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ABINIT Tutorial

Interatomic force constants and phonon dispersion curves

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Outline:

1. Energy derivatives and functional properties
2. Dynamical matrix and phonon frequencies
3. Interatomic force constants in real space
4. Phonon dispersion curves
5. What can we do with that ?
6. Thermodynamical properties

1. Energy derivatives and physical properties

X. Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)
R. W. Nunes and X. Gonze, Phys. Rev. B 63, 155107 (2001)

Energy functionals:

The energy functional minimized in terms of the electronic degrees of freedom within ABINIT is

- In zero field:

The Born-Oppenheimer energy :

$$E_{e+i}[\mathbf{R}_\kappa] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] \right)$$

with

$$E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] = \underbrace{\left(T_e[\psi_{n\mathbf{k}}] + E_H[\psi_{n\mathbf{k}}] + E_{xc}[\psi_{n\mathbf{k}}] + E_{ei}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] \right)}_{E_{el}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}]} + U_{ii}[\mathbf{R}_\kappa]$$

Energy functionals:

- In non-zero field:

The related functional *

$$F_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] - \Omega_0 \ \mathcal{E} \cdot \mathcal{P}[\psi_{n\mathbf{k}}] \right)$$

or the electric enthalpy

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \min_{\psi_{n\mathbf{k}}} \left(E_{e+i}[\mathbf{R}_\kappa, \psi_{n\mathbf{k}}] - \Omega_0 \ \mathcal{E} \cdot \mathcal{P}[\psi_{n\mathbf{k}}] \right) - \frac{\Omega_0}{8\pi} \mathcal{E}^2$$

** R. W. Nunes and X. Gonze, Phys. Rev. B 63, 155107 (2001)*
I. Souza, J. Iniguez and D. Vanderbilt, Phys. Rev. Lett. 89, 117602 (2002)

Energy expansion:

Various physical quantities are related to successive derivatives of E_{e+i} or $\mathscr{F}_{e+i}$ in terms of $\mathcal{E}$ and $\tau_\kappa = R_\kappa - R_\kappa^0$

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}_\kappa^0, 0]$$
$$+ \sum_\alpha \frac{\partial \mathscr{F}_{e+i}}{\partial \mathcal{E}_\alpha} \mathcal{E}_\alpha + \sum_\alpha \sum_\kappa \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha}} \tau_{\kappa\alpha}$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \frac{\partial \mathscr{F}_{e+i}}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta} \mathcal{E}_\alpha \mathcal{E}_\beta + \sum_{\alpha\beta} \sum_\kappa \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha} \partial \mathcal{E}_\beta} \tau_{\kappa\alpha} \mathcal{E}_\beta$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} \frac{\partial \mathscr{F}_{e+i}}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\beta}} \tau_{\kappa\alpha} \tau_{\kappa'\beta} + \ldots$$

Note : can be generalized to include strains → $\mathscr{F}_{e+i}[R_\kappa, \mathcal{E}, \eta]$

Physical quantities:

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}^0_\kappa, 0]$$

$$- \Omega_0 \sum_\alpha \mathcal{P}^s_\alpha \mathcal{E}_\alpha \; - \sum_\alpha \sum_\kappa F^0_\alpha \; \tau_{\kappa\alpha}$$

$$- \frac{\Omega_0}{8\pi} \sum_{\alpha\beta} \varepsilon^\infty_{\alpha\beta} \mathcal{E}_\alpha \mathcal{E}_\beta \; - \sum_{\alpha\beta} \sum_\kappa Z^*_{\kappa,\alpha\beta} \; \tau_{\kappa\alpha} \; \mathcal{E}_\beta$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} C_{\alpha\beta}(\kappa,\kappa') \tau_{\kappa\alpha} \tau_{\kappa'\beta}$$

Interatomic force constants (IFC)
in real space

Physical quantities:

- Atomic forces :

$$F_{\kappa\alpha}[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{d\mathcal{F}_{e+i}[\mathbf{R}_\kappa,\mathcal{E}]}{d\tau_{\kappa\alpha}}$$

$$= \underbrace{F^0_{\kappa\alpha}}_{=0} + \sum_\beta Z^*_{\kappa,\alpha\beta}\ \mathcal{E}_\beta - \sum_\beta \sum_{\kappa'} C_{\alpha\beta}(\kappa,\kappa')\tau_{\kappa'\beta}$$

- Electric displacement field :

$$\mathcal{D}_\beta[\mathbf{R}_\kappa,\mathcal{E}] = -\frac{4\pi}{\Omega_0}\ \frac{d\mathcal{F}_{e+i}[\mathbf{R}^0_\kappa,0]}{d\mathcal{E}_\beta}$$

$$= 4\pi\left(\underbrace{\mathcal{P}^s_\beta}_{=0} + \frac{1}{\Omega_0}\sum_\alpha\sum_\kappa Z^*_{\kappa,\alpha\beta}\ \tau_{\kappa\alpha}\right) + \sum_\alpha \varepsilon^\infty_{\alpha\beta}\,\mathcal{E}_\alpha$$

2. Dynamical matrix and phonon frequencies

X. Gonze, Phys. Rev. B 55, 10337 (1997)
X. Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Equation of motion for the ions (for $\mathcal{E} = 0$)

- Harmonic energy :

$$\mathscr{F}_{e+i}[\mathbf{R}_\kappa, \mathcal{E}] = \mathscr{F}_{e+i}[\mathbf{R}^0_\kappa, 0] + \frac{1}{2}\sum_{a\kappa\alpha}\sum_{b\kappa'\beta} C^{ab}_{\alpha\beta}(\kappa,\kappa')\tau^a_{\kappa\alpha}\tau^b_{\kappa'\beta}$$

- Equation of motion

$$M_\kappa \frac{\partial^2 \tau^a_{\kappa\alpha}}{\partial t^2} = F^a_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{ab}_{\alpha\beta}(\kappa,\kappa')\tau^b_{\kappa'\beta}$$

- Solution

$$\tau^a_{\kappa\alpha}(t) = \eta_{m\mathbf{q}}(\kappa\alpha)\, e^{i\,\mathbf{q}\cdot\mathbf{R}^a}\; e^{-i\omega_{m\mathbf{q}}t}$$

Dynamical equation

$$-M_\kappa \omega^2_{m\mathbf{q}} \eta_{m\mathbf{q}}(\kappa\alpha) = -\sum_{\kappa'\beta} \underbrace{\left(\sum_b C^{ab}_{\alpha\beta}(\kappa,\kappa') e^{i\,\mathbf{q}\cdot(\mathbf{R}^b-\mathbf{R}^a)}\right)}_{\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa') = \frac{1}{N}\sum_{ab} C^{ab}_{\alpha\beta}(\kappa,\kappa') e^{i\,\mathbf{q}\cdot(\mathbf{R}^b-\mathbf{R}^a)}} \eta_{m\mathbf{q}}(\kappa'\beta)$$

$$M_\kappa \omega^2_{m\mathbf{q}} \underbrace{\eta_{m\mathbf{q}}(\kappa\alpha)}_{\gamma_{m\mathbf{q}}(\kappa\alpha)/\sqrt{M_\kappa}} = \sum_{\kappa'\beta} \underbrace{\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa')}_{\tilde{D}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa')\sqrt{M_\kappa M_{\kappa'}}} \underbrace{\eta_{m\mathbf{q}}(\kappa'\beta)}_{\gamma_{m\mathbf{q}}(\kappa'\beta)/\sqrt{M_{\kappa'}}}$$

$$\omega^2_{m\mathbf{q}} \gamma_{m\mathbf{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \tilde{D}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa')\, \gamma_{m\mathbf{q}}(\kappa'\beta)$$

Phonon frequency

Dynamical matrix

Phonon eigenvector

Notations

- Force constant matrix ⟶ $\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa') = \dfrac{\partial^2 E_{e+i}}{\partial\tau^{\mathbf{q}}_{\kappa\alpha}\partial\tau^{\mathbf{q}}_{\kappa'\beta}}$
- Dynamical matrix ⟶ $\tilde{D}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa') = \dfrac{\tilde{C}^{\mathbf{q}}_{\alpha\beta}(\kappa,\kappa')}{\sqrt{M_\kappa M_{\kappa'}}}$
- Phonon eigenvector ⟶ $\gamma_{m\mathbf{q}}(\kappa\alpha)$

  with $\left\langle \gamma \middle| \gamma \right\rangle = 1$
- Phonon eigendisplacements ⟶ $\eta_{m\mathbf{q}}(\kappa\alpha) = \dfrac{\gamma_{m\mathbf{q}}(\kappa\alpha)}{\sqrt{M_\kappa}}$

  (with M in emu)

  with $\left\langle \eta \middle| M \middle| \eta \right\rangle = 1$
- Phonon frequency ⟶ $\omega_{m\mathbf{q}}$

Zone-center phonons ($q \rightarrow 0$)

(TO modes : $\mathcal{E} = 0$, LO modes : $\mathcal{D} = 0$):

- Force :

$$F_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{0b}_{\alpha\beta}(\kappa,\kappa')\tau^{b}_{\kappa'\beta} + \sum_{\beta'} Z^{*}_{\kappa,\alpha\beta'}\ \hat{q}_{\beta'}\left|\mathcal{E}\right|$$

- Displacement field

$$\mathcal{D}_{\alpha} = \frac{4\pi}{\Omega_0}\sum_{\alpha}\sum_{\kappa} Z^{*}_{\kappa',\alpha\beta}\ \tau^{b}_{\kappa'\beta} + \sum_{\beta}\varepsilon^{\infty}_{\alpha\beta}\,\hat{q}_{\beta}\ \left|\mathcal{E}\right|$$

Along q, $\mathcal{D}$ must be preserved : $q_{\alpha}.\mathcal{D}_{\alpha}=0$

$$\left|\mathcal{E}\right| = -\frac{4\pi}{\Omega_0}\frac{\sum_{b\kappa'}\sum_{\alpha'\beta} Z^{*}_{\kappa',\alpha'\beta}\ \tau^{b}_{\kappa'\beta}\,\hat{q}_{\alpha'}}{\sum_{\alpha'\beta'}\hat{q}_{\alpha'}\ \varepsilon^{\infty}_{\alpha'\beta'}\ \hat{q}_{\beta'}}$$

