

First-principles thermodynamic calculations in the harmonic and quasi-harmonic approximations using Quantum Espresso

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Outline

- Introduction

- The harmonic approximation
 - Basic principles
 - Equations of motions
 - Density Functional Perturbation Theory (DFPT) or Linear Response Method
 - Examples and limitations

- The Quasi Harmonic Approximation (QHA)
 - Basic principles
 - Examples

- The Quantum-Espresso code

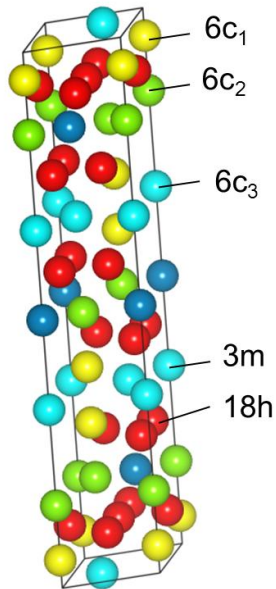
Introduction

We will consider **solids**...

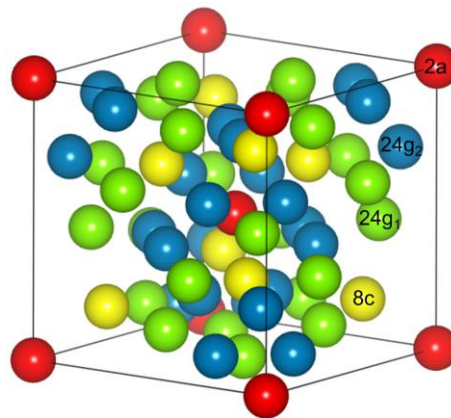
Most solids are **crystalline** (but not all! amorphous solids...)

Atoms are periodically distributed in a crystalline solid:

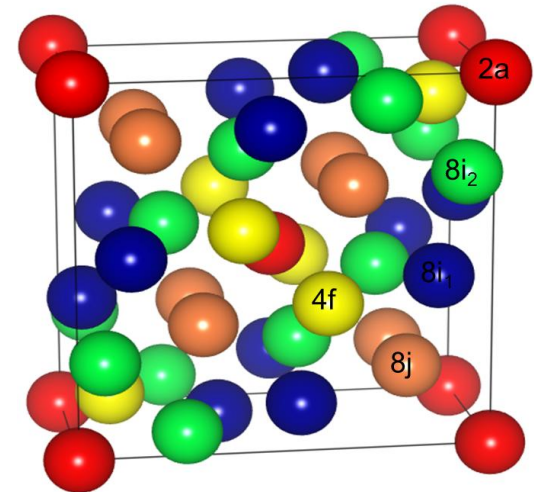
- **Unit cell (type, lattice parameters)**
- **Basis (number of atoms, atomic type, positions in the unit cell)**



