GreenALM

Virtual Psi-k GreenALM Hands-on Tutorial 2021

Introduction to thermo-mechanical properties

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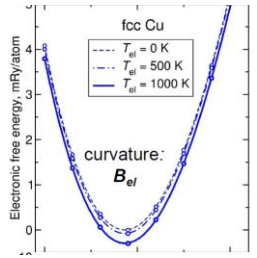
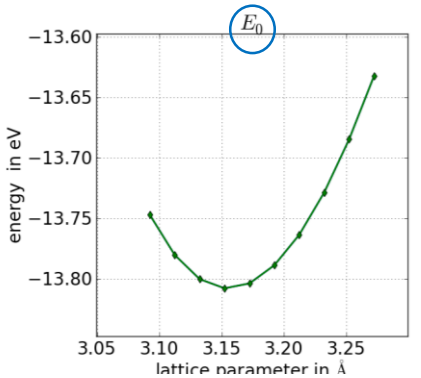
Free energy

Groundstate energy $\mathbf{E_0}$ from:

DFT groundstate calculation

$$F = E_0 + F_{vib} + F_{conf} + F_{mag} + F_{el} + F_{defects} + \dots$$





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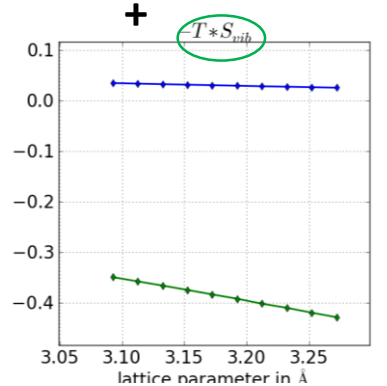

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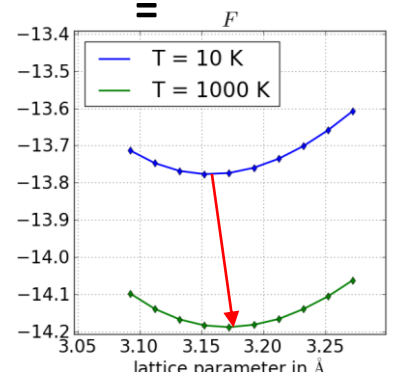
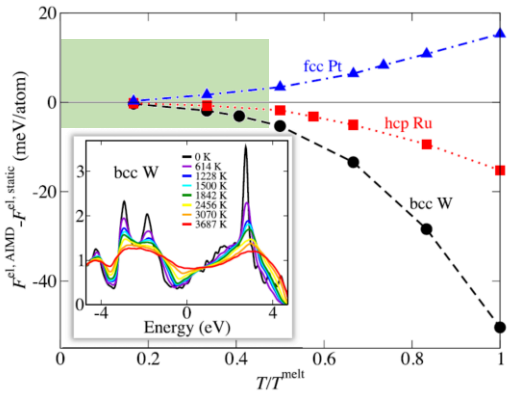


- F_{conf}: No volume dependence
- F_{el}: Typically small influence on curvature of F_{vib} (→ Talk by Pavel Korzhavyi)
- $F_{defects}$: Matters mostly at high temperatures (→ Talk by Blazej Grabowki)



Zhang, Grabowski et al, 2017
https://doi.org/10.1103/PhysRevB.95.165126

Low temperatures ($T < T_{melt}/2$), non-magnetic solid:
$\mathbf{F_{vib}}$ is leading contribution

Vibrational free energy $\mathbf{F_{vib}}$ e.g. from

a) Ab-initio MD

b) Quasiharmonic approximation (QHA):
Explicit phonon calculations, Debye Grüneisen model

