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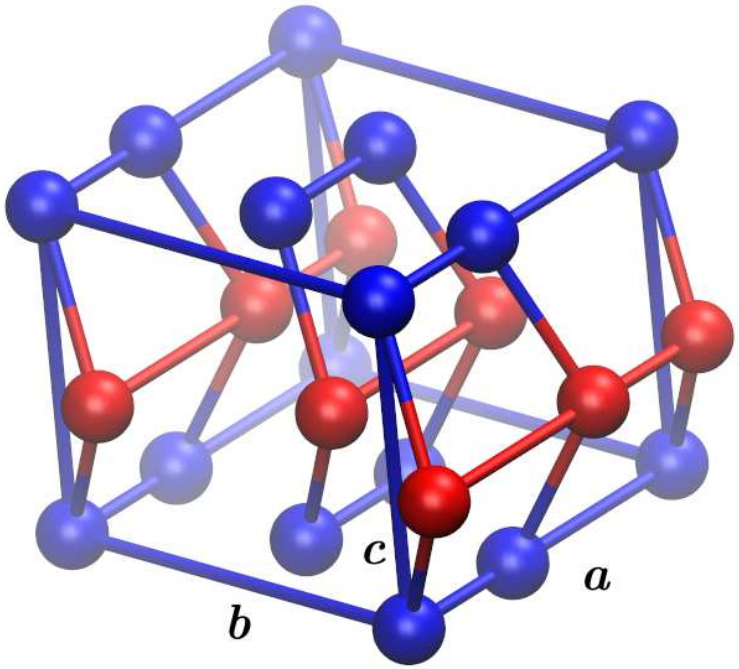
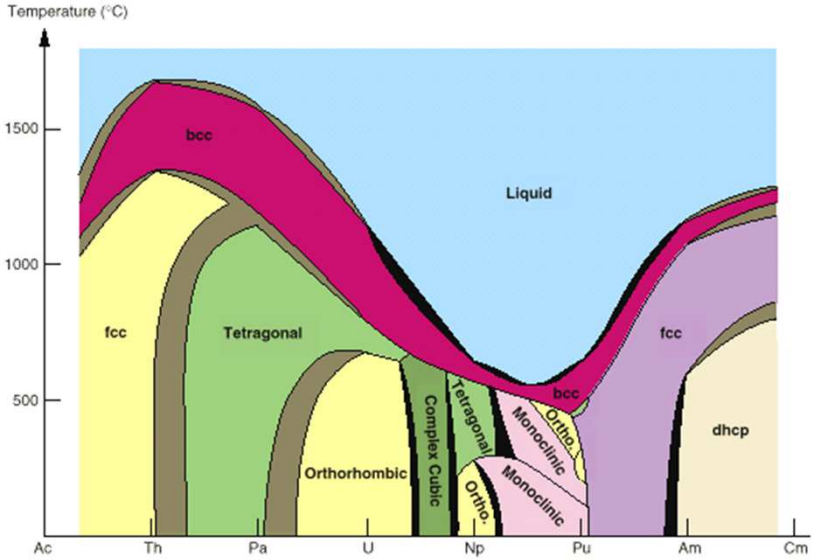
Anharmonic effects in solids : an implementation in ABINIT

J. BOUCHET, F. BOTTIN, J. BIEDER

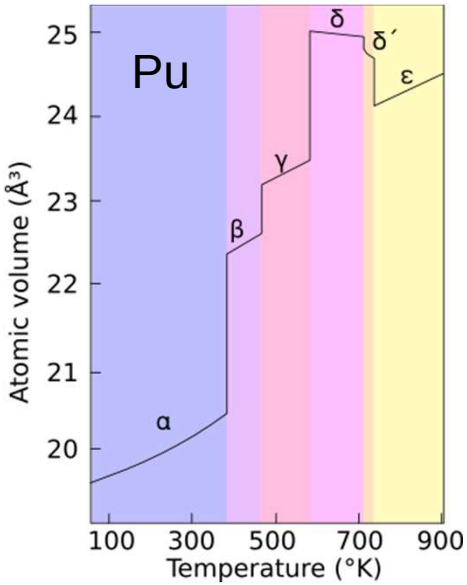


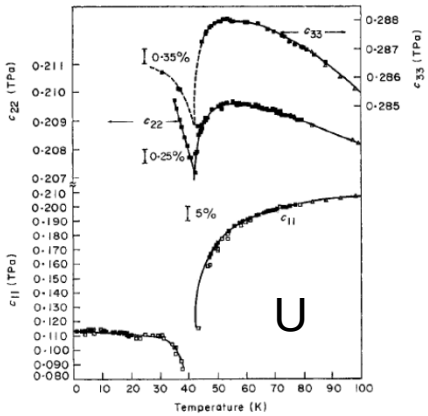
8TH ABINIT DEVELOPER'S WORKSHOP
9-12 MAY 2017

ACTINIDES : T ≠ 0 K ???



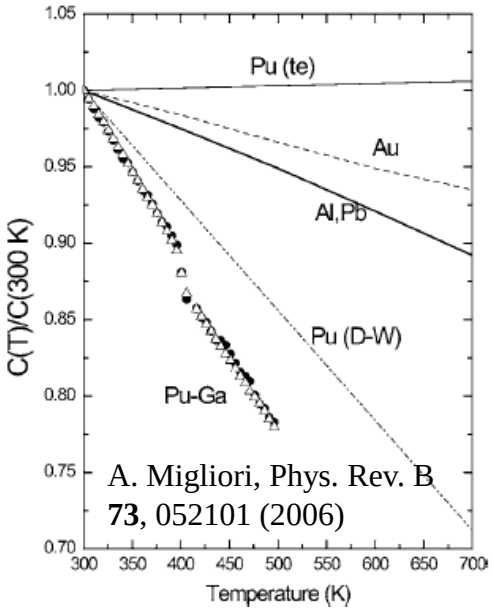
[Los Alamos Science, number **26**, 2000]



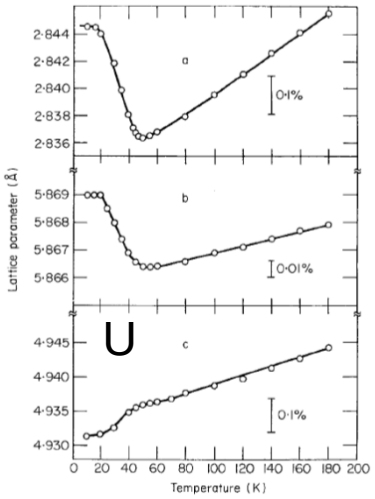


Fisher and McSkimin 1961

- Comparison with experiments at room temperature.
- Low melting points.
- Dynamical instability of the bcc structure at 0 K.
- 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)
- …

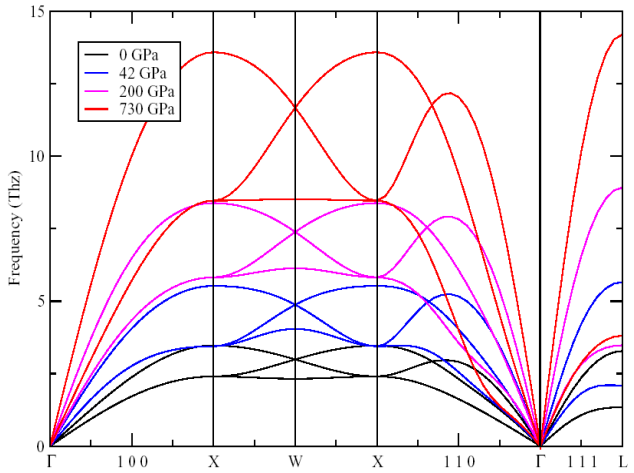


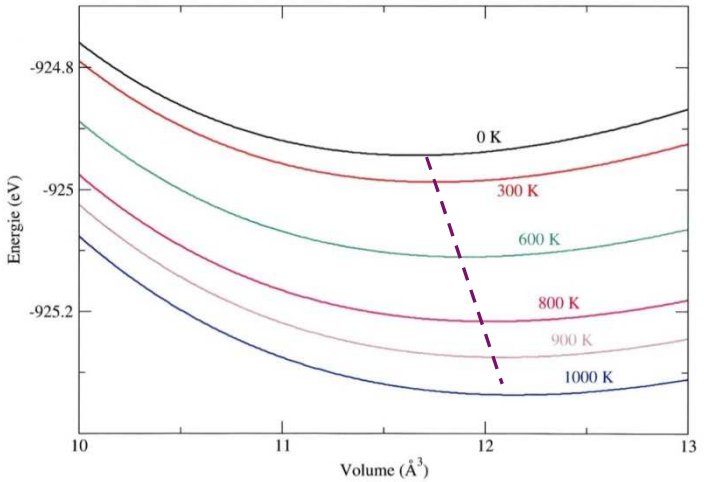
A. Migliori, Phys. Rev. B **73**, 052101 (2006)



