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Ab initio description of actinides: Hund's exchange, spin-orbit coupling and crystal structure

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Conference: *What about U ?*

Actinides in the periodic table

4*d* element: filling of the 4*d* band (Bonding states and antibonding): 4*d* electrons are delocalized.

Lanthanides:

4*f* electrons are localized, negligible overlap between 4*f* orbitals .

Actinide: intermediate case of localization.

At atmospheric pressure:

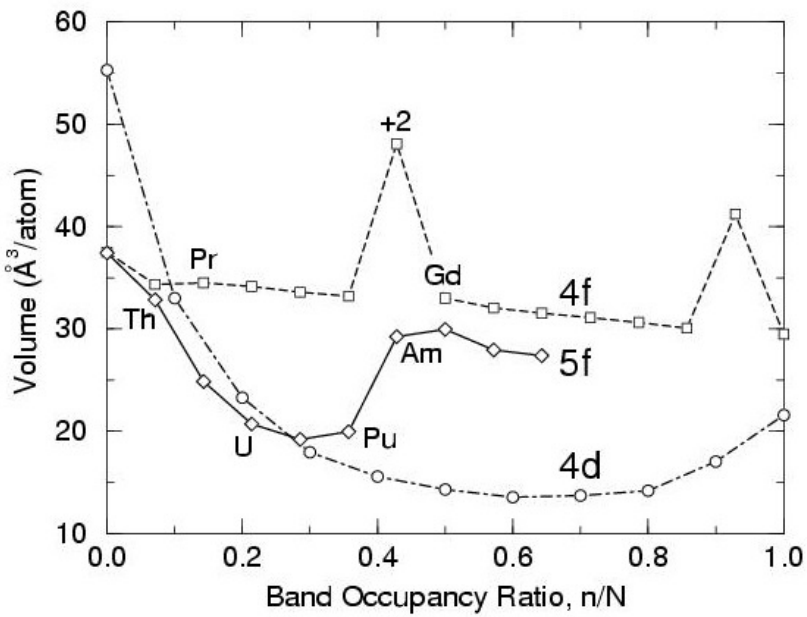
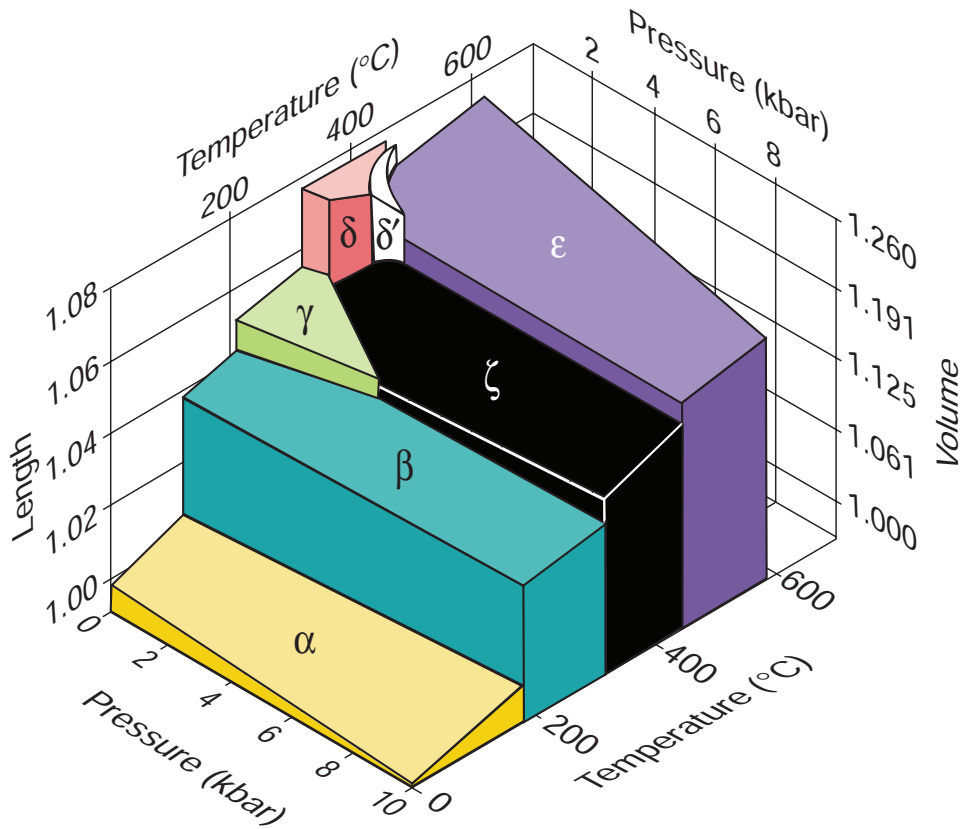


FIG. 2. Atmospheric pressure volumes of the $4d$ transition metals, the rare earths $(4f)$, and the actinides $(5f)$. The two rare earths with large volumes are divalent.

[Mac Mahan, et al J. Comp.-Aid. Mater. Des. 5, 131 (1998)]

Plutonium has a large number of difference phases

- Many phases
- Some phases with delocalized electrons (low volume) and phases with localized electrons (large volume).



From Kevin T. Moore and Gerrit van der Laan Rev. Mod. Phys. 81, 235 (2009)

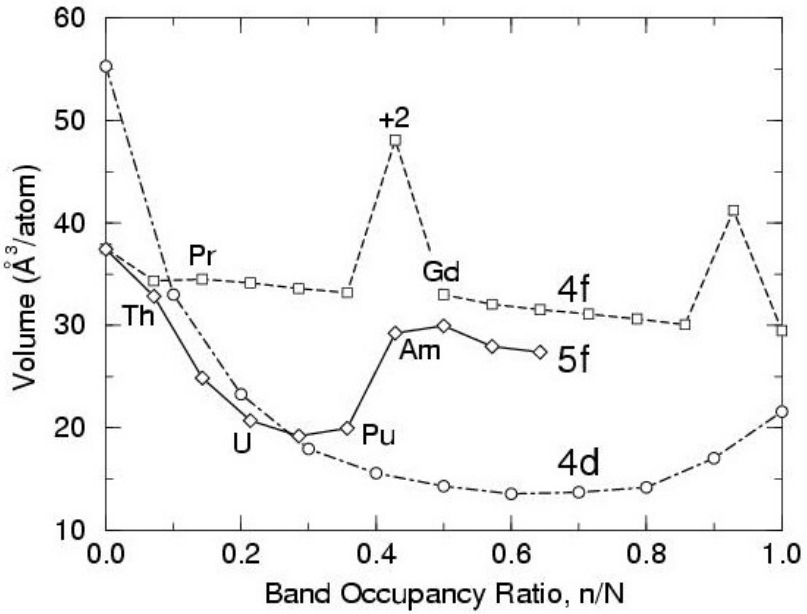
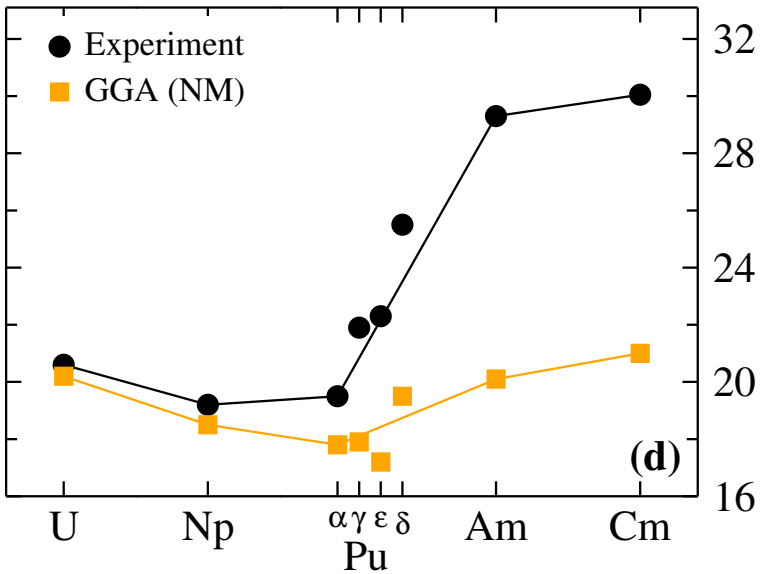


FIG. 2. Atmospheric pressure volumes of the $4d$ transition metals, the rare earths $(4f)$, and the actinides $(5f)$. The two rare earths with large volumes are divalent.

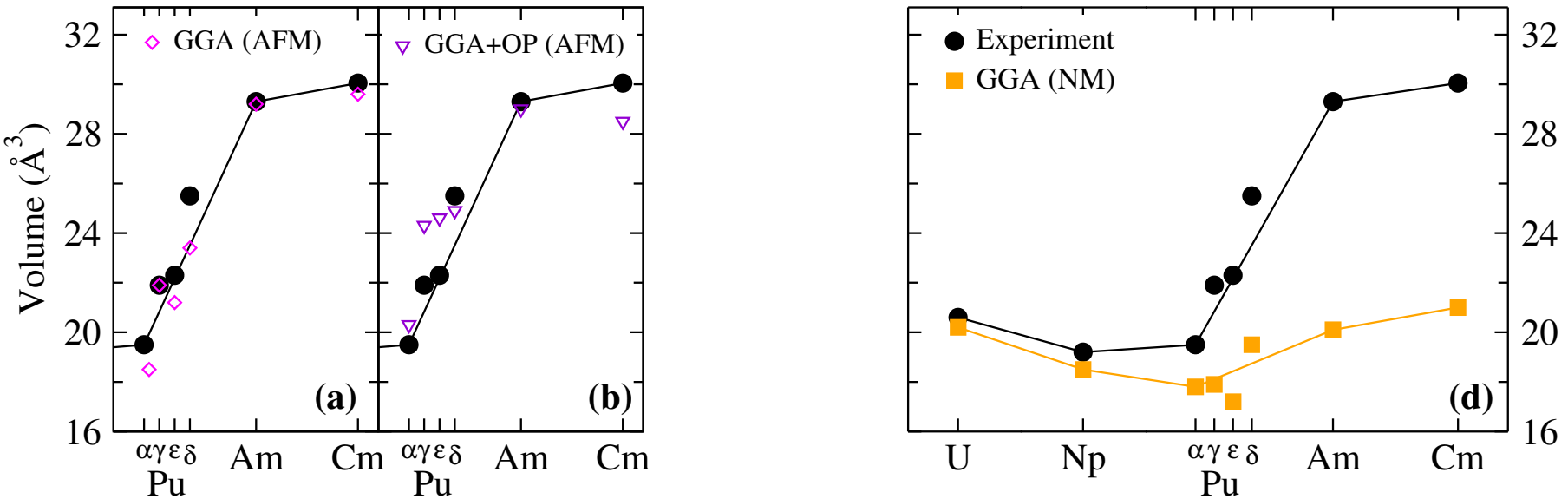
- α-U, α-Np, and α-Pu are low symmetry phases induced by chemical bonding of *f* electrons.
- δ-Pu, Am, and Cm have compact phases (as lanthanides).
- δ and α Plutonium, have no local moment, ordered or not. (J. C. Lashley, A. Lawson, R. J. McQueeney, and G. H. Lander, Phys. Rev. B 72, 054416 (2005))

