Light actinides – Magnetism and electron spectroscopy

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Actinides – 5f systems (analogy with lanthanides – 4f)
Seaborg (1945)

<table>
<thead>
<tr>
<th>5f</th>
<th>(Ra)</th>
<th>5f</th>
<th>(Xe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>6d(^1) 7s(^2)</td>
<td>La</td>
<td>5d(^1) 6s(^2)</td>
</tr>
<tr>
<td>Th</td>
<td>6d(^2) 7s(^2)</td>
<td>Ce</td>
<td>4f(^1) 5d(^1) 6s(^2)</td>
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<tr>
<td>Pa</td>
<td>5f(^2) 6d(^1) 7s(^2)</td>
<td>Pr</td>
<td>4f(^3) 6s(^2)</td>
</tr>
<tr>
<td>U</td>
<td>5f(^3) 6d(^1) 7s(^2)</td>
<td>Nd</td>
<td>4f(^4) 6s(^2)</td>
</tr>
<tr>
<td>Np</td>
<td>5f(^4) 6d(^1) 7s(^2)</td>
<td>Pm</td>
<td>4f(^5) 6s(^2)</td>
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<tr>
<td>Pu</td>
<td>5f(^6) 7s(^2)</td>
<td>Sm</td>
<td>4f(^6) 6s(^2)</td>
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<tr>
<td>Am</td>
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<td>Eu</td>
<td>4f(^7) 6s(^2)</td>
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<tr>
<td>Cm</td>
<td>5f(^7) 6d(^1) 7s(^2)</td>
<td>Gd</td>
<td>4f(^7) 5d(^1) 6s(^2)</td>
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<tr>
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<td>5f(^9) 7s(^2)</td>
<td>Tb</td>
<td>4f(^9) 6s(^2)</td>
</tr>
<tr>
<td>Cf</td>
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<td>Dy</td>
<td>4f(^{10}) 6s(^2)</td>
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<td>Es</td>
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<td>Ho</td>
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<tr>
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<td>5f(^{12}) 7s(^2)</td>
<td>Er</td>
<td>4f(^{12}) 6s(^2)</td>
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<tr>
<td>Md</td>
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<td>Tm</td>
<td>4f(^{13}) 6s(^2)</td>
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<tr>
<td>No</td>
<td>5f(^{14}) 7s(^2)</td>
<td>Yb</td>
<td>4f(^{14}) 6s(^2)</td>
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<tr>
<td>Lr</td>
<td>5f(^{14}) 7p(^\ast) 7s(^2)</td>
<td>Lu</td>
<td>4f(^{14}) 5d(^1) 6s(^2)</td>
</tr>
</tbody>
</table>

Larger extent (towards 3d)  Small extent of the 4f states
Participation in bonding reflects in atomic radii and crystal structures.
Overview of essential properties of elemental actinides, summarizing available data on the \( g \)-coefficient of the low-temperature specific heat, temperature independent susceptibility \( c_0 \), Néel temperature \( T_N \), Curie temperature \( T_C \), and paramagnetic Curie temperature \( \Theta_p \).

<table>
<thead>
<tr>
<th>Element</th>
<th>( \gamma ) (mJ/mol K(^2))</th>
<th>( \chi_0 ) (10(^{-8}) m(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>4</td>
<td>0.12</td>
</tr>
<tr>
<td>Pa</td>
<td>6.6</td>
<td>0.34</td>
</tr>
<tr>
<td>U</td>
<td>10</td>
<td>0.48</td>
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<tr>
<td>Np</td>
<td>14</td>
<td>0.68</td>
</tr>
<tr>
<td>Pu</td>
<td>22</td>
<td>0.64</td>
</tr>
<tr>
<td>Am.....</td>
<td>2...</td>
<td>0.85</td>
</tr>
</tbody>
</table>

**Pauli paramagnets** \( C_{el} = \frac{1}{3} \pi^2 N(E_F) k_B^2 T = \gamma T \)

**5f bonding**

<table>
<thead>
<tr>
<th>Element</th>
<th>( T_N ) (K)</th>
<th>( T_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm</td>
<td>64</td>
<td>51</td>
</tr>
<tr>
<td>Bk</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Cf</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Es</td>
<td>11.3 (?)</td>
<td></td>
</tr>
</tbody>
</table>

