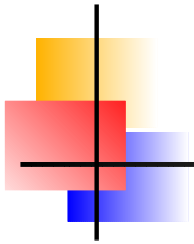


Electronic structure and non-magnetic character of δ-Pu-Am alloys

Alexander Shick, Jindřich Kolorenč, Václav Drchal

Ladislav Havela, Thomas Gouder, and Peter Oppeneer

Institute of Physics ASCR, Prague

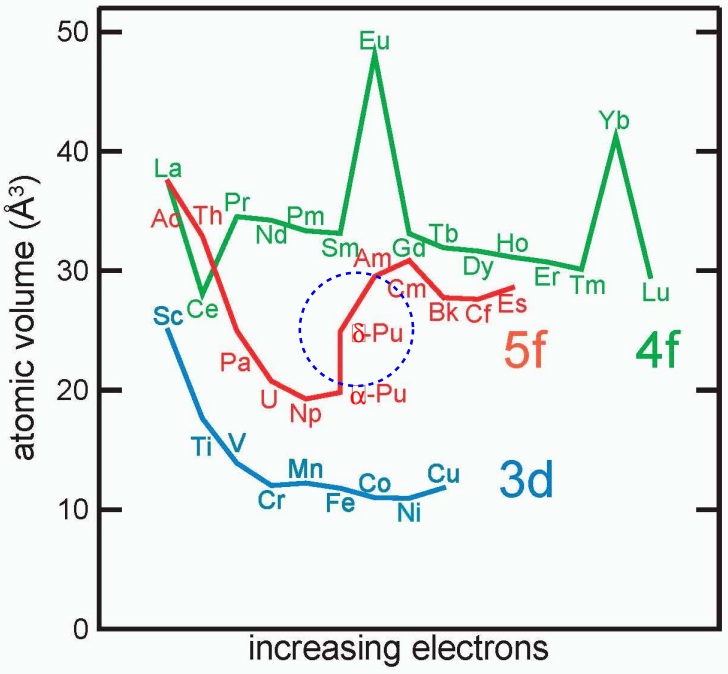
Charles University, Prague

Institute for Transuranium Elements, Karlsruhe

Department of Physics, Uppsala University

Motivation

- Electron-electron correlation effects in a proximity to the localization threshold of the $5f$: between Pu and Am.

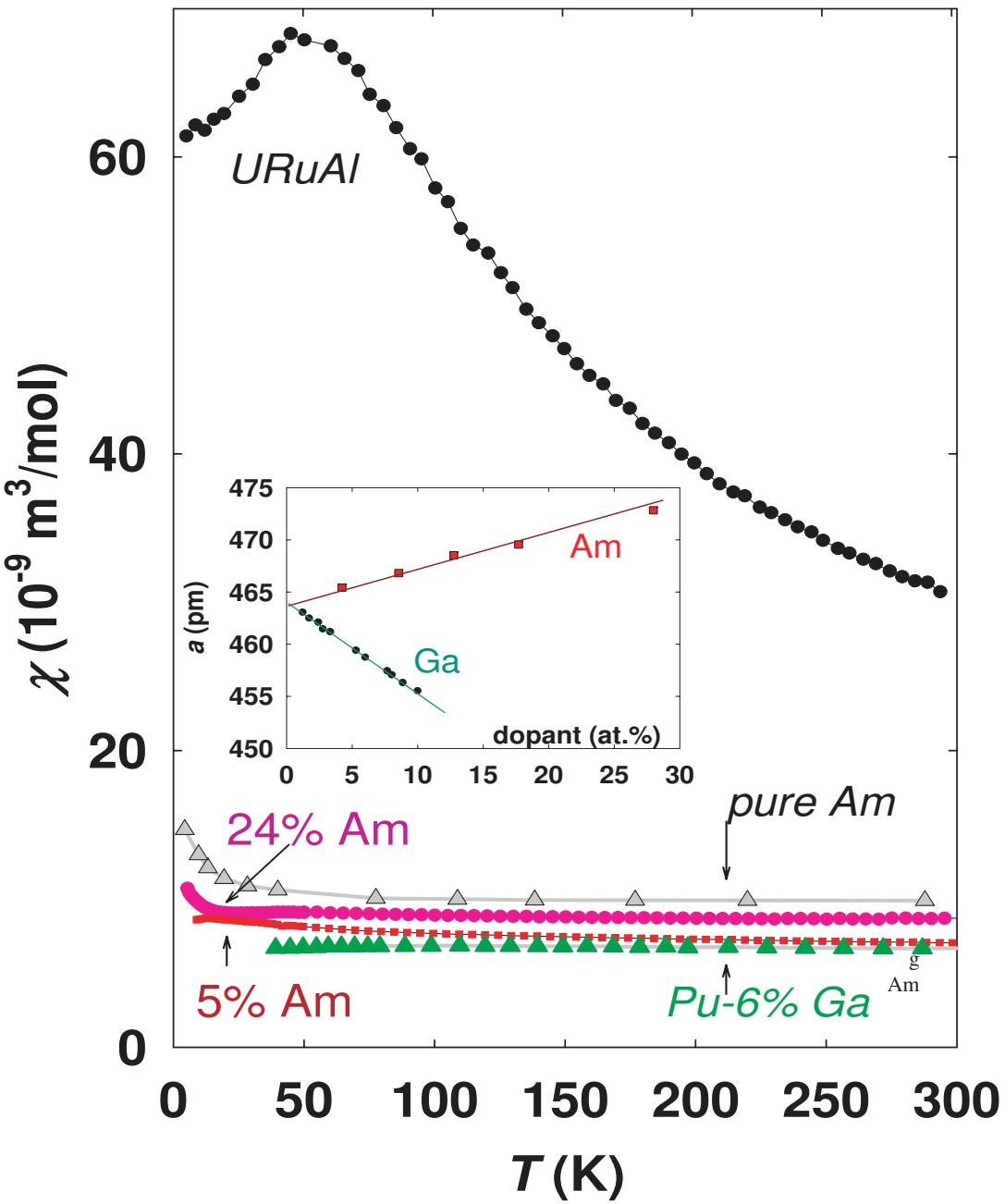


- Pu lies at the position intermediate between localized and itinerant behavior.
- Absence of magnetic moments in plutonium

J. C. Lashley, A. Lawson,
R. J. McQueeney, and G. H. Lander
Phys. Rev. **B72**, 054416 (2005)

- An important open issue: can a further $5f$ localization or onset of magnetism take place when expanding the lattice by Am doping?