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





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

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

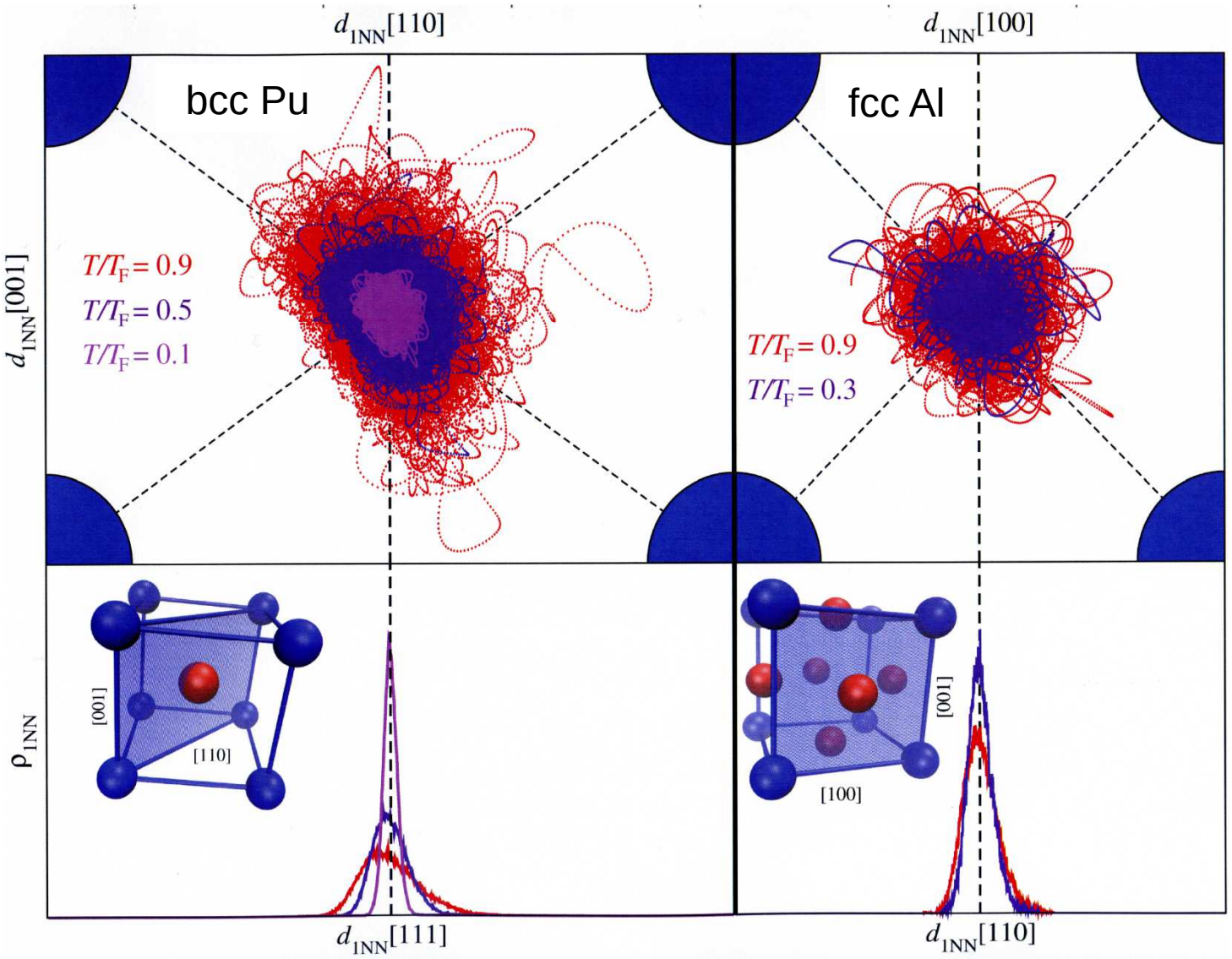
Structures dynamically stable at 0 K

Weak anharmonicity

Bcc unstable at 0 K

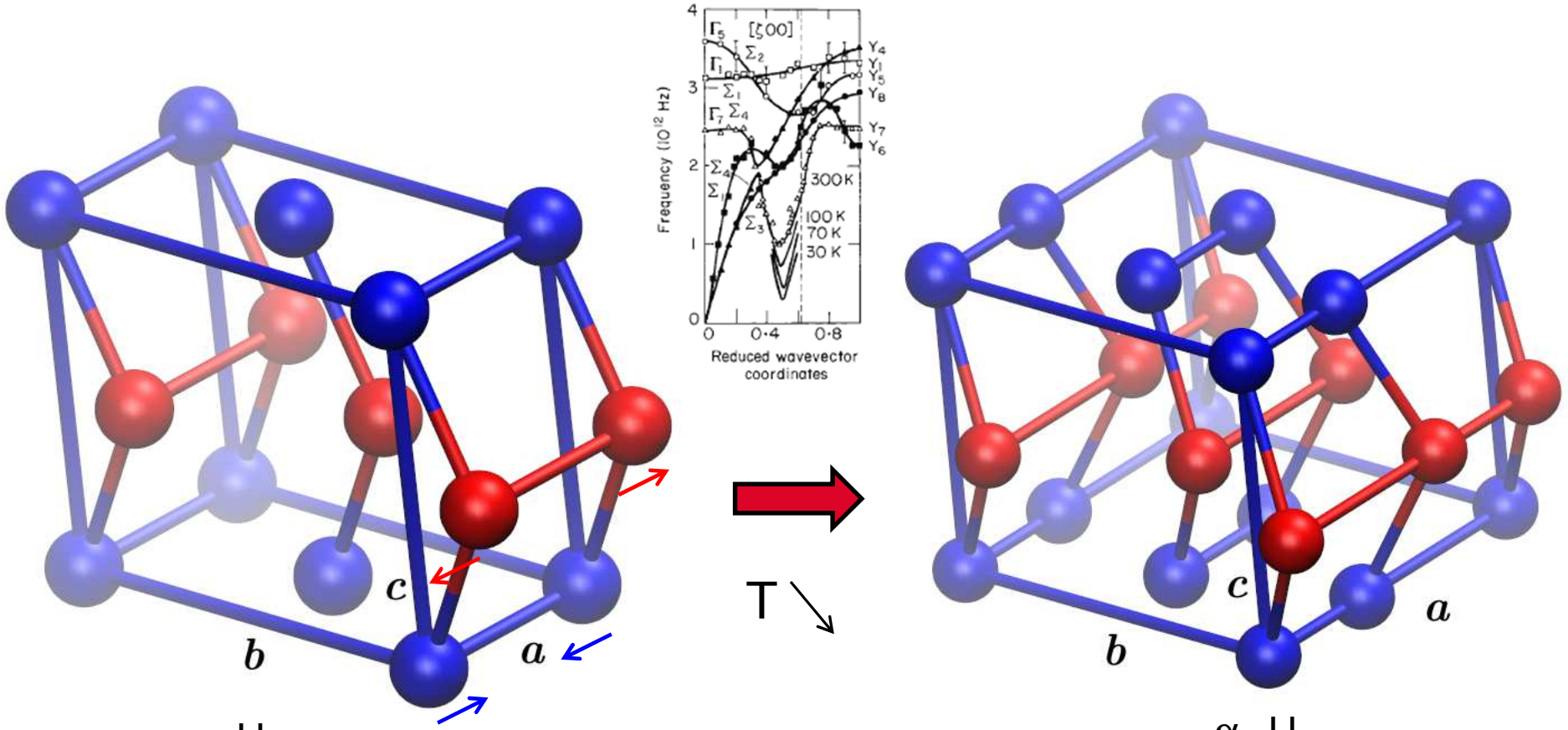
Low melting point, phase transitions

HARMONIC-ANHARMONIC : Al VS Pu



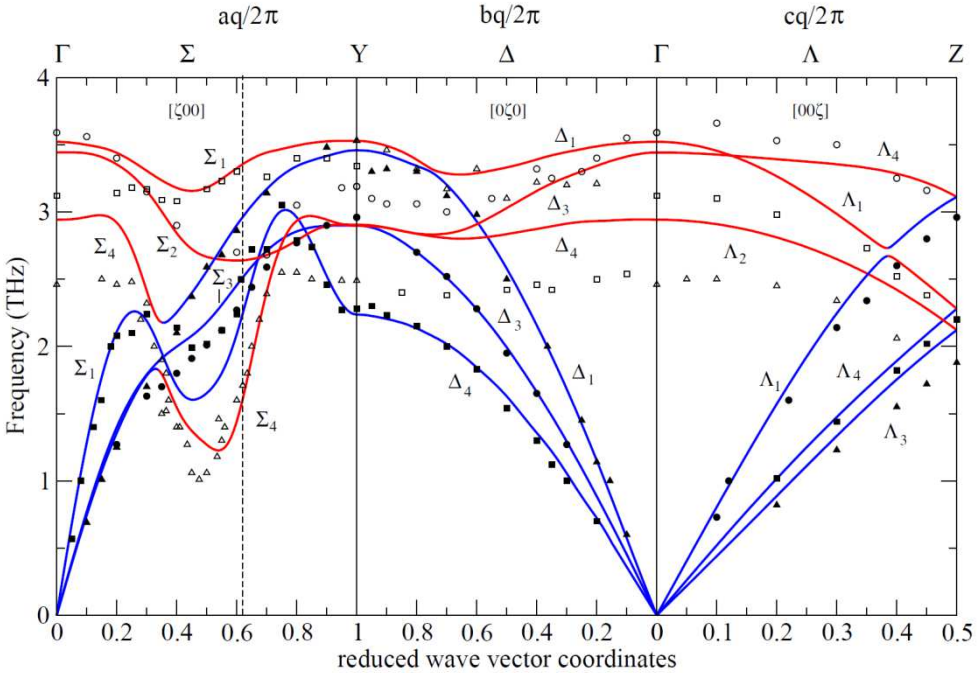
URANIUM : FAILURE OF THE QHA

The uranium metal shows a charge density wave at zero pressure, directly relied upon the presence of a soft mode in the [100] direction. Thus, the structure is twofold in this direction at very low temperature.

