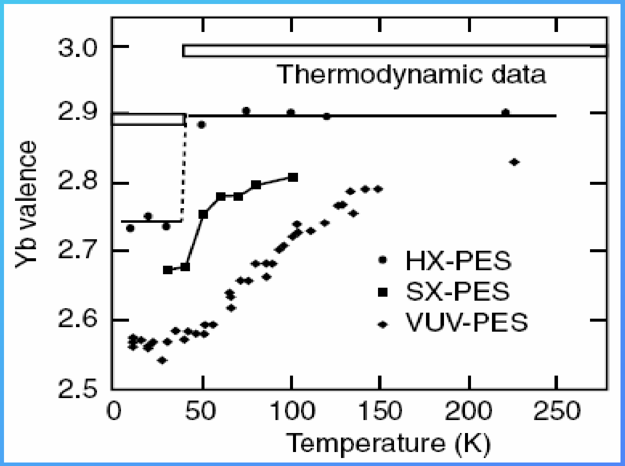
L.Moreschini, T. Durakiewicz (2006)

let's compare…



L.Moreschini *et al.* PRB **75**, 35113 (2007)

- valence jump in YbInCu$_4$ but the valence does not reach abruptly the low T value. disorder?
- HAXPES data too sparse to see the first order transition of YbInCu$_4$. must increase intensity
- relative changes very similar for all techniques
- HAXPES valence from the 3*d* always higher than from the 4*f*. wrong background or non-4*f* subtraction?
- RIXS valence always higher than with HAXPES. disorder in the scraped layer?
- smooth valence evolution in YbAl$_3$ and YbCu$_2$Si$_2$
- room T valence for YbCu$_2$Si$_2$ lower than expected. crystal field effect?

