DE LA RECHERCHE À L'INDUSTRIE

cea

4th International Workshop on Models and Data for Plasma-Material Interaction in Fusion Devices

MoD-PMI 2019

Date : 18-20 June 2019

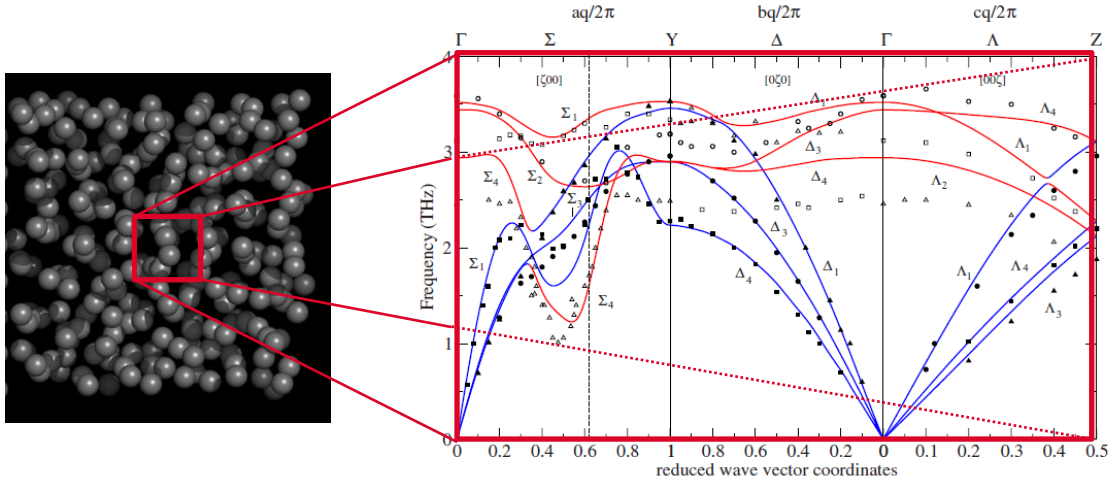
Venue : National Institute for Fusion Science (NIFS)
322-6 Oroshi-cho, Toki, Gifu 509-5292, JAPAN

www.cea.fr

VIBRATIONAL PROPERTIES OF URANIUM AND PLUTONIUM

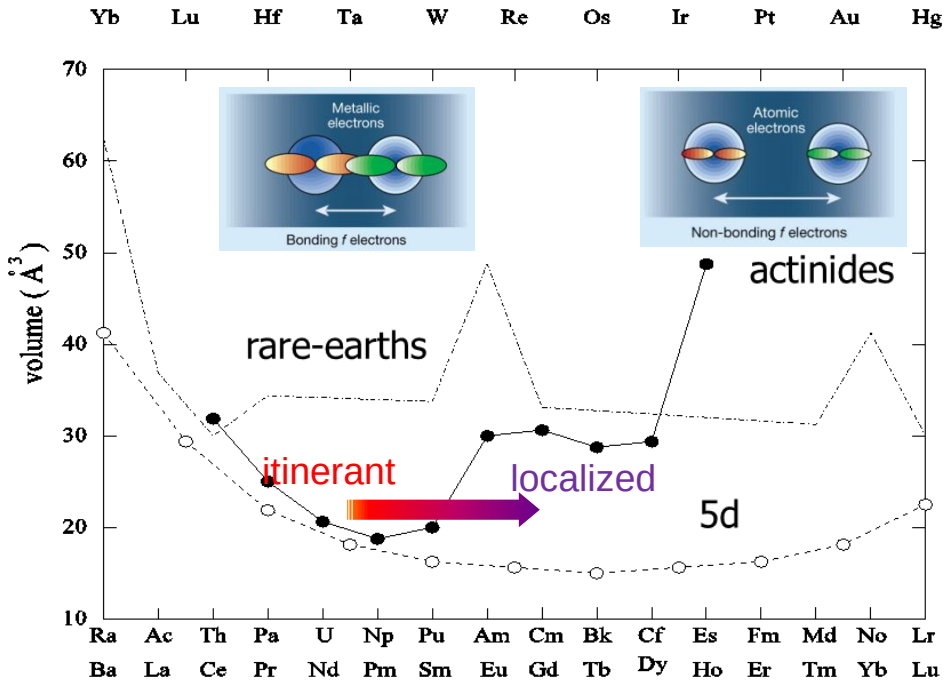
JOHANN BOUCHET,
FRANÇOIS BOTTIN,
BORIS DORADO,
ALOIS CASTELLANO

CEA, DAM, DIF, F-91297 ARPAJON, FRANCE

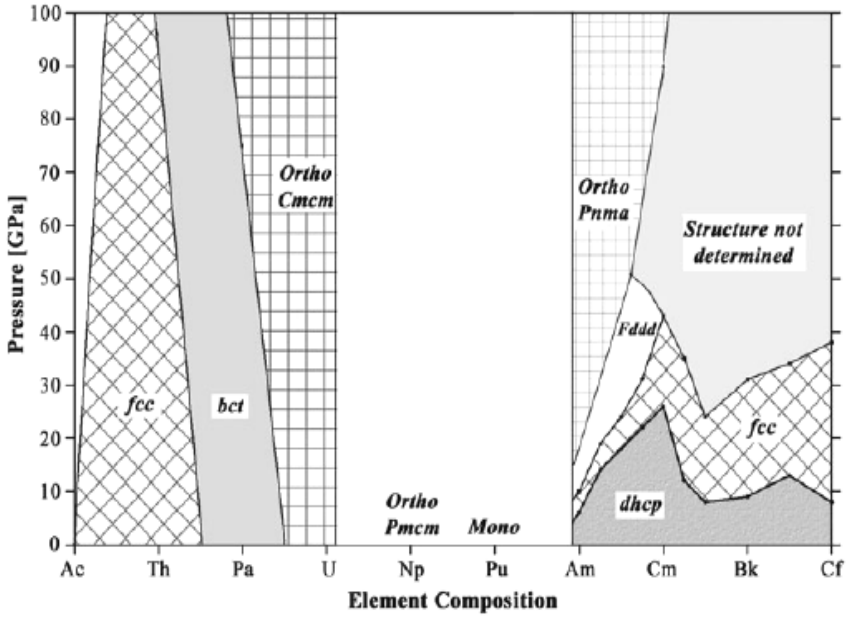


DENSITY FUNCTIONAL THEORY, T= 0 K

DFT (GGA, +U, +DMFT…) has been a successful tool to understand the ground state properties of the actinides and their compounds : Structures, Equilibrium volume, Bulk modulus, elastic constants, phase transitions in pressure…

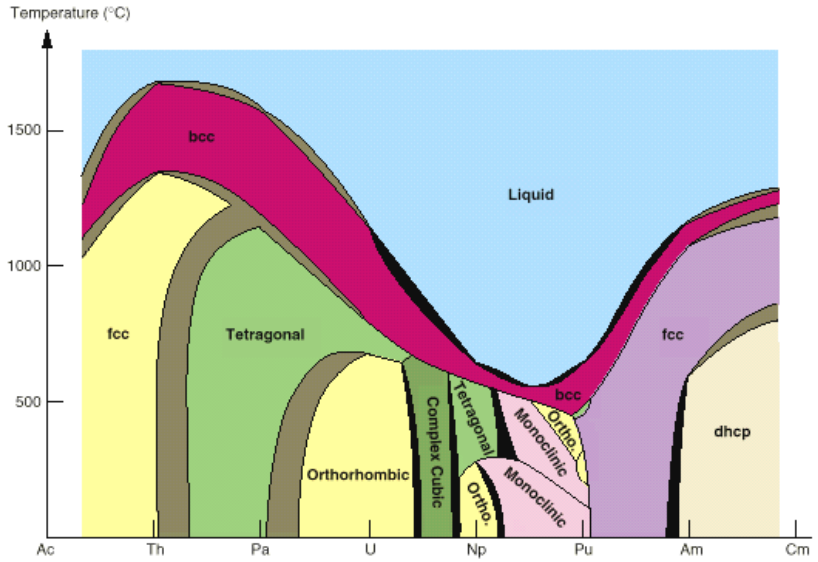


R. C. Albers, *Nature* **410**, 759-761 (2001)

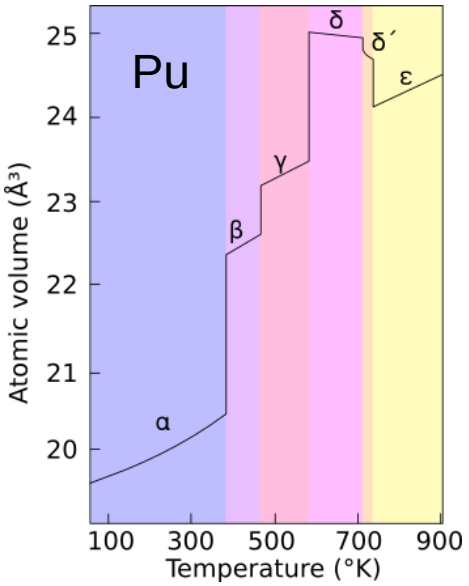


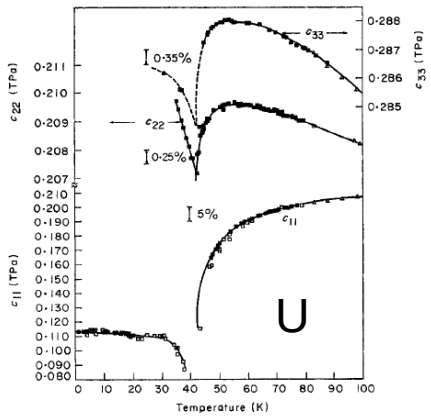
[A. Lindbaum *et al.* J. Phys Cond Matt **15**, S2297 (2003)]

T ≠ 0 K ???