The Quasi-harmonic approximation

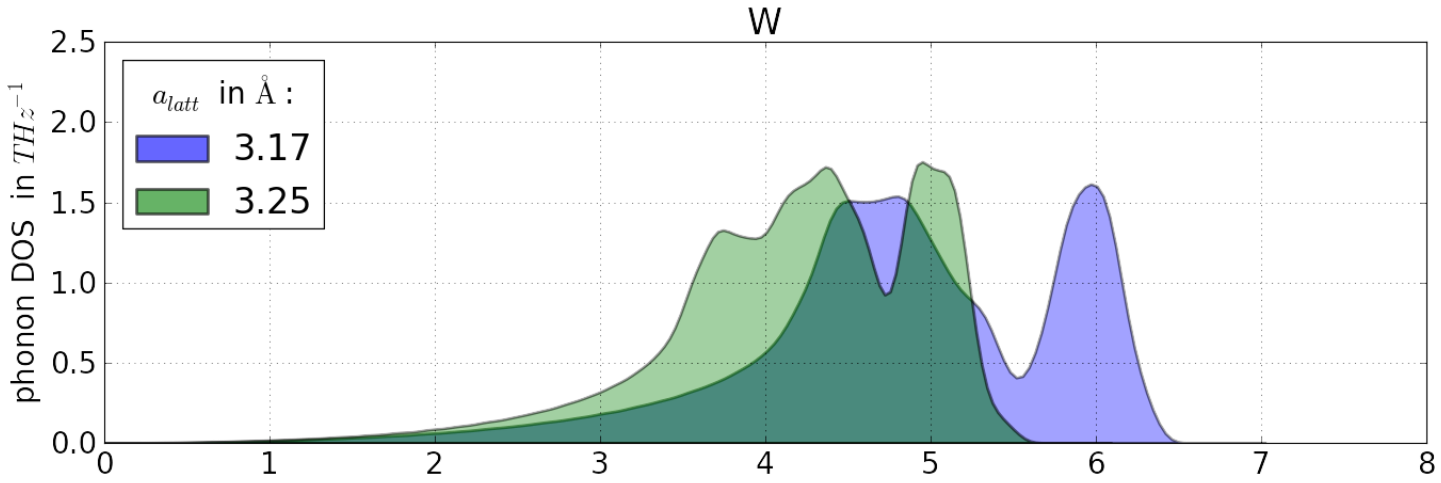
QHA with **explicit phonon calculations** (e.g. phonopy + VASP….)

- Finite displacements and forces → dynamical matrix
- Eigenvalues of dynamical matrix = phonon frequencies
- Intergration over phonon DOS → F_{vib}

zero-point vibrations

temperature excitations

$$F_{vib} = \frac{1}{2}\sum_{i}^{3N}\epsilon_i + \frac{1}{\beta}\sum_{i}^{3N}\ln(1-\exp^{-\beta\epsilon_i}) \qquad \epsilon_i = \hbar\omega_i \qquad \beta = \frac{1}{k_b T}$$

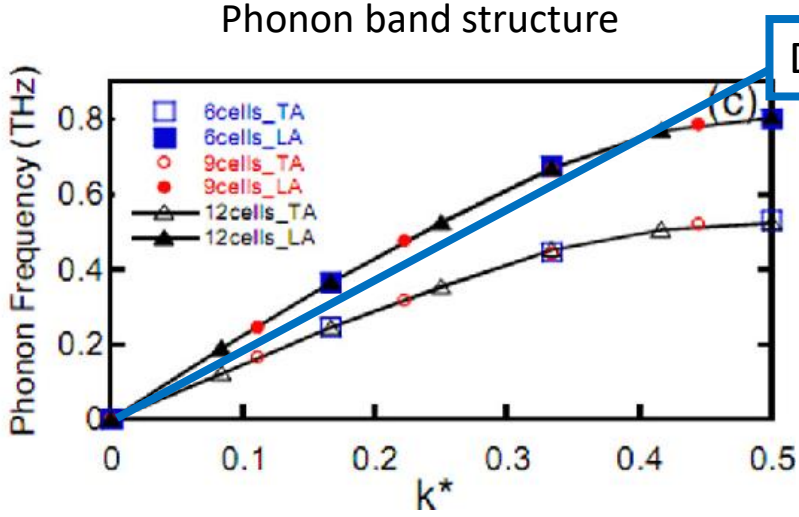


Debye model

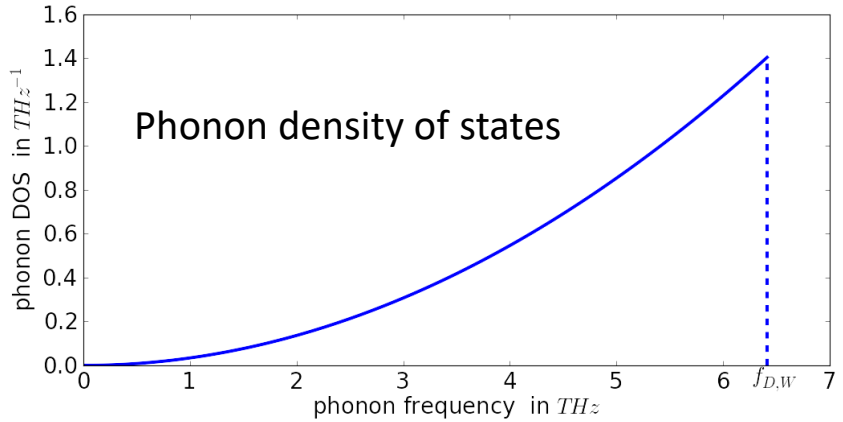
- Only one phonon branch: Averaged between longitudinal and transversal acoustic phonons
- Linear dispersion