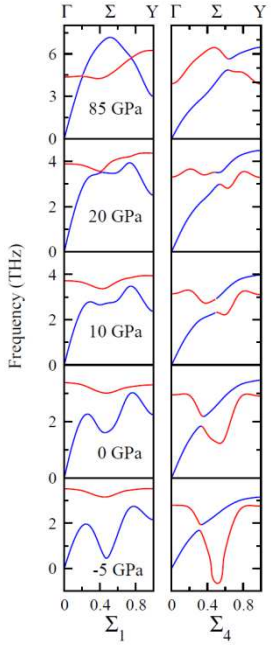


Smith *et al.*, *Phys. Rev. Lett.* (1980)

Uranium-Phonon spectrum with DFPT



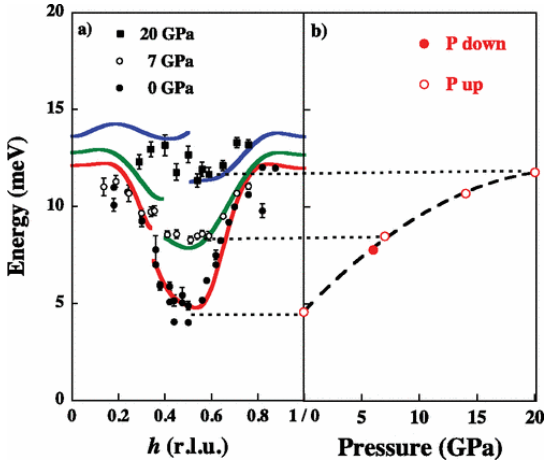
Pressure



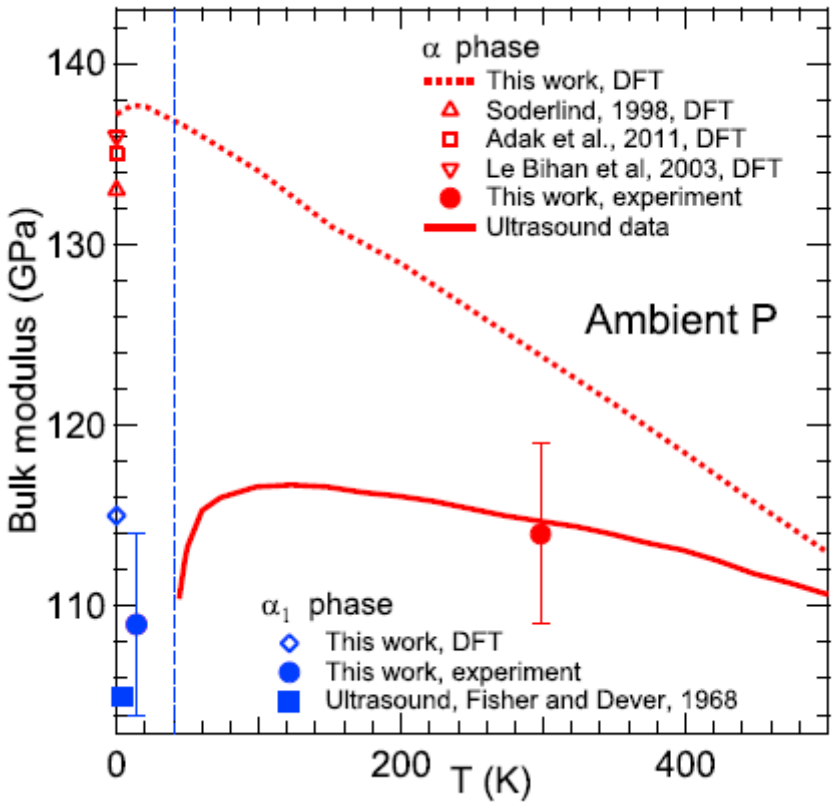
[W.P. Crummett *et al.* Phys. Rev. B **19**, 6028 (1979)]
[J. Bouchet Phys Rev B, **77** (2008)]

Pressure behavior confirmed by IXS

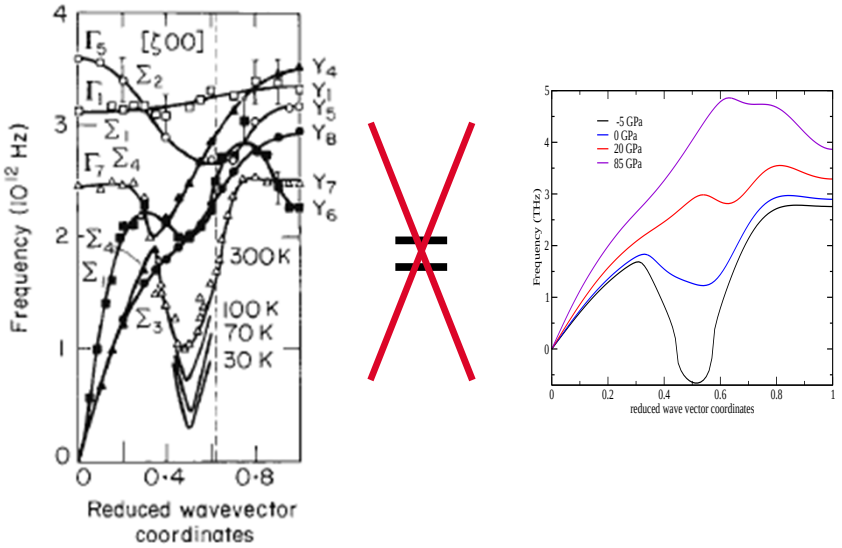
S. Raymond, J. Bouchet, G. H. Lander et al., Phys. Rev. Lett. 107, 136401 (2011).



URANIUM : FAILURE OF THE QHA



This mode increases experimentally with temperature whereas with the QHA it decreases when the volume increases.
→ Failure of the QHA.



The phonon spectrum has to depend **explicitly** on the temperature.

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

THE INTERATOMIC FORCES CONSTANTS

Series expansion of the total energy wrt the atomic displacements:

$$H = U_0 + \sum_{i,\alpha} \left(\frac{\partial U}{\partial u_i^\alpha}\right)_0 u_i^\alpha + \sum_{ij,\alpha\beta} \frac{1}{2!} \left(\frac{\partial^2 U}{\partial u_i^\alpha u_j^\beta}\right)_0 u_i^\alpha u_j^\beta + \sum_{ijk,\alpha\beta\gamma} \frac{1}{3!} \left(\frac{\partial^3 U}{\partial u_i^\alpha u_j^\beta u_k^\gamma}\right)_0 u_i^\alpha u_j^\beta u_k^\gamma + 0(u^4)$$

Around equilibrium: $(\mathcal{F}_i^\alpha)_0 = -\left(\frac{\partial U}{\partial u_i^\alpha}\right)_0 = 0$

The second order IFCs are defined by: $\Phi_{ij}^{\alpha\beta} = \left(\frac{\partial^2 U}{\partial u_i^\alpha u_j^\beta}\right)_0$

At the second order, the relation between total forces and atomic displacements becomes: $\mathcal{F}_i^\alpha = -\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta$

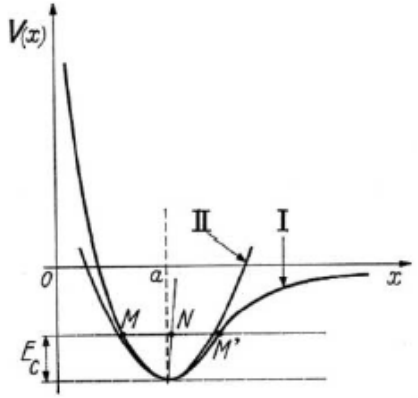
Then, we can compute the dynamical matrix : $\sum_{\beta,j} D_{ij}^{\alpha\beta}(\mathbf{q}) X_j^\beta(\mathbf{q}) = M_i \omega^2(\mathbf{q}) X_i^\alpha(\mathbf{q})$

And also the vDOS and Free Energy:

$$\begin{aligned} F(V,T) &= U_0(V_0) + F_{vib}(V,T) \quad \text{avec} \\ F_{vib}(V,T) &= \int_0^\infty g(\omega) \left[k_B T \ln\left(1 - \exp^{-\frac{\hbar\omega}{k_B T}}\right) + \frac{\hbar\omega}{2} \right] d\omega \end{aligned}$$

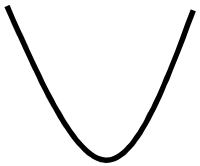
O. Hellman *et al.*, PRB 84, 180301(R) (2011), O. Hellman *et al.*, PRB 87, 104111 (2013).

