Light actinides –

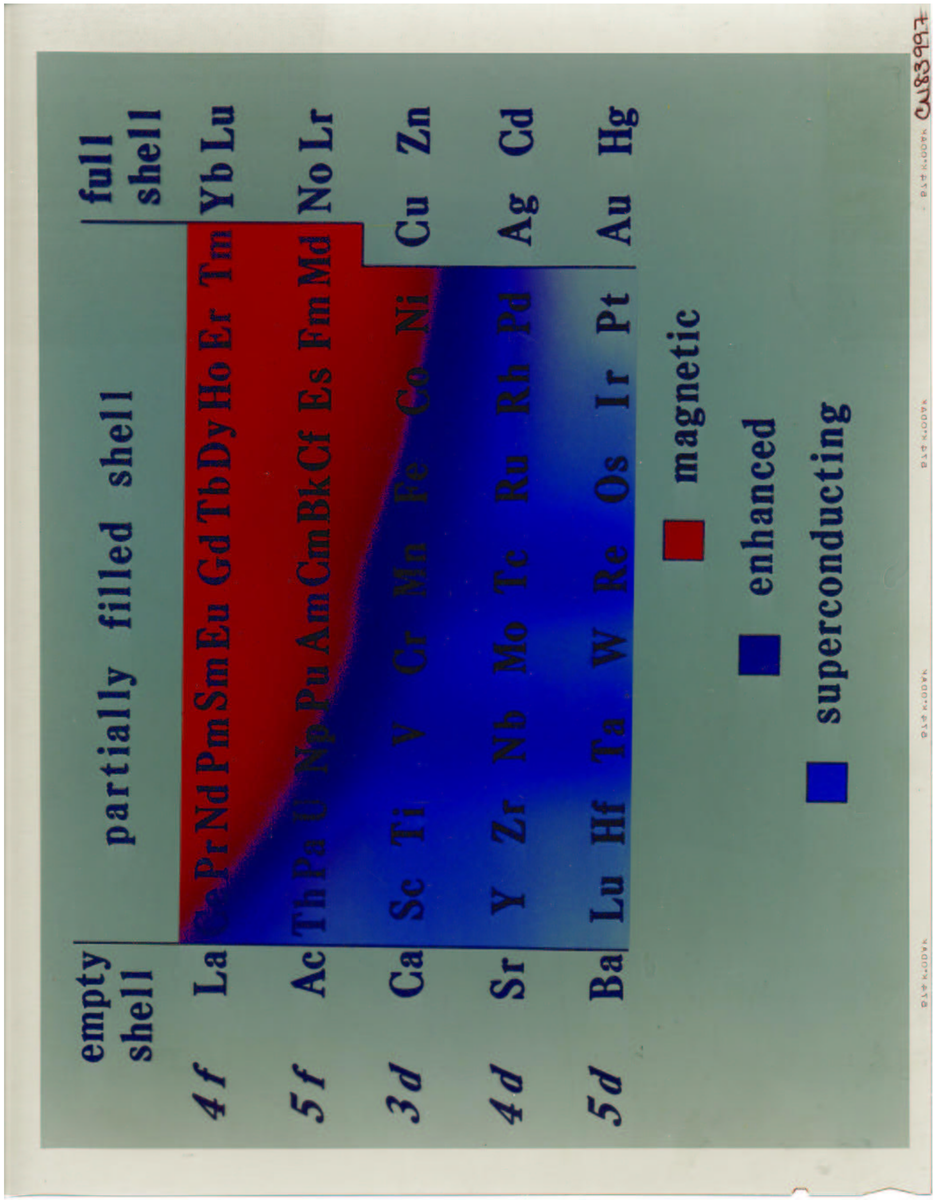
Magnetism and electron spectroscopy

L. Havela

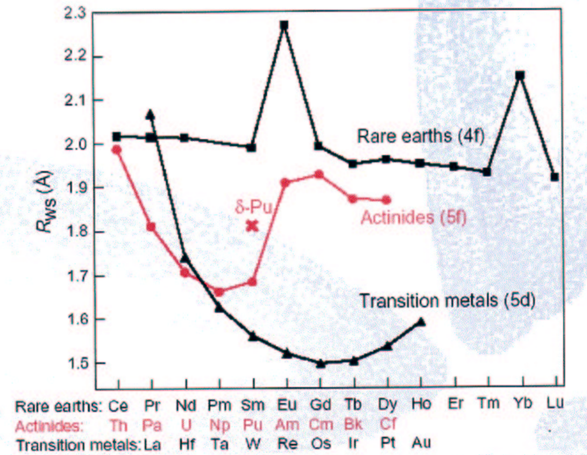
Actinides – *5f* systems (analogy with lanthanides – *4f*)
Seaborg (1945)

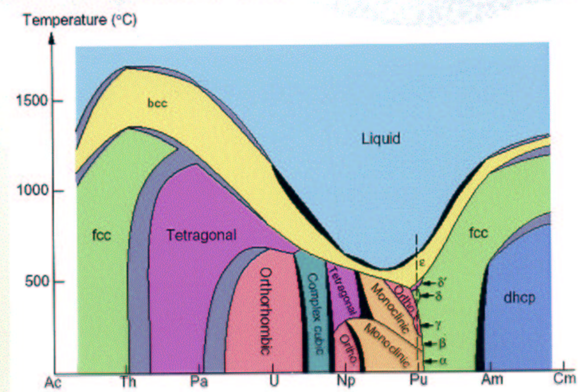
	~~4f~~ 5f	(Ra)		~~5f~~ 4f	(Xe)
Ac	$6d^1\,7s^2$		La	$5d^1\,6s^2$	
Th	$6d^2\,7s^2$		Ce	$4f^1\,5d^1\,6s^2$	
Pa	$5f^2\,6d^1\,7s^2$		Pr	$4f^3\,6s^2$	
U	$5f^3\,6d^1\,7s^2$		Nd	$4f^4\,6s^2$	
Np	$5f^4\,6d^1\,7s^2$		Pm	$4f^5\,6s^2$	
Pu	$5f^6\,7s^2$		Sm	$4f^6\,6s^2$	
Am	$5f^7\,7s^2$		Eu	$4f^7\,6s^2$	
Cm	$5f^7\,6d^1\,7s^2$		Gd	$4f^7\,5d^1\,6s^2$	
Bk	$5f^9\,7s^2$		Tb	$4f^9\,6s^2$	
Cf	$5f^{10}\,7s^2$		Dy	$4f^{10}\,6s^2$	
Es	$5f^{11}\,7s^2$		Ho	$4f^{11}\,6s^2$	
Fm	$5f^{12}\,7s^2$		Er	$4f^{12}\,6s^2$	
Md	$5f^{13}\,7s^2$		Tm	$4f^{13}\,6s^2$	
No	$5f^{14}\,7s^2$		Yb	$4f^{14}\,6s^2$	
Lr	$5f^{14}\,7p\,7s^2$		Lu	$4f^{14}\,5d^1\,6s^2$	

Larger extent (towards 3*d*) Small extent of the 4*f* 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 Θ_p.

	Th	Pa	U	Np	Pu	Am…..
γ (mJ/mol K^2)	4	6.6	10	14	22	2…….
χ_0 (10^{-8} m^3/mol)	0.12	0.34	0.48	0.68	0.64	0.85

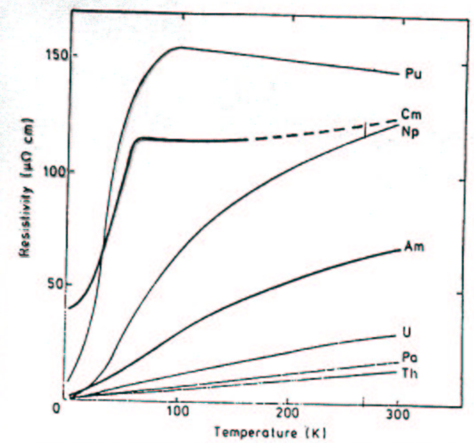
Pauli paramagnets $C_{el}= 1/3\pi^2 N(E_F)k_B{}^2T=\gamma T$

5*f* bonding

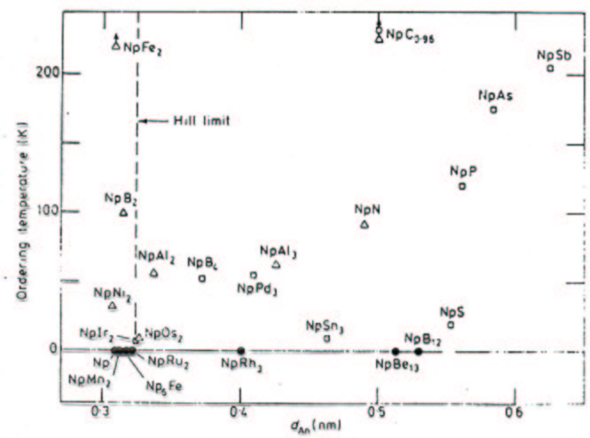
	Cm	Bk	Cf	Es
T_N (K)	64 …	34	51 (T_C)	
μ_{eff} (μ_B)	7.55	9.7	9.7	11.3 (?)

5*f* 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 γ means 5*f* states at E_F.



Electrical resistivity of pure actinides (Cm data of Schenkel (1977)).



Magnetic ordering temperatures of Np intermetallics plotted against interactinide spacing. (□) T_N; (△) T_C; (●) no ordering.

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_6Mn, U_6Fe, U_6Co, U_6Ni
$T_c < 3.7$ K

