Café com Física

Pressure Induced Phase-Transition of β-As_2Te_3

26 de fevereiro 14h00
Sala de Conferências
do 3º andar

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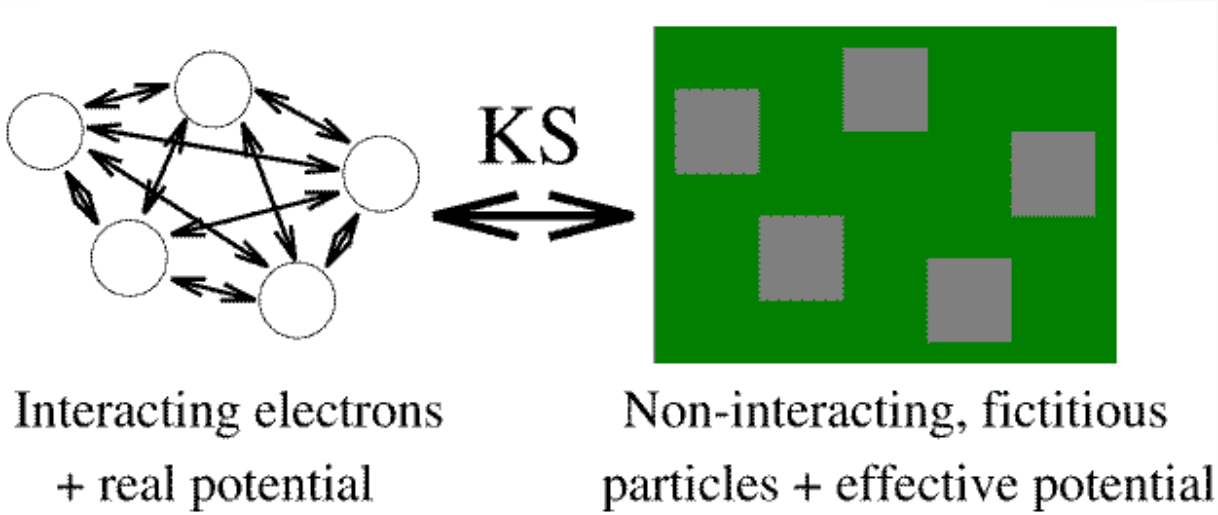
Ground-State Properties

Density Functional Theory



Kohn-Sham equations

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}[n(\mathbf{r})]\right]\varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

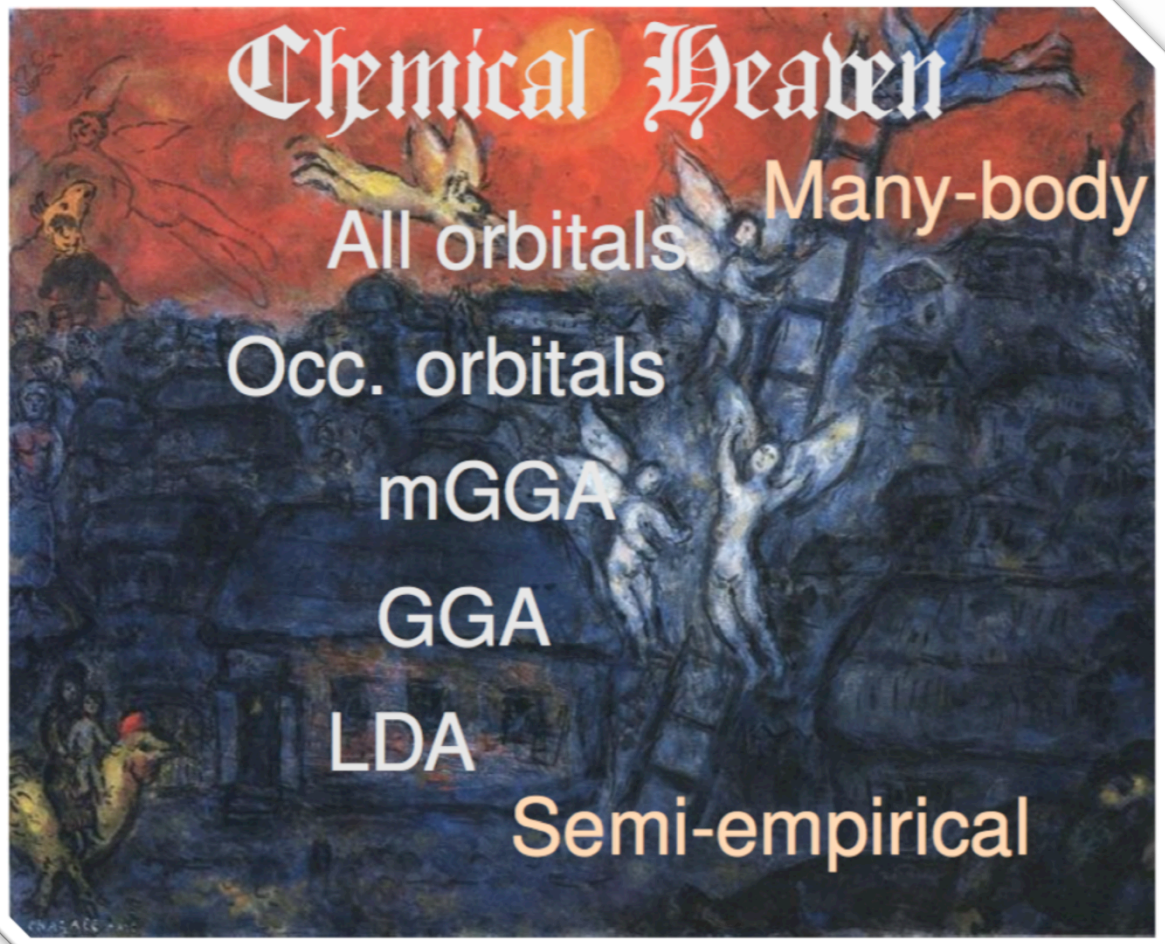
$$n(\mathbf{r}) = \sum_{i}^{occ} |\varphi_i(\mathbf{r})|^2$$

$$v_{\mathrm{KS}}[n(\mathbf{r})] = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}[n(\mathbf{r})] + v_{\mathrm{xc}}[n(\mathbf{r})]$$

$$v_{\mathrm{xc}}[n(\mathbf{r})] = \frac{\delta E_{\mathrm{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Ground-State Properties

Exchange-Correlation Functionals

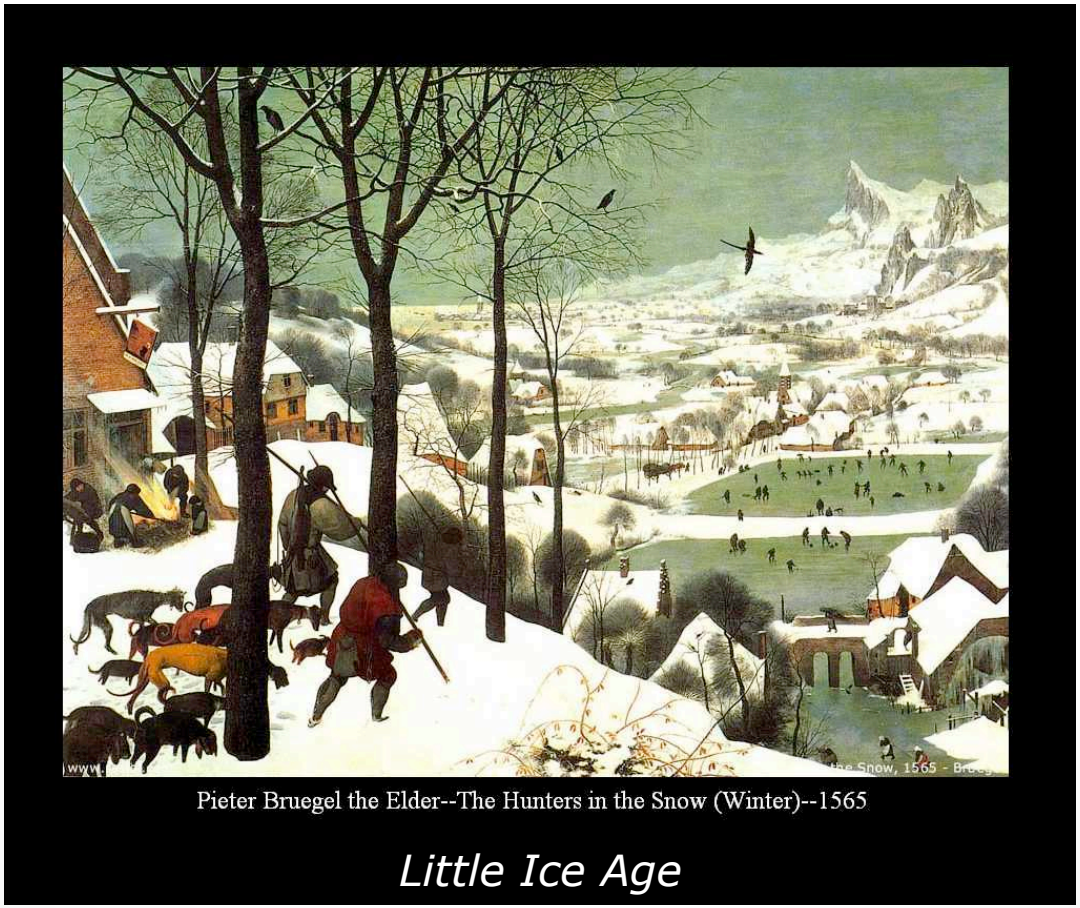


Marc Chagall – Jacob's dream

Lattice Dynamics

Systems perturbed by external stimuli

- Temperature
  - Phase transitions



Pieter Bruegel the Elder--The Hunters in the Snow (Winter)--1565

Little Ice Age

Lattice Dynamics

Mean energy of each vibrational mode, *v*

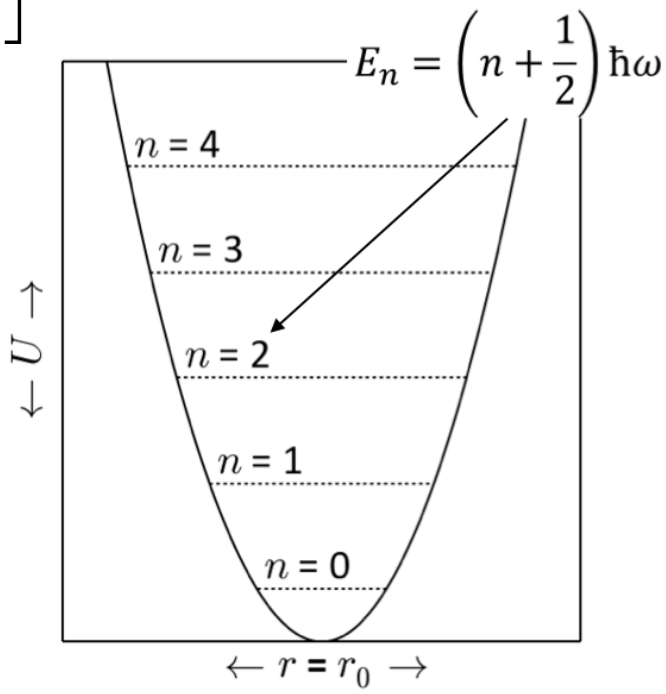
$$E(\vec{q},\nu) = \hbar\omega(\vec{q},\nu)\left[\frac{1}{2} + n(\vec{q},\nu)\right]$$

Bose-Einstein distribution

$$n(\vec{q},\nu) = n(\omega,T) = \left[\frac{1}{\exp\left(\hbar\omega(\vec{q},\nu)/k_B T\right) - 1}\right]$$