Experiment: are Pu-Am alloys magnetic?



- $\chi_{Pu-Am}(T)$ has a low-T upturn, which is more pronounced for pure Am, and is decreasing with decrease of Am content.
- $\chi_{Pu-Am}(T)$ remains very weak, not exceeding $10^{-8}\ m^3/mol$
- Curie term arises due to

  $\approx$ 0.1 % of Np

  α-decay of ^{241}Am $\rightarrow$ ^{237}Np
- No sign of magnetism in the specific heat of Pu-Am alloys

Are Pu-Am alloys magnetic?

- Experiment: no, it isn't!
- Conventional "band theory" (LSDA/GGA): yes it is!

  A. Landa and P. Söderlind, J. Alloys Comp. **376**, 62 (2004) claim the existence of the large local magnetic moments in Pu-Am alloys
- The same "story" as in elemental δ-Pu:
  P. Söderlind *et al.*, Europhys. Lett. **55**, 525 (2001); PRB **66**, 205109 (2002); PRL **92**, 185702 (2004).
  and elemental Am:
  P. Söderlind *et al.*, PRB **61**, 8119 (2000); Phys. Rev. B **72**, 024109 (2005).
  They claim the existence of the magnetic moments in elemental Pu and Am, and even attempt to explain the phase transitions due to different type of the magnetic order.

Beyond LDA

Full Potential Linearized Augmented Plane Wave (FP-LAPW) method +
Rotationally invariant *"Around-Mean-Field"* (AMF)-LSDA+U:

$$E_{AMF} = E^{LSDA} + \Delta E^{ee}$$

$$\Delta E^{ee} = \frac{1}{2} \sum_{\gamma_1,\gamma_2,\gamma_3,\gamma_4} \delta n_{\gamma_1,\gamma_2} \left[\langle \gamma_1, \gamma_3 | V^{ee} | \gamma_2, \gamma_4 \rangle - \langle \gamma_1, \gamma_3 | V^{ee} | \gamma_4, \gamma_2 \rangle \right] \delta n_{\gamma_3,\gamma_4}$$

$$n_{\gamma_1\gamma_2} \equiv n_{m_1\sigma_1,m_2\sigma_2} \ , \ \delta n_{\gamma_1,\gamma_2} = n_{\gamma_1,\gamma_2} - n^{\sigma_1} \delta_{\gamma_1,\gamma_2}, \quad n^\sigma = \frac{1}{2l+1} \sum_{m=-l}^{l} n_{m\sigma,m\sigma}$$

$$< \gamma_1, \gamma_3 | V^{ee} | \gamma_2, \gamma_4 > = \delta_{\sigma_1,\sigma_2} \delta_{\sigma_3,\sigma_4} \sum_k a_k(m_1, m_3, m_2, m_4) F_k$$

$$a_k(m_1, m_3, m_2, m_4) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} < lm_1 | Y_{kq} | lm_2 > \times < lm_3 | Y^*_{kq} | lm_4 >$$

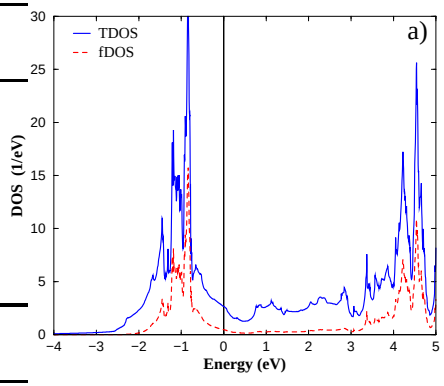
F_k are the Slater integrals $\Leftrightarrow$ Hubbard U and Exchange J

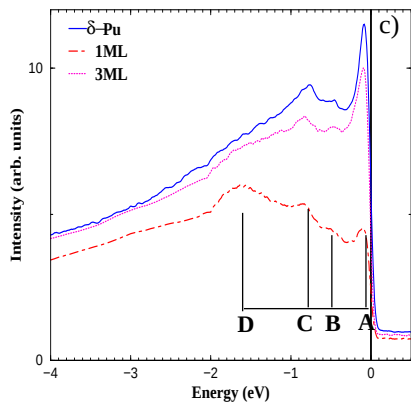
AMF-LSDA+U works for $\delta-$Plutonium

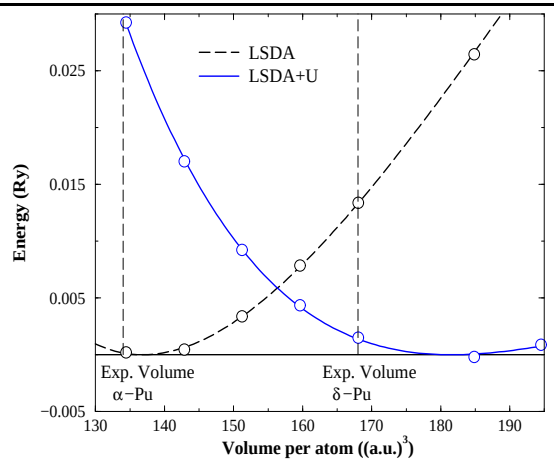
A. B. Shick, V. Drchal, and L. Havela, Europhys. Lett. 69, 588 (2005).

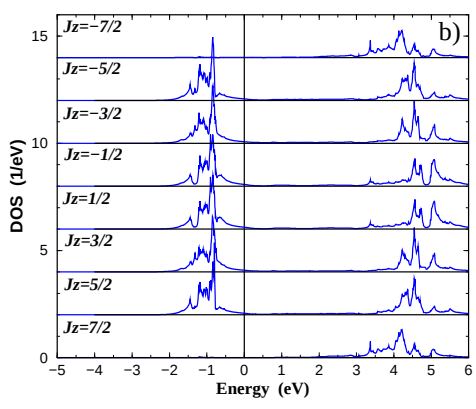
- AMF-LSDA+U yields non-magnetic $\delta-$Pu ground state with correct equilibrium V_{eq} and B. It also yields correct $5f$ manifold binding energy.