U_3Ir

U_3Si_2

UPt, UIr – *Ferro*

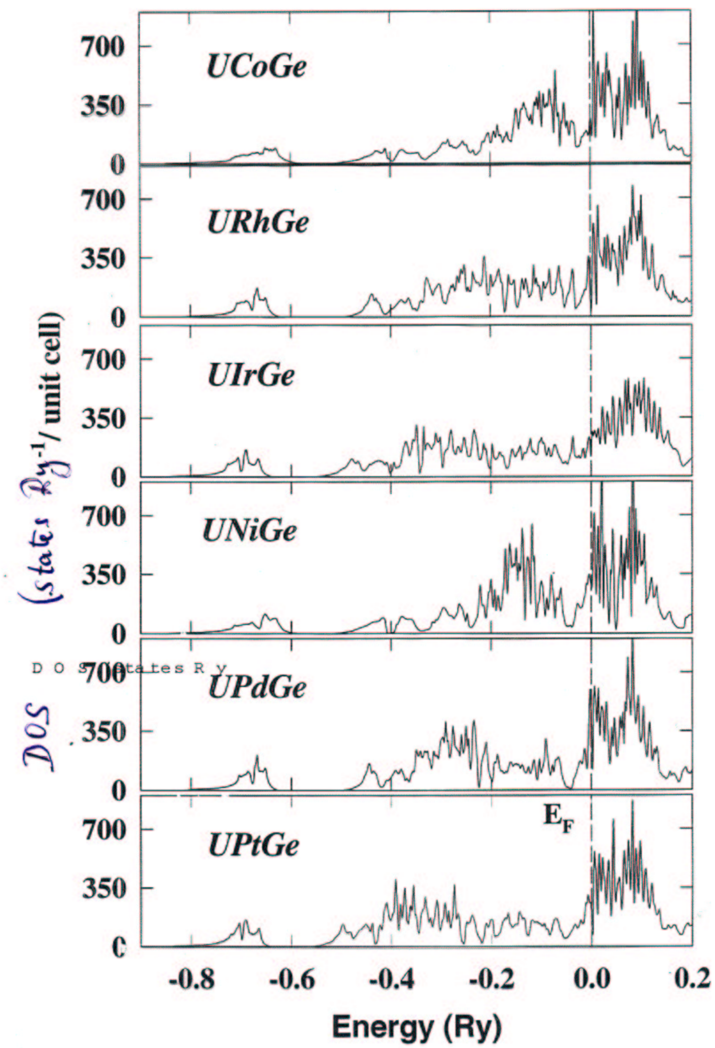
UFe_2, UNi_2 (Laves ph.) - *Ferro*

UGa_2 – *Ferro*

UGa_3, UIn_3, UPt_3 *AF*
UPd_3

UCu_5
U_2Zn_{17}, UBe_{13}

SC + AF UPd_2Al_3
SC + F URhGe



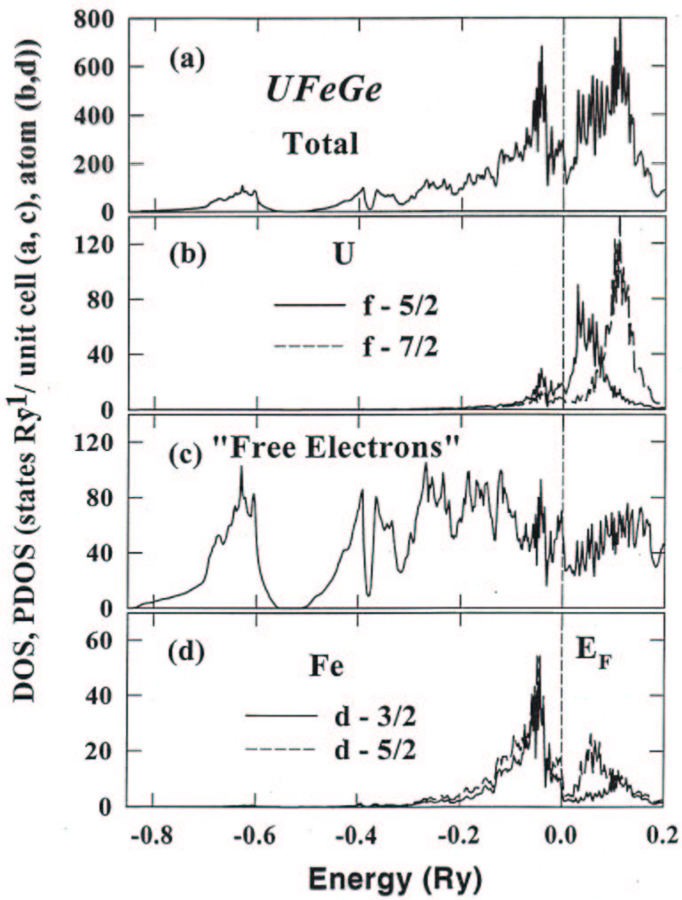
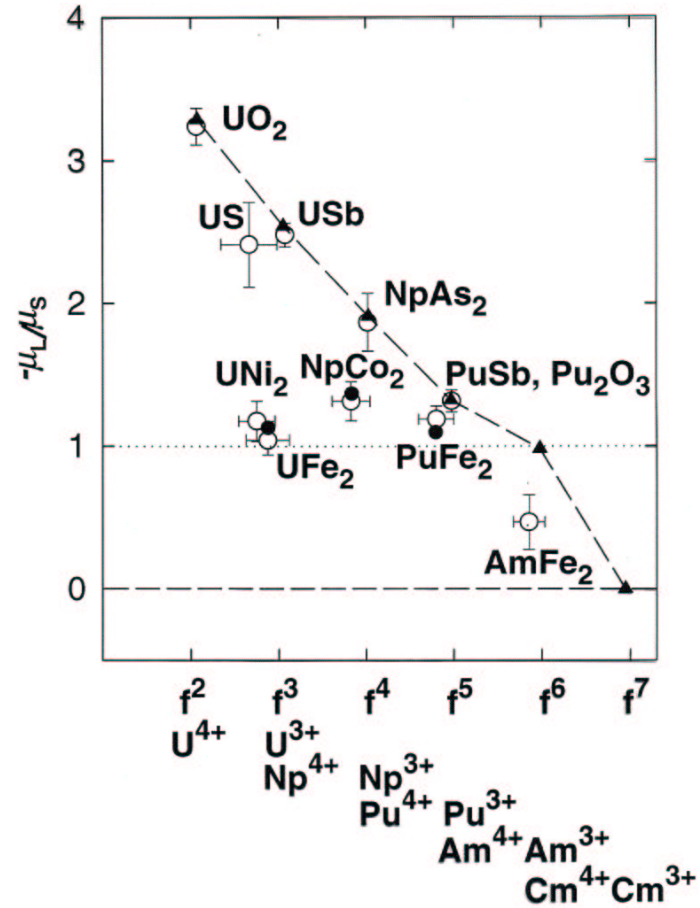


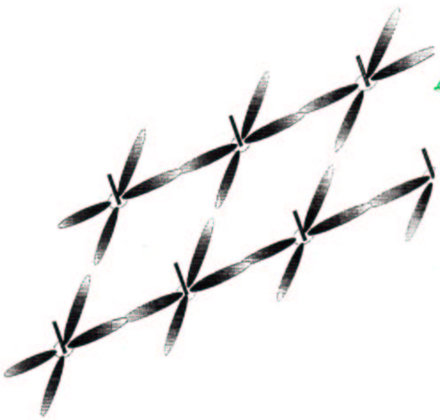
Fig.3. Calculated DOS and projected DOS of UFeGe.



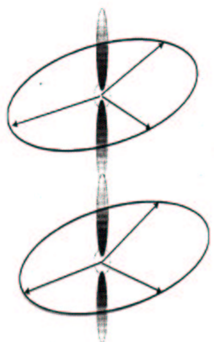
Strong spin-orbit interaction in actinides – orbital moments induced even in systems of itinerant electrons

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

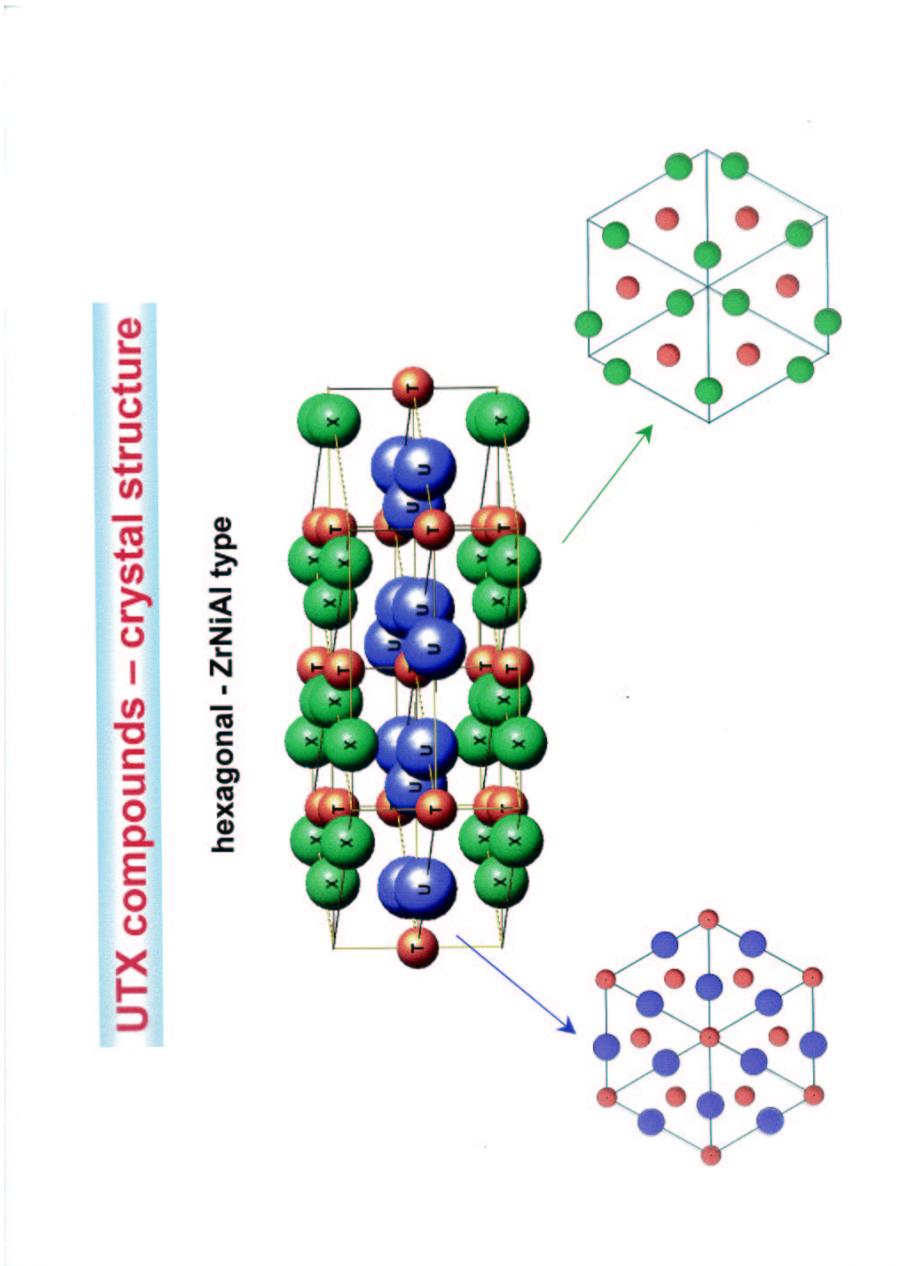
Two-ion anisotropy
(CEF ⟹ single ion anisotropy)

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 ⟹ any change of magnetic structure induces strong Fermi surface reconstruction (even if moments do not change much)


UTX compounds – crystal structure
hexagonal - ZrNiAl type

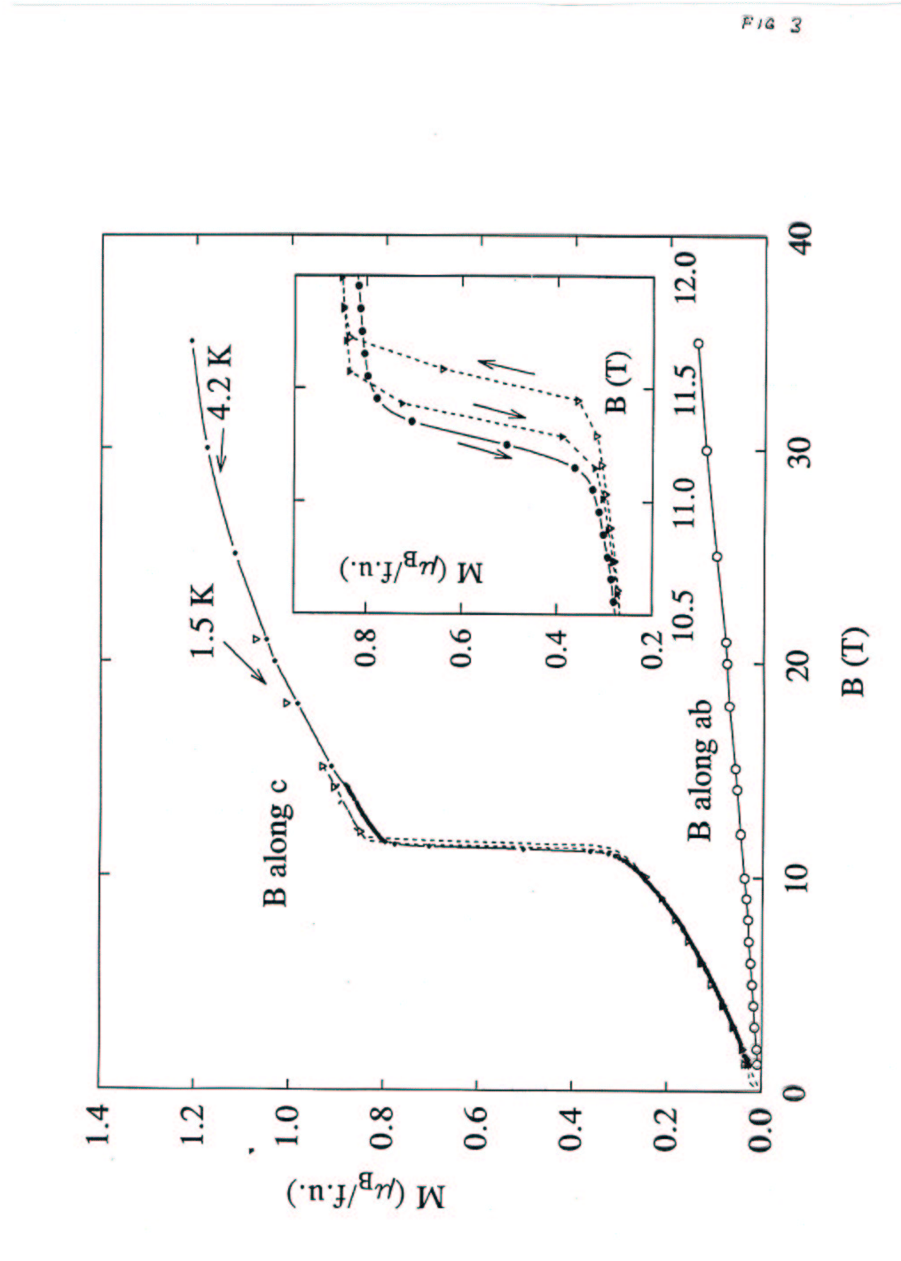


FIG 3
M (μB/f.u.)
B (T)
B along c
B along ab
1.5 K
4.2 K

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Electronic properties of UNiAl in high magnetic fields