Phonons modelled as waves with an associated reciprocal-space wavevector ***q*** (3N modes/***q***-point)

- *3 acoustic modes ω ➔ 0 and **q** ➔ 0 (atoms move in-phase)*
- *3N-3 optical modes (atoms move out-of-phase)*



Harmonic Approximation

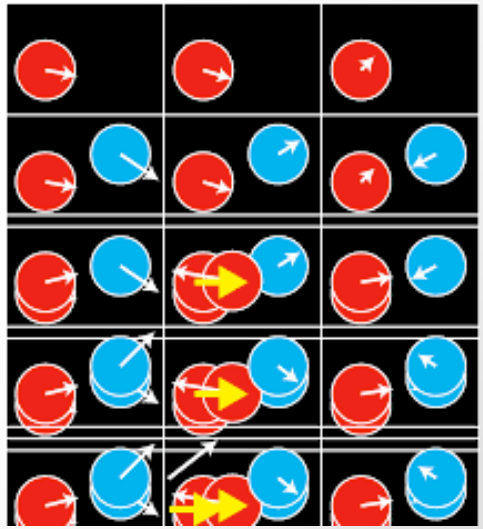
Potential Energy of a Phonon System

$$\phi = V_0 + \frac{1}{2} \sum_{\substack{j\,,\,j' \\ l\,,\,l'}} \frac{\partial^2 V}{\partial \mathbf{u}_{j,l} \partial \mathbf{u}_{j',l'}} \mathbf{u}_{j,l} \mathbf{u}_{j',l'} + \cdots$$

$$+ \frac{1}{n!} \sum_{\substack{j,\cdots,j^{(n)} \\ l,\cdots,l^{(n)}}} \frac{\partial^n V}{\partial \mathbf{u}_{j,l} \cdots \partial \mathbf{u}_{j^{(n)},l^{(n)}}} \mathbf{u}_{j,l} \cdots \mathbf{u}_{j^{(n)},l^{(n)}}$$

Harmonic phonon energy

$$E(q) = \sum_q \hbar\omega(q) \left[\frac{1}{2} + \frac{1}{\exp\left(\hbar\omega(q)/k_{\mathrm{B}}T\right) - 1} \right]$$



Harmonic Approximation

Helmoltz Free energy

$$F = -k_B T \ln Z$$

$$Z(T) = \exp\left(-\phi/k_B T\right) \prod_{\vec{q},\nu} \frac{\exp\left[-\hbar\omega(\vec{q},\nu)/2k_B T\right]}{1 - \exp\left[-\hbar\omega(\vec{q},\nu)/k_B T\right]}$$

$$F(V,T) = \phi + \frac{1}{2}\sum_{\vec{q},\nu} \hbar\omega(\vec{q},\nu) + k_B T \sum_{\vec{q},\nu} \ln\left[1 - \exp\left[-\hbar\omega(\vec{q},\nu/k_B T)\right]\right]$$

Harmonic Approximation

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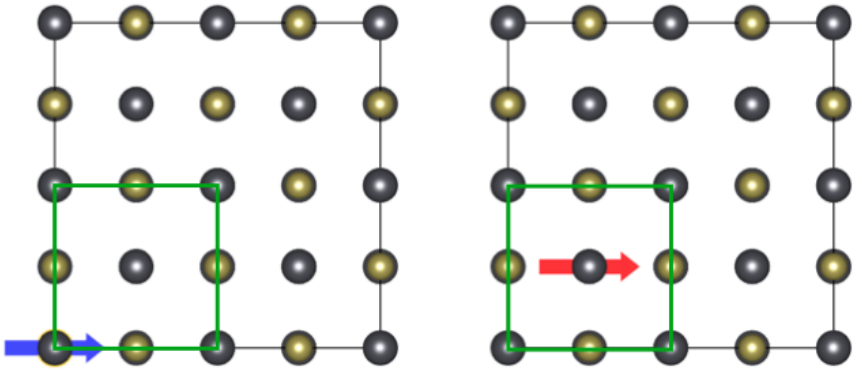
Lattice energy

Vibrational zero-point energy

Temperature dependence from phonon occupation

Harmonic Approximation

Phonon frequencies derived from the restoring force in response to ion displacements from equilibrium positions



Interactomic Force Constants (IFC)

$$\phi_{\alpha\beta}(jl,j'l') = \frac{\partial^2 V}{\partial u_\alpha(jl)\partial u_\beta(j'l')} = -\frac{\partial F_\beta(j'l')}{\partial u_\alpha(jl)}$$

- Density-Functional Perturbation Theory
- Finite displacement Parlinski-Li-Kawazoe supercell approach

  K. Parlinski *et al.*, Phys. Rev. Lett. 78, 4063 (1997)
  L. Chaput *et al.*, Phys. Rev. B 84, 094302 (2001)

$$\phi_{\alpha\beta}(jl,j'l') \simeq -\frac{F_\beta(j'l';\Delta u_\alpha(jl)) - F_\beta(j'l')}{\Delta u_\alpha(jl)}$$

Lattice Thermal Conductivity

The *lattice thermal conductivity* arises from contributions by phonons of all frequencies (lattice vibrations).
It is also possible to estimate lattice thermal conductivity from lattice dynamics calculations alone, by considering higher order terms in the Taylor expansion:

- Relaxation times
- Anharmonic frequencies

Boltzmann transport equation

$$\frac{\partial f_{\mathbf{q}\lambda}}{\partial t}(\mathbf{r}) = \frac{\partial f_{\mathbf{q}\lambda}}{\partial t}(\mathbf{r})_{\mathrm{diff}} + \frac{\partial f_{\mathbf{q}\lambda}}{\partial t}(\mathbf{r})_{\mathrm{ext}} + \frac{\partial f_{\mathbf{q}\lambda}}{\partial t}(\mathbf{r})_{\mathrm{scatt}} = 0$$

Relaxation-time approximation

$$-\frac{\partial f_{\mathbf{q}\lambda}}{\partial t}(\mathbf{r})_{\mathrm{scatt}} = \frac{f_{\mathbf{q}\lambda} - f^0_{\mathbf{q}\lambda}}{\tau_{\mathbf{q}\lambda}}$$

Mode group velocity

$$f_{\mathbf{q}\lambda} - f^0_{\mathbf{q}\lambda} = -\upsilon_{\mathbf{q}\lambda} - \frac{\partial f^0_{\mathbf{q}\lambda}}{\partial T}\Delta T \tau_{\mathbf{q}\lambda}$$

Lattice Thermal Conductivity

From the group velocity and relaxation time, the lattice thermal conductivity tensor can be obtained from a summation over modes:

$$\kappa = \sum_{\mathbf{q}\lambda} \omega_{\mathbf{q}\lambda} \frac{\partial f^0_{\mathbf{q}\lambda}}{\partial T} v_{\mathbf{q}\lambda} \otimes v_{\mathbf{q}\lambda} \tau_{\mathbf{q}\lambda} = \sum_{\mathbf{q}\lambda} C_{V,\mathbf{q}\lambda} v_{\mathbf{q}\lambda} \otimes v_{\mathbf{q}\lambda} \tau_{\mathbf{q}\lambda}$$

Phonon lifetimes $\tau_{\mathbf{q}\lambda} = \frac{1}{2\Gamma_{\mathbf{q}\lambda}}$

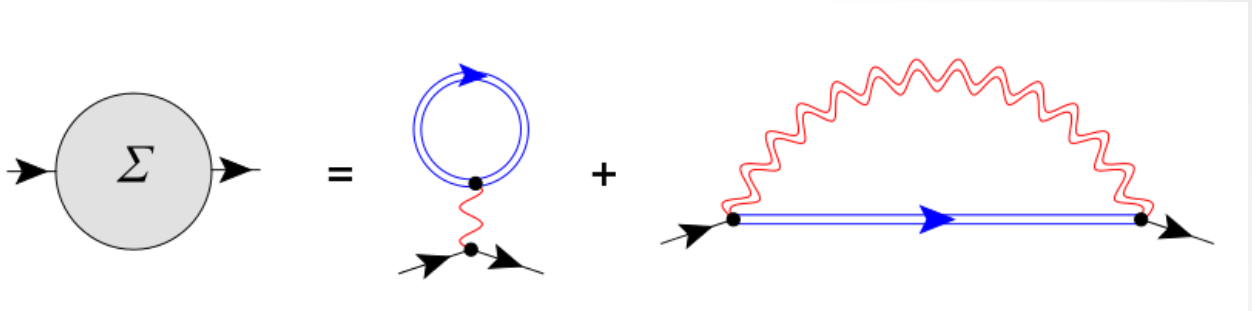
Regarding the RTA, it is worth noting that in bulk materials there may be other important scattering mechanisms, including those related to defects, the presence of different atomic isotopes, grain boundaries, etc. Moreover, the RTA only takes into account perturbations in phonon occupation numbers due to the temperature gradient for individual phonon modes, while assuming that all others maintain their equilibrium distribution. However, while neglecting the variation in occupation serves to reduce the thermal conductivity, not accounting for the effect of isotope scattering leads to an overestimation, and it is thought that these two approximations typically result ina fortuitous cancellation of errors, and so the RTA frequently gives values close to those observed experimentally.

Many-Body Perturbation Theory: *GW*

- Electron correlation: treating it as a small perturbation to the Hamiltonian of the system.
- MBPT can treat the many-body correlations as if these were composed by weakly interacting particles: quasiparticles and collective excitations. In order to calculate the properties of these particles one can resort to quantum field theoretical quantities such as Green's fucntions, also known as propogators.
- The conceptual tool of GW is the one-particle Green's function.
- Knowledge of the Green's function of a system provides the most important physical information such as the ground-state energy and other thermodynamic functions, the energy and lifetime of excited states, and linear response to external perturbations.

Many-Body Perturbation Theory: *GW*

$$\Sigma = iGW$$



In GW, the self-energy is given by the Hartree term, and the Fock term is supplemented by the screened Coulomb interaction, W, instead of the bare V. W is calculated within the RPA, in which the screening is given by the interaction with independent electron-hole pairs.
Feynman diagram: the interaction between two electrons is mediated via a virtual electron-hole pair (bubble) which causes a dynamical charge redistirbuition – electrons only perceive each other through a screened interaction.

