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A series of radioactive metallic elements in Group 3 of the periodic table including the 14 elements with atomic numbers 90 through 103.
As the atomic number increases in the series, added electrons enter the highly anisotropic 5f electron orbitals.

\[ \begin{align*} 
5fy^3 & \quad 5fx^3 & \quad 5fz^3 \\
5fx(z^2-y^2) & \quad 5fy(z^2-x^2) & \quad 5fz(x^2-y^2) \\
5fxyz & 
\end{align*} \]
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.
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

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

\[ ^{238}_{92} U + ^{1}_{0} n \rightarrow ^{239}_{92} U \rightarrow ^{239}_{93} Np \quad \text{23.5 min} \]

Neptunium

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

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

\[ ^{239}_{93} Np \rightarrow ^{239}_{94} Pu \quad \text{2.365 d} \]
• Actinides: the backbone of nuclear fission technologies

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

Tendency to form magnetic moments

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

P. Coleman
Narrow bands and large spin-orbit interaction

Decreasing width of dominant electron-energy band:

- Itinerant electrons (K, Al...) conventional superconductivity
- 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

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

Transition from itinerancy to localization
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

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

<table>
<thead>
<tr>
<th>Element</th>
<th>4f</th>
<th>5f</th>
<th>3d</th>
<th>4d</th>
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<tr>
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<td>Nd</td>
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<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cu</td>
</tr>
</tbody>
</table>

Increasing localization

Low temperature Superconductors

Smith and Kmetko (1983)

Magnetism
Electron physics of the actinides

Fe-based SC

Increasing localization

Low temperature Superconductors

Superconductivity
cuprates

Smith and Kmetko (1983)
Electron physics of the actinides

PuCoGa$_5$

Increasing localization

Unconventional heavy-fermion SC
Hidden order

URu$_2$Si$_2$

Smith and Knetko (1983)
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
Conventional “state of the art” DFT theory fails in describing in detail actinide materials.

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.
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

\[ \frac{2\langle \vec{\ell} \cdot \vec{s} \rangle}{3n_h} = -\frac{5}{2} \left( B - \frac{3}{5} \right) + \Delta \]
X-ray Magnetic Circular Dichroism

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

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

\[ T = \sum_i [s_i - 3r_i(r_i \cdot s_i)/r_i^2] \]

\[ \frac{3\langle T_z \rangle}{\langle S_z \rangle} \]

\(<T_z>\) 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

- Linearly polarised photons
- Elastic scattering
- Resonant anisotropic contributions to the x-ray susceptibility tensor
RXS experiments provide direct evidence for the ordering of electric quadrupole moments in UO$_2$ below $T_N$.

$Q_{yz} =$

$Q_{zx} =$

$Q_{xy} =$

$(0, 0, 0) \quad <Q> = +
\quad +
\quad +$

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

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

$(1/2, 1/2, 0) \quad <Q> = +
\quad -
\quad -$
Long-range order of electric quadrupoles in \( \text{UO}_2 \)

3-k transverse AF order of magnetic dipoles and \( \Gamma_5 \) e-quadrupoles

U point group: \( C_{2h} \)

U sublattice: simple cubic;
4 atoms in the base

Non-magnetic Space Group: Pa3

Magnetic Space Group: Pa3’
Low-T lattice dynamics

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

Quadrupolar waves.
Triakontadipole order in NpO$_2$

$\Gamma_8$ quartet ground state

Primary OP: $\nu^2$ electric multipoles

No crystal distortions: Same atomic positions as in the CaF$_2$ structure, but different Point Symmetry

Zero magnetic dipole moment

Longitudinal 3-k structure

Secondary OP: $2^2$ electric multipoles

Resonant X-Ray scattering
Triakontadipole order in NpO$_2$

Primary OP: $2^5$ magnetic multipoles

Magnetic field distribution around a Np ion
Hidden order in URu$_2$Si$_2$

- Quadrupoles
- Octupoles
- Hexadecapoles
- Triakontadipoles

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

Fermi surface reconstruction and dynamical symmetry breaking
Hidden order in URu$_2$Si$_2$

Search for electric quadrupole order

- $\sigma - \pi$
- $\sigma - \sigma$

$\sigma - \pi$ dipoles $\parallel [001]$

$\sigma - \pi$ $Q_{xy}$ quadrupoles

$\sigma - \sigma$ $Q_{xy}$ quadrupoles

Intensity (arb. units)

Azimuth $\Psi$ (degrees)

$x^2 - y^2$

$z\chi$

$yz$

$3z^2 - r^2$
Hidden order in URu$_2$Si$_2$

a-b component of the ordered magnetic dipole moment

$$\mu = 0.03 \times (h, 0, 1) \mu_B$$
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The plutonium magnetic conundrum

Experiments find no static magnetism in $\delta$-Pu.

LDA + Exact Diagonalization of an impurity Anderson model suggests that Pu has an intermediate-valence state $<n_{5f}> = 5.21$. 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.
Observation of magnetic fluctuations centred around 84 meV in agreement with theory.

Jánoschek et al., 2015
Actinide Research with neutrons and hard synchrotron radiation

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