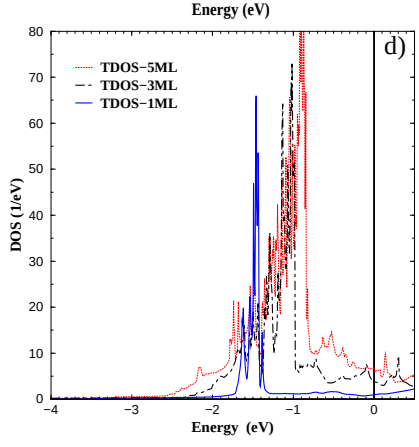
Model	M_J	V_{eq}	B (kbar)
LSDA	2.337	136.8	761
FLL LSDA+U	0.530	187.9	675
AMF LSDA+U	0	181.5	314
Experiment	0	168	299











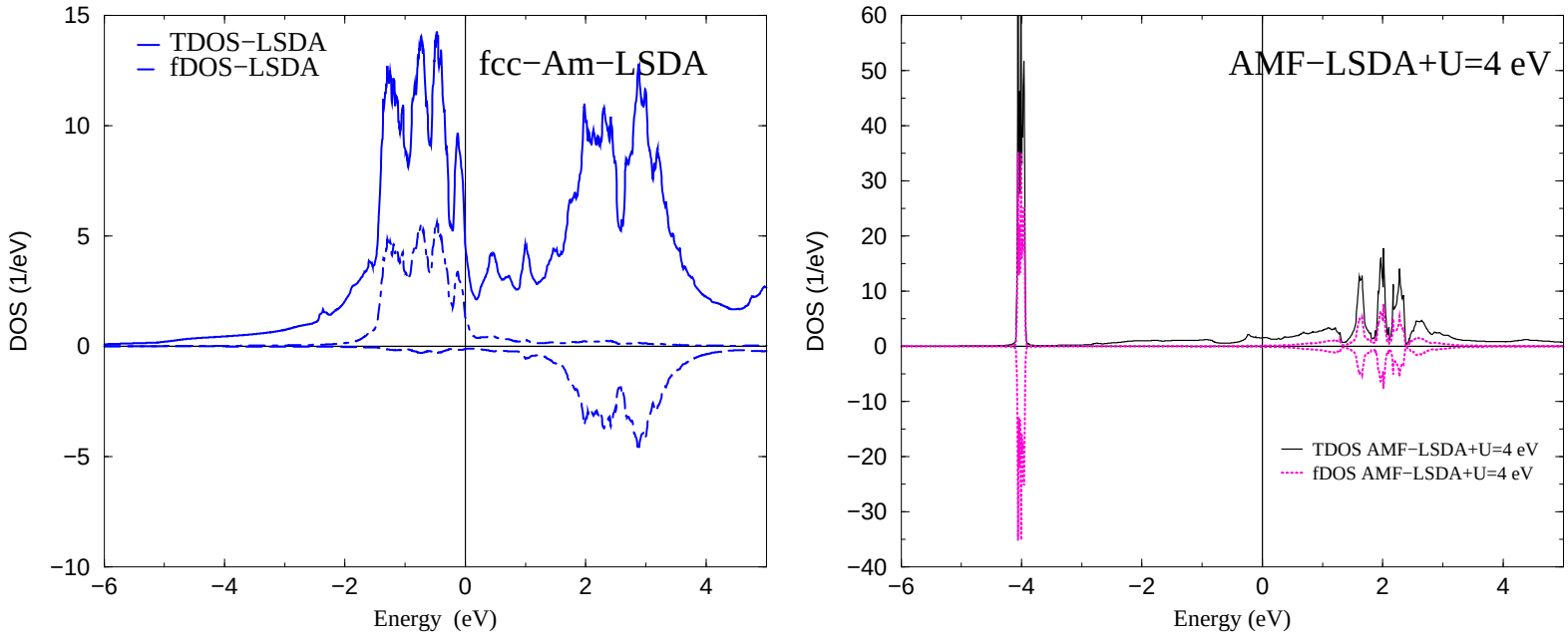
Does AMF-LSDA+U work for Americium?

fcc-Am: Coulomb-U = 4 eV, Exchange-J = 0.75 eV

Method	n_{5f}	M_s	M_l	M_j	V_{eq}	B
GGA	N/A	6	-1	5	170	430
open-core	6	0	0	0	202	468
open-core	6	0	0	0	180	460
LSDA-SIC	6	0	0	0	213	395
LSDA+U=3 eV	5.92	0	0	0	182.1	673
LSDA+U=4 eV	5.90	0	0	0	186.1	551
Exp.	6	-	-	0	198	299

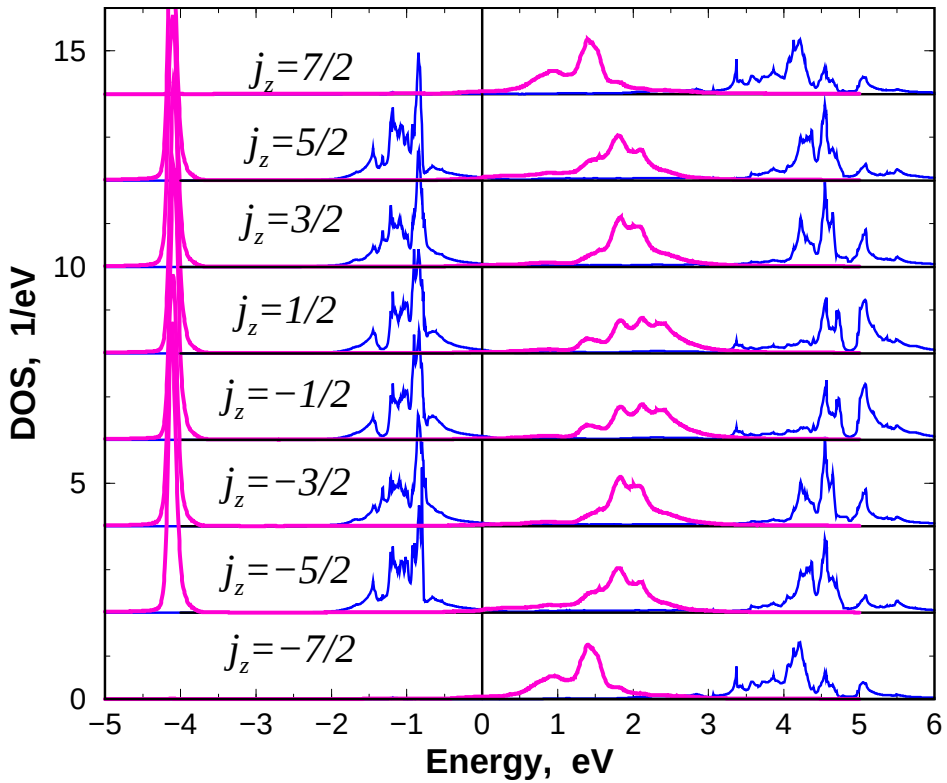
- The AMF-LSDA+U gives correctly non-magnetic Am ground state. Equilibrium V_{eq} and bulk modulus B are calculated in agreement with experiment.