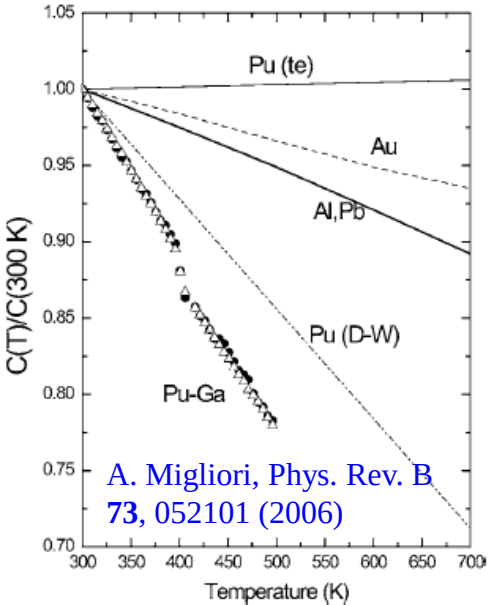


[Los Alamos Science, number **26**, 2000]

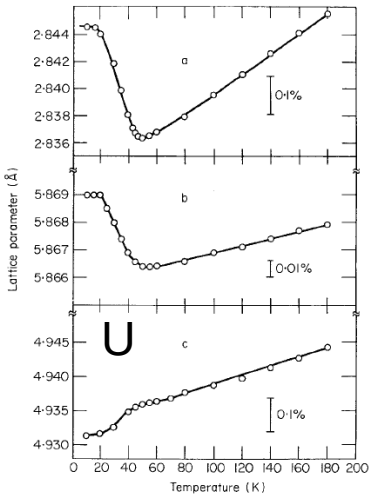




Fisher and McSkimin 1961

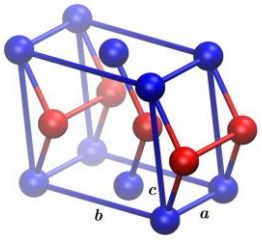


A. Migliori, Phys. Rev. B **73**, 052101 (2006)

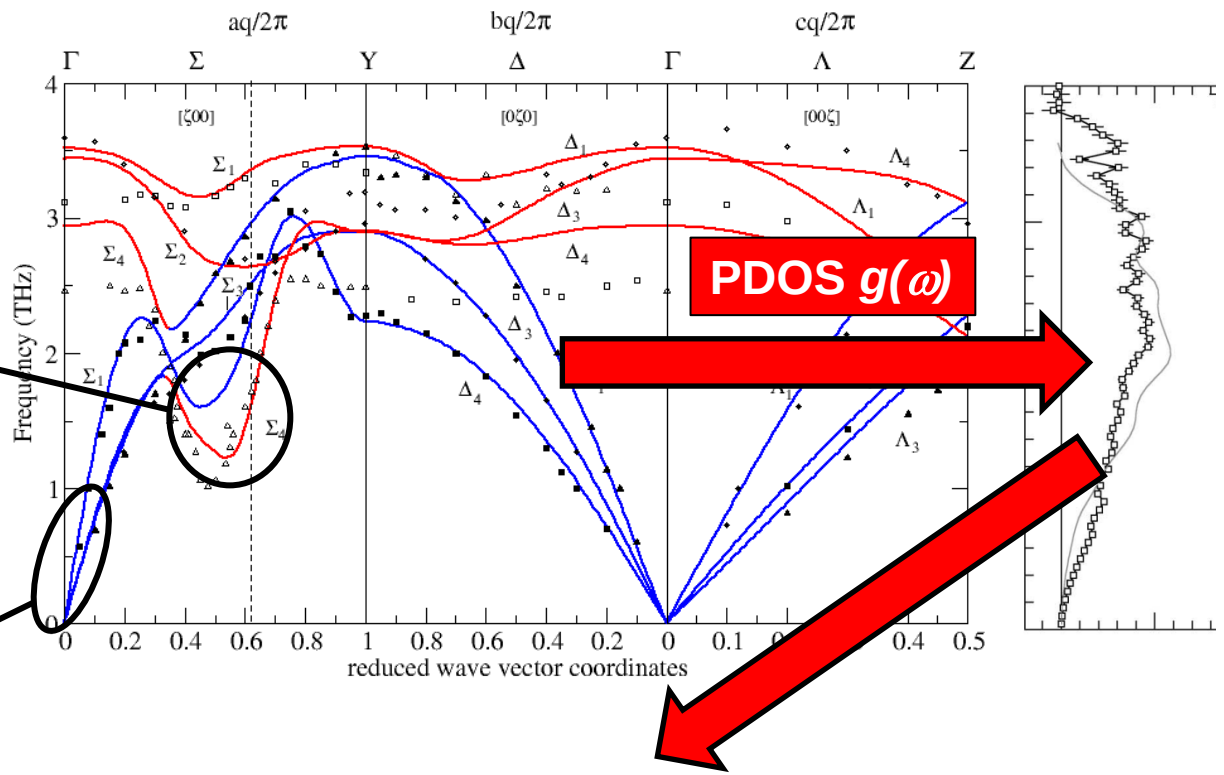


- Comparison with experiments at room temperature.
- Low melting points.
- Dynamical instability of the bcc structure.
- Elastic constants of uranium at low T.
- CDW in uranium
- Thermal conductivity of nuclear fuels
- Thermal dilation (uranium, plutonium)
- Softening of the bulk modulus of Pu
- Phase transitions (low symmetry vs high symmetry)
- …

PHONON SPECTRUM



α-U Phonon Spectrum



Soft modes, structural stability

PDOS $g(\omega)$

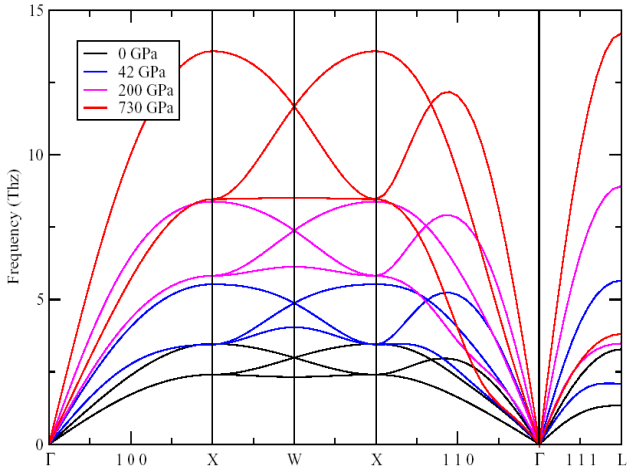
$$V_s = \sqrt{\frac{C_{ij}}{\rho}}$$

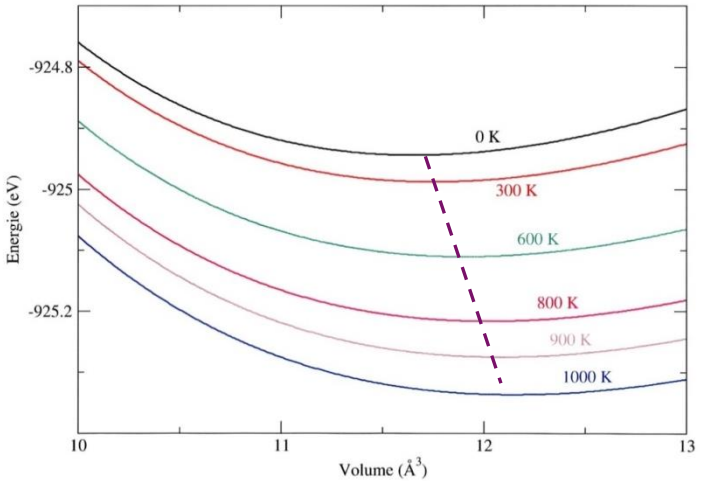
$$F_{ph}(V,T) = k_B T \sum_{q,j} \ln\left\{2\sinh\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right)\right\}$$

$$U,\ S_{vib},\ C_V \ldots$$

ATOMIC MOTIONS AND PHONON SPECTRA IN DFT

Density functional perturbation theory (DFPT) T= 0 K
Harmonic approximation : no thermal expansion, no phase transitions (melting)
Quasi harmonic approximation : phonon frequencies are **volume** dependent





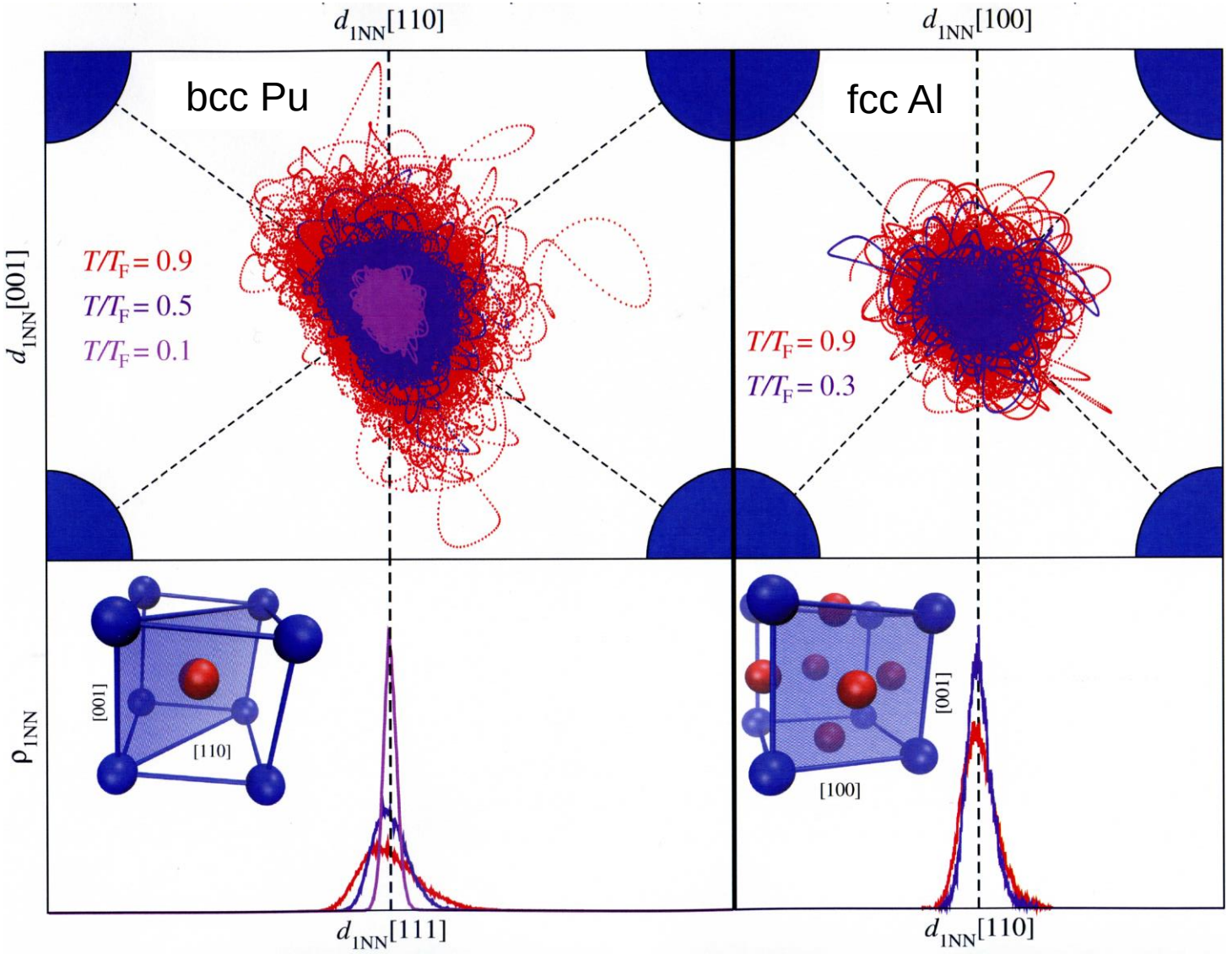
$$F(V,T) = E(V) + F_{ph}(\omega,T) + F_e(T)$$

$$F_{ph}(V,T) = k_B T \sum_{q,j} \ln\left\{2\sinh\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right)\right\}$$

