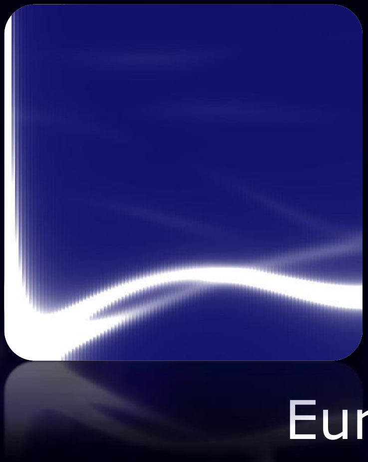
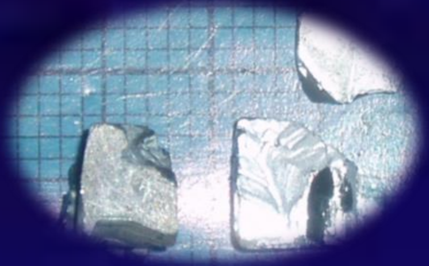
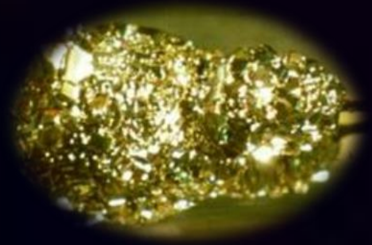
Actinide Research with Neutrons and hard Synchrotron Radiation

Roberto.Caciuffo@ec.europa.eu

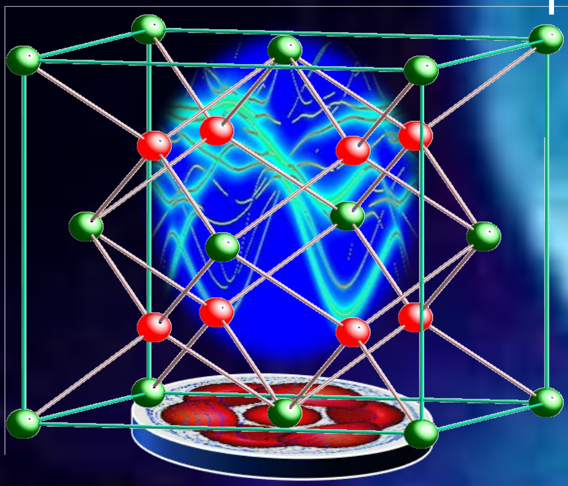


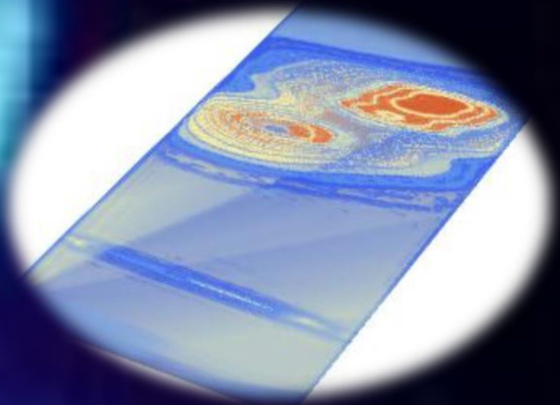




Roberto Caciuffo

European Commission, Joint Research Centre
Institute for Transuranium Elements,
Karlsruhe, Germany
roberto.caciuffo@ec.europa.eu



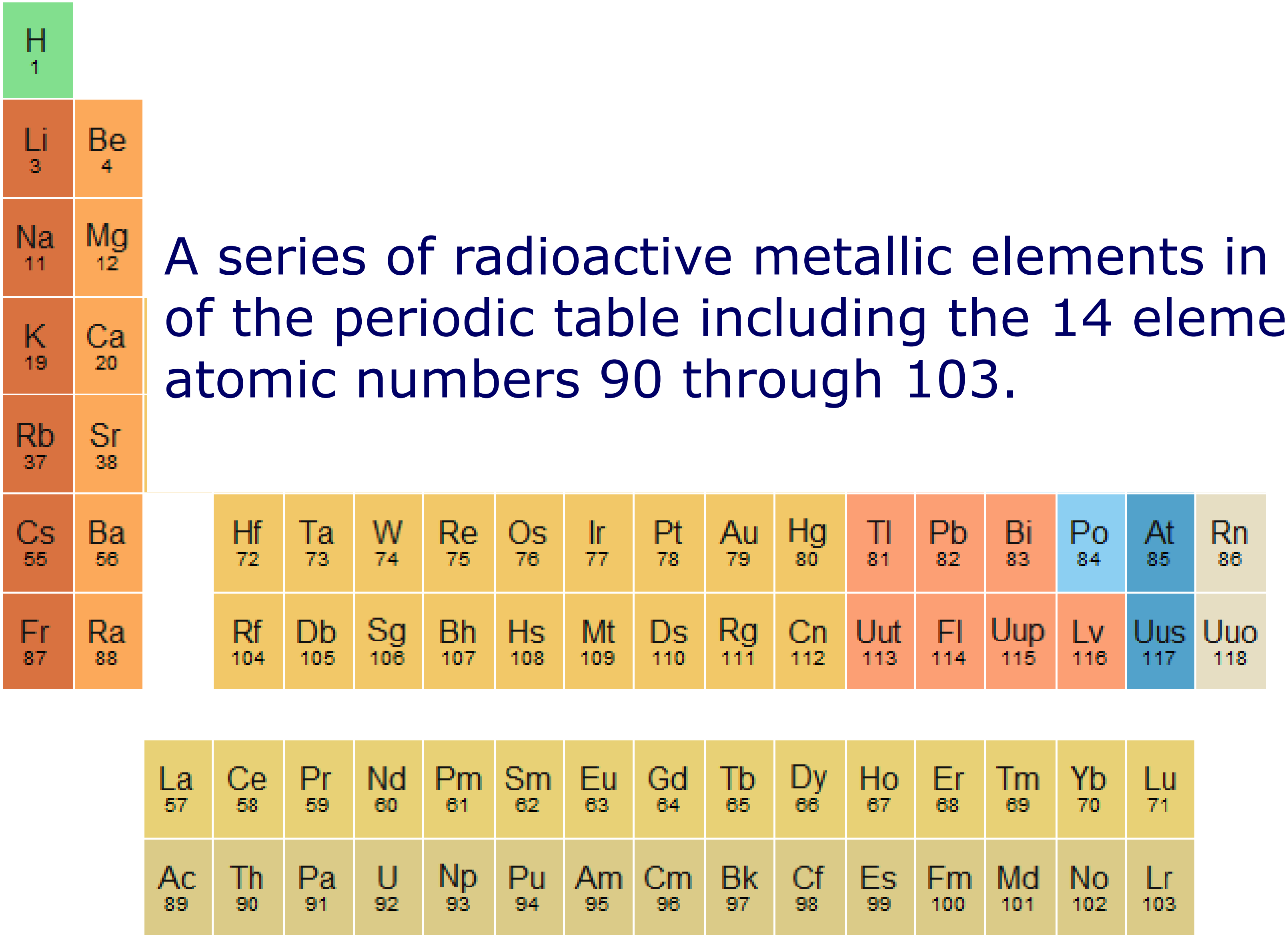


Hercules Specialized Courses, 14-18 September 2015, Grenoble

The Actinide Series

Roberto.Caciuffo@ec.europa.eu

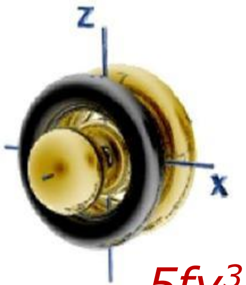
A series of radioactive metallic elements in Group 3 of the periodic table including the 14 elements with atomic numbers 90 through 103.



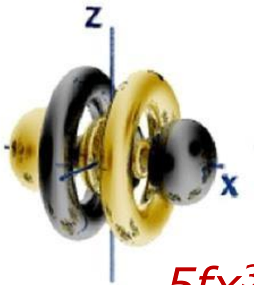
H 1																	
Li 3	Be 4																
Na 11	Mg 12																
K 19	Ca 20																
Rb 37	Sr 38																
Cs 55	Ba 56		Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88		Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Uut 113	Fl 114	Uup 115	Lv 116	Uus 117	Uuo 118
		La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	
		Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103	

The Actinide Series

As the atomic number increases in the series, added electrons enter the highly anisotropic 5f electron orbitals.



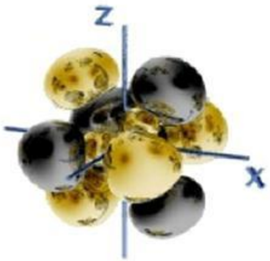
5fy³



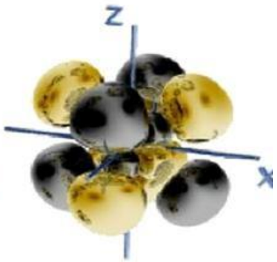
5fx³

5fz³

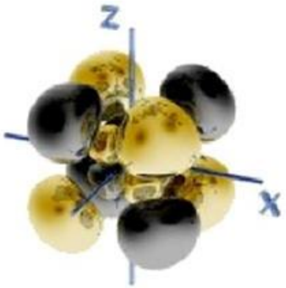
5fx(z²-y²)



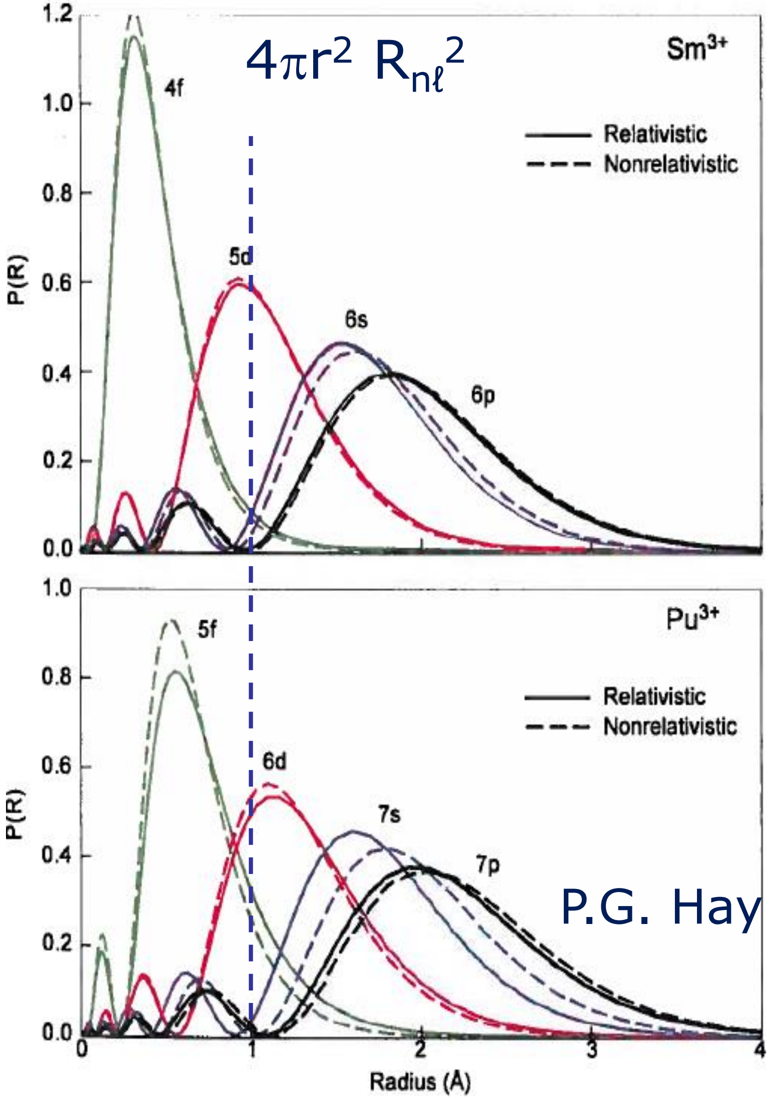
5fy(z²-x²)



5fz(x²-y²)



5fxyz



P.G. Hay

The Actinide Series

Thorium (1828)

Jens Esmark (N)

Jons J. Berzelius (S)

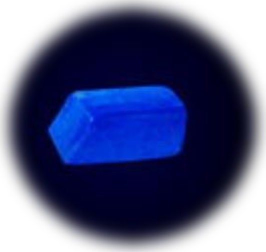
Uranium (1789)

Martin H. Klaproth (D)

Th and U are the only actinides found in the Earth's crust in large quantities.

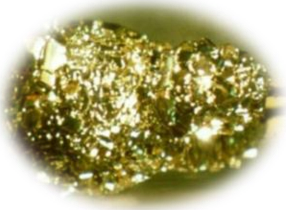
The Actinide Series

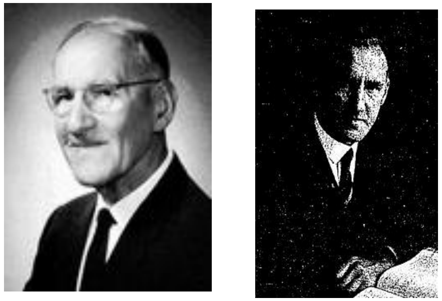
Roberto.Caciuffo@ec.europa.eu



Actinium (1899)

André-Louis Debierne (F)





Protactinium (1913)

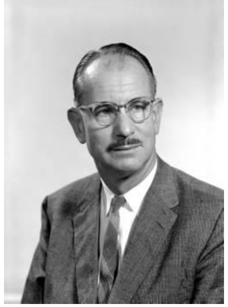
Kazimierz Fajans (P),
Oswald Helmuth Göhring (D)

Ac and Pa are found in nature as decay products of some Th and U isotopes. All the others An are synthetic elements. Their discovery is strictly linked to the progress in nuclear physics during the 1930 1940 decades. Small amounts of Np and Pu have been found in U ores.

The Actinide Series

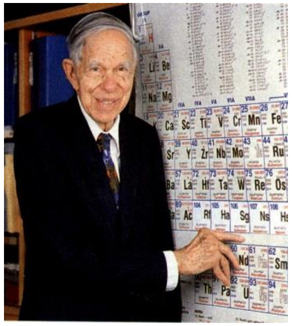
Roberto.Caciuffo@ec.europa.eu

Np(1940) discovered by Edwin M. McMillan and Philip Abelson



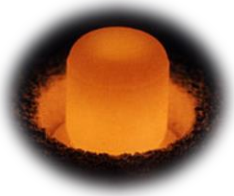
$${}^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U \xrightarrow[23.5\,\text{min}]{\beta-} {}^{239}_{93}Np$$

Neptunium



Pu: discovered in 1940 by
Glenn T. Seaborg, J. W.Kennedy,
E. M. McMillan, M. Cefola and A. Wahl

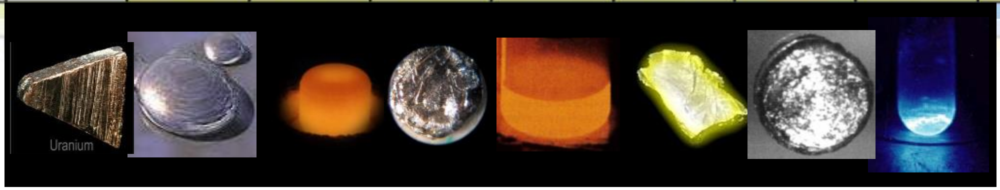
$${}^{238}_{92}U + {}^{2}_{1}D \rightarrow {}^{238}_{93}Np + 2\,{}^{1}_{0}n; \quad {}^{238}_{93}Np \xrightarrow[2.117\,d]{\beta-} {}^{238}_{94}Pu$$



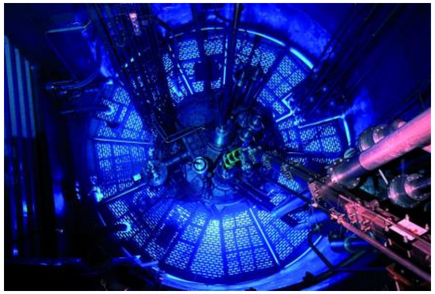
$${}^{239}_{93}Np \xrightarrow[2.365\,d]{\beta-} {}^{239}_{94}Pu$$

The Actinide Series

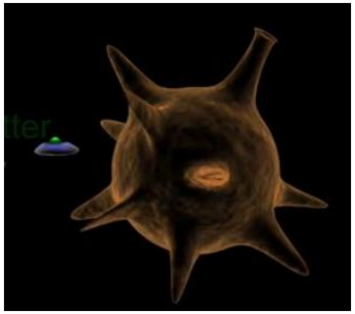
Actinides														
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
${}^2D_{3/2}$	${}^3F_2$	${}^4K_{11/2}$	${}^5L^\circ_6$	${}^6L_{11/2}$	${}^7F_0$	${}^8S^\circ_{7/2}$	${}^9D^\circ_2$	${}^6H^\circ_{15/2}$	${}^5I_8$	${}^4I^\circ_{15/2}$	${}^3H_6$	${}^2F^\circ_{7/2}$	${}^1S_0$	${}^2P^\circ_{1/2}$?
Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
(227)	232.0381	231.03588	238.02891	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)
[Rn]$6d7s^2$	[Rn]$6d^27s^2$	[Rn]$5f^26d7s^2$	[Rn]$5f^36d7s^2$	[Rn]$5f^46d7s^2$	[Rn]$5f^67s^2$	[Rn]$5f^77s^2$	[Rn]$5f^76d7s^2$	[Rn]$5f^97s^2$	[Rn]$5f^{10}7s^2$	[Rn]$5f^{11}7s^2$	[Rn]$5f^{12}7s^2$	[Rn]$5f^{13}7s^2$	[Rn]$5f^{14}7s^2$	[Rn]$5f^{14}7s^27p$?
5.17	6.3067	5.89	6.1941	6.2657	6.0260	5.9738	5.9914	6.1979	6.2817	6.42	6.50	6.58	6.65	4.9 ?