DOS



- AMF-LSDA+U: $5f$-manifold with binding energy $\sim$ 3.5 eV (U=3 eV); 4 eV (U=4 eV)
- Am-$5f$ states are narrower than Pu-$5f$ states, with the width of $\approx$ 0.1 eV
- when the volume is reduced by 30 %, the situation changes dramatically: Am-$5f$ states broaden nearly up to 1 eV, and are located just below the bottom of the valence band.

Character of Am ground state

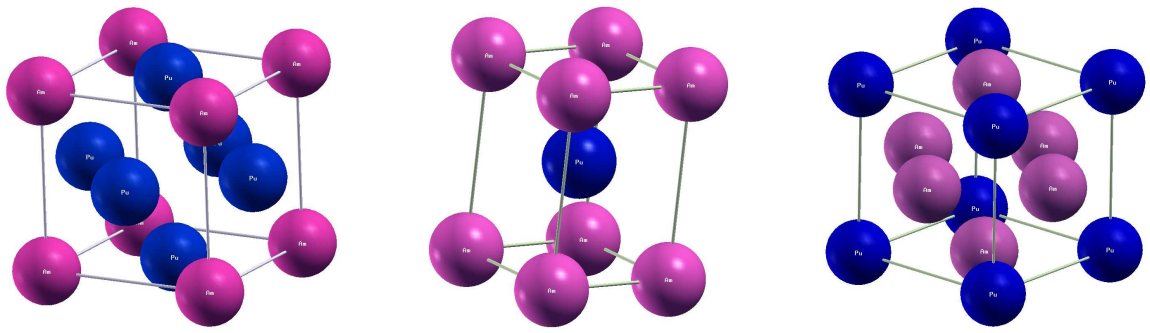


- AMF-LSDA+U: six filled $j = 5/2$ f-states (n_f =5.90).
- Am-5f^6 manifold is more localized than Pu-5f^6 (n_f = 5.5).
- Truly non-magnetic $S_z = L_z = J_z = 0$ $5f^6$ ground state

- The AMF-LSDA+U result can be interpreted as yielding the $J = 0$ singlet ground-state configuration that corresponds to the jj-coupled Slater determinant formed of fully and equally populated six $j = 5/2$ orbitals.

Pu-Am alloys

Now we consider Pu_xAm_{1-x} (x = 0.25, 0.5, 0.75) alloys:
The fcc-based super-cells: $L1_2$ for Pu_3Am ($Pu_{0.75}Am_{0.25}$) and $PuAm_3$ ($Pu_{0.25}Am_{0.75}$), and $L1_0$ for PuAm ($Pu_{0.5}Am_{0.5}$).



- LSDA: magnetic solutions for all considered Pu-Am alloys,

  $$M_{Am} \approx 5\ \mu_B \text{ and } M_{Pu} \approx 2.5\ \mu_B$$

  (like in A. Landa and P. Söderlind, J. Alloys Comp. **376**, 62 (2004))

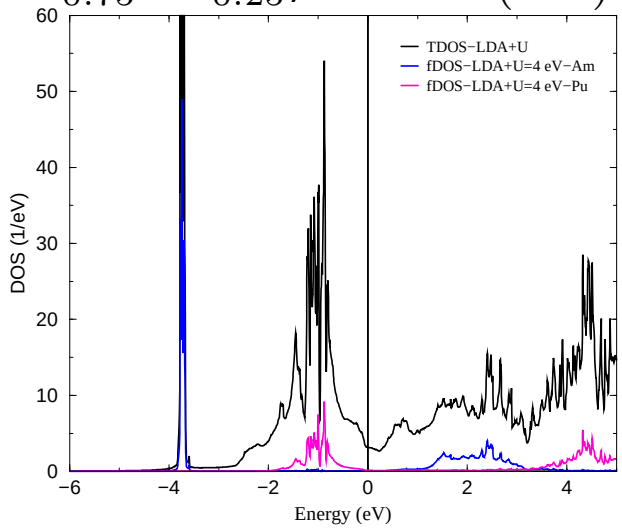
- Starting from spin-polarized LSDA, we apply AMF-LSDA+U.
  Am-U= 4 eV, and J=0.75 eV; Pu-U=4 eV, and J=0.70 eV

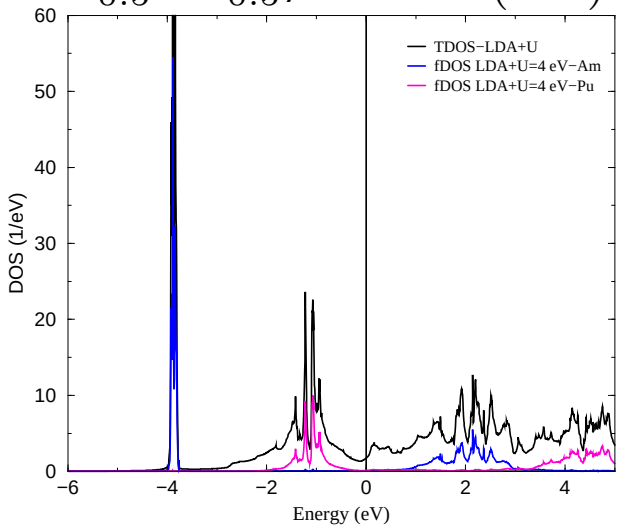
  .

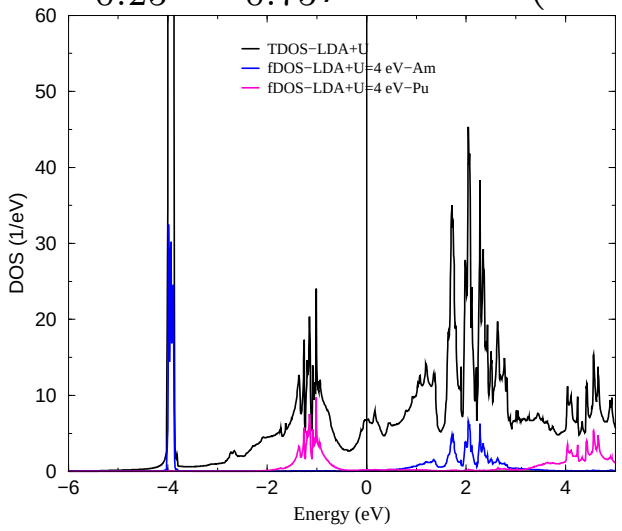
- The magnetism collapses in all cases, and Pu-Am alloys become non-magnetic, similarly to fcc-Am and δ-Pu.