Structures dynamically stable at 0 K
Weak anharmonicity

Bcc unstable at 0 K
Low melting point, phase transitions

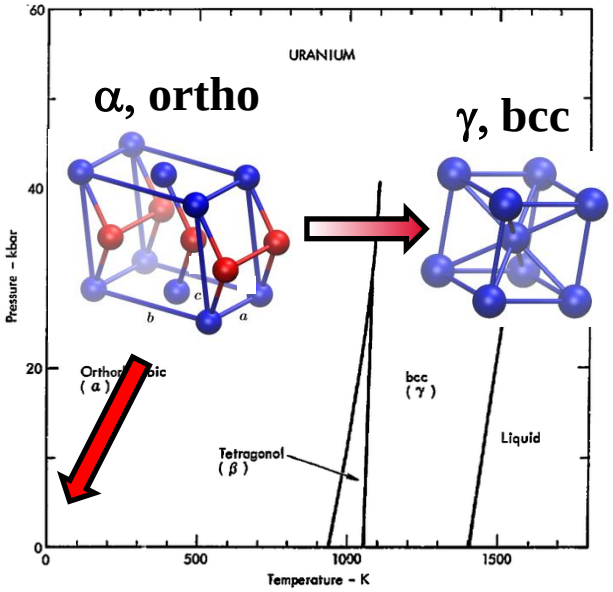
HARMONIC-ANHARMONIC : Al VS Pu

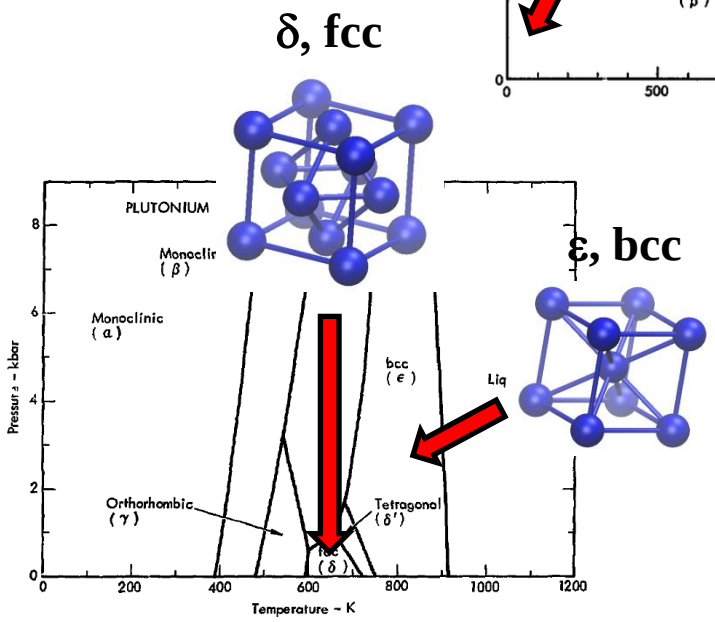


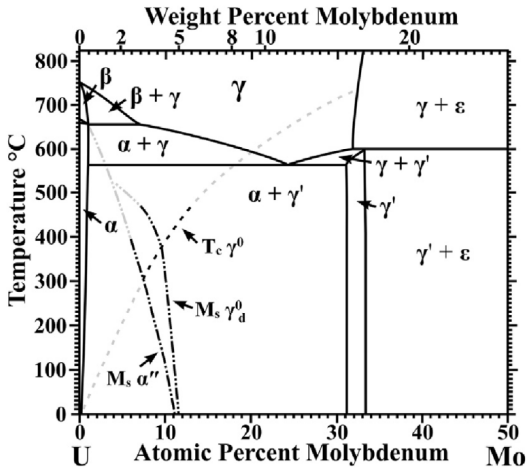
OUTLINE

- Introduction. DFT, a ground state theory (T=0 K)
- T≠0 K : DFPT and Quasi Harmonic approximation
- Failure of the QHA for uranium at low *T*.

  Introduction of a new method : TDEP
- Phase transitions in uranium
- The case of plutonium.
- U-Mo alloys

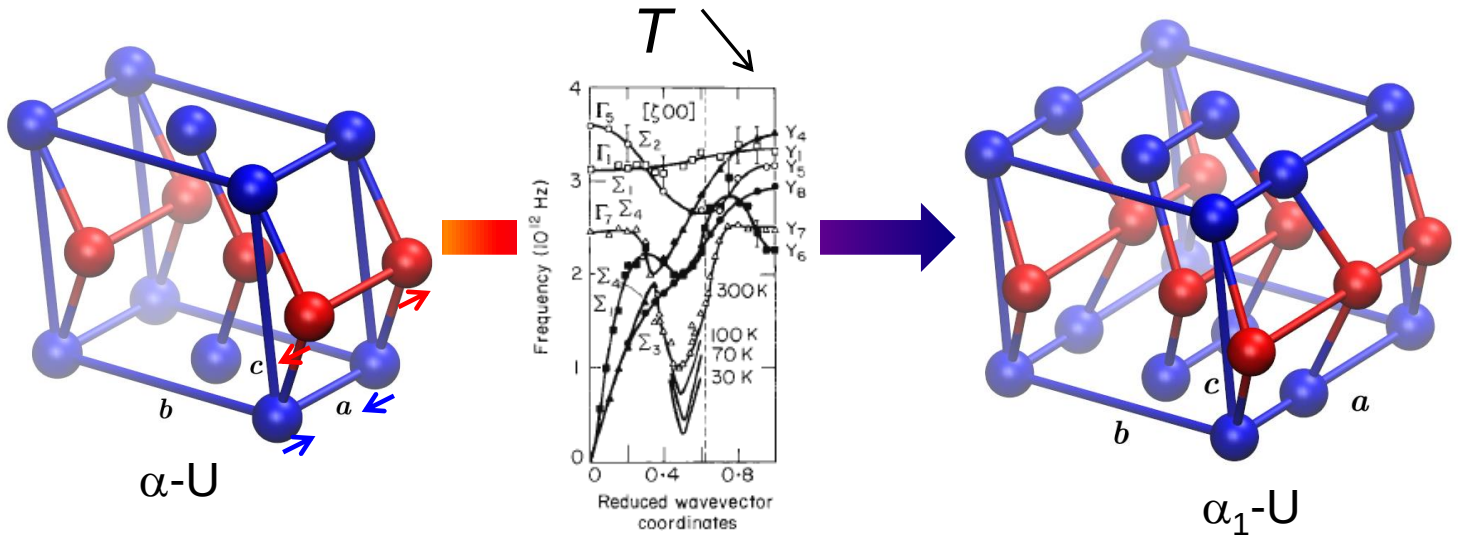






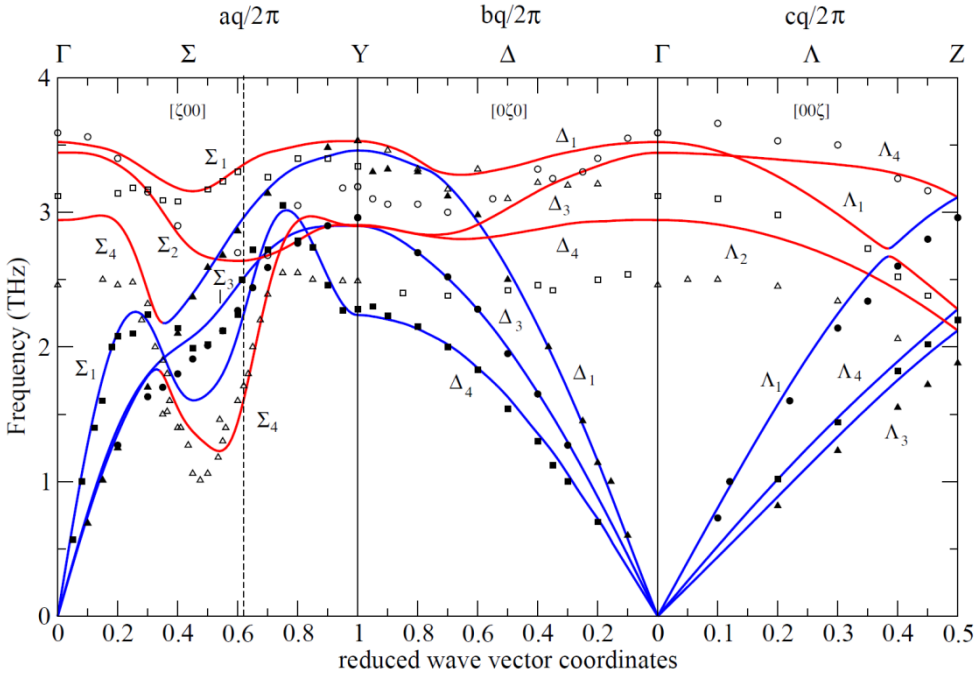
URANIUM METAL

Uranium is the only element discovered so far to exhibit CDW phase transitions at ambient pressure.
Evolution of the soft mode in temperature shows a phase transition and a doubling of the unit cell in the [100] direction.

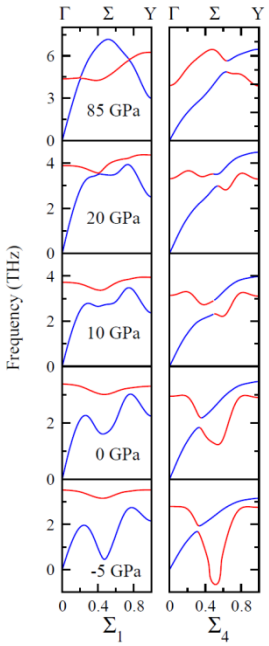


[Smith *et al.*, *Phys. Rev. Lett.* 1980]

Uranium-Phonon spectrum with DFPT (T=0 K)



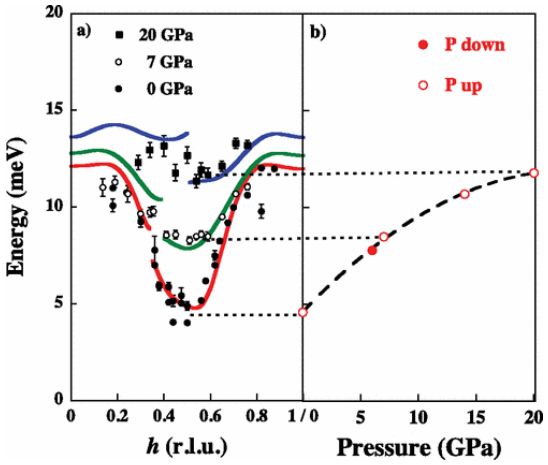
Pressure



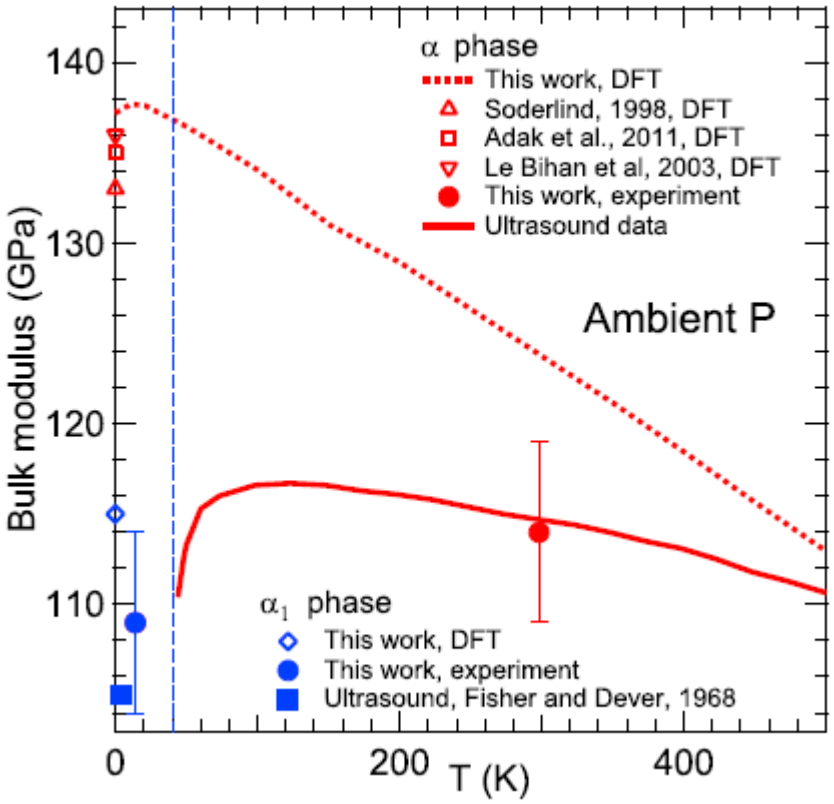
[W.P. Crummett *et al.* Phys. Rev. B **19**, 6028 (1979)]
[J. Bouchet Phys Rev B, **77** (2008)]

Pressure behavior confirmed by IXS

[S. Raymond, J. Bouchet, G. H. Lander et al., Phys. Rev. Lett. 107, 136401 (2011).]