- Actinides: the backbone of nuclear fission technologies

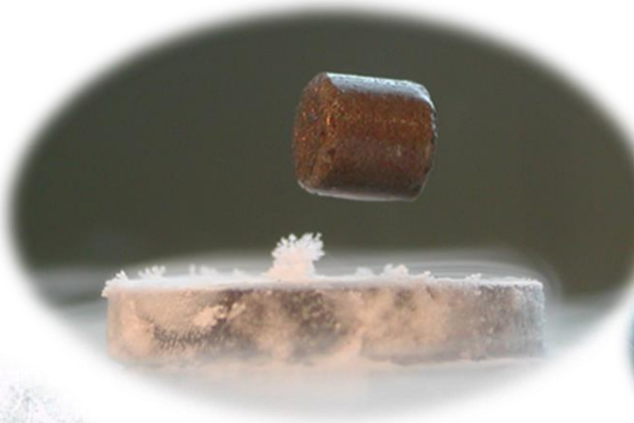


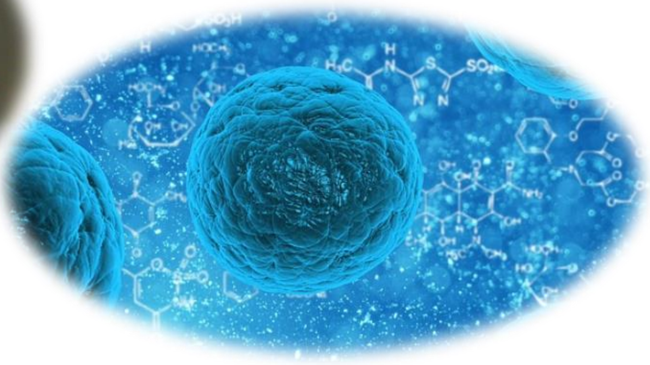
- Applications in many strategic fields, from space exploration to medical diagnostics and treatments.

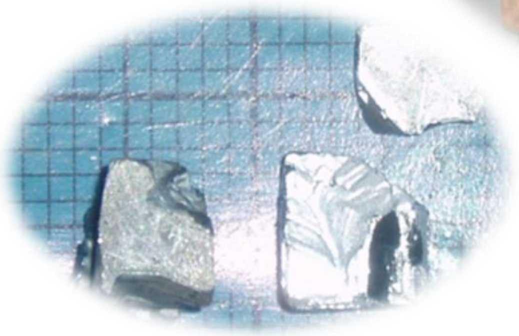


Electron physics of the actinides

Roberto.Caciuffo@ec.europa.eu





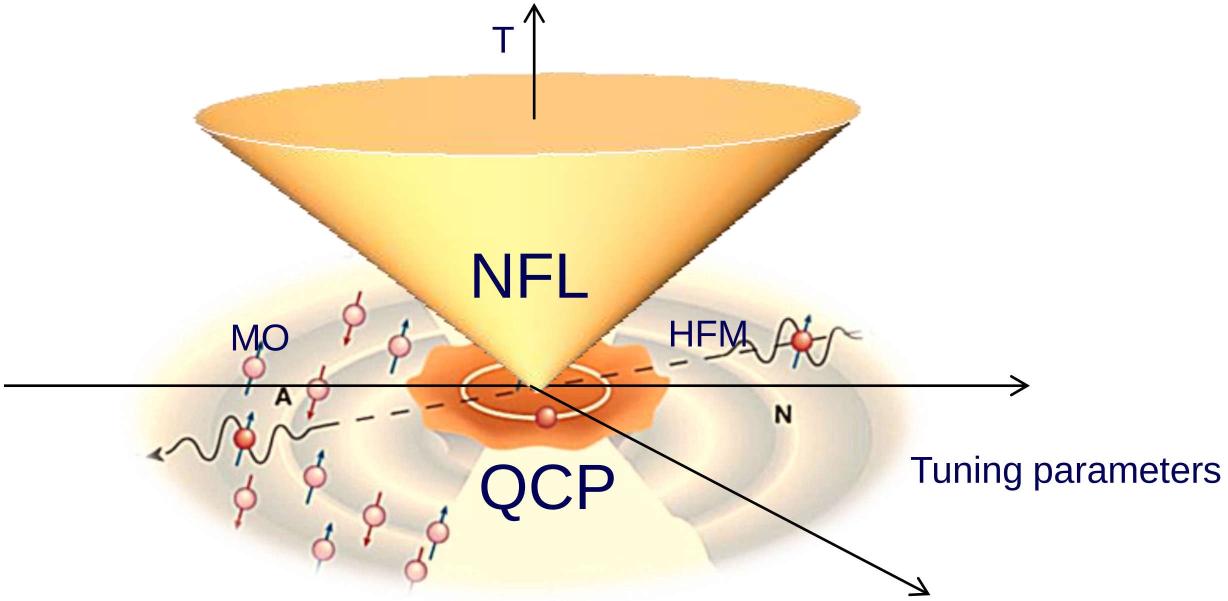


Actinide electron physics is playing a major role in exploring the frontier between the nm and the μm scale, where emergent properties are not yet understood.

Electron physics of the actinides

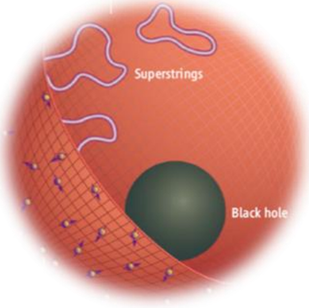
Roberto.Caciuffo@ec.europa.eu

- At the brink of magnetic instability, in a regime where quantum fluctuations of the magnetic and electronic degrees of freedom are strongly coupled. Novel electronic behaviour develops around the point of instability (quantum critical point).



- important test bed for the development of our understanding of quantum matter

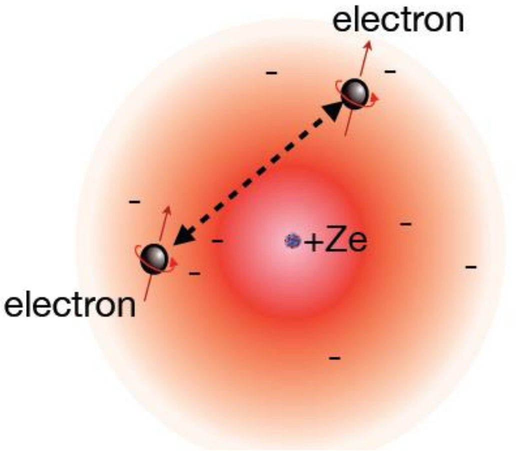
- investigating new classes of material behaviour.

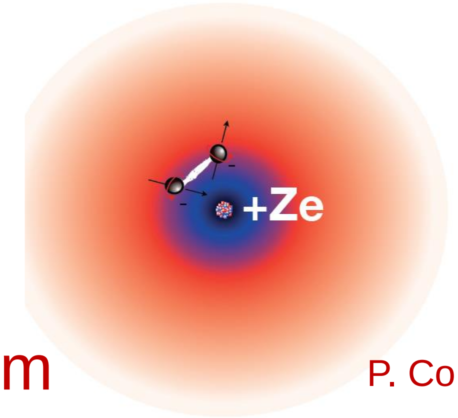


Electron physics of the actinides

Small number of protons:
electrons wide apart and weekly interacting

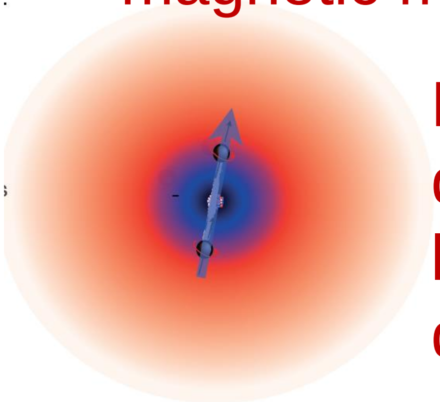
Large number of protons:
electrons closer to each other Interact strongly and are prone to correlated behaviour





P. Coleman

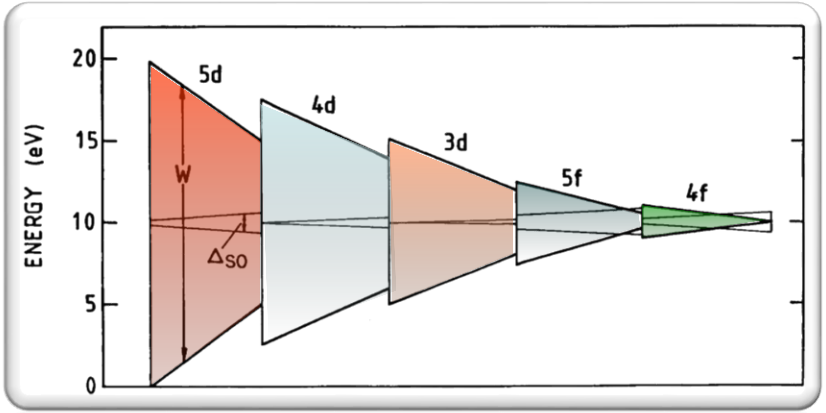
Tendency to form magnetic moments



But magnetism melts when quantum fluctuations are too large, and new physics may develop.

Narrow bands and large spin-orbit interaction

Roberto.Caciuffo@ec.europa.eu



Decreasing width of dominant electron-energy band:

Itinerant electrons (K, Al…) conventional super-conductivity → Higher density metal (Cu, Pd) d bonding → **Strongly Correlated Electron Systems** → Localised electrons (Gd) Local magnetism

Increasing electron correlations :