- Parabolic DOS

Phonon band structure



1-atom unit cell



Free energy: Debye Grüneisen model

- The Debye-Grüneisen approach is very powerful due to its computational efficiency and simplicity in terms of ingredients
- It works very nicely for a wide range of materials (as shown in the talk by P. Korzhavyi in the morning)
- It very versatile: Can be used with any method delivering total energy (at 0K) as function of volume

$$F_{vib} = \frac{9}{8} k_B \Theta_D - k_B T \left[D_3 \left(\frac{\Theta_D}{T} \right) - 3 \ln(1 - e^{-\frac{\Theta_D}{T}}) \right]$$

k_B … Boltzmann constant
Θ_D … Debye temperature
$D_3(z)$ … Debye-function

$$D_3(z) = \frac{3}{z^3} \int_0^z dx \frac{x^3}{e^x - 1}$$

Debye temperature at 0K: $\Theta_D(0K) \sim \left(\frac{V_0^{1/3} * B_0}{M} \right)^{1/2}$

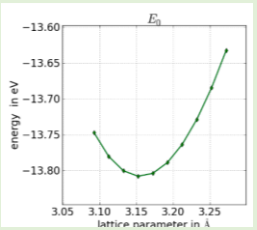
Debye temperature at finite T: $\Theta_D(T) = \Theta_D(0K) \left(\frac{V_0}{V(T)} \right)^{\gamma}$

Therodynanic Grüneisen parameter: $\gamma = -1 - \frac{V}{2} \frac{\partial^3 E / \partial V^3}{\partial^2 E / dV^2}$

B_0 ….. Bulk modulus at 0K
M ….. Atomic mass
V_0 …… volume 0K

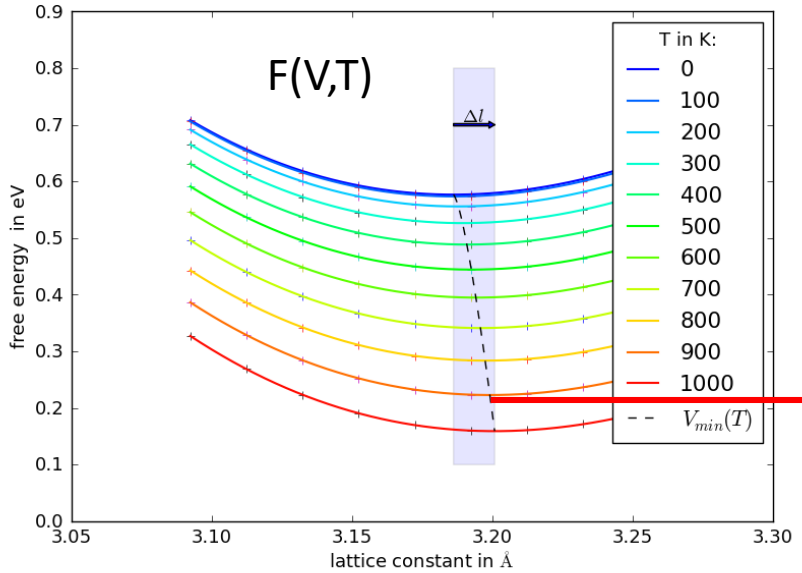
V ….. volume
E … total enegy

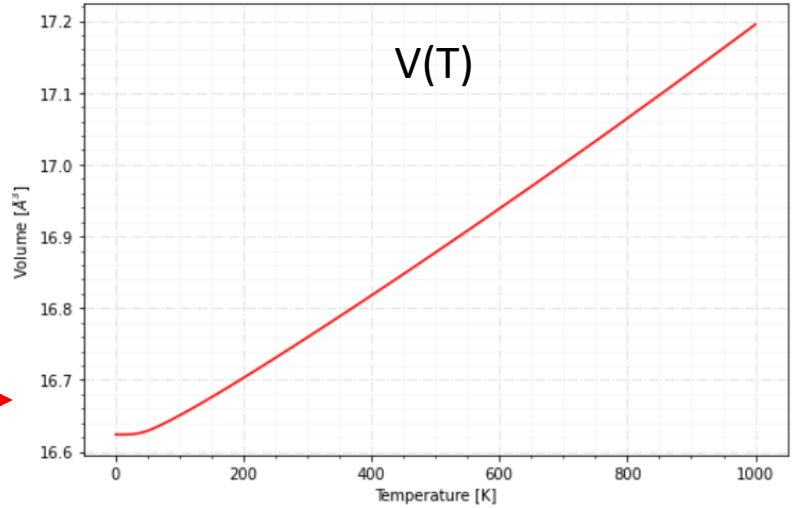
All input can be obtained from a simple equation of state