**5f localized – Hund's rules magnetic moments**

No such clear boundary in compounds. Local moments do not imply localized states.
U compounds-large variability of magnetic properties (Np, Pu parallels)
On-magnetic behaviour due to CEF?? NO.
High \( \gamma \) means 5f states at \( E_F \).
In compounds – no simple borderline
Local moment does not imply localized 5f states
Uranium compounds – large variety of magnetic properties
(Np, Pu – parallel)

CEF? No – weak paramagnets – low γ
Approaching magnetic ordering (spin fluctuations)
γ-enhancement

5f band intersected by $E_F$
5f-5f overlap ....... U-U spacing
Hill criterion – 340-360 pm

Superconducting  
Magnetic

α-U
$U_2$Mn, $U_2$Fe, $U_2$Co, $U_2$Ni
$T_c < 3.7$ K

$U_3$Ir
$U_3$Si$_2$

UPt, UIr – Ferro
UFe$_2$, UNi$_2$ (Laves ph.) – Ferro
UGa$_2$ – Ferro
UGa$_3$, UIn$_3$, UPt$_3$ AF
UPd$_3$
$UCu_5$
$U_2$Zn$_{17}$, UBe$_{13}$
SC + AF $U_{MgA}$
SC + F $UR_{GaGe}$
Fig. 3. Calculated DOS and projected DOS of UFeGe.
Strong spin-orbit interaction in actinides - orbital moments induced even in systems of itinerant electrons

Implications for relation of bonding directions and easy magnetization directions

The compression of the 5f charge towards the bonding directions

Population of the states with orbital moment perpendicular

Easy axis anisotropy for planar bonding

Hybridization

Easy-plane anisotropy for columnar bonding

Strong bonding directions often coincide with the shortest U-U links

Two-ion anisotropy
(CEF \rightarrow single ion anisotropy)

The same distinct type of anisotropy in paramagnetic and ordered state

Estimate:
- from intercept of hard- and easy-axis magnetization $10^2 - 10^3$ T
- from difference of respective paramagnetic Curie temperatures $10^2 - 10^3$ K

(similarity to monoatomic layers)

Electronic and magnetic structure strongly interconnected \rightarrow any change of magnetic structure induces strong Fermi surface reconstruction (even if moments do not change much)
II. MAGNETIC ORDERING AND ELECTRICAL RESISTIVITY

Metallic materials with atoms carrying magnetic moments:

\[ \rho = \rho_0 + \rho_{\text{ph}} + \rho_{\text{pd}} \]

Below magnetic ordering temperature:

- in simple ferromagnets \( \rho_{\text{pd}} \to 0 \) with \( T \to 0 \)
  (and since \( \rho_{\text{ph}} \to 0 \), as well) \( \Rightarrow \)
  \[ \rho \to \rho_0 \]
- in other magnetic structures
  (especially in antiferromagnets)
  often:
  \[ \rho > \rho_0 \text{ or even } \rho >> \rho_0 \]

1) R.J. Elliot and F.A. Wedgwood (1963)

Fermi level gauging
- crystallographic \( \rightarrow \) magnetic
- periodicity

\[ \rho = \frac{S_0 + S_{\text{ph}} + S_{\text{pd}}}{1 - g_m(T)} \]

2) Spin dependent scattering
Other approach – LSD calculations ab initio, total energy, orbital polarization, ASW (Sandrauskil and Kähler) U\textsubscript{3}Pd\textsubscript{5}Sn

L and S need not be necessarily collinear

Narrow 5f-band system

One-band Hubbard model:
- Intratomic Coulomb interaction U
- Band width

Minimum 2 bands + hybridization

decay of magnetism - monotonous decay of $T_C$ and $\mu$
(e.g. as a function of pressure)

unrealistic

Moment washout

Exchange coupling non-monotonous
In most of cases – U moment vanishes in the dilution limit
Exception - 0.3% U in gold (Hillebrecht, Sechovsky) – XPS, susceptibility

Amitsuka – diluted heavy fermions

YRu$_2$Si$_2$ – U .......... Kondo
ThRu$_2$Si$_2$ – U .......... local moment
ThPd$_2$Si$_2$ – U .......... local moment
\[ \Delta E_{\text{kin}} = N(E_F)(\delta E)^2 \]
\[ \Delta E_{\text{int}} = -U[N(E_F)(\delta E)]^2 \]