μ phase



χ phase



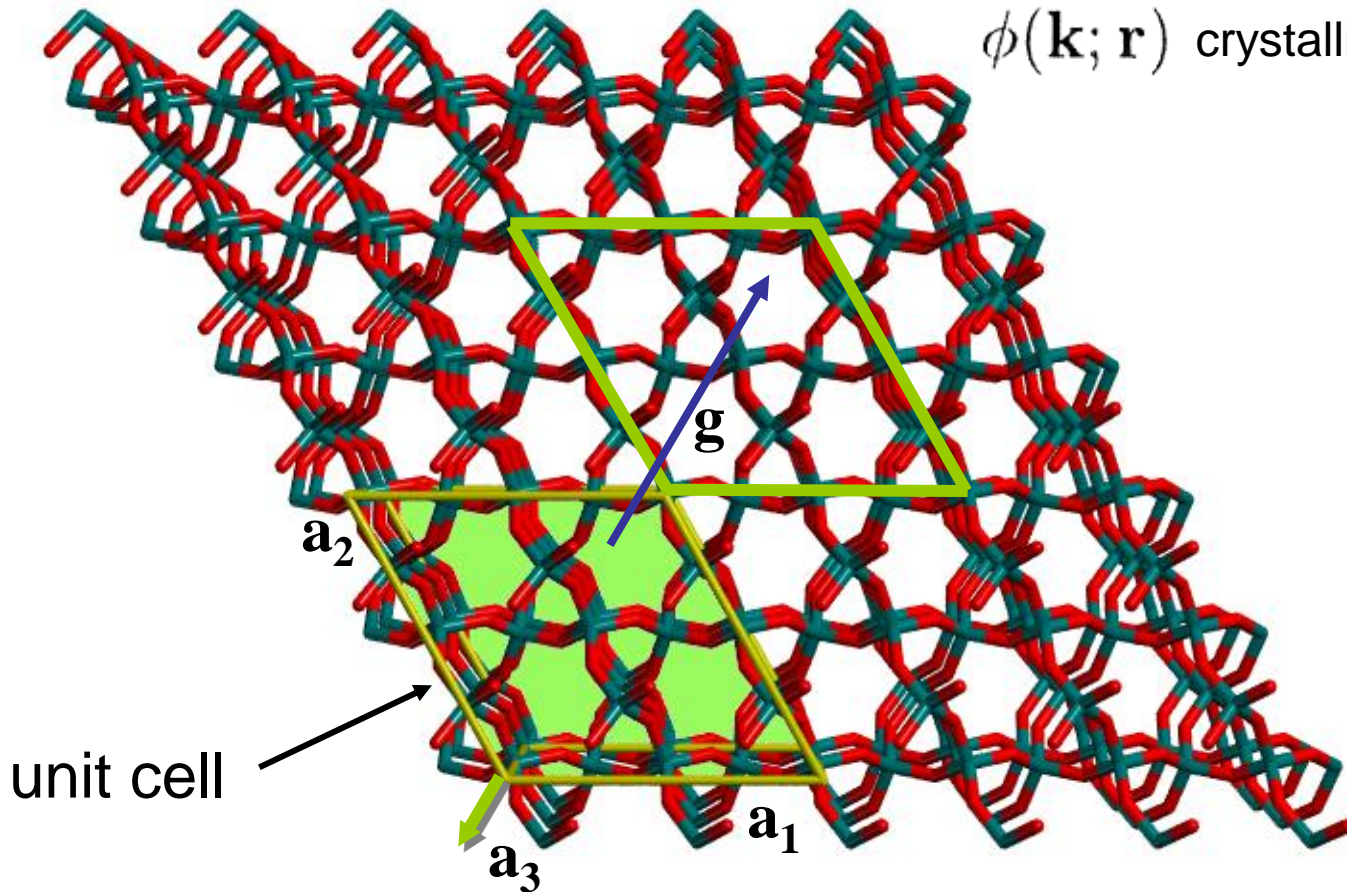
σ phase

Periodic treatment for crystals

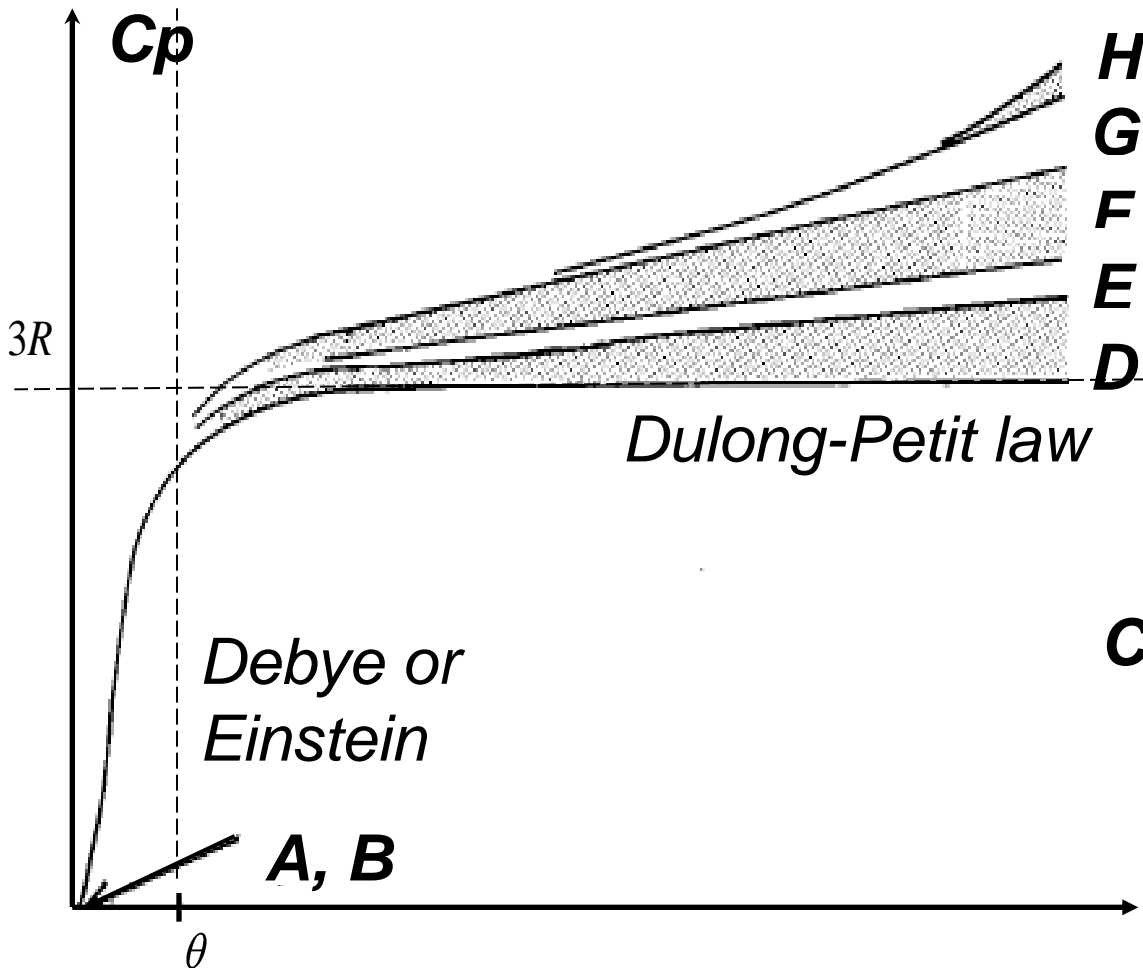
Born Von-Karman rule: $\Psi(\mathbf{r} + N_i \mathbf{a}_i) = \Psi(\mathbf{r}) \quad i = 1, 2, 3$

Bloch theorem: $\phi(\mathbf{k}; \mathbf{r} + \mathbf{g}) = \phi(\mathbf{k}; \mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{g}}, \quad \mathbf{g} = l \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3$

$\phi(\mathbf{k}; \mathbf{r})$ crystalline orbitals



Temperature dependence of heat capacity in real metals



From G. Grimvall, *Thermophysical properties of materials*, North-Holland 1986

(H) contribution to heat capacity because of vacancies formation, varies exponentially with T_m/T . Usually low for metals, but significant close to T_m

(G) correction factor to C_{el} because of non constant $N(E_F)$ at high T. For some metals, can be 50% or more of C_{el} at T_m

(F) electronic contribution, linear in T. No enhancement factor ($\lambda=0$, no phonons-electrons coupling). Low T data cannot be extrapolated at high T

(E) explicit anharmonic contributions to C_V , linear in T to leading order.

(D) $C_p - C_V$ contribution. Usually dominated by vibrational part, linear in T. Higher order contributions come from higher order anharmonicity and electronic high T excitations.

(C) main contribution from harmonic vibrational heat capacity. Asymptotic value $3R$ at high T.

(B) phonons contribution (Debye or Einstein model, Debye approximation for low T)

(A) electronic heat capacity (linear in T, enhancement factor for phonon coupling)

The harmonic approximation

Two fundamental assumptions:

1. ***atoms oscillates around a mean equilibrium position which is a Bravais lattice site***
2. ***typical excursions of each atom from its equilibrium position is small compared to the interatomic spacing*** (how much small?)

Let's consider a periodic solid. We indicate with

$$\mathbf{R}_l = \mathbf{R}_\mu + \mathbf{d}_s$$

the equilibrium positions of the atoms. \mathbf{R}_μ indicate the Bravais lattice vectors and \mathbf{d}_s the positions of the atoms in one unit cell ($s = 1, \dots, N_{at}$).

We take N unit cells with Born-von Karman periodic boundary conditions. Ω is the volume of one cell and $V = N\Omega$ the volume of the solid.

At time t , each atom is displaced from its equilibrium position. $\mathbf{u}_l(t)$ is the displacement of the atom l .

The equations of motion

$$H = \sum_{I\alpha} \frac{\mathbf{P}_{I\alpha}^2}{2M_I} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta}$$

where \mathbf{P}_I are the momenta of the nuclei and M_I their masses. The classical motion of the nuclei is given by the $N \times 3 \times N_{at}$ functions $\mathbf{u}_{I\alpha}(t)$. These functions are the solutions of the Hamilton equations:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\partial H}{\partial \mathbf{P}_{I\alpha}} = \frac{\mathbf{P}_{I\alpha}}{M_I} \\ \dot{\mathbf{P}}_{I\alpha} &= -\frac{\partial H}{\partial \mathbf{u}_{I\alpha}} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \end{aligned}$$

or:

$$M_I \ddot{\mathbf{u}}_{I\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} = F_{J\beta}$$

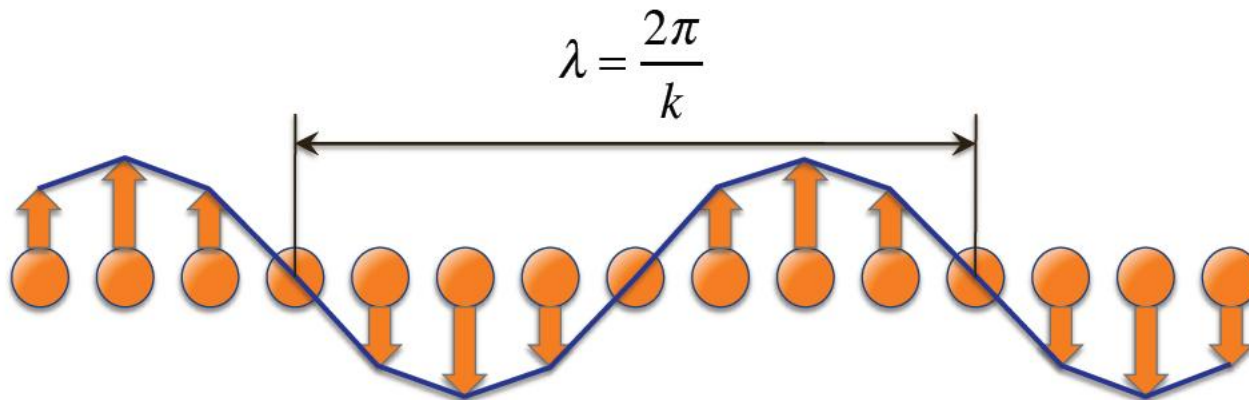
Linear system of $3N$ 2nd order differential equations of motion

Phonons solutions

We can search the solution in the form of a phonon. Let's introduce a vector \mathbf{q} in the first Brillouin zone. For each \mathbf{q} we can write:

$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_{\mathbf{q}}t)}$$

where the time dependence is given by a simple exponential $e^{i\omega_{\mathbf{q}}t}$ and the displacement of the atoms in each cell identified by the Bravais lattice \mathbf{R}_μ can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to $\mathbf{R}_\mu = 0$: $\frac{1}{\sqrt{M_s}} \mathbf{u}_{s\alpha}(\mathbf{q})$.