LO-TO correction at Γ

$$F_{\kappa\alpha} = -\sum_{b\kappa'\beta} C^{0b}_{\alpha\beta}(\kappa,\kappa')\tau^{b}_{\kappa'\beta} + \sum_{\beta'} Z^{*}_{\kappa,\alpha\beta'}\ \hat{q}_{\beta'} \left(-\frac{4\pi}{\Omega_0} \frac{\sum_{b\kappa'}\sum_{\alpha'\beta} Z^{*}_{\kappa',\alpha'\beta}\ \tau^{b}_{\kappa'\beta}\ \hat{q}_{\alpha'}}{\sum_{\alpha'\beta'} \hat{q}_{\alpha'}\ \varepsilon^{\infty}_{\alpha'\beta'}\ \hat{q}_{\beta'}} \right)$$

$$= -\sum_{b\kappa'\beta} \tau^{b}_{\kappa'\beta} \left(C^{0b}_{\alpha\beta}(\kappa,\kappa') + \frac{4\pi}{\Omega_0} \frac{\sum_{\beta'}\left(Z^{*}_{\kappa,\alpha\beta'}\hat{q}_{\beta'}\right)\sum_{\alpha'}\left(Z^{*}_{\kappa',\alpha'\beta}\ \hat{q}_{\alpha'}\right)}{\sum_{\alpha'\beta'} \hat{q}_{\alpha'}\ \varepsilon^{\infty}_{\alpha'\beta'}\ \hat{q}_{\beta'}} \right)$$

Non-analytical term to be added to $C_{\alpha\beta}(\kappa, \kappa')$ to compute the LO-TO splitting in the limit of $q \rightarrow 0$

3. Interatomic force constants in real space

X. Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Interatomic force constants

- If the dynamical matrix was known at any q

$$C_{\kappa\alpha,\kappa'\beta}(0,b)=\frac{(2\pi)^3}{\Omega_0}\int_{\mathrm{BZ}}\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_b}d\mathbf{q}.$$

- Since the dynamical matrix is only known on a regular (lxmxn) grid, we can only approximate IFC in a box of (lxmxn) unit cells

$$C_{\kappa\alpha,\kappa'\beta}(0,b)=\frac{1}{N_{\mathbf{q}}}\sum_{\mathbf{q}\in\mathrm{grid}(l\times m\times n)}\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_b}\quad\text{if}\quad\mathbf{R}_b+\boldsymbol{\tau}_\kappa-\boldsymbol{\tau}'_\kappa\in\mathrm{box}$$

$$=0\qquad\qquad\text{if}\quad\mathbf{R}_b+\boldsymbol{\tau}_\kappa-\boldsymbol{\tau}'_\kappa\notin\mathrm{box}$$

Range of the IFC

- Are the IFC in real space really short range ?

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) + C^{\mathrm{LR}}_{\kappa\alpha,\kappa'\beta}(0,b)$$

Short-range chemical forces

For materials with non-vanishing Z*
Long-range Coulomb forces

Dominant DD interaction

Isotropic: $$C_{\kappa\alpha,\kappa'\beta}(0,a) = \frac{Z_\kappa Z'_\kappa}{\epsilon}\left(\frac{\delta_{\alpha\beta}}{d^3} - 3\frac{d_\alpha d_\beta}{d^5}\right) \quad \text{with} \quad \mathbf{d} = \mathbf{R}_a + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa$$

Anisotropic: $$C^{\mathrm{DD}}_{\kappa\alpha,\kappa'\beta}(0,a) = \sum_{\alpha'\beta'} Z^*_{\kappa,\alpha\alpha'} Z^*_{\kappa',\beta\beta'}\left(\frac{(\epsilon^{-1})_{\alpha'\beta'}}{D^3} - 3\frac{\Delta_{\alpha'}\Delta_{\beta'}}{D^5}\right) \times (\det\epsilon)^{-1/2}$$

Model interaction valid at large distances
Estimated in real and reciprocal space from Z* and ε^∞.

IFC in real space

- Substract the long-range DD part in recirpocal space

$$\widetilde{C}^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \widetilde{C}^{\mathrm{DD}}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q})$$

- Fourier transform the SR part on a finite grid

$$C^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}\in \mathrm{grid}\ (l\times m\times n)} \widetilde{C}^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_b} \quad \text{if } \mathbf{R}_b + \boldsymbol{\tau}_\kappa - \boldsymbol{\tau}'_\kappa \in \mathrm{box}$$

$$= 0 \qquad \text{if } \mathbf{R}_b + \boldsymbol{\tau}_\kappa - \boldsymbol{\tau}'_\kappa \notin \mathrm{box}$$

- Add back the DD part in real space

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) + C^{\mathrm{DD}}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(0,b)$$

Decomposition provided by anaddb

4. Phonon dispersion curves

X. Gonze and Ch. Lee, Phys. Rev. B 55, 10355 (1997)

Dynamical matrix at any q

- Start from the IFC in real space

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) + C^{\mathrm{DD}}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(0,b)$$

- Fourier transform back the SR part to q-space and add back the DD part

$$\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \sum_{\mathbf{d}_b \in \mathrm{box}\ (l\times m\times n)} C^{\mathrm{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} + \widetilde{C}^{\mathrm{DD}}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}).$$

- Diagonalize the dynamical matrix at q

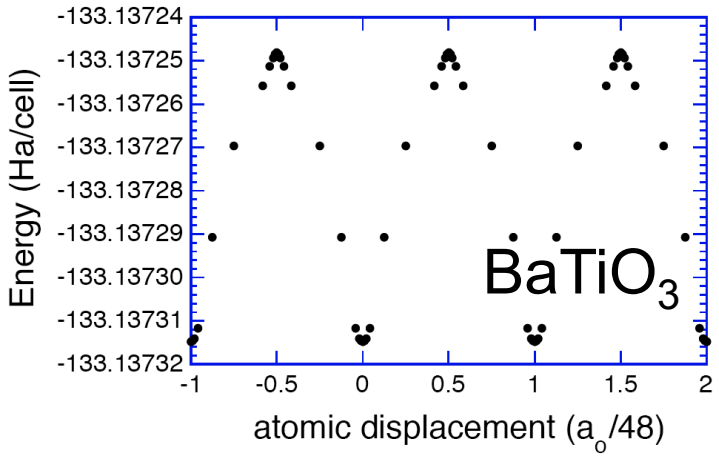
Acoustic sum rule

The crystal energy must be invariant under global translation of the whole crystal ($\omega^{AC}=0$).

- This imposes a constraint on the force constant matrix known as the **acoustic sum rule** (ASR) :

$$\sum_{\kappa'} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0})=0 \quad \text{or} \quad \sum_{\kappa' b} C_{\kappa\alpha,\kappa'\beta}(a,b)=0$$

- This relation is slightly broken due to the use of a real space grid to evaluate the exchange-correlation energy.



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Acoustic sum rule

- The ASR is restored using :

$$\widetilde{C}^{\mathrm{New}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) = \widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) - \delta_{\kappa\kappa'}\sum_{\kappa''}\widetilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0})$$

- The same “q=0 correction” used at all q

$$\widetilde{C}^{\mathrm{New}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \delta_{\kappa\kappa'}\sum_{\kappa''}\widetilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0})$$

- This is equivalent to correct the “on-site” IFC in real space

$$C^{\mathrm{New}}_{\kappa\alpha,\kappa\beta}(a,a) = -\sum_{(\kappa'',b)\neq(\kappa,a)} C_{\kappa\alpha,\kappa''\beta}(a,b)$$

Summary : ABINIT 2nd DDB

$$
\begin{array}{c} \\ \tau_A \\ \tau_B \\ E \\ \sigma \end{array}
\begin{array}{c}
\begin{array}{cccc} \tau_A & \tau_B & E & \sigma \end{array} \\
\begin{pmatrix}
D^{anal}_{AA} & D^{anal}_{AB} & Z^*_A & \zeta_A \\
D^{anal}_{AB} & D^{anal}_{BB} & Z^*_B & \zeta_B \\
Z^*_A & Z^*_B & \varepsilon^\infty & \bar{e} \\
\zeta_A & \zeta_B & \bar{e} & \bar{C}
\end{pmatrix}
\end{array}
$$

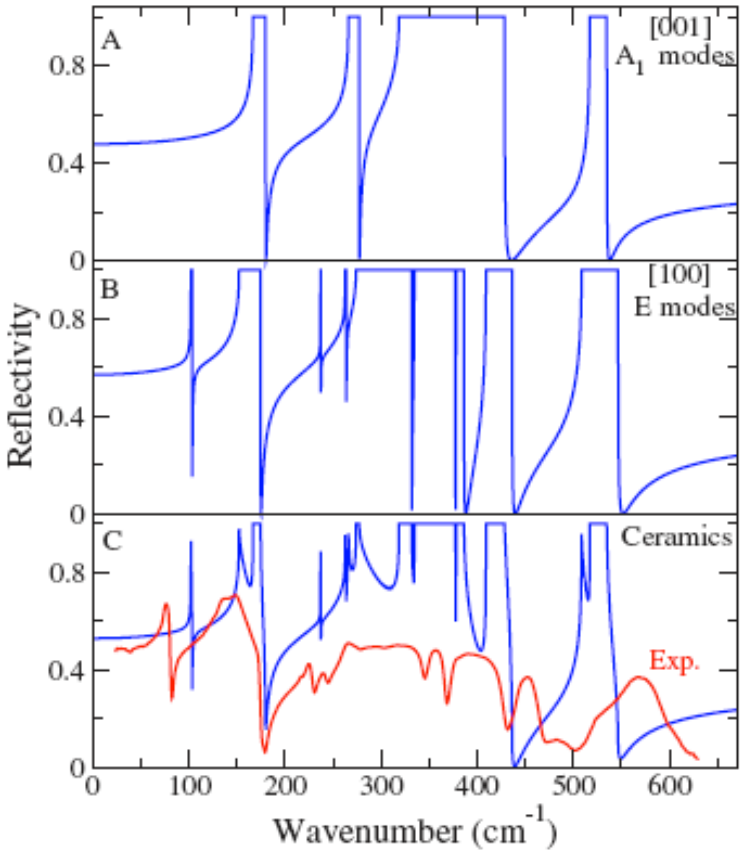
$$D = D^{anal} + \frac{Z^* Z^*}{\varepsilon^\infty} \qquad \varepsilon^0 = \varepsilon^\infty + \frac{Z^* \cdot Z^*}{D^{anal}} + \frac{e \cdot e}{C}$$

$$C = \bar{C} + \frac{\zeta\zeta}{D^{anal}} \qquad e = \bar{e} + \frac{Z^* \cdot \zeta}{D^{anal}}$$

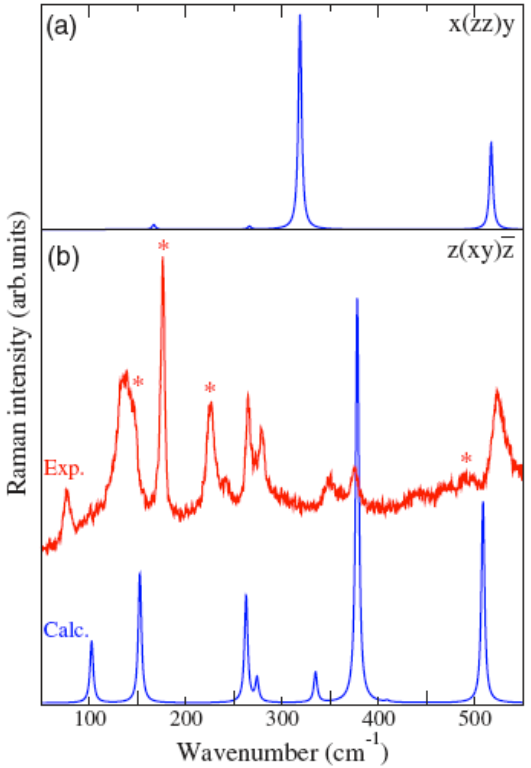
4. What can we do with that ?