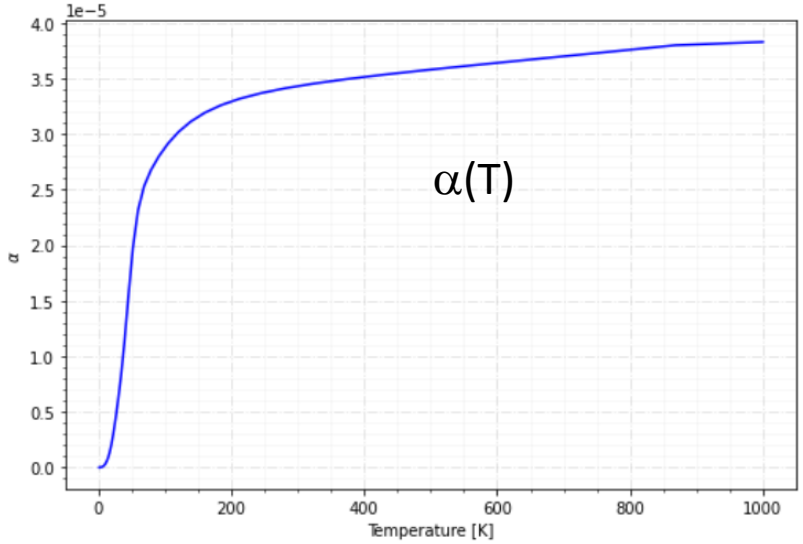


Moruzzi et al. 1988, https://doi.org/10.1103/PhysRevB.37.790
Korzhavyi et al. 1994, https://doi.org/10.1103/PhysRevB.49.14229
Dengg et al. 2017, https://doi.org/10.1103/PhysRevB.96.035148
Bodlos et al. 2021, https://doi.org/10.1103/PhysRevMaterials.5.043601