Free-electron behaviour

Low resistivity

Low density of states

Low electronic-heat capacity

→

Heavy-fermion behaviour

High resistivity

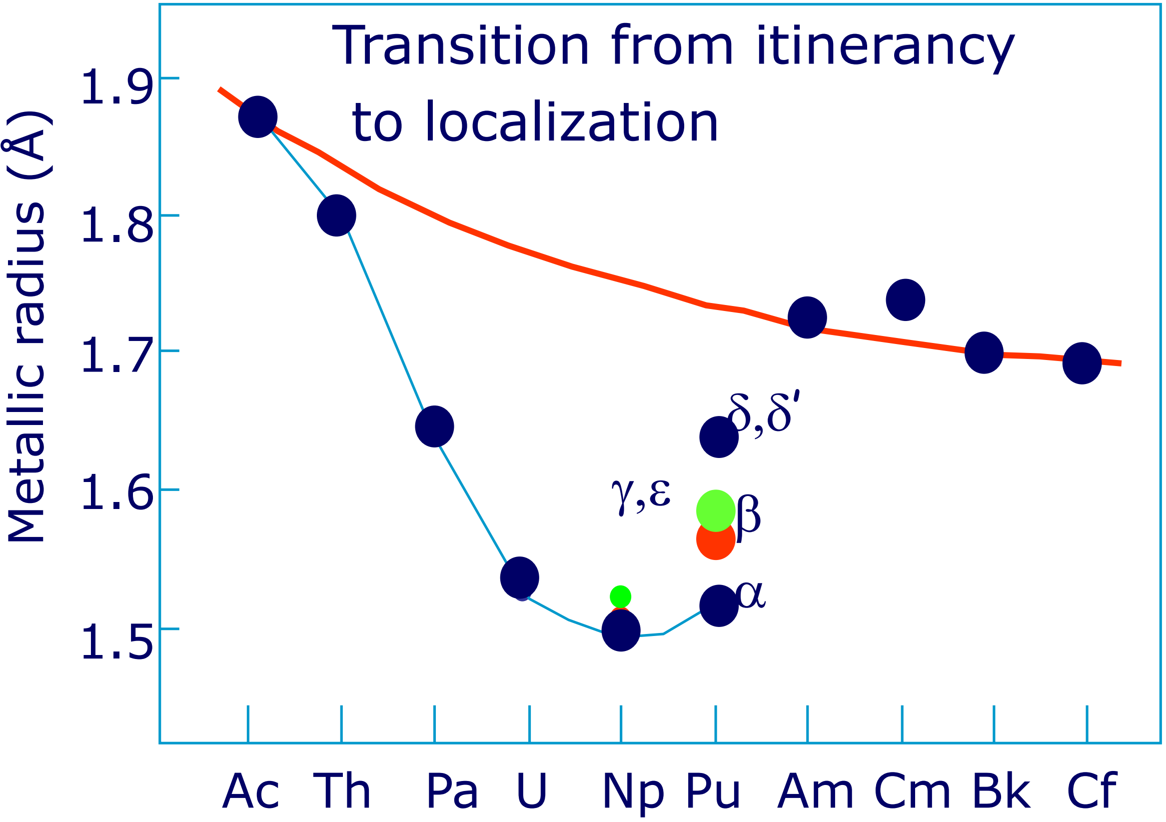
High density of states

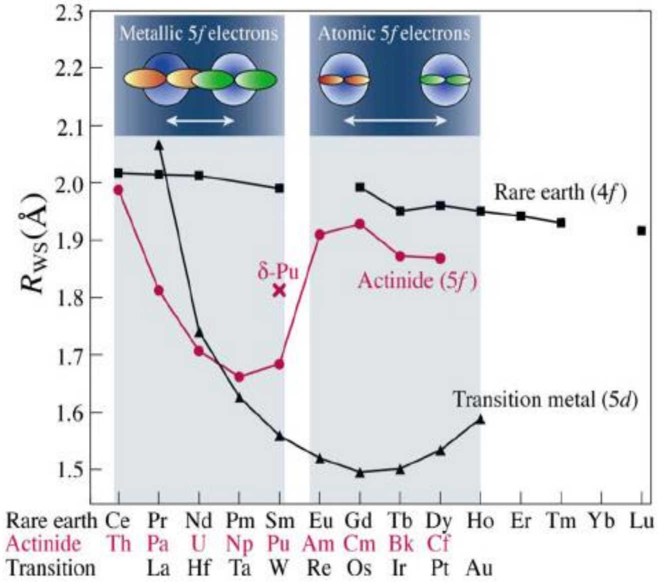
High electronic-heat capacity

Elemental volumes in the actinide series

Roberto.Caciuffo@ec.europa.eu

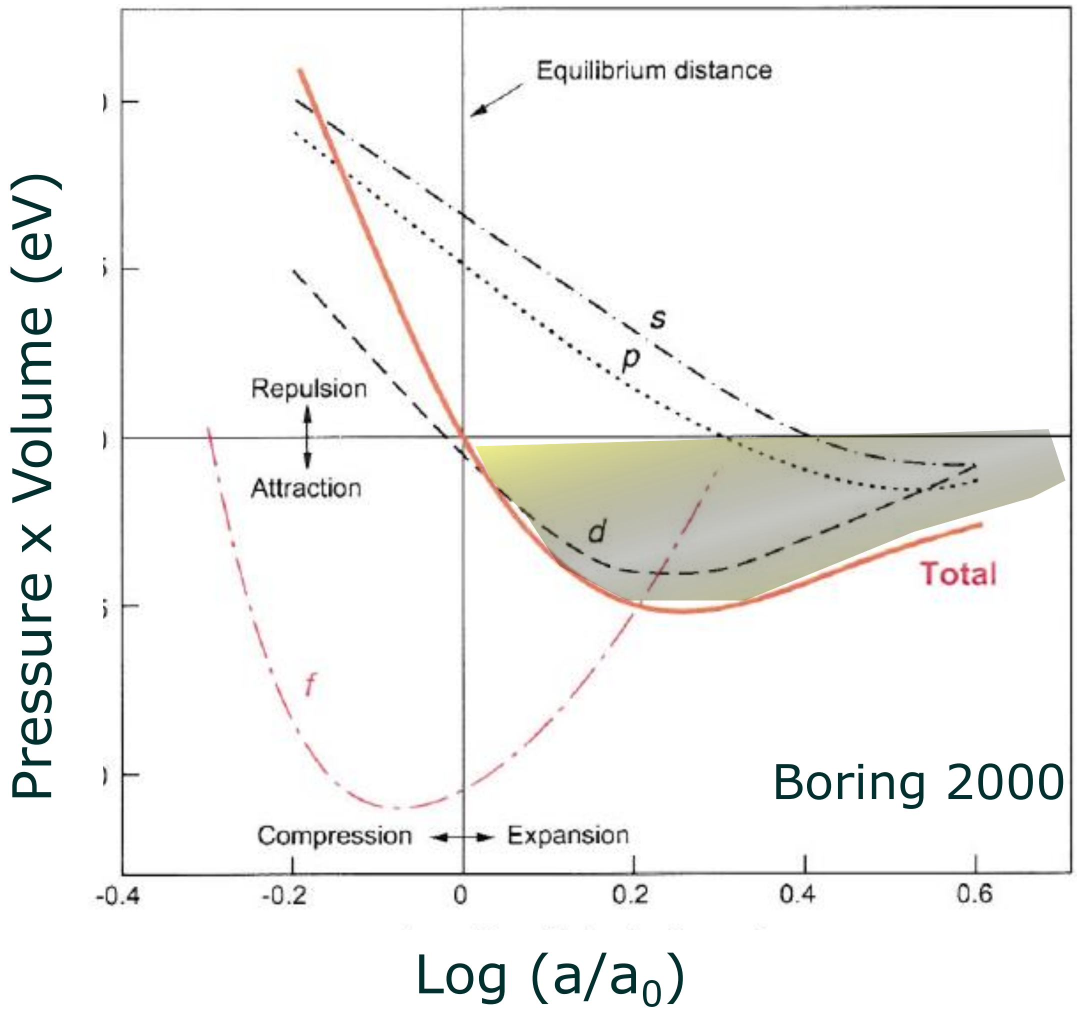
5f-e poised at the edge between localized (bonding as in rare earth) and itinerant (non-bonding as in transition metals) configurations





Bonding curve and narrow 5f bands in δ-Pu

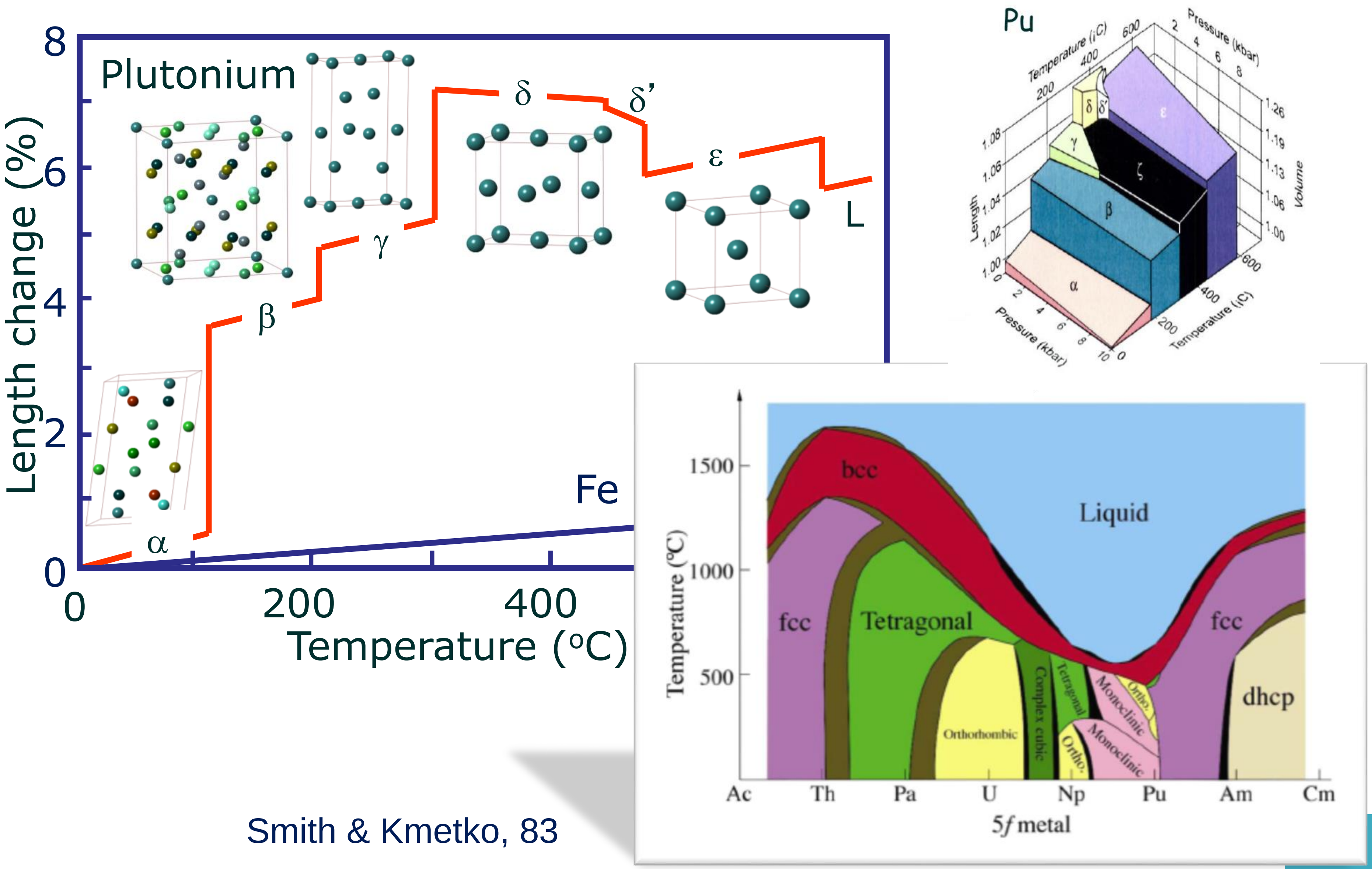
Roberto.Caciuffo@ec.europa.eu



Boring 2000

The strong competition between sp and f bands is a sign of instability near the ground state.

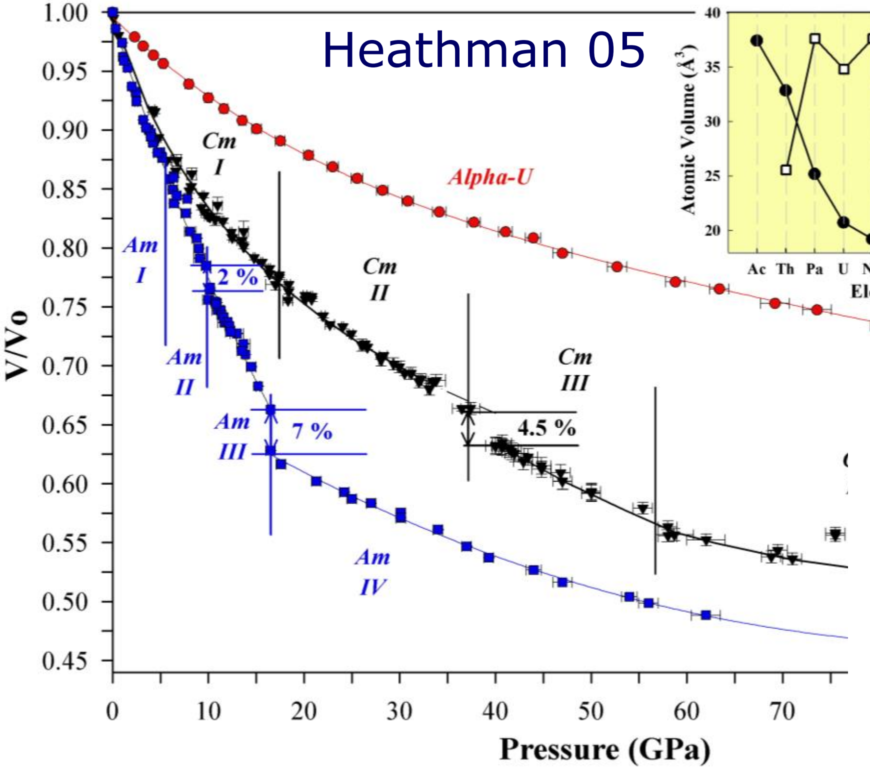
Prone to lattice instabilities

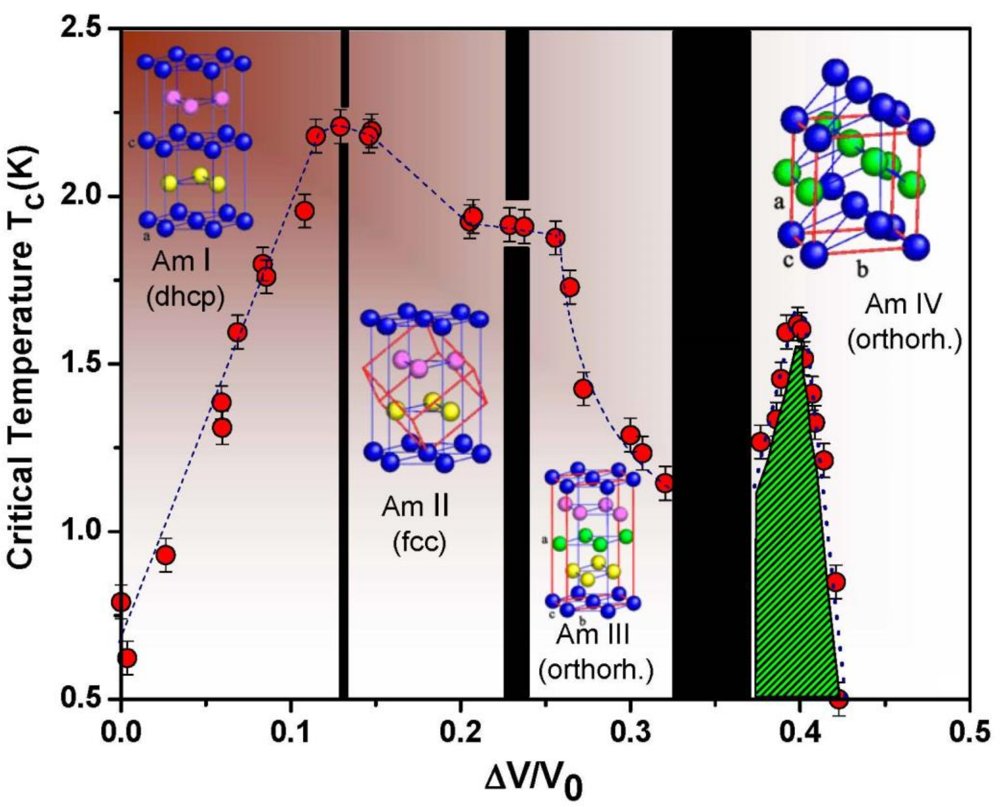


Smith & Kmetko, 83

Pressure-induced delocalization of 5f electrons

Roberto.Caciuffo@ec.europa.eu





Volume collapses signify the stepwise delocalization of the 5f electrons and their subsequent participation in the metallic bonding

Roberto.Caciuffo@ec.europa.eu

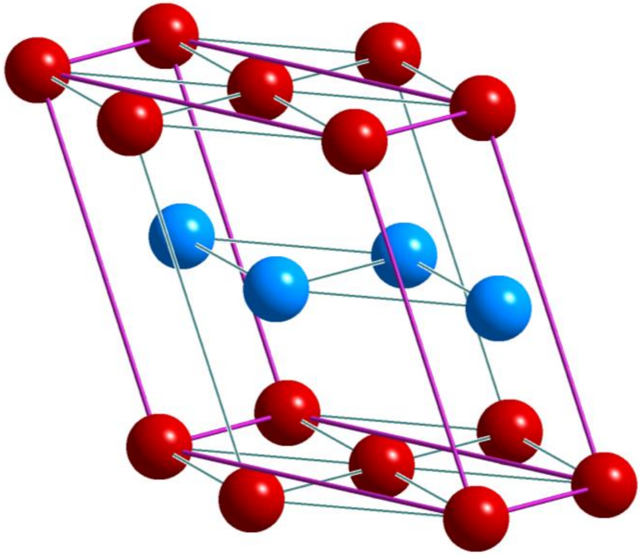
Cm III structure unique

Cm is one of a few elements (Co, Fe) that has a lattice structure stabilized by magnetic interactions

Cm III stable between 37-56 Gpa

Monoclinic, Space Group C2/c

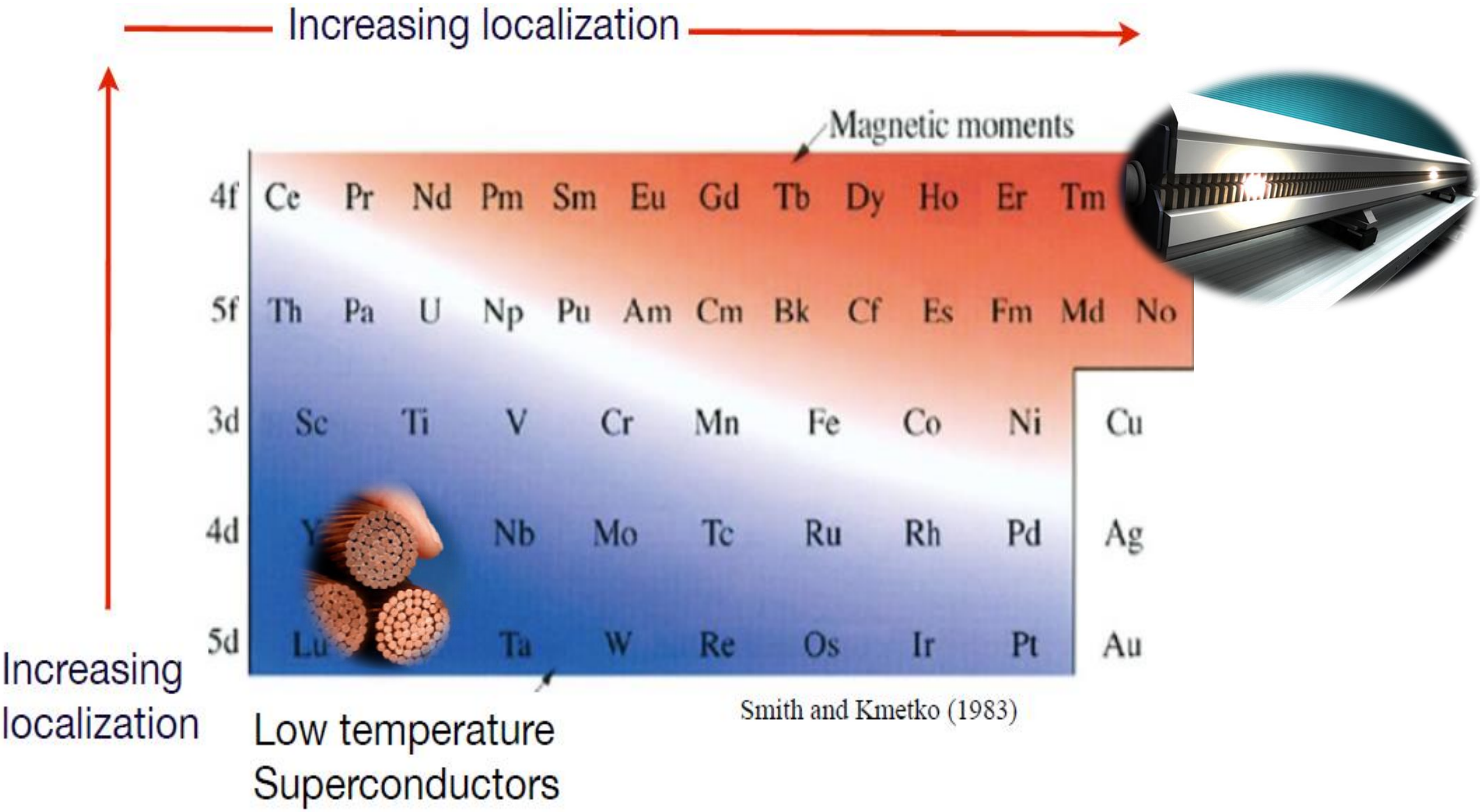
In the Cm IV there is no magnetic moment and 5f electrons are itinerant