Infrared and Raman spectra

$BiFeO_3$ – IR spectra



$BiFeO_3$ – Raman spectra

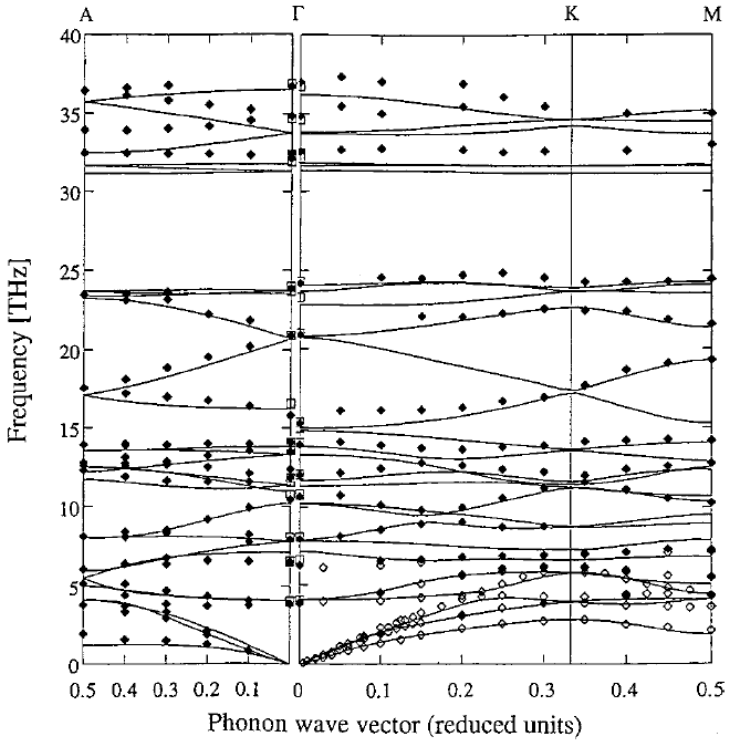


P. Hermet,[1] M. Goffinet,[1] J. Kreisel,[2] and Ph. Ghosez[1]

PHYSICAL REVIEW B **75**, 220102(R) (2007)

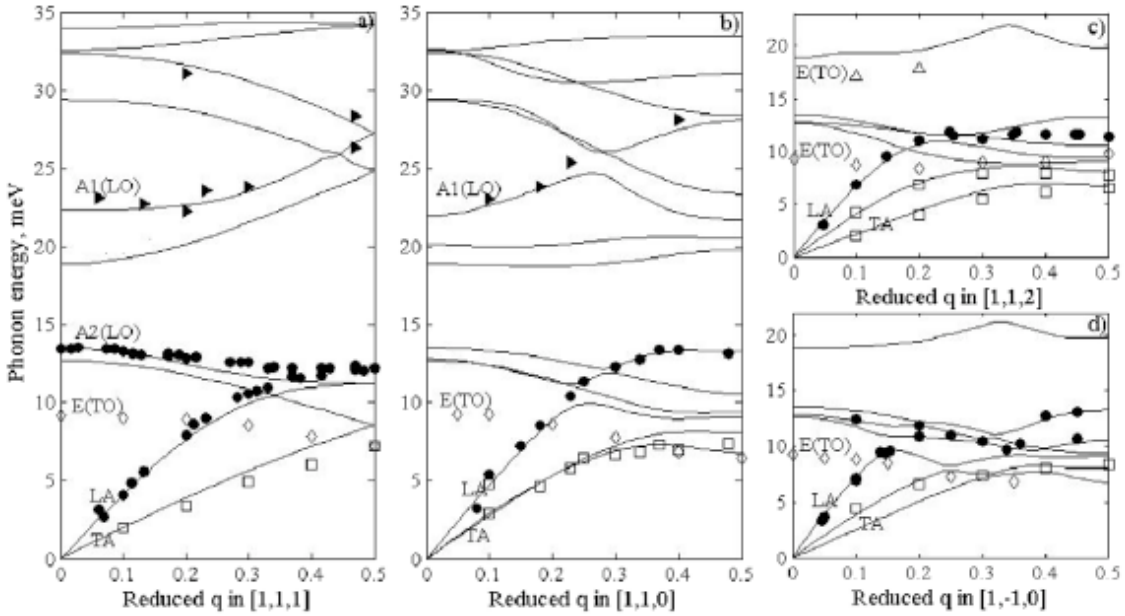
Phonon dispersion curves

α-quartz



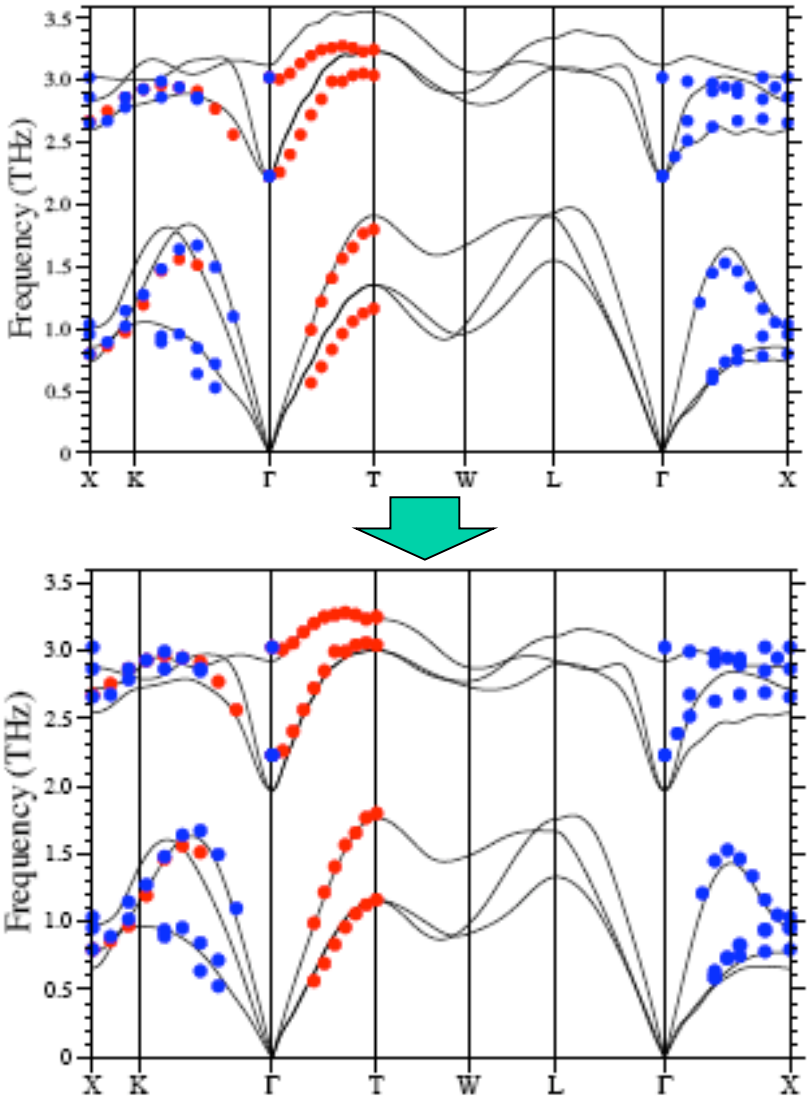
Gonze, X., J.-C. Charlier, D. C. Allan, and M. P. Teter, 1994, Phys. Rev. B **50**, 13035.

$BiFeO_3$



Borissenko et al., J. Phys. Condens. Matter 25, 102201 (2013)

Dispersion curves of Bi



Full line DFPT without spin-orbit

Only very old experimental data available

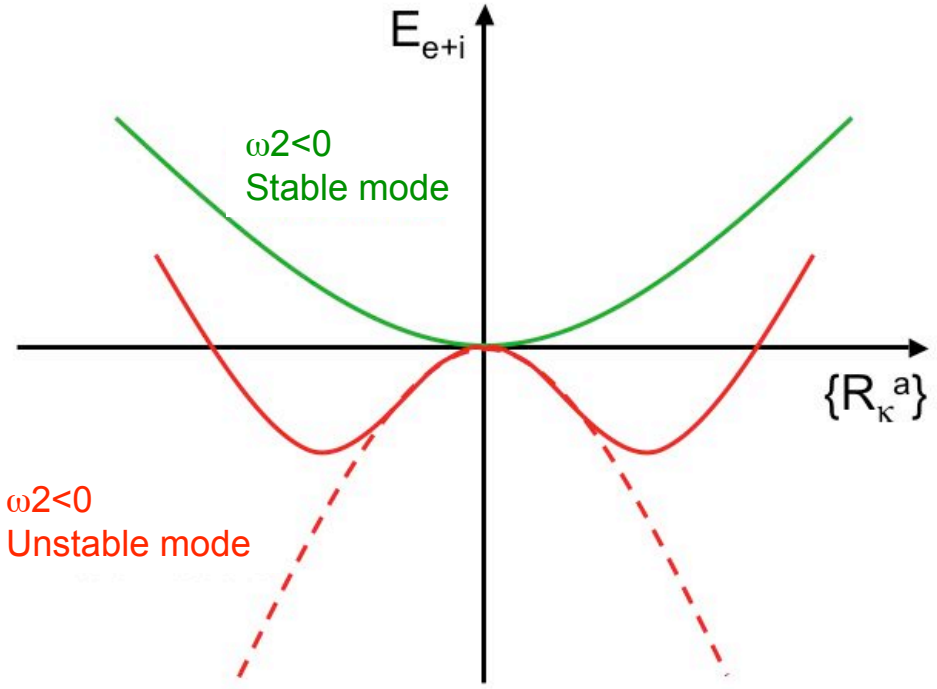
- Yarnell et al, IBM J.Res. Dev. 1964
- Smith, internal report Los Alamos 1967

10-15% change due to Spin-orbit coupling

Full line DFPT with spin-orbit

LE. Diaz-Sanchez, A.H. Romero, X. Gonze, Phys. Rev. B 76, 104302 (2007)