QHA AND TDEP APPROXIMATIONS



The QHA gives good results except when the phonon spectrum depends **EXPLICITLY** on the temperature.

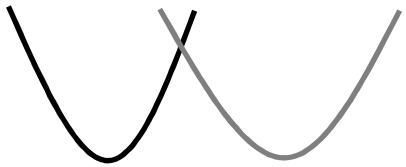
ω (0 K)



Harm. Approx.

Temperature effects are only taken into account through the Bose-Einstein statistic. The phonon spectrum is constant.

ω (0 K, *V*)

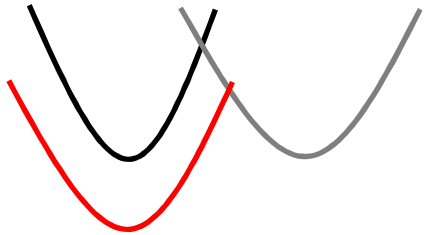


QHA

Temperature effects are taken into account **IMPLICITLY** through the thermal expansion. The phonon spectrum is function of volume.

Static ab initio calculations

ω (*T*, *V*)



TDEP

Temperature effects are **EXPLICTLY** taken into account through into the phonon spectrum.

AIMD simulations

$$\mathcal{F}_i^{\alpha}(t) = -\sum_{j,\beta} \Phi_{ij}^{\alpha\beta} u_j^{\beta}(t)$$

THE 2ND AND 3RD ORDER IFCS MATRICES

The number of coefficients in the 2nd and 3rd order IFCs matrices could be very huge. For 100 atoms, $(3*100)^2$ at the 2nd order and $(3*100)^3$ at the 3rd order.

These number could be strongly reduced using symmetries; up to 10-20 at the 2nd order and around 100 at the 3rd order.

1. The IFCs are symmetric: $\Phi_{ij}^{\alpha\beta} = \Phi_{ji}^{\beta\alpha}$

$$\Psi_{ijk}^{\alpha\beta\gamma} = \Psi_{jki}^{\beta\gamma\alpha} = \Psi_{kij}^{\gamma\alpha\beta} = \Psi_{ikj}^{\alpha\gamma\beta} = \Psi_{jik}^{\beta\alpha\gamma} = \Psi_{kji}^{\gamma\beta\alpha}$$

2. The acoustic sum rule :

$$\sum_j \Phi_{ij}^{\alpha\beta} = 0 \quad \forall\, i \;\&\; (\alpha,\beta) \qquad \Big| \qquad \sum_k \Psi_{ijk}^{\alpha\beta\gamma} = 0 \quad \forall\, i,j \;\&\; (\alpha,\beta,\gamma)$$

3. The symmetries of the crystal (I) : from ef(g) → to ij(k)

$$\Phi_{ij}^{\alpha\beta} = \sum_{\mu\nu} S_{ef\to ij}^{\alpha\mu} S_{ef\to ij}^{\beta\nu} \Phi_{ef}^{\mu\nu} \qquad \Big| \qquad \Psi_{ijk}^{\alpha\beta\gamma} = \sum_{\mu\nu\xi} S_{efg\to ijk}^{\alpha\mu} S_{efg\to ijk}^{\beta\nu} S_{efg\to ijk}^{\gamma\xi} \Psi_{efg}^{\mu\nu\xi}$$

4. The symmetries of the crystal (II) : if the interaction is kept invariant or reversed

PROCEDURE

Forces and displacements (MD, MC…)

Define structure : Compare average positions and ideal ones

Define the bonds and the shells of NN (Rcut)

Find the symmetries which keep invariant or reversed the bonds : number of coefficients