FAILURE OF THE QHA (T≠ 0 K)

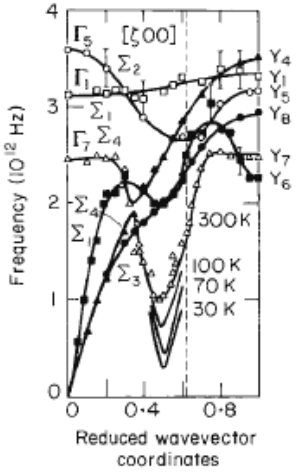


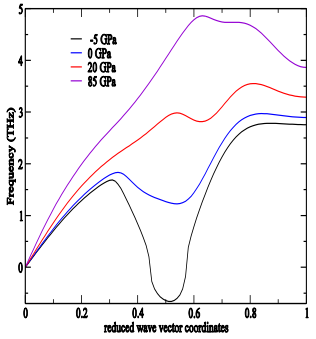
A. Dewaele, J. Bouchet, F. Occelli, M. Hanfland, and G. Garbarino, Phys. Rev. B **88**, 134202 (2013)

- QHA only takes into account the thermal dilatation

$$\omega(T)= \omega(V)$$

- Inadequate for uranium because of the soft modes
- α-U is NOT the correct structure at 0 K

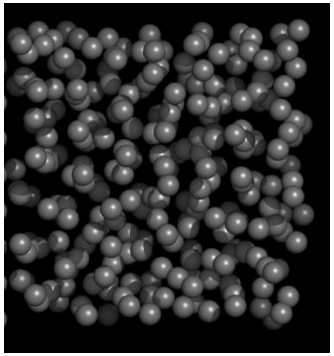




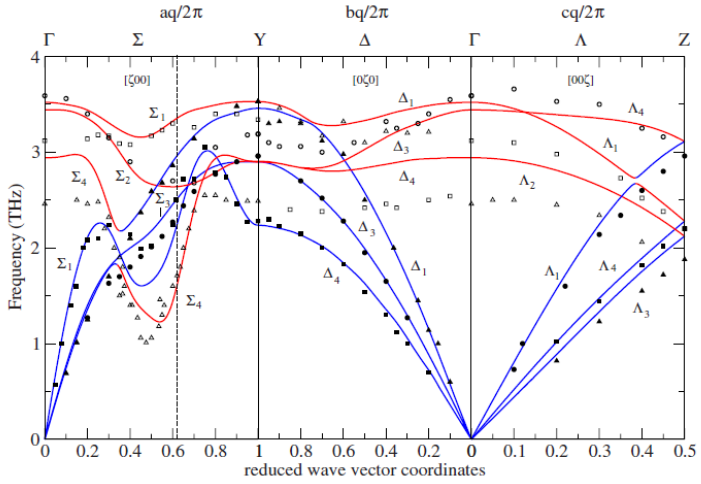
The phonon frequencies have to be explicitly dependent of the temperature

HOW TO TAKE INTO ACCOUNT THE TEMPERATURE? AB INITIO MOLECULAR DYNAMICS

Ab-initio Molecular Dynamics (AIMD)



?



FT

At each time step τ :

$$F_i(\tau) = \sum_j \boldsymbol{\Phi_{ij}} u_j(\tau)$$

$$\sum_{\beta,j} D_{ij}^{\alpha\beta}(\mathbf{q}) X_j^{\beta}(\mathbf{q}) = M_i \omega^2(\mathbf{q}) X_i^{\alpha}(\mathbf{q})$$

Equation of motion

Forces are related to displacements by the interatomic force constants (IFC)

$\boldsymbol{\Phi_{ij}}$ and then ω will be temperature dependent

Temperature-dependent effective potential (TDEP)

O. Hellman *et al.* PRB **84** 180301 (2011)

TDEP METHOD

At each time step of the AIMD, we have the forces and the displacements :

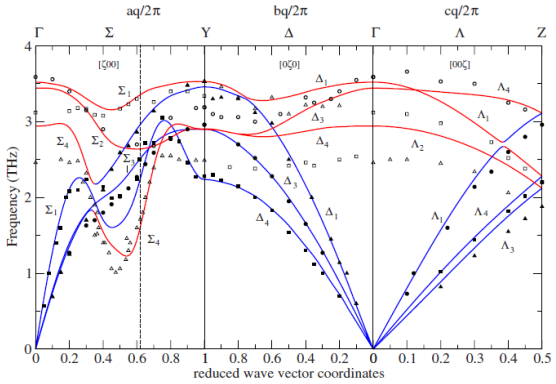
$$\mathcal{F}_i^{\alpha}(t) = -\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^{\beta}(t) - \frac{1}{2} \sum_{jk,\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_j^{\beta}(t) u_k^{\gamma}(t) + 0(u^3)$$

FT

Second Order : Phonon frequencies

$$\sum_{\beta,j} D_{ij}^{\alpha\beta}(\mathbf{q}) X_j^{\beta}(\mathbf{q}) = M_i \omega^2(\mathbf{q}) X_i^{\alpha}(\mathbf{q})$$

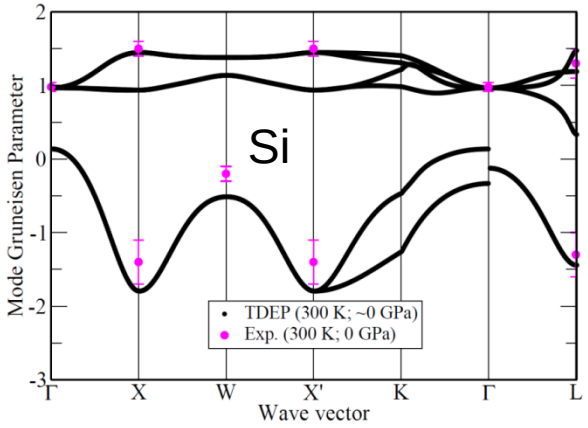
$\omega\,(T)$



Third Order : Grüneisen parameter

$$\gamma_s(\mathbf{q}) = -\frac{1}{6\omega_s^2(\mathbf{q})} \sum_{ijk,bc,\alpha\beta\gamma} \Psi_{ijk}^{\alpha\beta\gamma}(0,b,c) \frac{X_{is}^{\star\alpha}(\mathbf{q}) X_{js}^{\beta}(\mathbf{q})}{\sqrt{M_i M_j}} \tau_k^{\gamma} \exp\left[i\mathbf{q}.\mathbf{R}(b)\right]$$

$$\gamma_s(\mathbf{q}) = -\frac{V}{\omega_s(\mathbf{q})} \left(\frac{\partial \omega_s(\mathbf{q})}{\partial V}\right)_T \qquad \gamma = \frac{\sum_{i=1}^{3N_a} \gamma_i C_{V,i}}{C_V}$$



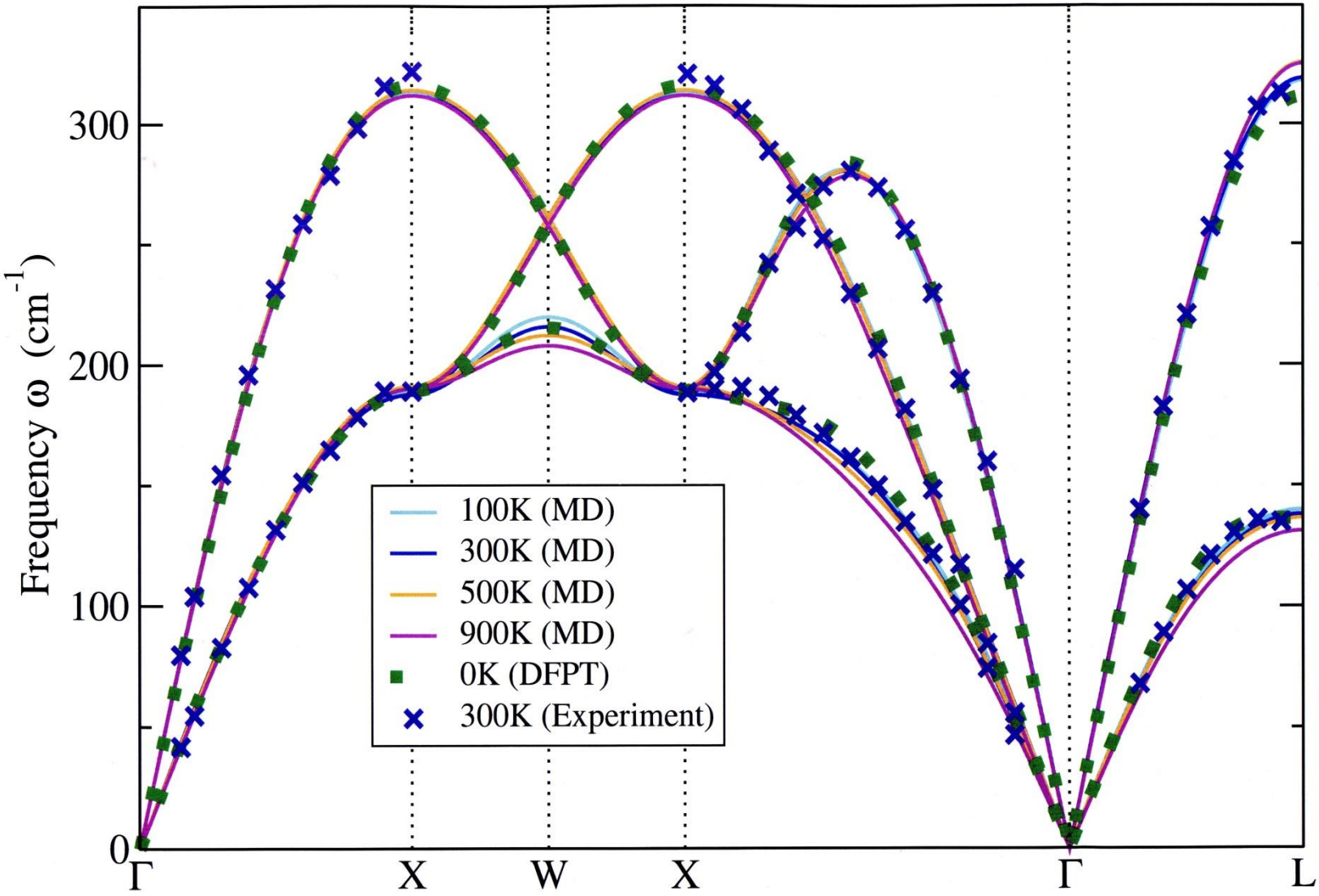
O. Hellman *et al.* PRB **84** 180301 (2011)