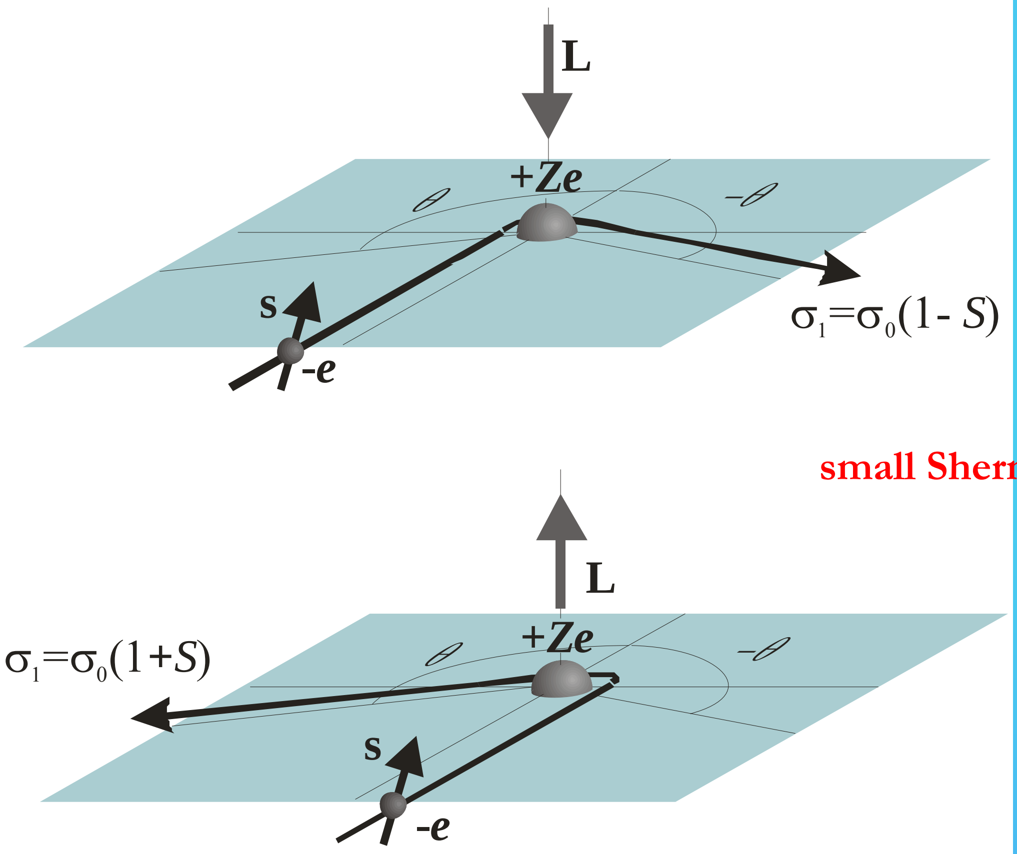


H. Sato *et al.* PRL **93**, 246404 (2004)

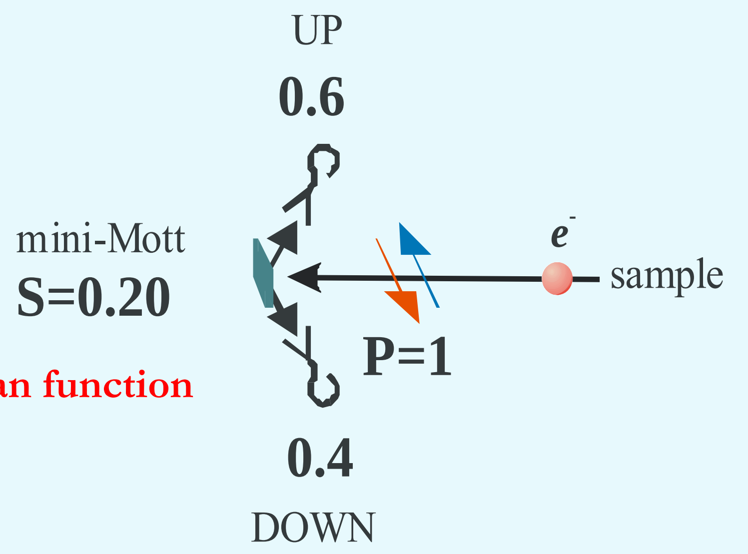
SP-PES with a mini-Mott

backscattering of electrons from a heavy nucleus target

$$P=\frac{I^{\uparrow}-I^{\downarrow}}{I^{\uparrow}+I^{\downarrow}}$$



small Sherman function



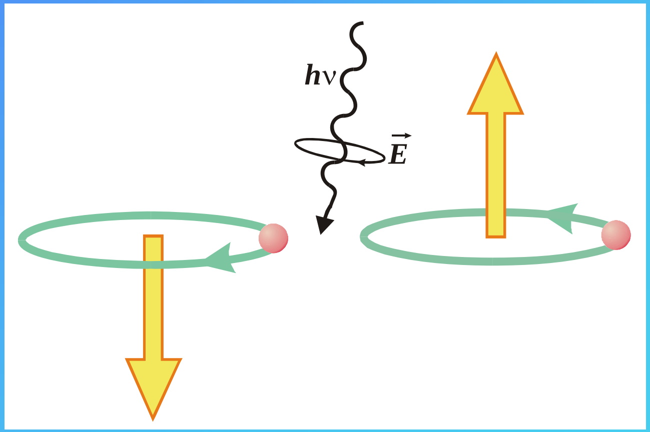
mini-Mott

S=0.20

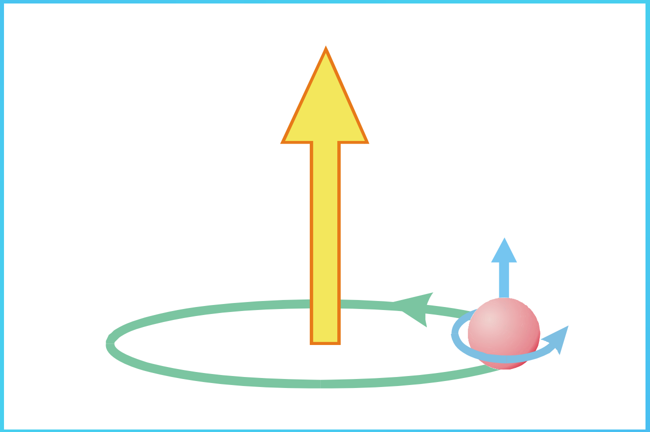
$$\frac{\mathrm{UP-DN}}{\mathrm{UP+DN}}=\frac{0.6-0.4}{0.6+0.4}=PS=0.2$$

J.Kessler, *Polarized electrons* (1976)

SP-PES with circularly polarised light



coupling between photon and photoelectron angular moments (***dipole selection rules***)

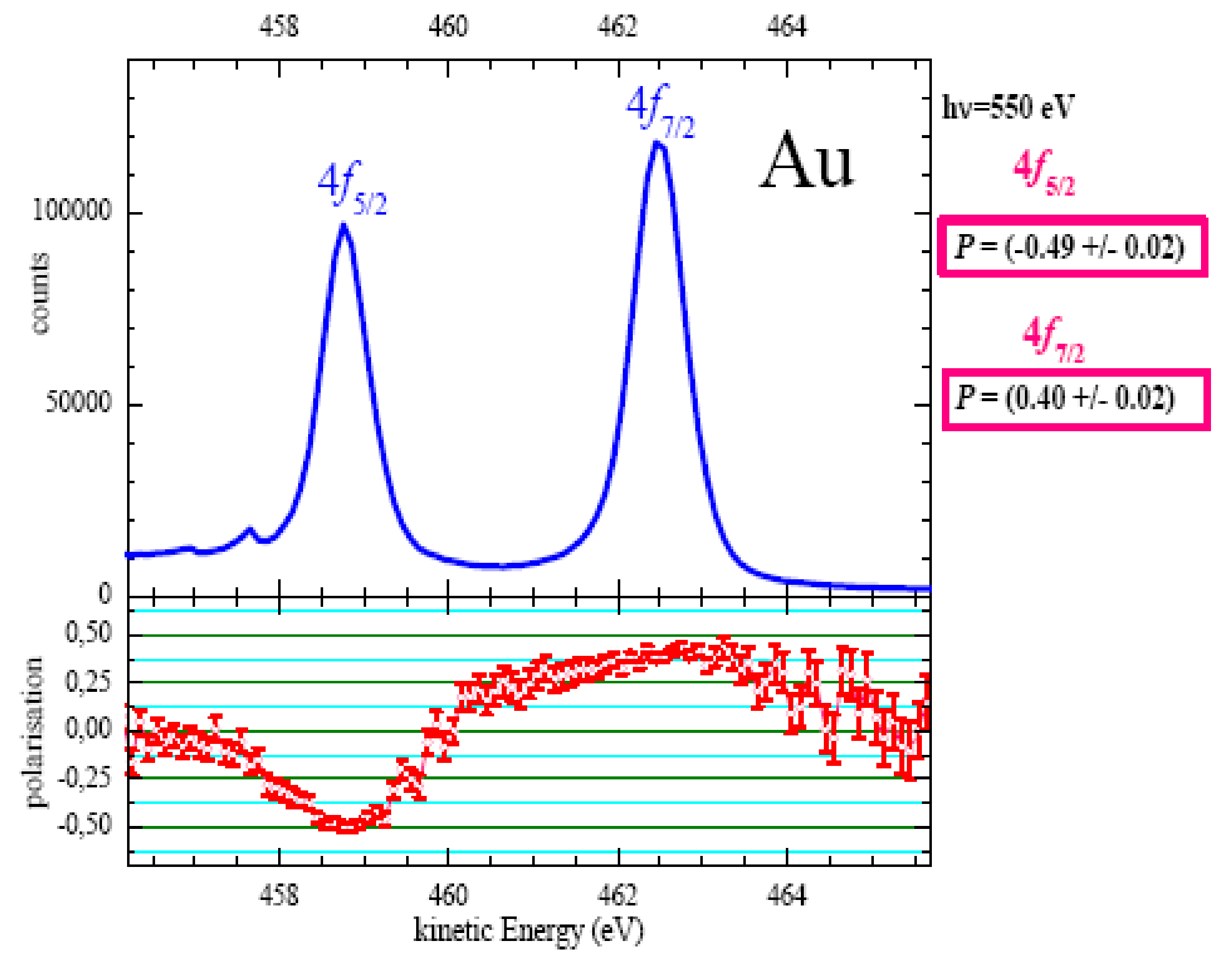


coupling between photoelectron spin and orbital moment (***spin-orbit interaction***)