Stoner criterion
\[ U N(E_F) \geq 1 \ldots \text{spontaneous splitting} \]

magnetic field can help to bring up to instability
Local probes

- Neutron diffraction
  Analysis of form factor in high-field state
  in $B = 1\, \text{T}$: $\mu_L = 0.60\, \mu_B$, $\mu_S = -0.28\, \mu_B$, $\mu_{Co} = 0.06\, \mu_B$
  in $B = 8\, \text{T}$: $\mu_L = 0.79\, \mu_B$, $\mu_S = -0.40\, \mu_B$, $\mu_{Co} = 0.07\, \mu_B$
  Javorsky et al. 2002

- NMR
  Decrease of the spin-lattice relaxation time $1/T_1$ at the metamagnetic transition (on Co)
  Iwamoto et al. 2001
Critical field $B_c$ of metamagnetic transition vs squared temperature for fixed powders of Ni-substituted alloys under ambient pressure. The lowest curve is for UCoAl single crystal along the c axis.
Magnetization isotherms of fixed powders of UCoAl-based alloys with 1% substitutions at 4.2 K under ambient pressure.
Critical point – minimization of free energy $F = U - T^S$

Increase of entropy due to thermal fluctuations

Decay of magnetism due to other ‘control’ parameter $\xi$ (concentration, pressure)

If $T_C \to 0$, quantum fluctuations start to be important

Hubbard Hamiltonian

\[ \hat{H} = \sum_\xi \epsilon_\xi c_\xi^\dagger c_\xi + \sum_\xi \xi_\text{Hubb} n_\xi \]

Quantum fluctuations at the critical point adding extra degrees of freedom – like extra dimensions, depending on propagation and damping of magnetic fluctuations

Non-Fermi liquid behaviour

Landau Fermi liquid theory

\[ FL - C = \gamma T \]

\[ \rho \sim T^2 \quad \rho \sim T^{2/3} \quad NFI \]

\[ T^{3/2} \quad AF \]
Effects of pressure

\[ M(\mu_B/\text{U-atom}) \]

\[ H \parallel c\text{-axis} \]
\[ T = 4.2 \text{ K} \]

\[ U_{0.9}\text{Co}_{1.05}\text{Al}_{1.05} \]

\[ M(\mu_B/\text{U-atom}) \]

\[ H \parallel c\text{-axis} \]
\[ T = 4.2 \text{ K} \]

\[ U_{1.1}\text{Co}_{0.98}\text{Fe}_{0.02}\text{Al} \]

Magnetization isotherms of alloy with 2% Fe measured on fixed powder under several pressures at 4.2 K (top). Bottom: field dependence of differential susceptibility dM/dB.
These things are not really new – theory of weak itinerant ferromagnetism.

Mathon 1968 \( \rho = bT^{6/3} \ldots ZrZn_{2}, TiBe_{2}, Ni_{3}Al \)

Selfconsistent spin fluctuation theory – Moriya, Ueda 1970-90

AF \( n = 3/2 \) \((a \text{ is diverging})\)

Mishra and Sreeram PRB 1998 \( n \) decreases with decreasing dimensionality

Band metamagnetism \( YCo_{2} \)

Theories –
1. Spin fluctuations – Landau Ginzburg; free energy expansion including \( M^{2} \) term (Yamada)
2. Two competing states, one with zero spontaneous magnetization

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![Diagram](image-url)
Rule of magnetovolume effects in itinerant systems

\[ \Delta V \propto M_s^2 \]

In UCoAl

\[ \Delta a / a \propto (\Delta M)^2 \]

\[ \Delta M = \Delta M_0 - k\delta a \]

\[ \text{i.e. not } \delta p, \text{ or } \delta V \]

Critical pressure to suppress metamagnetism – about 60-70 kbar

Landau-Ginzburg theory

\[ F = a M^2 + b M^4 + c M^6 \]

\[ b < 0, a > 0, c > 0 \]

Yamada – extended the Moriya SF theory

\[ 1/\chi(T) = a + 5/3b \xi(T)^2 + 35/9c \xi(T)^4 \]

\[ \xi(T)^2 \] – mean square amplitude of spin fluct.