From F_{vib} to α



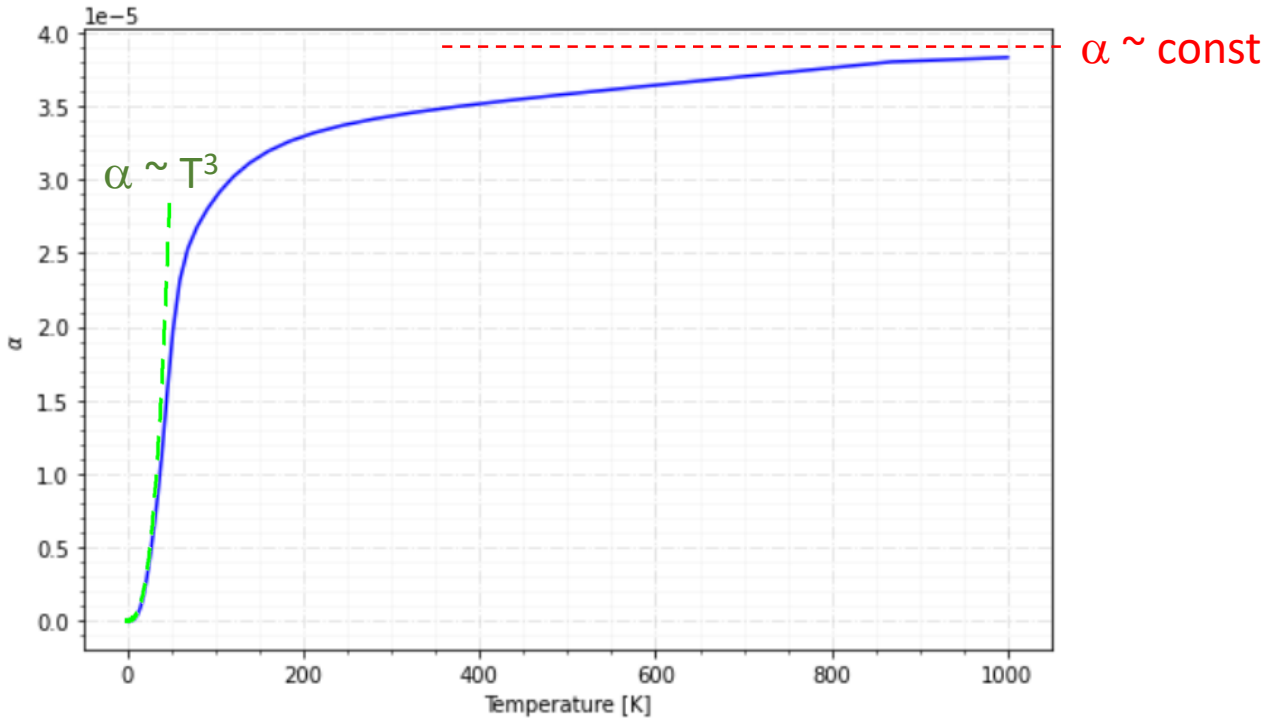




$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$$

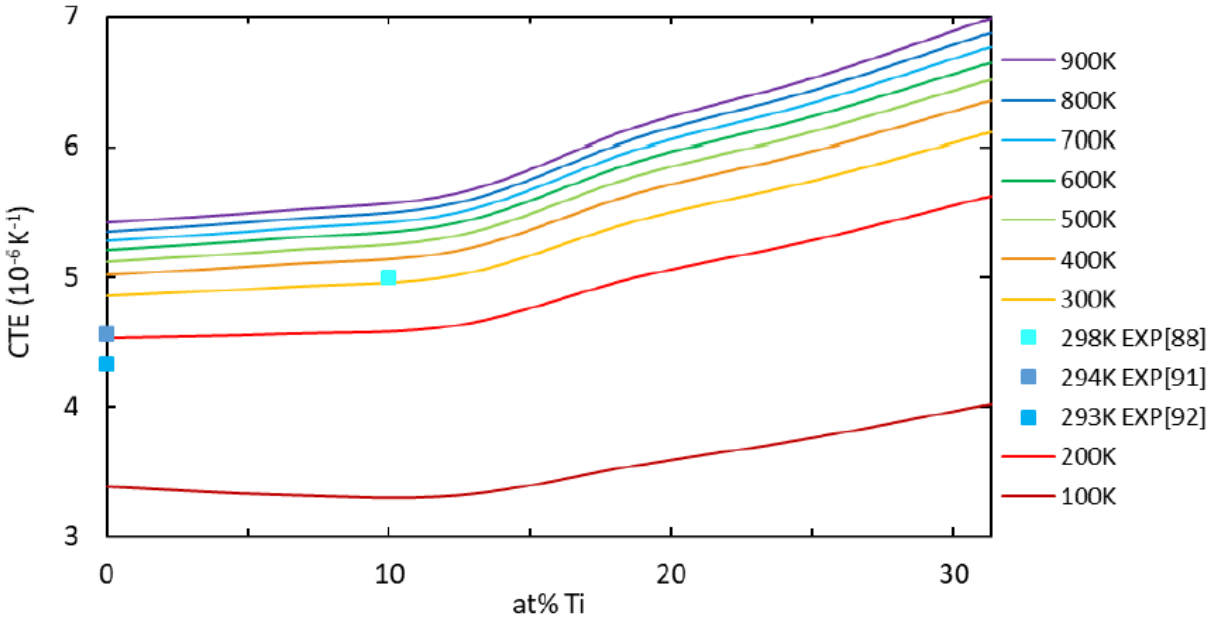
Thermal expansion … basic considerations

- The volumetric coefficient of thermal expansion is defined as $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$
- It is related to c_v (the specific heat at constant volume) and the bulk modulus as $\alpha = \frac{\gamma c_v}{B}$ (see e.g. Ashcroft-Mermin)
- In the two limits of very low and infinte temp
  - T → 0: $\alpha \sim T^3$
  - T → inf: $\alpha \sim$ const