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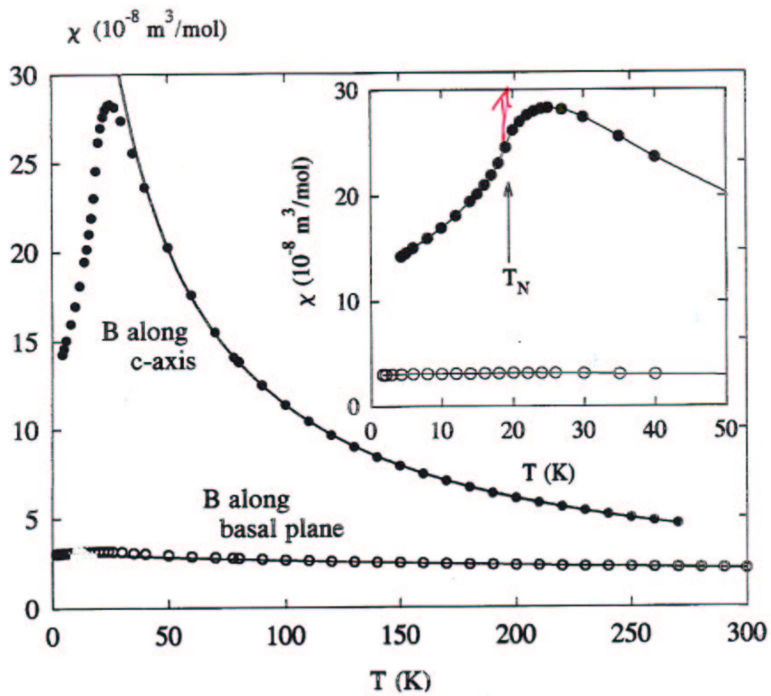
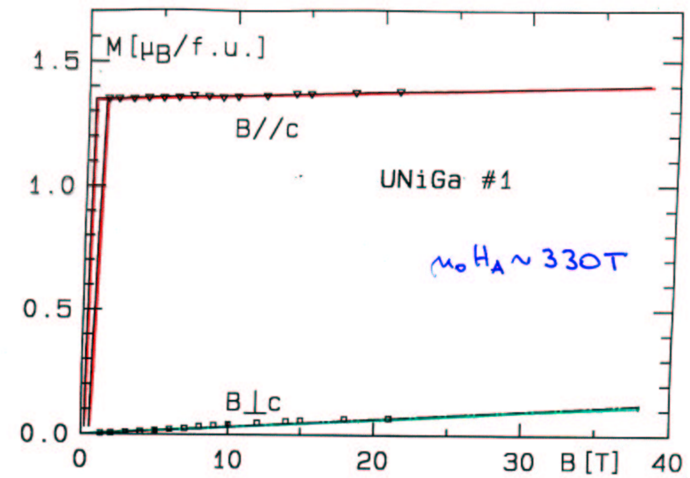
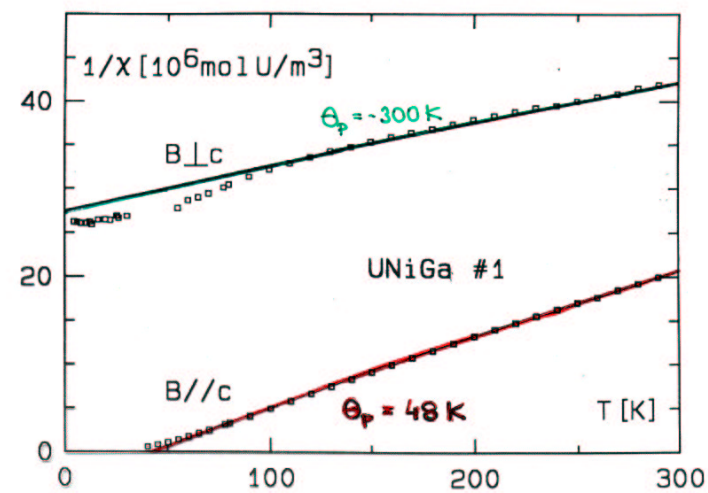
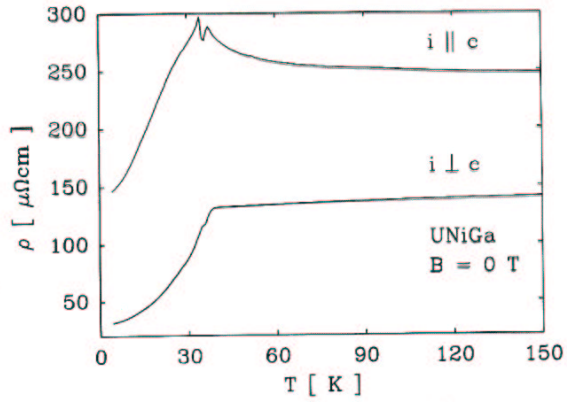
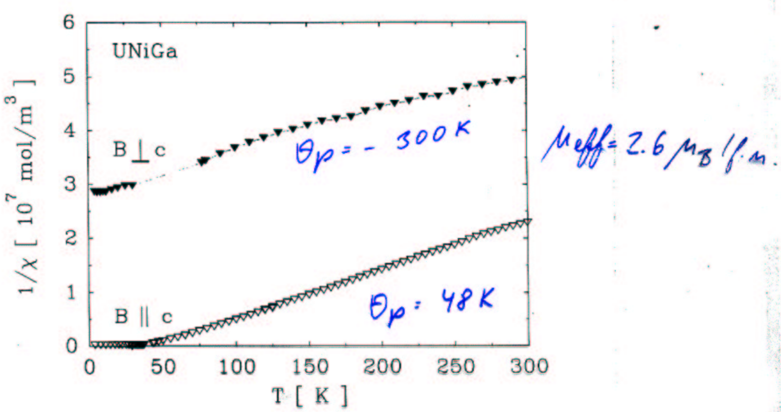


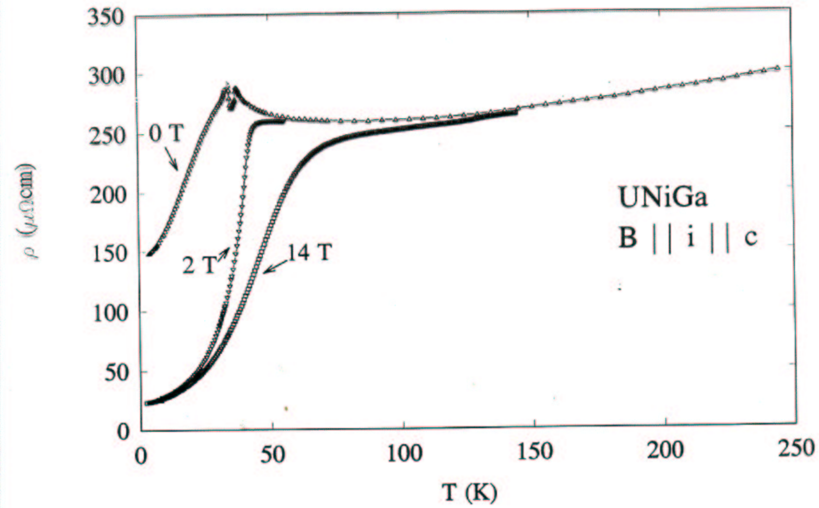


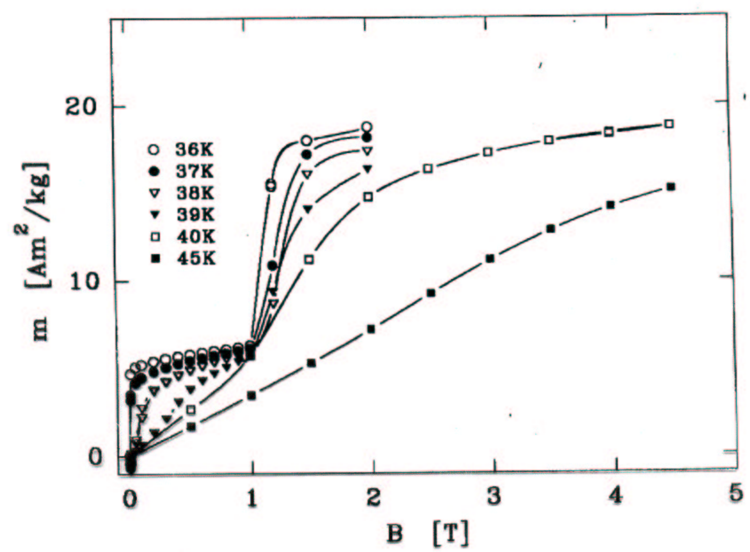






Resistance of UNiGa long the c-axis in various fields along c.





II. MAGNETIC ORDERING AND ELECTRICAL RESISTIVITY

Metallic materials with atoms carrying magnetic moments:

$$\rho = \rho_0 + \rho_{ph} + \rho_{spd}$$

Below magnetic ordering temperature:

- in simple ferromagnets $\rho_{spd} \to 0$ with $T \to 0$ (and since $\rho_{ph} \to 0$, as well) $\Rightarrow$

$$\rho \to \rho_0$$

- in other magnetic structures (especially in antiferromagnets) often:

$$\rho > \rho_0 \text{ or even } \rho >> \rho_0$$

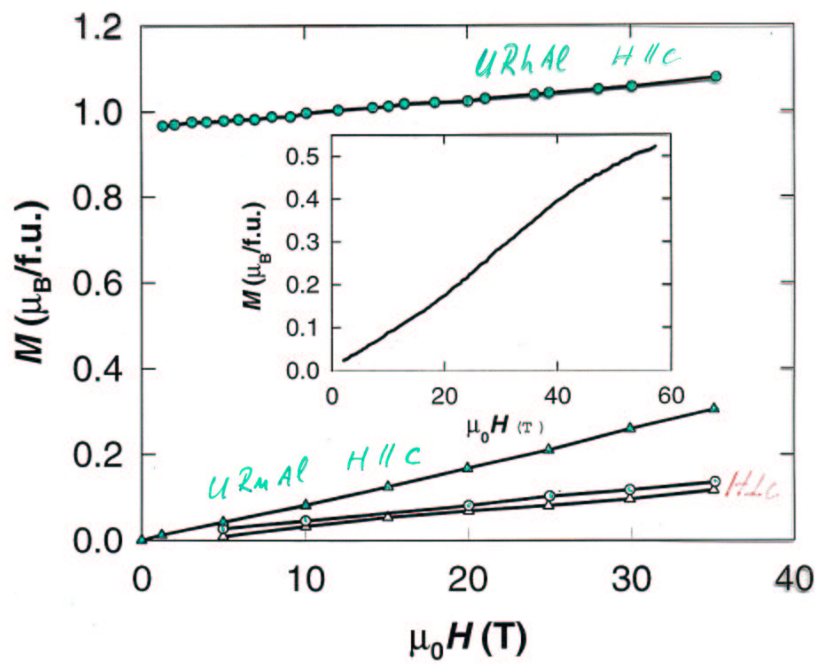
1) R.J. Elliot and F.A. Wedgwood (1963)

Fermi level gapping

- crystallographic <—> magnetic - periodicity

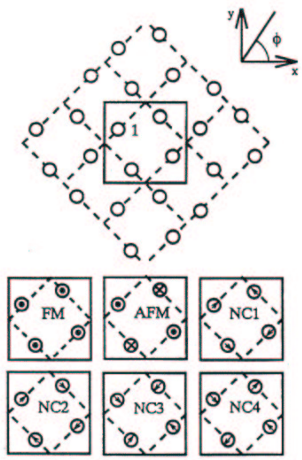
$$\rho = \frac{\rho_0 + \rho_{ph} + \rho_{spd}}{1 - g\, m(T)}$$

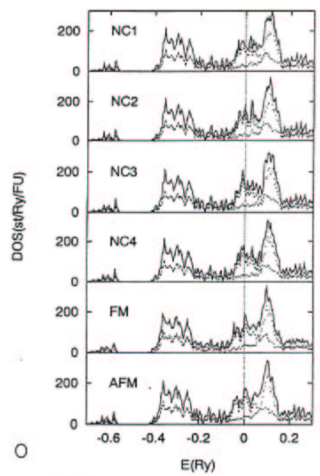
2) Spin dependend scattering

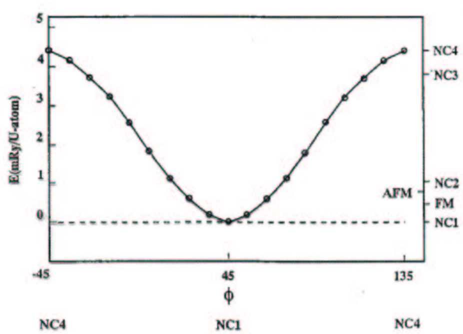


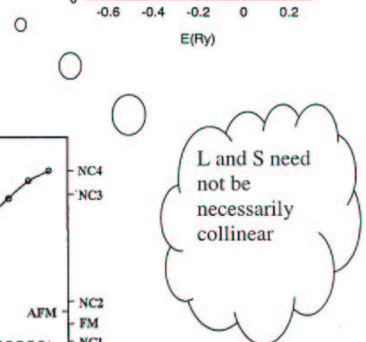
Other approach – LSDF calculations *ab initio*, total energy, orbital polarization, ASW