- increases with increasing T

archetypal band metamagnet YCo₂

\[ B_s = 70 \ T \]
Models

- Yamada theory extended to uniaxial case (but needs still the 6th order term on the free energy expansion series)
- Takahashi-Sakai two different phases, each without the 6th order term. Both with spin fluctuations, one with zero-point SF. The high-field state equivalent to Ferro state (linear Arrott plots above the transition)
- But none explains so far the NFL behaviour

Plutonium
An element at odds with itself

Plutonium is a physicist's dream but an engineer's nightmare. With little provocation, the metal changes its density by as much as 25 percent. It can be as brittle as glass or as malleable as aluminum; it expands when it solidifies—mush like water freezing to ice; and its shiny, silvery, finely machined surface will tarnish in minutes. It is highly reactive in air and strongly reducing in solution, forming multiple compounds and complexes in the environment and during chemical processing. It transmutes by radioactive decay, causing damage to its crystaline lattice and leaving behind tellurium, americium, americium, neptunium, and other impurities. Plutonium damages materials on contact and is therefore difficult to handle, store, or transport. Only physicists would ever dream of making and using such a material. And they did make it—in order to take advantage of the extraordinary nuclear properties of plutonium-239.

Plutonium, the Most Complex Metal

Plutonium, the sixth member of the actinide series, is a metal, and like other metals, it conducts electricity (albeit quite poorly), is electropositive, and dissolves in mineral acids. It is extremely dense—more than twice as dense as iron—and as it is heated, it begins to show its incredible sensitivity to temperature, undergoing dramatic length changes equivalent to density changes of more than 20 percent.
Background information - Th to Pu just plain band picture

J. Naegele, 1980s
of states is found to be contained in a narrow region within 0.5 eV of the Fermi energy (similar to uranium results). This result is clearly at odds with experiment and attests to the notion that at least some of the 5f electrons are localized.

The α-platinum calculation and measured spectrum are compared in Figure 1(c). Some puzzling problems become evident because the sharp structure near $E_F$ clearly observed experimentally, is not well reproduced in an unconstrained GGA calculation. Conventional wisdom states that α-platinum is much like a transition metal with conventional bands. A sharp peak at the Fermi energy would suggest that even this transition-like material exhibits strong correlation effects. But the sharp features in the α-platinum spectrum occur at 100 meV below $E_F$ and therefore calls into question the correlation effects. Moreover, one would not anticipate electron-electron correlations in a system with a temperature-independent susceptibility as well as a densely packed crystal structure, in which direct f-f overlap is possible. Nonetheless, we must recall that α-platinum's 4f core levels show satellite behavior similar to, yet not as intense as, that in δ-platinum. Perhaps correlation phenomena are important in spite of the 5f maximum occurring at 100 meV below $E_F$. A reasonable calculational approach for α-platinum might be one of renormalized bands, in which the Hubbard Hamiltonian is introduced as a perturbation on GGA-derived bands. Variation of the Coulomb correlation energy introduction $U$ controls the strength of the electron-electron correlations. This approach may solve the problem for α-platinum but is more problematic for δ-platinum, whose GGA-calculated bands are too narrow compared with experiment. The structure at 1 eV may not be reproduced by renormalization.
**α-Pu surface prepared at various temperatures**

![Graph showing binding energy vs. intensity for different temperatures.]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Intensity (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77 K</td>
<td>4000</td>
</tr>
<tr>
<td>423 K</td>
<td>3000</td>
</tr>
<tr>
<td>383 K</td>
<td>2000</td>
</tr>
<tr>
<td>363 K</td>
<td>1000</td>
</tr>
<tr>
<td>303 K</td>
<td>1000</td>
</tr>
</tbody>
</table>

Elucidates the discrepancies between different authors:
low-\(T\) preparation - triangular shape, no details
high-\(T\) - features of \(\delta\)-Pu

Explained by theoretical work Eriksson et al., PRB 1992. Shows that \(\delta\)-Pu should be stable at the surface of \(\alpha\)-Pu due to lower coordination.

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**Monoatomic Pu layers on Mg**

Very small intermixing of Pu and Mg

Deposition at room \(T\) - Pu islands

Deposition at approx. 100 K - nearly homogeneous coverage

- New feature at 1.7 eV - \(5f\) states - localized
- Intermediate thickness
  - 3 peaks
  - (0.85 eV, 0.5 eV, \(E_g\))
- Large thickness
  - \(\alpha\)-Pu
**Pu/Mg**
**HeII VB Study**

- Transition from itinerant to localised 5f
- In between: correlation satellites (Three peak structure)
Peak A - not pure 5f