Heathman05

Electron physics of the actinides

Roberto.Caciuffo@ec.europa.eu

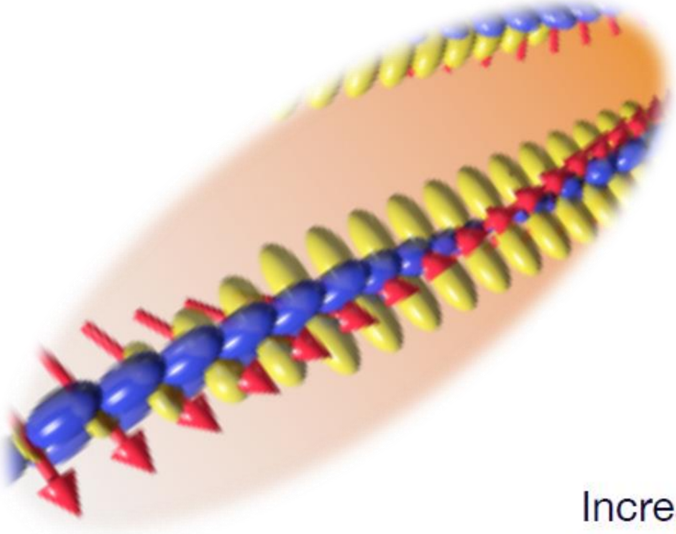


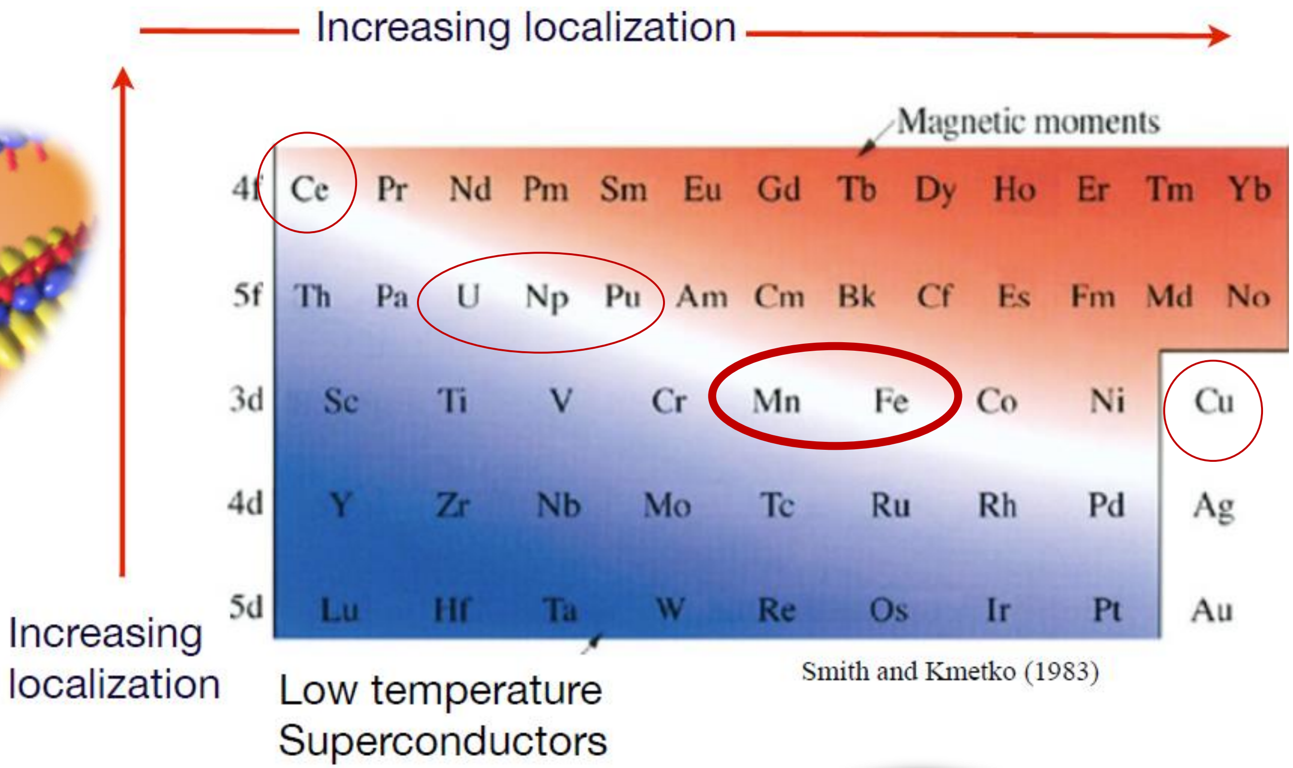
Smith and Kmetko (1983)

The white band running diagonally is where f or d valence electrons change from itinerant and bonding (blue region) to localized and magnetic (red region). Slight changes in temperature, pressure, or chemistry will move metals located on the white band to either more conductive or more magnetic behavior.

Electron physics of the actinides

Roberto.Caciuffo@ec.europa.eu





Increasing localization

Increasing localization

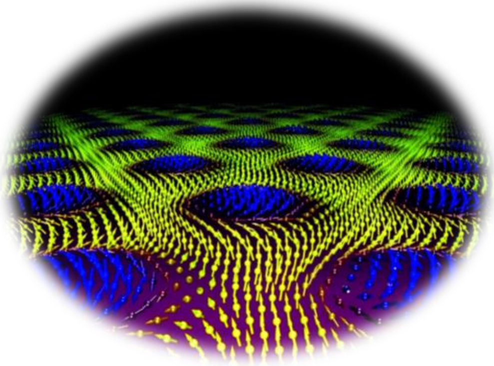
Magnetic moments

4f	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu				
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag				
5d	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au				

Low temperature Superconductors

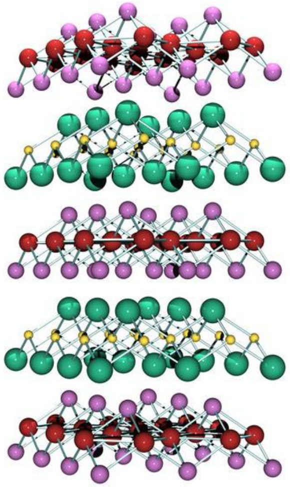
Smith and Kmetko (1983)

Magnetism

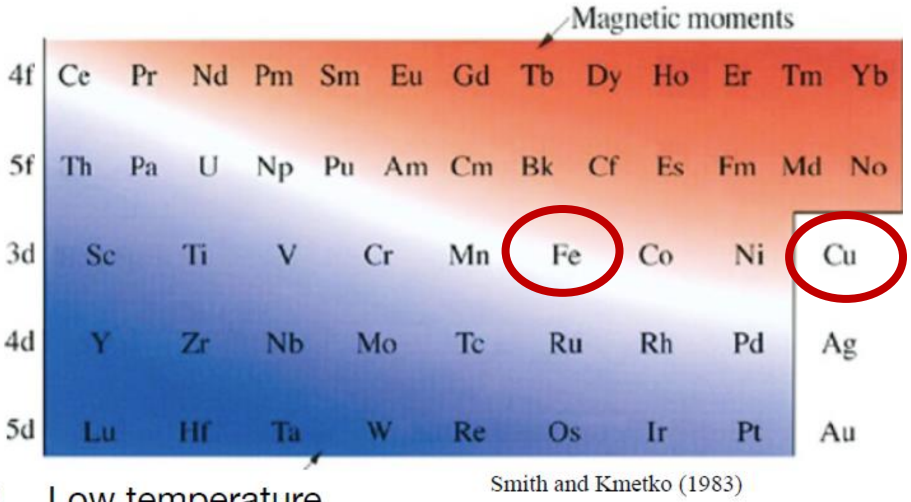


Electron physics of the actinides

Roberto.Caciuffo@ec.europa.eu



Fe-based SC



Increasing localization

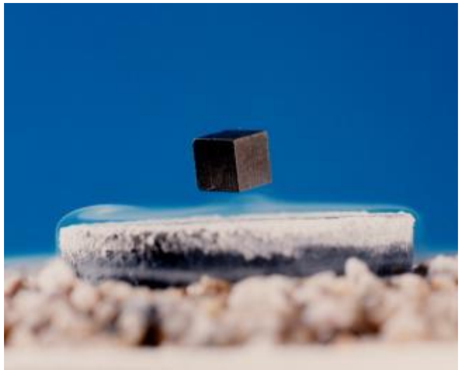
Magnetic moments

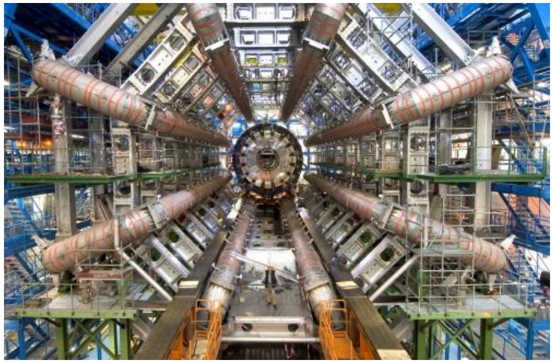
4f	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu				
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag				
5d	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au				

Smith and Kmetko (1983)

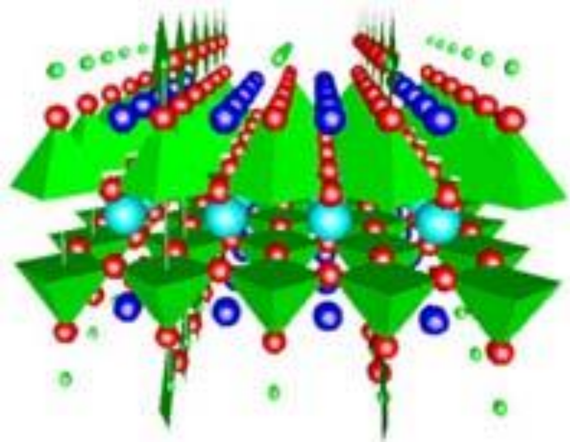
Increasing localization

Low temperature Superconductors





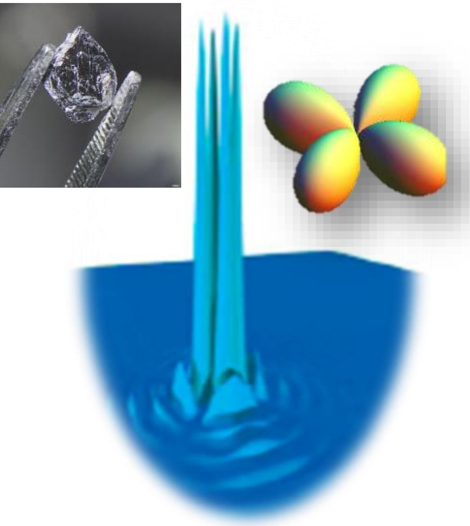
Superconductivity

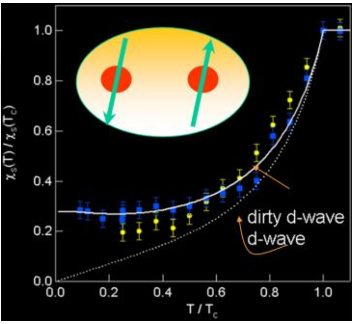


cuprates

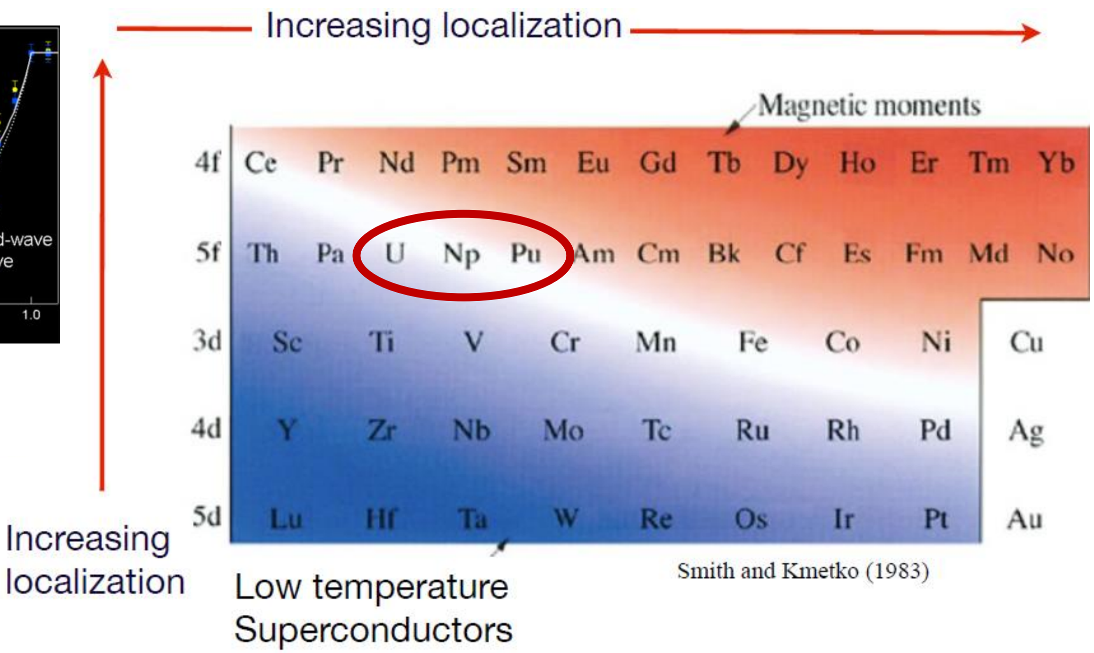
Electron physics of the actinides

Roberto.Caciuffo@ec.europa.eu



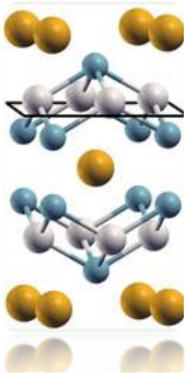


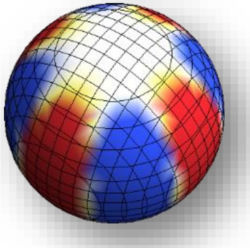
PuCoGa$_5$



4f	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu				
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag				
5d	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au				

Smith and Kmetko (1983)