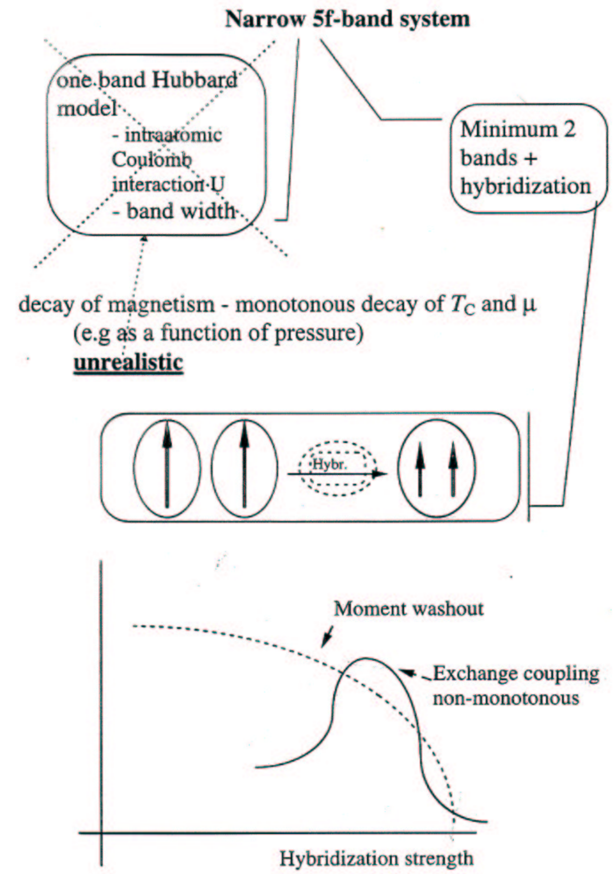
(Sandratskii and Kübler) U_2Pd_2Sn











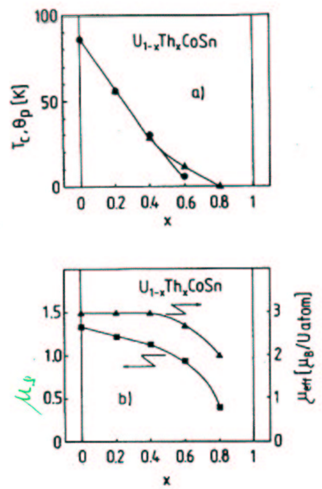


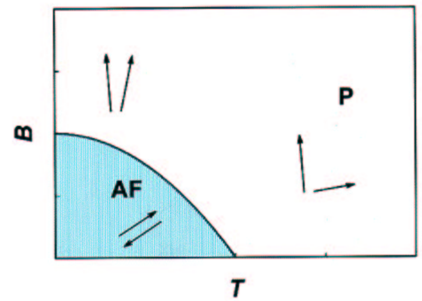
FIG. 2. (a) Concentration dependence of T_C (●) and θ_p (▲). (b) Concentration dependence of the magnetic moment in 4T (■) and the effective moment (▲).

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

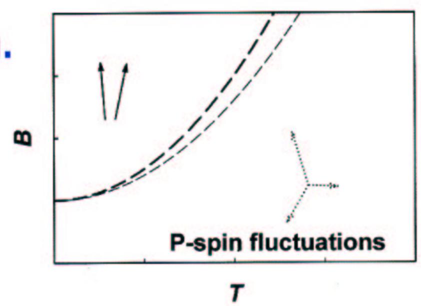
Amitsuka – diluted heavy fermions

YRu_2Si_2 – U ....Kondo
$ThRu_2Si_2$ – U ....local moment
$ThPd_2Si_2$ – U ....local moment

Metamagnetism



Band Metamagn.



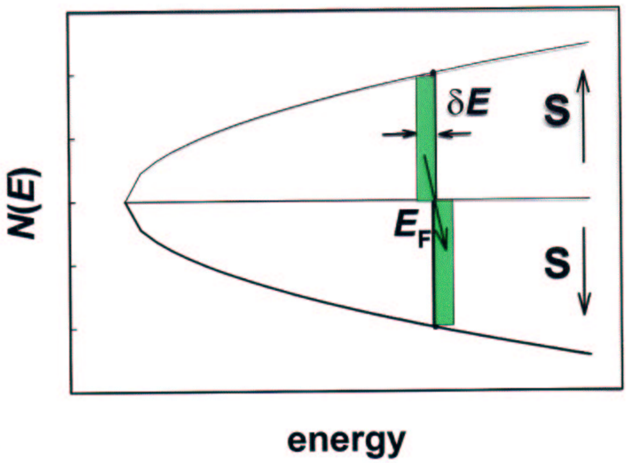
Thermodynamics:

(Clausius-Clapeyron)

$$\Delta Q = -\Delta M \; T(\partial B_c / \partial T)$$

$$\Delta S = \Delta Q / T$$

$$\Delta S = -\frac{\Delta M}{\Delta T}\left(\frac{\partial B_c}{\partial T}\right)$$



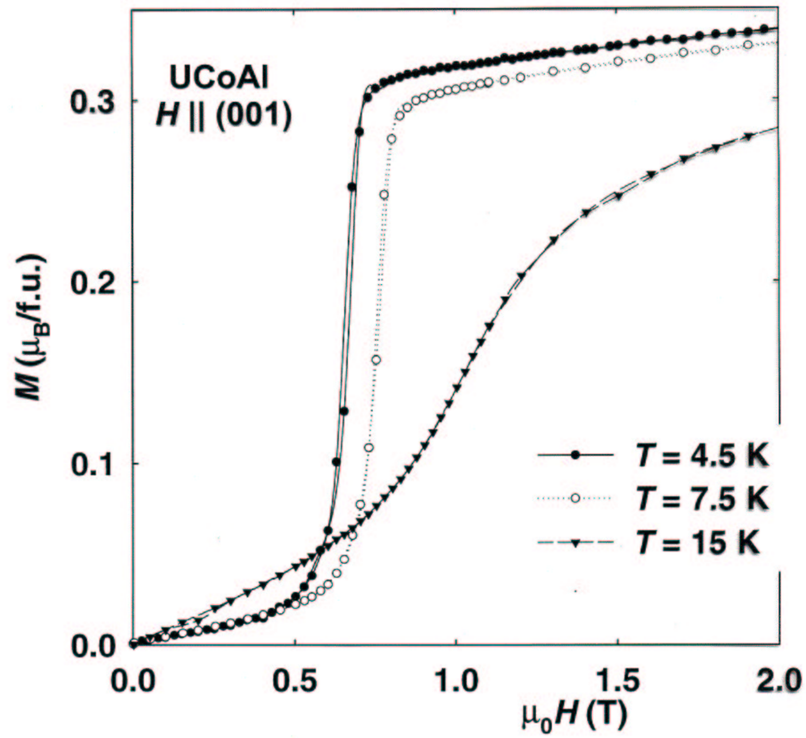
$$\Delta E_{\mathrm{kin}} = N(E_{\mathrm{F}})(\delta E)^2$$

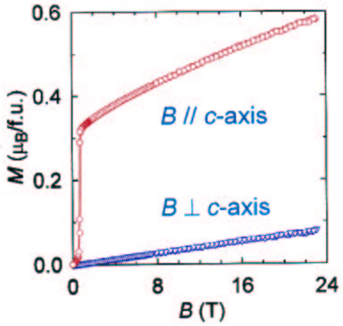
$$\Delta E_{\mathrm{int}} = -U\left[N(E_{\mathrm{F}})(\delta E)\right]^2$$

Stoner criterion

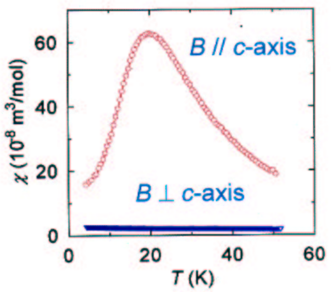
$U\, N(E_{\mathrm{F}}) \geq 1$.....spontaneous splitting

magnetic field can help to bring up to instability





magnetization at 2 K



susceptibility

Local probes

- Neutron diffraction

Analysis of form factor in high-field state

in B = 1 T: μ_L= 0.60 μ_B μ_S= -0.28 μ_B μ_{Co}= 0.06 μ_B

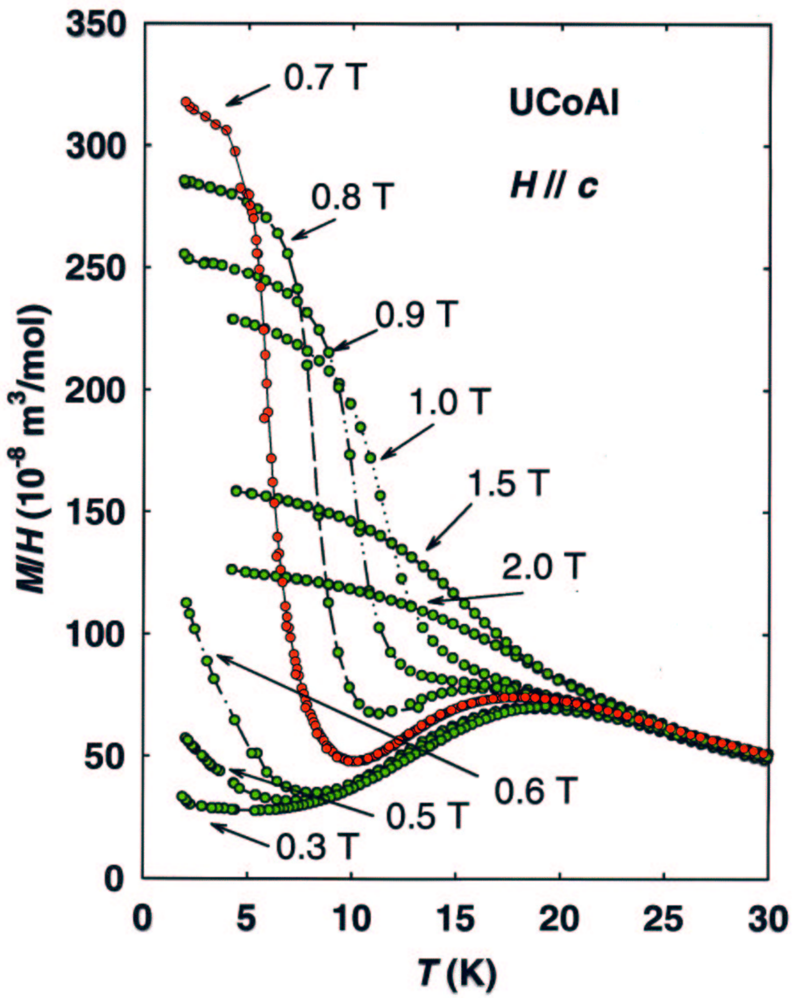
in B = 8 T: μ_L= 0.79 μ_B μ_S= -0.40 μ_B μ_{Co}= 0.07 μ_B

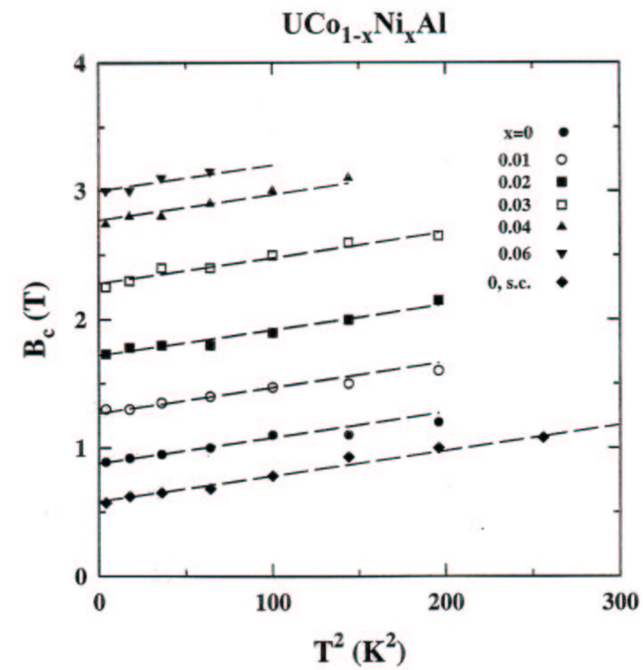
Javorsky et al. 2002

- NMR

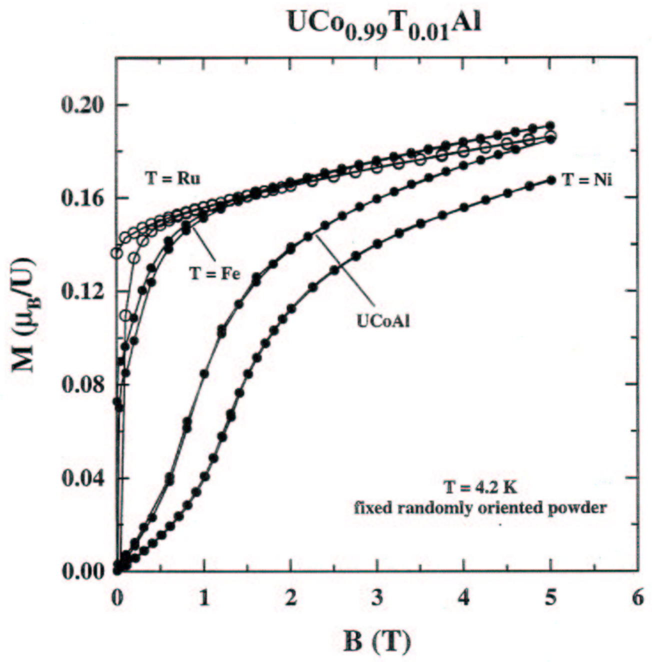
Decrease of the spin-lattice relaxation time $1/T_1$ at the metamagnetic transition (on Co)