→ **the photoemitted electrons are spin polarised also for non ferromagnetic samples**

Fano, Phys. Rev. **178**, 131 (1969)

an easy spectrum: the Au 4*f* levels



calculated

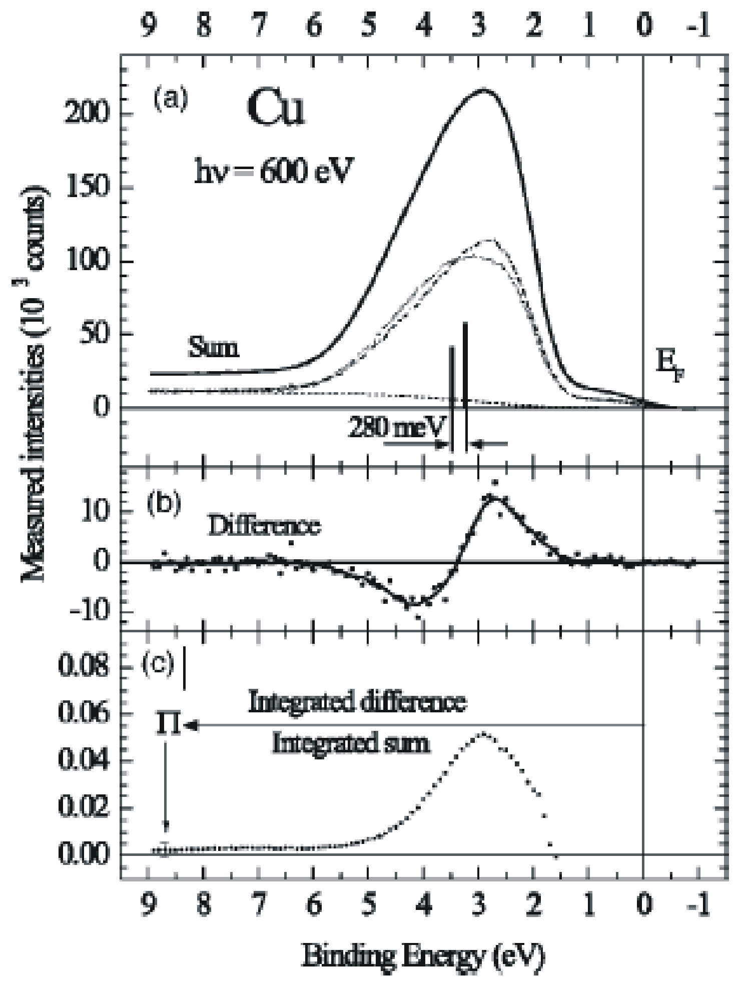
polarization of $4f_{5/2}$ peak:

P = -1/2

polarization of $4f_{7/2}$ peak:

P = 3/8

a not so easy spectrum: the Cu 3*d* states



- band-like system: the spin-orbit coupling is the only interaction

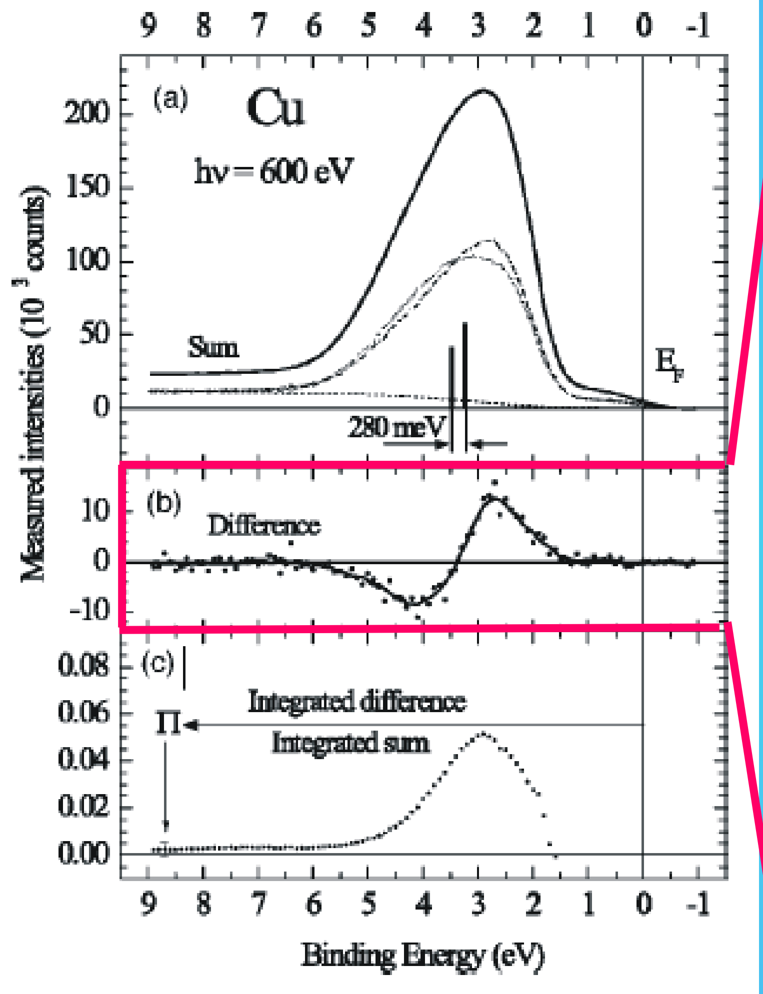
from the shape of the spectrum we can get an estimate of the 3*d* band spin-orbit splitting **($\Delta E_{SO} \approx$ 280 meV)**

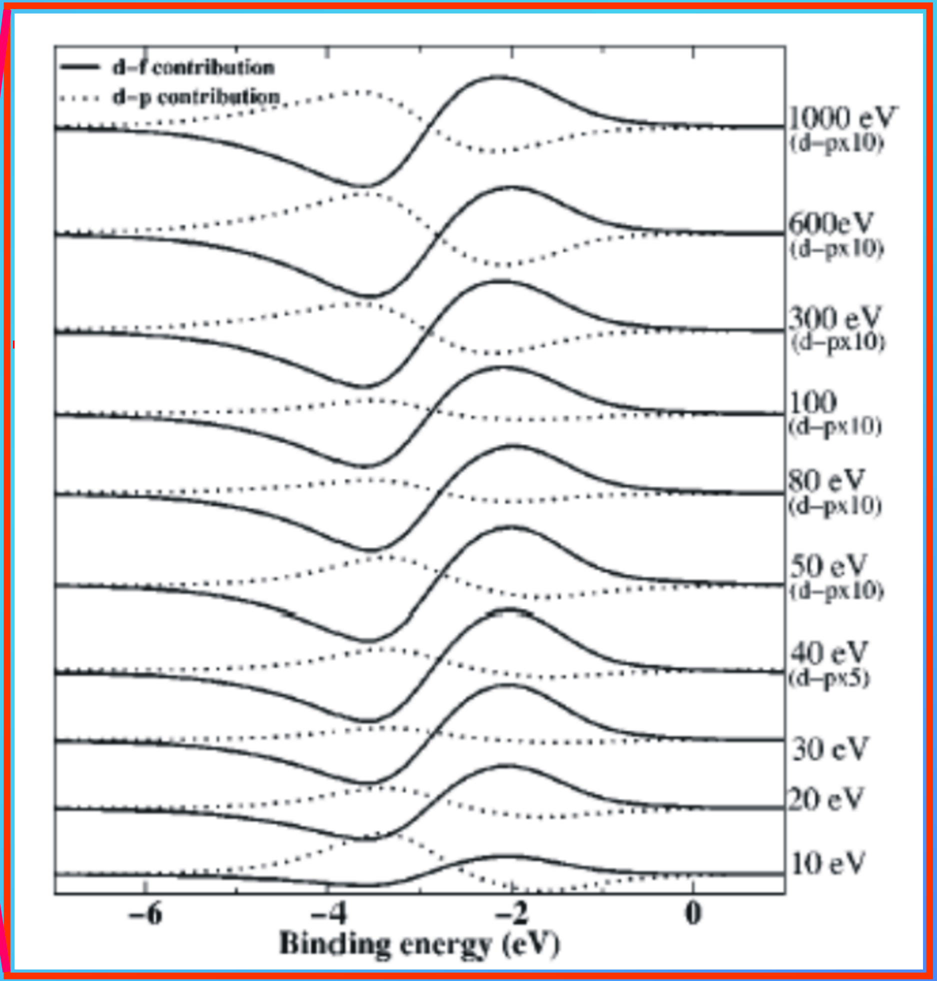
- the 3*d* shell is complete

The integral of the spectrum gives a null value

G.Ghiringhelli *et al.*, Phys. Rev. B **66**, 75101 (2002)

a not so easy spectrum: the Cu 3*d* states

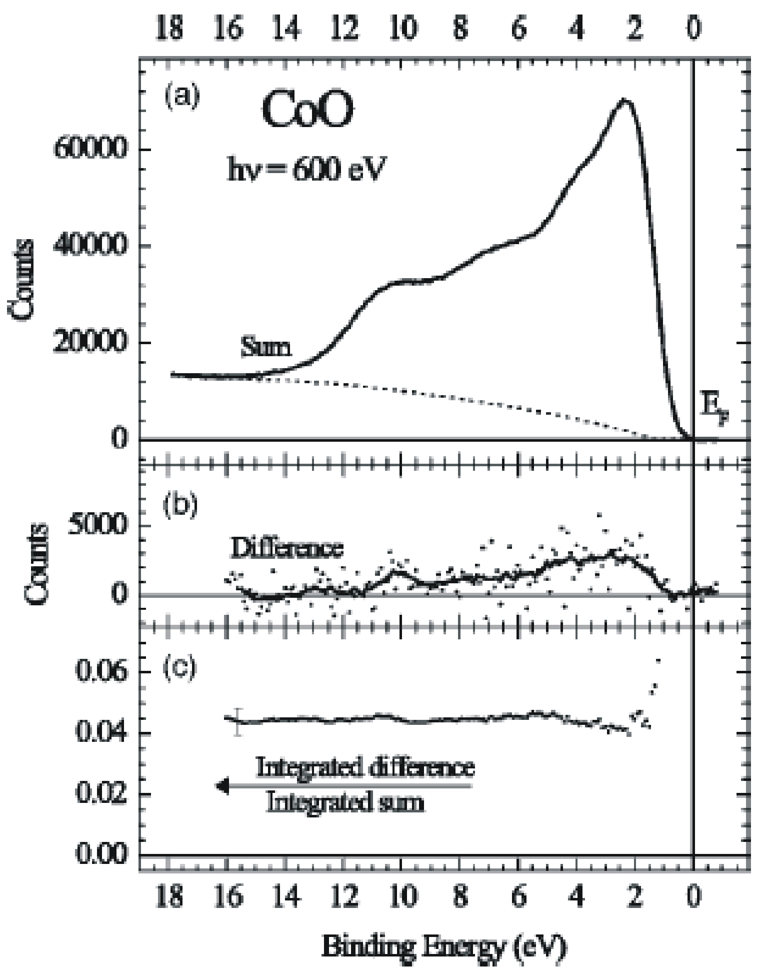




Minar *et al.*, Phys. Rev. B. **63**, 144421 (2001)

G.Ghiringhelli *et al.*, Phys. Rev. B **66**, 75101 (2002)

3*d* correlations: CoO



- strongly correlated system: Coulomb interaction is stronger than spin-orbit coupling

→ there is no evidence of spin-orbit splitting of the 3*d* states

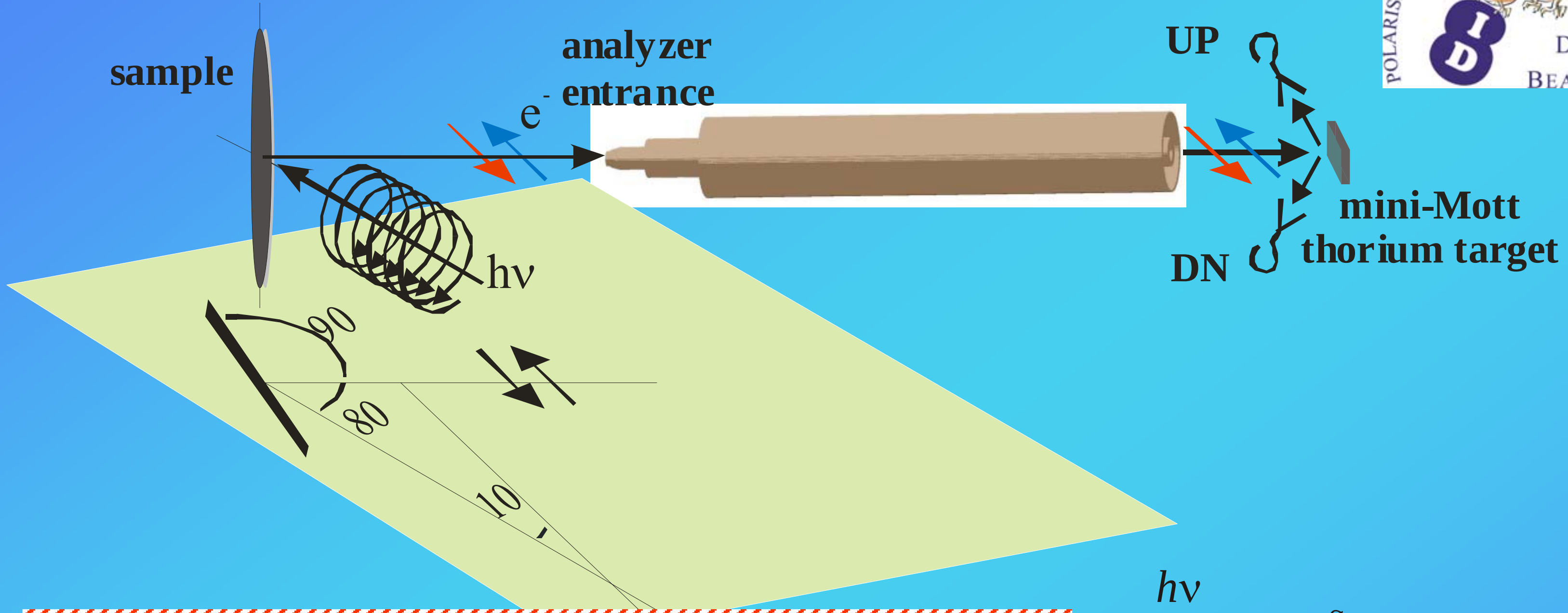
- from the integral of the spectrum we can find out the value of the spin-orbit coupling in 3*d* states of Co in CoO

→ $\langle L_z S_{z'} \rangle \approx (-0.33 \pm 0.04)\hbar^2$

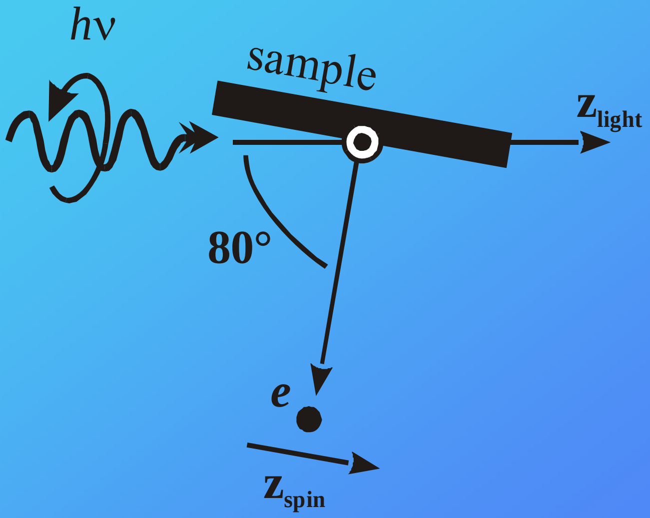
- by a cluster model calculation it is possible to infer the value of the orbital moment at 0 K: $\langle L_z \rangle \approx 1.36\mu_B$

G.Ghiringhelli *et al.*, Phys. Rev. B **66**, 75101 (2002)

a new TOF-Mott analyser



optimized for the 16-bunch mode of the ESRF (one bunch each 176 ns)