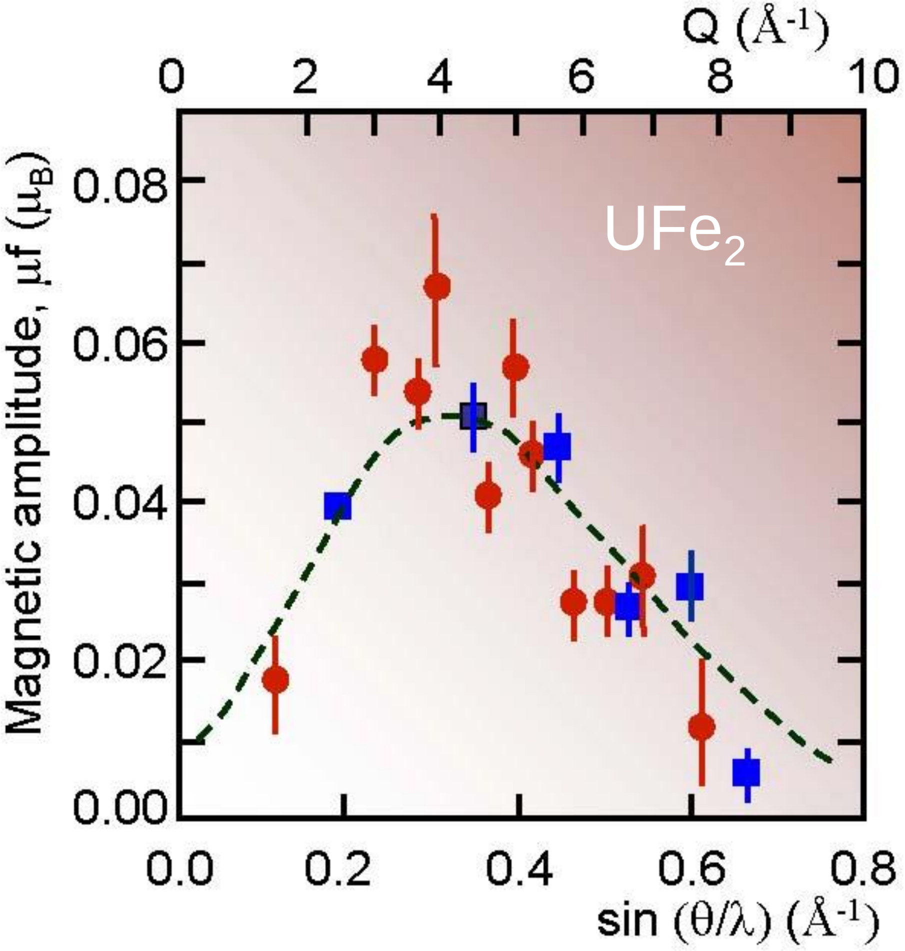
URu$_2$Si$_2$

Unconventional heavy-fermion SC

Hidden order

Polarized neutron diffraction and spin density distribution

Roberto.Caciuffo@ec.europa.eu



Magnetic structure factors are determined in amplitude and phase if the crystallographic structure is known.

The magnetization density distribution can therefore be determined.

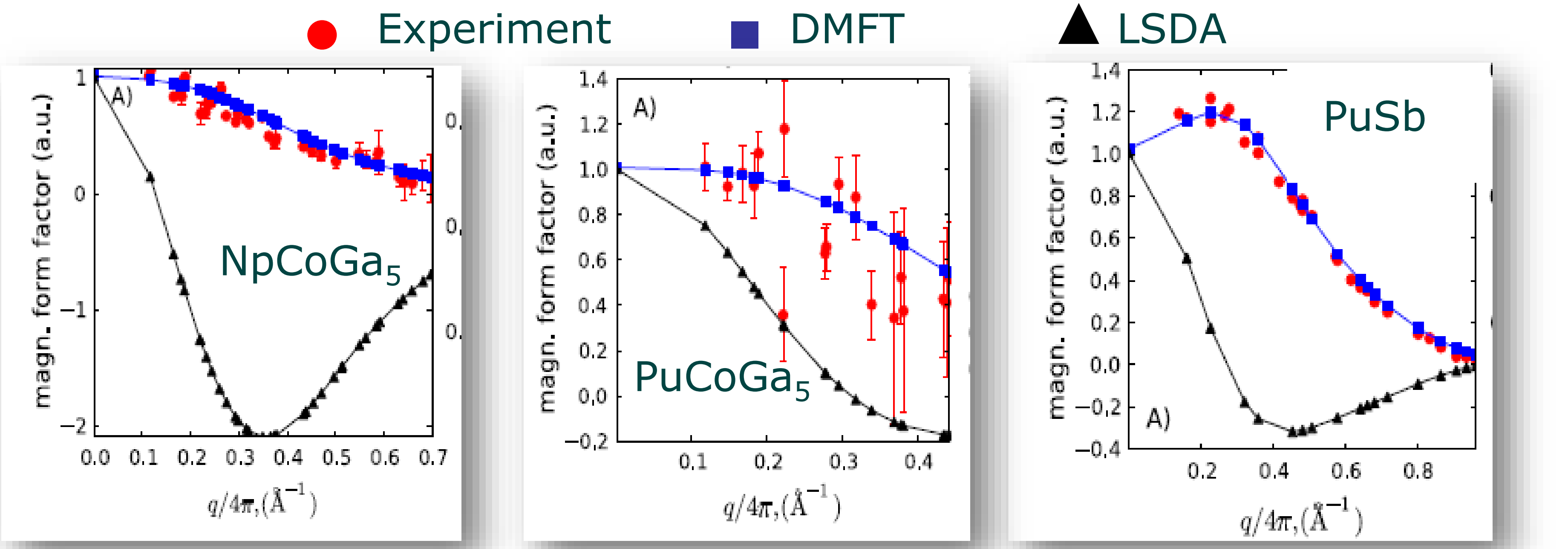
Analysis of the form factors allows determining spin and orbital components of the magnetic moment.

Wulff et al. 89

Polarized neutron diffraction and spin density distribution

Roberto.Caciuffo@ec.europa.eu

Conventional “state of the art” DFT theory fails in describing in detail actinide materials.



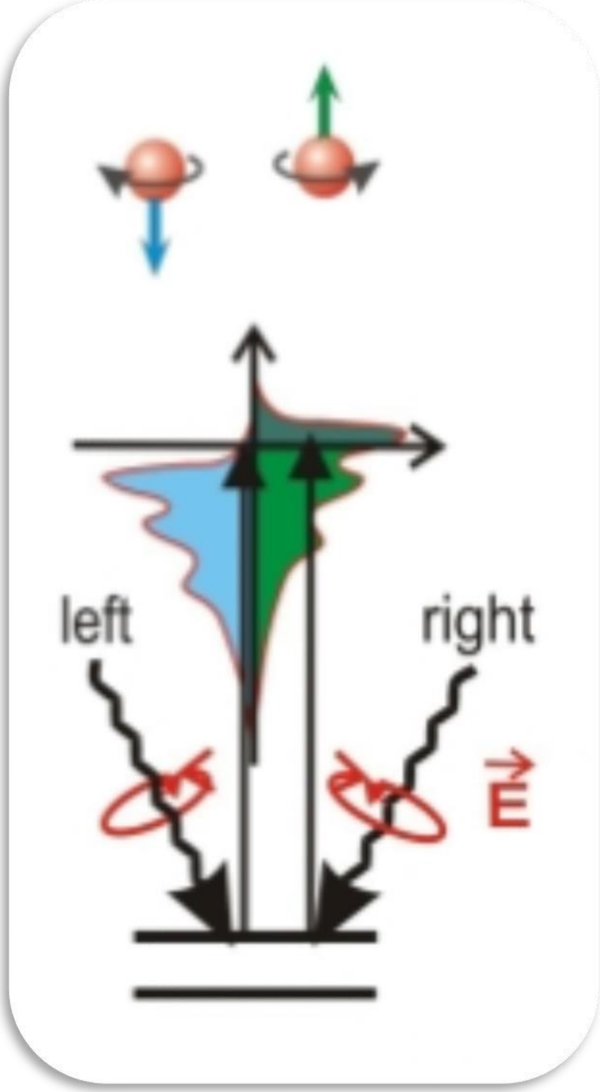
Pezzoli 2011

Magnetic form factor in some actinide compounds

Improvement obtained by empirical corrections (DFT+U or DMFT). However, DFT+U can converge to metastable states, DFT+DMFT is computationally expensive.

X-ray Magnetic Circular Dichroism

Roberto.Caciuffo@ec.europa.eu



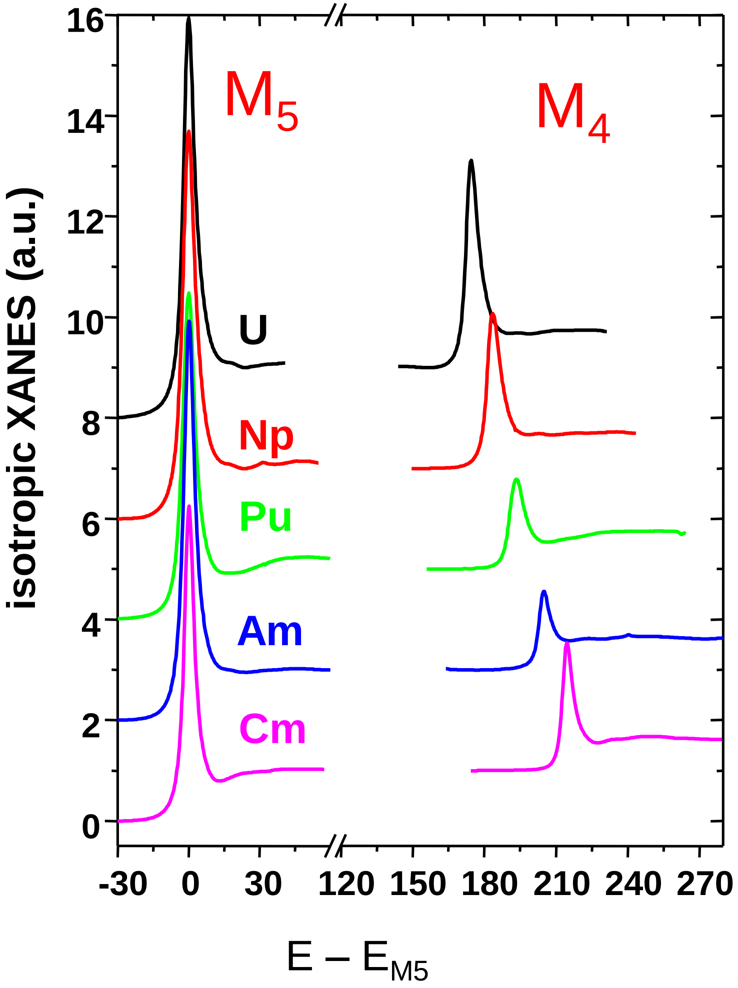
Polarized neutron diffraction (PND) requires single crystals of relatively large mass.

XMCD requires much smaller samples than PND (by a factor 10^{-4}), which is a big advantage when working with actinides.

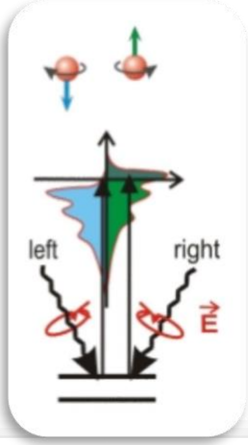
Only Q = 0 information, but allows determining $<L_z>$ and $<S_z>$ with high accuracy.

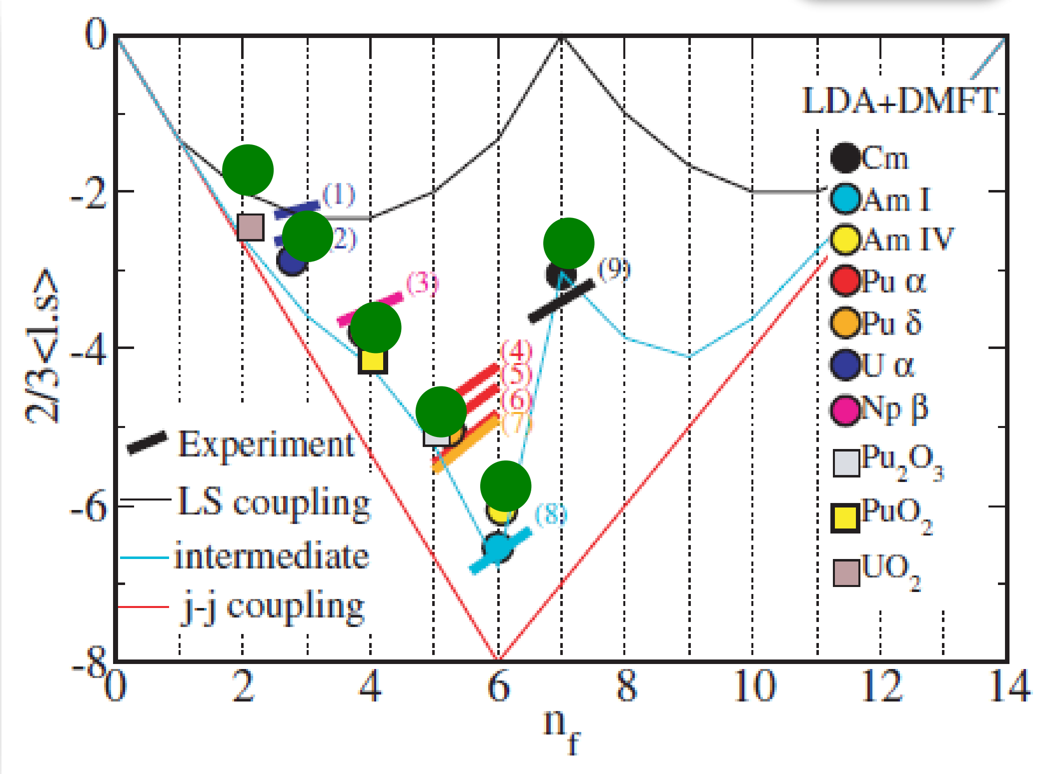
X-ray Magnetic Circular Dichroism

Roberto.Caciuffo@ec.europa.eu



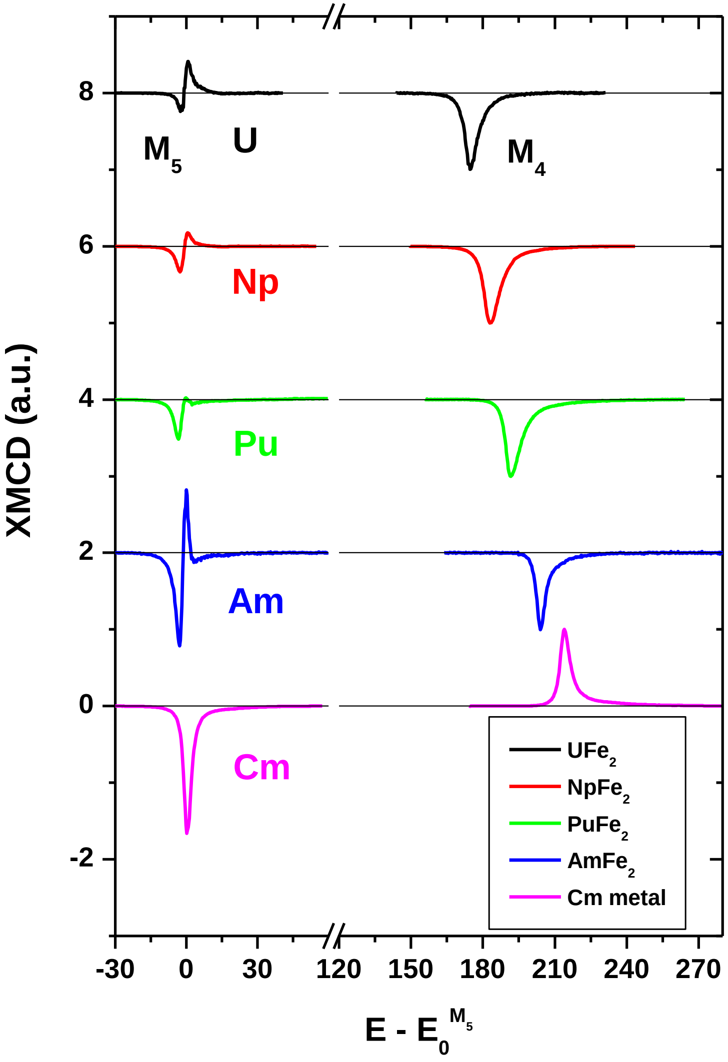
$$\frac{2\langle \vec{\ell}\cdot\vec{s}\rangle}{3n_h} = -\frac{5}{2}\left(B-\frac{3}{5}\right)+\Delta$$