Iwamoto et al. 2001

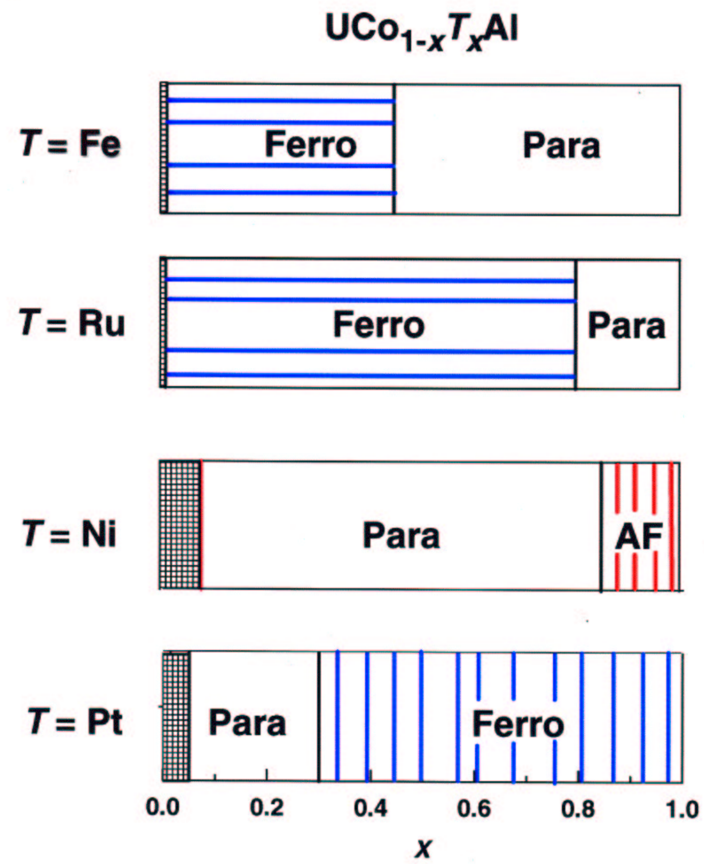




Critical field B_c of metamagnetic transition vs squared temperature for fixed powders of Ni-substituted alloys under ambient pressure. The lowest curve is for UCoAl single crystal along the c axis.



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
ξ (concentration, pressure)

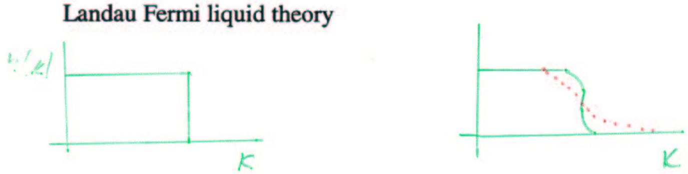
If $T_C \to 0$, quantum fluctuations start to be important

Hubbard Hamiltonian $\hat{H} = \sum_k \varepsilon_k c_k^+ c_k + \sum_i U n_{i\uparrow} n_{i\downarrow}$

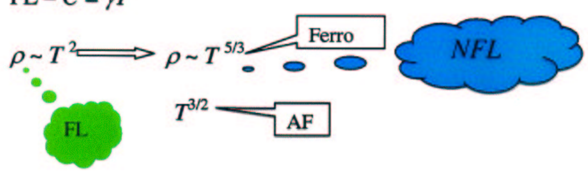
Quantum fluctuations at the critical point adding extra degrees of freedom – like extra dimensions, depending on propagation and damping of magnetic fluctuations