The dynamical matrix

Inserting this solution in the equations of motion and writing $I = (\mu, s)$, $J = (\nu, s')$ we obtain an eigenvalue problem for the $3 \times N_{at}$ variables $\mathbf{u}_{s\alpha}(\mathbf{q})$:

$$\omega_{\mathbf{q}}^2 \mathbf{u}_{s\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q})$$

where:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})}$$

is the dynamical matrix of the solid.

The dynamical matrix elements can be calculated by first principles calculations with 2 methods:

- ✓ *Supercell method* (or Small Displacement Method)
- ✓ *Linear Response Method* (Density Function Perturbation Theory, DFPT)

Properties of the dynamical matrix

- The dynamic matrix is a $3N_{\text{at}} * 3N_{\text{at}}$ Hermitean matrix

- Symmetrical with respect to $\mathbf{q} \rightarrow -\mathbf{q}$ change:

$$D_{s\alpha s'\beta}(-\mathbf{q}) = D_{s\alpha s'\beta}(\mathbf{q})$$

- If all atoms are moved by the same displacement \mathbf{d} from equilibrium, the dynamical matrix is zero:

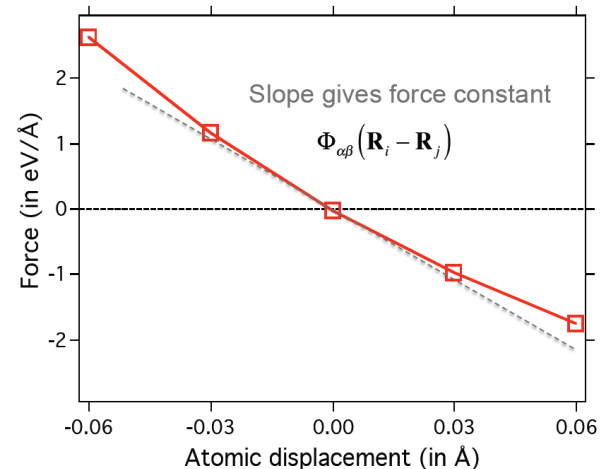
$$\sum_{\mathbf{q}} D_{s\alpha s'\beta}(\mathbf{q}) = 0$$

The supercell method

- Set up a “large” supercell
- Displace atoms by a “small” amount
- Linearize and fit atom forces
- Assemble the dynamical matrix
- Diagonalize the dynamical matrix (solve the equations of motion)

$$M_I \ddot{\mathbf{u}}_{I\alpha} = - \sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} = - \sum_{J\beta} \Phi_{J\beta} u_{J\beta} = F_{I\alpha}$$

- Works with any DFT total energy code
- Needs to check supercell is large enough, atomic displacements are small enough,...
- Code available: PHON (Dario Alfe)
 - PHONONS (K. Parliski)



Density Functional Perturbation Theory (DFPT)

Within DFT the ground state total energy of the solid, calculated at fixed nuclei, is:

$$E_{tot} = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{loc}(\mathbf{r}) \rho(\mathbf{r}) d^3r + E_H[\rho] + E_{xc}[\rho] + U_{II}$$

where $\rho(\mathbf{r})$ is the density of the electron gas:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

and $|\psi_i\rangle$ are the solution of the Kohn and Sham equations. E_H is the Hartree energy, E_{xc} is the exchange and correlation energy and U_{II} is the ion-ion interaction. According to the Hellmann-Feynman theorem, the first order derivative of the ground state energy with respect to an external parameter is:

$$\frac{\partial E_{tot}}{\partial \lambda} = \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d^3r + \frac{\partial U_{II}}{\partial \lambda}$$

Density Functional Perturbation Theory (DFPT)

Deriving with respect to a second parameter μ :

$$\begin{aligned} \frac{\partial^2 E_{tot}}{\partial \mu \partial \lambda} &= \int \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mu \partial \lambda} \rho(\mathbf{r}) d^3 r + \frac{\partial^2 U_{II}}{\partial \mu \partial \lambda} \\ &+ \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r \end{aligned}$$

So the new quantity that we need to calculate is the charge density induced, at first order, by the perturbation:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial \mu}$$

To fix the ideas we can think that $\lambda = \mathbf{u}_{\mu s \alpha}$ and $\mu = \mathbf{u}_{\nu s' \beta}$

Density Functional Perturbation Theory (DFPT)

The wavefunctions obey the following equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where $V_{KS} = V_{loc}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$. $V_{KS}(\mathbf{r}, \mu)$ depends on μ so that also $\psi_i(\mathbf{r}, \mu)$, and $\varepsilon_i(\mu)$ depend on μ . We can expand these quantities in a Taylor series:

$$V_{KS}(\mathbf{r}, \mu) = V_{KS}(\mathbf{r}, \mu = 0) + \mu \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} + \dots$$

$$\psi_i(\mathbf{r}, \mu) = \psi_i(\mathbf{r}, \mu = 0) + \mu \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} + \dots$$

$$\varepsilon_i(\mu) = \varepsilon_i(\mu = 0) + \mu \frac{\partial \varepsilon_i}{\partial \mu} + \dots$$

Density Functional Perturbation Theory (DFPT)

Inserting these equations and keeping only the first order in μ we obtain:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -\frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r}) + \frac{\partial \varepsilon_i}{\partial \mu} \psi_i(\mathbf{r})$$

where: $\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$ and

$$\frac{\partial V_H}{\partial \mu} = \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d^3 r'$$
$$\frac{\partial V_{xc}}{\partial \mu} = \frac{dV_{xc}}{d\rho} \frac{\partial \rho(\mathbf{r})}{\partial \mu}$$

depend self-consistently on the charge density induced by the perturbation.

The DFPT self-consistent cycle

DFT

$$V_0(\mathbf{r}) \Leftrightarrow n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$(-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

DFPT

$$V'(\mathbf{r}) \Leftrightarrow n'(\mathbf{r})$$

$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

$$n'(\mathbf{r}) = 2 \operatorname{Re} \sum_{\epsilon_v < E_F} \phi_v^*(\mathbf{r}) \phi'_v(\mathbf{r})$$

$$(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r}) \phi_v(\mathbf{r})$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

The ph.x code

The program `ph.x` solves this self-consistent linear system for $3 \times N_{at}$ perturbations at a fixed vector \mathbf{q} . With $\frac{\partial \rho(\mathbf{r})}{\partial \mu}$ for all the perturbations it calculates the dynamical matrix

$$D_{s\alpha s'\beta}(\mathbf{q})$$

at the given \mathbf{q} . Diagonalizing this matrix we obtain $3 \times N_{at}$ frequencies $\omega_{\mathbf{q}}$. By repeating this procedure for several \mathbf{q} we could plot $\omega_{\mathbf{q}}$ as a function of \mathbf{q} and display the phonon dispersions. However, it is more convenient to adopt a different approach that requires the calculation of the dynamical matrix in a small set of points \mathbf{q} .