Build the matrix relating forces and coefficients

Moore Penrose Inverse

Build the IFC matrix with a reference bond and the symmetries

Dynamical matrix, DOS…

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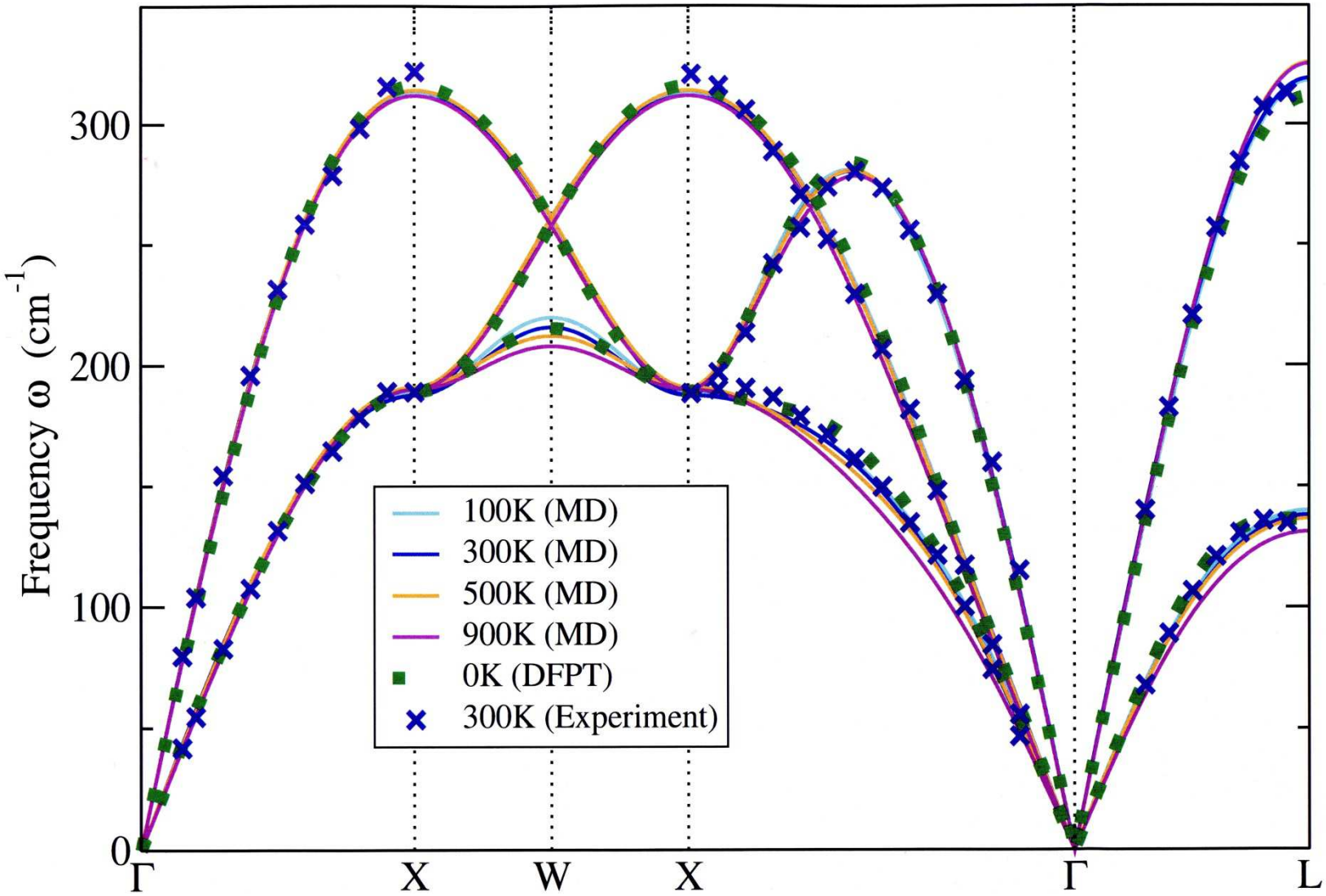
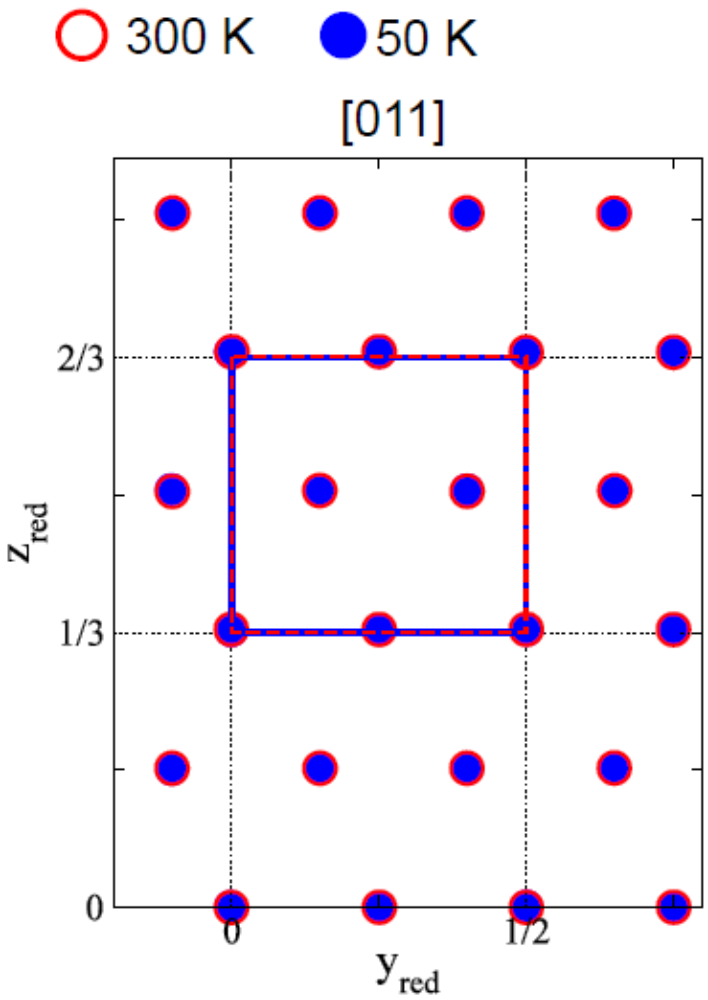
IN THE ABINIT PACKAGE

```
 Analysis of interatomic force constants

 column 1 is related to the displacement
       of the generic atom along x,
 column 2 is related to the displacement
       of the generic atom along y,
 column 3 is related to the displacement
       of the generic atom along z,

  NOTE: Open file ifcinfo.out, for the output of interatom
force constants. This is because prt_ifc==1.

 generic atom number   1
 with cartesian coordinates  0.00000000E+00  0.00000000E+0
0.00000000E+00

 Third atom defining local coordinates :
     ib =    1   irpt =   54

   1 interaction with atom     1 cell     105
 with coordinates     0.000000E+00    0.000000E+00
0.000000E+00
 and distance     0.000000E+00
   0.08028  0.00000  0.00000
   0.00000  0.08028  0.00000
   0.00000  0.00000  0.10244
  Trace          0.26300
 Transformation to local coordinates
 First  local vector :        0.000000        0.000000
1.000000
 Second local vector :       -0.707107        0.707107
0.000000
 Third  local vector :       -0.707107        0.707107
0.000000
   0.10244  0.00000  0.00000
   0.00000  0.08028  0.00000
   0.00000  0.00000  0.08028

   2 interaction with atom     1 cell      56
 with coordinates    -2.667425E+00   -2.667425E+00
2.667425E+00
 and distance     4.620116E+00
  -0.00756 -0.01320  0.01246
  -0.01320 -0.00756  0.01246
   0.01246  0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :       -0.577350        0.577350
0.577350
 Second local vector :        0.408248        0.408248
0.816497
 Third  local vector :       -0.707107        0.707107
0.000000
  -0.03083  0.00339  0.00000
   0.00339  0.00895  0.00000
   0.00000  0.00000  0.00564

   3 interaction with atom     1 cell     104
 with coordinates     2.667425E+00    2.667425E+00   -
2.667425E+00
 and distance     4.620116E+00
  -0.00756 -0.01320  0.01246
  -0.01320 -0.00756  0.01246
   0.01246  0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :        0.577350        0.577350
0.577350
 Second local vector :       -0.408248       -0.408248
0.816497
 Third  local vector :       -0.707107        0.707107
0.000000
  -0.03083  0.00339  0.00000
   0.00339  0.00895  0.00000
   0.00000  0.00000  0.00564

   4 interaction with atom     1 cell      54
 with coordinates    -2.667425E+00   -2.667425E+00   -
3.853670E+00
 and distance     5.392688E+00
  -0.00756 -0.01320 -0.01246
  -0.01320 -0.00756 -0.01246
  -0.01246 -0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :       -0.494637       -0.494637
0.714610
 Second local vector :        0.505306        0.505306
0.699523
 Third  local vector :        0.707107       -0.707107
0.000000
  -0.02835  0.01020  0.00000
   0.01020  0.00647  0.00000
   0.00000  0.00000  0.00564

   5 interaction with atom     1 cell     106
 with coordinates     2.667425E+00    2.667425E+00
3.853670E+00
 and distance     5.392688E+00
  -0.00756 -0.01320 -0.01246
  -0.01320 -0.00756 -0.01246
  -0.01246 -0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :        0.494637        0.494637
0.714610
 Second local vector :       -0.505306       -0.505306
0.699523
 Third  local vector :        0.707107       -0.707107
0.000000
  -0.02835  0.01020  0.00000
   0.01020  0.00647  0.00000
   0.00000  0.00000  0.00564

   6 interaction with atom     1 cell      63
 with coordinates    -3.260548E+00    3.260548E+00   -
3.260548E+00
 and distance     5.647434E+00
  -0.00756  0.01320 -0.01246
   0.01320 -0.00756  0.01246
  -0.01246  0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :       -0.577350        0.577350
0.577350
 Second local vector :        0.408248       -0.408248
0.816497
 Third  local vector :       -0.707107       -0.707107
0.000000
  -0.03083  0.00339  0.00000
   0.00339  0.00895  0.00000
   0.00000  0.00000  0.00564

   7 interaction with atom     1 cell      65
 with coordinates    -3.260548E+00    3.260548E+00
3.260548E+00
 and distance     5.647434E+00
  -0.00756  0.01320  0.01246
   0.01320 -0.00756 -0.01246
   0.01246 -0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :       -0.577350        0.577350
0.577350
 Second local vector :        0.408248       -0.408248
0.816497
 Third  local vector :        0.707107        0.707107
0.000000
  -0.03083  0.00339  0.00000
   0.00339  0.00895  0.00000
   0.00000  0.00000  0.00564

   8 interaction with atom     1 cell      95
 with coordinates     3.260548E+00   -3.260548E+00   -
3.260548E+00
 and distance     5.647434E+00
  -0.00756  0.01320  0.01246
   0.01320 -0.00756 -0.01246
   0.01246 -0.01246 -0.00112
  Trace          -0.01625
 Transformation to local coordinates
 First  local vector :        0.577350       -0.577350
0.577350
 Second local vector :       -0.408248        0.408248
0.816497
 Third  local vector :        0.707107        0.707107
0.000000
  -0.03083  0.00339  0.00000
   0.00339  0.00895  0.00000
   0.00000  0.00000  0.00564
```

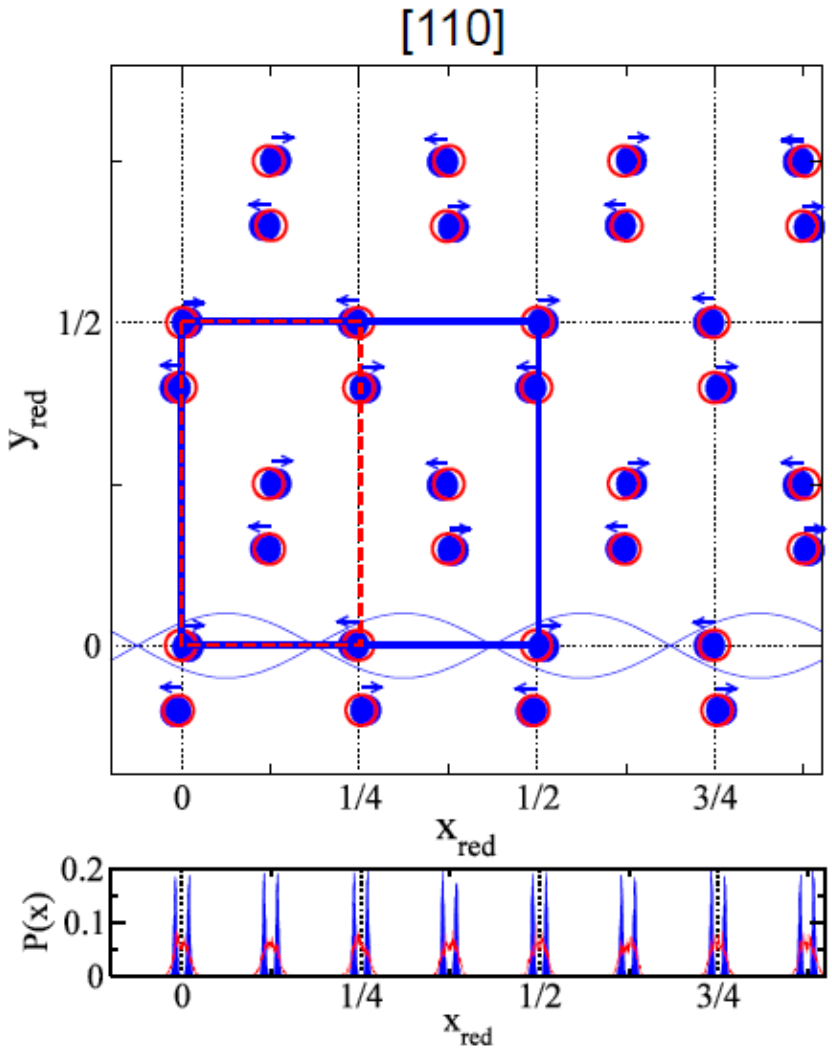
TEST CASE: Al


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)