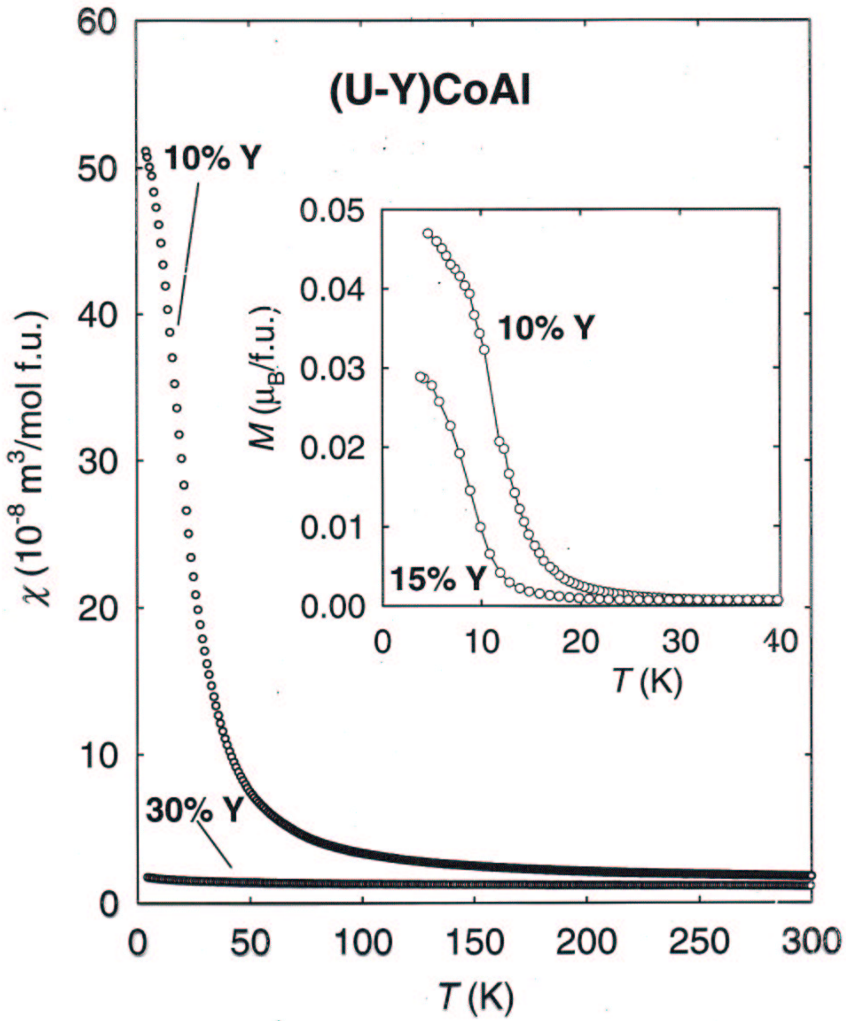
Non-Fermi liquid behaviour

Landau Fermi liquid theory

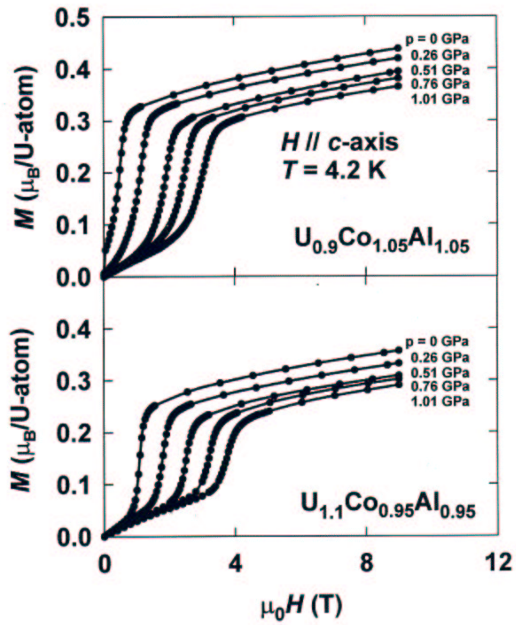


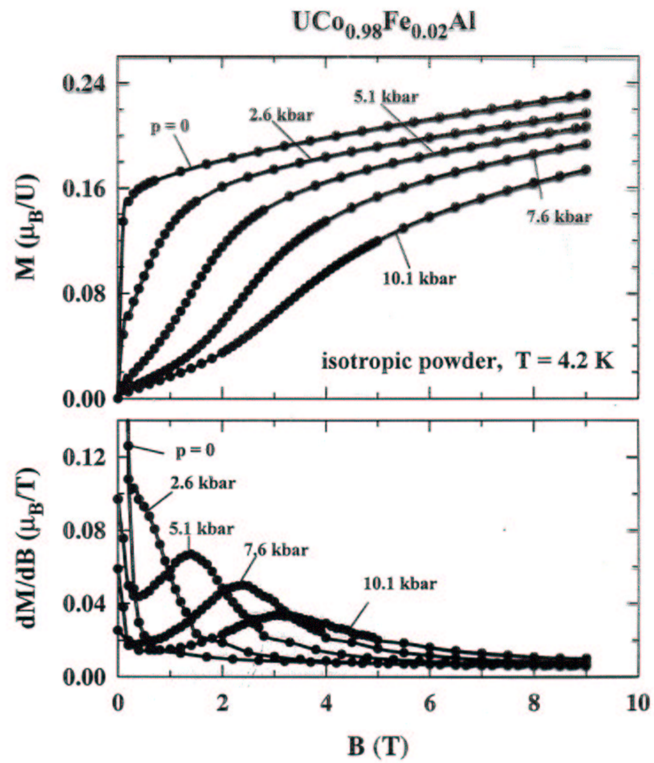
FL – $C = \gamma T$



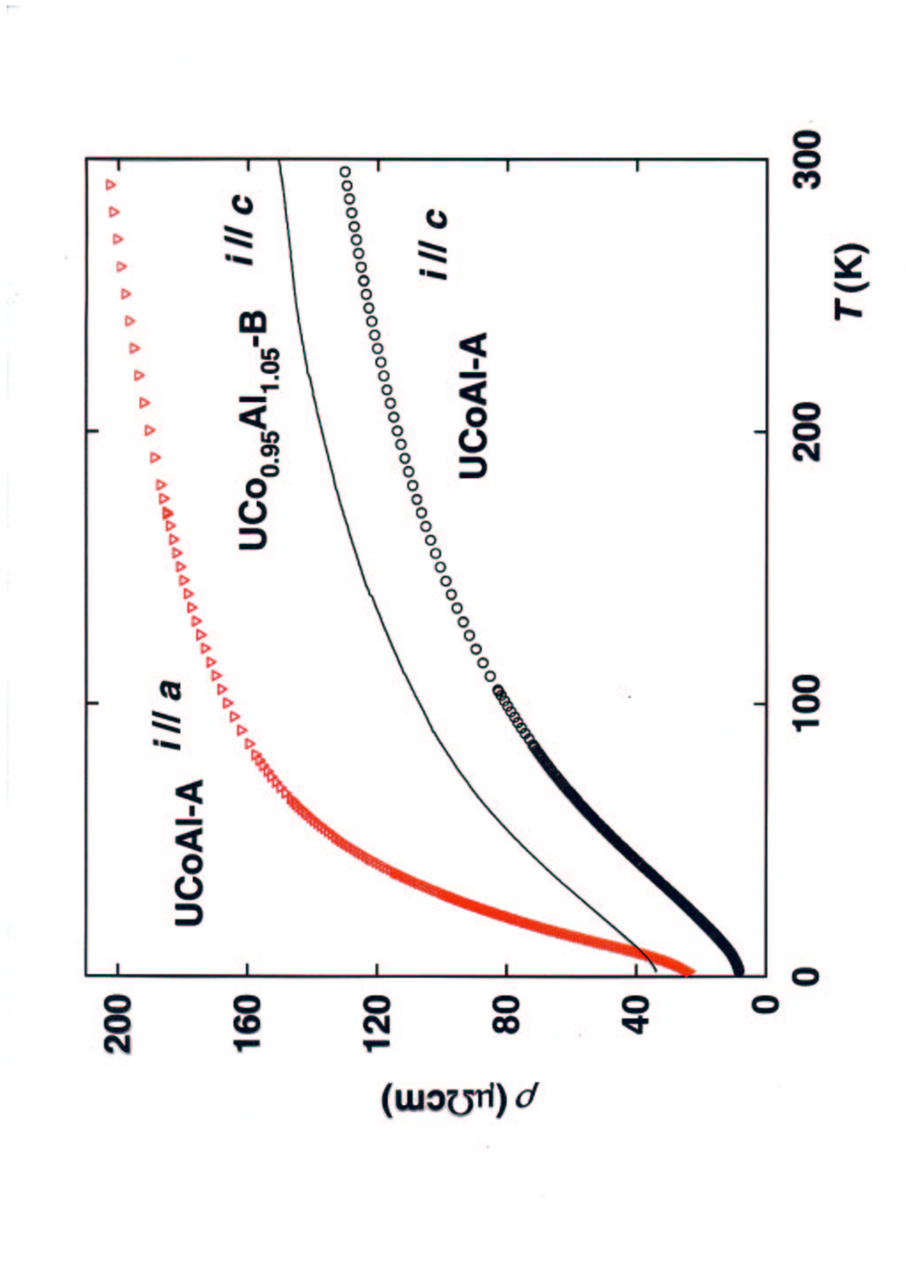


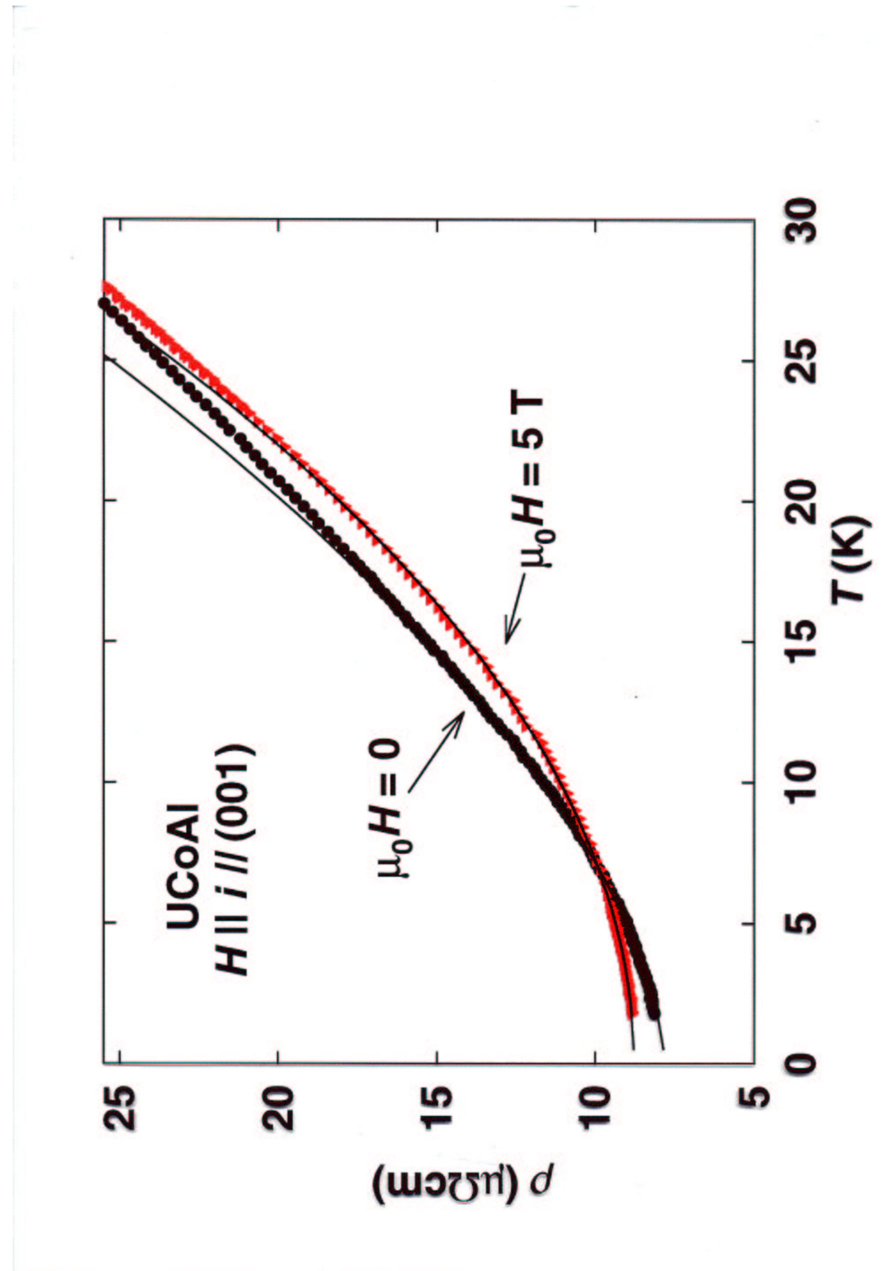
Effects of pressure





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.


UCoAl-A
i // a
UCo0.95Al1.05-B
i // c
UCoAl-A
i // c
ρ (μΩcm)
T (K)
0
40
80
120
160
200
0
100
200
300


UCoAl
H || i // (001)
μ0H = 0
μ0H = 5 T
ρ (μΩcm)
T (K)
5
10
15
20
25
0
5
10
15
20
25
30

These things are not really new – theory of weak itinerant ferromagnetism

Mathon 1968 $\rho = bT^{5/3}$……$ZrZn_2$, $TiBe_2$, Ni_3Al

Selfconsistent spin fluctuation theory – Moriya, Ueda 1970-90

AF n = 3/2 (*a* is diverging)

Mishra and Sreeram PRB 1998 *n* decreases with decreasing dimensionality

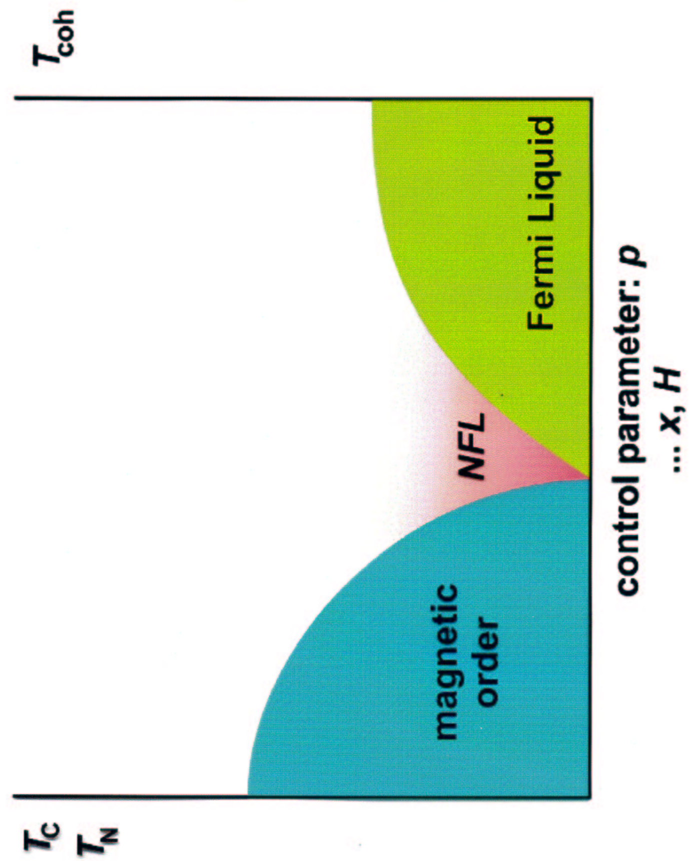
Band metamagnetism YCo_2

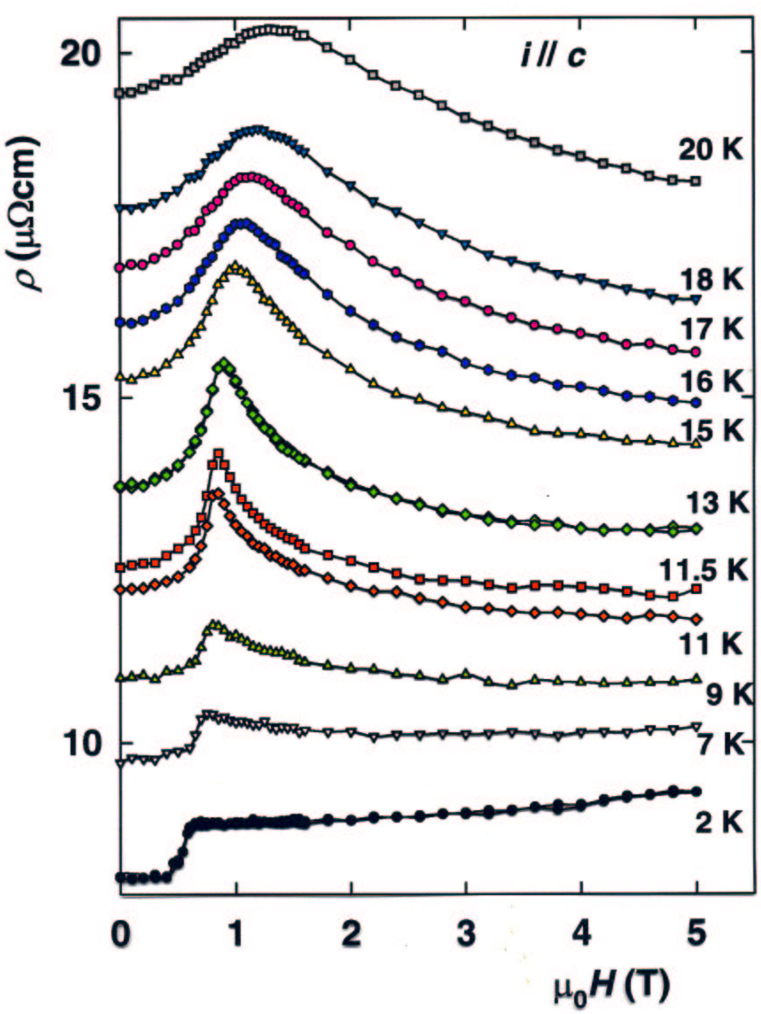
Theories -

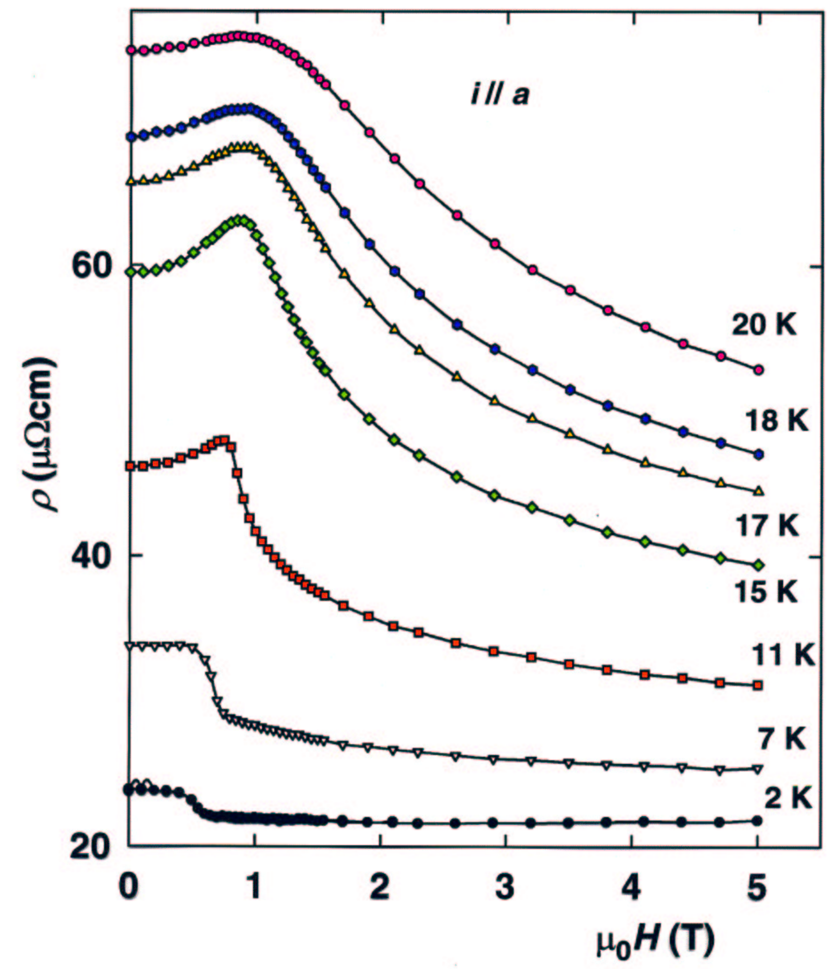
1. Spin fluctuations – Landau Ginzburg; free energy expansion including M^5 term

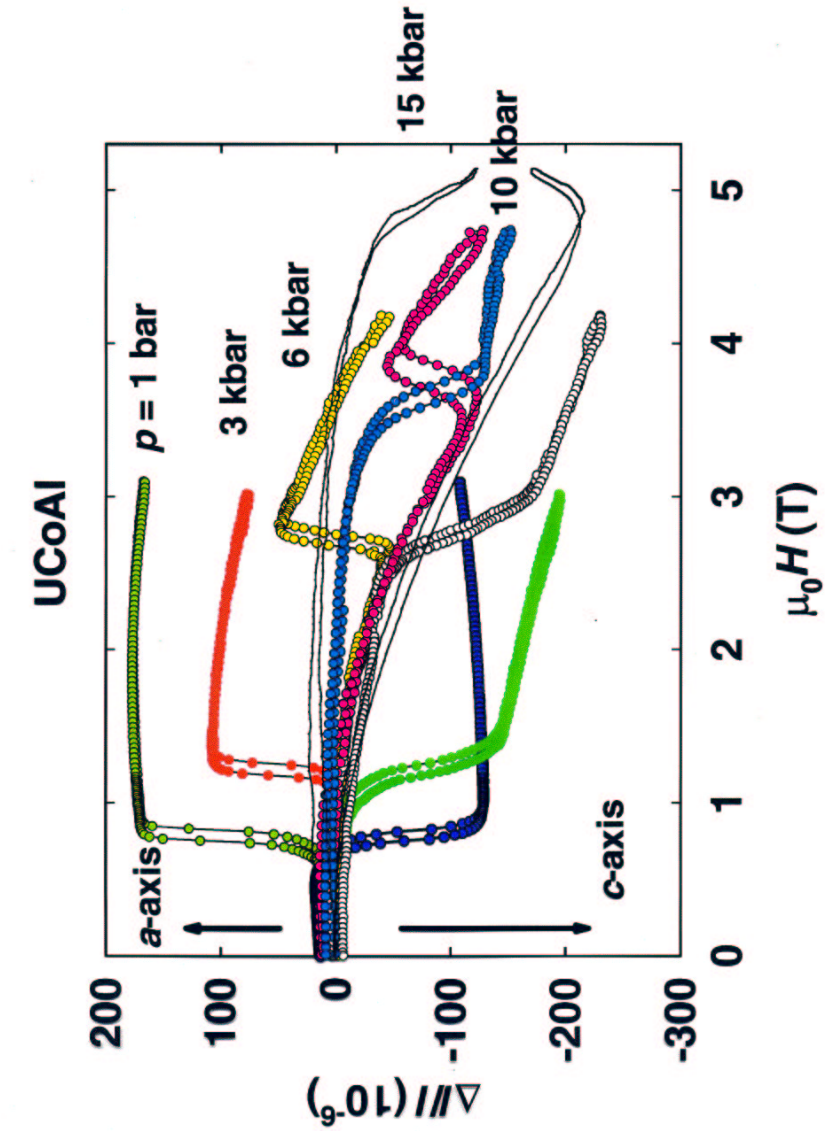
(Yamada)