Structural instabilities



Structural instability : Negative curvature

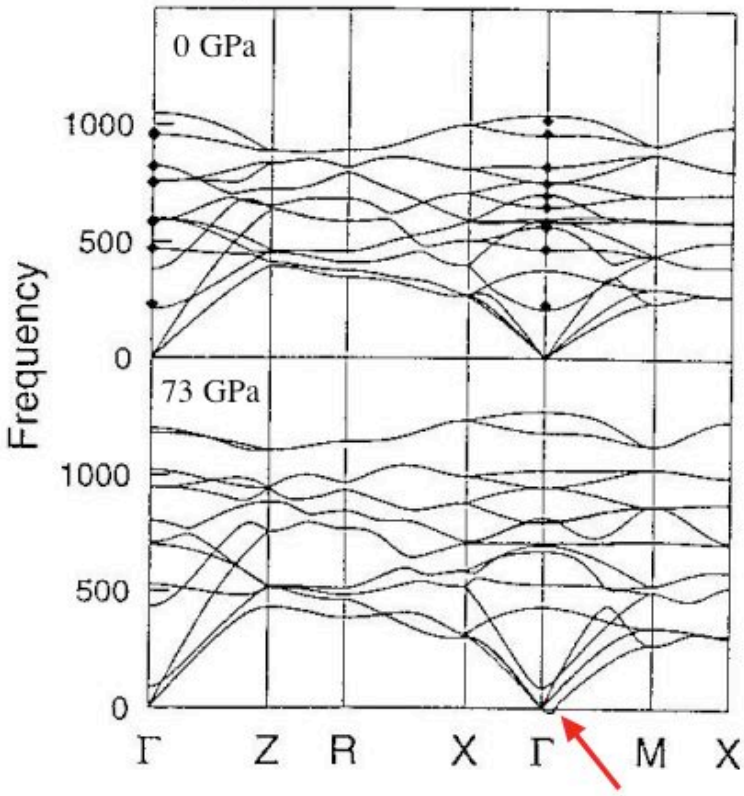
$\omega^2<0$

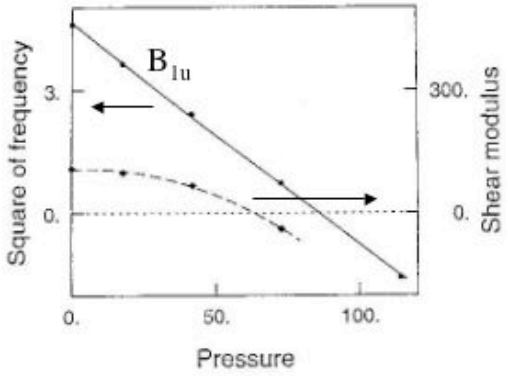
ω *imaginary* (unstable mode)

Instability of stishovite under pressure

Phonon softening under pressure

SiO_2 - stishovite

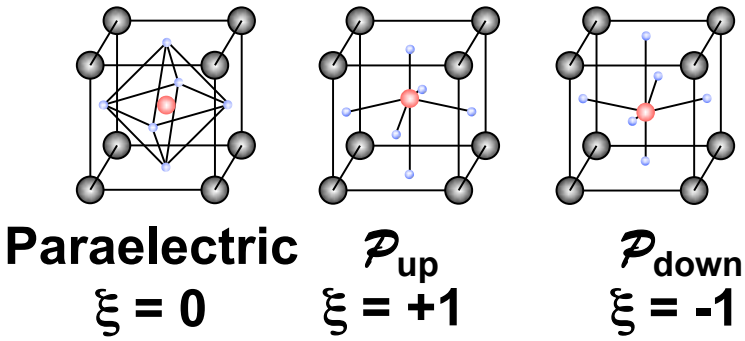


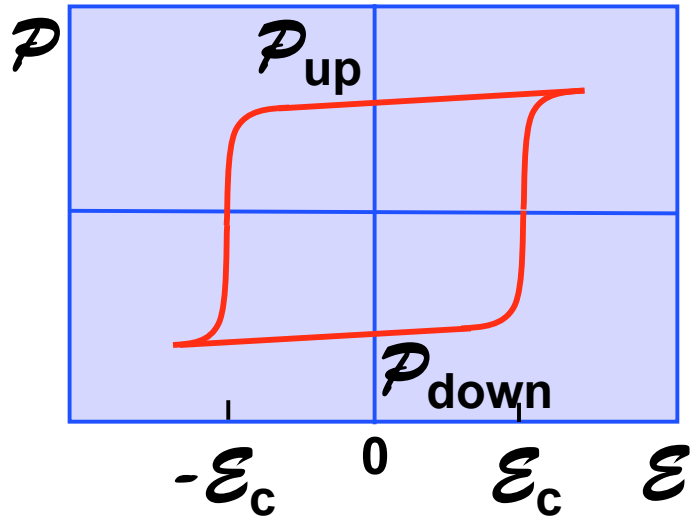


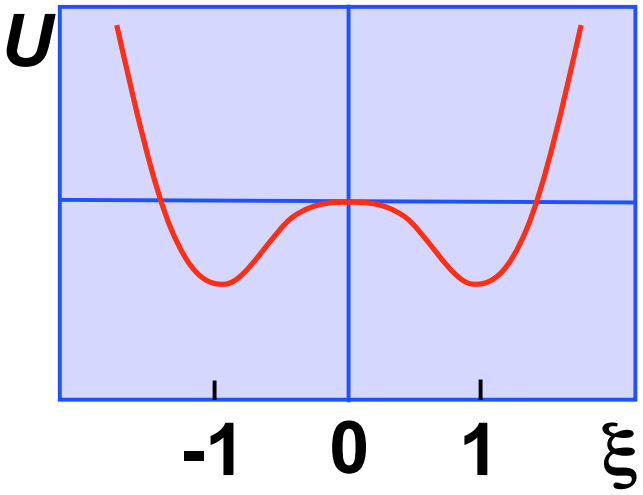
Ferroelastic transition from stishovite to rutile-type structure

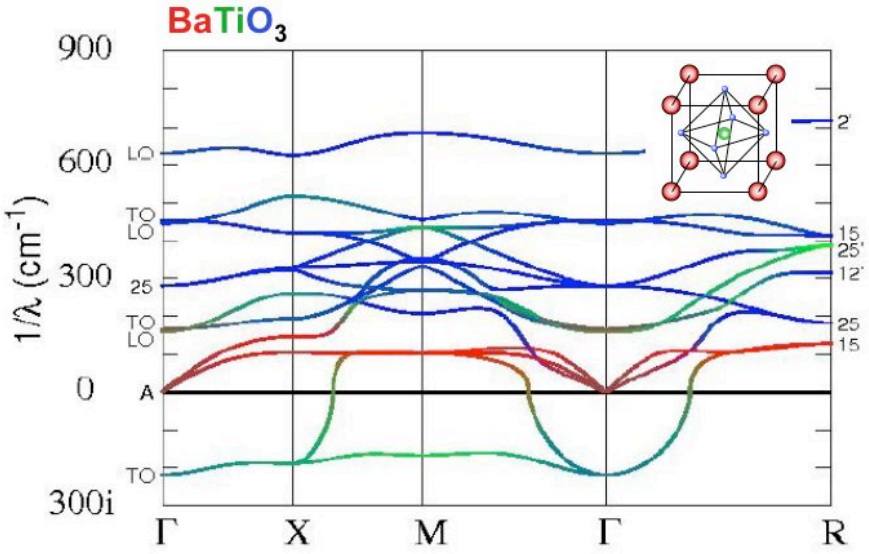
Ch. Lee and X. Gonze, Phys. Rev. B 56, 7321 (1997)