DOS

$Pu_{0.75}Am_{0.25}$, $V = 177\ (a.u.)^3$ $Pu_{0.5}Am_{0.5}$, $V = 183\ (a.u.)^3$ $Pu_{0.25}Am_{0.75}$, $V = 190\ (a.u.)^3$





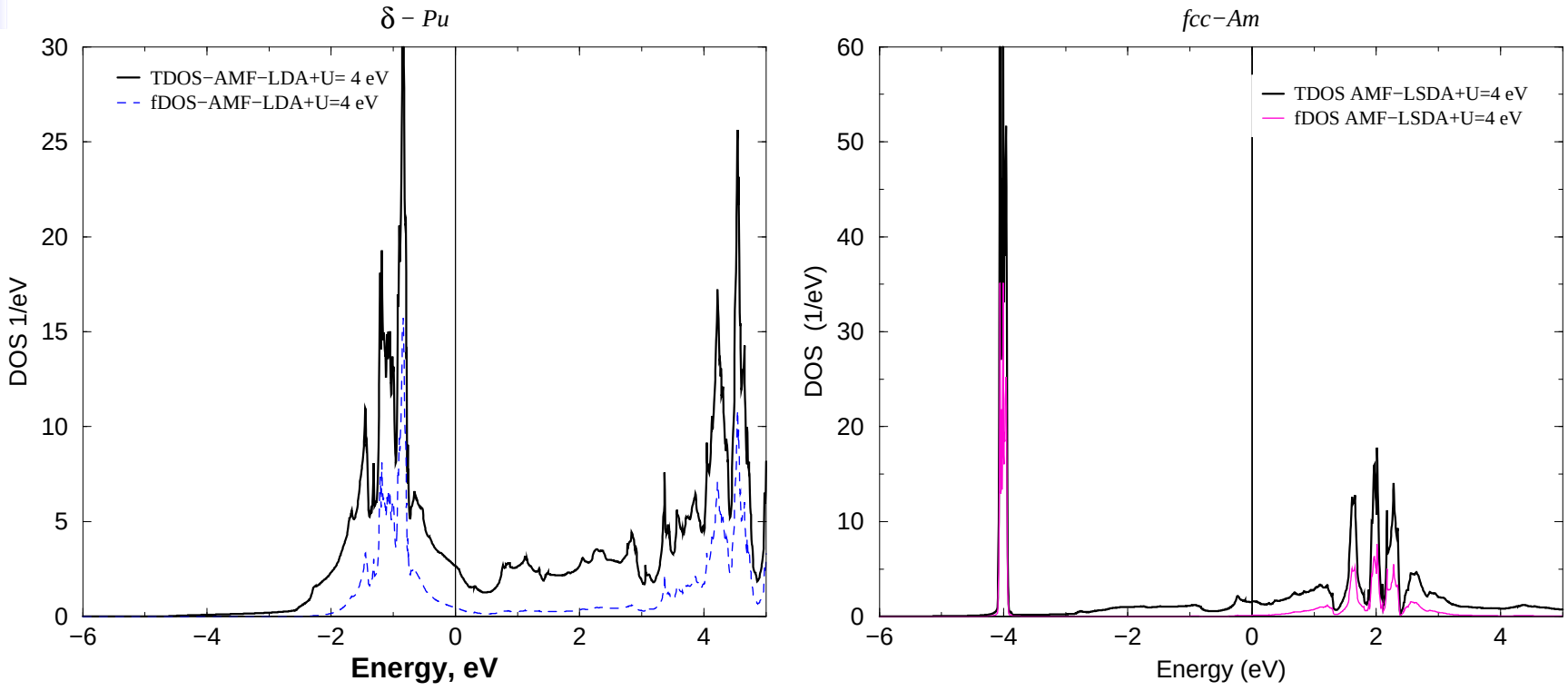


(Am-$n_{5f} = 6.02$, Pu-$n_{5f} = 5.43$) (Am-$n_{5f} = 5.98$, Pu-$n_{5f} = 5.41$) (Am-$n_{5f} = 5.96$, Pu-$n_{5f} = 5.40$)

Pu- and Am $5f$-manifolds are well separated. We find no sizable change in the Pu-$5f$ and Am-$5f$ manifold occupations. Pu-$5f$ and Am-$5f$ binding energies are slightly increasing ($\approx$ 0.2 eV) with an increase of Am content. Considering the lattice expansion with an increase of Am content, we did not find any sizeable effect on Pu- and Am-$5f$ states.

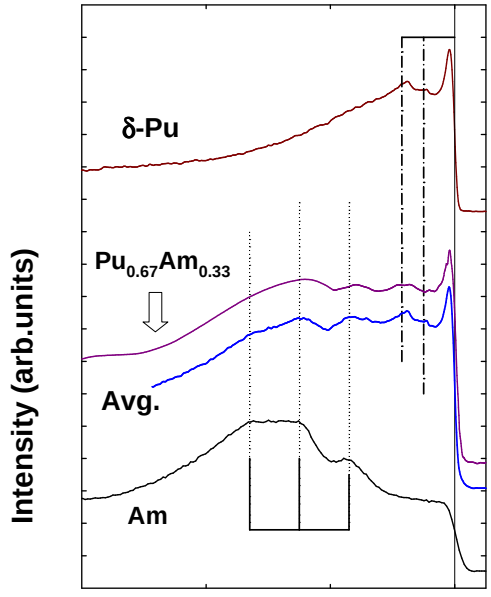
As the difference between V_{eq} of δ-Pu and fcc-Am is relatively small ($\approx$ 15 %), Am remains in the AmI phase, i.e. below the first phase transition at 6 GPa.

Is it "f^6"?



- Pu: six partly filled $j = 5/2$ f-states (n_f = 5.44) hybridized with a broad valence band.
- Am: six filled $j = 5/2$ f-states n_f = 5.92 $\Rightarrow$ fully localized f^6.
- *fcc* Pu-Am alloys are very much a simple weighted superposition of elemental Pu and Am with very little (if any) interaction between plutonium and americium $5f$-states.