Non magnetic GGA underestimates volume for late actinides



GGA: Cohesion is overestimated, not enough correlation

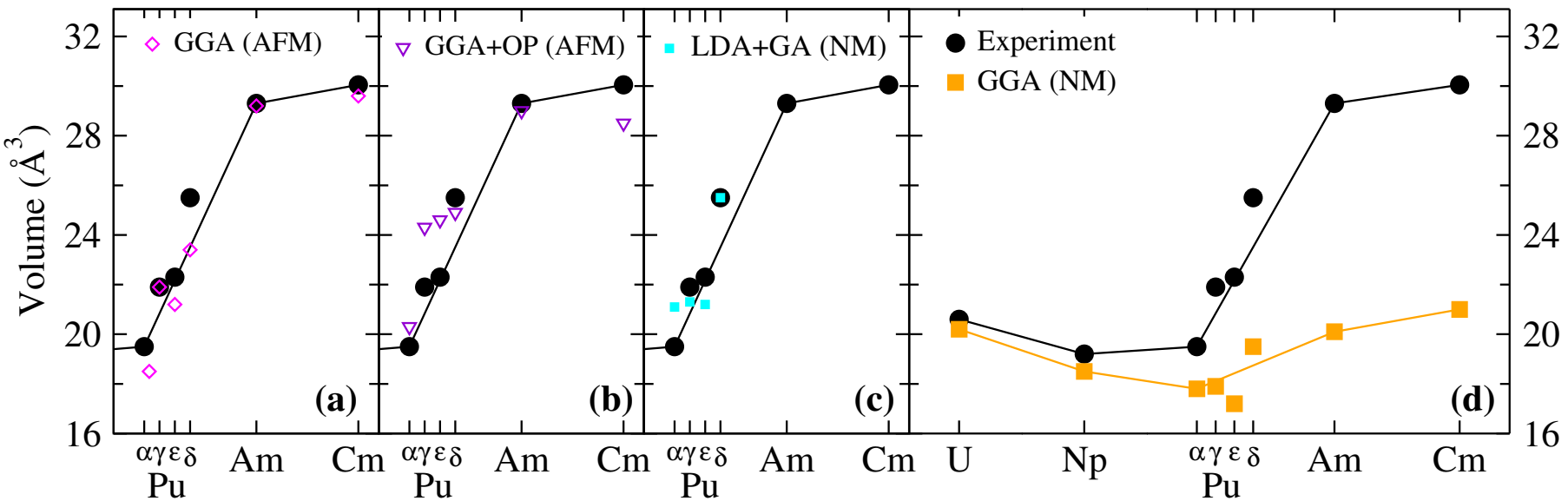
GGA-AFM improves volumes



GGA-AFM: good description of volumes but magnetism is wrong

GGA(AFM) G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A. Kutepov and S. Kutepova J. Magn. Magn. Mater. 272, E329 (2004)
GGA+OP P. Söderlind and B. Sadigh Phys. Rev. Lett. 92, 185702 (2004), P. Söderlind *al* MRS Bull. 35, 883 (2010)

LDA+GA results



Gutzwiller with U=4.5 eV, J_{H}=0.36 eV: good volumes and magnetism

GGA(AFM) G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A. Kutepov and S. Kutepova J. Magn. Magn. Mater. 272, E329 (2004)
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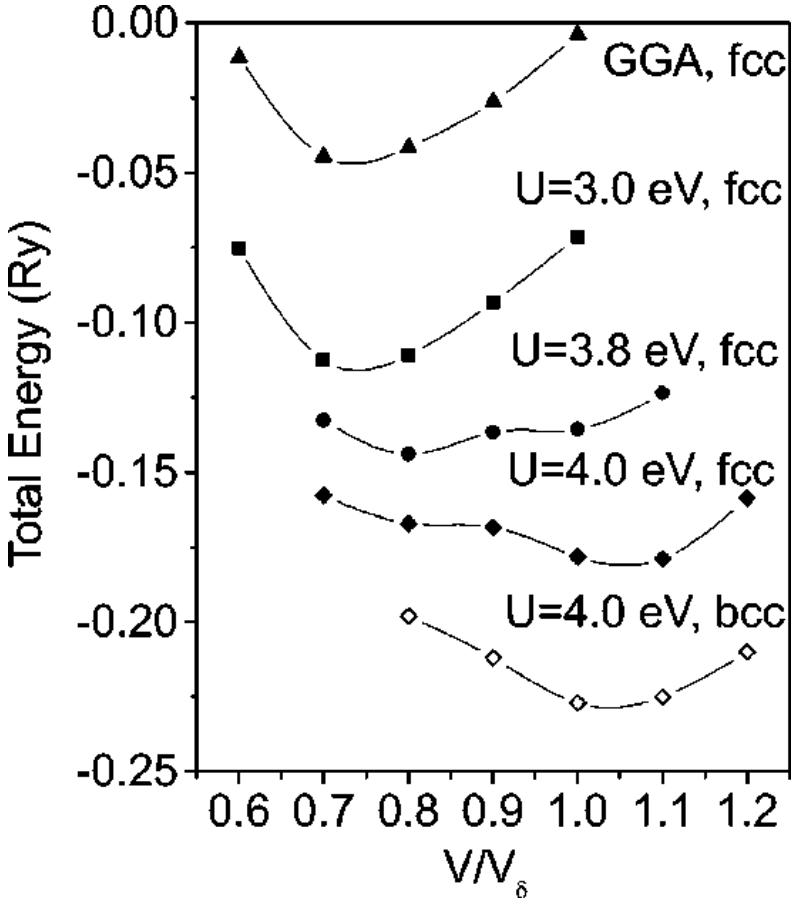


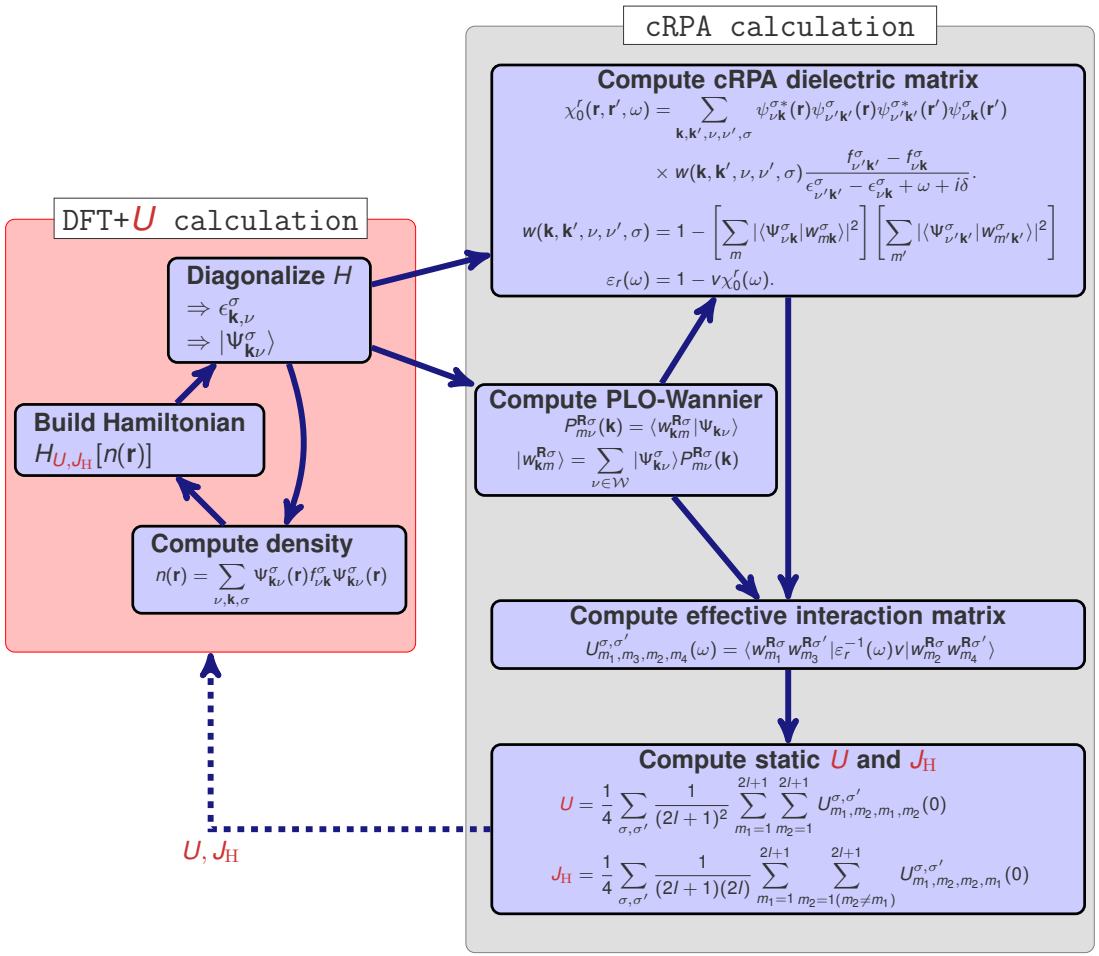
Pioneering DFT+DMFT calculation with U=4 eV and J_{H}=0 eV.

(S. Y. Savrasov, G. Kotliar, and E. Abrahams, Nature (London) 410, 793 (2001))

Is it possible to describe all actinides with a single framework ?

- Calculation of effective interactions U and J_{H} with cRPA ?
- Does DFT+DMFT calculations with cRPA interactions give good structural properties ?
- What is the role of crystal structure ?
- Role of SOC and Hund's exchange J_{H} ?