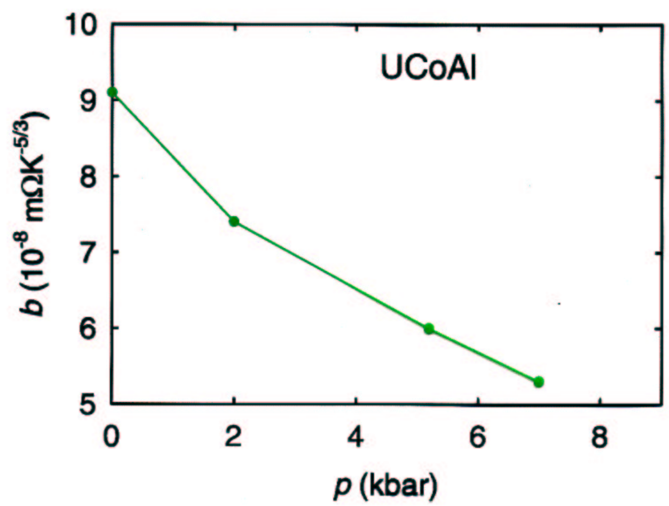
2. Two competing states, one with zero spontaneous magnetization




i // c
ρ (μΩcm)
20
15
10
20 K
18 K
17 K
16 K
15 K
13 K
11.5 K
11 K
9 K
7 K
2 K
0
1
2
3
4
5
μ0H (T)


i // a
ρ (μΩcm)
60
40
20
20 K
18 K
17 K
15 K
11 K
7 K
2 K
0
1
2
3
4
5
μ0H (T)


UCoAl
p = 1 bar
3 kbar
6 kbar
15 kbar
10 kbar
a-axis
c-axis
μ0H (T)
Δl/l (10-6)


UCoAl
b (10-8 mΩK-5/3)
p (kbar)

Rule of magnetovolume effects in itinerant systems

$$\Delta V \propto M_s^2$$

In UCoAl

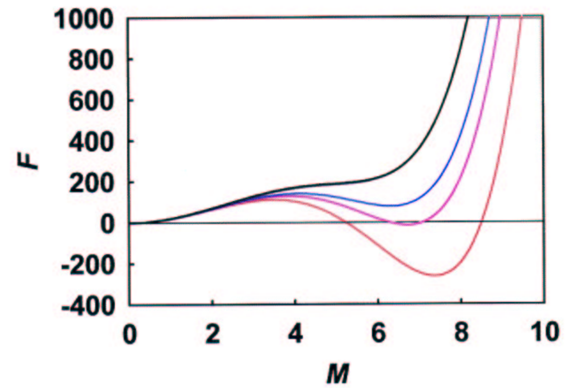
$$\Delta a / a \propto (\Delta M)^2$$

$$\Delta M = \Delta M_0 - k\delta a$$

......................*i.e.* not δp, or δV

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

b – mode – mode coupling

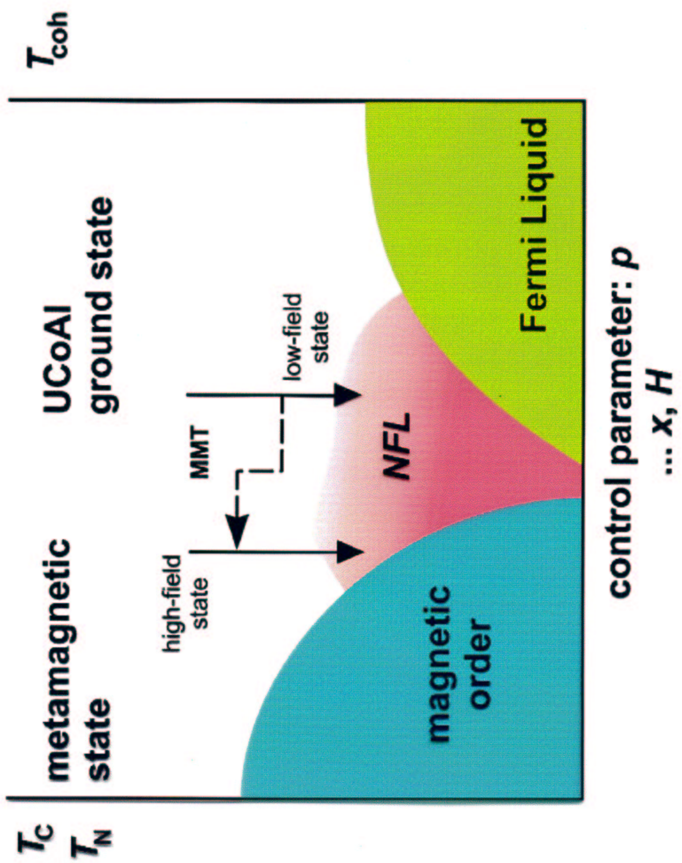
$1/\chi(T) = a + 5/3b\, \xi(T)^2 + 35/9c\, \xi(T)^4$

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

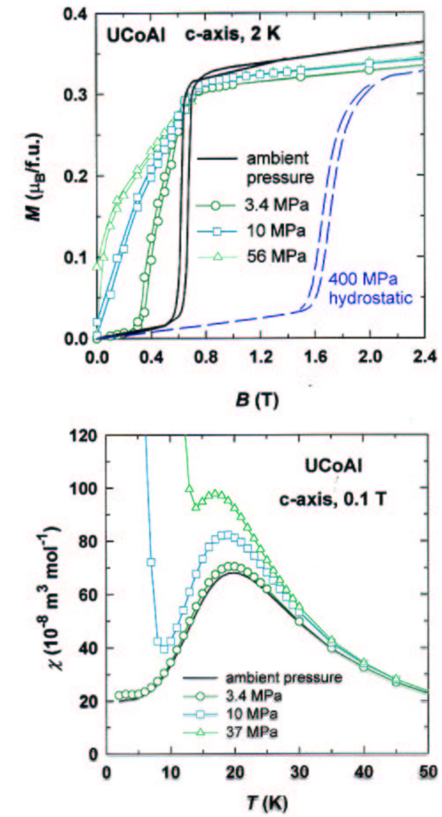
- increases with increasing T

archetypal band metamagnet YCo_2

$B_c \approx 70$ T

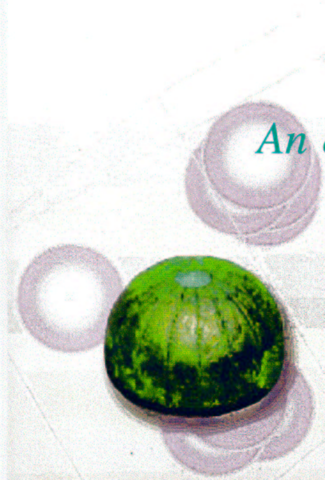


Uniaxial pressure



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



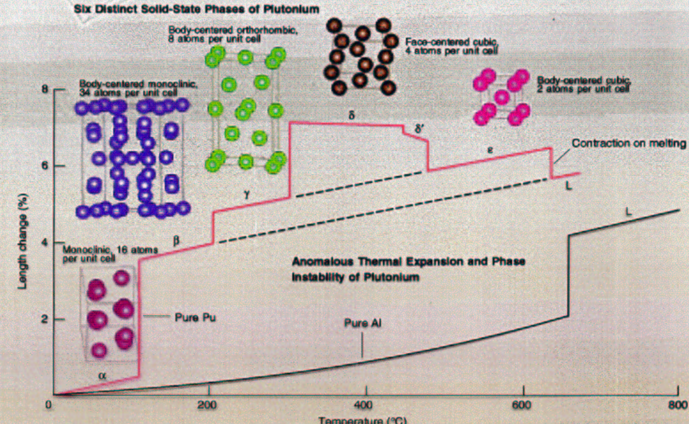
Plutonium

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—much like water freezing to ice; and its shiny, silvery, freshly 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 crystalline lattice and leaving behind helium, americium, uranium, 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

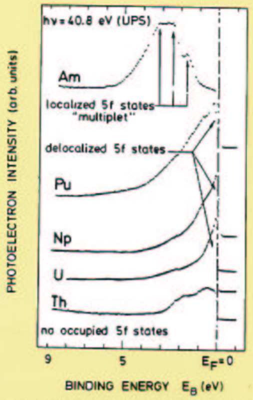
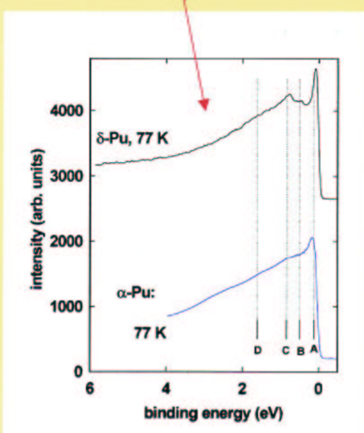
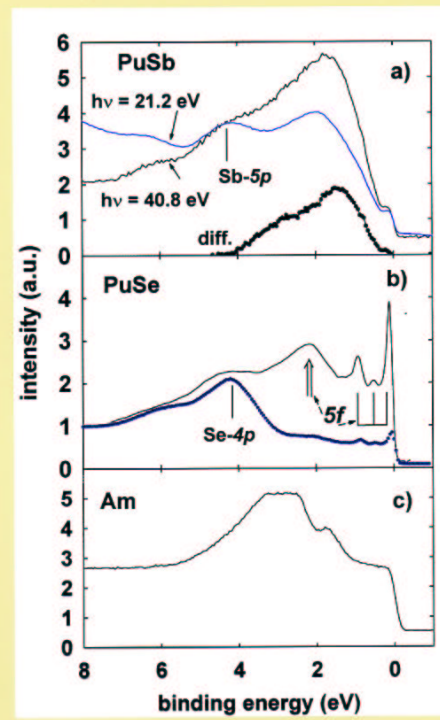


Fig. 5. UPS conduction band spectra for actinide metals from Th to Am for 40.8 eV excitation.

J. Naegele, 1980s





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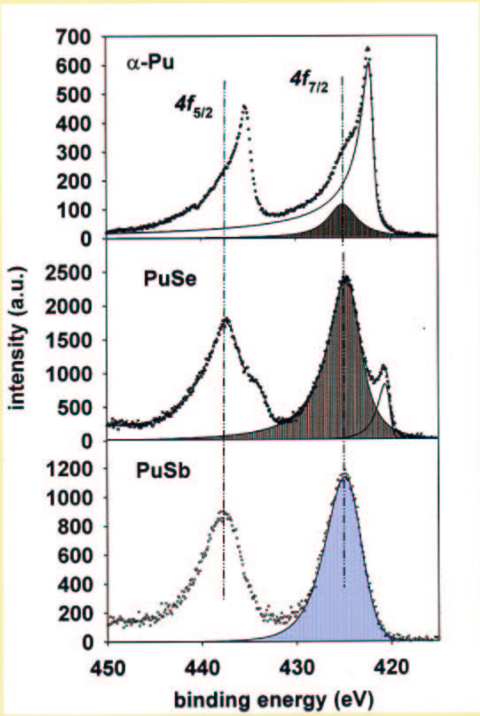
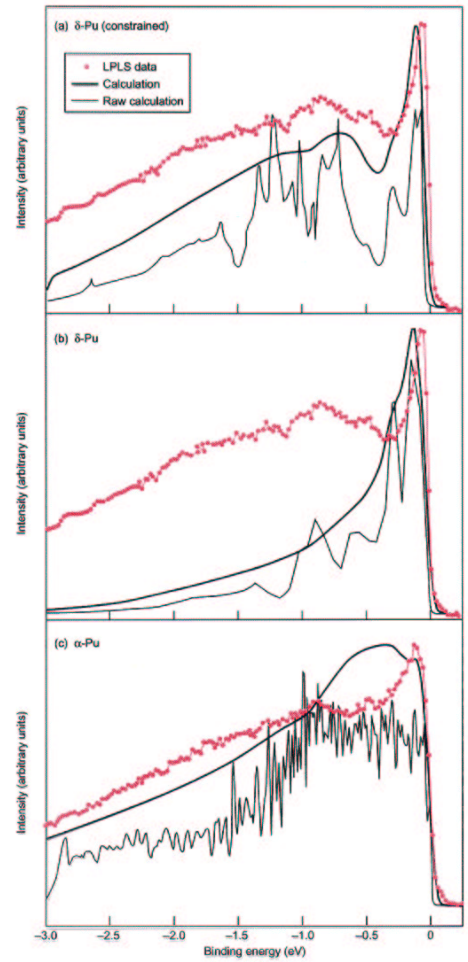
4f lines





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 reinforces the notion that at least some of the 5f electrons are localized.