The ph.x code

The dynamical matrix of the solid:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})} \quad (26)$$

is a periodic function of \mathbf{q} with $D_{s\alpha s'\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha s'\beta}(\mathbf{q})$ for any reciprocal lattice vector \mathbf{G} . Moreover, since in a solid all Bravais lattice points are equivalent, it does not depend on μ . Eq.26 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values \mathbf{R}_{ν} of the Bravais lattice and we can write:

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} = \frac{\Omega}{(2\pi)^3} \int d^3\mathbf{q} D_{s\alpha s'\beta}(\mathbf{q}) e^{-i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})} \quad (27)$$

The ph.x code

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of points \mathbf{q} . This will give the interatomic force constants only for a set of \mathbf{R}_ν neighbors of \mathbf{R}_μ . The code `q2r.x` reads a set of dynamical matrices calculated in a uniform mesh of \mathbf{q} points and calculates, using Eq. 27, the interatomic force constants for a few neighbors of the point $\mathbf{R}_\mu = 0$.

The ph.x code

then we can calculate:

$$\tilde{c}_n = \frac{1}{N} \sum_{j=0}^{N-1} f(x_j) e^{-i\frac{2\pi}{N}nj} \quad (30)$$

\tilde{c}_n is a periodic function of n and $\tilde{c}_{n+N} = \tilde{c}_n$. So, if N is sufficiently large that $c_n = 0$ when $|n| \geq N/2$ then \tilde{c}_n is a good approximation of c_n for $|n| < N/2$ and the function

$$f(x) = \sum_{n=-N/2}^{n=N/2} \tilde{c}_n e^{ik_n x} \quad (31)$$

is a good approximation of the function $f(x)$ also on the points x different from x_j .

The ph.x code

Therefore, if the dynamical matrix is a sufficiently smooth function of \mathbf{q} and the interatomic force constants decay sufficiently rapidly in real space, we can use Eq. 26 to calculate the dynamical matrix at arbitrary \mathbf{q} , limiting the sum to a few \mathbf{R}_ν neighbors of $\mathbf{R}_\mu = 0$. The program `matdyn.x` reads the interatomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary \mathbf{q} using Eq. 26.

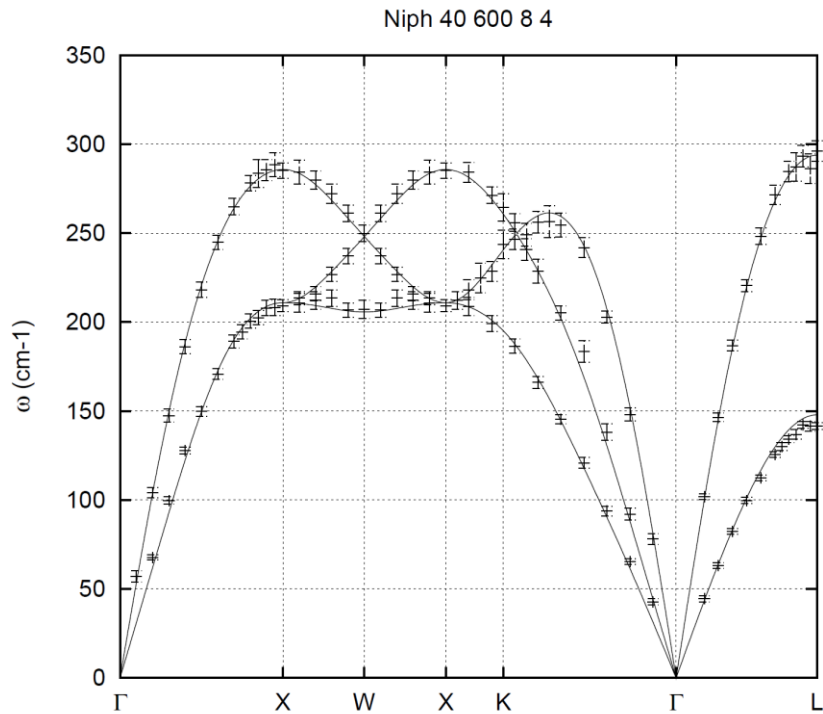
Thermodynamic functions in the harmonic approximation

$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log \left(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}} \right)$$

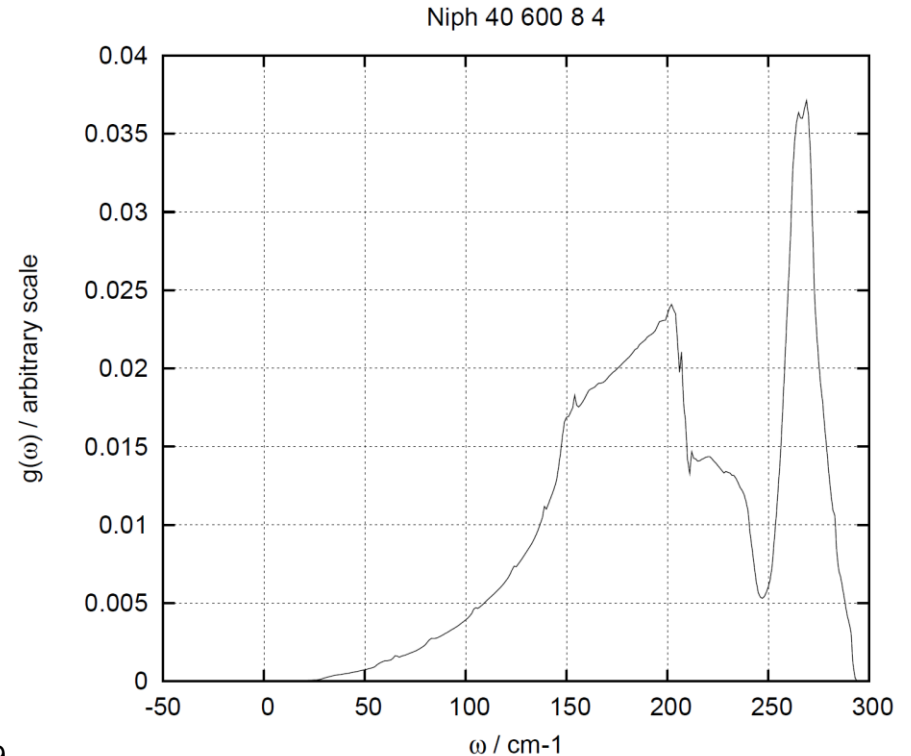
$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

- The vibrational free energy and all other thermodynamic properties in the harmonic approximation can be determined from the phonon frequencies calculated at the equilibrium volume V_0
- These frequencies, phonon dispersion curves in the BZ and phonon DOS can be calculated by first principles by:
 - ✓ *Supercell method (or Small Displacement Method)*
 - ✓ *Linear Response Method (Density Functional Perturbation)*