URANIUM : AVERAGE POSITIONS AT 300 AND 50 K



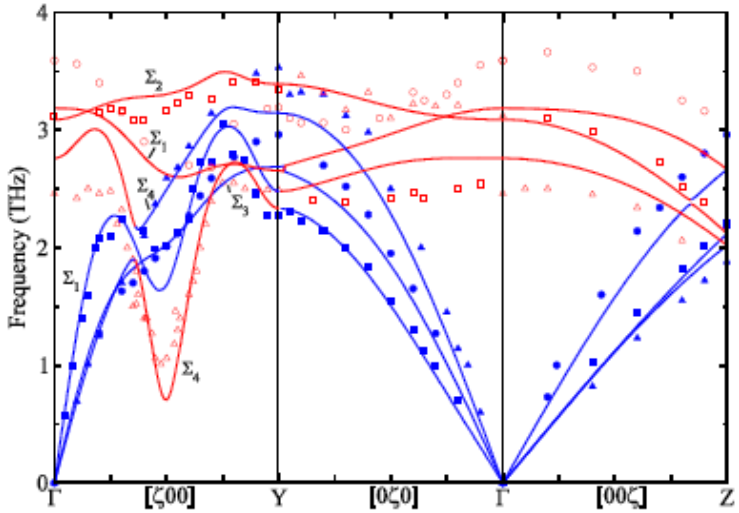
No change in the [011] plane, the atoms stay in the ideal positions

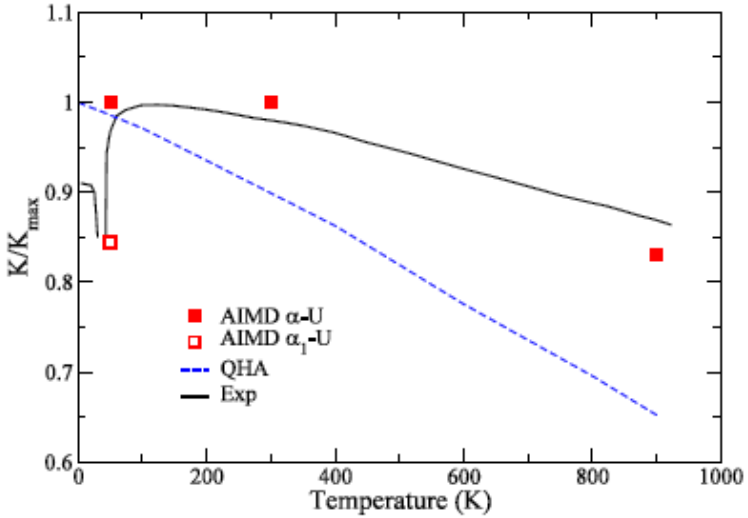


At 50 K, the atoms adopt new equilibrium positions with a small displacement in the *x* direction