Thermal expansion via QHA vs Debye … example of W-Ti

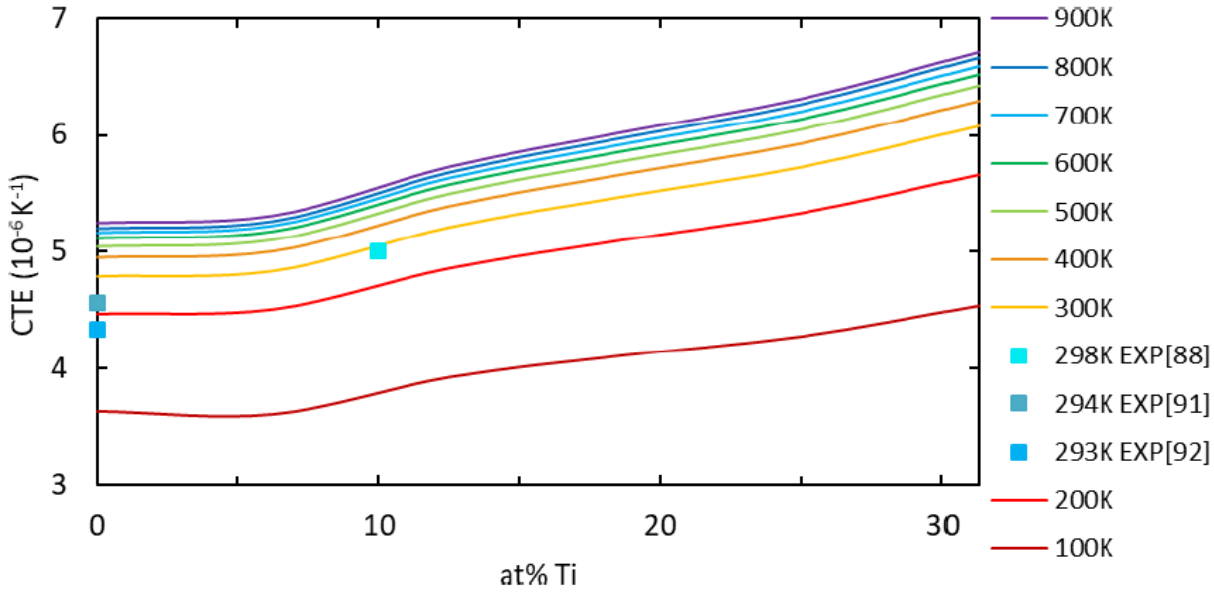
Explicit phonon calcs



- VASP + phonopy, 128-atom supercell
- For each volume and concentration:
  20-40 displacements per supercell

➔ Total of ~ **1000 calculations of 128-atom supercells**

Debye-Grüneisen model



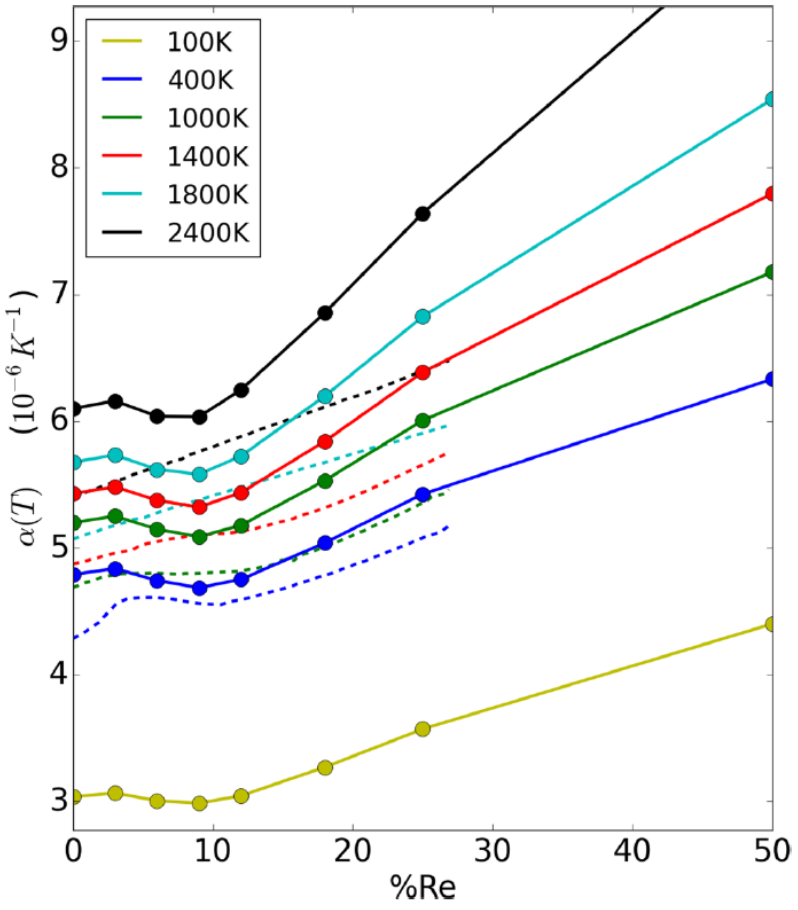
- VASP 16-atom supercell
- For each volume and concentration: 7 calculations