First principles phonons for Ni: harmonic



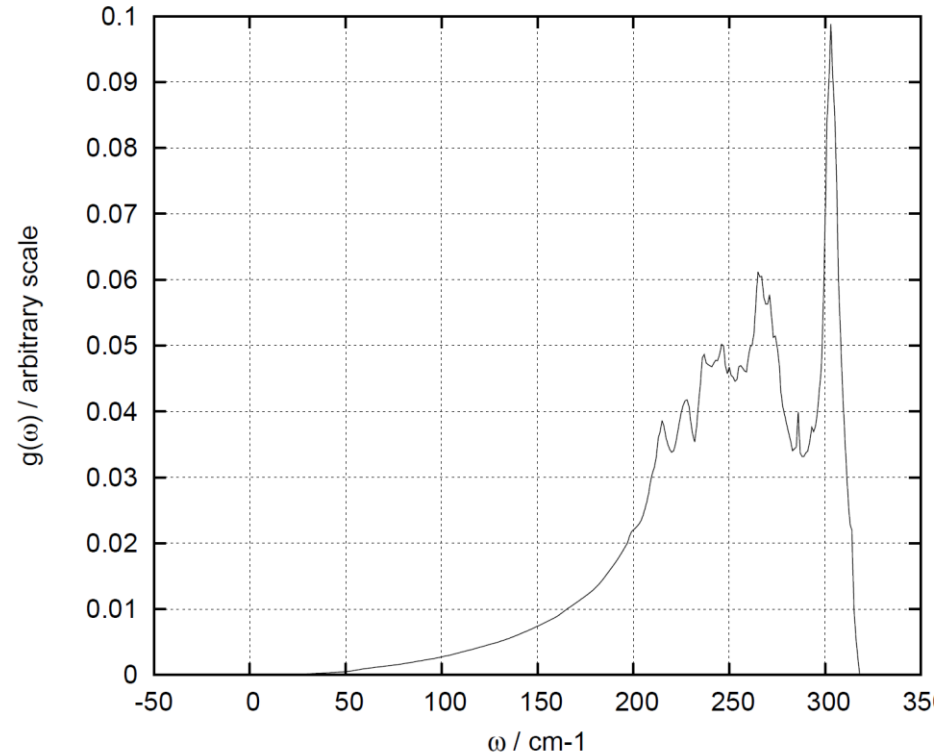
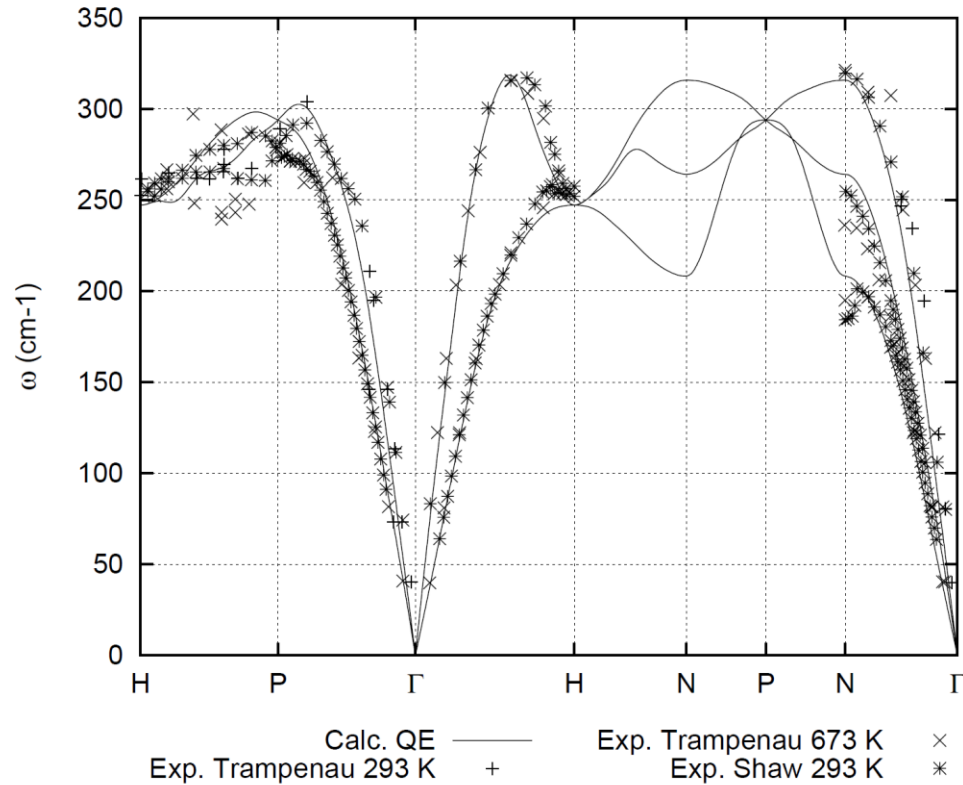
Exp. Data from R. J. Birgenau et al., Phys Rev 136 (1964) 1359



Phonons dispersion and DOS calculated by first principles with Quantum-Espresso and the Linear Response Method

PBE potential, ultrasoft pseudopotentials, Ecut=40 Ry, k-points mesh 8*8*8, q-points mesh (4*4*4)

First principles phonons for Cr: harmonic



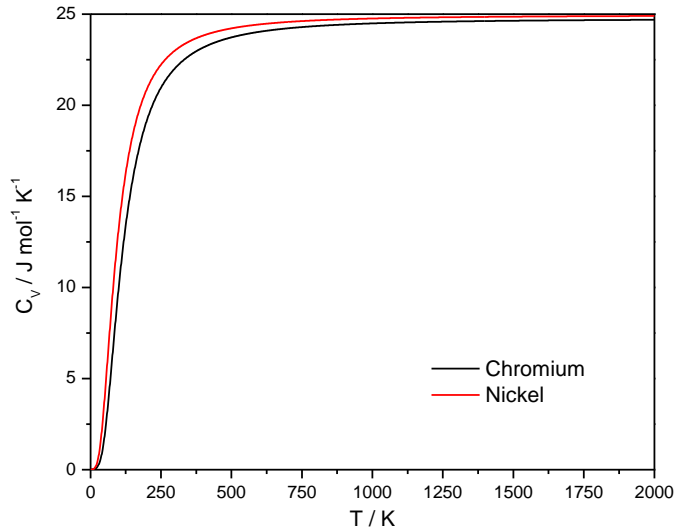
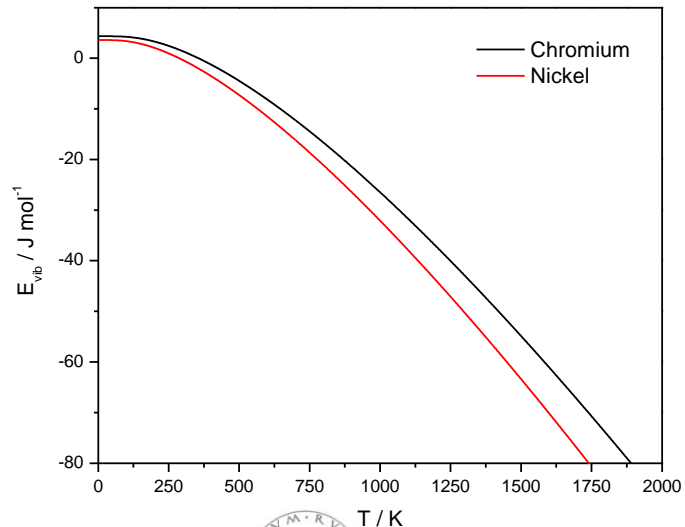
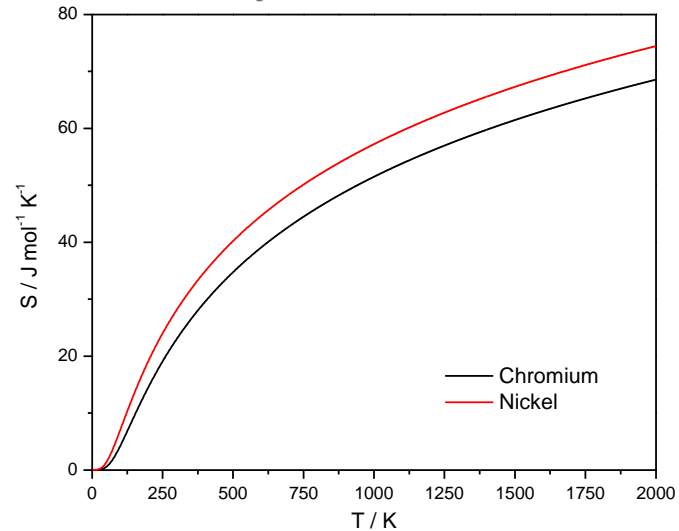
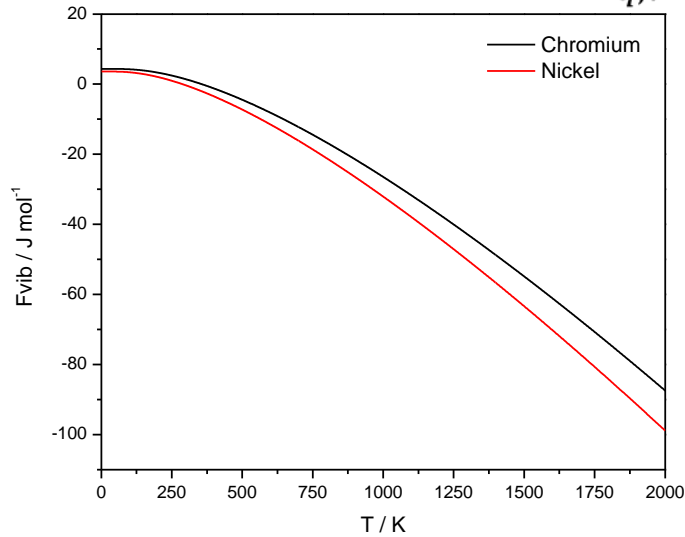
Exp. data from Trampenau et al. Phys Rev B 47 (1993) 3132 and Shaw et al., Phys Rev B 4 (1971) 969