NEW METHODS TO TREAT ANHARMONICITY BEYOND THE QHA

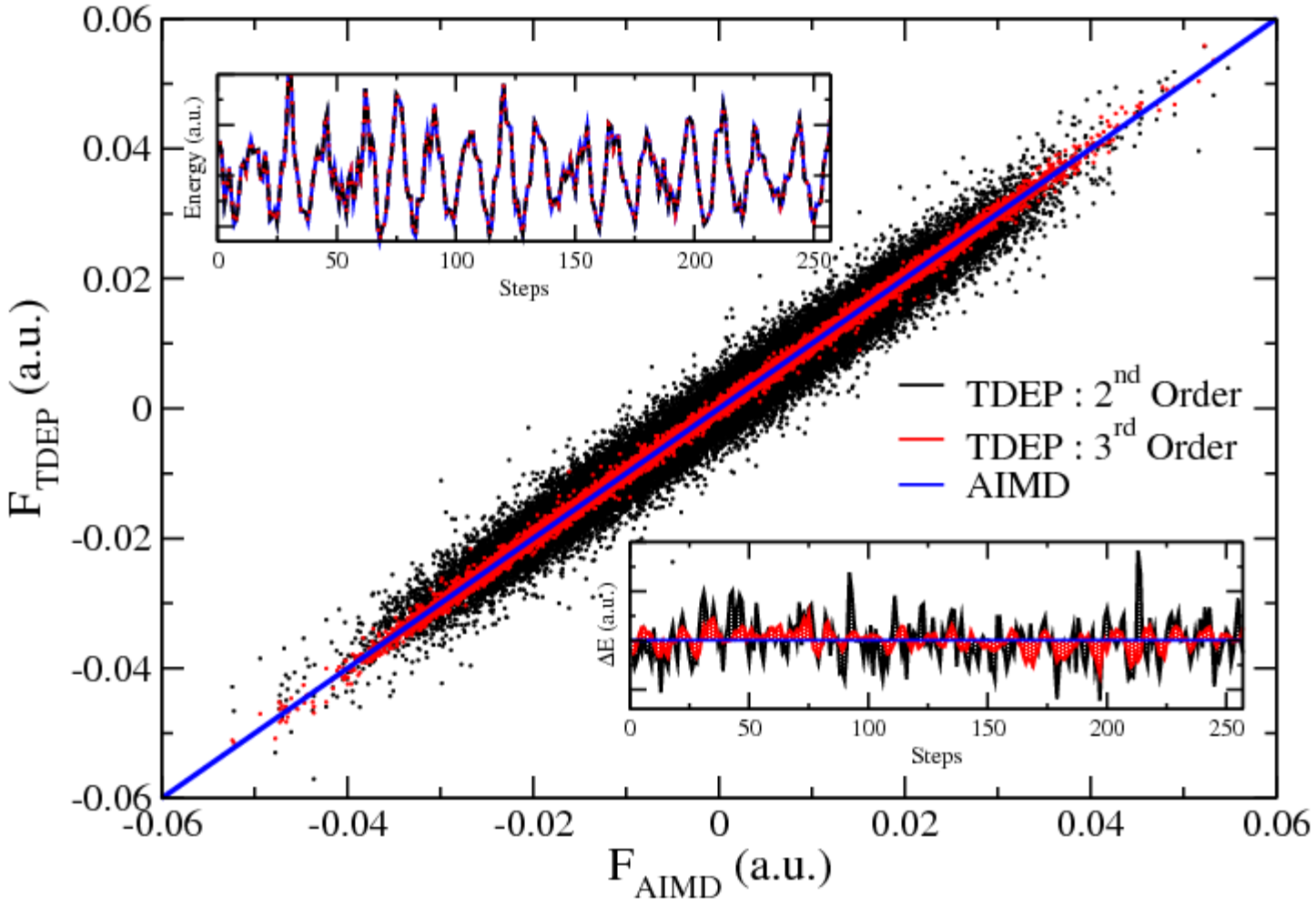
- Self-Consistent Ab-Initio Lattice Dynamics (SCAILD) [P. Souvatzis et al. 2008, P. Souvatzis et al. 2009, W. Luo et al. 2010],
- Stochastic Self-Consistent Harmonic Approximation (SSCHA) [I. Errea et al. 2014, I. Errea et al. 2014, L. Paulatto et al. 2015, M. Borinaga et al. 2016],
- **Temperature Dependent Effective Potential (TDEP)** [O. Hellman et al. 2011, O. Hellman 2013, P. Steneteg et al. 2013, J. Bouchet et al. 2015],
- Anharmonic LAttice MODEl (ALAMODE) [Tadano et al. 2014, Tadano et al. 2015],
- Compressive Sensing Lattice Dynamics [L. J. Nelson et al. 2013, F. Zhou et al. 2014].
- DynaPhopy [A. Carreras, A. Togo, and I. Tanaka, 2017, T. Sun, D. Zhang D., R. Wentzcovitch 2014]
- Other methods obtain anharmonic contributions via a derivation of the Gibbs energy [A. Glensk et al. 2015],

WORKSHOP CECAM : “Anharmonicity and thermal properties of solids”
January, 10-12th 2018, PARIS

TEST CASE: Al


Frequency ω (cm^{-1})
300
200
100
0
Γ
X
W
X
Γ
L
100K (MD)
300K (MD)
500K (MD)
900K (MD)
0K (DFPT)
300K (Experiment)

FORCES : TDEP VS AIMD

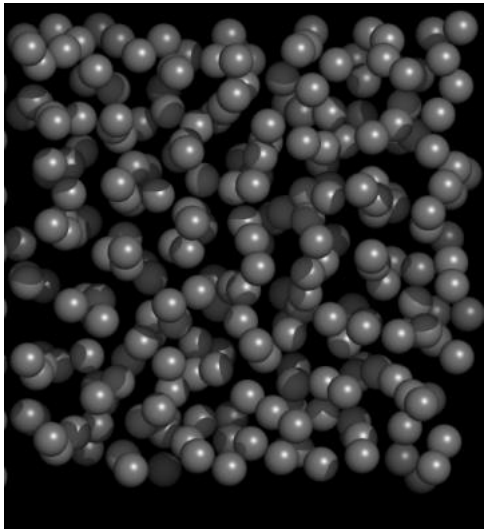


CALCULATIONS DETAILS OF AIMD FOR U

- Supercell : 4x2x3 of α–U = 96 atoms of uranium (up to 11th shell of nearest neighbors)
- 32 kpoints
- Experimental parameters (Llyod, Barrett J. Nucl. Mater. 1966)
- 50, 300 and 900 K starting with the ideal positions
- Around 3 000 time steps

Around 1-2 millions CPU hours

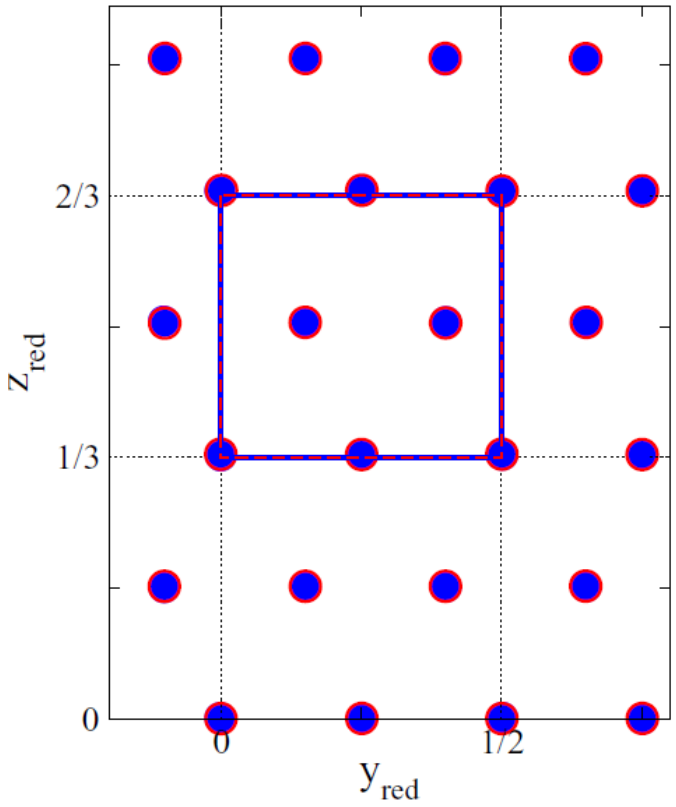
All the calculations have been performed using the ABINIT package, PAW (14 valence electrons), GGA.



URANIUM : AVERAGE POSITIONS AT 300 AND 50 K

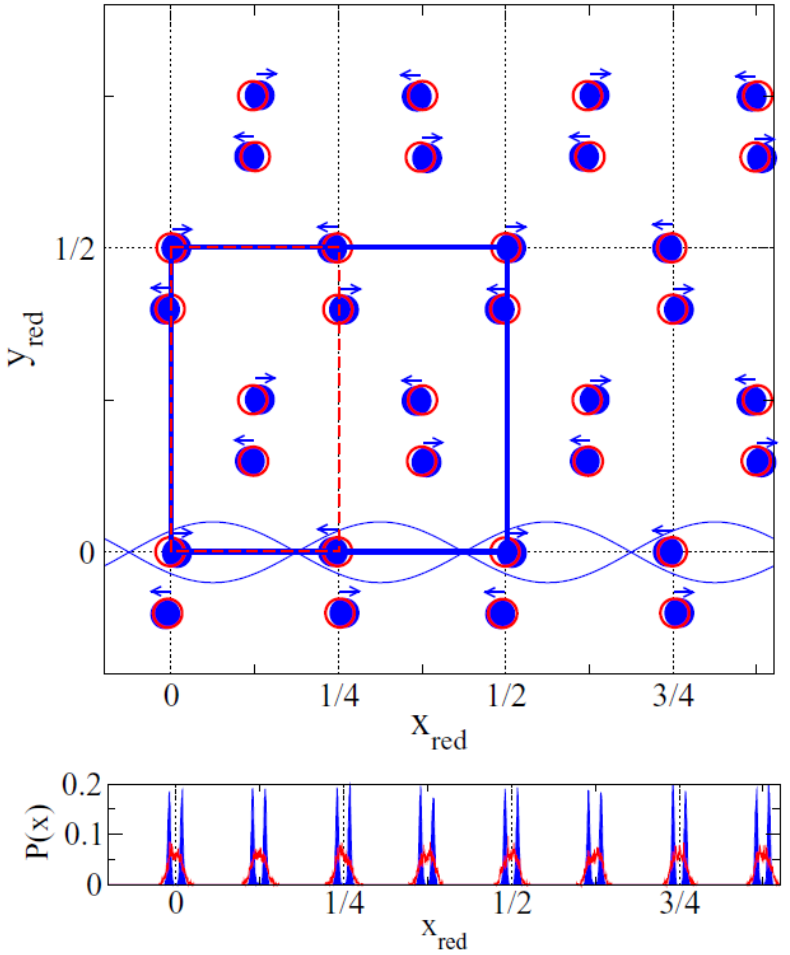
300 K 50 K

[011]