Self-consistent calculation of U in ABINIT



F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein PRB 70, 195104 (2004)
K. Karlsson, F. Aryasetiawan, and O. Jepsen Phys. Rev. B 81, 245113 (2010)

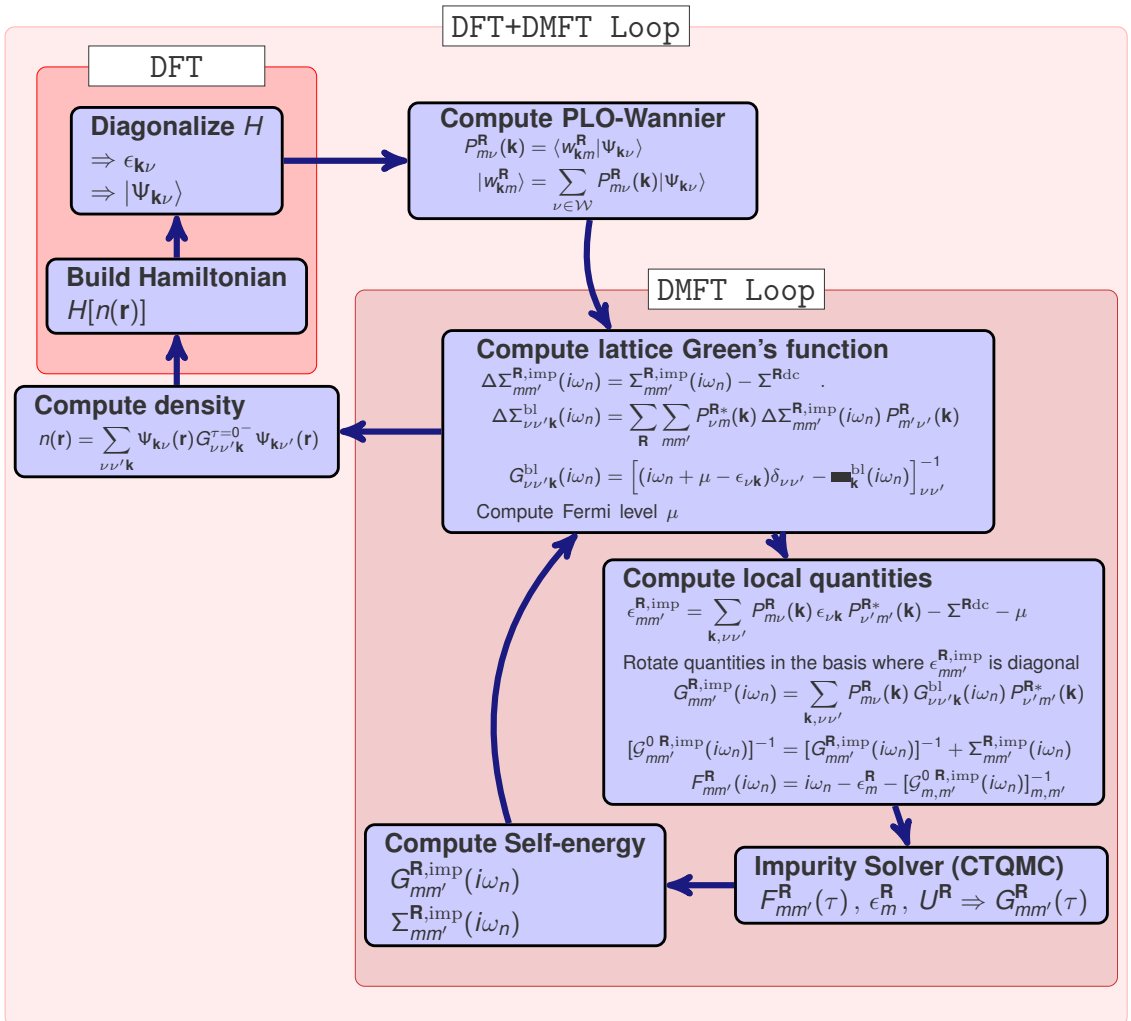
B. Amadon, T. Applencourt, F. Bruneval, Physical Review B **89**, 125110 (2014)

What about U ? U is small for plutonium and americium

	U	Np	Pu	Am	Cm
U	0.8	1.0	0.95	1.5	3.4
U_{diag}	1.5	1.7	1.7	2.3	4.3
J_{H}	0.4	0.4	0.45	0.4	0.55

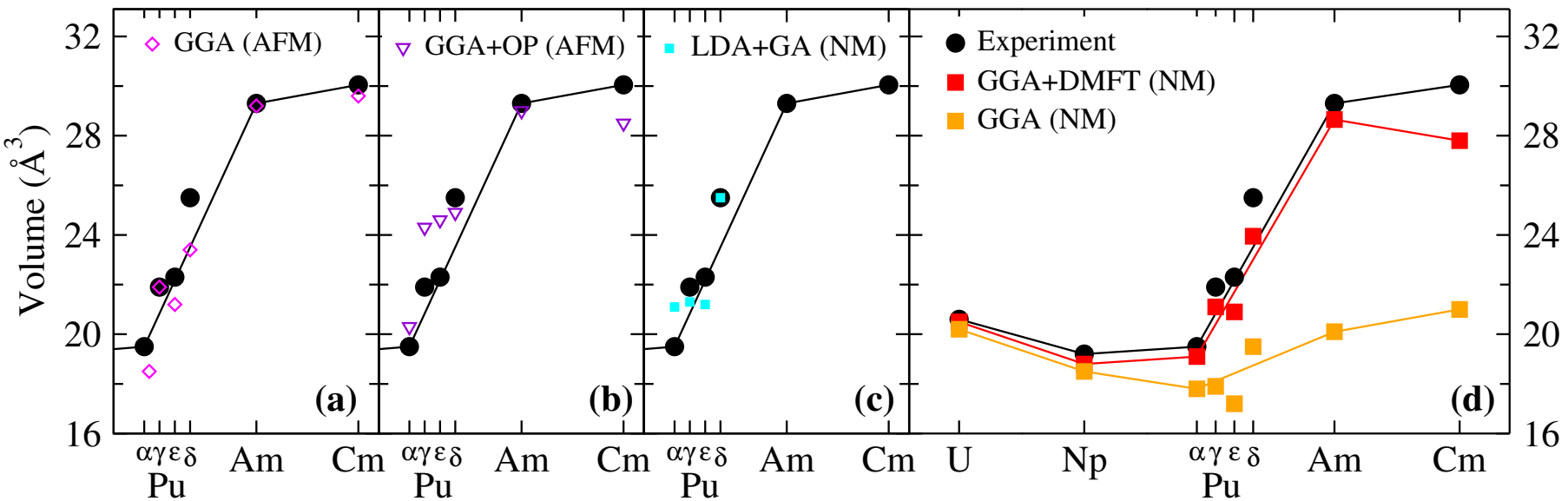
- U is weaker than expected in Pu and Am

DFT+DMFT in ABINIT



B. Amadon Journal of Phys.: Cond. Matter **24**, 075604 (2012).
J. Bieder, B. Amadon, Phys. Rev. B **89**, 195132 (2014)

U and J_H are used to compute structural properties in DFT+DMFT.



A good description of structural and magnetic properties

GGA(AFM) G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A. Kutepov and S. Kutepova J. Magn. Magn. Mater. 272, E329 (2004)
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GGA+DMFT B. Amadon, Phys. Rev. B **94**, 115148 (2016)

Comparison with previous works

	U, J_{H} (eV)	$V(\mathrm{\AA}^3)$	B_0(GPa)
δ-Plutonium			
GGA	0.00, 0.00	19.8	
GGA+DMFT Savrasov *et al* (2001)	4.00, 0.00	26.5	
GGA+DMFT/CTQMC (this work)	4.00, 0.00	25.8	28

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GGA+DMFT/CTQMC (this work)	0.94, 0.46	24.0	46
Exp (600 K)		25.0	30
Exp (Extrapolated at 0 K)		25.5	

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Exp (600 K)		25.0	30
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Americium			
LDA+DMFT/HI (Savrasov *et al* 2006)	4.50, 0.60	27.4	45
LDA+DMFT/CTQMC (this work)	4.50, 0.60	28.0	44

Not in contradiction with previous works.

U and *J* are here computed.

Analysis: Three key points

- Role of interactions on phases of Pu with different structures ?
- Role of structure on the volume jump ?
- Role of SOC and J_{H} on the volume jump ?

Role of interaction on phases of Pu with different structures.

