Bulk-sensitive x-ray spectroscopies on Yb Kondo systems

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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

Au + TM

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

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

\[ H = -J (\mathbf{S} \cdot \mathbf{s}) \]

impurity spin

cond \( e^- \) spin density

negative exchange constant
Yb and Ce on the periodic table

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

Ce ground state: \([\text{Xe}] \, 5d^1 \, 6s^2 \, 4f^1\) \text{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 \(\approx 2\text{eV}\)

\(4f^{13} - 4f^{14}\) energy separation in Yb compounds \(\approx \text{some 100 meV}\)
Valence fluctuations

The lowest E configuration is $3^+$

**Ce**
- $1$ electron: $\text{Ce}^{3+} (4f^1)$
- $1$ hole: $\text{Yb}^{3+} (4f^{13})$

**Yb**
- $0$ electrons: $\text{Ce}^{4+} (4f^0)$
- $0$ holes: $\text{Yb}^{2+} (4f^{14})$

The hybridization between $\text{Ce}^{3+} (4f^1)$ and $\text{Yb}^{3+} (4f^{13})$, and $\text{Ce}^{4+} (4f^0)$ and $\text{Yb}^{2+} (4f^{14})$ demonstrates the concept of valence fluctuations.
the mixed ground state in Ce compounds

\[ |\Psi_0\rangle = \alpha |f^1\rangle + \beta |f^0\rangle \quad \text{SINGLET} \]

\[ k_B T_K \approx 1 - 2 \text{ eV} \]

\[ \chi(T) = C/T \quad \text{Curie law at high } T \]
\[ \chi(T) = \text{constant non-magnetic at low } T \]

Pauli (compensation of the moments by the conduction electrons)

local moments (Curie-Weiss)
the mixed ground state in Yb compounds

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\[ k_B T_K \approx 1 - 100 \text{ meV} \]
the Kondo effect and the Anderson impurity model

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

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

AIM more general than the Kondo Hamiltonian


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

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

first excited state at $k_B T_K$
solving the AIM: the $T/T_K$ scaling

4f occupation

\[ |\Psi_{\text{excited}}\rangle = 4f^{13}\rangle \]

Ce
lowest E configuration
$\ell^1_{5/2} \to N=6$

Yb
lowest E configuration
$\ell^1_{7/2} \to N=8$

thermal depopulation
of the singlet state

MAGNETIC
EXCITED STATES

SINGLET
GROUND STATE

$T \ll T_K$ only $|\Psi_G\rangle$ is occupied
$T > T_K$ the excited states are progressively occupied

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

4f electrons in Ce and Yb

DOS of the KR mainly in the unoccupied states

DOS of the KR mainly in the occupied states
spectroscopies for Kondo systems

\[ \alpha - Ce \]

Energy (eV)

PES / IPES Intensity

\[ f^0 \]
\[ \approx f^1 \]
\[ f^2 \]

probing the Kondo scale with photoemission

\[ h\nu = 102 \text{ eV} \]


\[ T_K \approx 400 \text{K} \]

"nearly" heavy fermion

\[ h\nu = 102 \text{ eV} \]

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

to complicate the issue:

surface contributions

non-\(f\) contributions
probing the Kondo scale with photoemission


$\nu = 102 \text{ eV}$

YbAl$_3$

$T_K \approx 400K$

"nearly" heavy fermion

$\nu = 120 \text{ eV}$

YbCu$_2$Si$_2$

$T_K \approx 40-60K$

to complicate the issue:

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

surface contributions

non-$f$ contributions
probing the Kondo scale with photoemission

**YbInCu$_4$**

$T_v = 42K$

first order transition

0.5% volume collapse at T>T$_v$

$T_K \approx 20K$  T>T$_v$

$T_K \approx 400K$  T<T$_v$

to complicate the issue:

rapid oxidation

temperature cycling
probing the Kondo scale with photoemission?!?
**Why not trying something else? PFY-XAS**