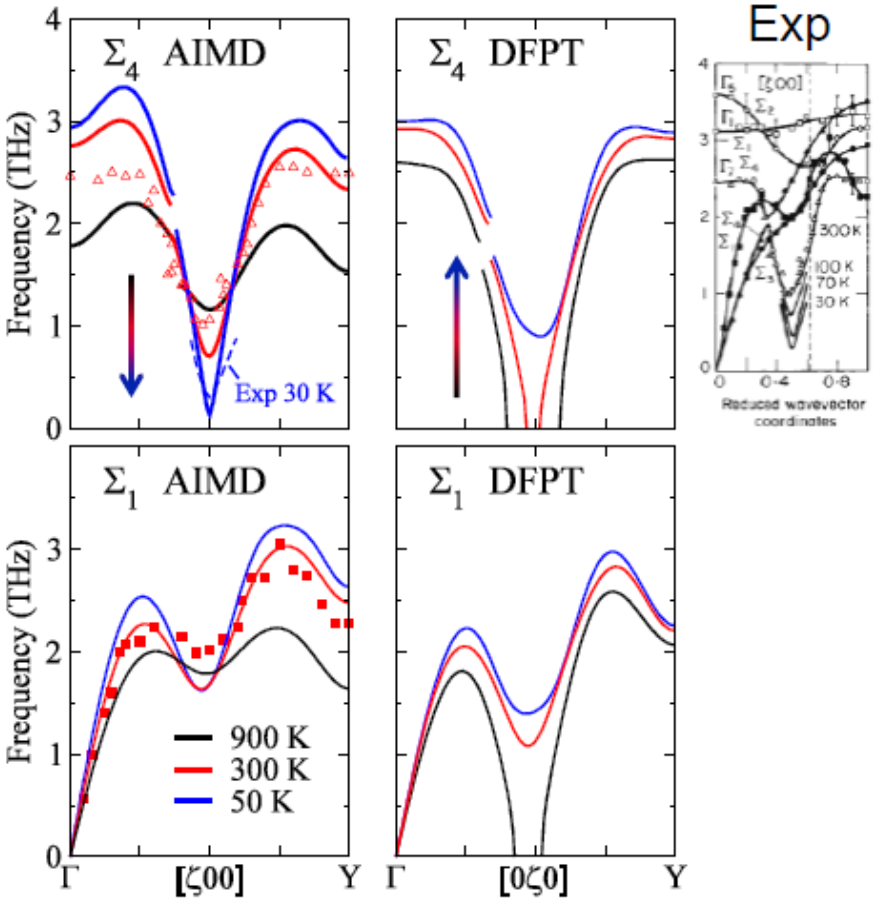
URANIUM : FAILURE OF THE QHA

Comparison AIMD-Exp at 300 K





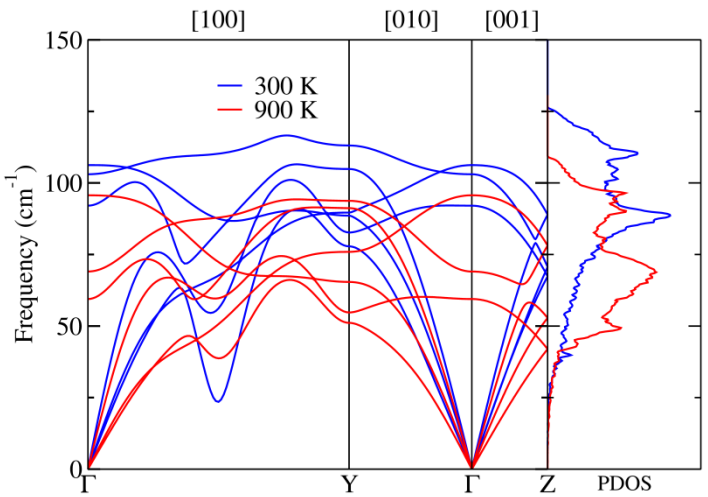
Comparison AIMD-DFPT



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

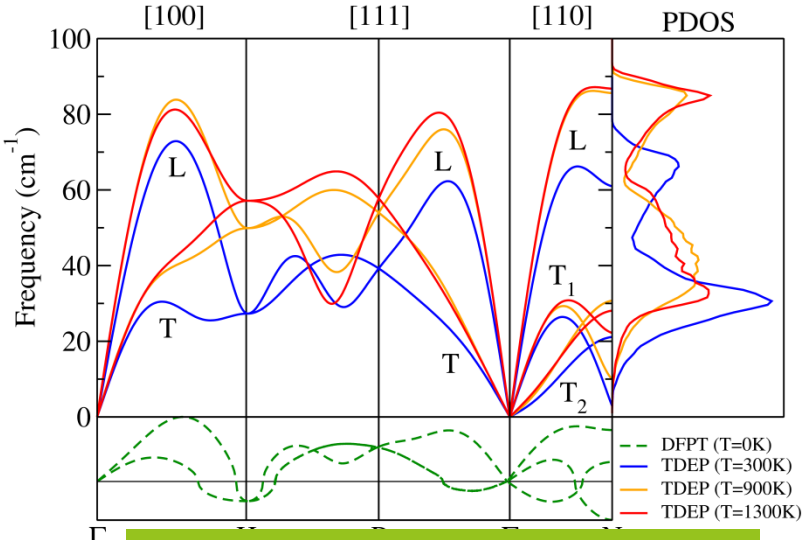
URANIUM : PHASE DIAGRAM

« alpha » phase

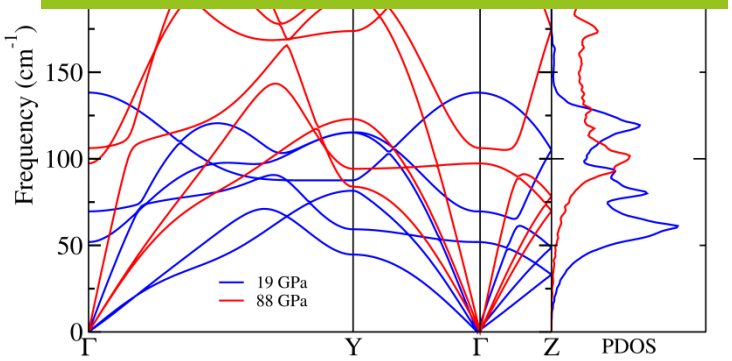


Temperature

« gamma » phase

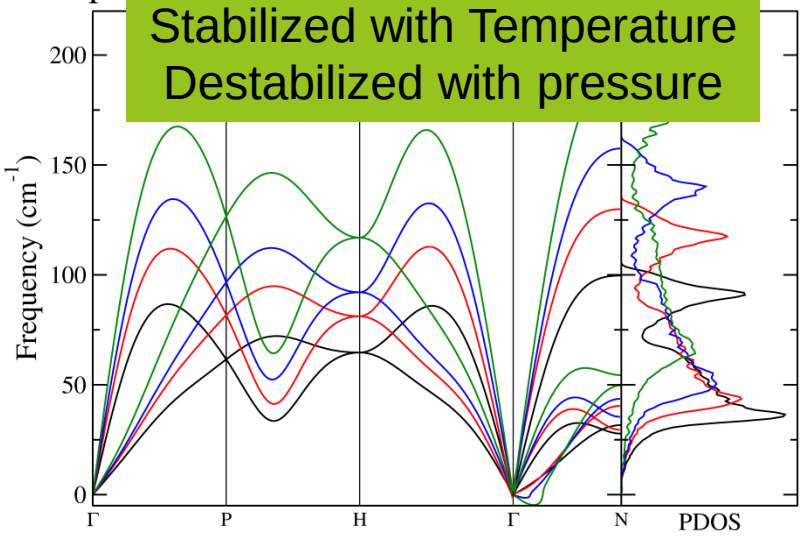


Destabilized with Temperature
Stabilized with pressure



Pressure

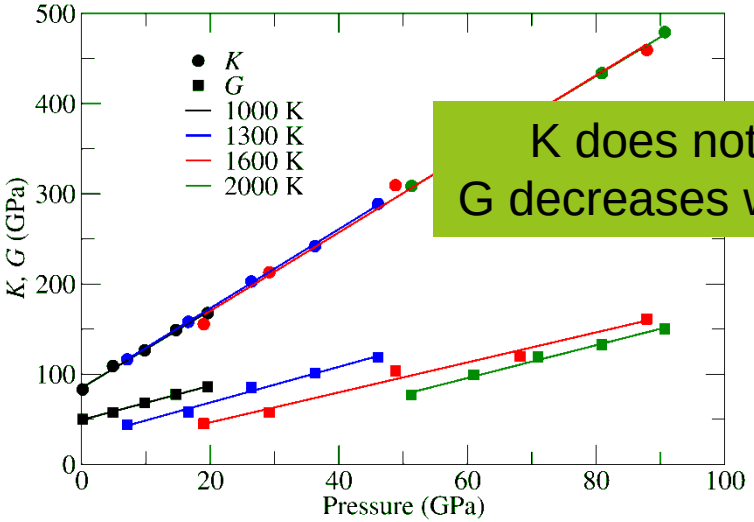
Stabilized with Temperature
Destabilized with pressure



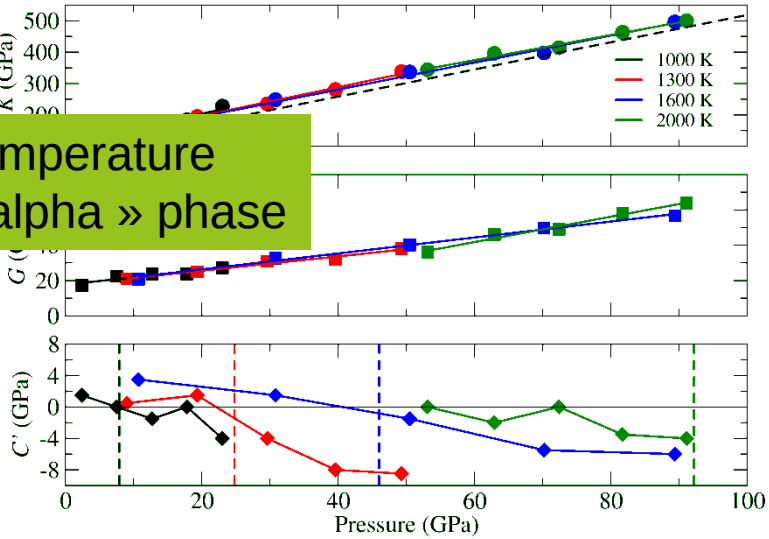
J. Bouchet & F. Bottin., Phys. Rev. B **95**, 054113 (2017)