Phonons dispersion and DOS calculated by first principles with Quantum-Espresso and the Linear Response Method

PBE potential, ultrasoft pseudopotentials, Ecut=100 Ry, k-points mesh 16*16*16, q-points mesh 8*8*8

Thermodynamics of Cr and Ni: harmonic approximation

$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log\left(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}}\right)$$



The quasi-harmonic approximation (QHA)

$$F(V, T) = U_0(\mathbf{V}) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu, \mathbf{V}) + k_B T \sum_{\vec{q}, \nu} \log\left(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu, \mathbf{V})}{k_B T}}\right)$$

Phonons calculations are performed at different volumes, then F is minimized

$$U(S, V) = F + TS$$

$$G(T, p) = F + pV$$

Bulk modulus

$$B_T = V \left(\frac{\partial^2 F}{\partial V^2} \right)_T$$

Thermal expansion

$$\beta = V^{-1} \left(\frac{\partial V}{\partial T} \right)_P$$

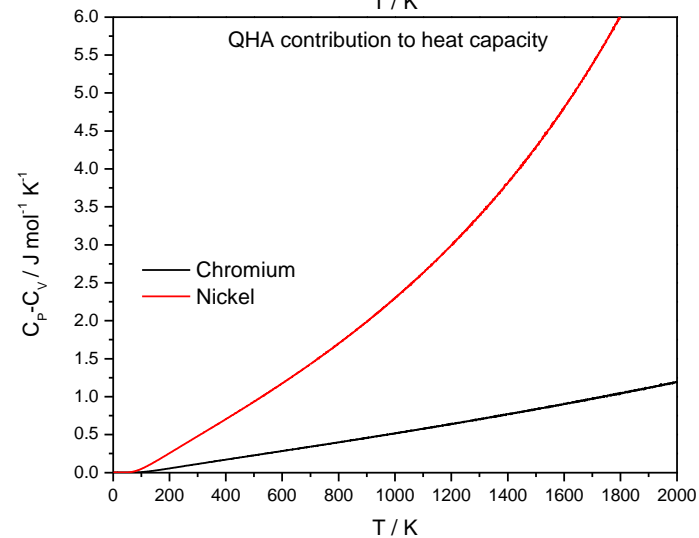
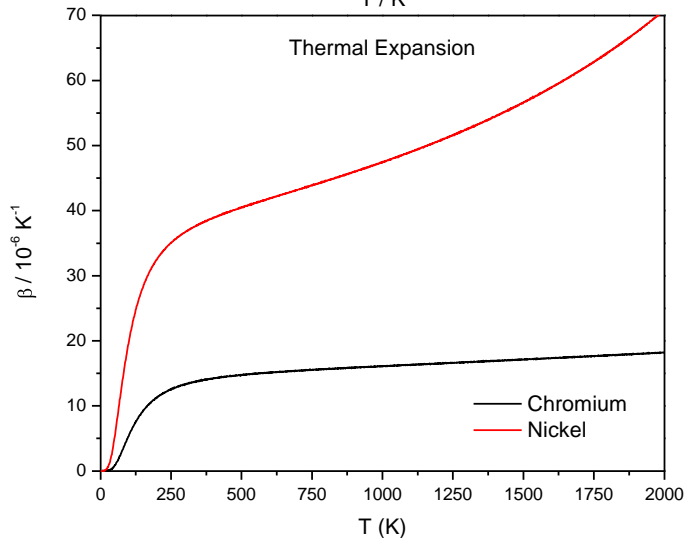
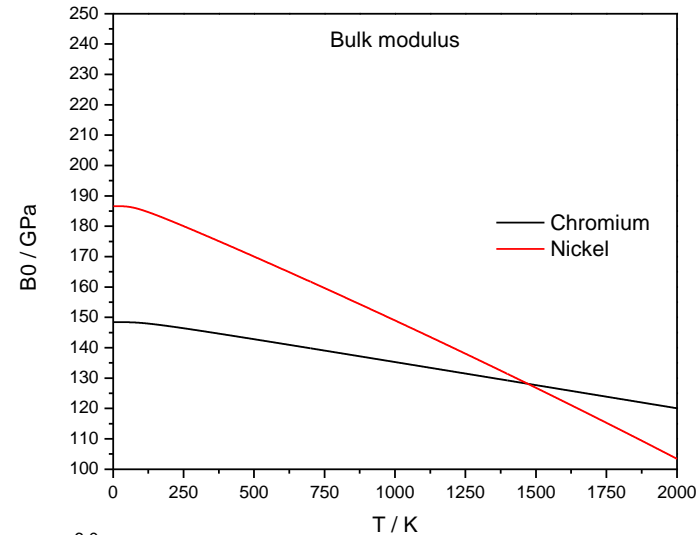
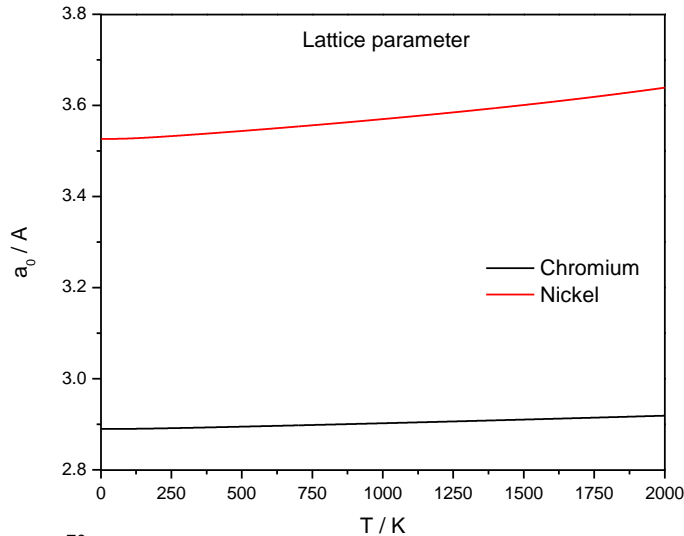
Heat capacity