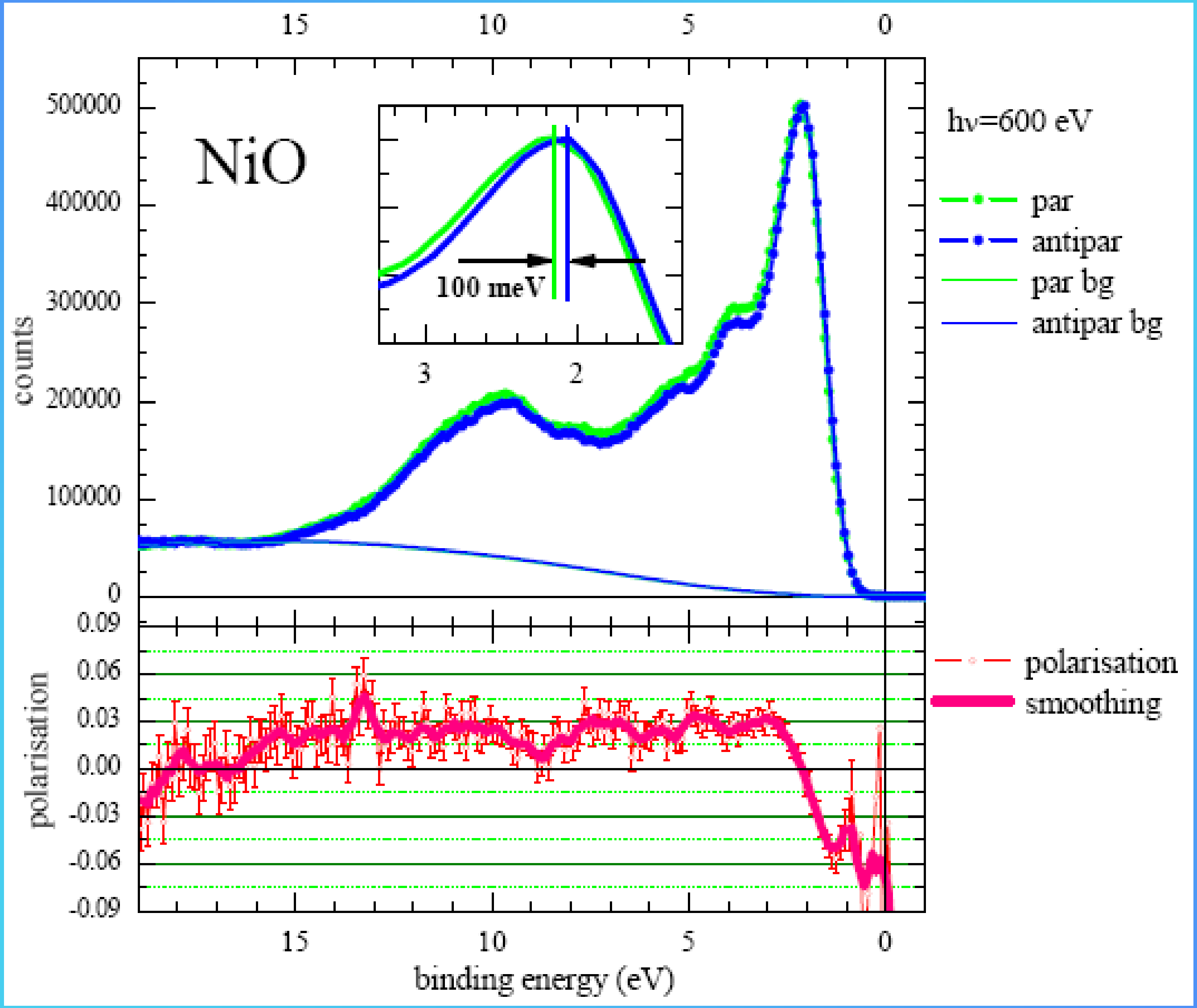
80° scattering angle, meaning a 10° difference between

- quantization axis defined by the photon angular moment
- spin component to which the polarimeter is sensitive, defined by the position of the energy analyzer

→ must correct the polarisation by cos(10°)

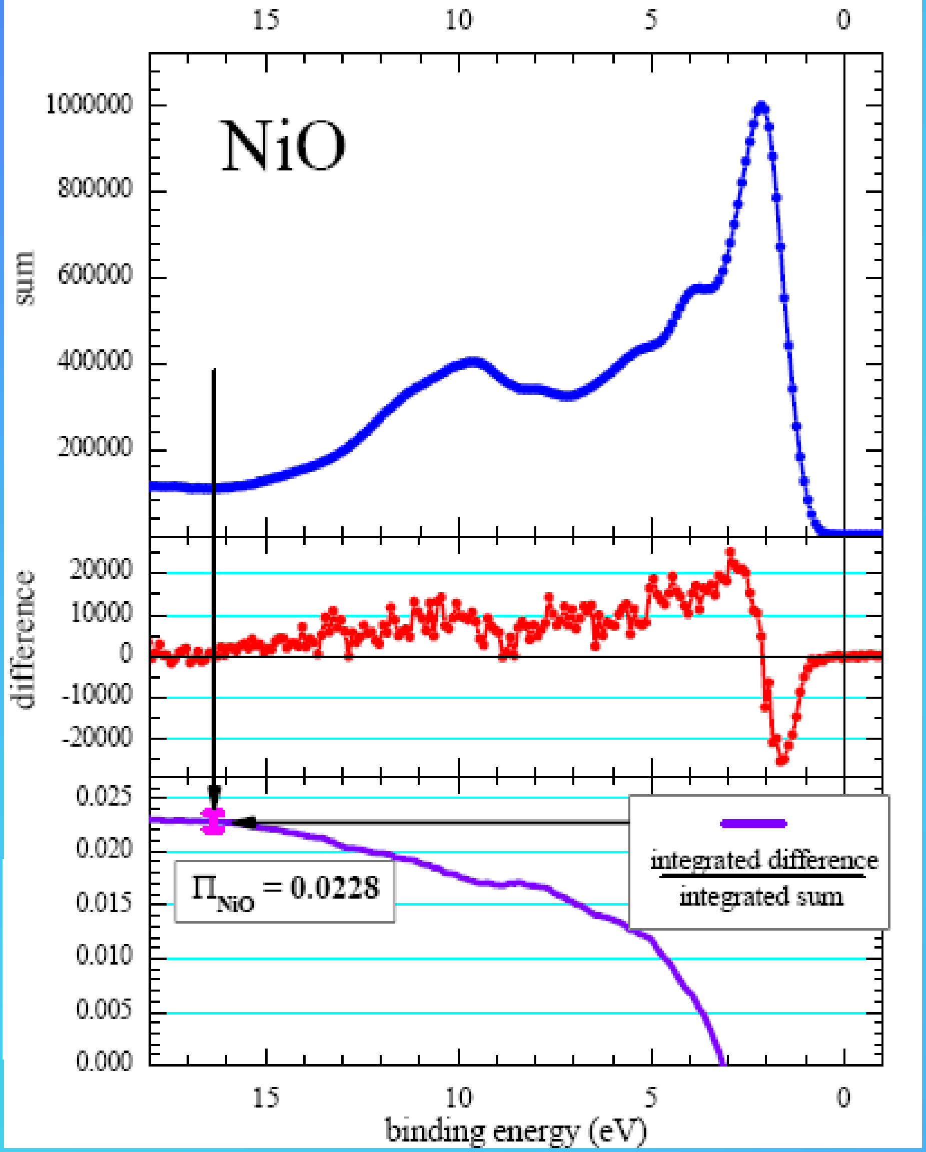
L.Moreschini *et al.*, to be submitted to Rev. Sc. Instrum.