URANIUM : PHASE DIAGRAM

« alpha » phase



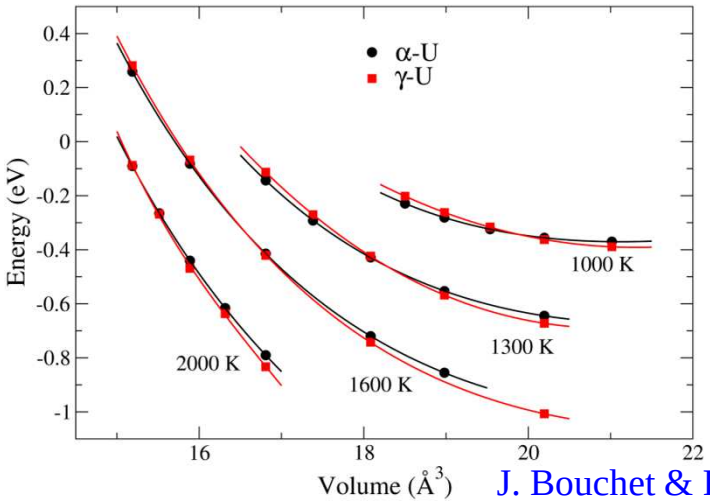
« gamma » phase

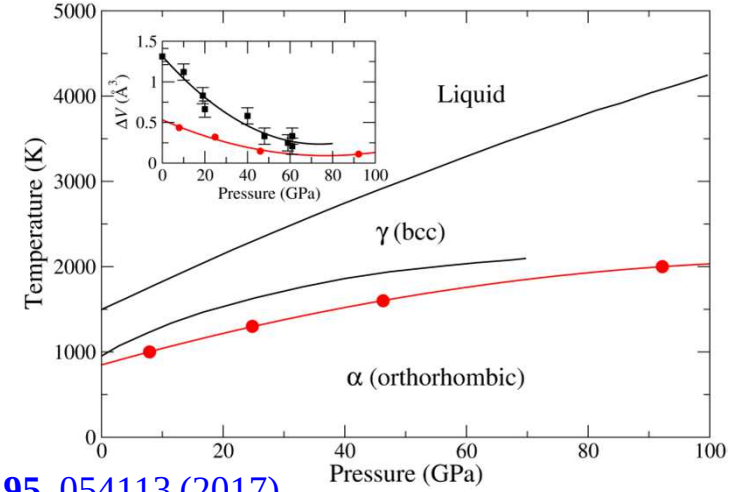


K does not depend on Temperature
G decreases wrt T for the « alpha » phase

Bulk & Shear

Free energy and phase diagram

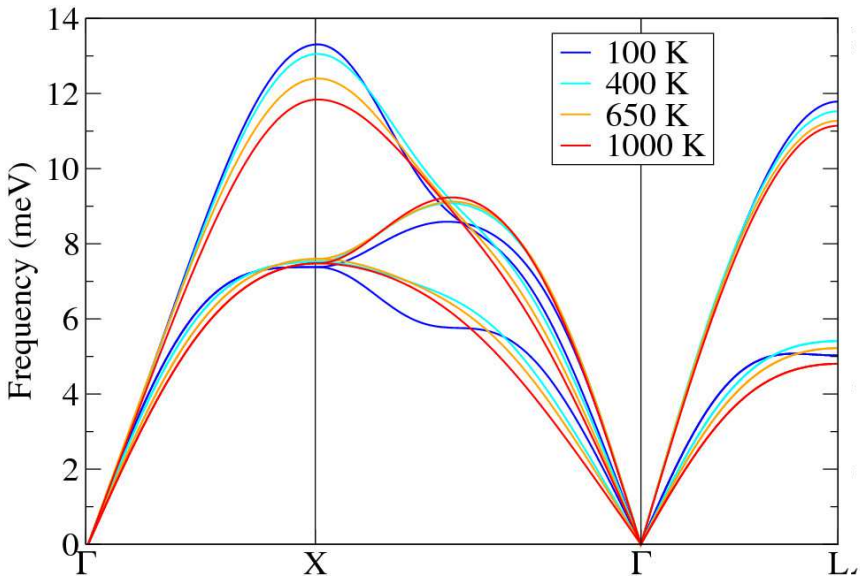




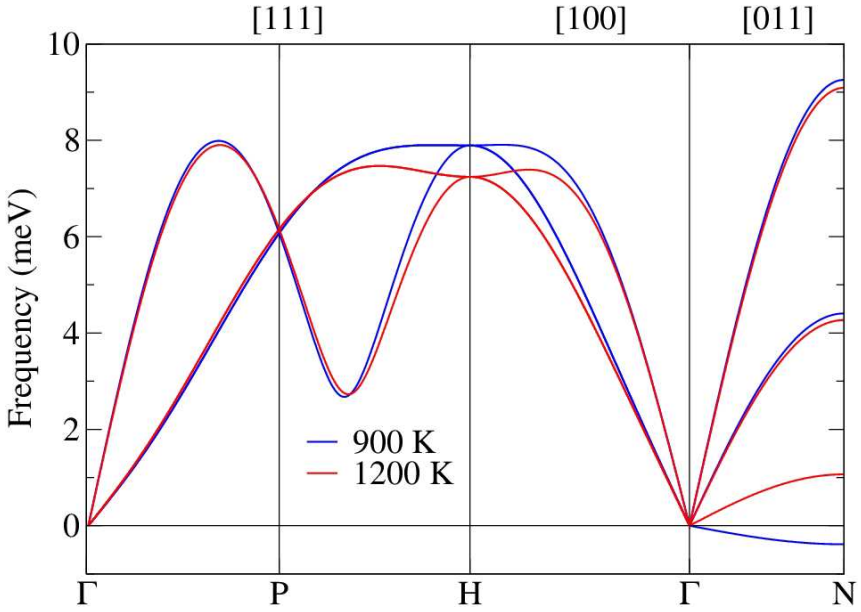
J. Bouchet & F. Bottin., Phys. Rev. B **95**, 054113 (2017)

PLUTONIUM: δ & ε PHASES STABILIZATION

« delta » phase



« epsilon » phase



Calculated transition temperature = 1000K (exp=750K)

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

IRON : ELASTIC CTS & SOUND VELOCITIES

Vibrational Density Of States

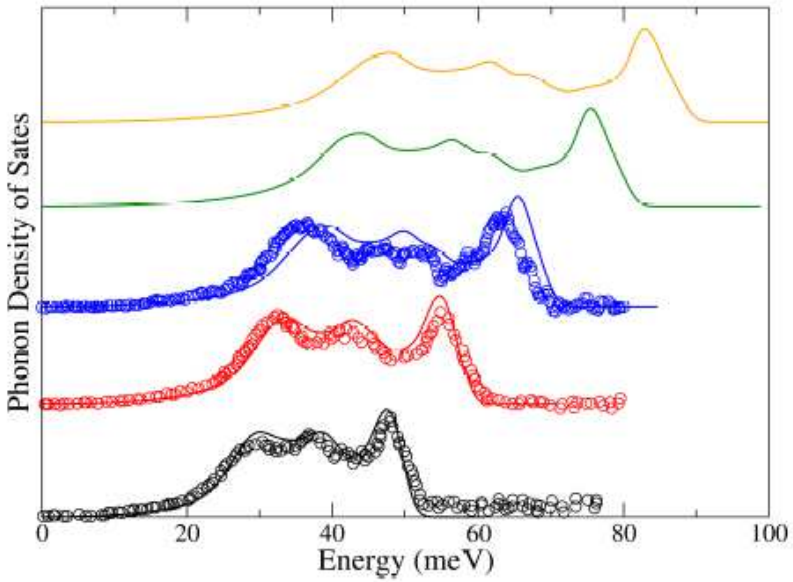


FIG. 3. (Color online) Room temperature phonon density of states of hcp Fe at different pressures. Straight lines : our work at 51 (black), 87 (red), 158 (blue), 245 (green) and 323 (orange) GPa. Open circles : NRIXS measurements[31,34] at 51 (black), 85 (red) and 151 (blue) GPa.

Entropy and Specific Heat

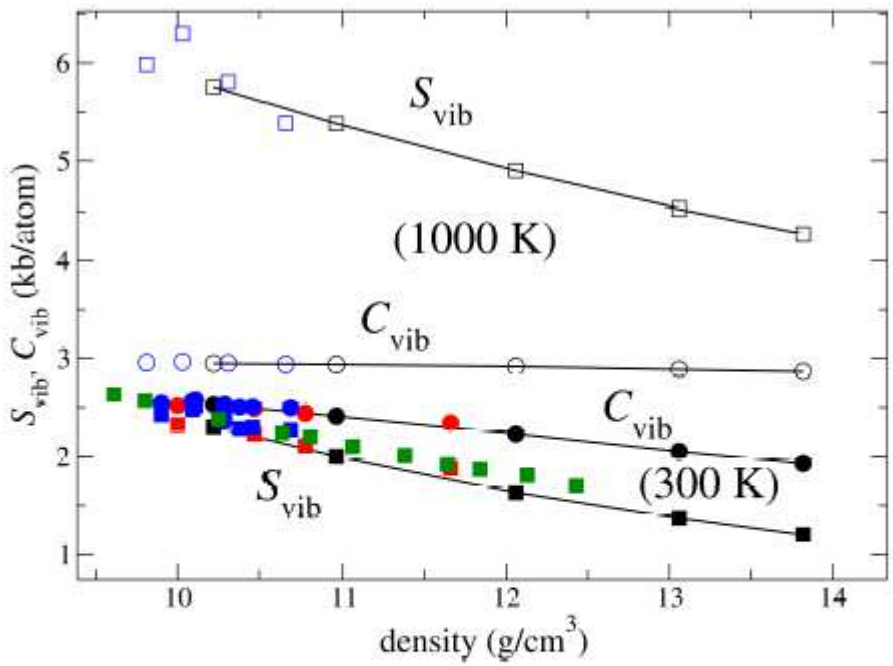


FIG. 5. (Color online) Vibrational entropy (squares) and vibrational heat capacity (circles) as a function of density for hcp Fe on isotherms T=300 K (filled symbols) and 1000 K RIXS measurements of green, red and blue.

Very good agreement between simulations and experiments.
The temperature effects are very well reproduced.

J. Bouchet & F. Bottin., in preparation

BEYOND THE 2ND ORDER

Beyond the 2nd order (in progress) :

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

Transport: the ionic thermal conductivity

$$\kappa_{\alpha\alpha} = \frac{1}{V} \sum_{\mathbf{q}s} C_{\mathbf{q}s} v_{\alpha\mathbf{q}s}^2 \tau_{\alpha\mathbf{q}s}$$

$$\frac{1}{\tau_{\mathbf{q}s}} = \Gamma_{\mathbf{q}s}$$

$$\Gamma_{\mathbf{q}s} = \sum_{s's''} \frac{\hbar\pi}{16} \iint_{\mathrm{BZ}} \left| \Psi_{ss's''}^{\mathbf{q}\mathbf{q}'\mathbf{q}''} \right|^2 \Delta_{\mathbf{q}\mathbf{q}'\mathbf{q}''} \times \left[(n_{\mathbf{q}'s'} + n_{\mathbf{q}''s''} + 1)\delta(\omega_{\mathbf{q}s} - \omega_{\mathbf{q}'s'} - \omega_{\mathbf{q}''s''}) + 2(n_{\mathbf{q}'s'} - n_{\mathbf{q}''s''})\delta(\omega_{\mathbf{q}s} - \omega_{\mathbf{q}'s'} + \omega_{\mathbf{q}''s''}) \right] d\mathbf{q}' d\mathbf{q}''$$

Equations of states : the Grüneisen parameters

$$\gamma_{\mathbf{q}s} = -\frac{V}{\omega_{\mathbf{q}s}} \frac{\partial \omega_{\mathbf{q}s}}{\partial V} = -\frac{1}{6\omega_{\mathbf{q}s}^2} \sum_{ijk\alpha\beta\gamma} \frac{\epsilon_{i\alpha}^{\mathbf{q}s*} \epsilon_{j\beta}^{\mathbf{q}s}}{\sqrt{M_i M_j}} r_k^{\gamma} \Psi_{ijk}^{\alpha\beta\gamma} e^{i\mathbf{q}\cdot\mathbf{r}_j}$$

Workshop CECAM : « Anharmonicity and thermal properties of materials » with O. Hellmann (CalTech) and M. Verstraete (Univ. Liège), January 2018