The GW approximation is an approximation to the self-energy which attempts to account for the complicated correlation effects in a many-body system. The simplest approximation results from the expansion of the Hedin's equation, which stem from five coupled equations

Hedin's Equation

The Schwinger-Dyson equation, the screened interaction, the polarisation vector, the standard relations between irreducible and reducible vertex, and self-energy

The Schwinger-Dyson equation relating the self-energy to the Green's function

$$G(12) = G^0(12) + \int d[34]\, G^0(13)\Sigma(34)G(42)$$

Hedin's Equation

Screened interaction

$$W(12) = \int [d3]\ \epsilon^{-1}(13)V(32)$$

Related to the polarisation vector through the dielectric function

$$\epsilon(13) = \delta(13) - \int d[4]\ V(14)\Pi(43)$$

Inverse of the Green's function

$$\delta(13) = \int d[4]\ G(14)G^{-1}(43)$$

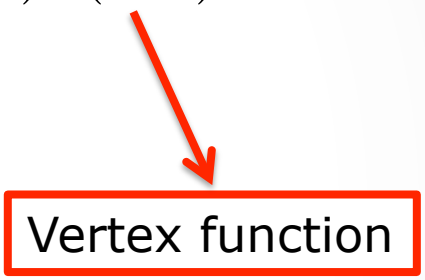
Dynamically screened interaction between electrons in a general medium

$$W(12) = V(12) + \int [d34]\ V(13)\Pi(34)W(42)$$

Hedin's Equation

The polarisation operator is the standard relation between two particle Green functions (response functions) and forms another of Hedin's equation

$$\Pi(12) = -i \int d[34]\; G(13)G(41)\Gamma(342)$$



Hedin's Equation

The polarisation operator is the standard relation between two particle Green functions (response functions) and forms another of Hedin's equation

$$\Pi(12) = -i \int d[34]\, G(13)G(41)\Gamma(342)$$

Vertex function

$$\Gamma(123) = \delta(12)\delta(13) + \int d[4567] \frac{\partial \Sigma(12)}{\partial G(45)} G(46)G(57)\Gamma(673)$$

a functional derivative of the Green's function

Hedin's Equation

Self-energy

$$\Gamma(123) = -\frac{\delta G^{-1}(12)}{\partial V(3)}$$

Simplest approximation: neglect the vertex corrections

$$\Pi(12) = -iG(12)G(21)$$

Self-energy reduces to

$$\Sigma(12) = -iG(12)W(12)$$

Thus obtaining the GW approximation

Quasiparticle Self-Consistent *GW*

The one-body Hamiltonian has the form

$$H^0 = -\frac{\nabla^2}{2m} + V^{\text{eff}}(\mathbf{r}_1, \mathbf{r}_2)$$

The potential is static and Hermitian and can be non-local

Although if $V^\textrm{eff}$ is generated by the Kohn-Sham relations it becomes local, such that

$$V^{\text{eff}}(\mathbf{r}_1, \mathbf{r}_2) = V^{\text{eff}}(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2)$$

Quasiparticle Self-Consistent *GW*

One-body Hamiltonian

$$H(\mathbf{r}_1, \mathbf{r}_2, \omega) = -\frac{\nabla^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}_1, \mathbf{r}_2) + V^{\mathrm{H}}(\mathbf{r}_1, \mathbf{r}_2) + \Sigma(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

Omega-dependent one-body effective potential

$$V^{\mathrm{GW}}(\mathbf{r}_1, \mathbf{r}_2, \omega) = V^{\mathrm{ext}}(\mathbf{r}_1, \mathbf{r}_2) + V^{\mathrm{H}}(\mathbf{r}_1, \mathbf{r}_2) + \Sigma(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

Perturbative correction to the one-particle potential

$$\Delta V(\mathbf{r}_1, \mathbf{r}_2, \omega) = V^{\mathrm{GW}}(\mathbf{r}_1, \mathbf{r}_2, \omega) - V^{\mathrm{eff}}(\mathbf{r}_1)$$

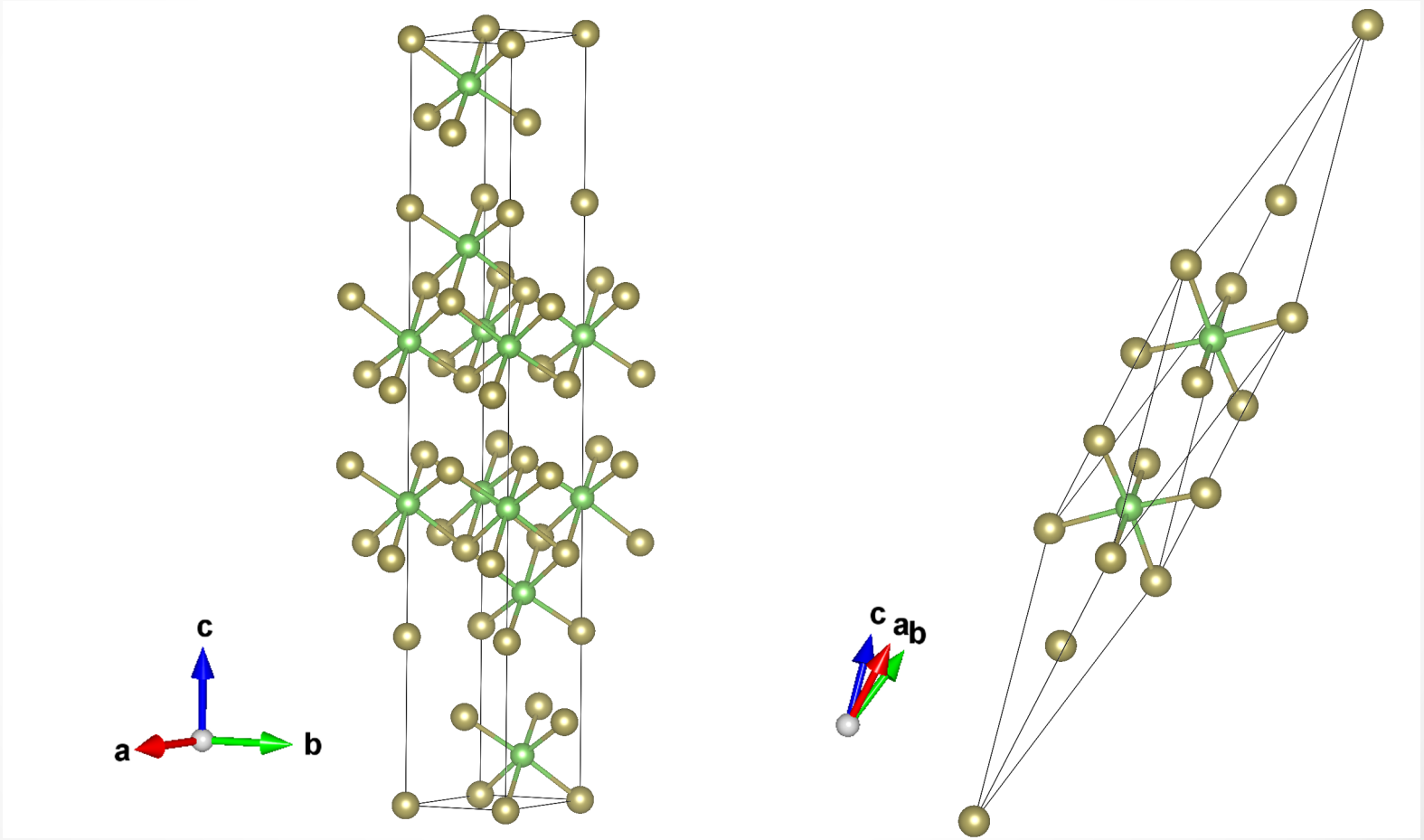
One-shot-GW: GW^0

- H^0 is generated by DFT (semi-)local functionals

Quasiparticle Self-Consistent *GW*

QSGW is an ab-initio method that determines the non-interacting Hamiltonian in a self-consistent manner and does not depend on the ground-state wavefunction