X-ray Magnetic Circular Dichroism

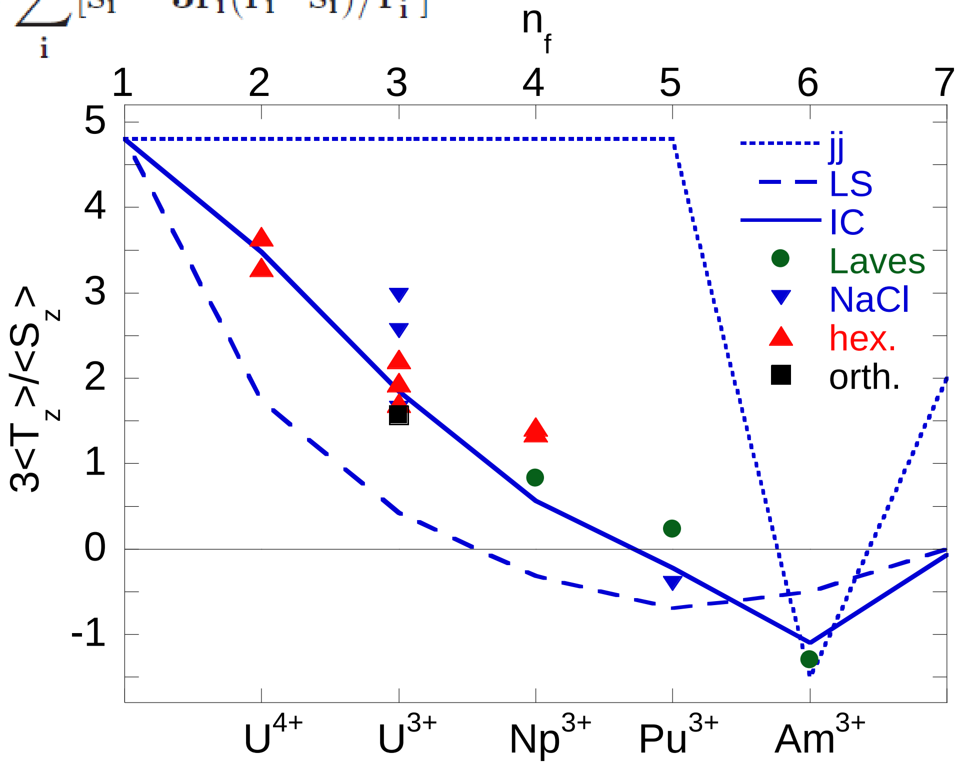
Roberto.Caciuffo@ec.europa.eu



$$\langle L_z \rangle = \frac{n_h}{I_{M_5} + I_{M_4}} \left(\Delta I_{M_5} + \Delta I_{M_4} \right)$$

$$\langle S_z \rangle + 3\langle T_z \rangle = \frac{n_h}{2(I_{M_5} + I_{M_4})} \left(\Delta I_{M_5} - \frac{3}{2} \Delta I_{M_4} \right)$$

$$\mathbf{T} = \sum_i [\mathbf{s}_i - 3\mathbf{r}_i(\mathbf{r}_i \cdot \mathbf{s}_i)/\mathbf{r}_i^2]$$

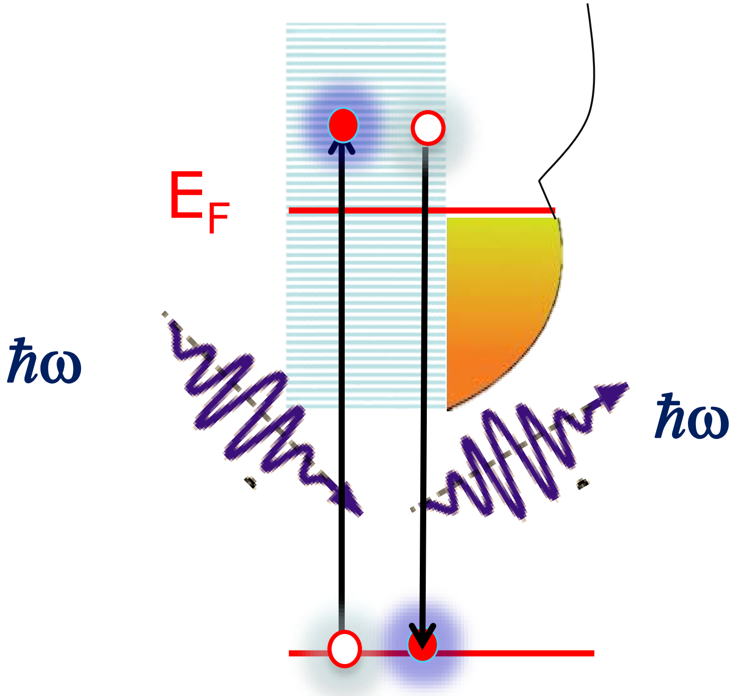


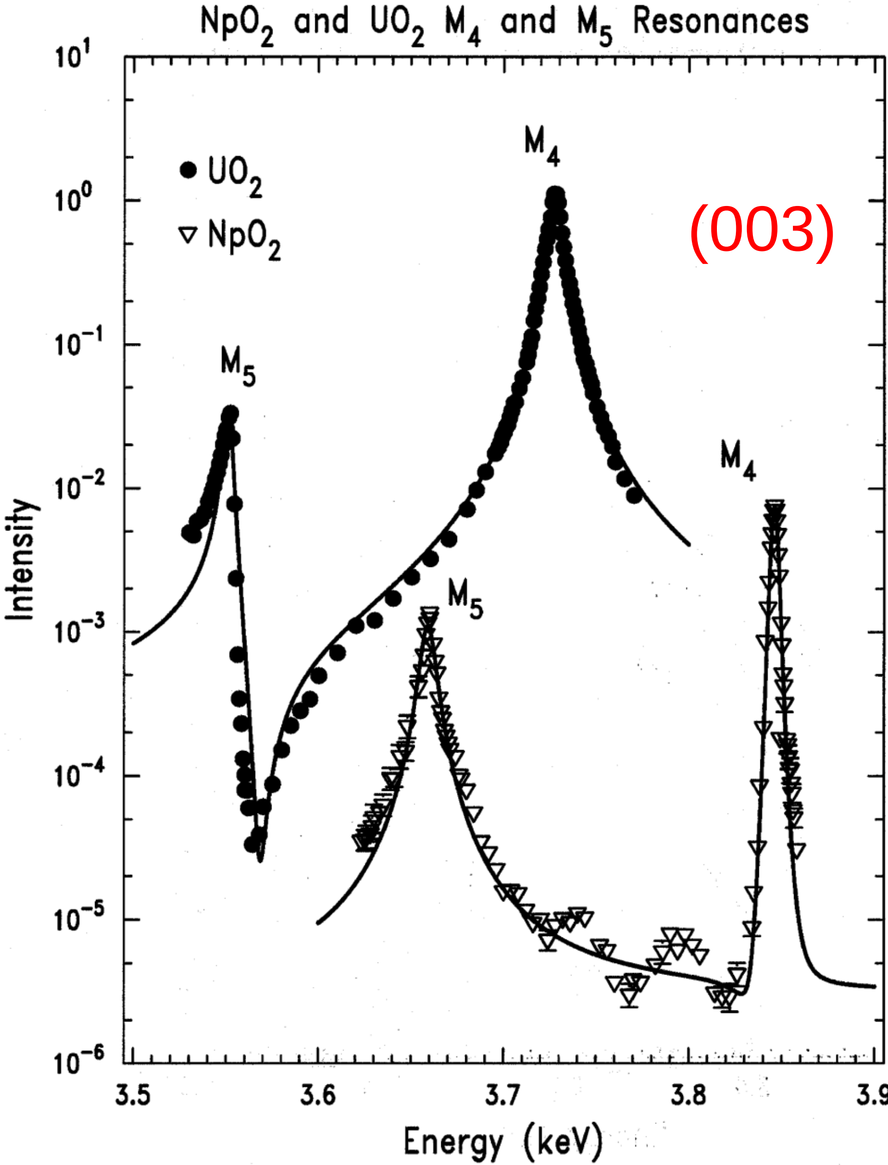
$\langle T_z \rangle$ is a measure of a spin moment anisotropy induced either by a charge quadrupole moment or by the spin-orbit interaction

Resonant x-ray scattering

Roberto.Caciuffo@ec.europa.eu

- Linearly polarised photons
- Elastic scattering
- Resonant anisotropic contributions to the x-ray susceptibility tensor

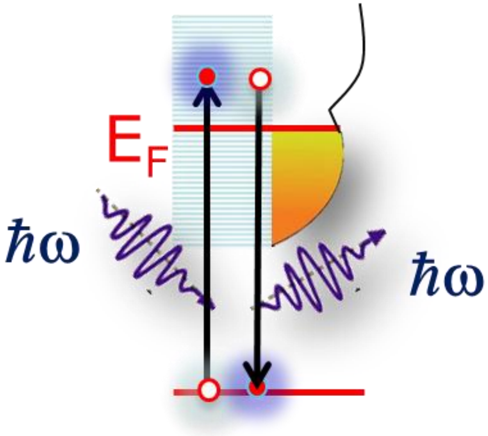


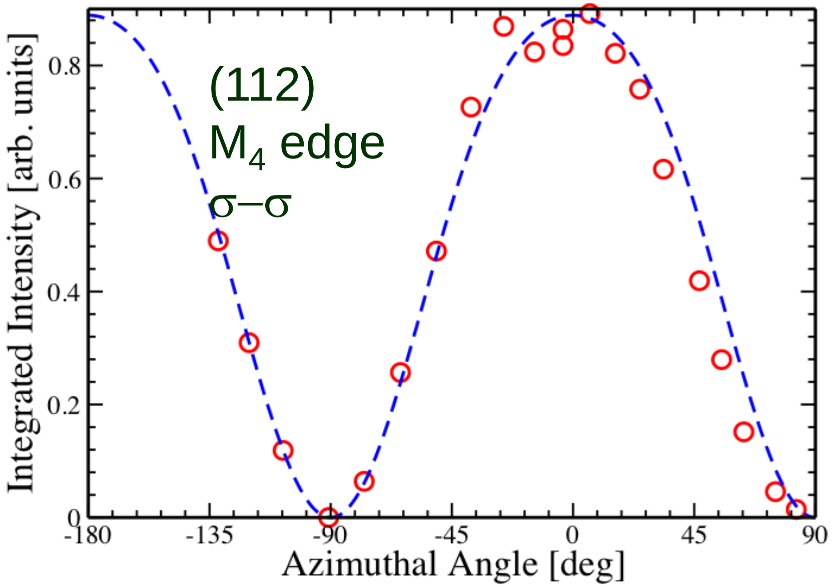


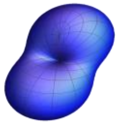
Long-range order of electric quadrupoles in UO_2

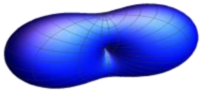
Roberto.Caciuffo@ec.europa.eu

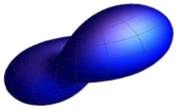
RXS experiments provide direct evidence for the ordering of electric quadrupole moments in UO_2 below T_N

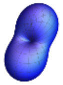
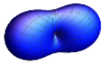
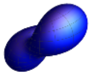


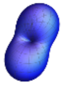
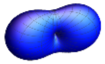
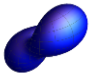


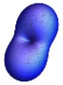
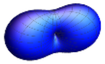
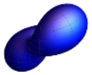
Q_{yz} = 

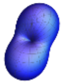
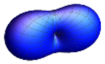
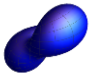
Q_{zx} = 

Q_{xy} = 

(0, 0, 0) <Q> = +  +  + 

(0, 1/2, 1/2) <Q> = -  +  - 

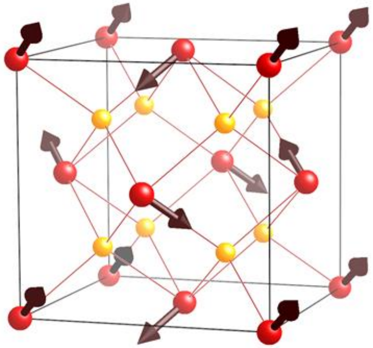
(1/2, 0, 1/2) <Q> = -  -  + 

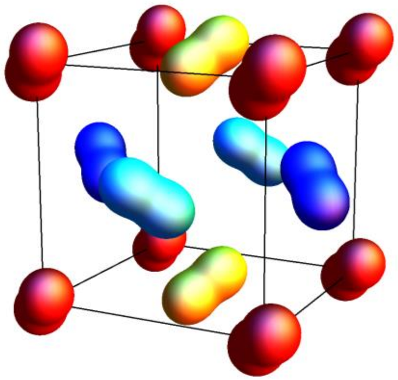
(1/2, 1/2, 0) <Q> = +  -  - 

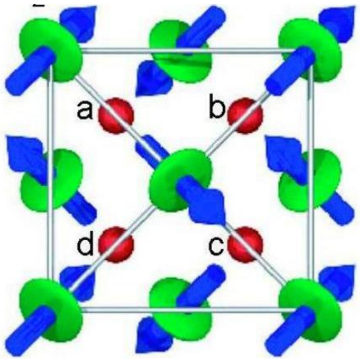
Long-range order of electric quadrupoles in UO_2

Roberto.Caciuffo@ec.europa.eu

3-k transverse AF order of magnetic dipoles and Γ_5 e-quadrupoles





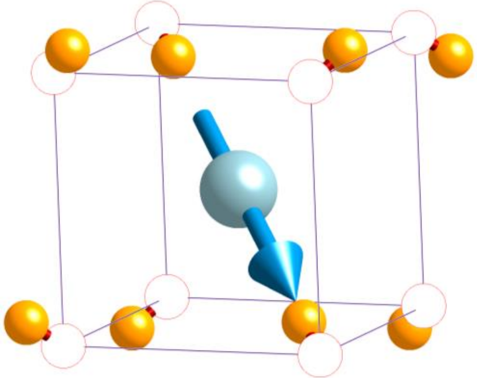


U point group: C_{2h}

U sublattice: simple cubic;