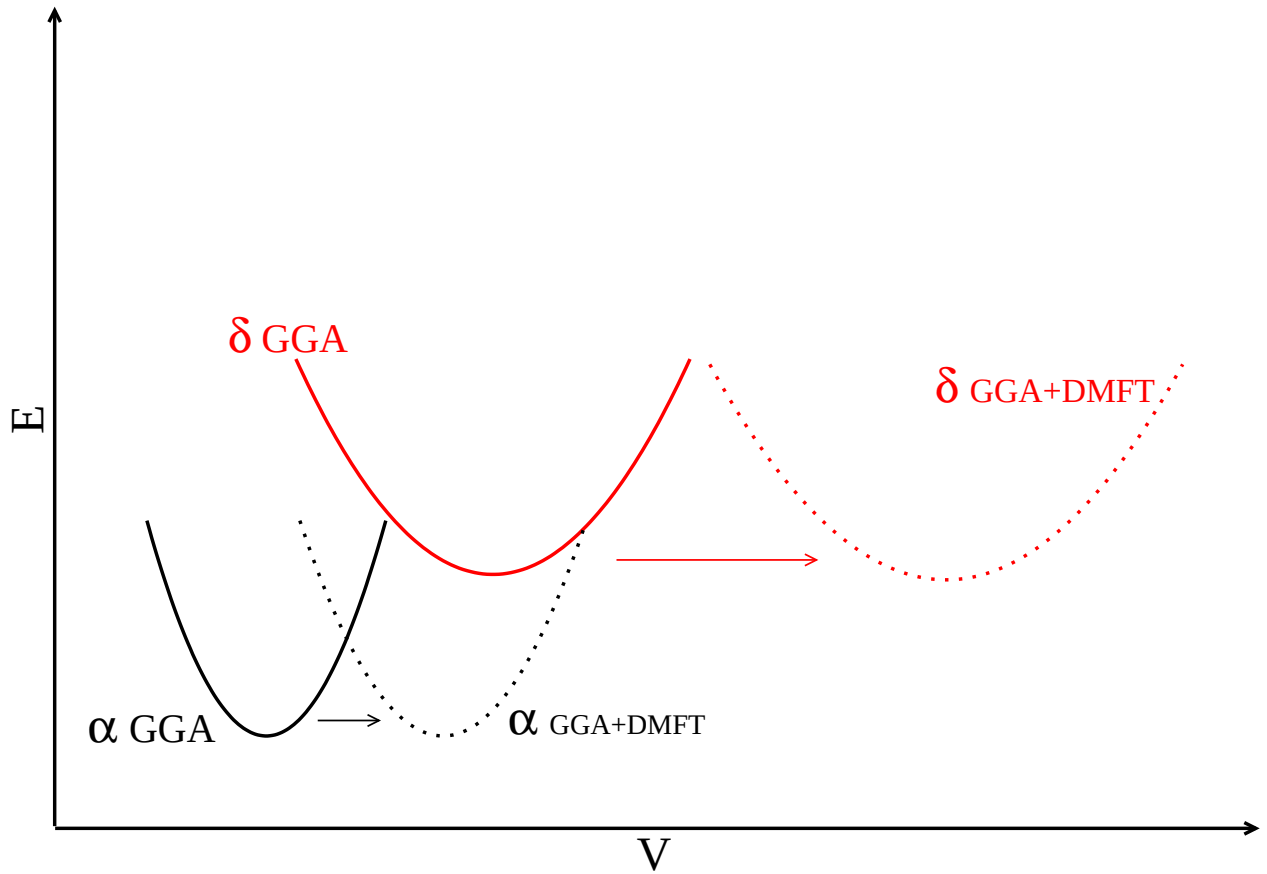
Phase	Number of neighbors	$d^{\min}_{Pu-Pu}$
α (pseudo-α)	4	2.51
δ	12	2.96

- δ phase has more neighbors, but they are farther apart.
- α phase has less neighbors, but they are closer.
- Chemical bonding is larger in α phase.

- The α phase is less sensitive to interactions.

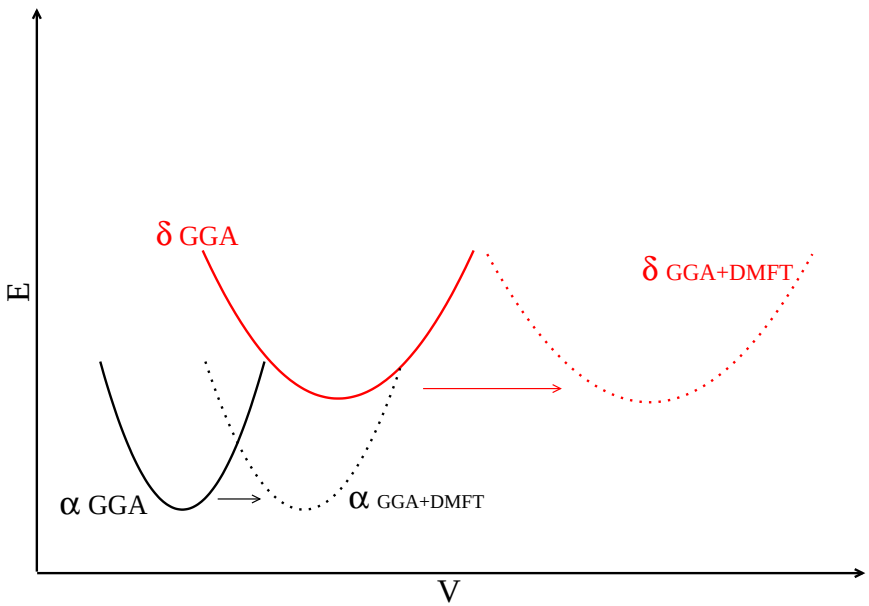
Pseudo-α phase: J. Bouchet, R. C. Albers, M. D. Jones, and G. Jomard Phys. Rev. Lett. 92, 095503 (2004).

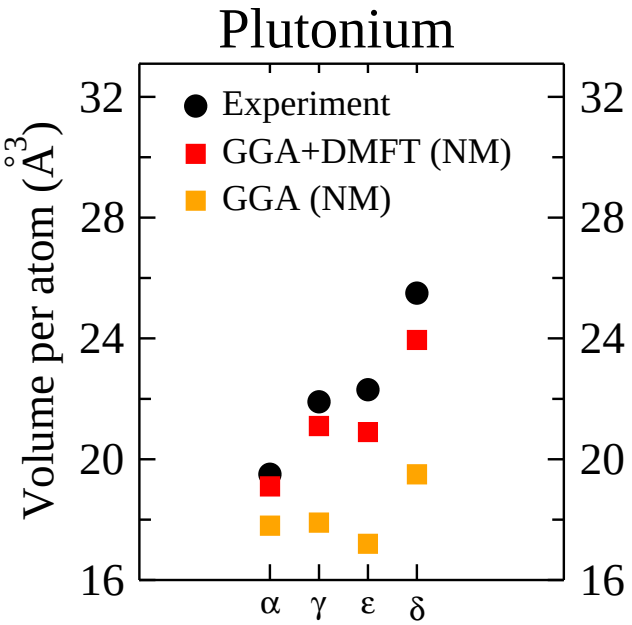
Role of interaction on phases of Pu with different structures.



- Chemical bonding stronger in the α phase, less sensitive to interactions.
- Chemical bonding weaker in the δ phase, more sensitive to interactions.

Role of interaction on phases of Pu with different structures.





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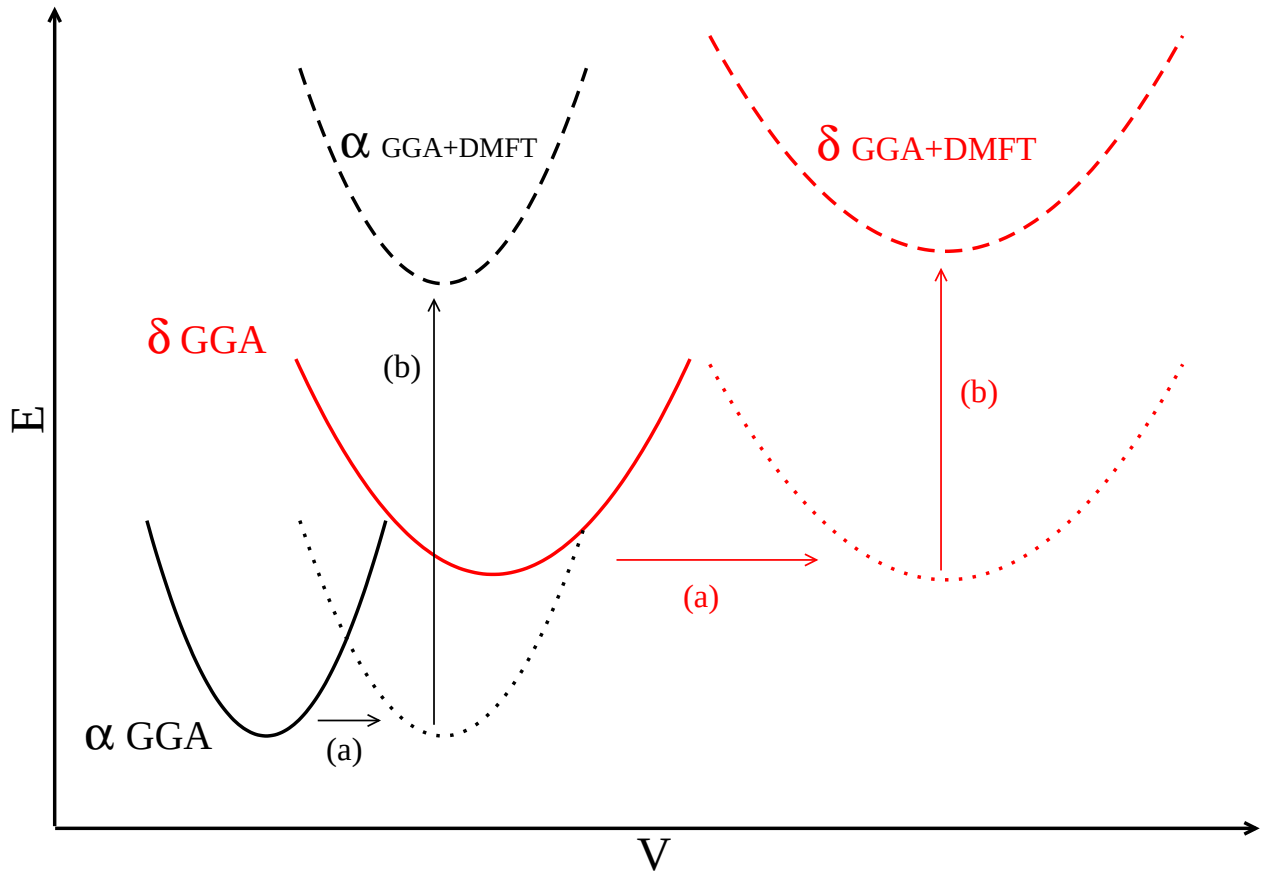

- (a) Chemical bonding stronger in α phase, less sensitive to interactions.
- (b) Electrons are more delocalized: interaction larger in the α phase.