➔ Total of ~ **200 calculations of 16-atom supercells**

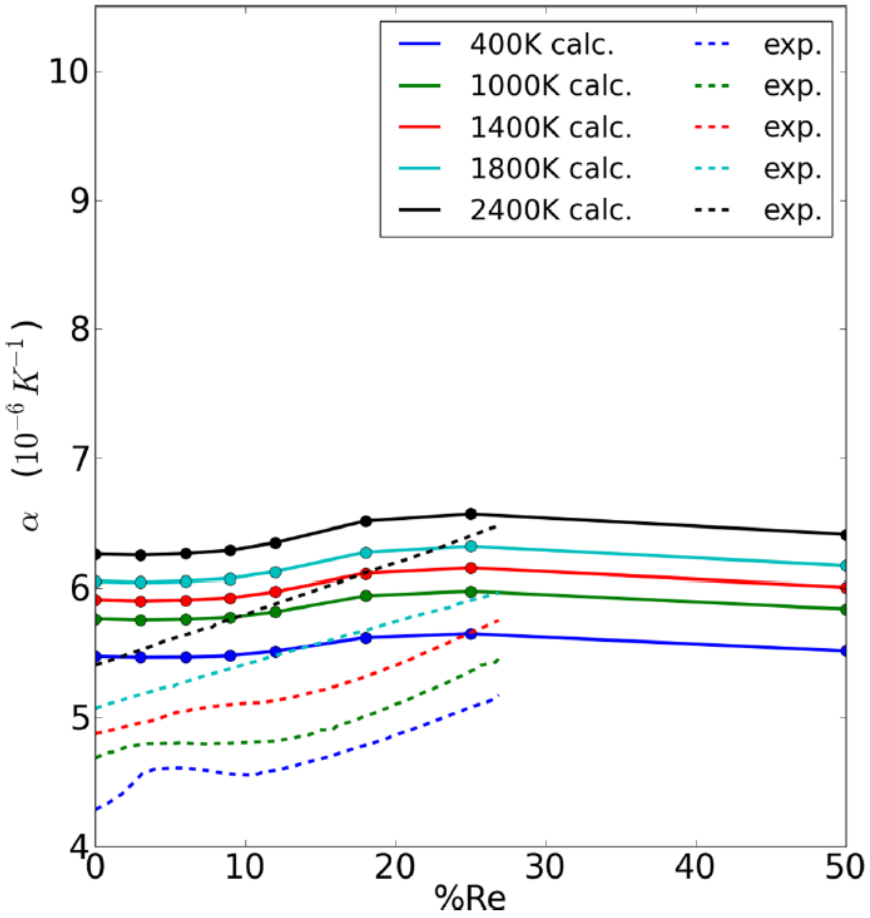
Bodlos et al. 2021 https://doi.org/10.1103/PhysRevMaterials.5.043601