4 atoms in the base

Static 3-k J-T distortion of the oxygen sublattice

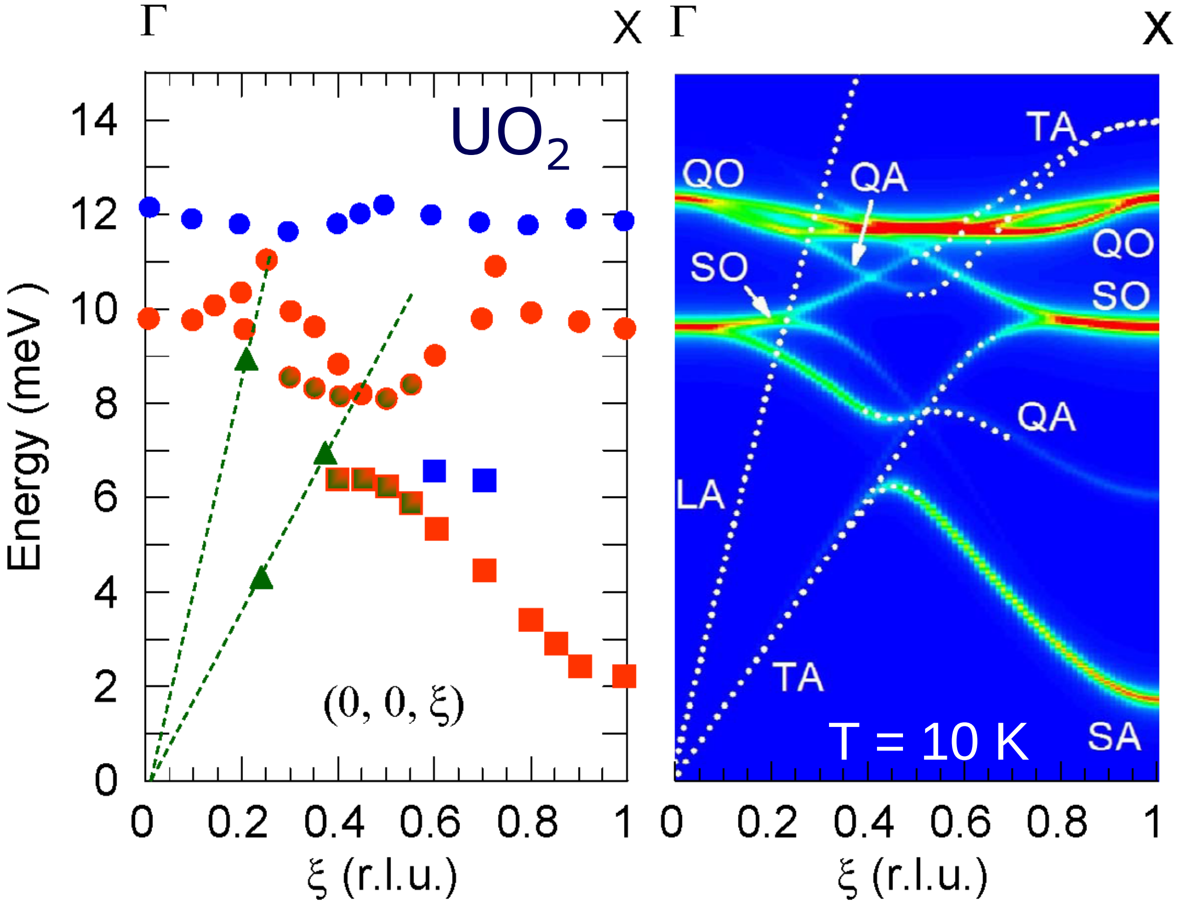


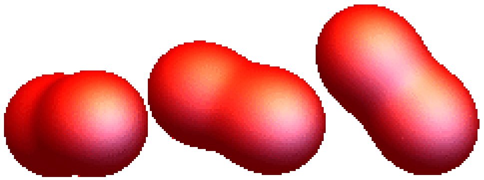
Non-magnetic Space Group: Pa3

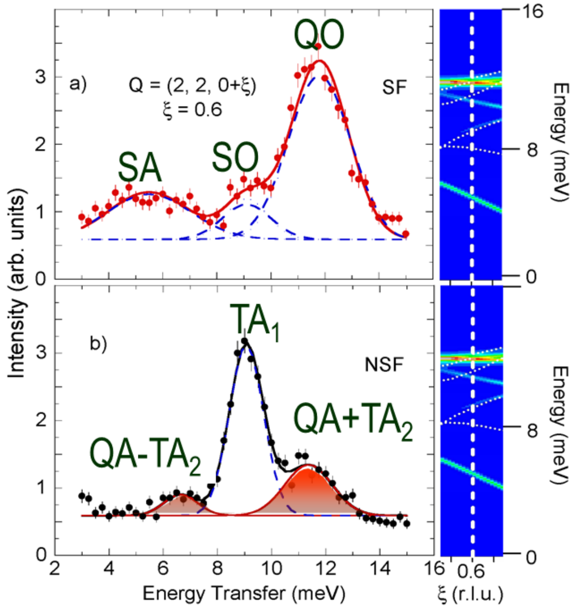
Magnetic Space Group: Pa3’

Low-T lattice dynamics

Roberto.Caciuffo@ec.europa.eu







Avoided crossings due to magnon-phonon interactions mediated by quadrupoles.

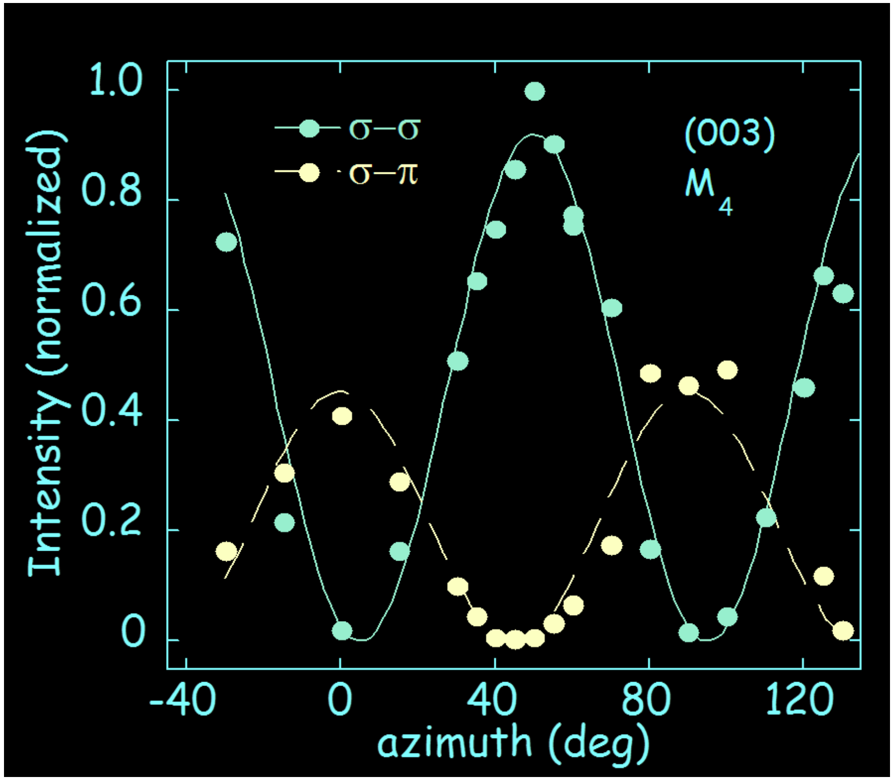
Quadrupolar waves.

Triakontadipole order in NpO_2

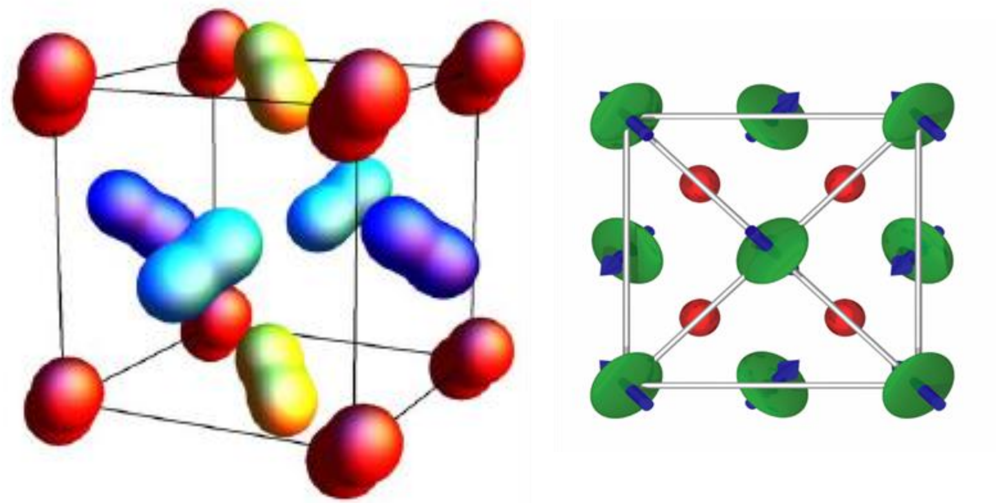
Roberto.Caciuffo@ec.europa.eu

Γ_8 quartet ground state

Resonant X-Ray scattering



Longitudinal 3-k structure



Secondary OP: 2^2 electric multipoles

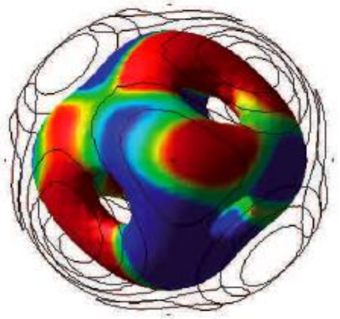
Zero magnetic dipole moment

No crystal distortions:

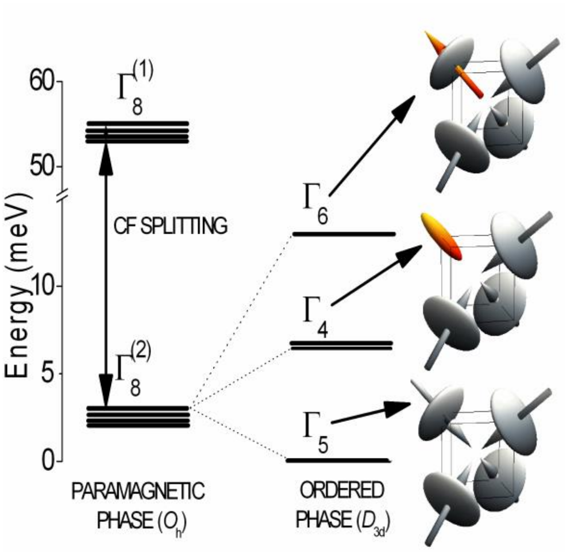
Same atomic positions as in the CaF_2 structure, but different Point Symmetry

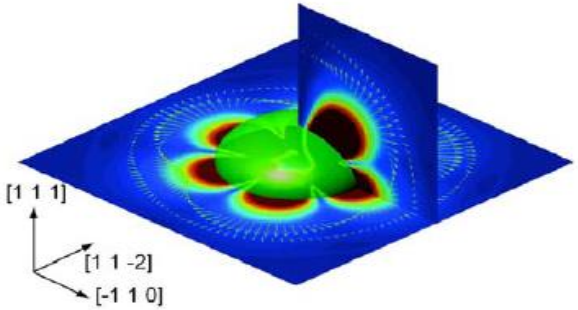
Triakontadipole order in NpO$_2$

Roberto.Caciuffo@ec.europa.eu

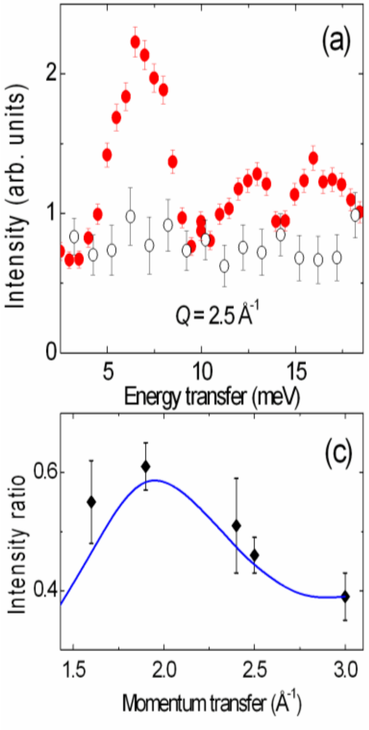


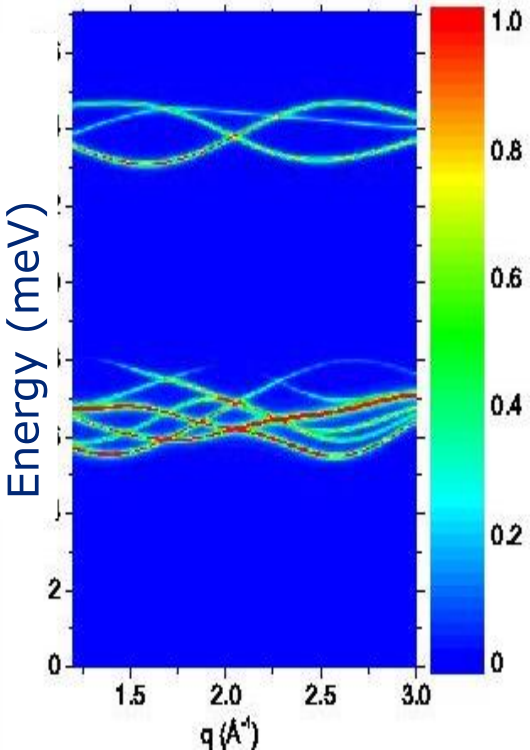
Primary OP: 2^5 magnetic multipoles





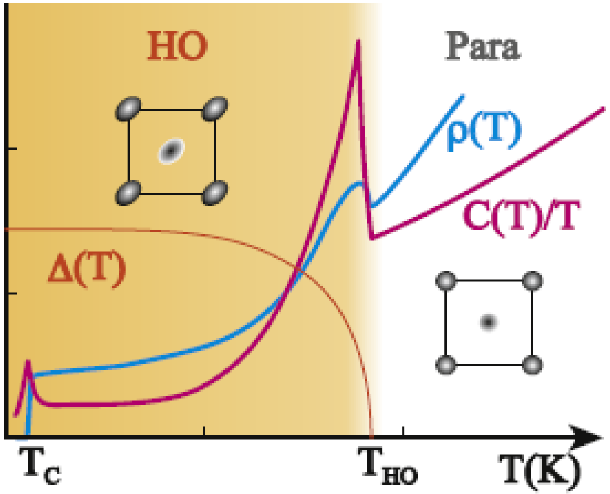
Magnetic field distribution around a Np ion