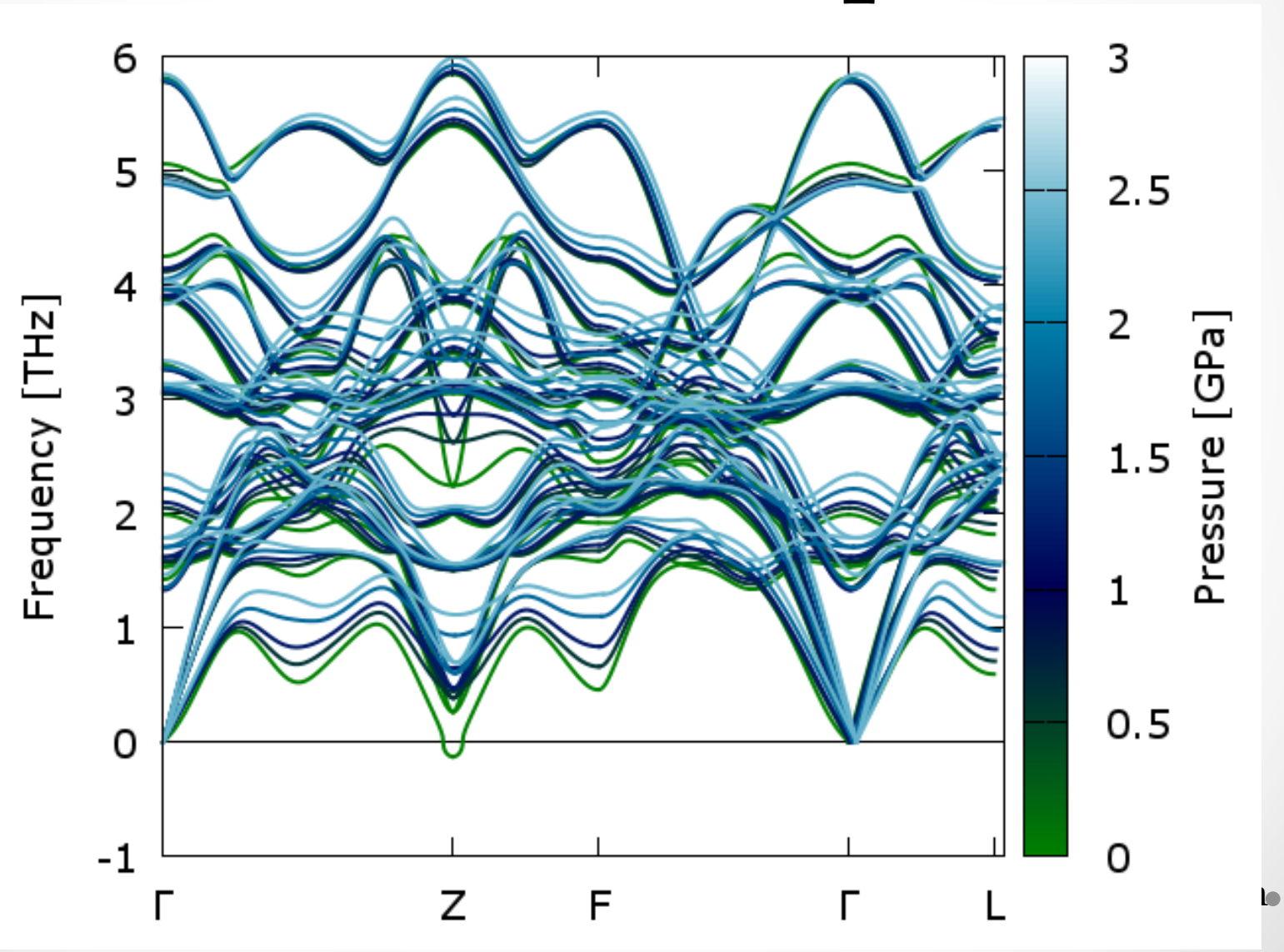
β-As_2Te_3
R-3m Space Group 166



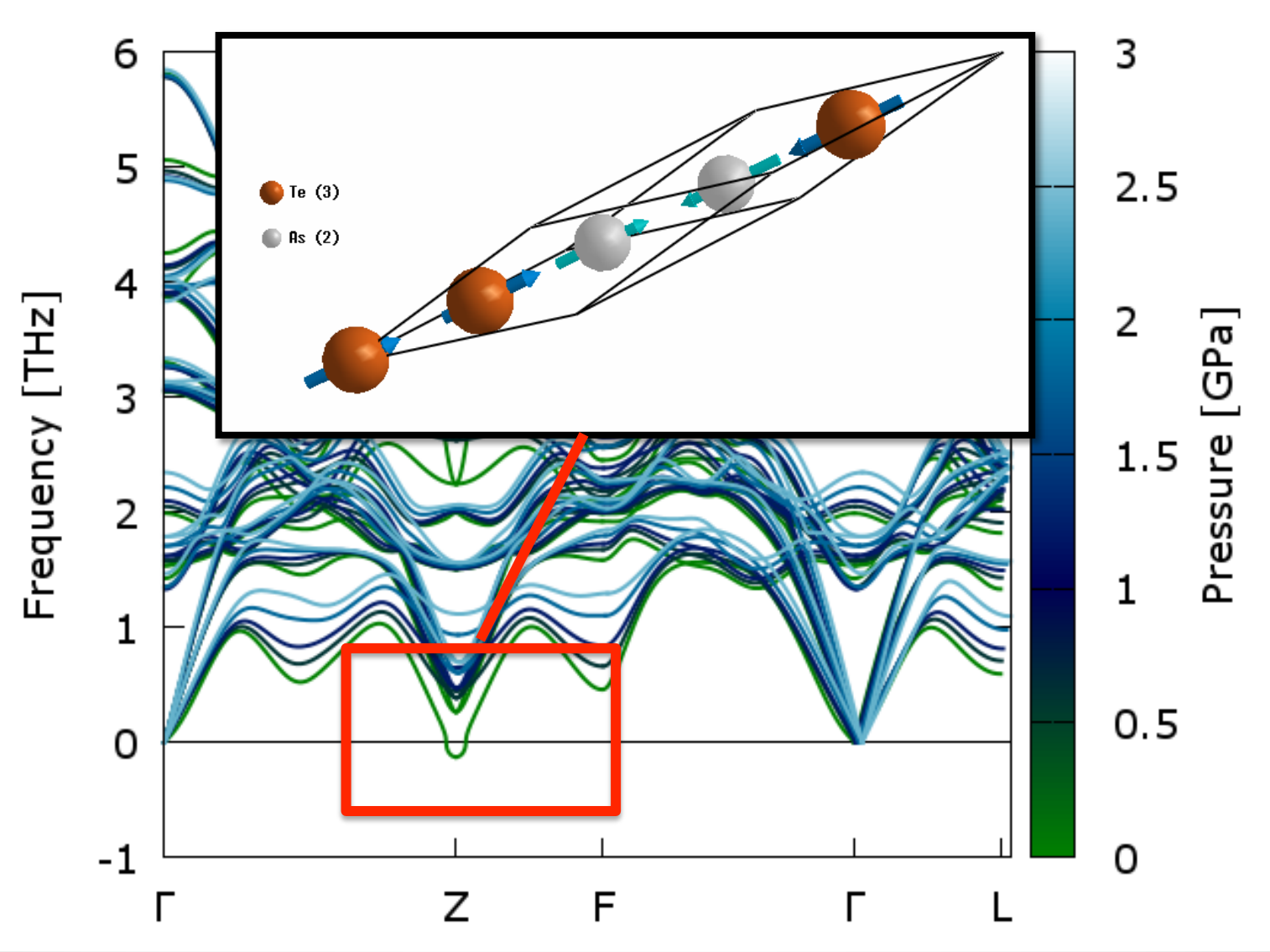
Unit-Cell
Hexagonal representation

Conventional-Cell
Rhombohedral representation

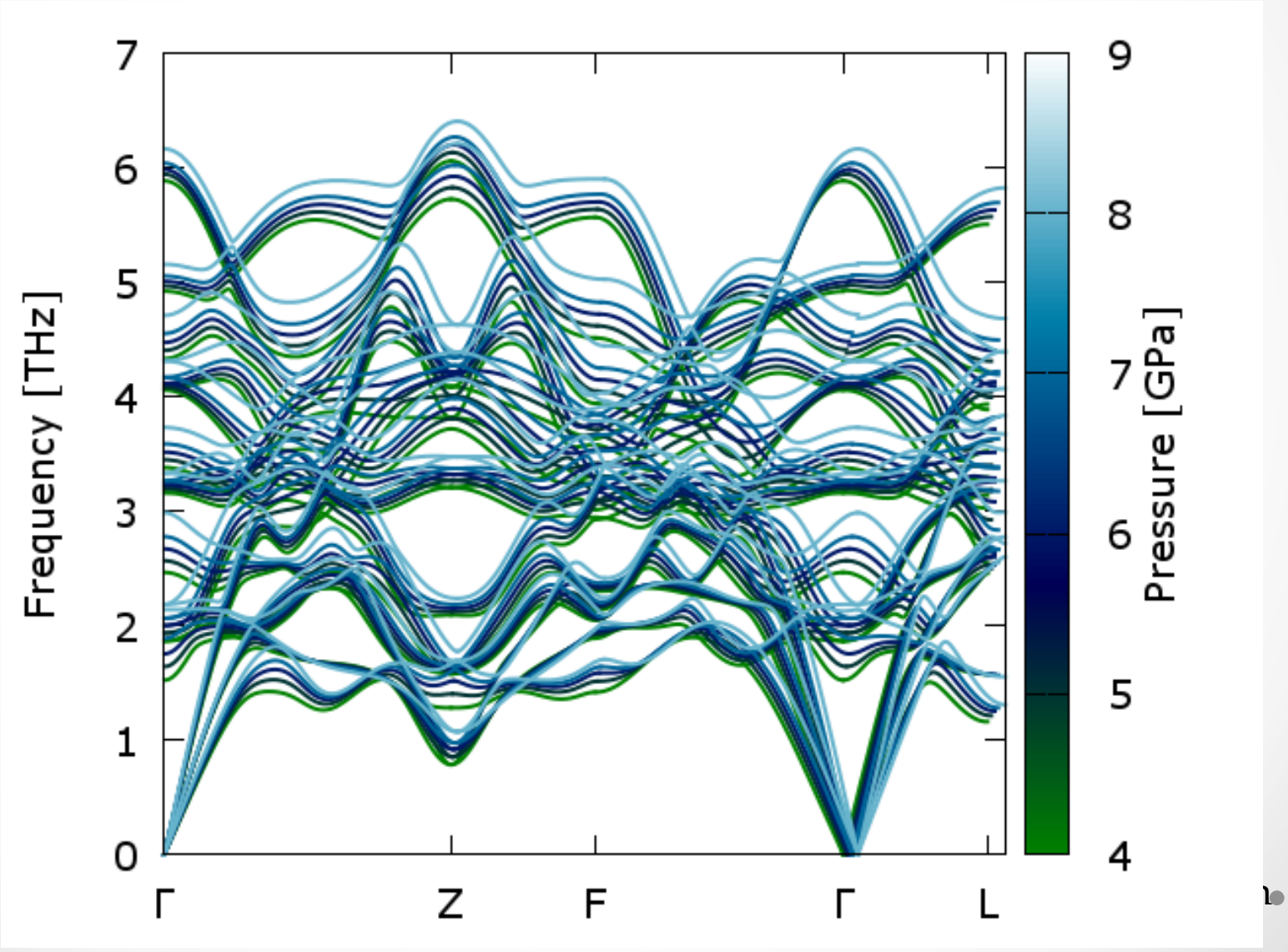
β-As_2Te_3 Phonon Band-Dispersion



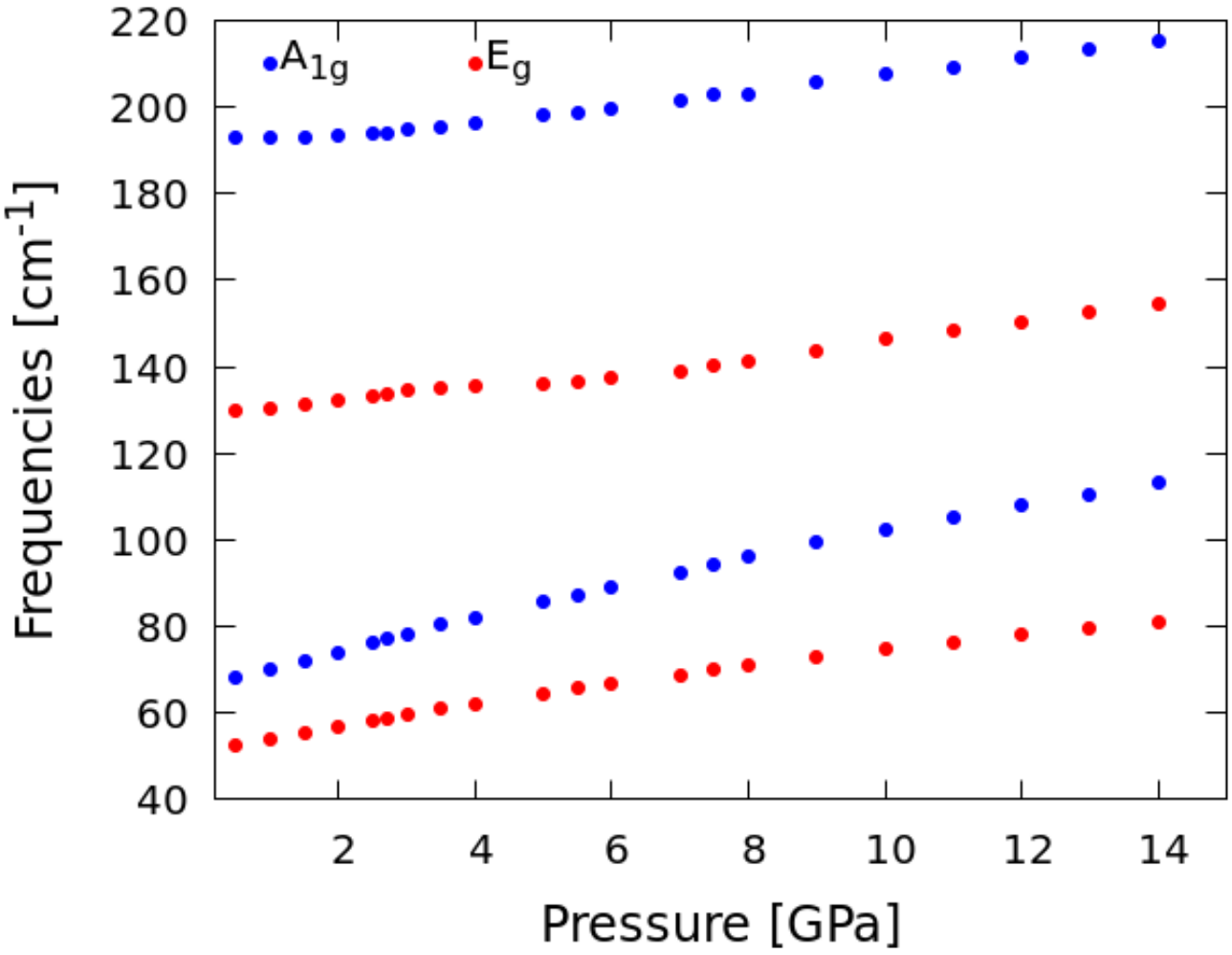