Ferroelectric instability of $BaTiO_3$

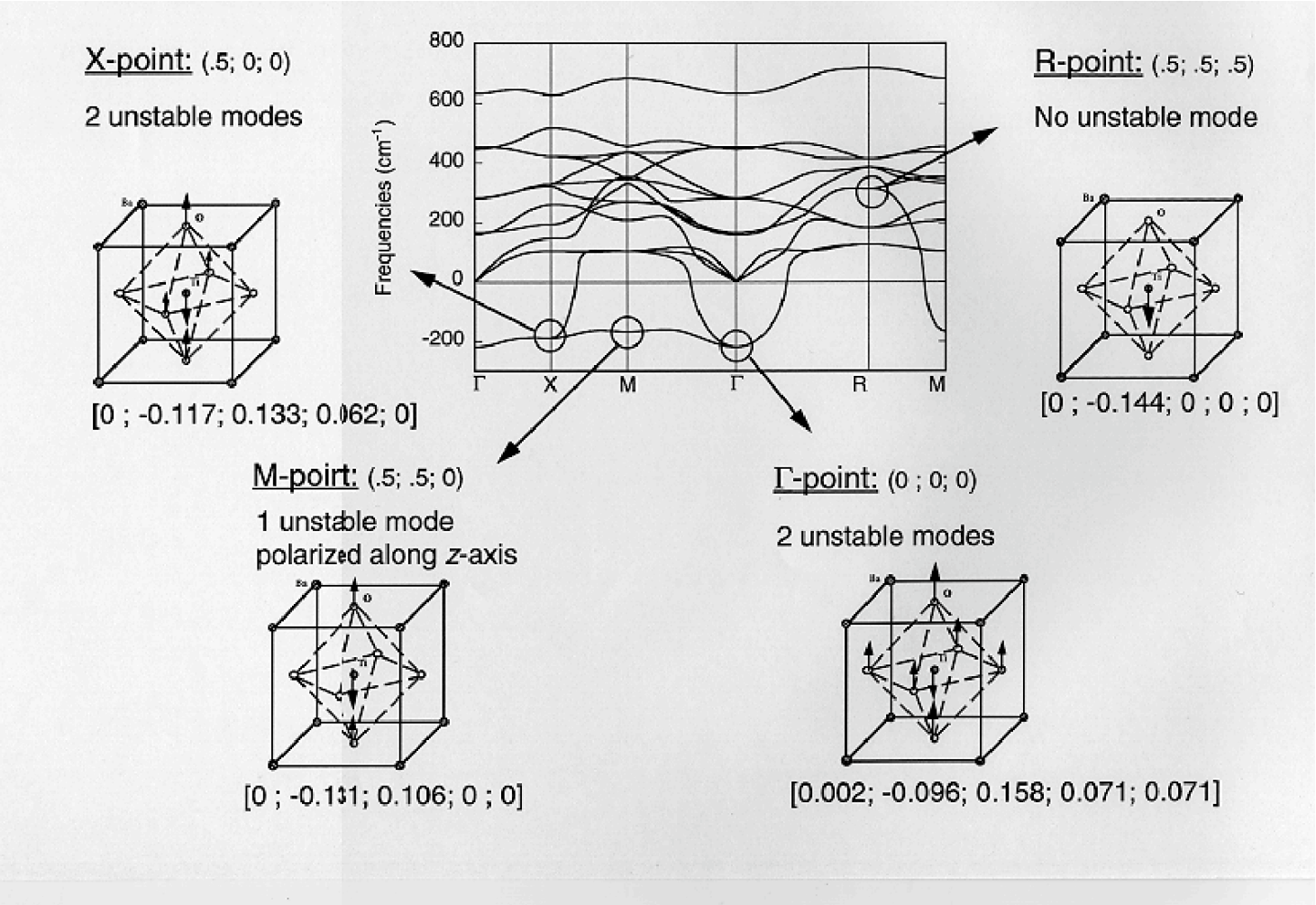




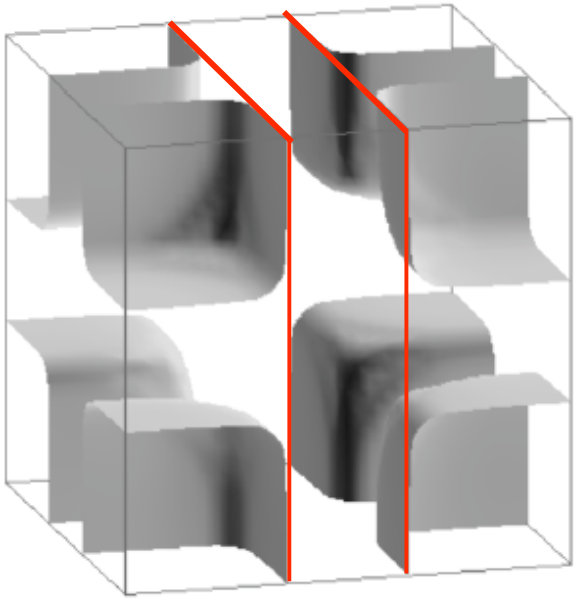


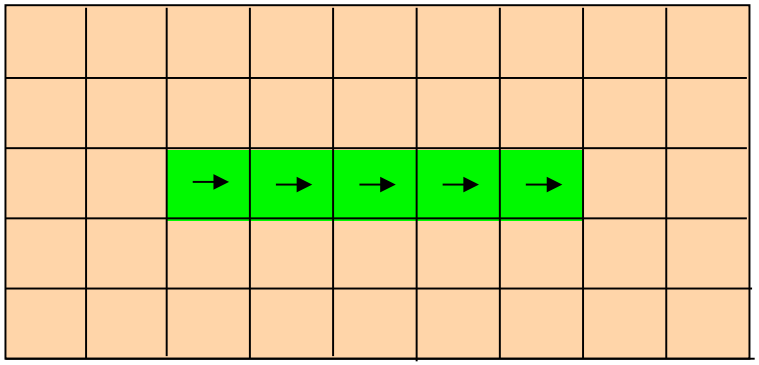


Ferroelectric instability of $BaTiO_3$



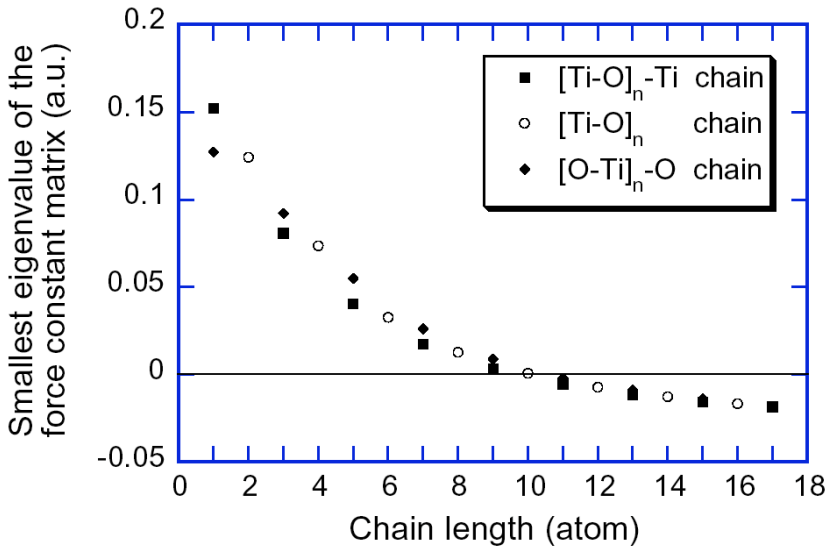
Ferroelectric instability of $BaTiO_3$





Instability for correlated displacements only

2-D instability in reciprocal space
Chain of correlation in real space



*Ph. Ghosez, X. Gonze and J.-P. Michenaud.*Ferroelectrics 206, 205-217 (1998).

Ferroelectric instability of $BaTiO_3$

Cochran's model:

Competetion between SR and LR forces

$$\underbrace{\langle \eta | D | \eta \rangle}_{\omega^2} = \underbrace{\langle \eta | D^{SR} | \eta \rangle}_{\omega^2_{SR}} + \underbrace{\langle \eta | D^{DD} | \eta \rangle}_{\omega^2_{DD}}$$

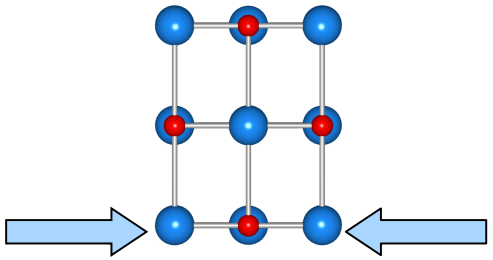
<0 >>0 <<<0

	$F_{1u}(TO1)$	$F_{1u}(TO2)$	$F_{1u}(TO3)$	F_{2u}
ω^2_{DD}	-625897	7232	-130549	109745
	(-745610)	(8615)	-155518)	130736)
ω^2_{SR}	613107	26538	361998	-26951
	(732820)	(25155)	(386967)	(-47942)
ω^2	-12790	33770	231449	82794

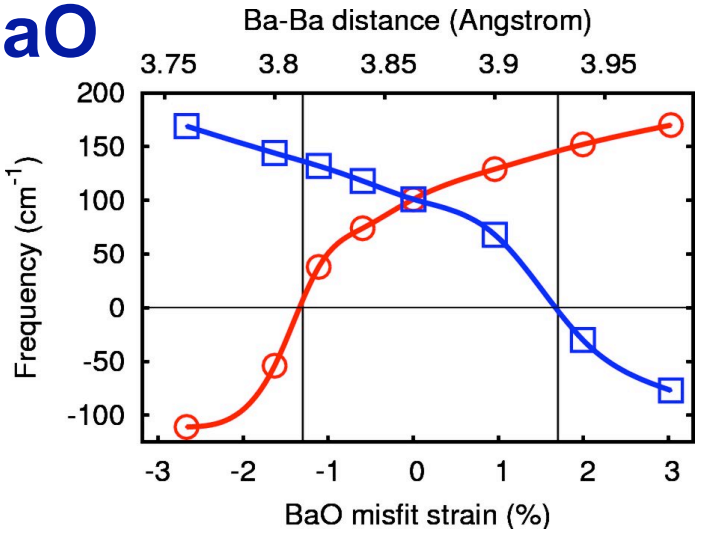
Ph. Ghosez, X. Gonze and J.-P. Michenaud, Europhys. Lett. 33, 713-718 (1996).

Strain induced ferroelectricity

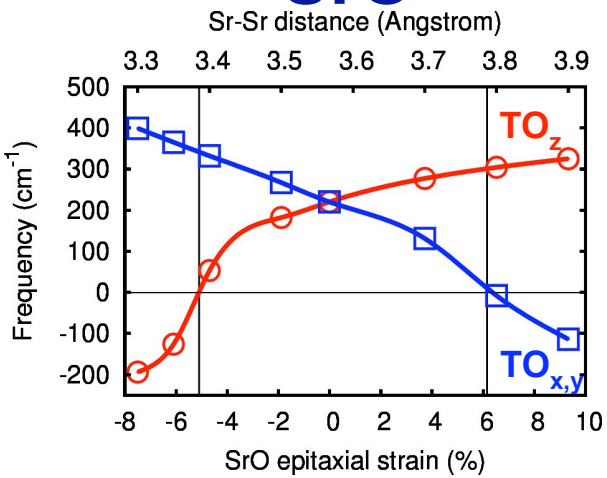
Role of epitaxial strain on rocksalt binary oxides