Photoemission (PES)



- The exp. Pu-Am alloy PES

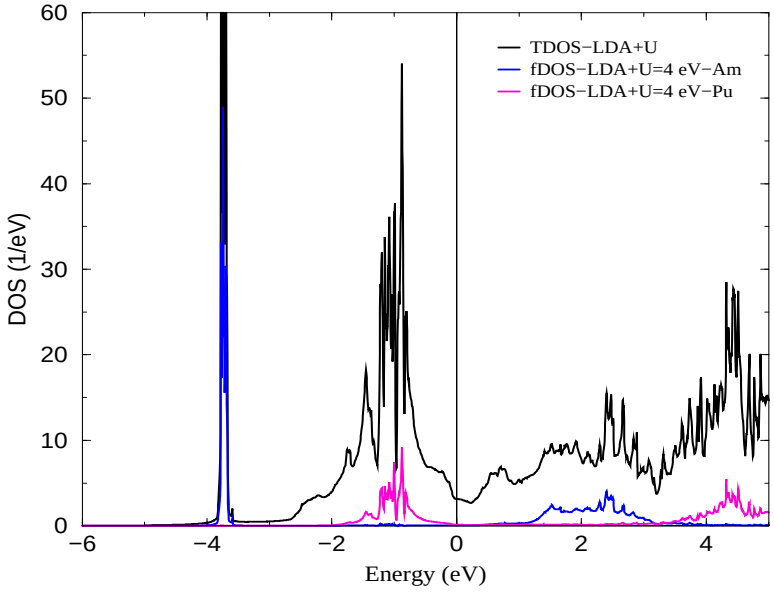
$\Rightarrow$ weighted average of pure Pu and Am PES

- The Pu-Am alloy DOS

$\Rightarrow$ weighted average of pure Pu and Am DOS

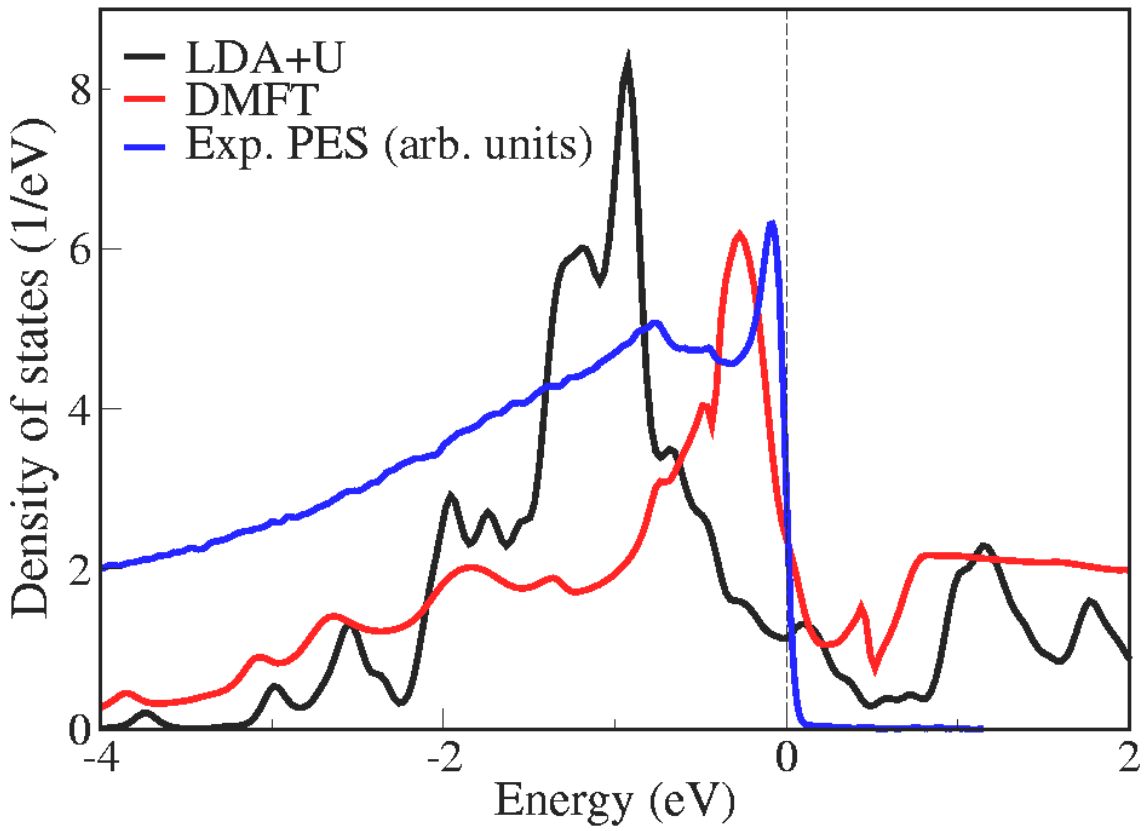
- It is no big surprise that DOS from AMF-LSDA+U fails for PES.

LSDA+U $\Rightarrow$ static ground state "one-electron" (Hartree-Fock) approach.



- PES describes the photoexcitations $\Rightarrow$ multiplets and dynamical fluctuations are needed.

δ-Pu PE



DMFT (T-matrix FLEX) for δ-Pu

L.V. Pourovskii, M.I. Katsnelson, A.I. Lichtenstein L. Havela, T. Gouder, F. Wastin, A. B. Shick, V. Drchal and G. H. Lander, Europhys. Lett. **74**, 479 (2006).

Towards DMFT

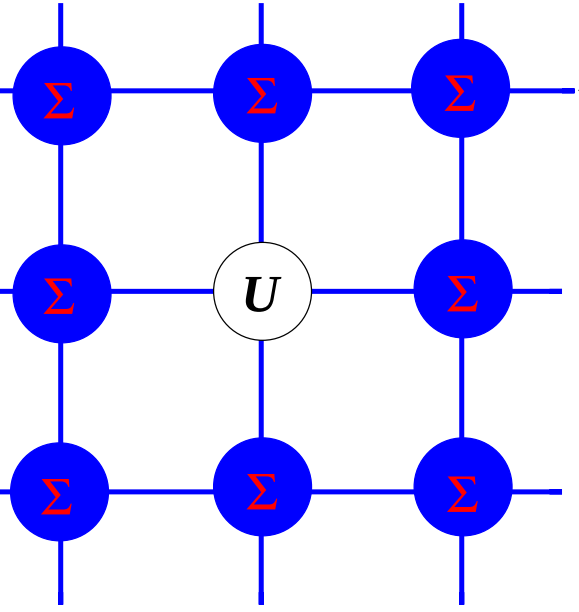
Interacting fermions on the lattice

$$\hat{H}_0 = \sum_{i,m,j,m',\sigma} \mathbf{t}^{i,j}_{m,m'} \mathbf{c}^{\dagger}{}_{i,m,\sigma} \mathbf{c}_{j,m',\sigma} + \sum_{i,m_1,m_2,\sigma,\sigma'} \xi_i(\vec{s} * \vec{l})_{m_1,\sigma,m_2,\sigma'} \mathbf{c}^{\dagger}_{i,m_1,\sigma} \mathbf{c}_{i,m_2,\sigma'}$$