β-As_2Te_3 Phonon Band-Dispersion

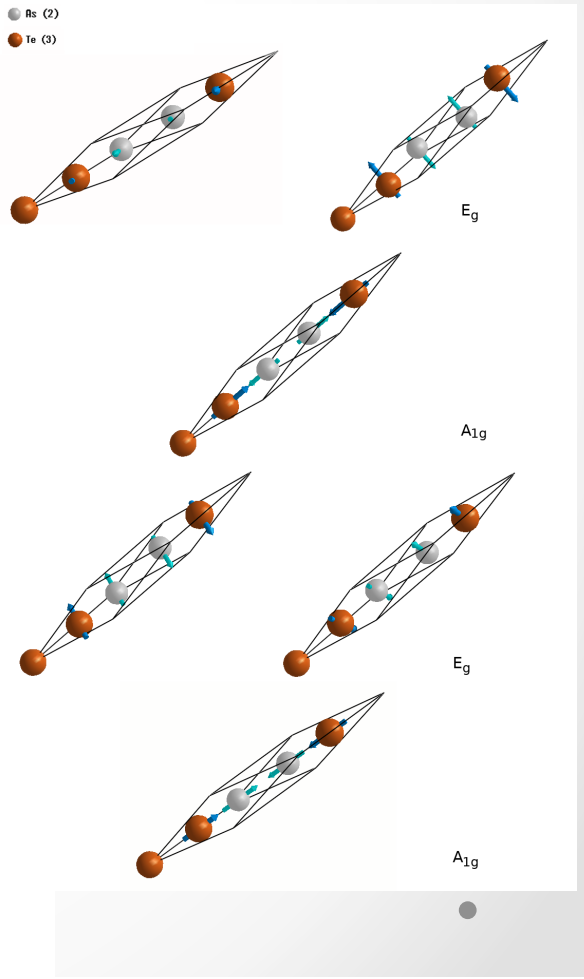


β-As_2Te_3 Phonon Band-Dispersion

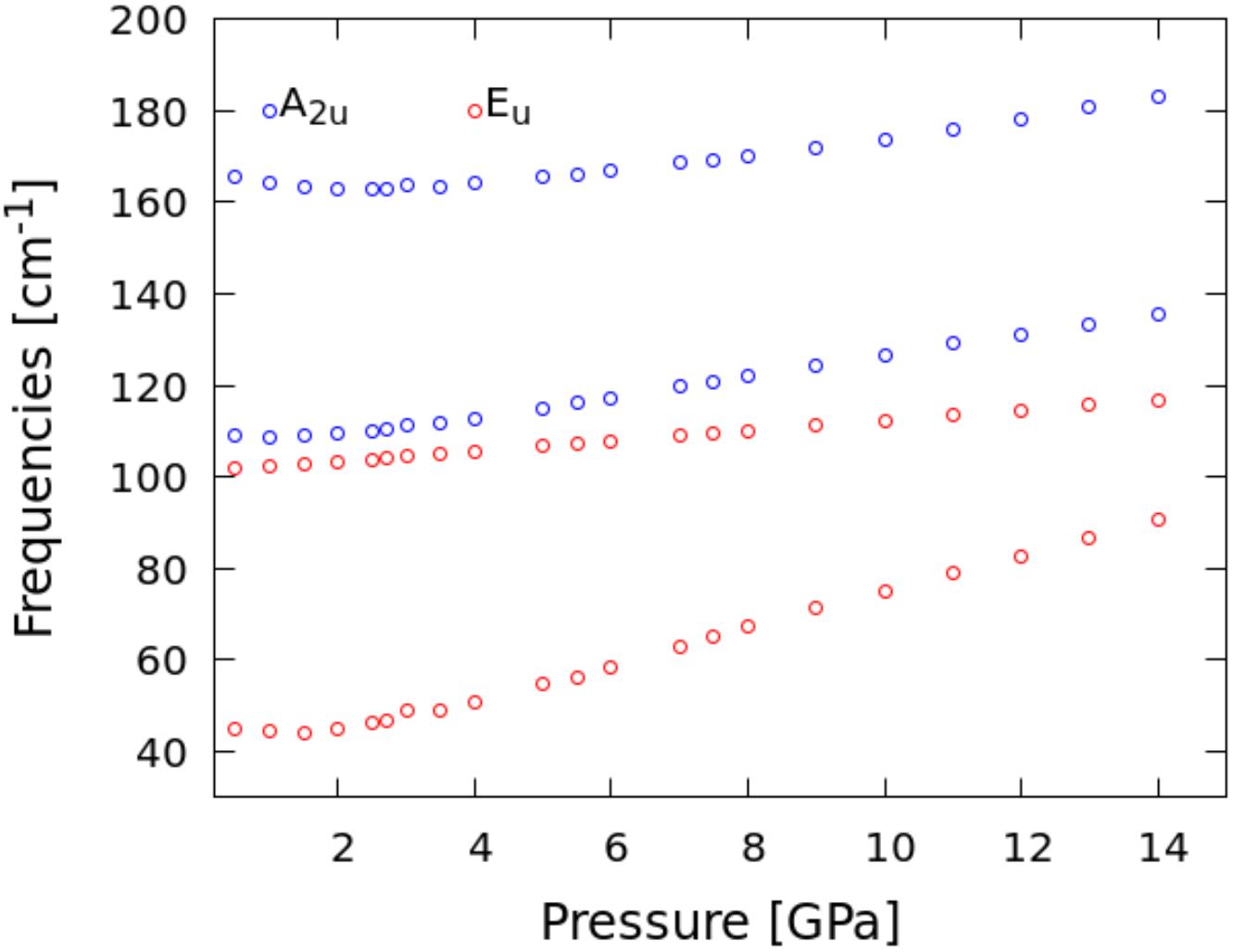


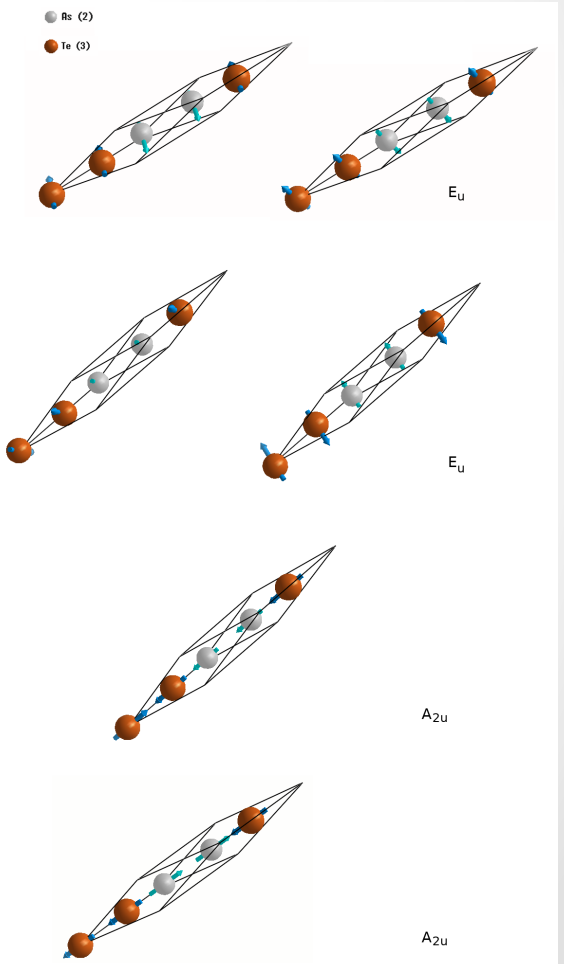
β-As_2Te_3 Raman Active Frequencies





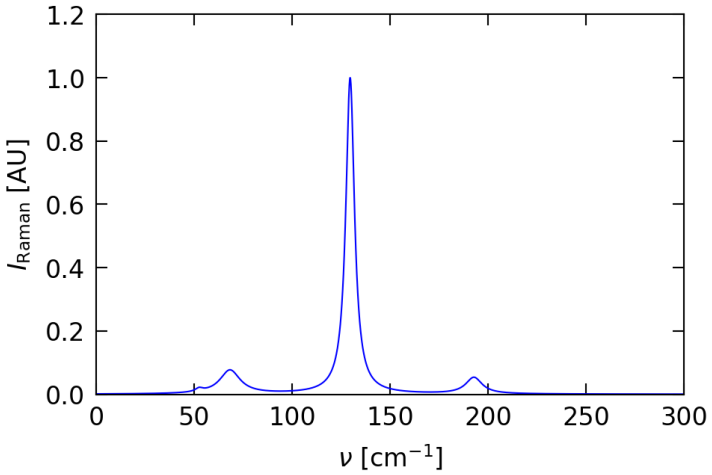
β-As_2Te_3 Infra-Red Active Frequencies