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

Absorption

$\nu_{in} \sim 8945$ eV

$\nu_{in} \sim 8948$ eV

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

**TFY**

Increased bulk sensitivity

The analysis assumes two replicas of the same lineshape

even better…RIXS

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

the weaker 2+ channel is resonantly enhanced
probing the Kondo scale with RIXS

\[ n_h = \frac{I_{3+}}{I_{3+} + I_{2+}} = \frac{I_{3+}}{I} \]

\[ \frac{dI_{3+}}{dn_h} = \frac{I}{I_{3+}} \left( \frac{dI_{2+}}{dn_h} = -\frac{I}{I_{3+}} \left( \frac{I}{I_{2+}} \right) \right) \]

the minority component is the more affected by valence changes

L. Moreschini et al. PRB 75, 35113 (2007)
probing the Kondo scale with RIXS

$\text{YbCu}_2\text{Si}_2$

$\text{L}_3\text{XAS (PFY)}$

$\text{L}_{\alpha_1}\text{RIXS}$

hv$_x$ = 8940 eV

$\text{YbCu}_2\text{Si}_2$

RIXS

$3^+ \text{ component evaluated far from the resonance}$

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

quadrupole transition

L. Moreschini et al. PRB 75, 35113 (2007)
RIXS on YbAgCu$_4$

YbAgCu$_4$

\[ L\alpha_1 \]

\[ T = 15 \text{ K} \]

\[ \alpha_1 \]

\[ T_k = 70 \text{ K} \]

\[ k_BT_k \approx 7 \text{ meV} \]

\[ 2^+ \]

\[ 3^+ \]

\[ h\nu_{\text{in}} \]

\[ \text{Transferred energy (keV)} \]

\[ \text{Incident energy (keV)} \]

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

$$T_k = 70 \, \text{K}$$

$$k_B T_k \approx 7 \, \text{meV}$$
RIXS measurements under pressure

Si spherical crystal analyzer (Rowland geometry)

ESRF ID26

Hard x-ray range (> 2 keV)

-15 -10 -5 0 5 10

Probability Amplitude

Radius (angstrom)

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

\[ I_{2+} + I_{3+} = I_{\text{valence}} \]

HAXPES - bulk sensitive photoemission

G. Panaccione et al. Nucl. Instr. and Meth. 547, 56 (2005)
valence band HAXPES

\[ \nu = 2 + n_h = 2 + \frac{14I_{3+}}{14I_{3+} + 13I_{2+}} \]

L. Moreschini et al. PRB 75, 35113 (2007)
core levels HAXPES - another way around


\[ v = 2 + n_h = 2 + \frac{I_{3+}}{I_{3+} + I_{2+}} \]
recent HAXPES - looking for high count rate

\[ h\nu = 8 \text{ keV} \]

YbCu2Si2

intensity ↑
resolution ↓
let's compare…

- valence jump in YbInCu₄ but the valence does not reach abruptly the low T value. disorder?
- HAXPES data too sparse to see the first order transition of YbInCu₄. must increase intensity
- relative changes very similar for all techniques
- HAXPES valence from the 3d always higher than from the 4f. wrong background or non-4f subtraction?
- RIXS valence always higher than with HAXPES. disorder in the scraped layer?
- smooth valence evolution in YbAl₃ and YbCu₂Si₂
- room T valence for YbCu₂Si₂ lower than expected. crystal field effect?
SP-PES with a mini-Mott

backscattering of electrons from a heavy nucleus target

\[ \sigma_1 = \sigma_0 (1 - S) \]

\[ \sigma_1 = \sigma_0 (1 + S) \]

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

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

an easy spectrum: the Au $4f$ 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 3d 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 3d band spin-orbit splitting ($\Delta E_{\text{SO}} \approx 280 \text{ meV}$)

• the 3d shell is complete

The integral of the spectrum gives a null value

a not so easy spectrum: the Cu 3d states


3d correlations: CoO

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

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

- from the integral of the spectrum we can find out the value of the spin-orbit coupling in 3d 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: \[ \langle L_z \rangle \approx 1.36 \mu_B \]

a new TOF-Mott analyser

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
The NiO case

\[ \Pi_{\text{NiO}} = 0.0228 \pm 0.0008 \ h^2 \]

the oxygen 2\(p\) contribution has to be subtracted

\[ \Pi_{\text{Ni}} = \frac{\Pi_{\text{NiO}}}{0.938} = 0.0245 \pm 0.0009 \ h^2 \]

\[ \left\langle \sum_{i} l_{z,i} s_{z',i} \right\rangle \approx 0.196 \pm 0.007 h^2 \]
What about YbInCu$_4$?

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