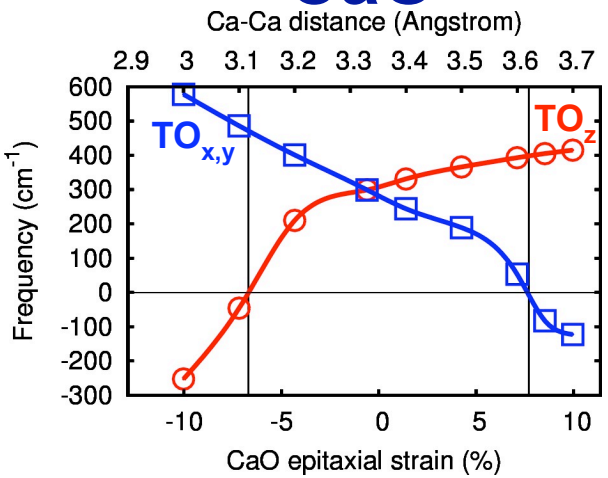
BaO



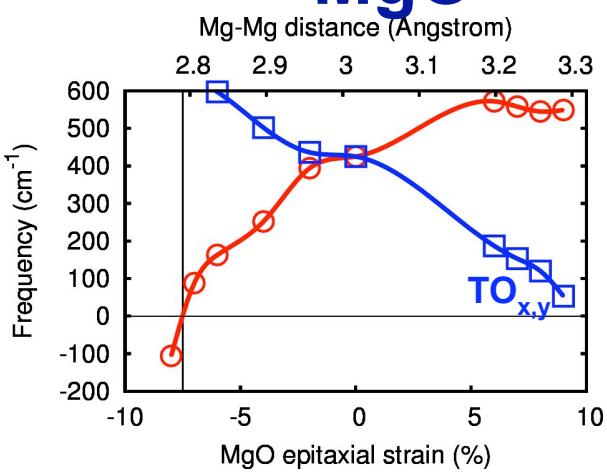
SrO



CaO

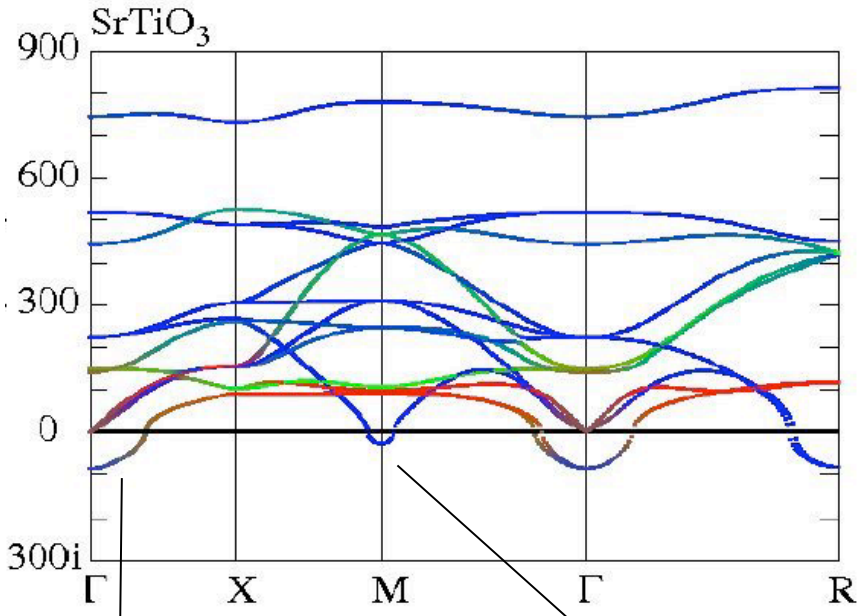


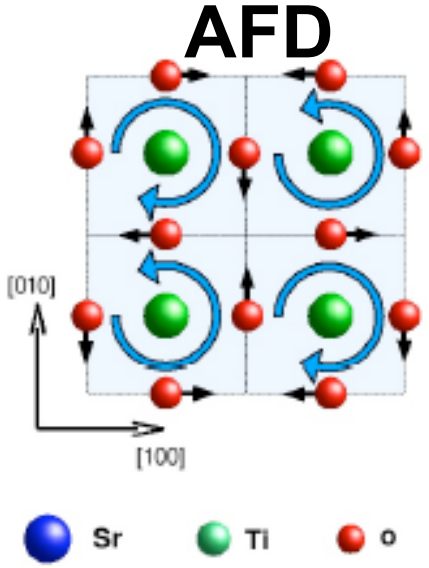
MgO

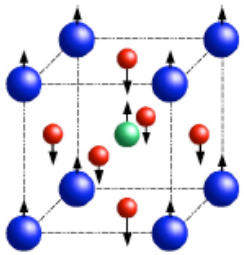


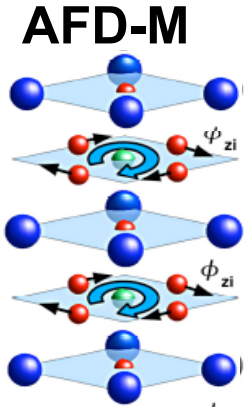
E. Bousquet, N. Spaldin and Ph. Ghosez, Phys. Rev. Lett. 104, 037601 (2010)

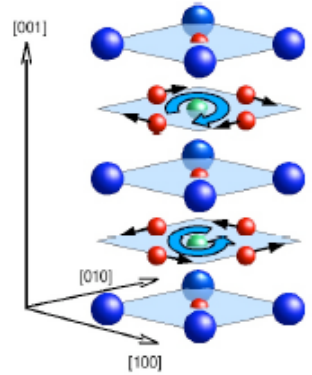
FE and AFD instabilities of $SrTiO_3$

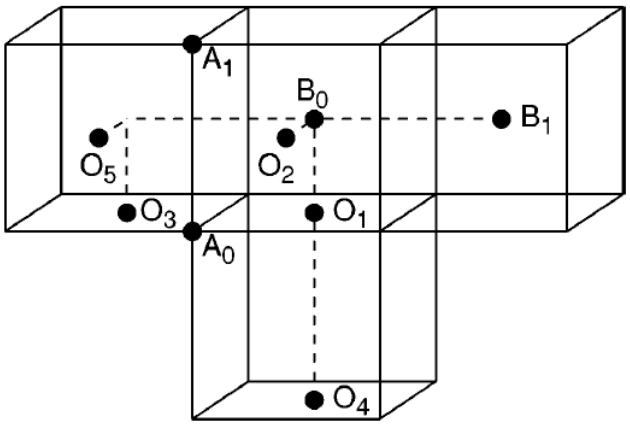












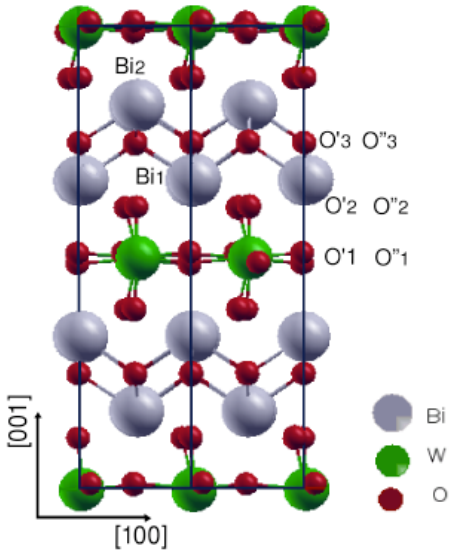
Analysis of IFC

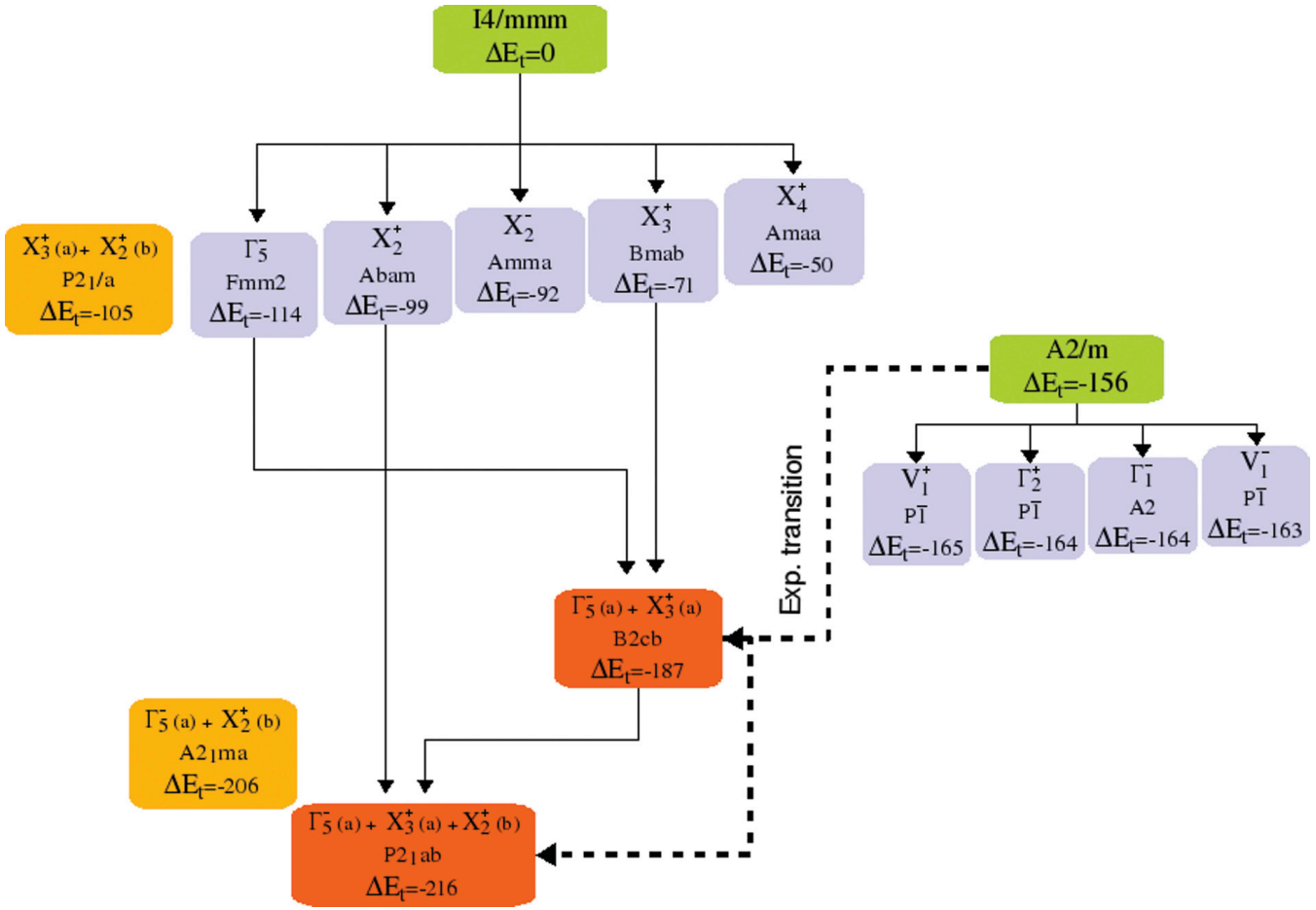
Comparison of the IFC between different perovskites

Atom		$BaTiO_3$ Total	$BaTiO_3$ DD	$BaTiO_3$ SR	$PbTiO_3$ Total	$PbTiO_3$ DD	$PbTiO_3$ SR	$PbZrO_3$ Total	$PbZrO_3$ DD	$PbZrO_3$ SR
B_0-O_1	(∥)	+0.0094	+0.2325	−0.2231	−0.0012	+0.1865	−0.1877	−0.0687	+0.1380	−0.2067
	(⊥)	−0.0211	−0.0430	+0.0218	−0.0178	−0.0417	+0.0239	−0.0100	−0.0358	+0.0258
B_0-B_1	(∥)	−0.0672	−0.0368	−0.0304	−0.0615	−0.0285	−0.0330	−0.0499	−0.0211	−0.0288
	(⊥)	+0.0075	+0.0184	−0.0109	+0.0065	+0.0142	−0.0077	+0.0054	+0.0105	−0.0052
B_0-O_4	(∥)	+0.0156	+0.0086	+0.0070	+0.0135	+0.0069	+0.0066	+0.0106	+0.0051	+0.0055
	(⊥)	+0.0009	−0.0016	+0.0007	+0.0015	−0.0015	+0.0006	+0.0012	−0.0013	+0.0002
B_0-A_0	(∥)	−0.0286	−0.0212	−0.0074	−0.0277	−0.0241	−0.0036	−0.0271	−0.0216	−0.0054
	(⊥)	+0.0134	+0.0106	+0.0028	+0.0157	+0.0121	+0.0036	+0.0145	+0.0108	+0.0037
	(xx)	−0.0006	+0.0000	−0.0006	+0.0012	+0.0000	+0.0012	+0.0007	+0.0000	+0.0007
A_0-O_1	(∥)	−0.0004	+0.0114	−0.0118	+0.0108	+0.0162	−0.0054	+0.0139	+0.0169	−0.0030
	(zz)	−0.0108	−0.0154	+0.0045	−0.0110	−0.0181	+0.0071	−0.0103	−0.0163	+0.0060
A_0-A_1	(∥)	−0.0112	−0.0052	−0.0060	−0.0108	−0.0086	−0.0022	−0.0094	−0.0093	−0.0001
	(⊥)	+0.0038	+0.0025	+0.0012	+0.0054	+0.0043	+0.0011	+0.0056	+0.0047	+0.0009