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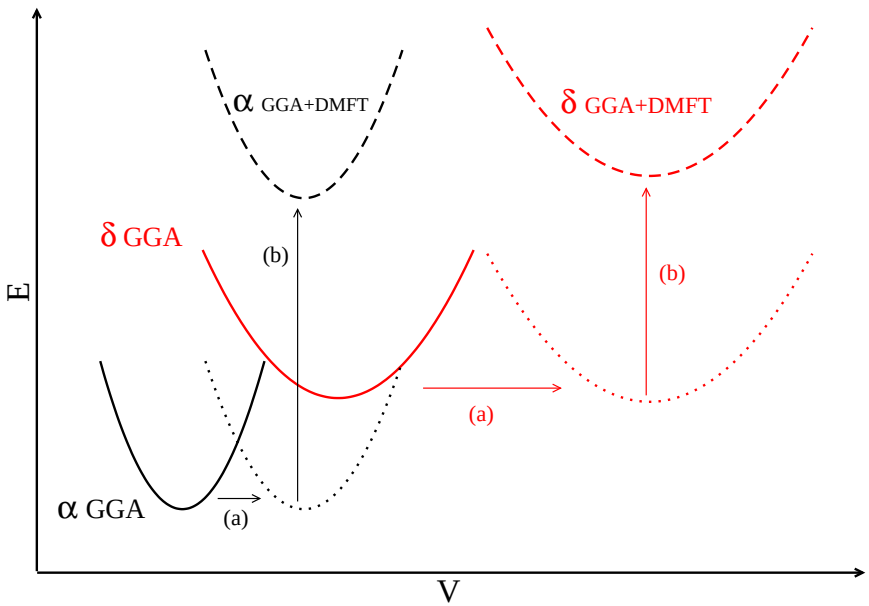
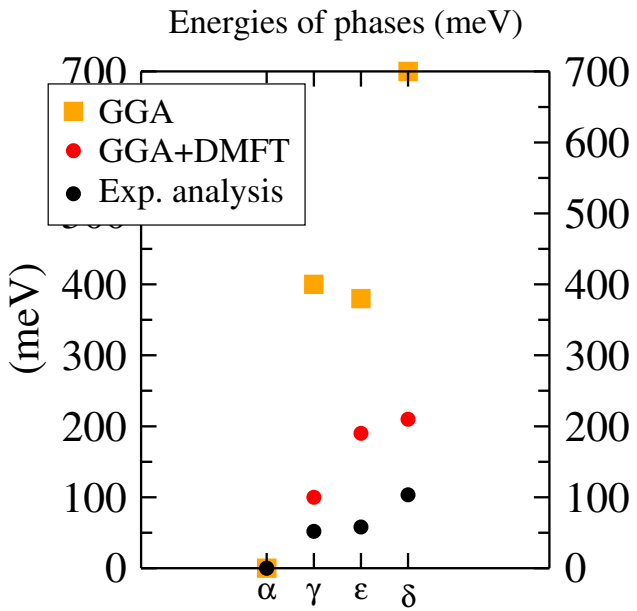




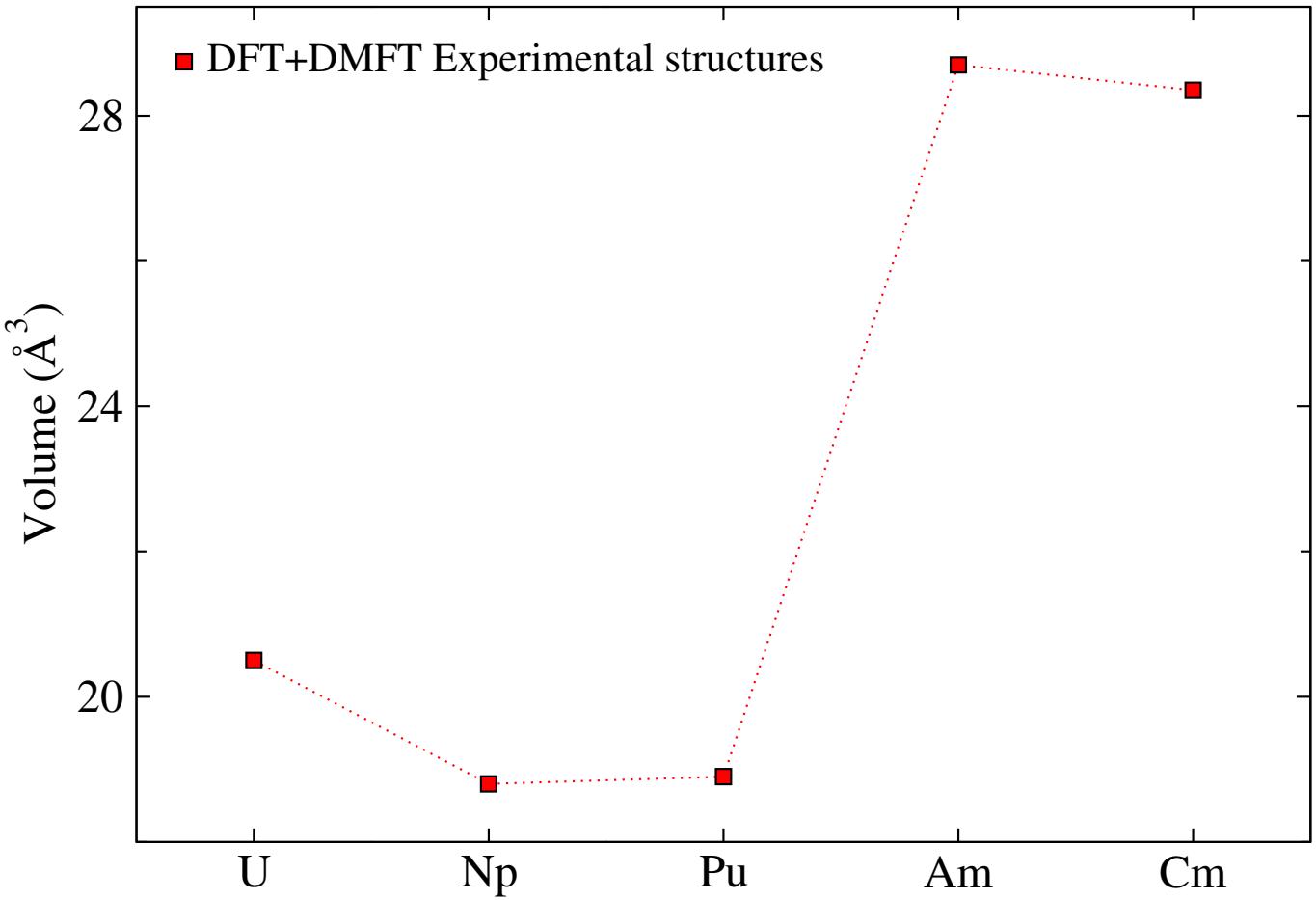
- (a) Chemical bonding stronger in α phase, less sensitive to interactions.
- (b) Electrons are more delocalized: interaction larger in the α phase.

Exp analysis: Duane C. Wallace Phys. Rev. B 58, 15433 (1998)

The volume jump: Impact of crystal structure.

- The jump in volumes in actinides involves a different structure for each element
- Does the volume jump persists if all elements are in the same (fictituous) structure ?

Role of structure in the volume jump



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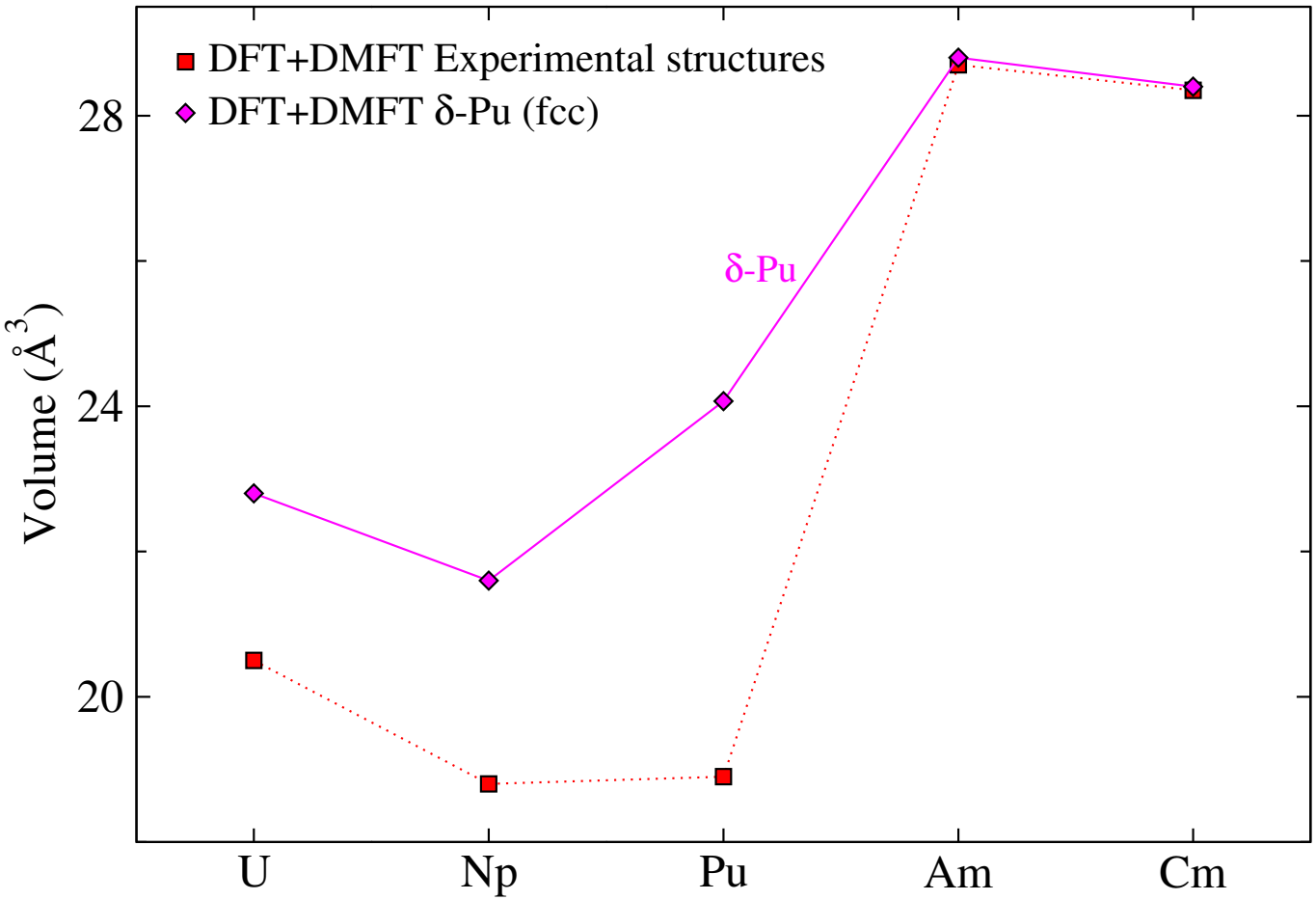