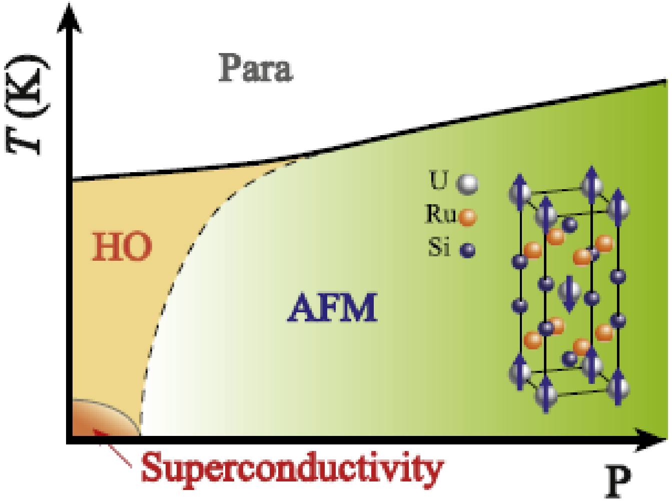


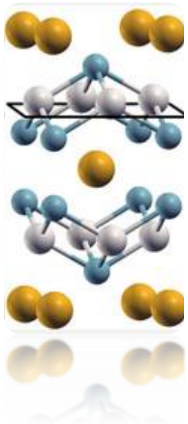


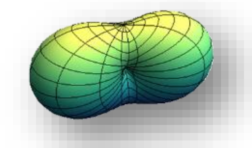
Hidden order in URu_2Si_2

Roberto.Caciuffo@ec.europa.eu

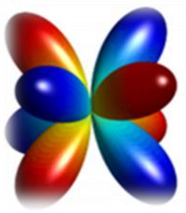




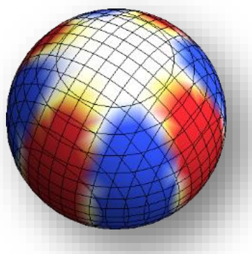




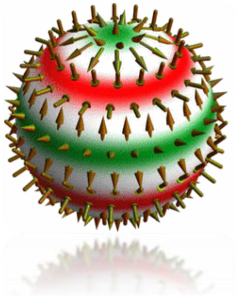
quadrupoles



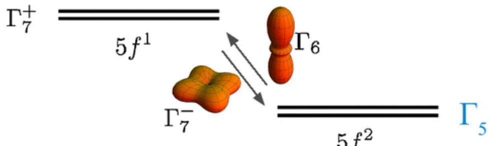
octupoles

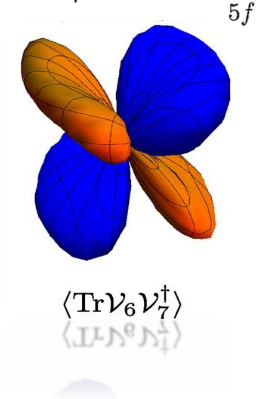


hexadecapoles

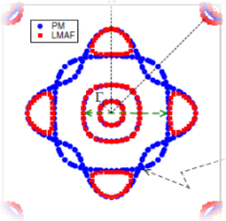


triakontadipoles





Broken single+double time-reversal and Ising quasi-particles

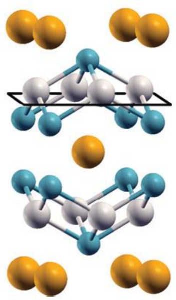


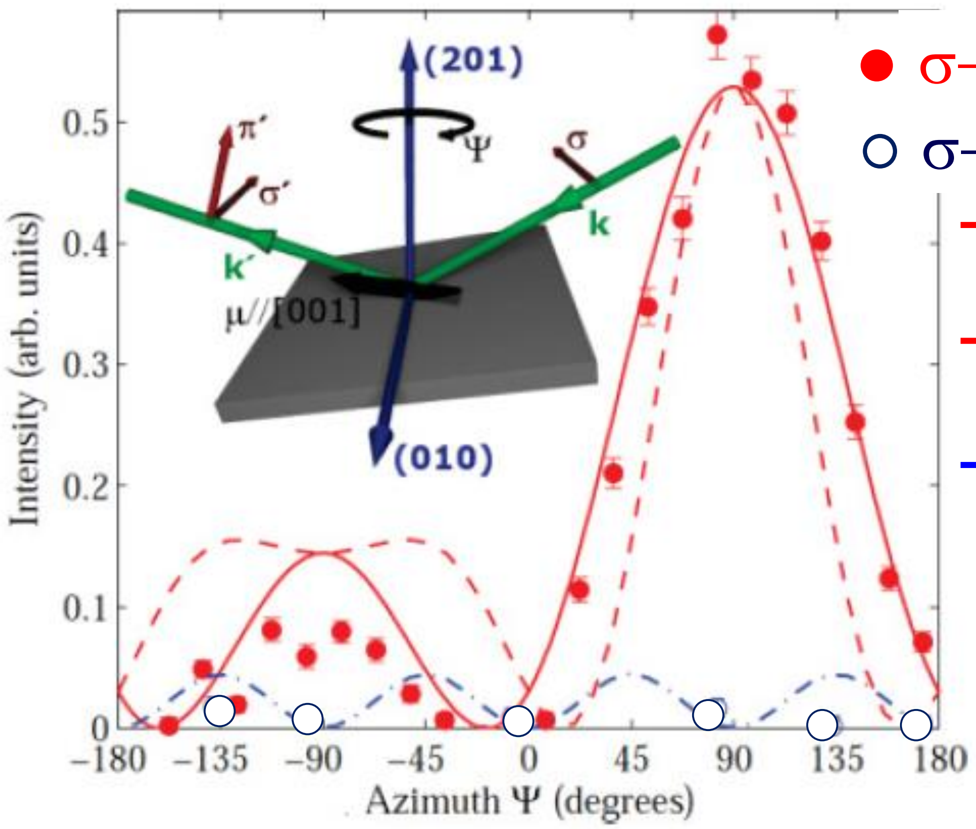
Fermi surface reconstruction and dynamical symmetry breaking

Hidden order in URu_2Si_2

Roberto.Caciuffo@ec.europa.eu

Search for electric quadrupole order





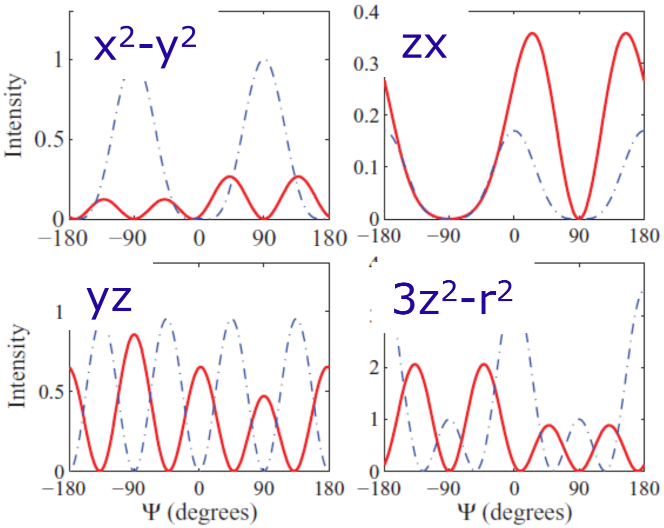
● σ–π

○ σ–σ

——— σ–π dipoles ∥ [001]

- - - - - σ–π Q_{xy} quadrupoles

- - - - - σ–σ Q_{xy} quadrupoles

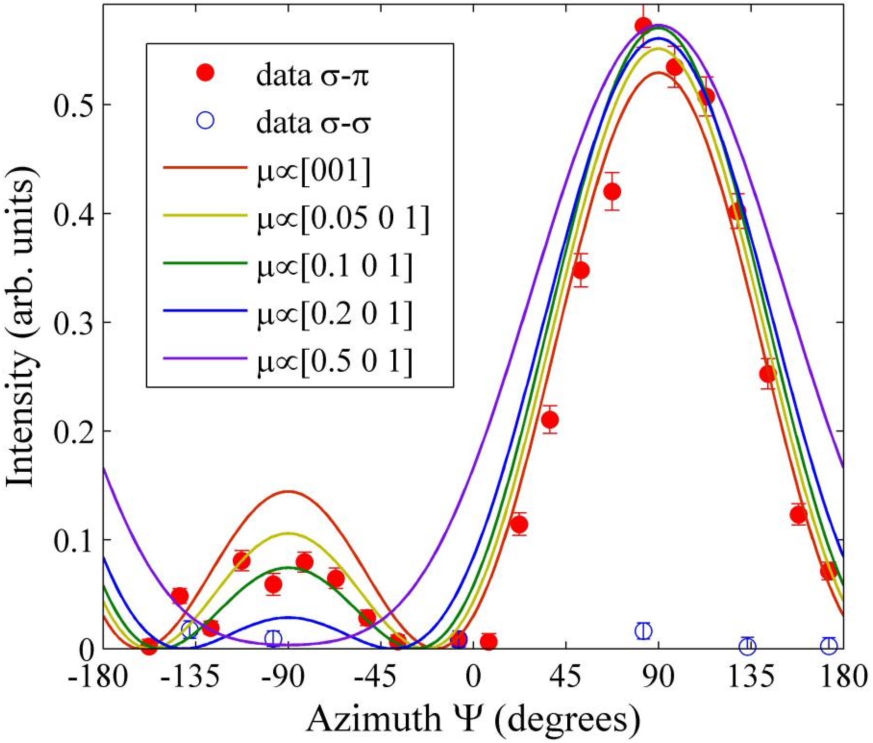


Hidden order in URu_2Si_2

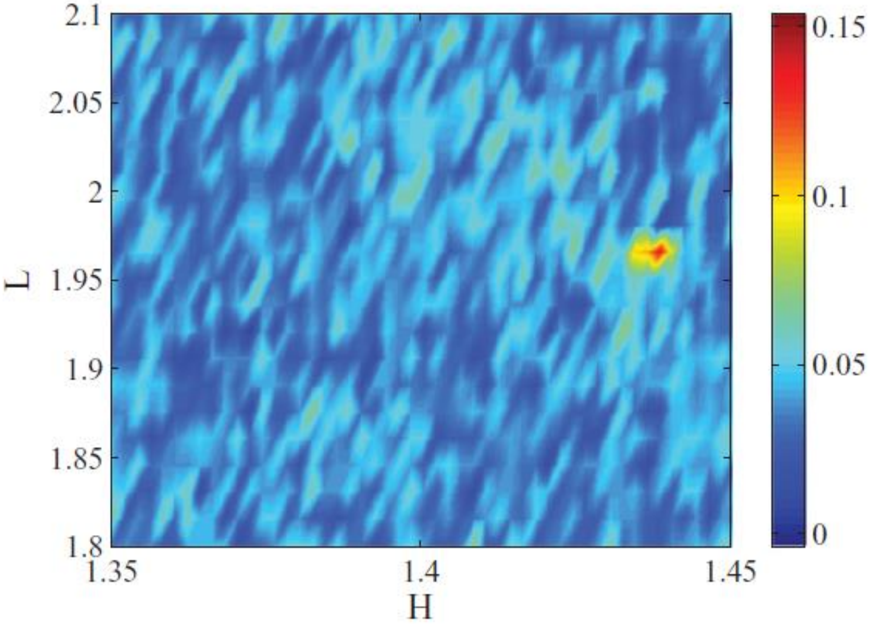
Roberto.Caciuffo@ec.europa.eu

a-b component of the ordered magnetic dipole moment

$$\mu = 0.03 \times (h, 0, 1)\ \mu_B$$



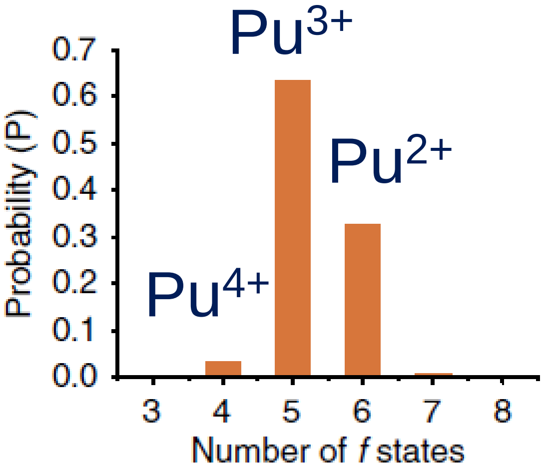
incommensurate quadrupole order



The plutonium magnetic conundrum

Experiments find no static magnetism in δ-Pu.

LDA + Exact Diagonalization of an impurity Anderson model suggests that Pu has an intermediate-valence state $\langle n_{5f} \rangle = 5.21$.
Similar results from DMFT.

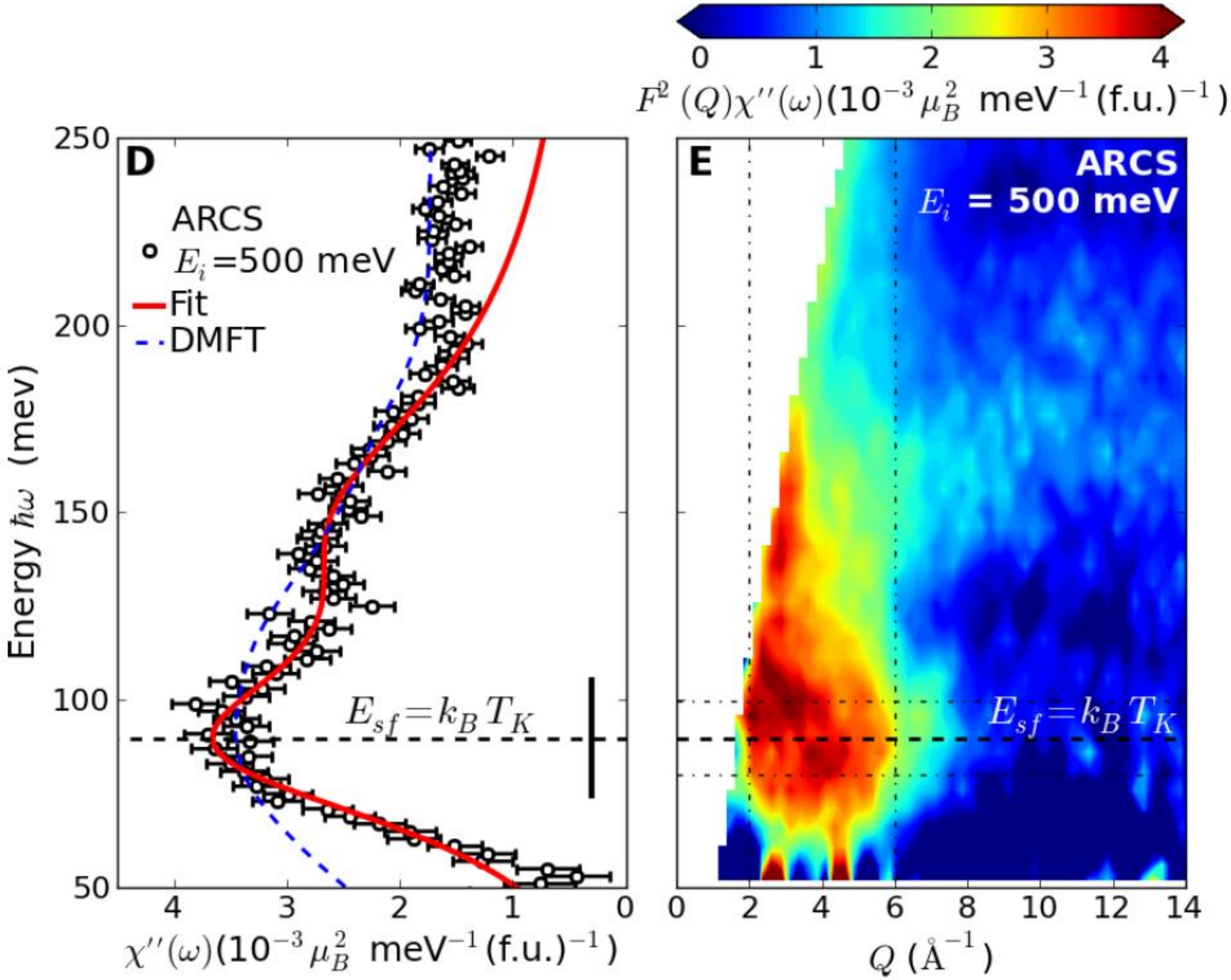


The hybridized ground state of the impurity is a nonmagnetic singlet (S = L = J = 0)

The 5f shell magnetic moment fluctuates in time because of the intermediate valence, but is dynamically compensated by the moment of the conduction electron bath

The plutonium magnetic conundrum

Roberto.Caciuffo@ec.europa.eu



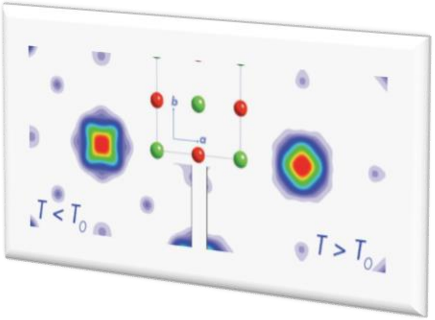
Janoschek et al., 2015

Observation of magnetic fluctuations centred around 84 meV in agreement with theory.

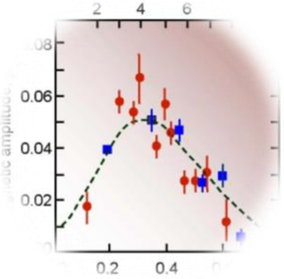
Actinide Research with neutrons and hard synchrotron radiation

Roberto.Caciuffo@ec.europa.eu

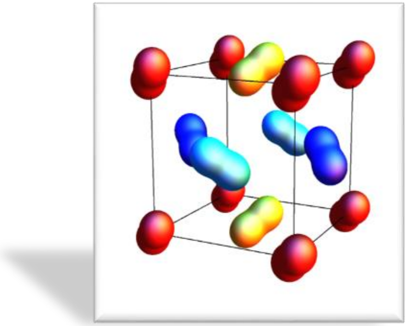
Magnetic structures and spin-density distributions



Collective excitations



Spin and orbital moments



Multipolar order

Oxidation states and mixed valence

Valence electron excitations

Core electrons excitations