No change in the [011] plane, the atoms stay in the ideal positions

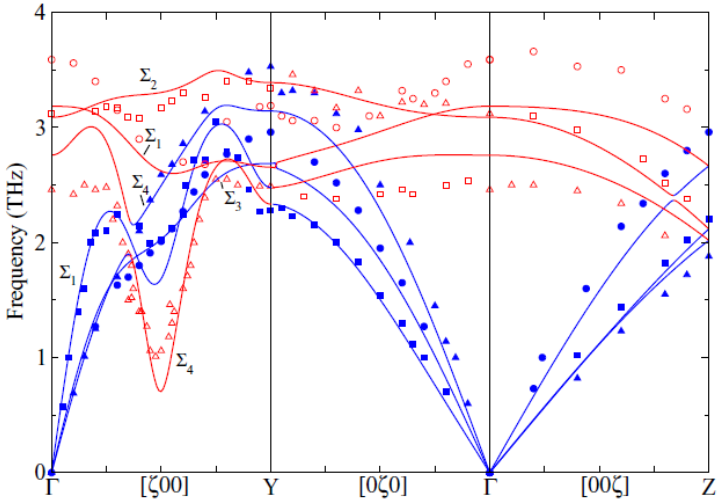
[110]

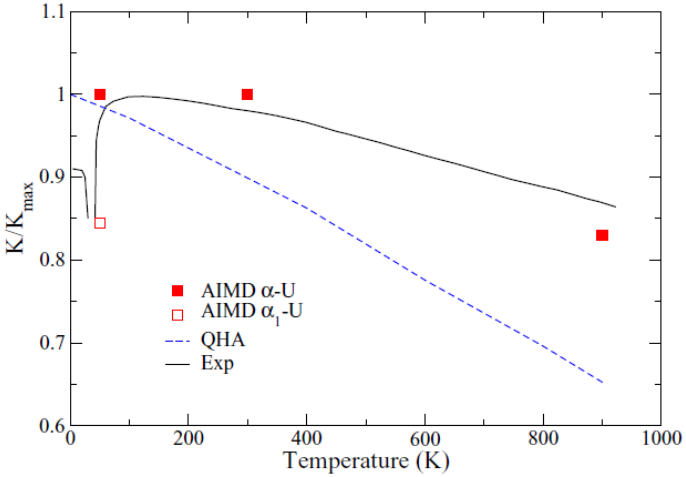


At 50 K, the atoms adopt new equilibrium positions with a small displacement in the *x* direction

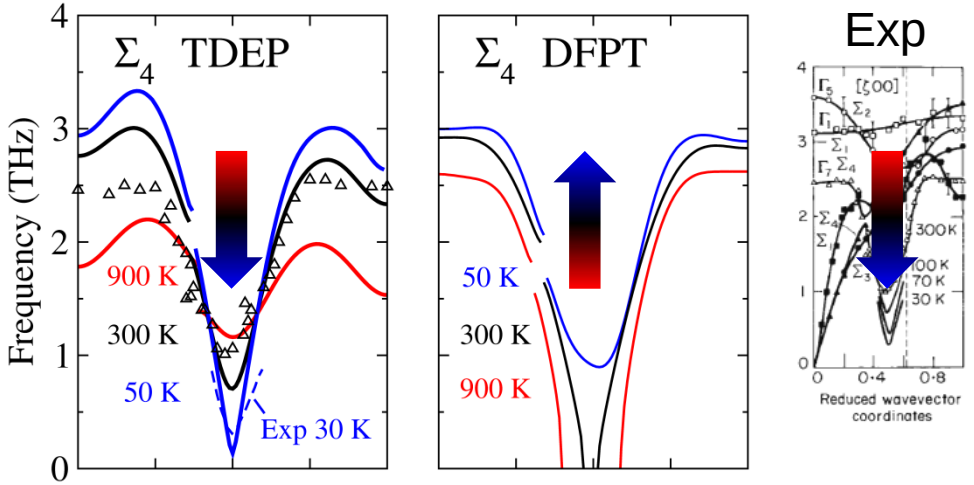
URANIUM : TDEP (T≠ 0K) VS DFPT(T=0K)

Comparison TDEP-Exp at 300 K





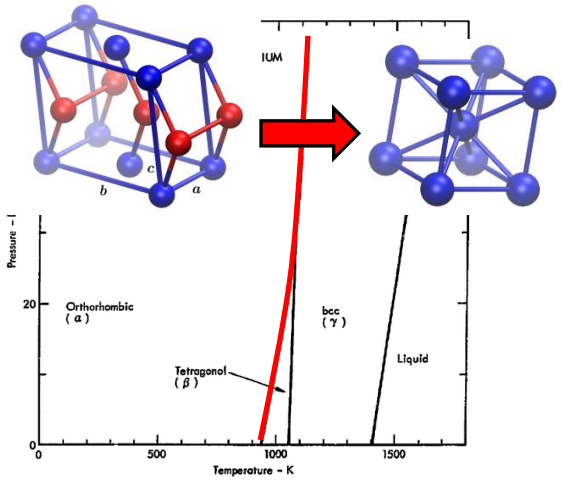
Comparison TDEP-DFPT



- At *V*(900 K), the α-U structure is unstable with DFPT
- At *V*(300 K), TDEP gives results comparable to exp while DFPT still predict a destabilization of α-U
- At *V*(50 K), TDEP predicts the phase transition towards the CDW state

J. Bouchet & F. Bottin., Phys. Rev. B **92**, 174108 (2015)

URANIUM : PHASE DIAGRAM

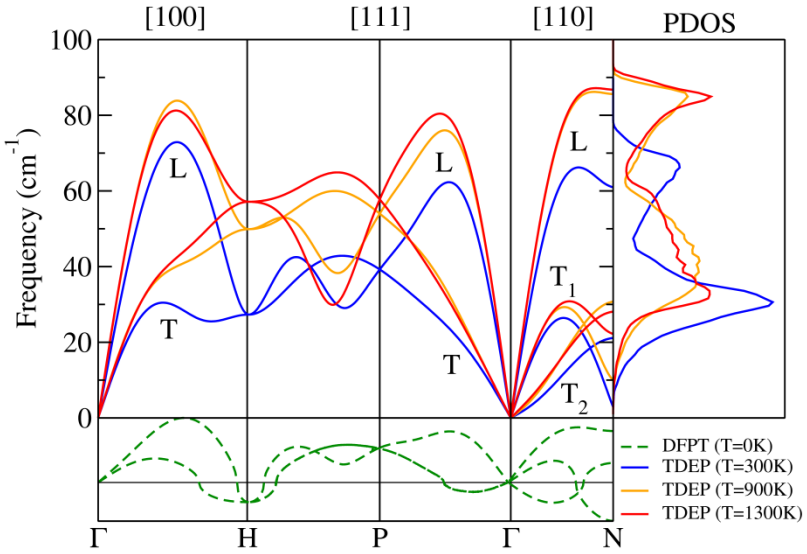


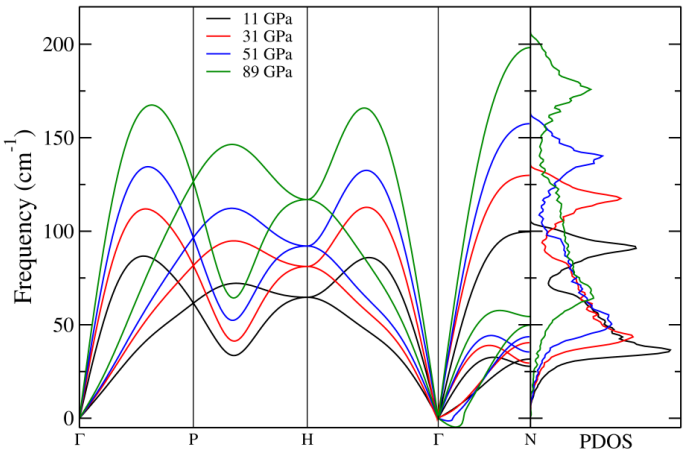
To find the transition line between two structures we need to compare their Gibbs energies :

$$G(P,T) = F(P,T)+PV(P,T)$$

With $F(T,V)=E(0,V)+F_{vib}(V,T)+F_{el}(V,T)$

bcc γ phase

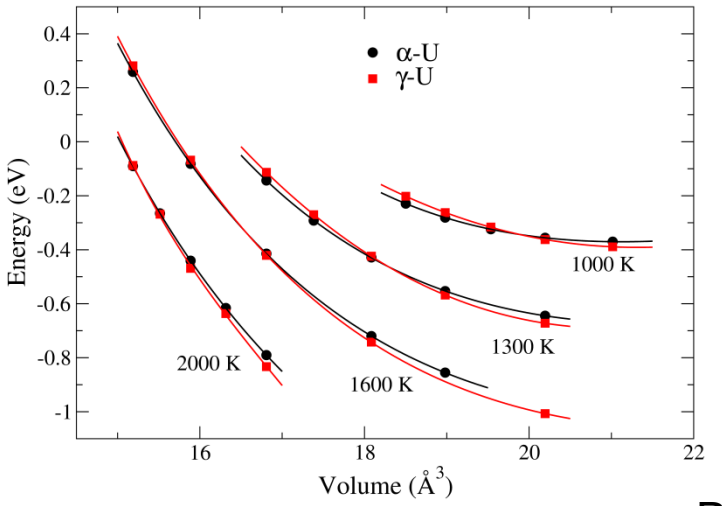




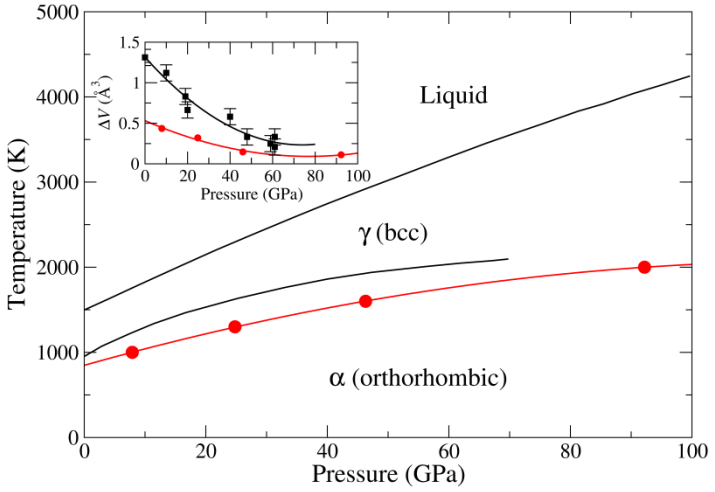
[J. Bouchet & F. Bottin., Phys. Rev. B **95**, 054113 (2017)]

URANIUM : PHASE DIAGRAM

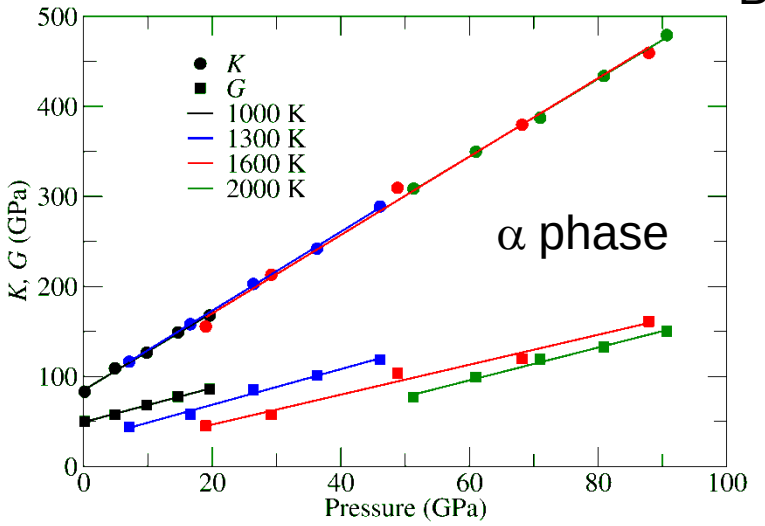
$F(T,V)=E(0,V)+F_{vib}(V,T)+F_{el}(V,T)$

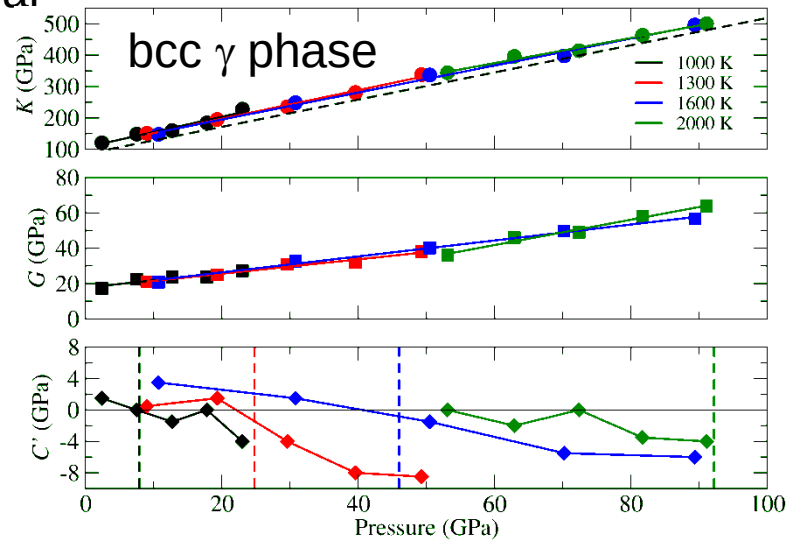


CS Yoo *et al*, Phys. Rev. B **57** 10359 (1998)



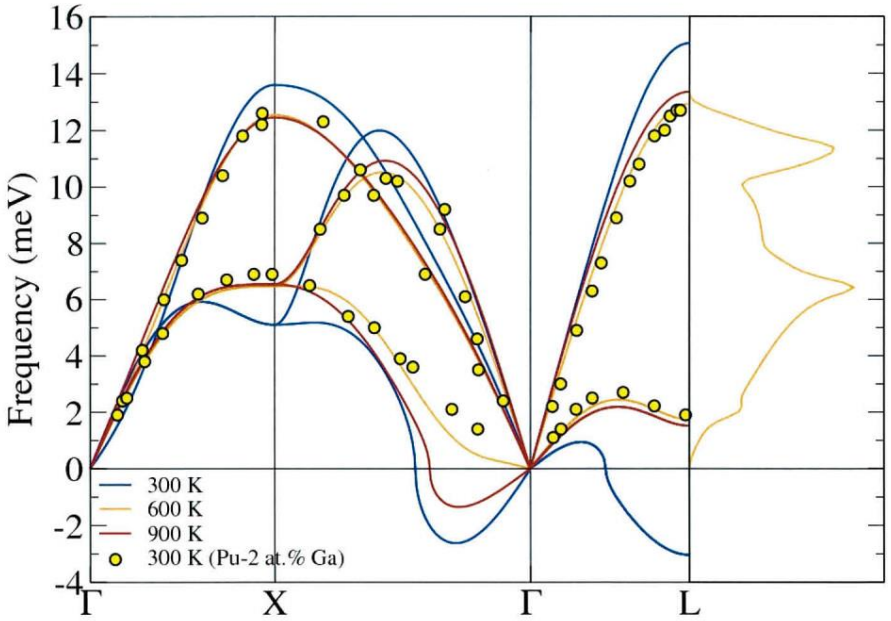
Bulk & Shear

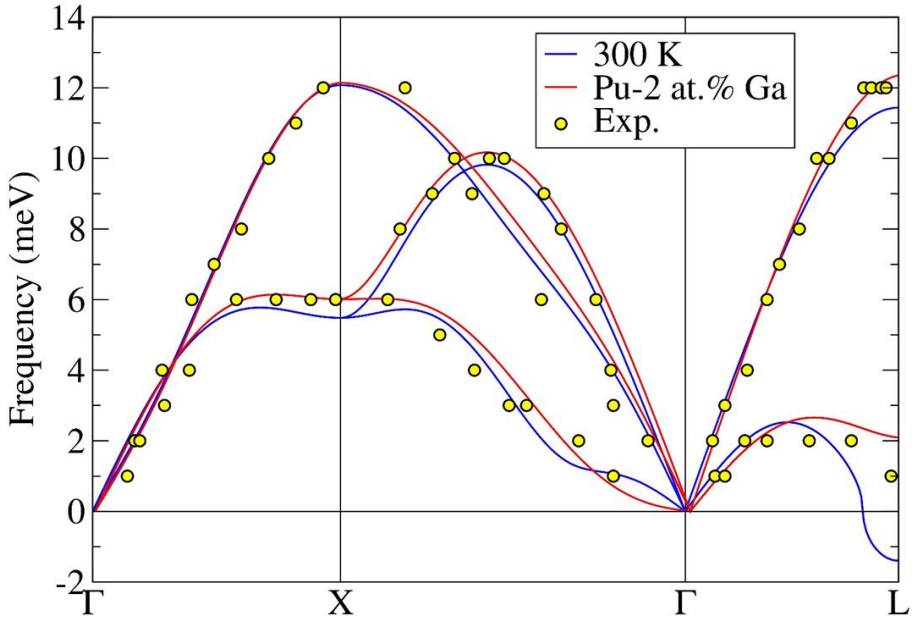




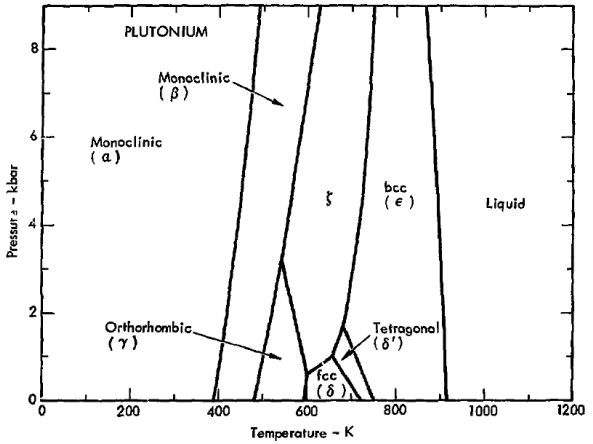
PHONONS IN δ-PU

Exp: J. Wong *et al.*, Science **301**, 1078 (2003)





- All the unusual features are reproduced at 600 K
- The δ phase is unstable at 300 K (α-Pu) and at 900 K (ε-Pu)
- At 300 K, the δ phase is stabilized by a small amount of Ga



[B. Dorado, F. Bottin & J. Bouchet , Phys. Rev. B **95**, 104303 (2017)]

NEGATIVE THERMAL EXPANSION

- Experimentally, δ-Pu has a NTE. Until now, no theory has ever been able to capture it.

- Grüneisen and thermal expansion coefficients in δ-Pu:

$$\gamma = \frac{\alpha B}{\rho c_v} \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Influence of volume change on phonon frequencies

Volume variation as a function of T

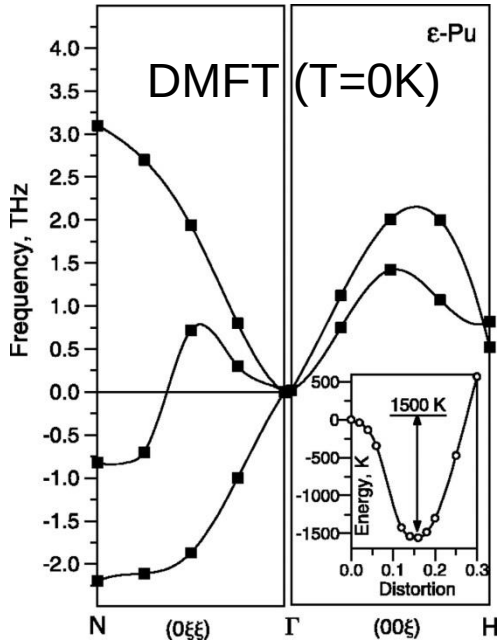
	300 K	600 K	900 K	Exp.
γ	−1.48	−1.23	0.49	−0.25
α	−56	−58	24	−26

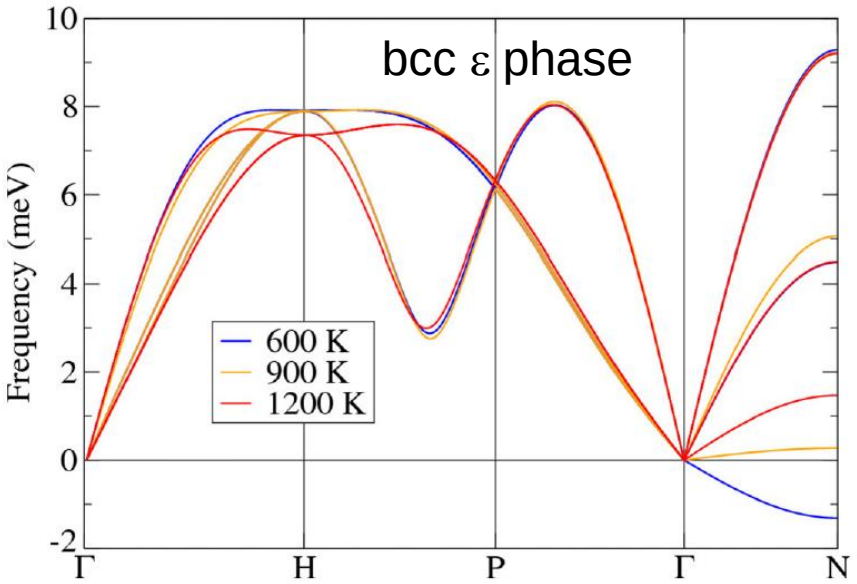
D. C. Wallace
Phys. Rev. B **58**, 15433 (1998)

- **δ-Pu NTE also correctly reproduced** (though larger than experiments).

- Analysis shows the **soft mode in Γ-L is responsible** for the NTE.