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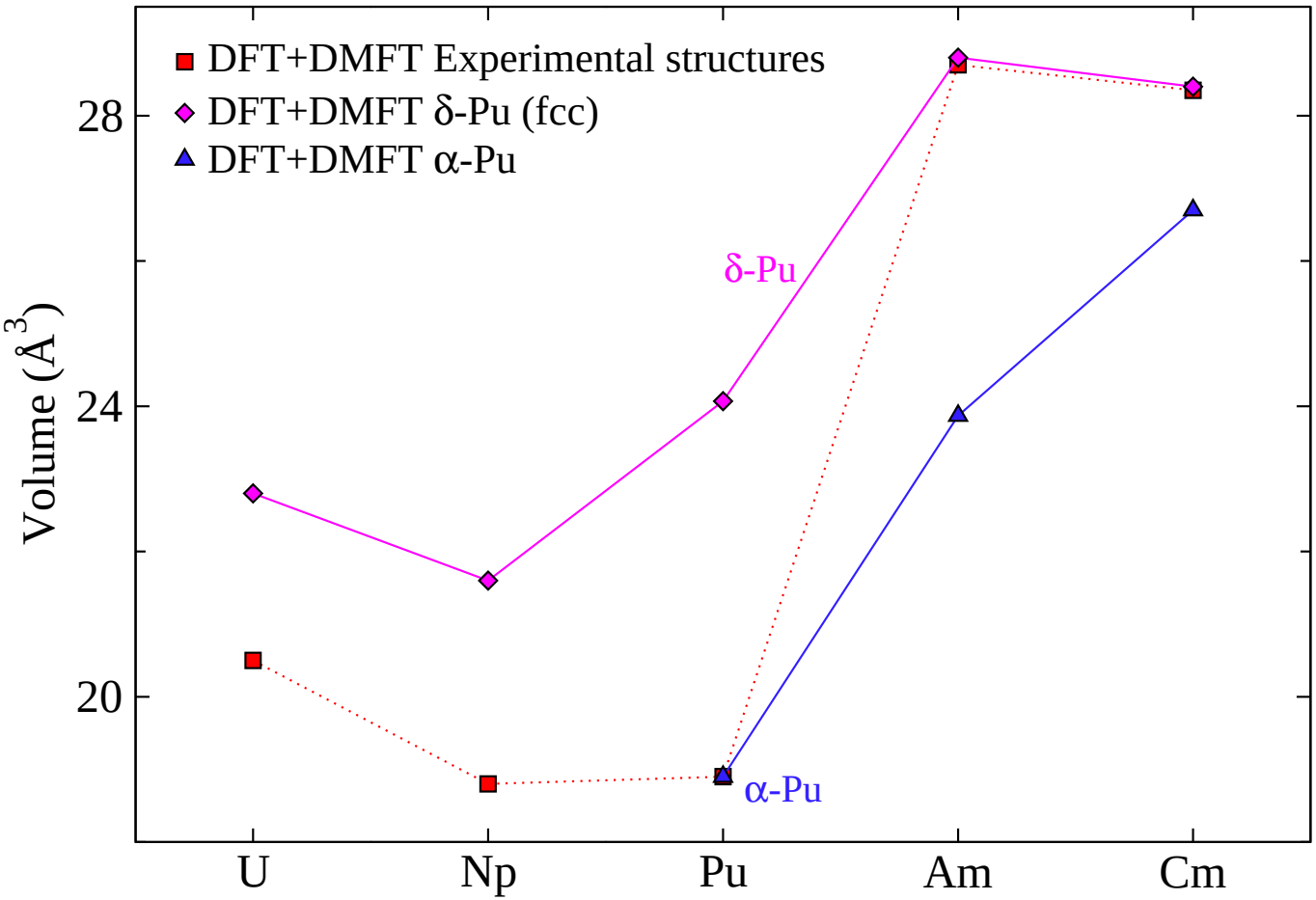

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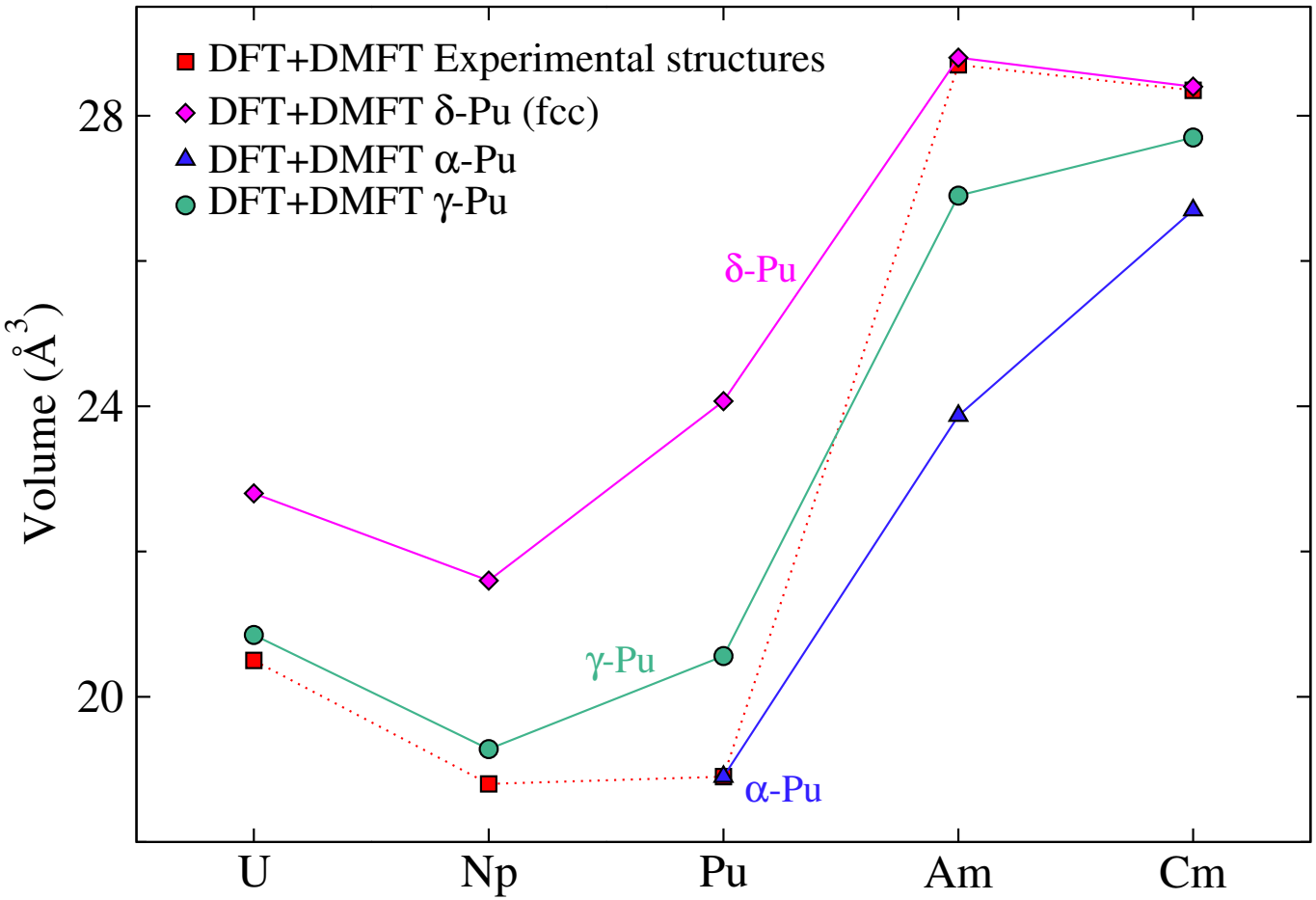