On-site Coulomb Interaction: $\hat{H}^{int}$

$$\frac{1}{2} \sum_{i,m_1,m_2,m_3,m_4}^{\sigma,\sigma'} < m_1, m_2 | V^{ee} | m_3, m_4 > \mathbf{c}^{\dagger}_{i,m_1,\sigma} \mathbf{c}^{\dagger}_{i,m_2,\sigma'} \mathbf{c}_{i,m_3,\sigma'} \mathbf{c}_{i,m_4,\sigma}$$

- Lattice periodicity + a single-site M-body problem



$$\hat{H}(\vec{k}) = \hat{H}_0(\vec{k}) + \mathbf{\Sigma} \Rightarrow \hat{G}_{m,m'} = \frac{1}{V_{BZ}} \int d^3\mathbf{k} [z - \hat{H}_0(\vec{k}) - \mathbf{\Sigma}]^{-1}_{m,m'}$$

"Bath": $\hat{G}_0^{-1} = \hat{G}^{-1} + \mathbf{\Sigma} \Rightarrow$ Impurity Solver : $\hat{G} = F[\hat{G}_0, \hat{H}_{int}]$

$$\mathbf{\Sigma}^{new} = \hat{G}_0^{-1} - \hat{G}^{-1}$$

Simplifications

"Static" LDA+U: $\hat{G}_{m,m'} \Rightarrow n_{m,m'} = -\frac{\mathrm{Im}}{\pi} \int dz [\hat{G}(z)]_{m,m'}$

$$\mathbf{\Sigma} = V_{m,m'} \sim U \left(n_{m,m'} - \frac{1}{(2l+1)} Tr[n_{m,m'}] \delta_{m,m'} \right)$$

"Hubbard I": Atomic limit $\mathbf{\Sigma}$

Atomic hamiltonian with SOC

Program written by Jindřich Kolorenč

$$\hat{H}_{\text{atom}} = \sum_{m_1,m_2,\sigma,\sigma'} \xi(\vec{s} * \vec{l})_{m_1,\sigma,m_2,\sigma'} \mathbf{c}^{\dagger}_{i,m_1,\sigma} \mathbf{c}_{i,m_2,\sigma'} \; +$$

$$\frac{1}{2} \sum_{m_1,m_2,m_3,m_4,\sigma,\sigma'} < m_1, m_2 | V^{ee} | m_3, m_4 > \mathbf{c}^{\dagger}_{i,m_1,\sigma} \mathbf{c}^{\dagger}_{i,m_2,\sigma'} \mathbf{c}_{i,m_3,\sigma'} \mathbf{c}_{i,m_4,\sigma}$$

Exact diag.: $\hat{H}_{\text{atom}} | \nu >= E_\nu | \nu > \; ; \; < N >= \frac{1}{Z} Tr \Big[\exp(-\beta(H^{at} - \mu N)) \; N \Big]$

Given $< N > \Rightarrow$ the "chemical potential" μ (or E_F).

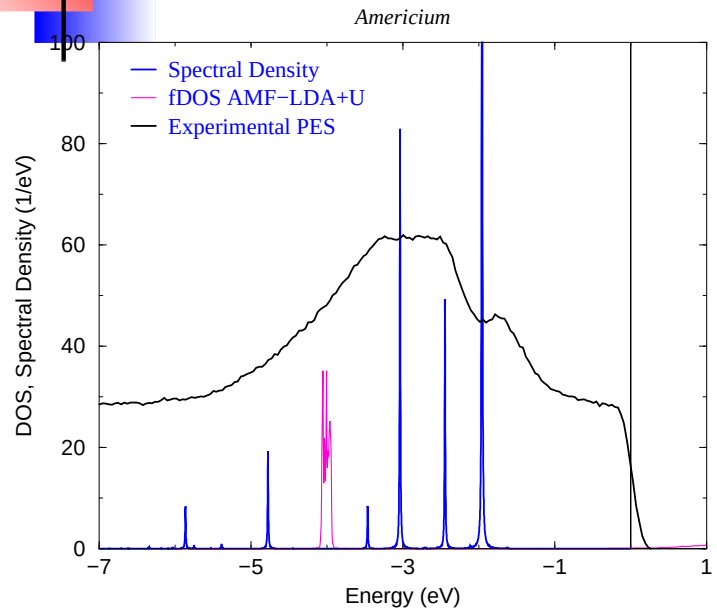
The Green function:

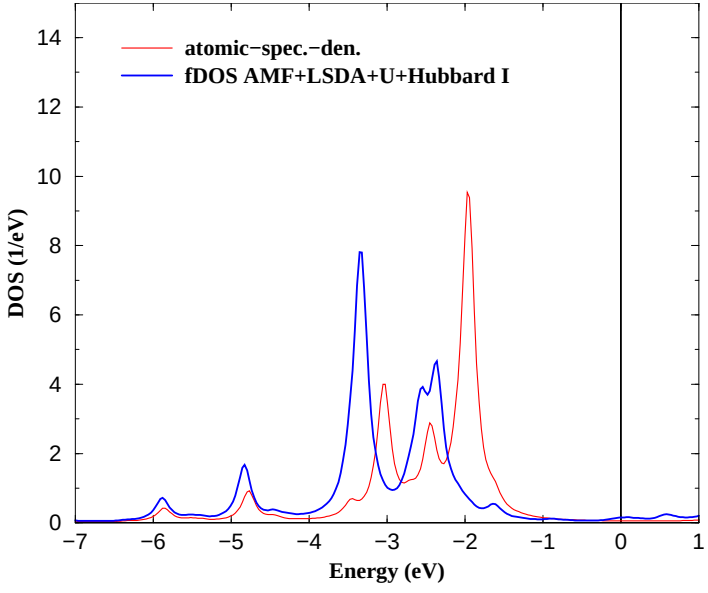
$$\hat{G}_{m_1,\sigma,m_2,\sigma'}(z-\mu) = \frac{1}{Z} \sum_{\nu,\lambda} \frac{< \lambda | c_{m_1,\sigma} | \nu >< \nu | c^{\dagger}_{m_2,\sigma'} | \lambda >}{z - \mu + (E_\lambda - \mu N_\lambda) - (E_\nu - \mu N_\nu)} \; *$$

$$(\exp(-\beta(E_\nu - \mu N_\nu)) + \exp(-\beta(E_\lambda - \mu N_\lambda)))$$

Spectral Density $= -\frac{\text{Im}}{\pi} Tr[\hat{G}_{m_1,\sigma,m_2,\sigma'}(z-\mu)]$