The NiO case



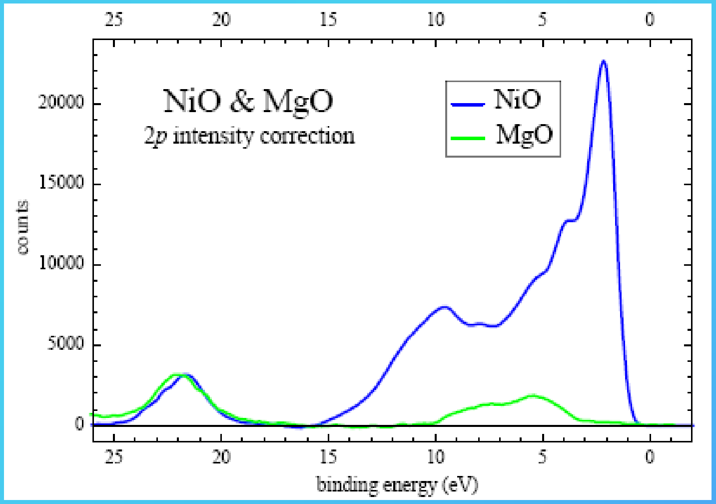
NiO
hν=600 eV
par
antipar
par bg
antipar bg
100 meV
3
2
counts
500000
400000
300000
200000
100000
0
polarisation
0.09
0.06
0.03
0.00
-0.03
-0.06
-0.09
polarisation
smoothing
15
10
5
0
binding energy (eV)