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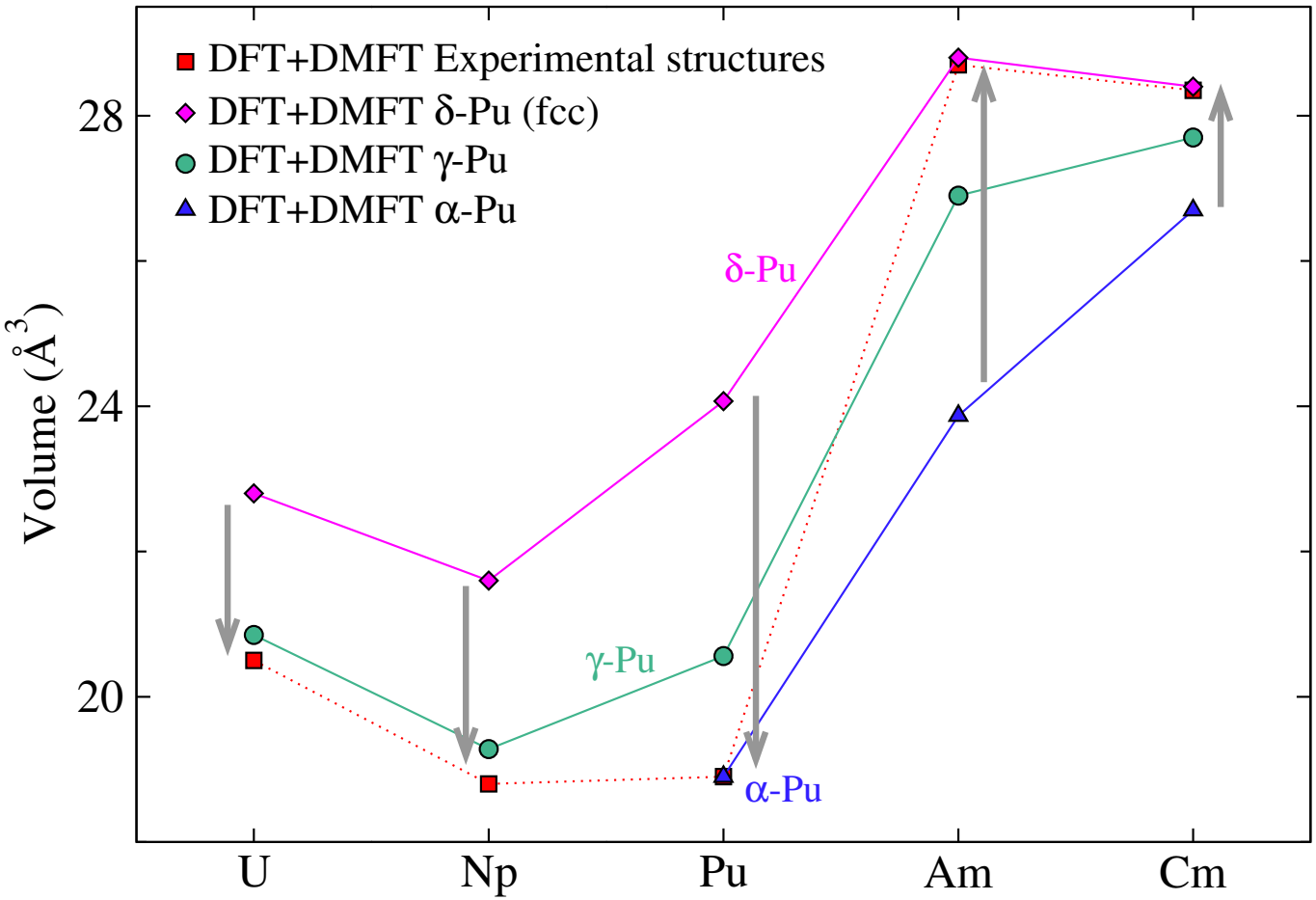
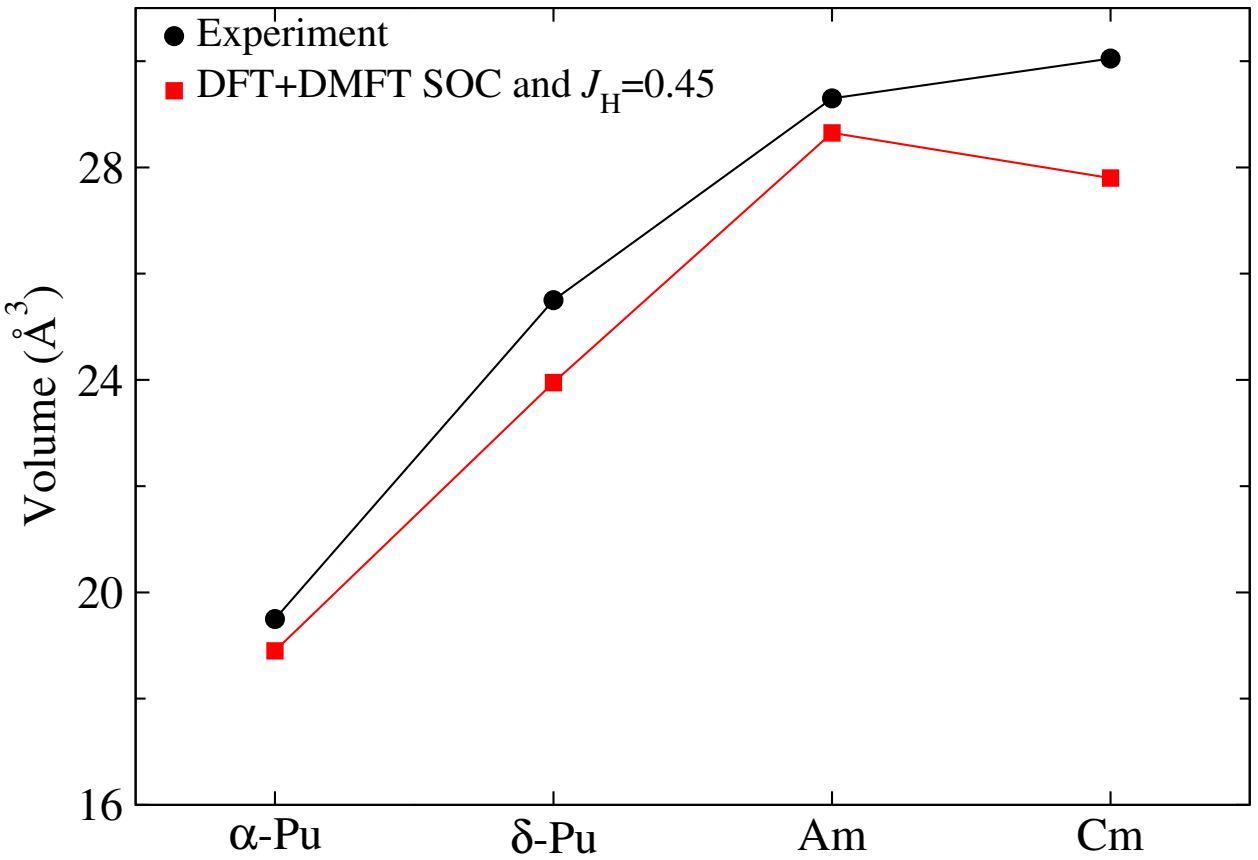


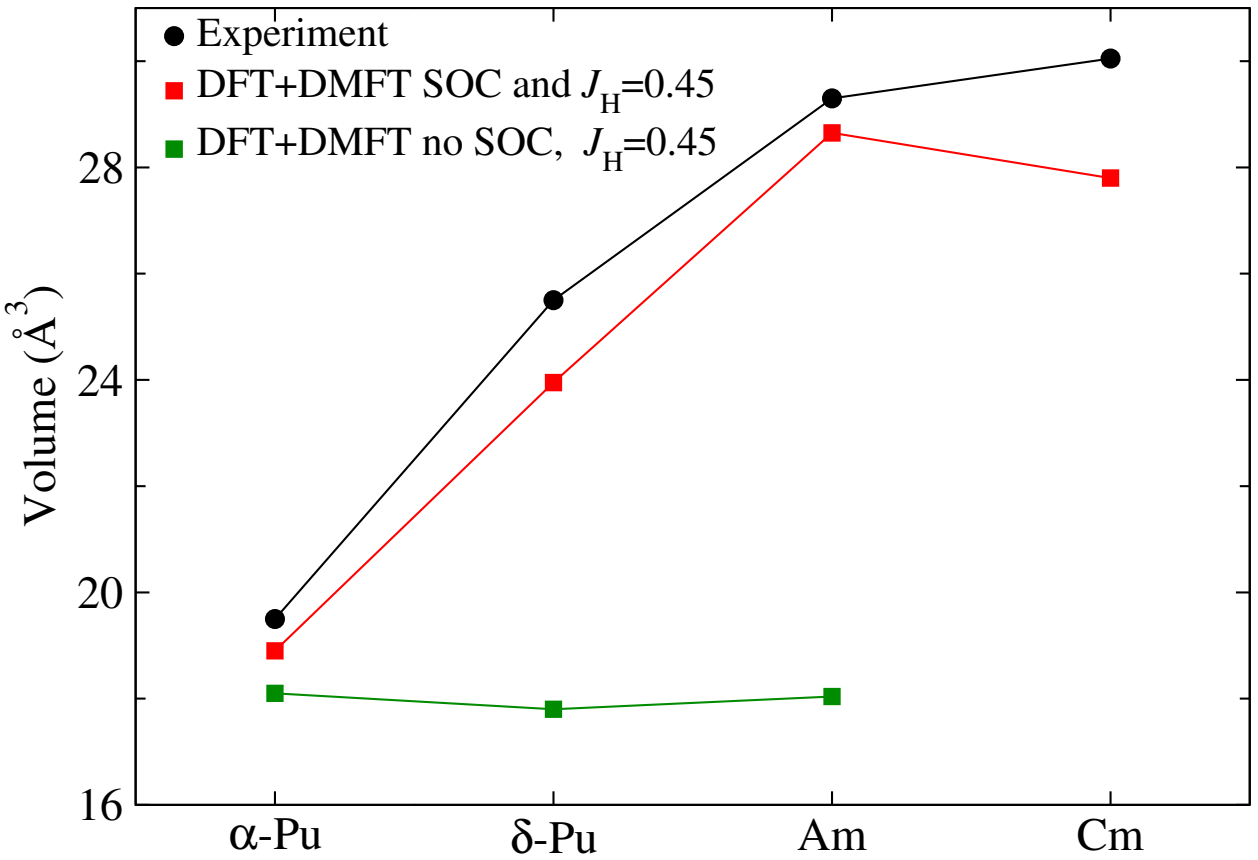
Electronic origin of the transition ?

Role of SOC and J_{H} ?

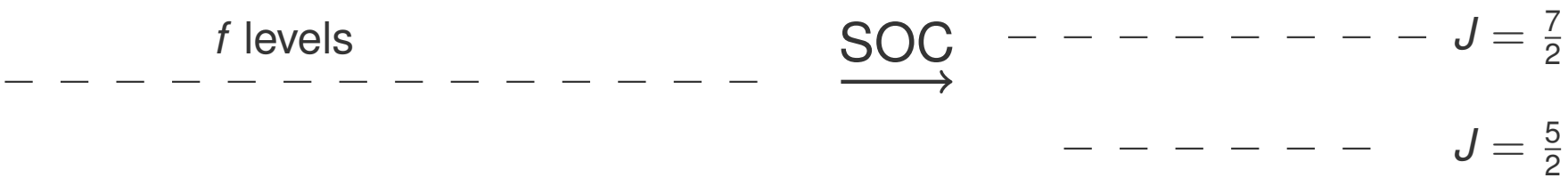
Role of spin-orbit coupling



Spin-orbit coupling is mandatory !