The α-plutonium 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-plutonium 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 feature in the α-plutonium spectrum occurs at 100 meV below E_F, and it 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-plutonium 4f core levels show satellite behavior similar to, yet not as intense as, that in δ-plutonium. Perhaps correlation phenomena are important in spite of the 5f maximum occurring at 100 meV below E_F. A reasonable calculational approach for α-plutonium 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 interaction U controls the strength of the electron-electron correlations. This approach may solve the problem for α-plutonium but is more problematic for δ-plutonium, whose GGA-calculated bands are too narrow compared with experiment. The structure at 1 eV may not be reproduced by renormalization. ■

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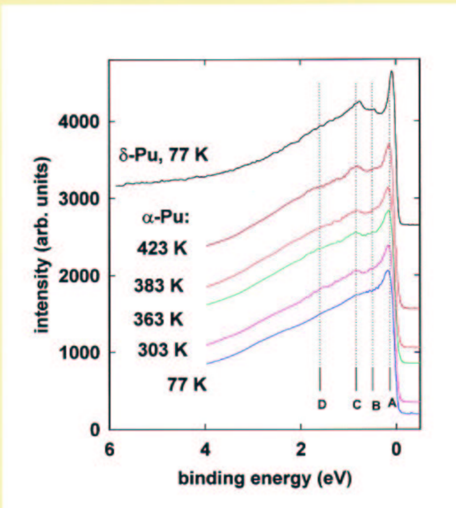
α-Pu surface prepared at various temperatures



Elucidates the discrepancies between different authors:

low-*T* preparation - triangular shape, no details

high-*T* - features of δ-Pu

Explained by theoretical work Eriksson et al., PRB 1992.
Shows that δ-Pu should be stable at the surface of α-Pu due to lower coordination.

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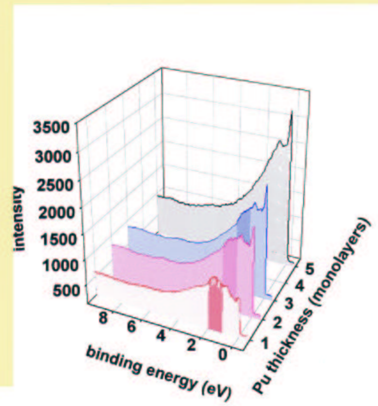
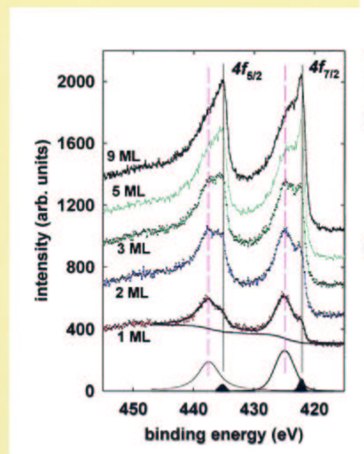
Monoatomic Pu layers on Mg

Very small intermixing of Pu and Mg

Depostion 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_F)

Large thickness

α-Pu

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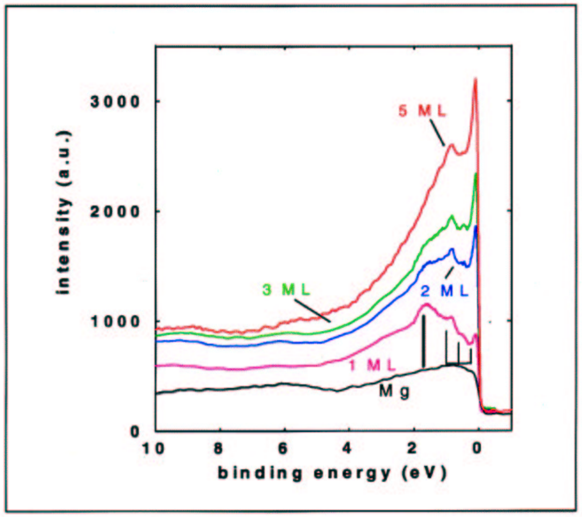
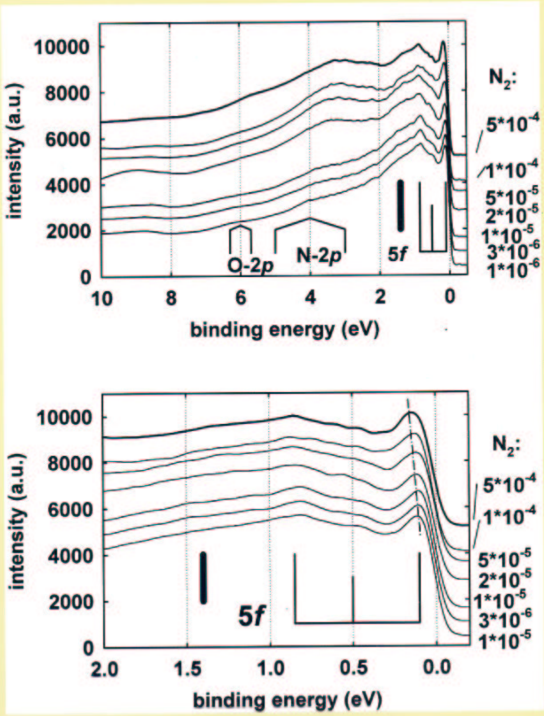
Pu/Mg
HeII VB Study

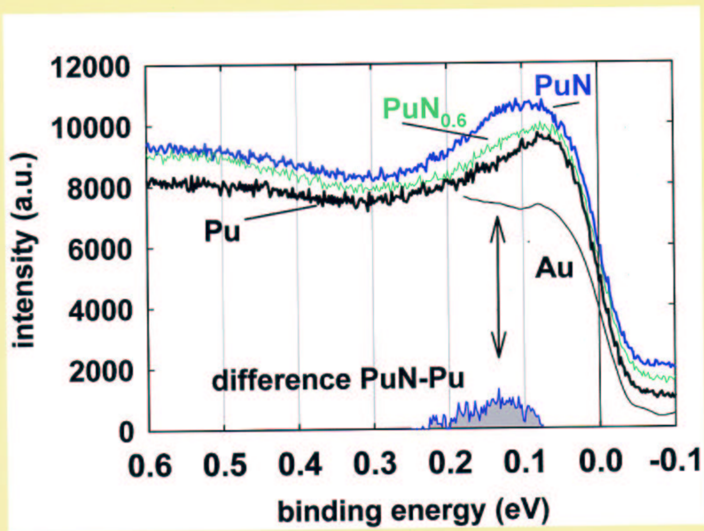


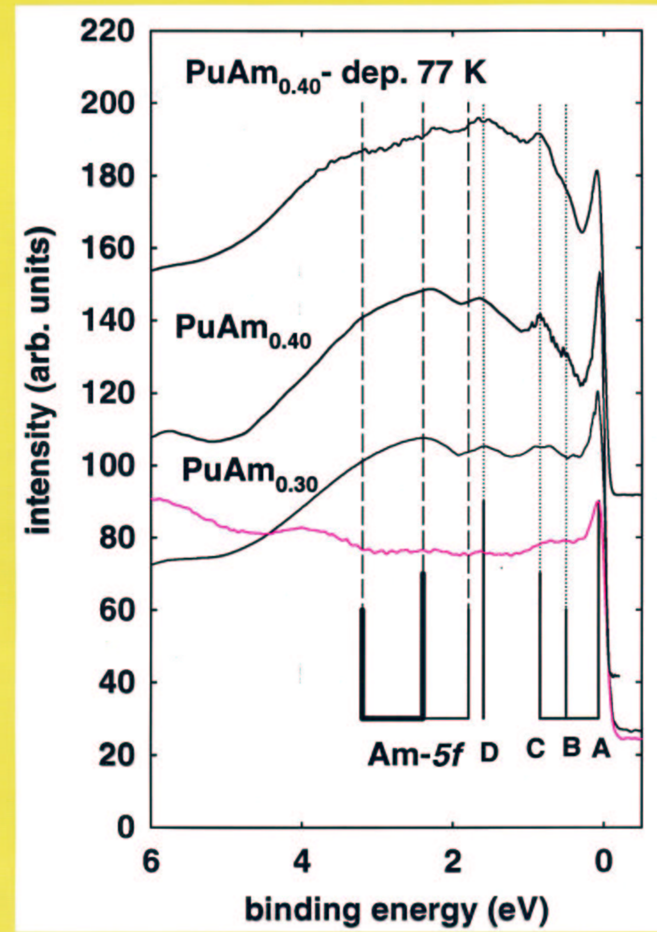
- Transition from itinerant to localised 5f
- In between: correlation satellites (Three peak structure)

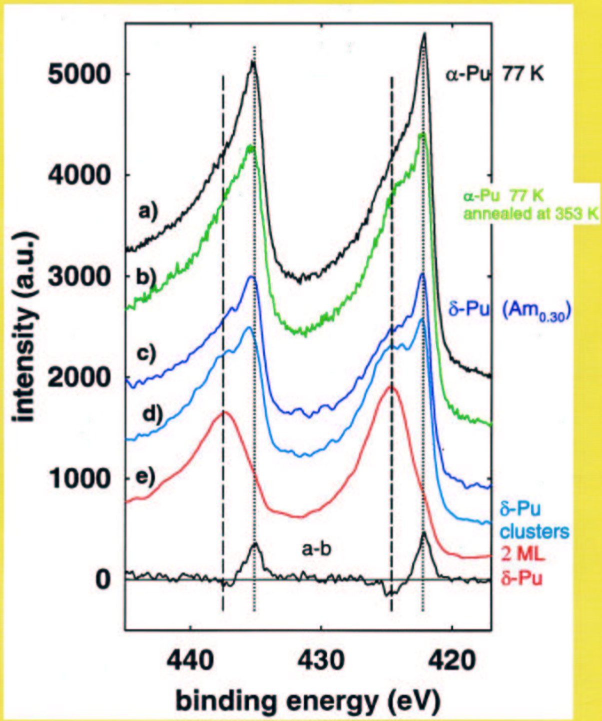
Pu-N

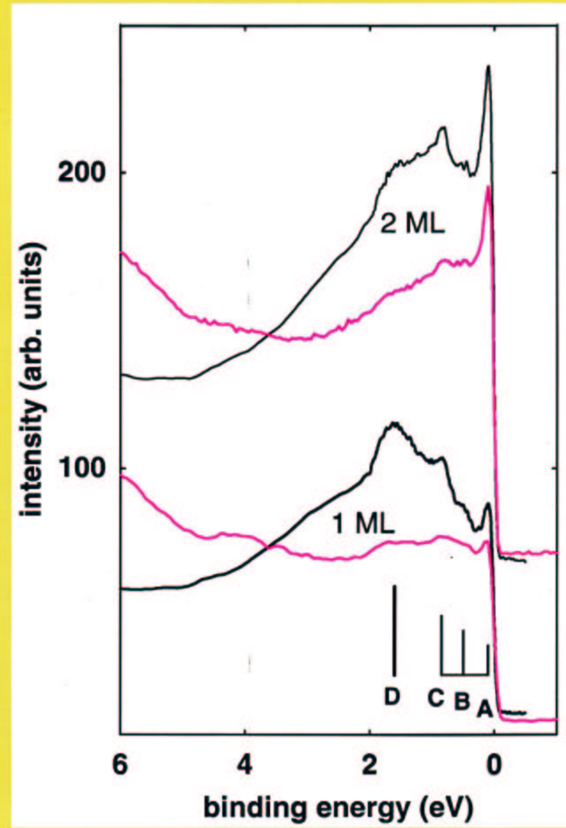


Pu-N detail


intensity (a.u.)
12000
10000
8000
6000
4000
2000
0
0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1
binding energy (eV)
PuN
PuN0.6
Pu
Au
difference PuN-Pu


PuAm0.40- dep. 77 K
PuAm0.40
PuAm0.30
intensity (arb. units)
220
200
180
160
140
120
100
80
60
40
20
0
6 4 2 0
binding energy (eV)
Am-5f
D
C
B
A





Peak A - not pure 5f