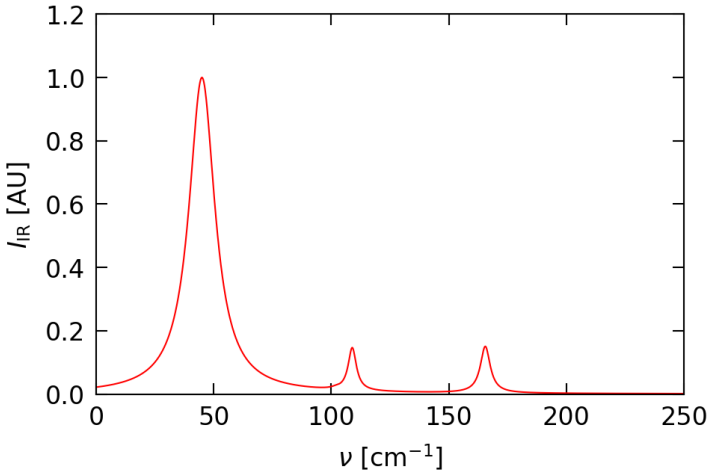




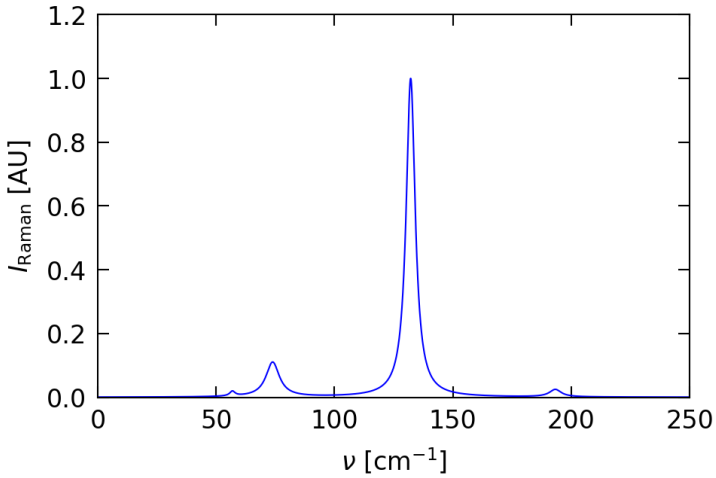
β-As2Te3
Raman and Infra-Red Spectra

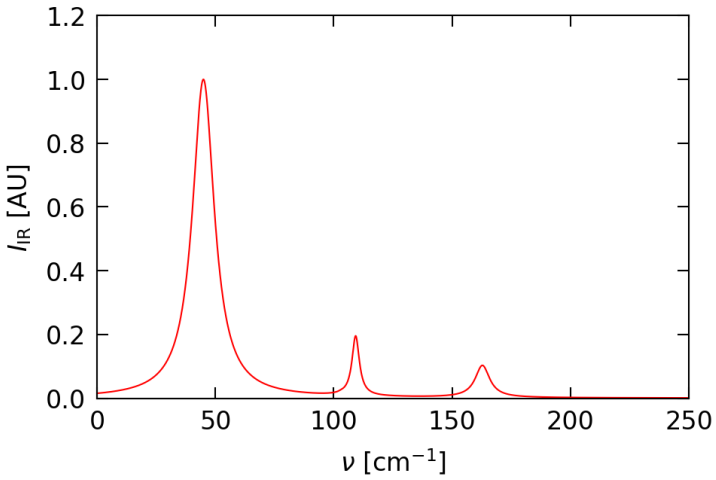
0.5 GPa





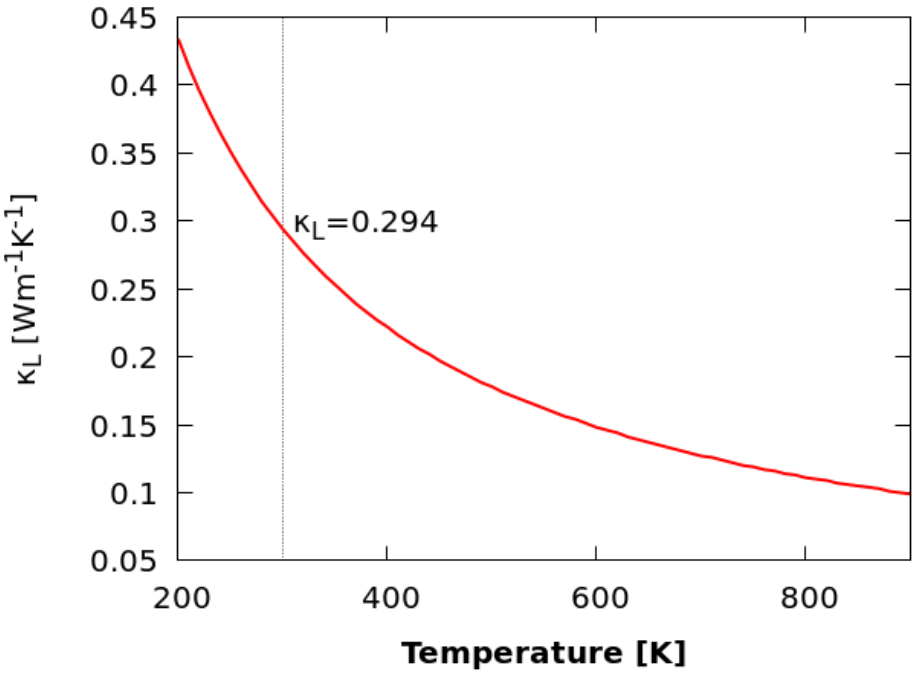
2.0 GPa



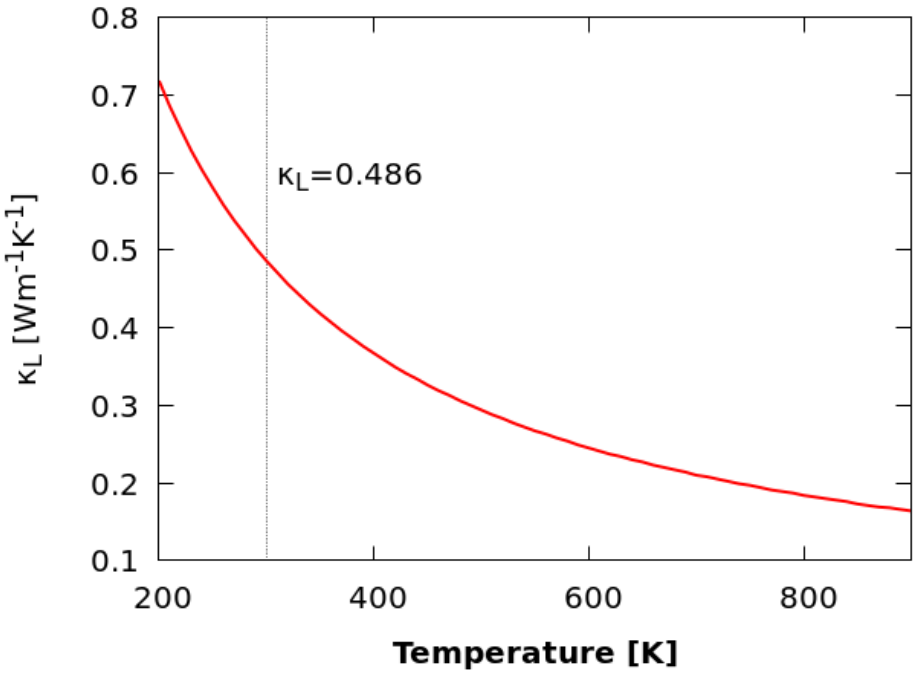


β-As2Te3
Lattice Thermal-Conductivity

0.5 GPa