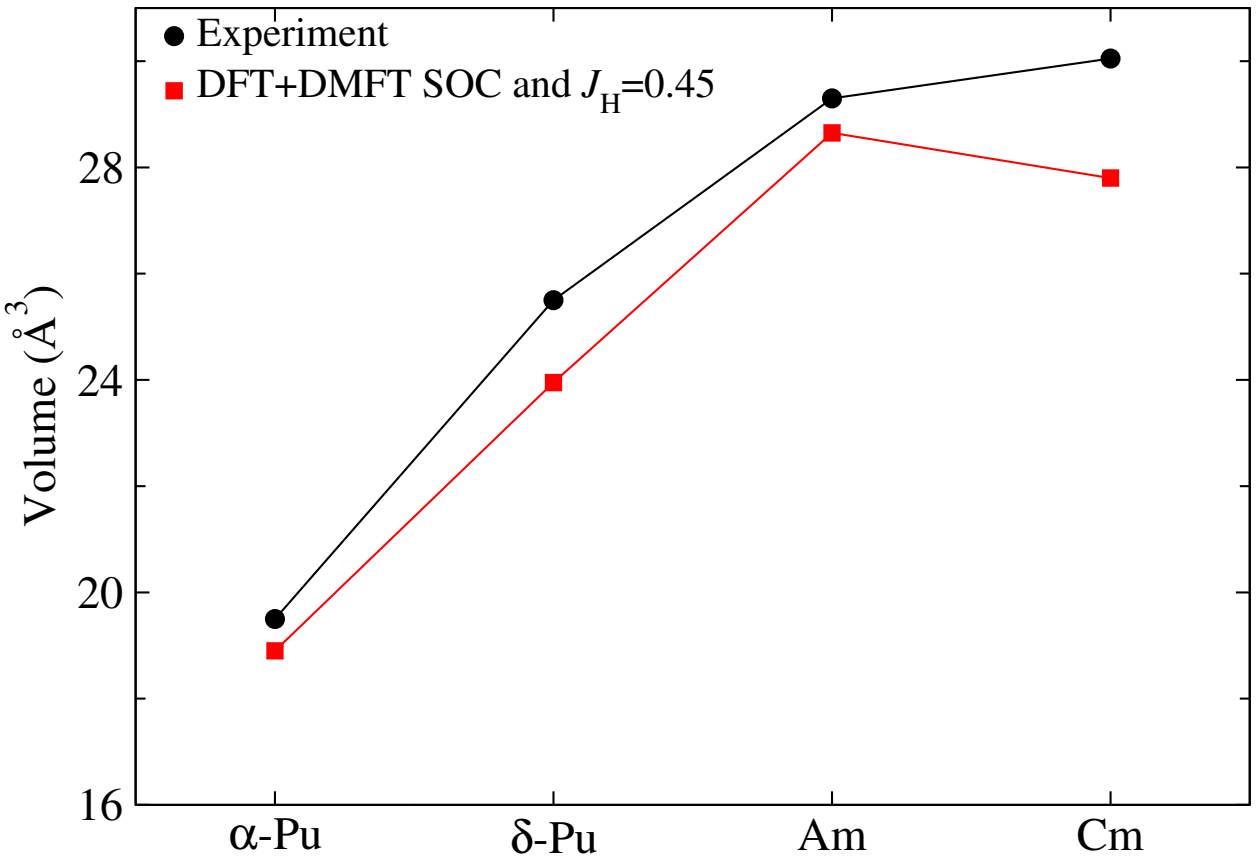


Effect of SOC on *f* levels.



- As in multibands Hubbard models, degeneracy is reduced, thus correlations are enhanced.

Hund's Exchange is important



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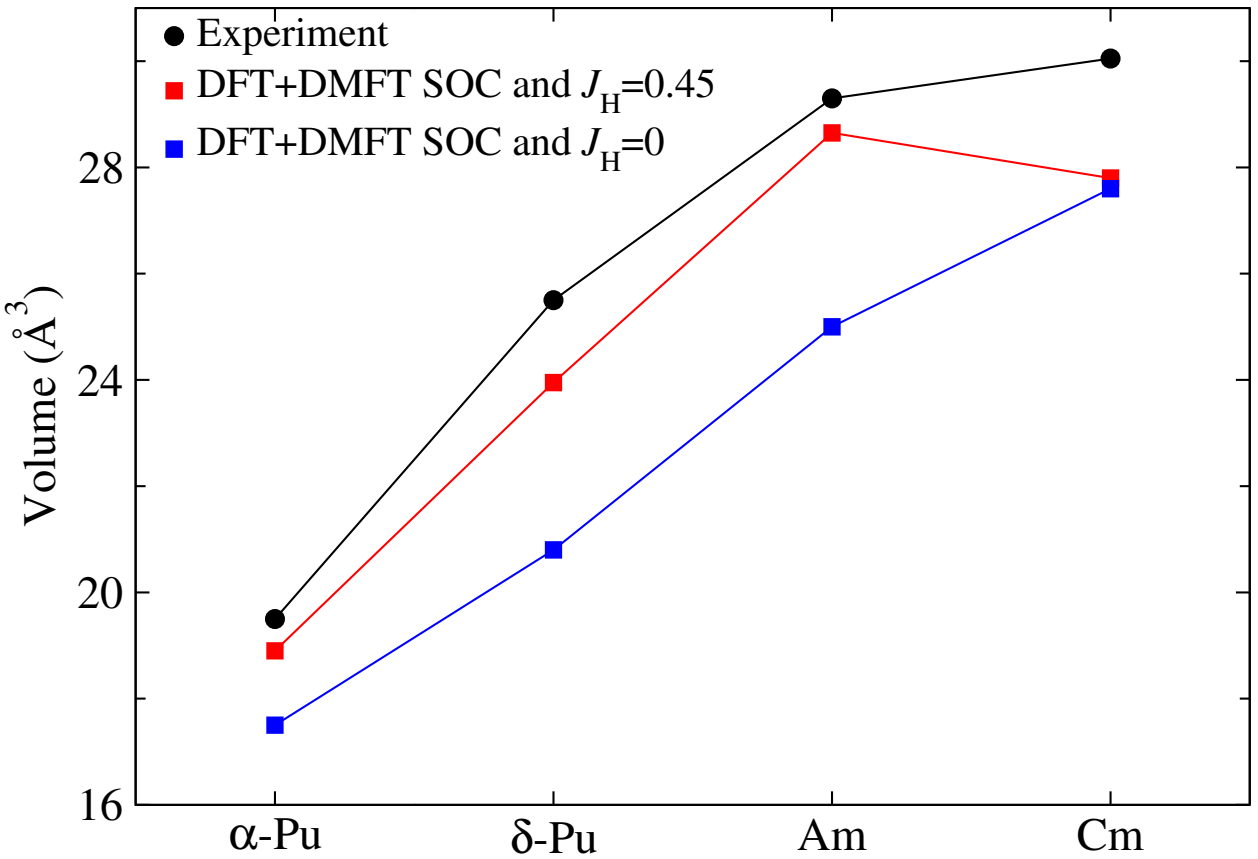
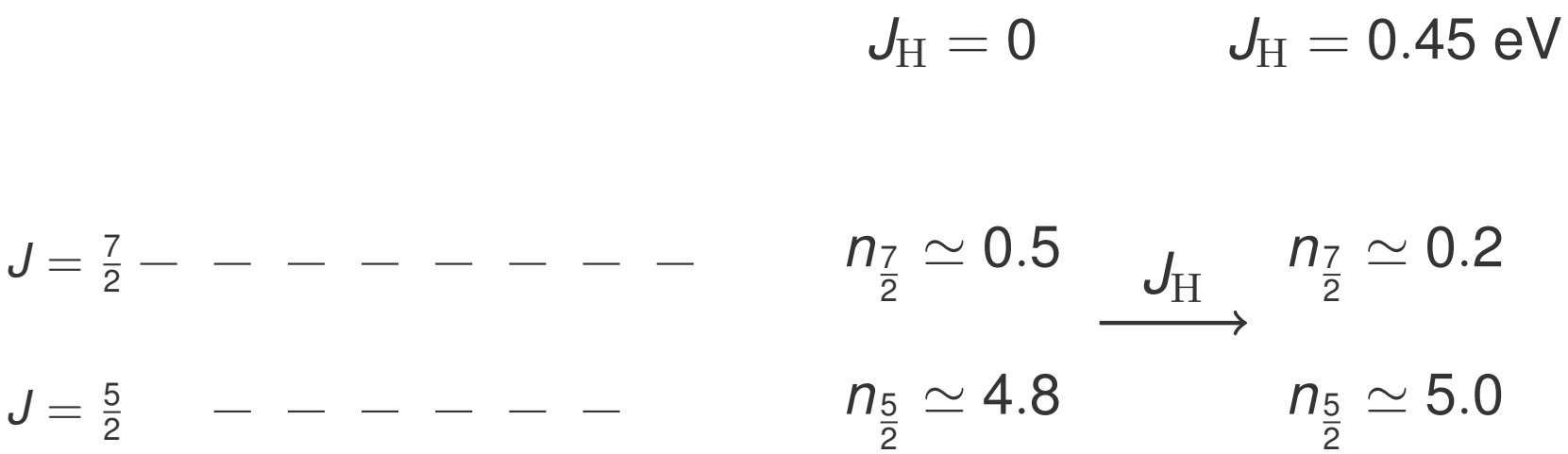
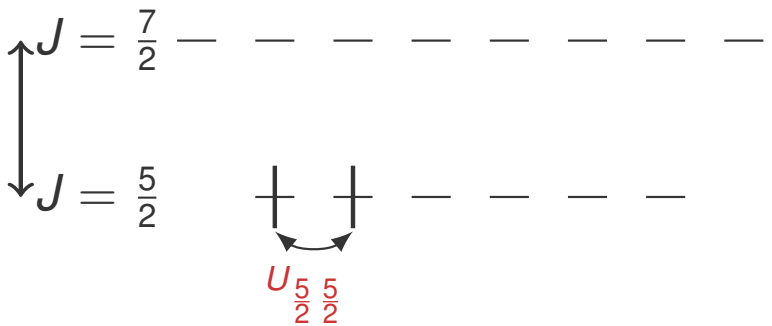


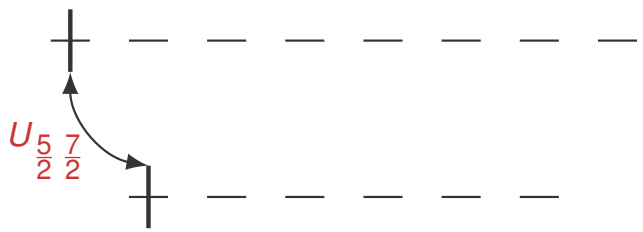
Role of J_{H} in δ Plutonium



- Hund's coupling J_{H} increases the polarization of $\frac{5}{2}$ orbitals.
- why ?

J_{H} enhances the polarization of J=5/2 orbitals.





$$E = U_{\frac{5}{2}\frac{5}{2}} \qquad E = U_{\frac{5}{2}\frac{7}{2}} + \lambda_{\mathrm{SOC}}$$

$U_{\frac{5}{2}\frac{7}{2}} > U_{\frac{5}{2}\frac{5}{2}} \Rightarrow$ The weight of Slater determinants involving $\frac{7}{2}$ states is reduced not only by SOC but also by Hund's interaction.

For interactions, see also J.-P. Julien, J.-X. Zhu, and R. C. Albers, Phys. Rev. B 77, 195123 (2008)

Conclusion

- U and J_{H} are computed: U is small
- The **same** theoretical description for low volume actinides and high volume actinides.
- Key role of SOC and Hund's exchange.

B. Amadon, Phys. Rev. B **94**, 115148 (2016)

Thanks to F. Bottin, J. Bouchet, C. Denoual, B. Dorado, F. Jollet, and G. Robert for useful discussions