Plutonium: bcc ε phase stabilization





- bcc is unstable at 0 K even with DMFT or LDA+*U*
- AIMD with LDA shows a disordered structure
- AIMD with LDA+*U* gives a gradual stabilization of the bcc structure around 900 K
- Calculated transition temperature = 1000K (exp=750K)
- See also P. Söderlind, Scientific Reports **7**, 1116 (2017)

B. Dorado, J. Bouchet & F. Bottin., Phys. Rev. B **95**, 104303 (2017)

Uranium-Molybdenum Alloys

❑ Motivations

Uranium metals are promising nuclear fuels
Pure uranium has three allotropes :
α-U orthorombic, β-U tetragonal, γ-U body centered cubic

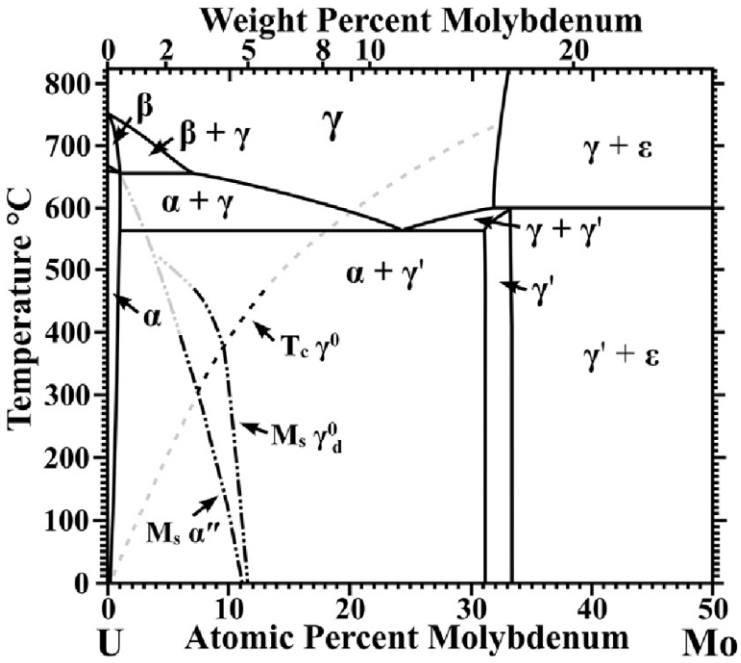
The γ-U phase is a good option for nuclear fuel, but it's unstable at low temperature (T<1000K)

Stabilize the γ phase by alloying uranium with a bcc metal such as Mo

❑ Goals

Construct the phase diagram of the bcc U-Mo system

Study the γ-stabilization effect of molybdenum

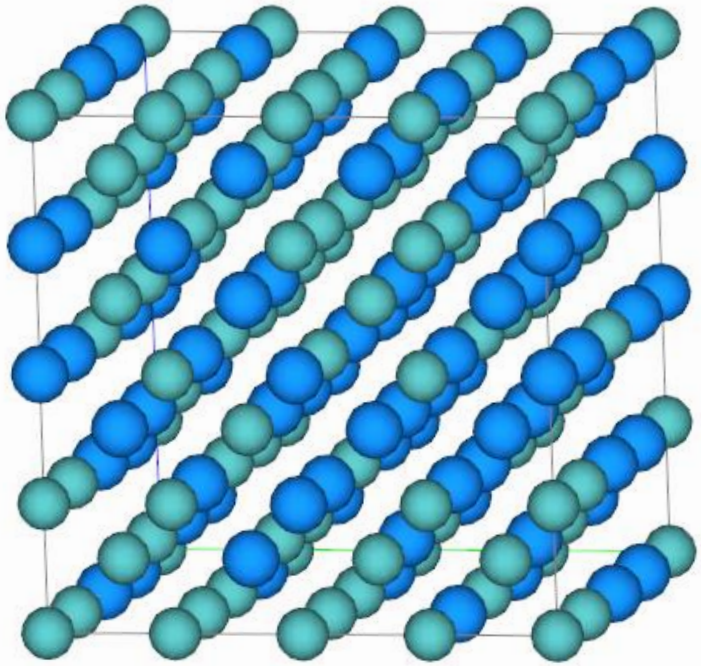


Steiner et al, J Nucl. Mater. 500 (2018) 184

Ab-initio computation

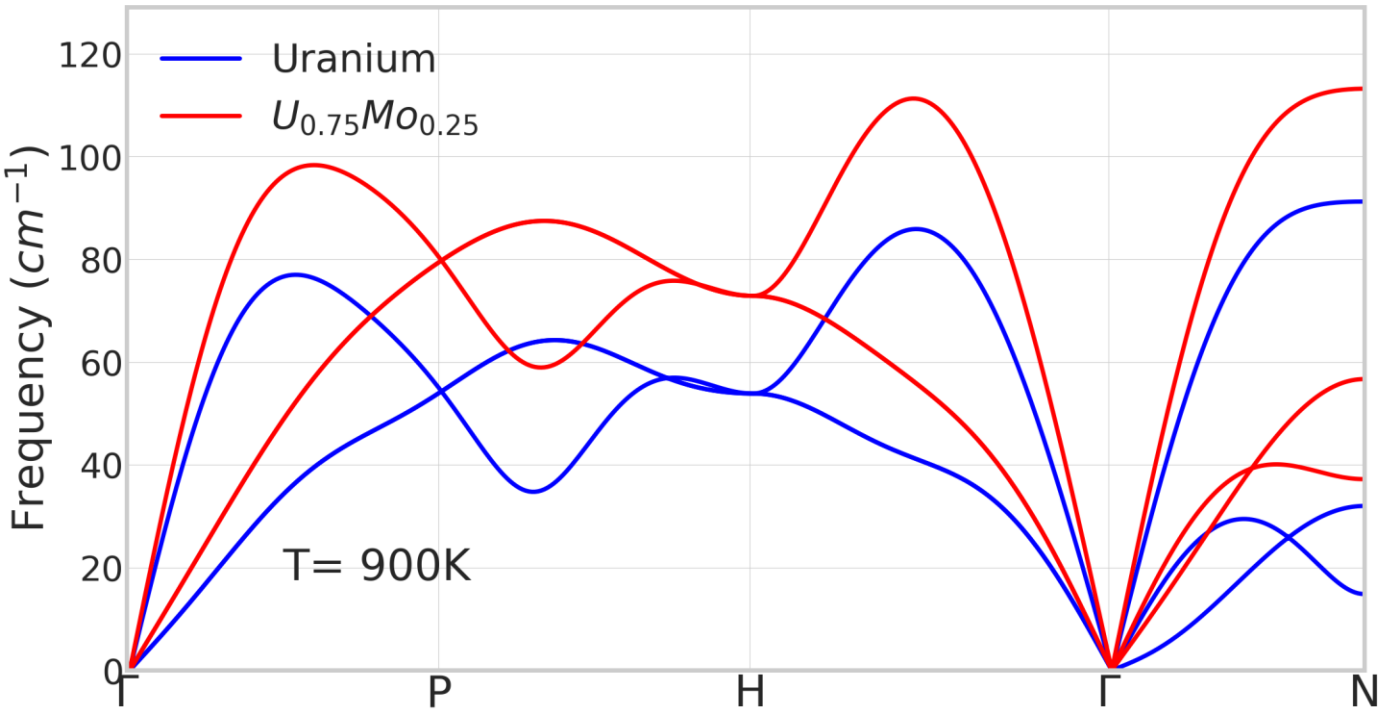
- Ab-initio Molecular Dynamics (AIMD) in the NVT ensemble
- GGA functional with the PAW formalism as implemented in Abinit

- 4x4x4 supercells with 128 atoms
- Random alloys are modeled by Special Quasirandom Structures (SQS)



Zunger et al. Phys. Rev. Lett. **65**, 353 (1990)

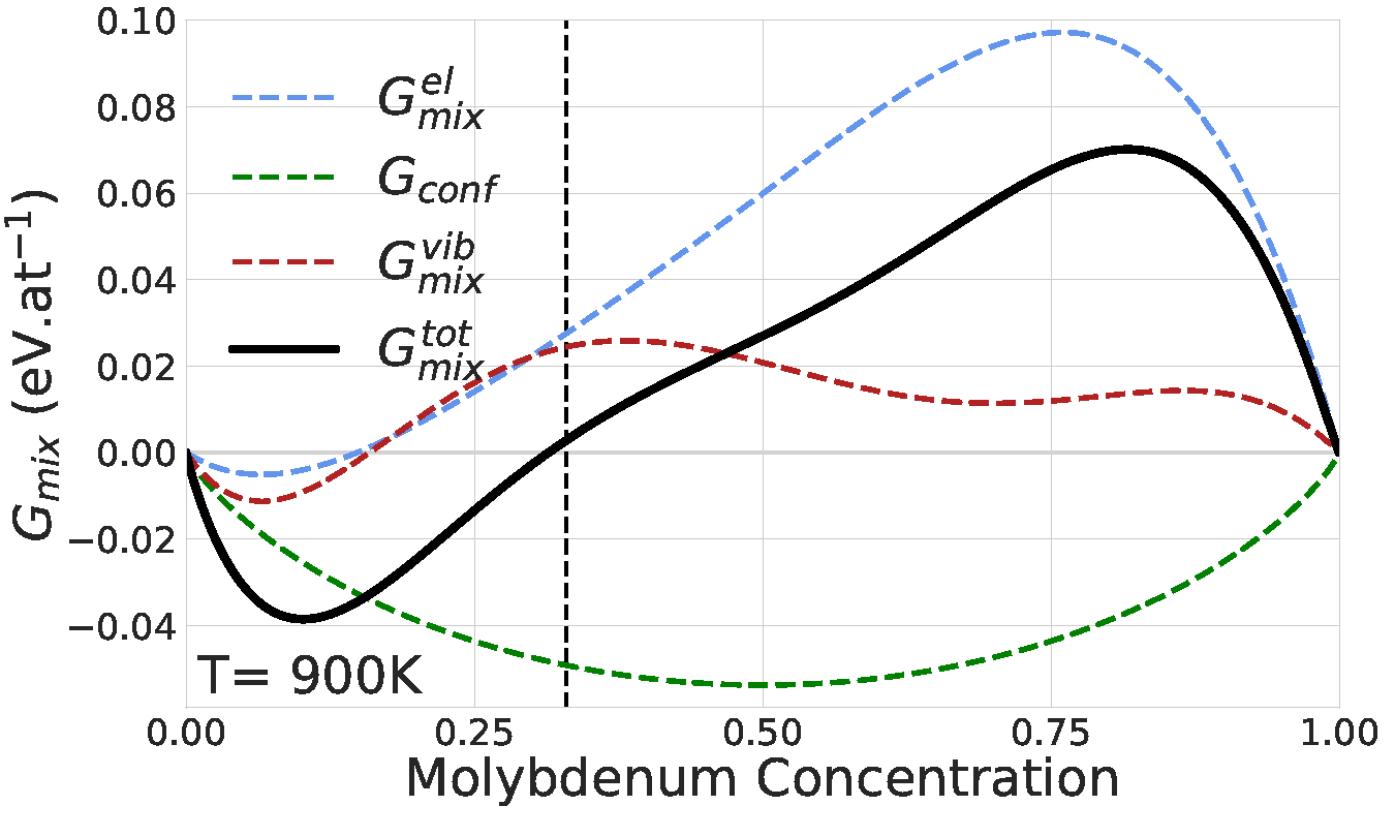
γ-stabilization effect in UMo



Stabilization of the bcc phase in UMo

MIXING FREE ENERGY

$$G_{mix}(T,x) = G_{U_{1-x}Mo_x}(T) - xG_{Mo}(T) - (1-x)G_U(T)$$



CONCLUSIONS

- The standard methods (DFPT, QHA) have limited applications for the actinides.
- AIMD and TDEP give phonon frequencies with an explicit temperature dependence.
- The CDW phase transition is well predicted as the transition line between α and γ-U
- The high temperature phases of Pu are found stable with TDEP
- Stabilization of bcc U by Mo

- Phase transitions mechanisms between α and δ plutonium
- Phase diagram of Pu
- Higher orders terms (phonon lifetime, thermal conductivity…)

Arigatou gozaimasu
Thank you for your attention