The NiO case



$$\Pi_{NiO} = 0.0228\pm0.0008\ h^2$$

the oxygen 2*p* contribution has to be subtracted

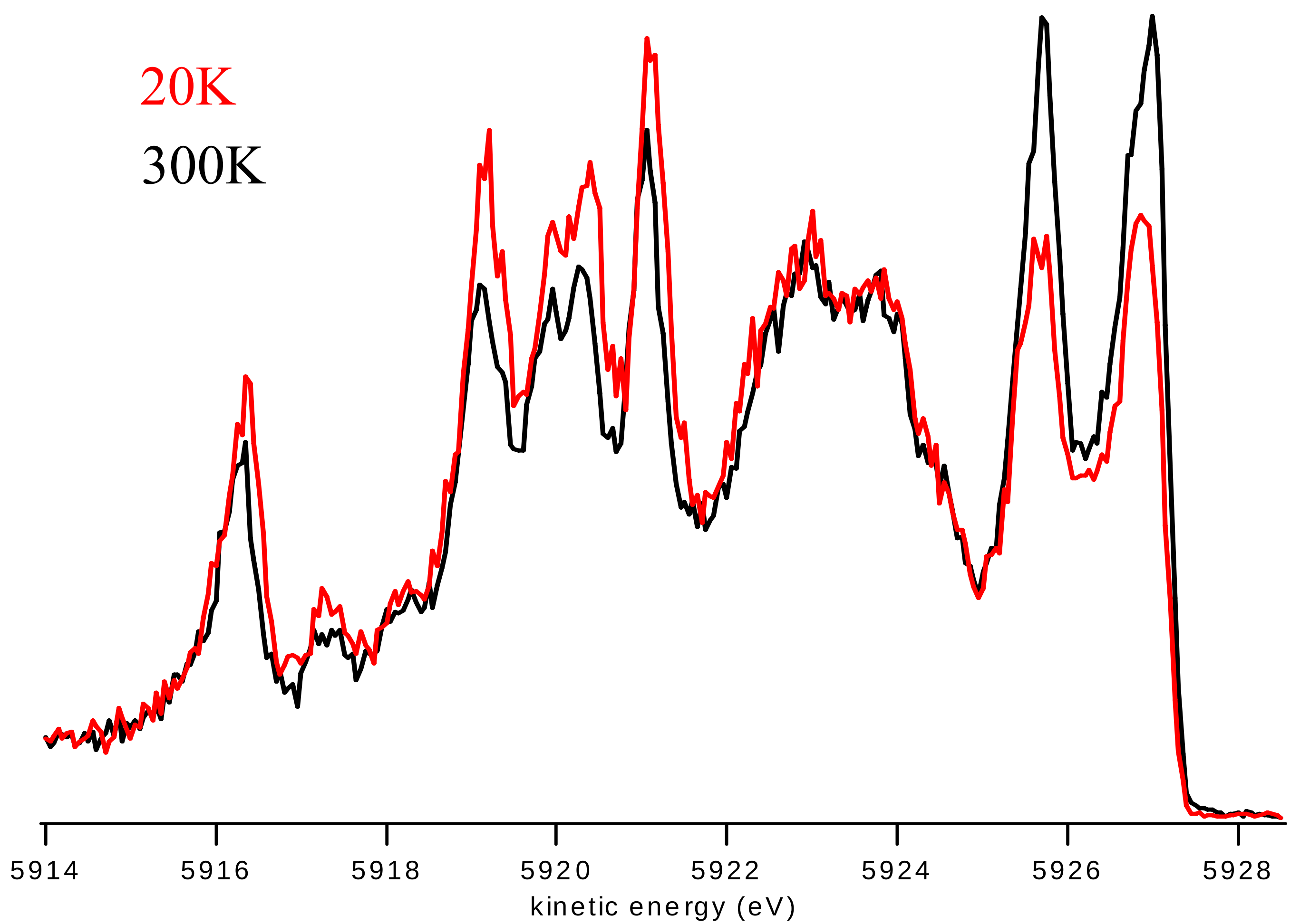


$$\Pi_{Ni} = \Pi_{NiO}/0.938 = 0.0245\pm0.0009\ h^2$$

$$\boxed{\left\langle \sum_i l_{z,i} S_{z',i} \right\rangle \approx 0.196 \pm 0.007\hbar^2}$$

What about $YbInCu_4$?

looking for the role of the Yb atom in the first order transition…



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- Giulio Monaco (ID16)
- the VolPE team

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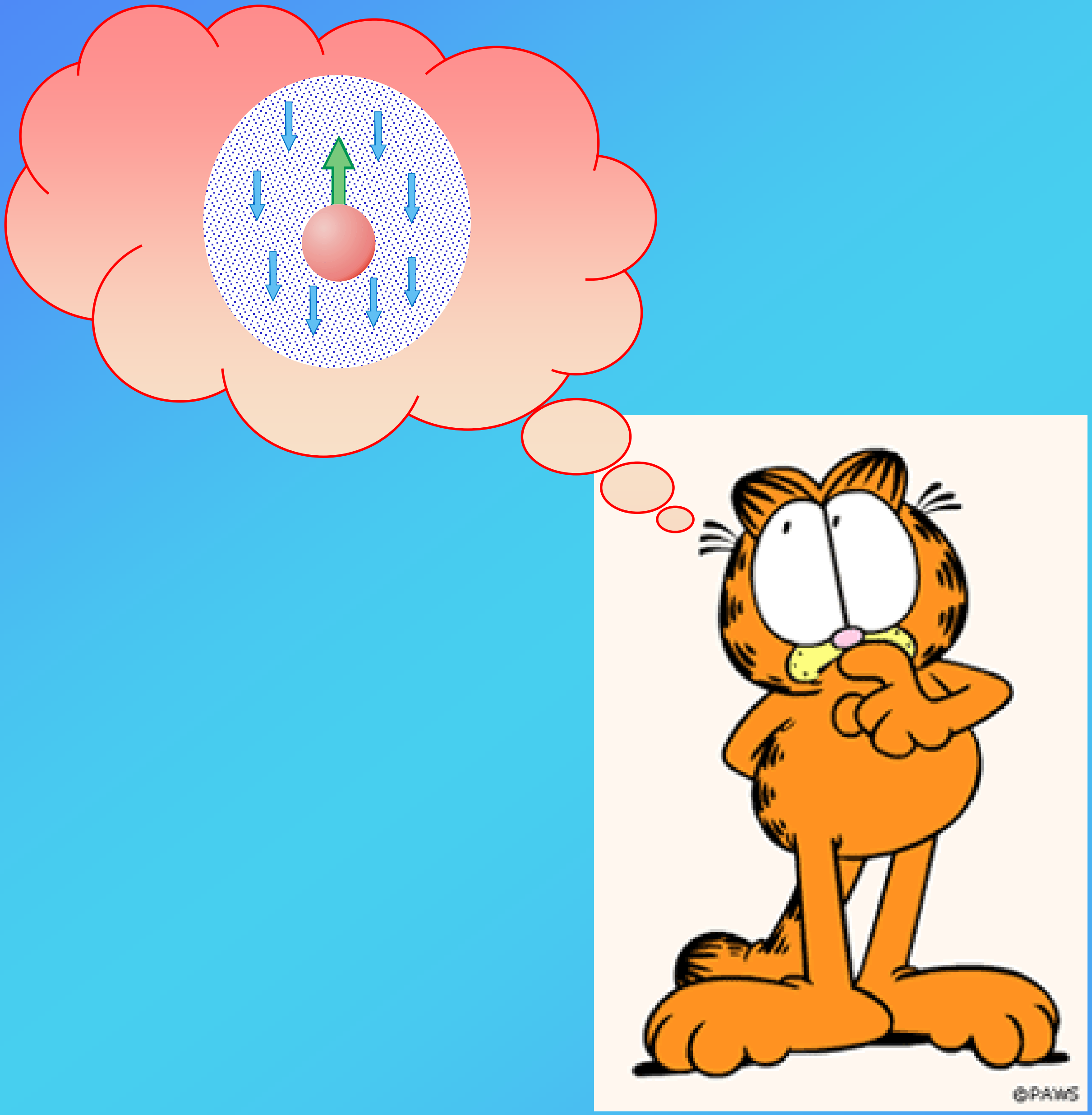
- Lucio Braicovich
- Claudia Dallera
- Ettore Carpene

at the LANL

- John Joyce
- Tomasz Durakiewicz
- crystal growers (John Sarrao, Eric Bauer, …)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