Thermal expansion via QHA vs Debye … example of W-Re

Explicit phonon calcs



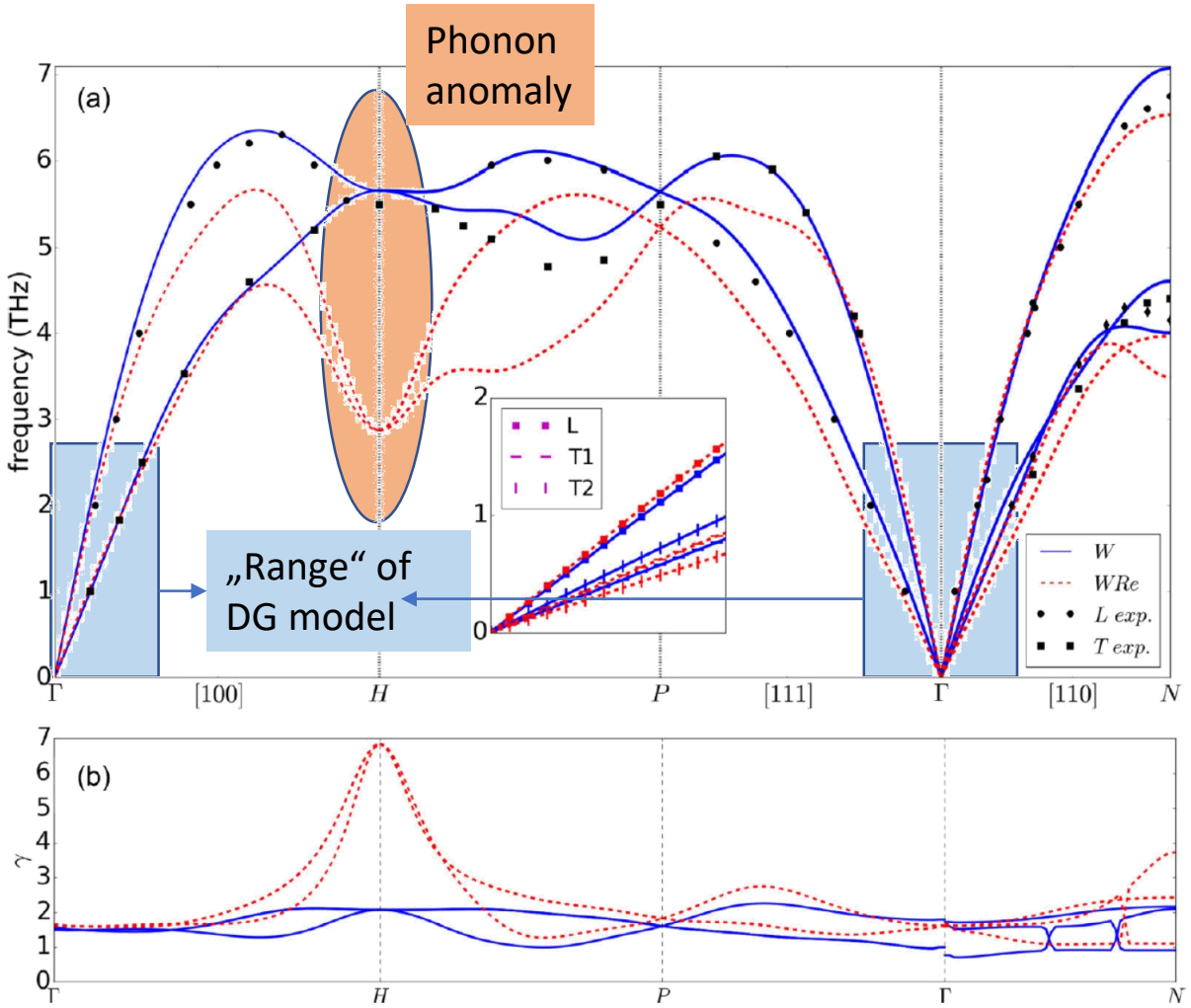
Debye-Grüneisen model

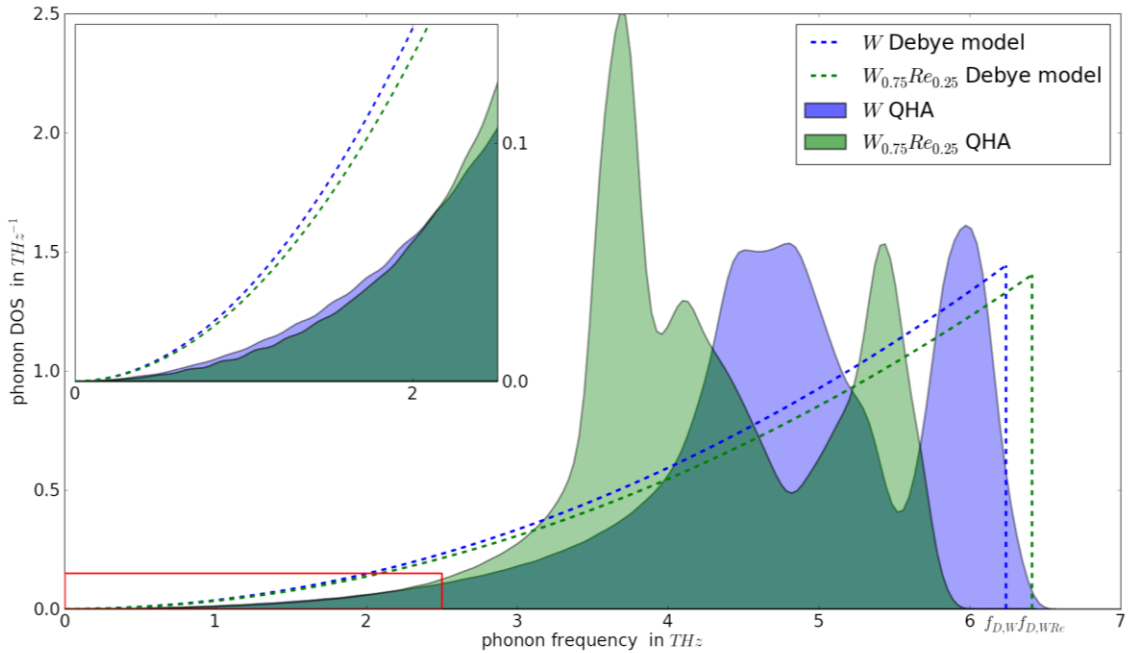


What's going on with the Debye-Grünesen model In W-Re?

Dengg et al. 2017 https://doi.org/10.1103/PhysRevB.96.035148

Thermal expansion via QHA vs Debye … example of W-Re





Dengg et al. 2017 https://doi.org/10.1103/PhysRevB.96.035148

Conclusions

- Thermal expansion is closely related to the phonons in a system
- The quasi-harmonic approximation is the „work-horse“ of calculating thermal expansion
- Debye-Grüneisen DG) model delivers vibrational free energy as function of volume just based on the equation of states
- DG model is versatile and can be combined with existing CPA implementations → perfect for random alloys
- DG model gives a very useful approximation in many cases
- Be careful in systems with phonon anomalies away from the Γ point