Ph. Ghosez, E. Cockayne, U.V. Waghmare and K. M. Rabe, Phys. Rev. B 60, 836 (1999)

Analysis of distorted structure





Hania Djani,[1,2,*] Eric Bousquet,[3,4] Abdelhafid Kellou,[2] and Philippe Ghosez[3]

PHYSICAL REVIEW B **86**, 054107 (2012)

Analysis of distorted structure

Phase	A	Γ_5^- [198i]	X_2^- [183i]	X_2^+ [135i]	X_3^+ [104i]	X_4^+ [98i]	Γ_5^- [29]	X_2^- [80]	X_3^+ [107]	Γ_5^- [137]
Phases arising from single-mode condensation										
$Fmm2$	361.0	0.84					0.51			0.11
$Amma$	395.6		0.79					0.60		
$Abam$	444.7			0.99						
$Bmab$	444.5				0.98				0.14	
$Amaa$	384.0					0.99				
Experimentally observed phases										
$B2cb$	601.0	0.53			0.79		0.24			0.09
$P2_1ab$	582.7	0.52		0.59	0.55		0.04		0.1	0.09
Hypothetical phases										
$A2_1ma$	514.5	0.58		0.78			0.01			0.11
$P2_1/a$	455.0			0.76	0.62				0.11	

$$\Delta = \sum_i Q_i \eta_i,$$

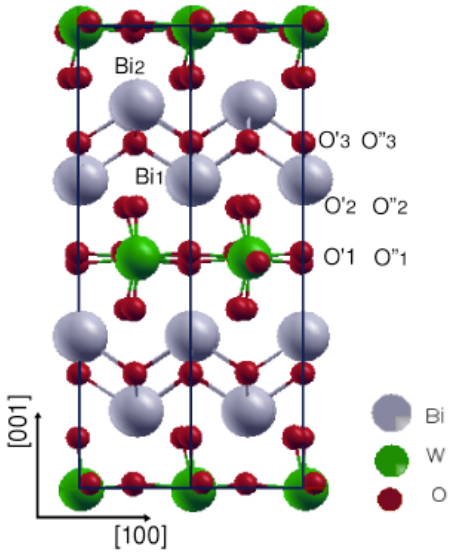
$$Q_i = A\alpha_i = \langle \eta_i | M | \Delta \rangle.$$

$$A = \langle \Delta_i | M | \Delta \rangle$$

$$\begin{aligned}
&\Delta E_t\left(Q_{\Gamma_5^-}, Q_{X_2^+}, Q_{X_3^+}\right) \\
&\quad = -2.50 Q_{\Gamma_5^-}^2 - 7.50 \times 10^{-1} Q_{X_3^+}^2 - 1.03 Q_{X_2^+}^2 \\
&\qquad + 1.36 \times 10^{-5} Q_{\Gamma_5^-}^4 + 1.97 \times 10^{-6} Q_{X_3^+}^4 \\
&\qquad + 2.65 \times 10^{-6} Q_{X_2^+}^4 + 2.10 \times 10^{-6} Q_{\Gamma_5^-}^2 Q_{X_3^+}^2 \\
&\qquad - 1.79 \times 10^{-9} Q_{\Gamma_5^-}^2 Q_{X_2^+}^2 + 1.79 \times 10^{-6} Q_{X_3^+}^2 Q_{X_2^+}^2 .
\end{aligned}$$

Analysis of distorted structure

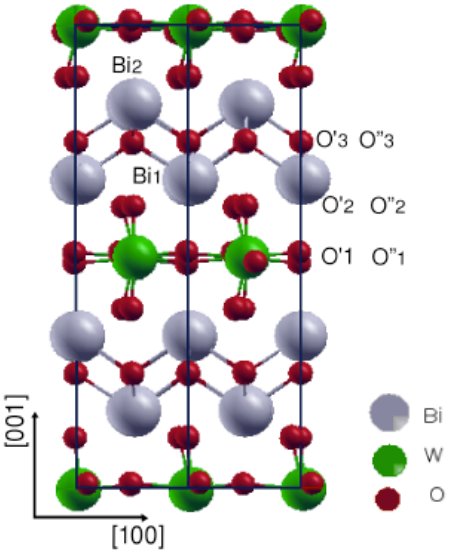
$P2_1ab$ ferroelectric phase of Bi_2WO_6



Atoms	Calculated (0 K)			Experimental (300 K)		
	x/a	y/b	z/c	x/a	y/b	z/c
Bi_1	-0.0109	0.5102	0.1698	-0.0126	0.5191	0.1726
Bi_2	-0.0036	0.4872	-0.1698	-0.0113	0.4839	-0.1722
W	0.0000	-0.0055	0.0000	0.0000	0.0077	-0.0004
O'_1	0.1679	0.7039	-0.0108	0.2679	0.7015	-0.0151
O''_1	0.2682	0.1951	0.0109	0.3342	0.2297	0.0159
O'_2	0.4532	0.5363	0.1114	0.5703	0.5603	0.1082
O''_2	-0.0355	0.0491	-0.1108	0.0854	0.0526	-0.1076
O'_3	0.2464	0.2519	0.2483	0.2740	0.2403	0.2511
O''_3	0.2541	0.2468	0.7484	0.2728	0.2585	0.7485

Good of bad agreement ?

Analysis of distorted structure



$P2_1ab$ ferroelectric phase of Bi_2WO_6

Modes	frequencies	Experimental		Calculated	
		α_i	$Q_i = \mathrm{A}\ \alpha_i$	α_i	$Q_i = \mathrm{A}\ \alpha_i$
Γ_5^-	i198 cm^{-1}	0.56	-4.28.23	0.52	303.73
X_2^+	i135 cm^{-1}	0.30	231.48	0.59	344.90
X_3^+	i104 cm^{-1}	0.59	455.26	0.55	-325.51
Γ_5^-	29 cm^{-1}	0.35	-266.02	0.04	26.022

More relevant comparison between relaxed and experimental structure !

5. Thermodynamical properties

Ch. Lee and X. Gonze, Phys. Rev. B 51, 8610 (1995)
G.-M. Rignanese, J.-P. Michenaud and X. Gonze, Phys. Rev. B 53, 4488 (1996)

Statistical physics :

In the harmonic approximation, the vibrations of the lattice (also called **phonons**) can be treated as gas of independent particles. They obey the Bose-Einstein statistics :

$$n(\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

The internal energy of the boson gas can be calculated directly using the standard formula:

$$U_{phon} = \int_0^{\omega_{\max}} \hbar\omega \left(n(\omega) + \frac{1}{2} \right) g(\omega) d\omega$$

Energy of the harmonic oscillator

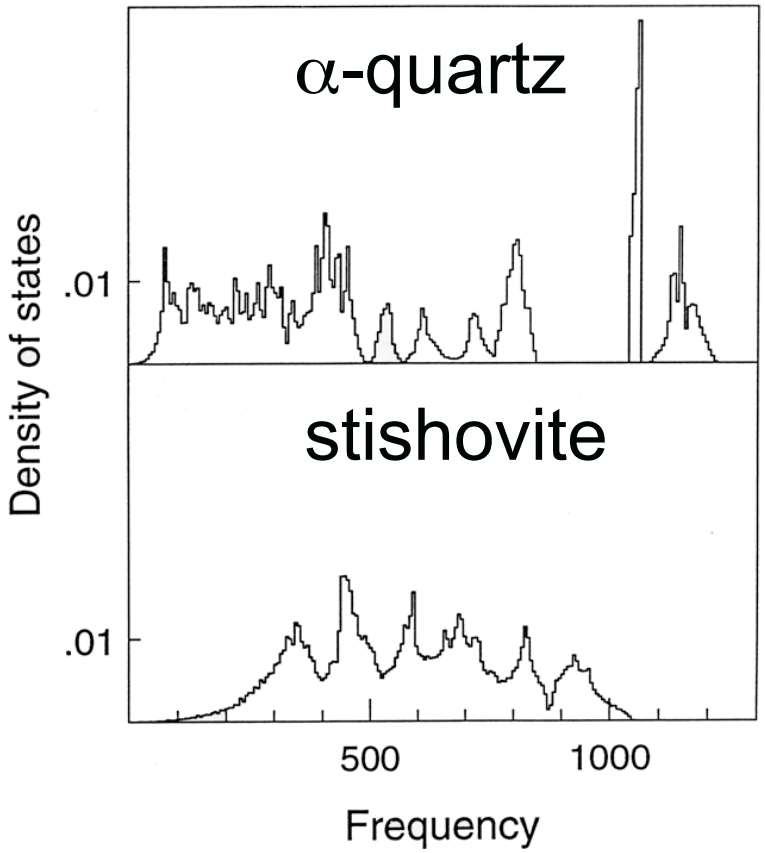
Phonon density of states

All vibrational contributions to thermodynamic properties, in the harmonic approximation, can be calculated in this manner.

Phonon density of states (DOS)

For each frequency channel, one counts the “number” of phonon modes

$$g_{norm}(\omega) = \frac{1}{3n_{at}N} \sum_{m\vec{q}} \delta(\omega - \omega_{m\vec{q}})$$



Thermodynamical properties

- Phonon DOS gives access to the vibrational contribution to various quantities:

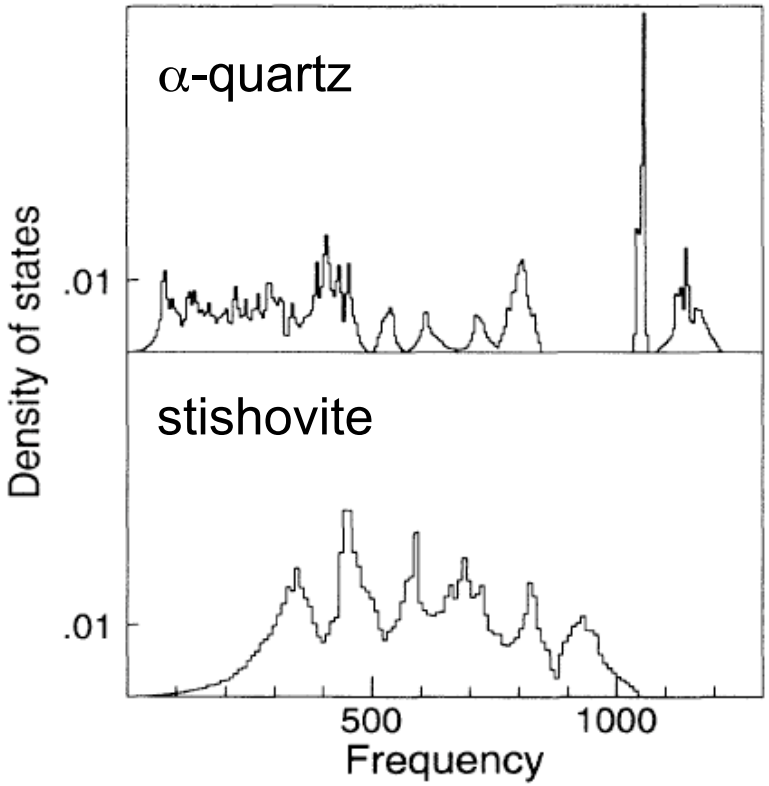
$$\Delta F = 3nNk_BT \int_0^{\omega_L} \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\} g(\omega)d\omega \ , \qquad (1)$$