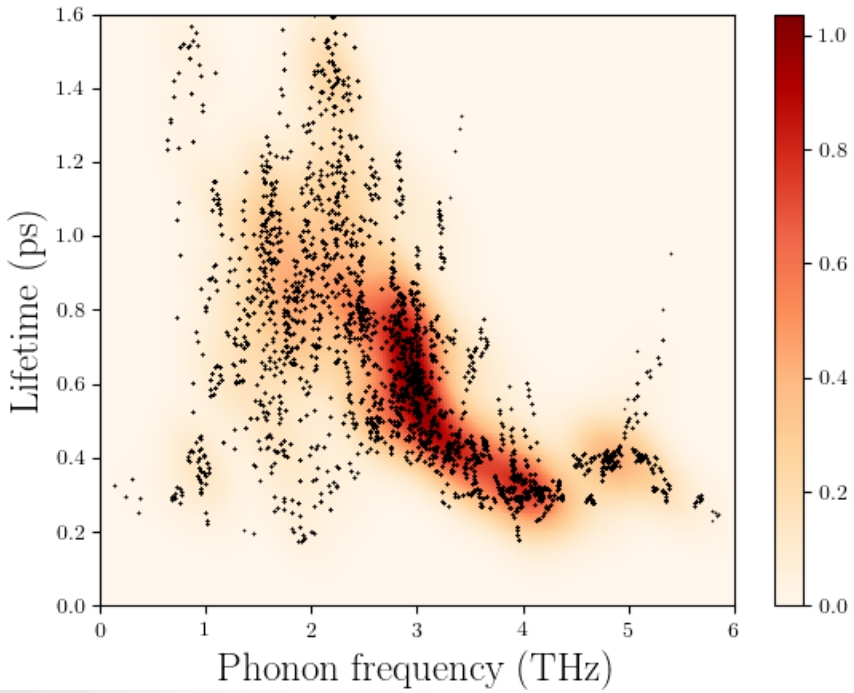


2.0 GPa

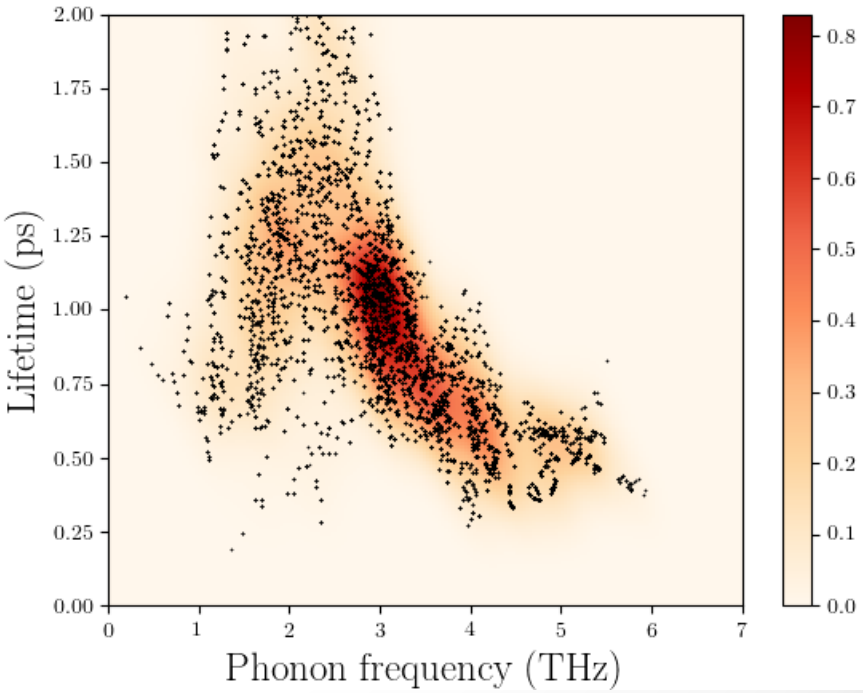


β-As2Te3
Phonon Lifetimes

0.5 GPa

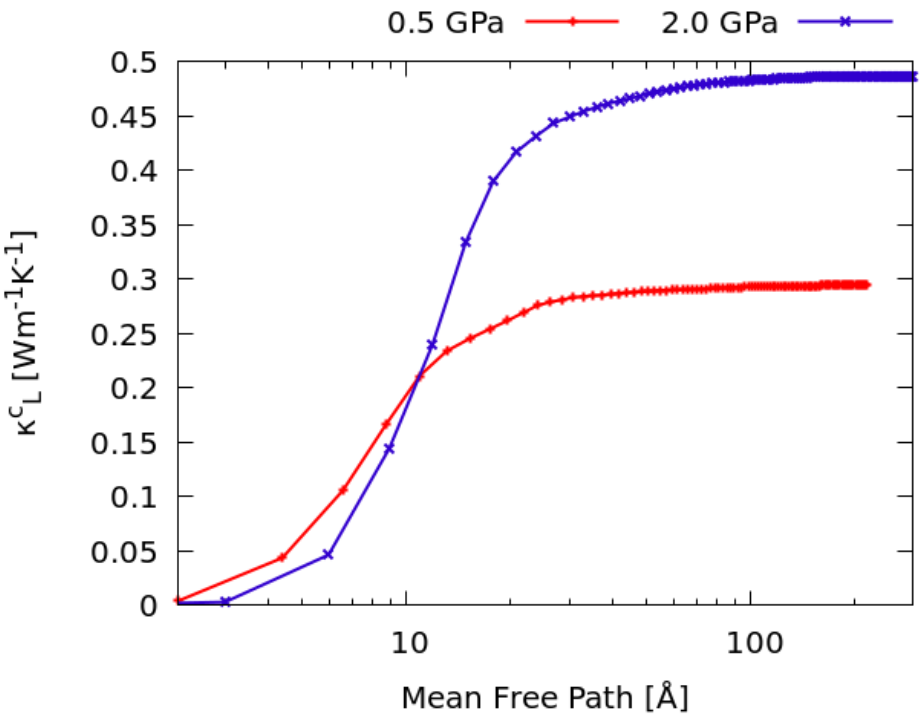


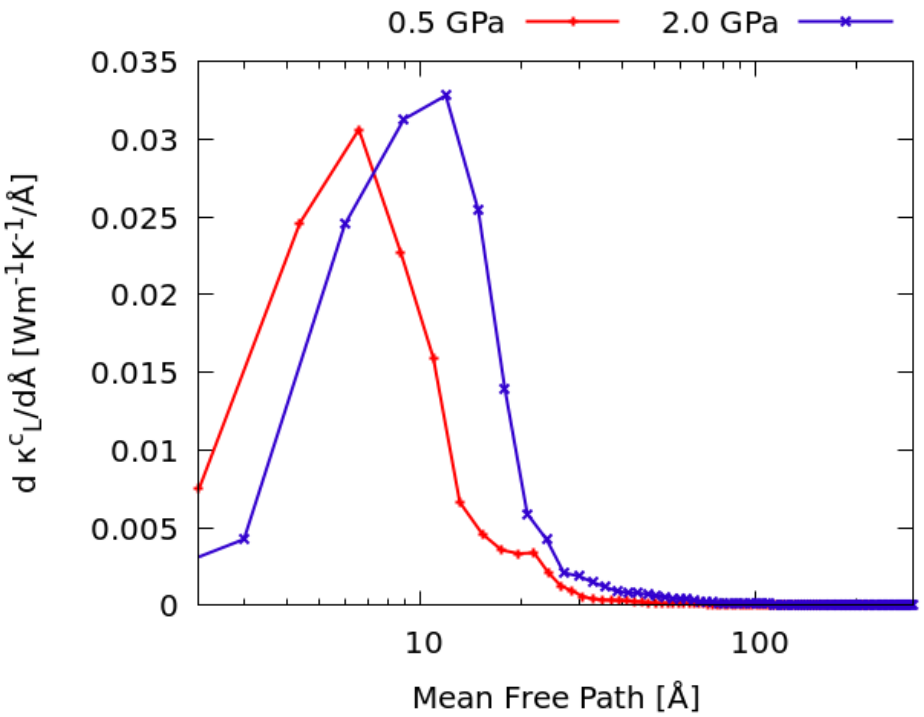
2.0 GPa



β-As_2Te_3

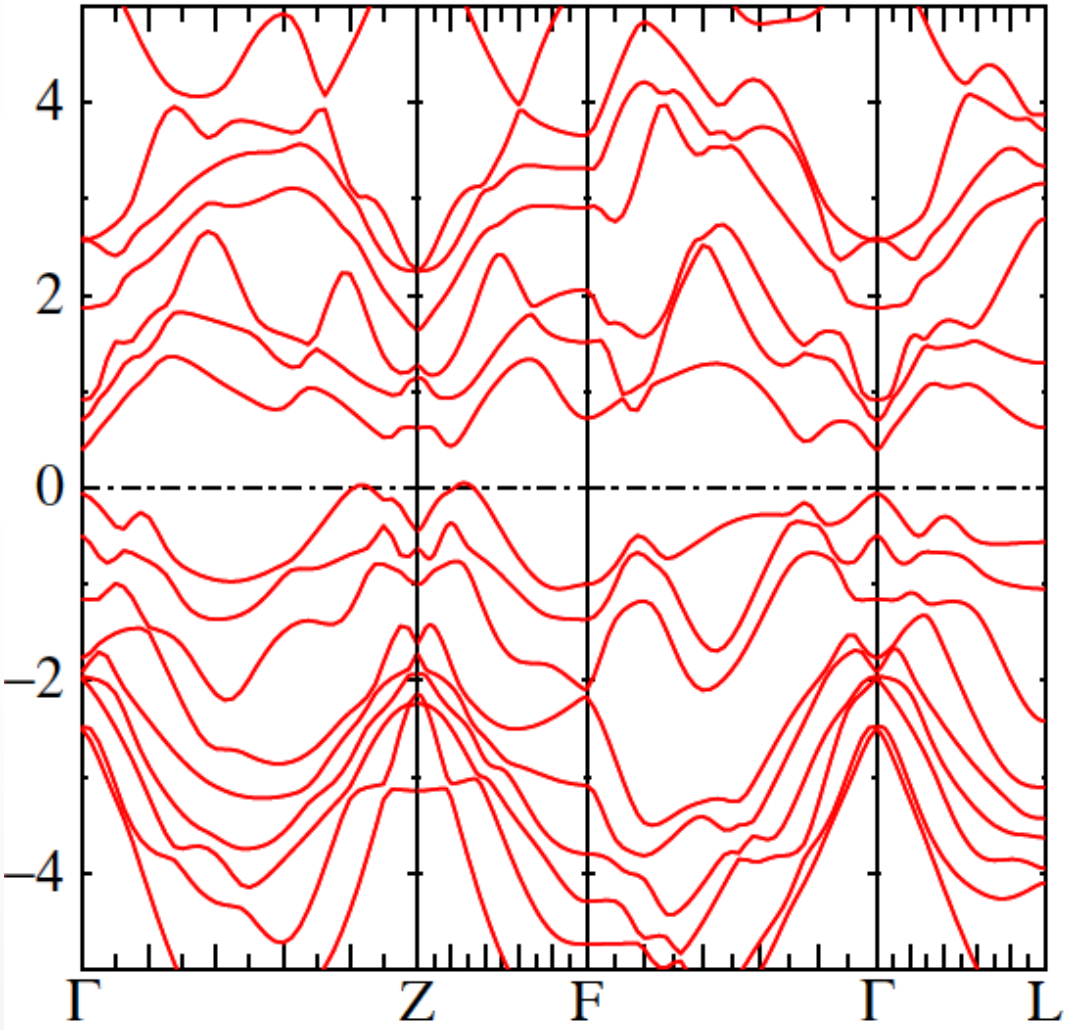
Cumulative physical properties with respect to mean free path





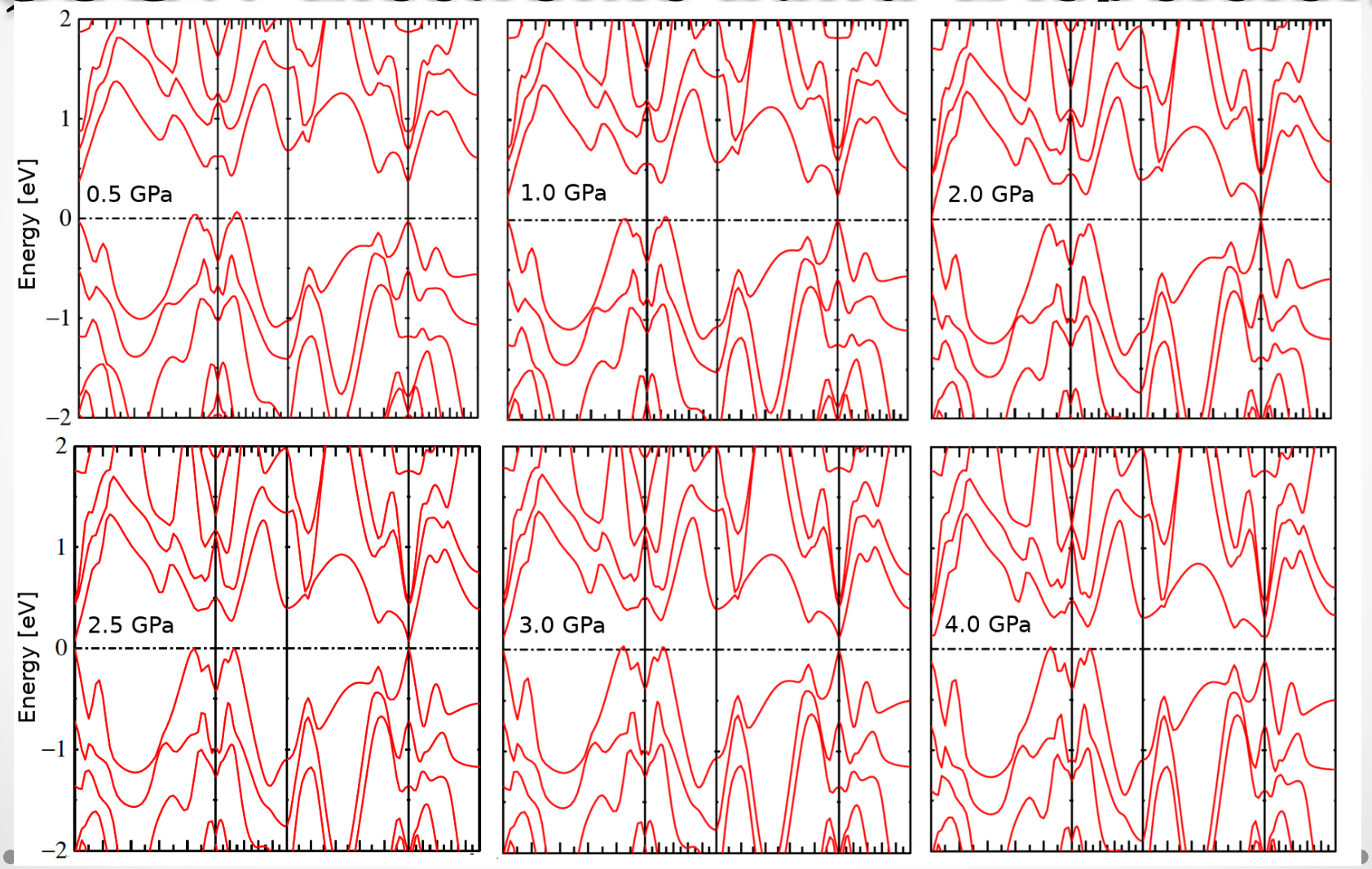
β-As2Te3

QSGW Electronic Band-Dispersion



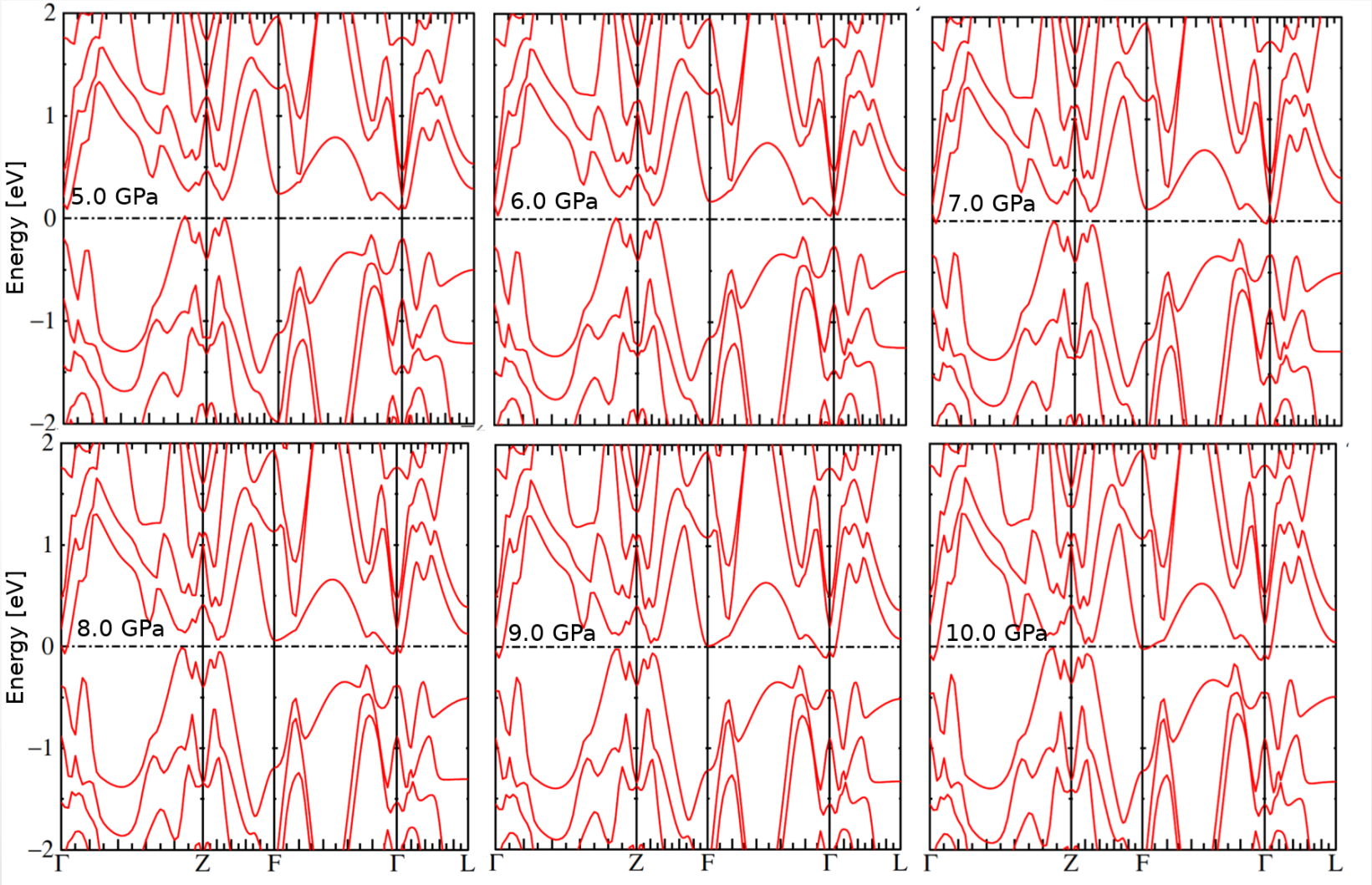
β-As2Te3

QSGW Electronic Band-Dispersion



β-As2Te3

QSGW Electronic Band-Dispersion



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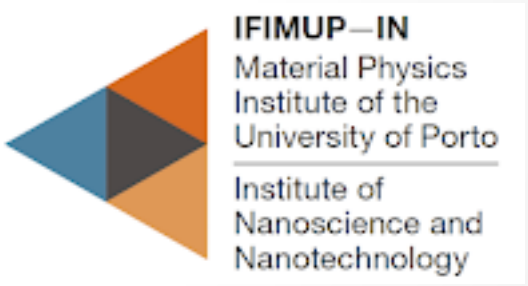
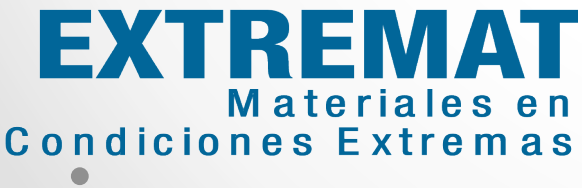
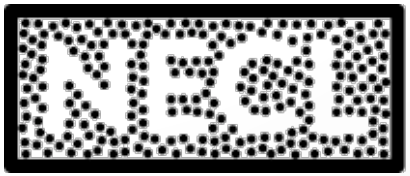
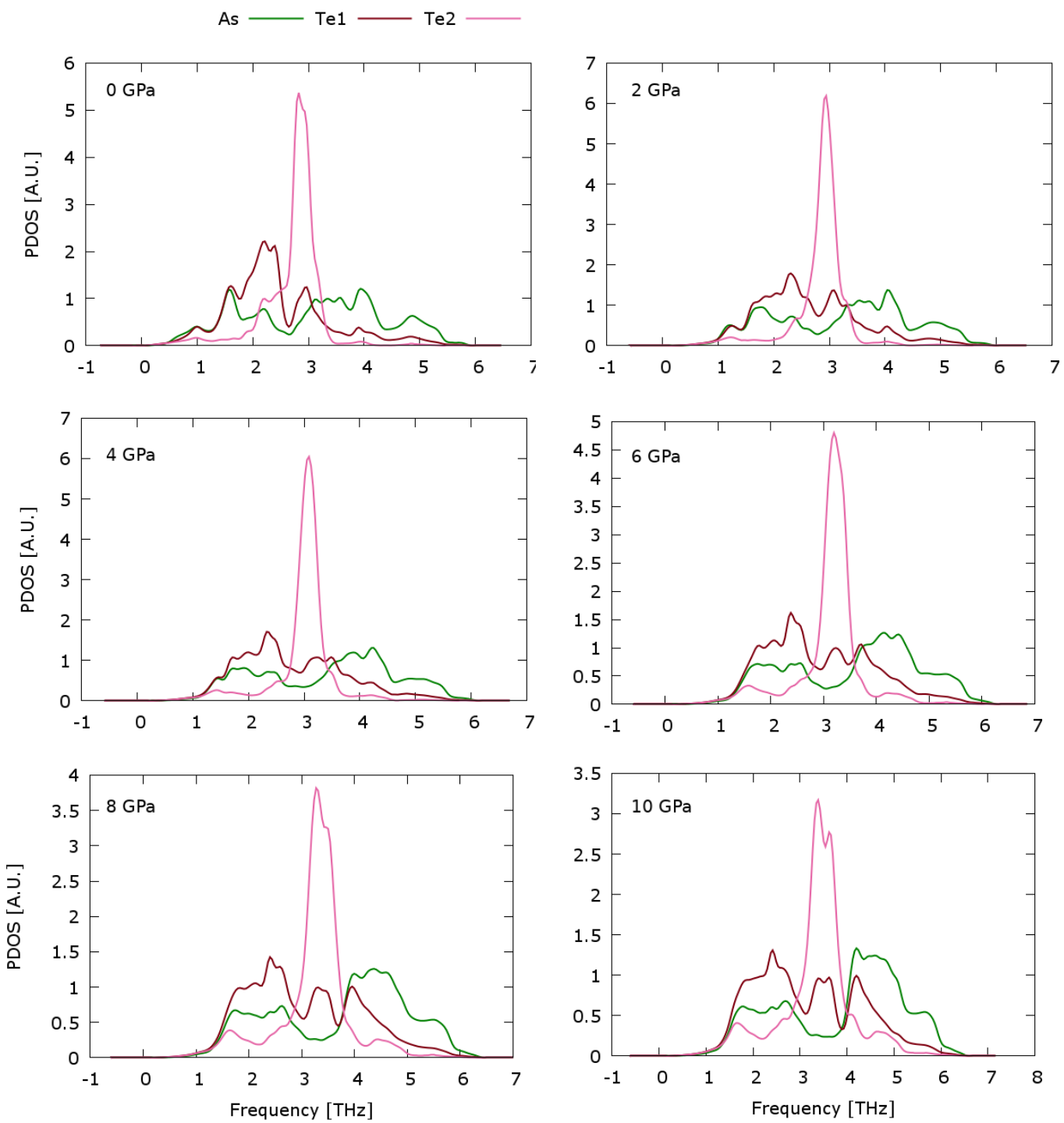







As
Te1
Te2
0 GPa
2 GPa
4 GPa
6 GPa
8 GPa
10 GPa
PDOS [A.U.]
Frequency [THz]

Quasi-Harmonic Approximation

Harmonic approximation

- Equilibrium distance between atoms is independent of temperature

Quasi-Harmonic Approximation (QHA)

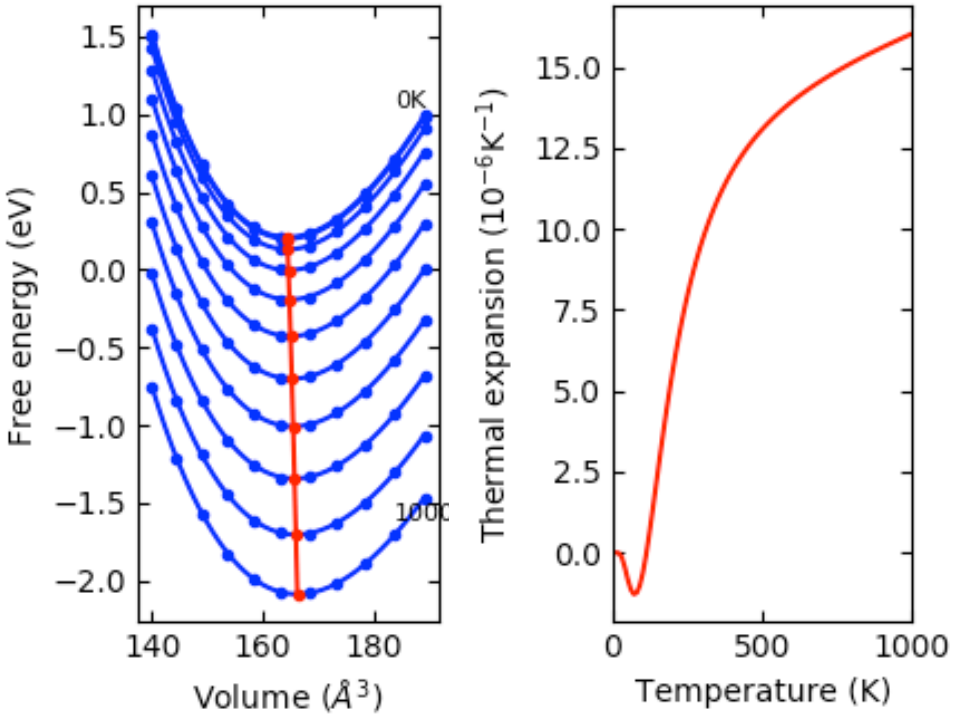
- Thermal expansion

  Volume dependence of phonon frequencies

Phonon frequencies computed for a range of expansions and compressions about the 0 K equilibrium volume

- *F(T)* evaluated as a function of temperature

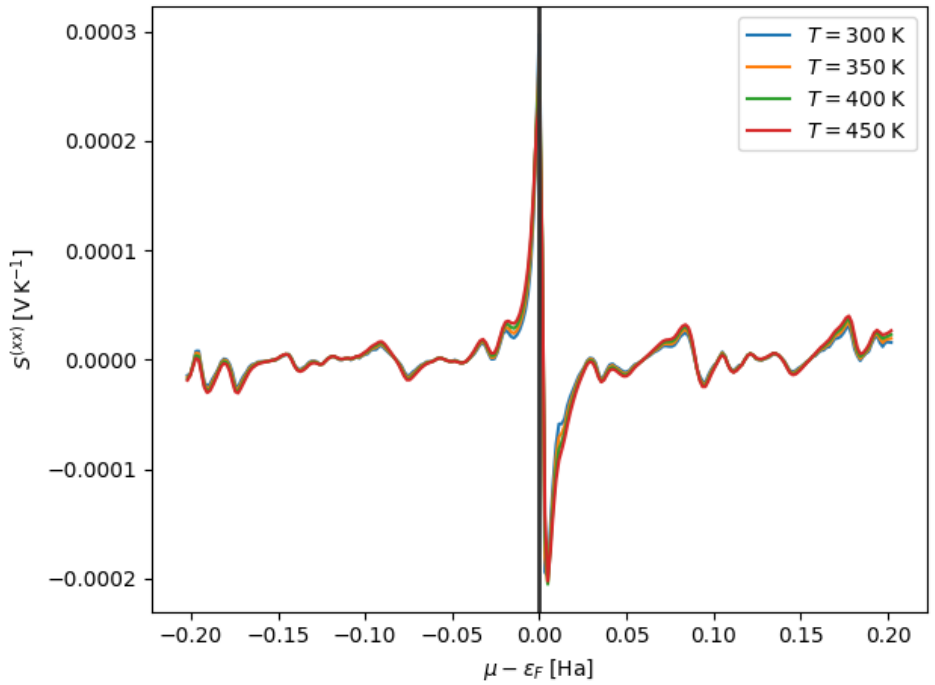
Valid only up to ~ 2/3 T_m



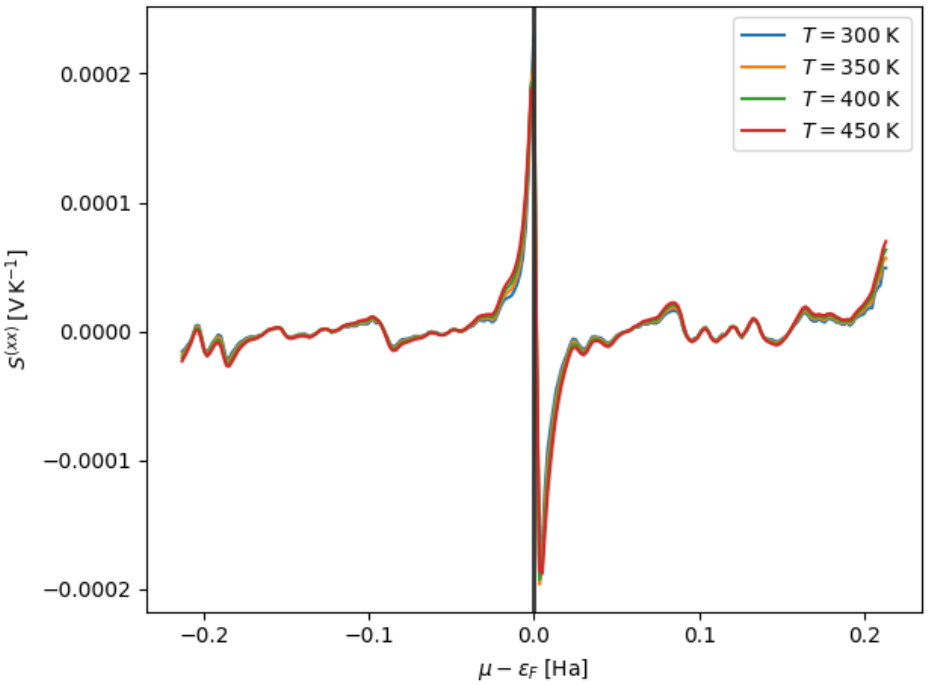
β-As_2Te_3

Seebeck Coeficcient

0.5 GPa



2.0 GPa



β-As_2Te_3

Phonon Band-Dispersion