Am PE





- The exp. Am PES

$\Rightarrow$ Am "f^6" Spectral Density: $f^5 \rightarrow f^6$ & $f^6 \rightarrow f^7$

(U= 4 eV; J= 0.7 eV), ξ = 0.34 eV

(in agreement with A. Svane, arXiv:cond-mat/0508311)

Multiplet transitions determine PES

Am f^6 AMF-LSDA+U DOS $\rightarrow$ f^6 ground state

G.S. DOS $\neq$ Spectral density

- Static mean-field

LDA+U: $\hat{H}(\vec{k}) = \hat{H}_0(\vec{k}) + \mathbf{V}_{m\sigma,m'\sigma'}$

$$\hat{G}_{m,m'} = \frac{1}{V_{BZ}} \int d^3\mathbf{k} [z - \hat{H}_0(\vec{k}) - \mathbf{V}]^{-1}_{m\sigma,m'\sigma'}$$

Static mean-field "bath": $\hat{G}_0^{-1} = \hat{G}^{-1} + \mathbf{V}$

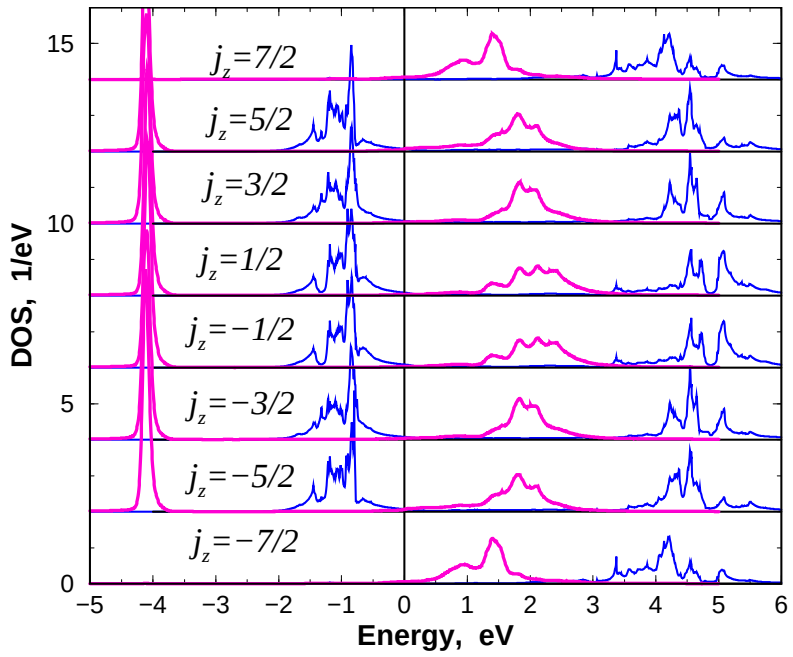
SIAM: $\hat{G}_0(z) = [z - \epsilon_f - \Delta]^{-1}$

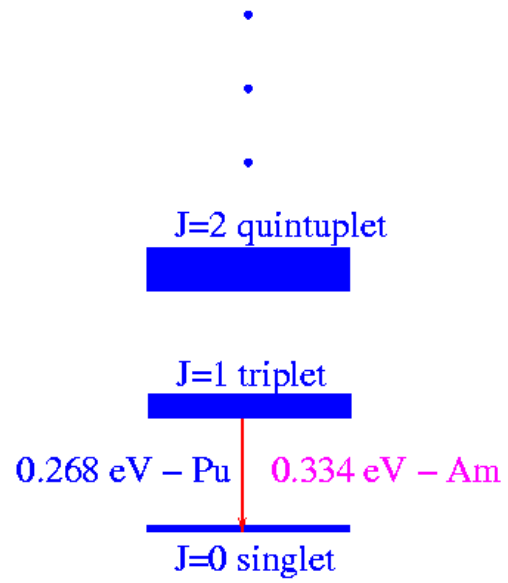
$$\Delta(z)_{m\sigma,m'\sigma'} = \frac{1}{V_{BZ}} \int d^3\mathbf{k} \frac{V^*_{\mathbf{k}m\sigma} V_{\mathbf{k}m'\sigma'}}{z - \epsilon_k}$$

Substitute LDA+U $\mathbf{V}$ by Hubbard I $\mathbf{\Sigma}(z)$

Spectral Density $= -\frac{\mathrm{Im}}{\pi} Tr[\hat{G}_{m_1,\sigma,m_2,\sigma'}(z)]$

Can Am make Pu magnetic?





- Am-atom: f^6 - singlet, $< J^2 >= J(J+1) = 0 \rightarrow J = 0$

$< S^2 >= S(S+1) \rightarrow S = 2.47$ & $< L^2 >= L(L+1) \rightarrow L = 2.47$ - it is not $^7F_0$

AMF-LSDA+U: six filled $j = 5/2$ f-states, $J_z = S_z = L_z = 0$

- Pu-atom: f^6 - singlet, $J = 0$, $S = 2.52$ & $L = 2.52$

AMF-LSDA+U: six partly filled $j = 5/2$ f-states, $J_z = S_z = L_z = 0$

By no means Am-induced lattice expansion can help to close the 0.27 eV gap between $J = 0$ singlet and $J = 1$ triplet

Summary

- The "around-mean-field" version of LSDA+U method gives a unified picture of δ-Pu, Am and δ-Pu-Am alloys.
- We demonstrate the non-magnetic character of $Pu - Am$ alloys, in agreement with experiment.
- Electronically and "non-magnetically" the *fcc* Pu-Am alloys: a simple weighted superposition of elemental Pu and Am.
- AMF-LSDA+U and Many-Body Atomic Exact Diagonalization suggest that $\delta - Pu$ and *fcc*-Am have $5f^6$-like J=0 singlet ground state.

A. B. Shick, V. Drchal, and L. Havela, Europhys. Lett. 69, 588 (2005).
A. B. Shick, L. Havela, J. Kolorenč, V. Drchal, T. Gouder, P. M. Oppeneer, Phys. Rev. B 73, 104415 (2006).
L. V. Pourovskii *et al.* Europhys. Lett. 74 479 (2006).