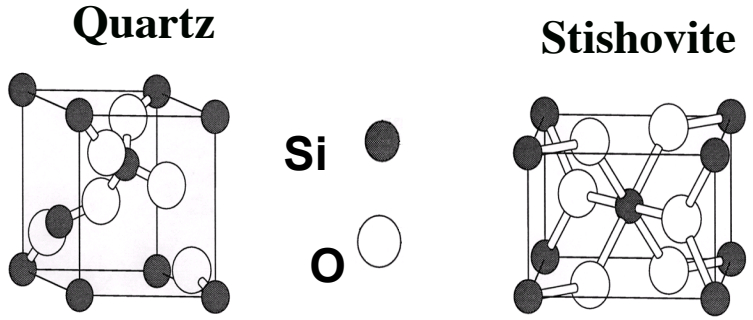
$$\Delta E = 3nN\frac{\hbar}{2} \int_0^{\omega_L} \omega\coth\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \ , \qquad (2)$$

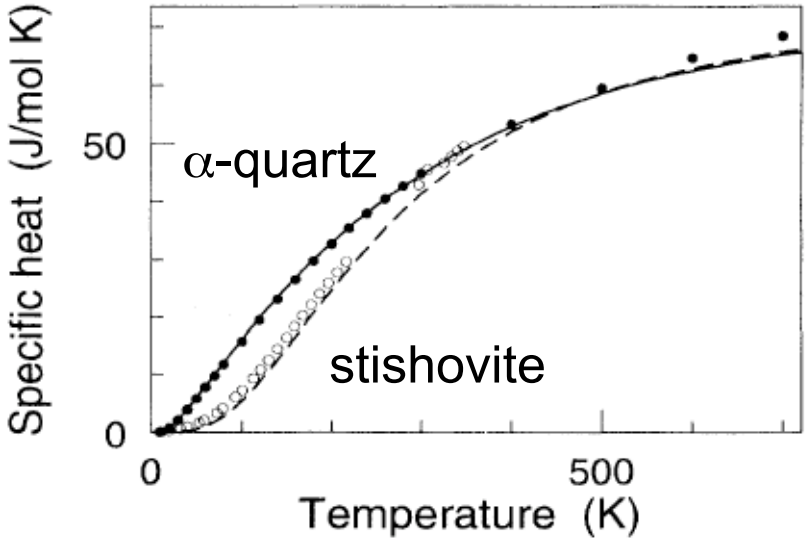
$$C_v = 3nNk_B \int_0^{\omega_L} \left(\frac{\hbar\omega}{2k_BT}\right)^2 \mathrm{csch}^2\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \ , \qquad (3)$$

$$S = 3nNk_B \int_0^{\omega_L} \left[\frac{\hbar\omega}{2k_BT}\coth\frac{\hbar\omega}{2k_BT} - \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\}\right] \times g(\omega)d\omega \ , \qquad (4)$$

SiO_2 α-quartz versus stishovite







Ch. Lee and X. Gonze, Phys. Rev. B 51, 8610 (1995)

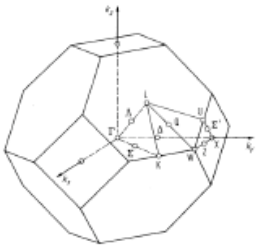
Thermal expansion

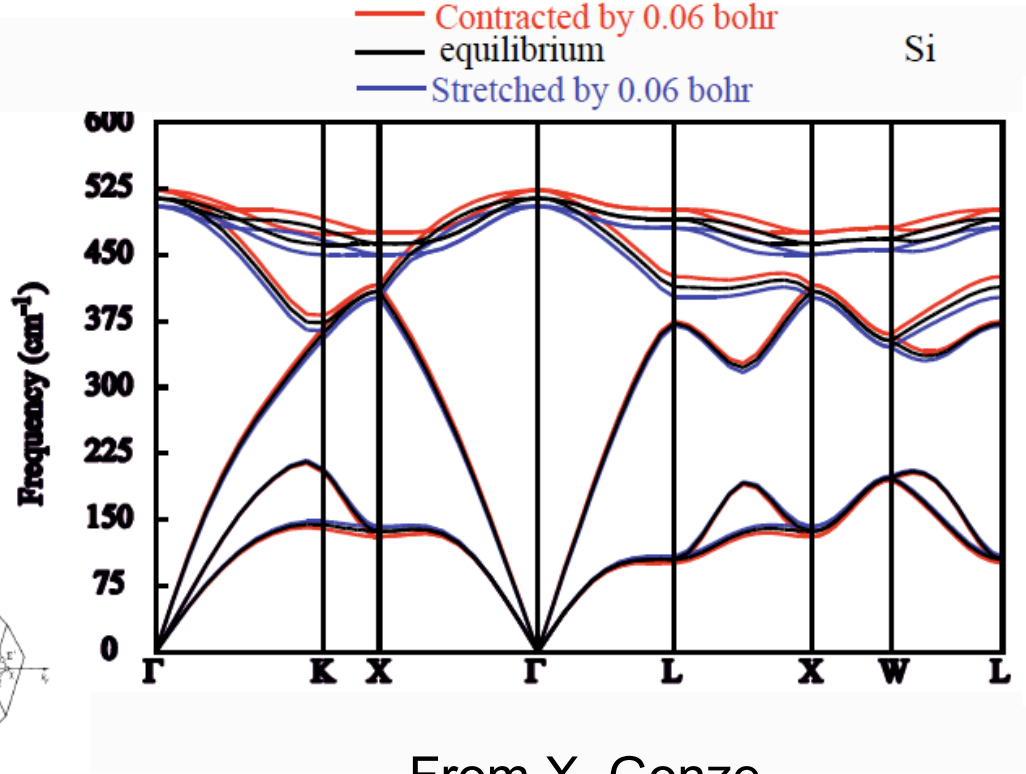
$$\alpha(T) = \frac{V}{3B}\sum_{\vec{q},m}\frac{1}{\hbar\omega_{\vec{q},m}}\gamma_{\vec{q},m}\frac{\partial n(\omega_{\vec{q},m})}{\partial T}$$

Grüneisen parameters :

$$\gamma_{m,\vec{q}} = -\frac{\partial(\ln\omega_{m,\vec{q}})}{\partial(\ln V)}$$

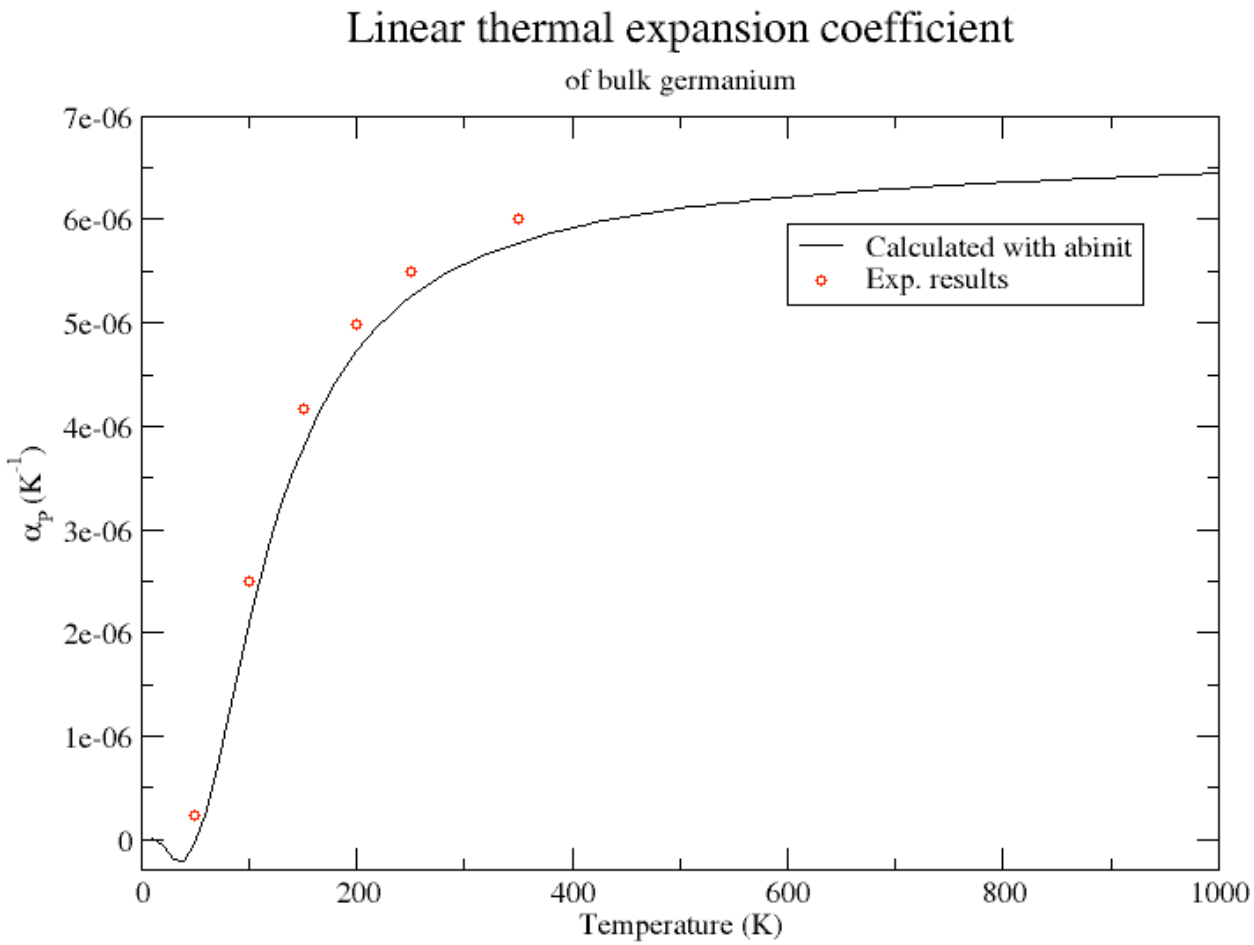
To be computed from finite differences





From X. Gonze

Thermal expansion



From X. Gonze