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log\left(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}}\right)$$

$$C_p - C_V = TV\beta^2 B_T \quad C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

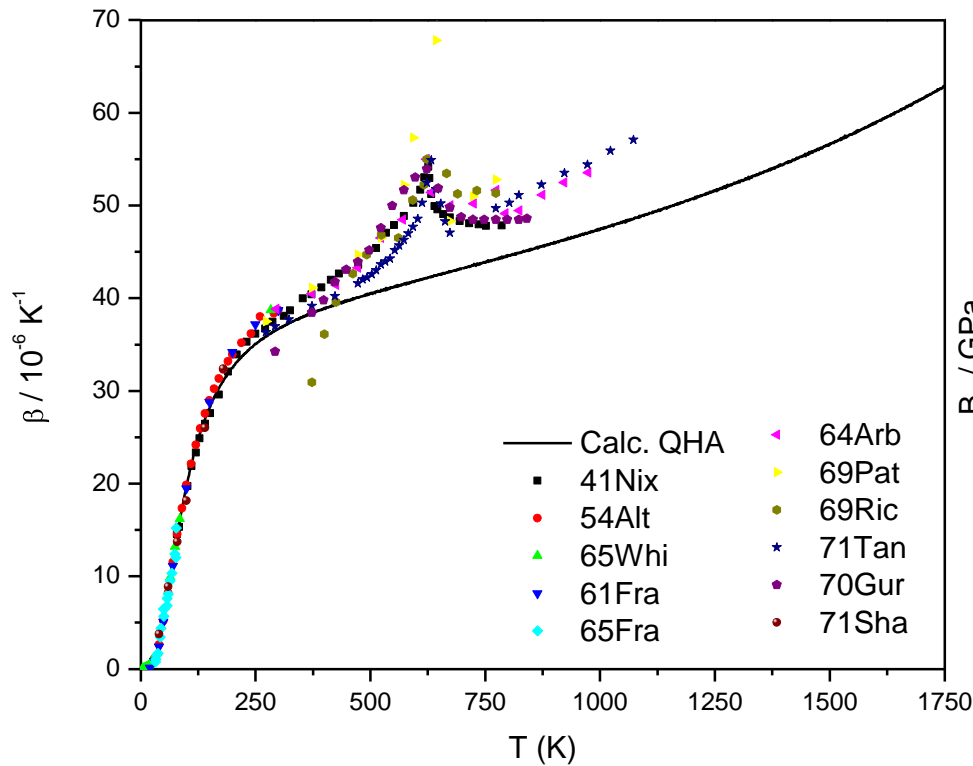
Thermophysical properties for Cr and Ni in the QHA



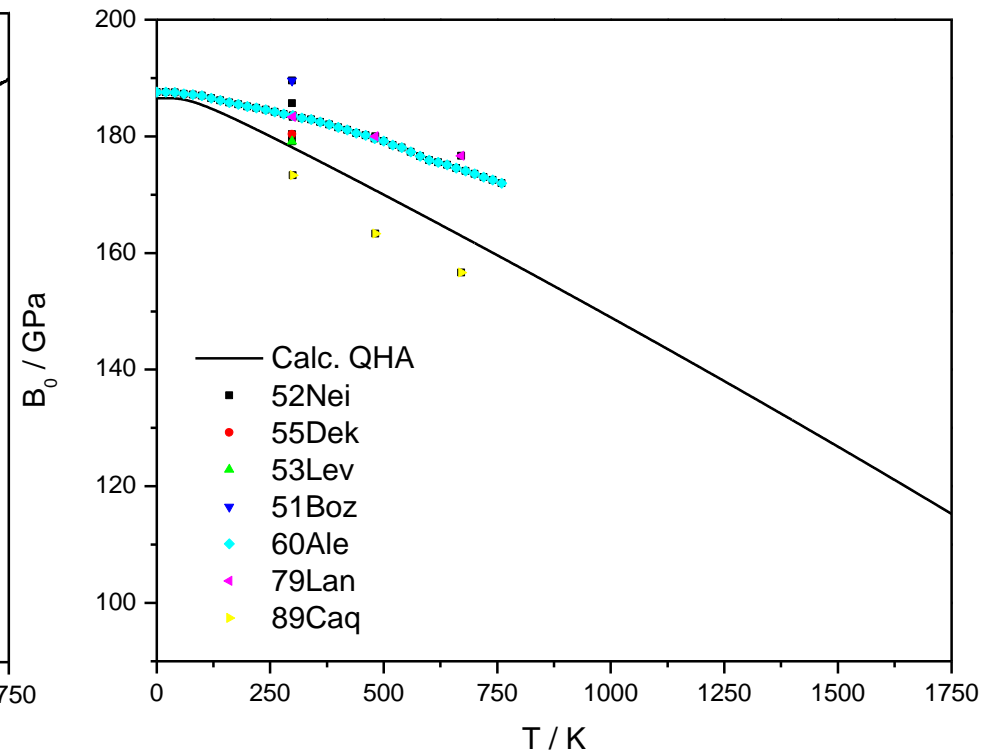
Thermophysical functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation

Quasi Harmonic Approximation: comparison with experimental data for Ni

Thermal expansion

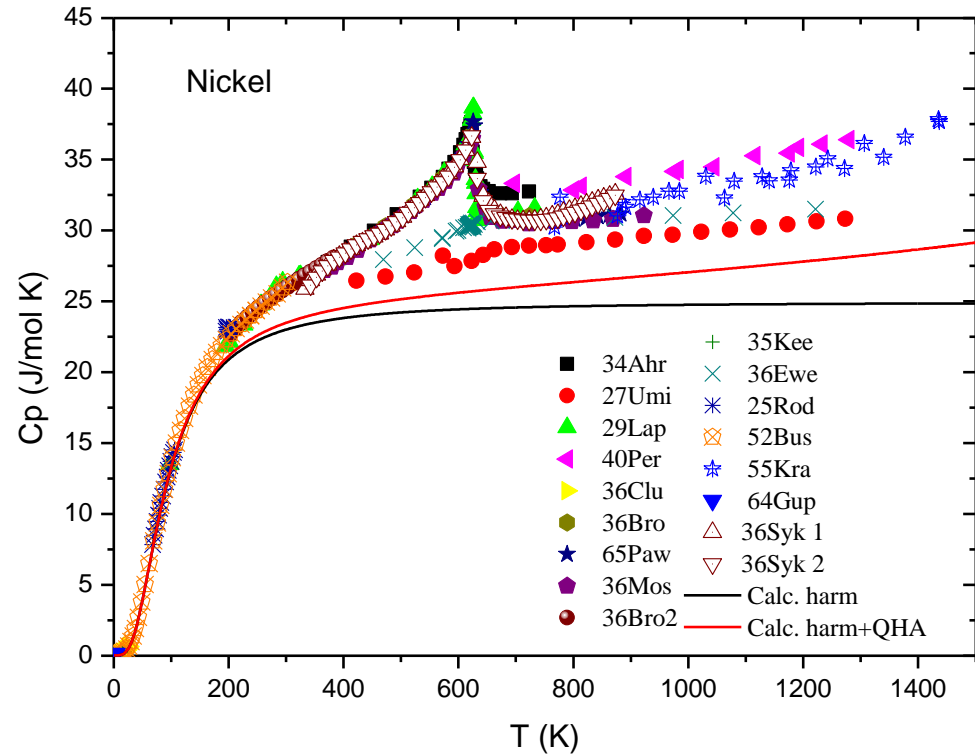
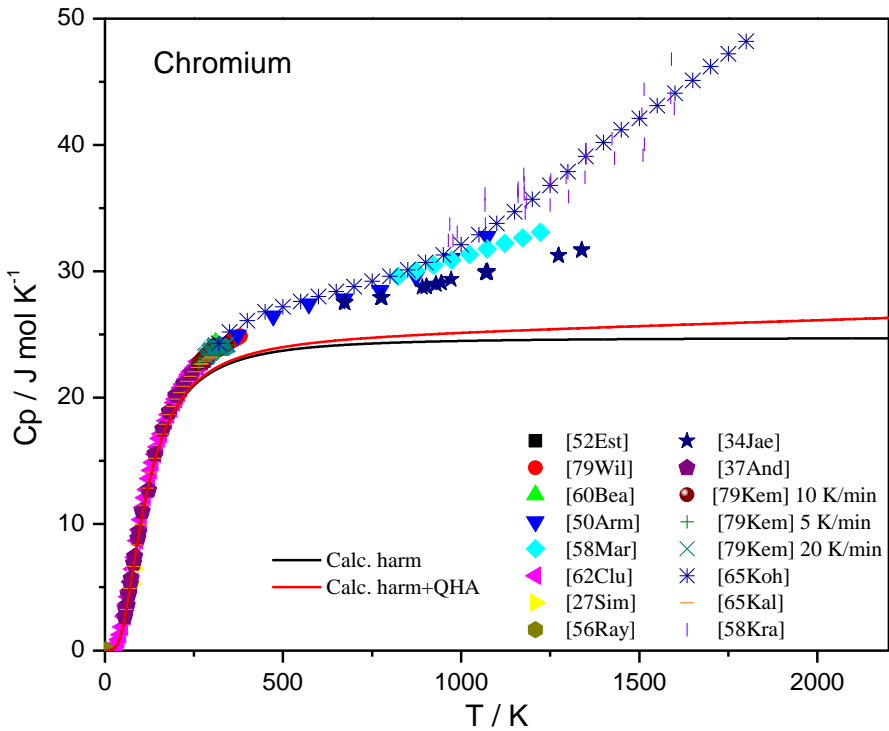


Bulk modulus



Thermophysical functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation

First principles heat capacity for Cr and Ni (Quasi Harmonic Approximation)



Thermodynamic functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation

The Quantum Espresso open source code

Many modules and tools are available:

pwscf.x

ph.x

matdyn.x

q2r

plotdos

....

GUI

(Graphical User Interface)

Other software codes for phonons calculations

- PHON, Dario Alfe', <http://www.homepages.ucl.ac.uk/~ucfbdx/phon/>
- PHONONS (K. Parlinski) <http://wolf.ifj.edu.pl/phonon/>
- VASP 5.2, <http://cms.mpi.univie.ac.at/vasp/>
- ABINIT, <http://www.abinit.org/>

Aknowledgments

For support...

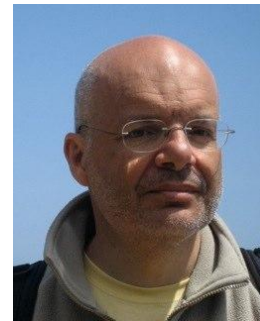
*ICAMS, International Centre for Advanced
Materials Simulations, Ruhr University Bochum*

For comments, discussions, slides,...

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Suzana G. Fries, ICAMS, Bochum, Germany

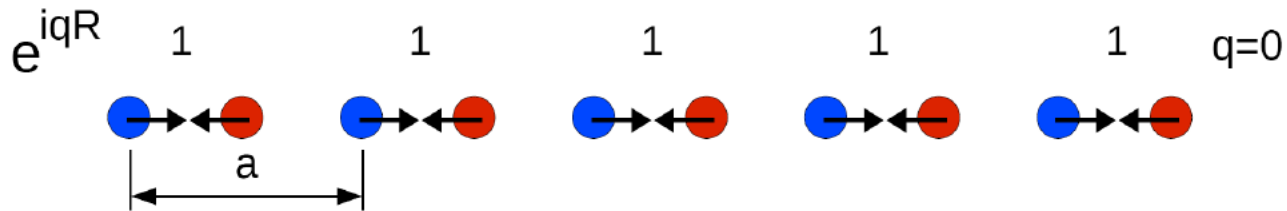


You for listening...

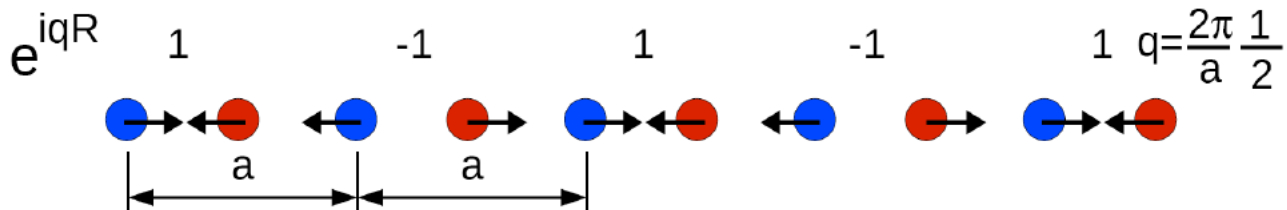
*Many thanks to Andrea Dal Corso for providing
some of these slides*

Characteristic of phonons

A Γ -point phonon has the same displacements in all unit cells ($\mathbf{q} = 0$):

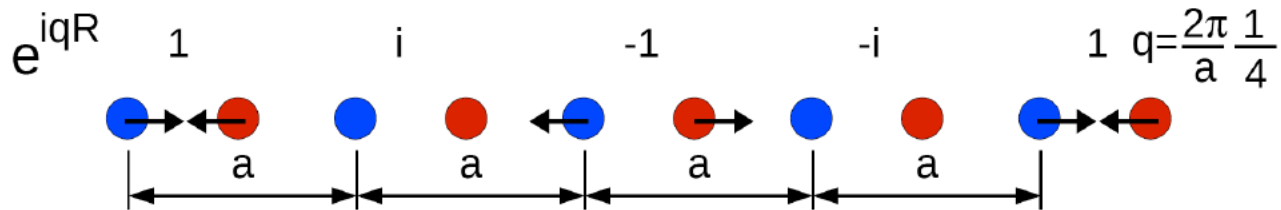


A zone border phonon with $\mathbf{q}_{ZB} = \mathbf{G}/2$, where \mathbf{G} is a reciprocal lattice vector, has displacements which repeat periodically every two unit cells:



Characteristic of phonons

A phonon with $\mathbf{q} = \mathbf{q}_{\text{ZB}}/2$ has displacements which repeat every four unit cells:



A phonon at a general wavevector \mathbf{q} could be incommensurate with the underlying lattice:

