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Département de Physique
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ABINIT School

Analysis of atomic distortions

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Born-Oppenheimer energy

Solid : interacting electrons and nuclei

- General problem :

$$H(\mathbf{r},\mathbf{R})\,\Phi(\mathbf{r},\mathbf{R}) = E\,\Phi(\mathbf{r},\mathbf{R})$$

$$\downarrow$$

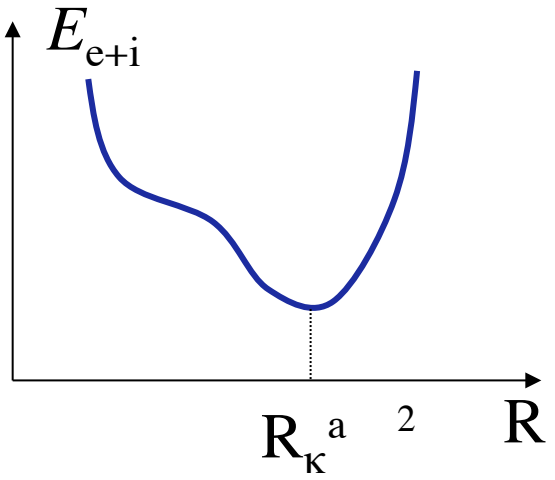
$$H(\mathbf{r},\mathbf{R}) = T_i(\mathbf{R}) + U_{ii}(\mathbf{R}) + T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{ie}(\mathbf{r},\mathbf{R})$$

- Born-Oppenheimer approximation

$M_\kappa >> m_e \rightarrow T_i(\mathbf{R})$

$$H_{e+i}(\mathbf{r},\mathbf{R}) = T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{ie}(\mathbf{r},\mathbf{R}) + U_{ii}(\mathbf{R})$$

$$H_{e+i}(\mathbf{r},\mathbf{R})\,\varphi(\mathbf{r},\mathbf{R}) = E_{e+i}(\mathbf{R})\,\varphi(\mathbf{r},\mathbf{R})$$



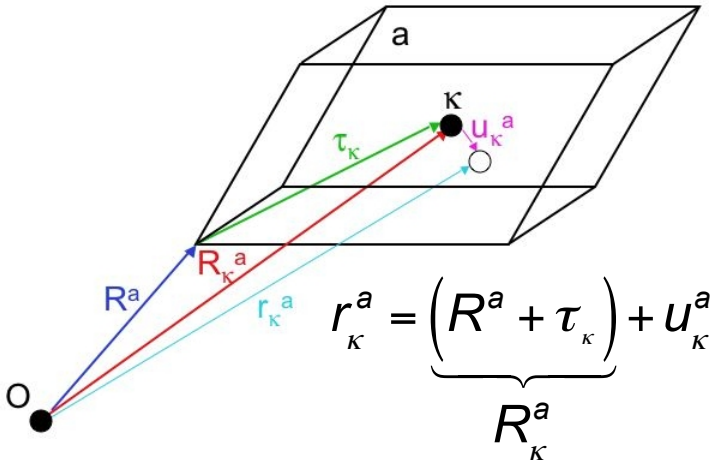
ABINIT total energy $E_{tot}(R)$ corresponds to the Born-Oppenheimer energy $E_{e+i}(R)$

Background

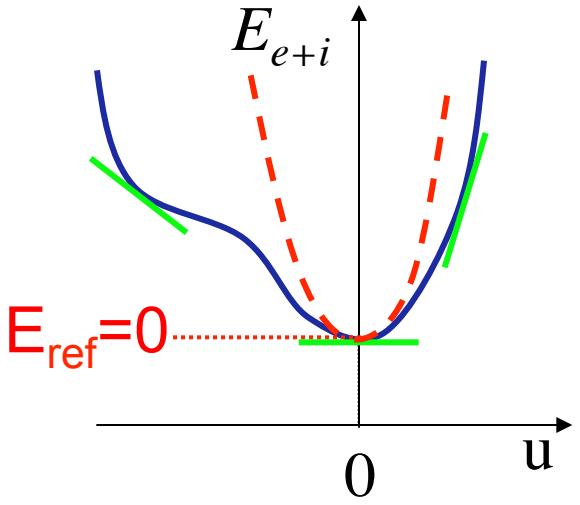
Phonons: harmonic approximation

$$E_{e+i}\left(r_\kappa^a\right) = E_{e+i}\left(R_\kappa^a\right) - \sum_{\kappa\alpha a} \underbrace{F_{\kappa\alpha}^a}_{\frac{\partial E}{\partial r_{\kappa\alpha}^a}} u_{\kappa\alpha}^a$$

$$+\frac{1}{2}\sum_{\substack{\kappa\alpha a \\ \kappa'\beta b}} \underbrace{C_{\kappa\alpha,\kappa'\beta}^{ab}}_{\frac{\partial^2 E}{\partial r_{\kappa\alpha}^a \partial r_{\kappa'\beta}^b}} u_{\kappa\alpha}^a u_{\kappa'\beta}^b$$



- Interatomic Force Constant (IFC) :
  - $\kappa \neq \kappa'$: $C_{\kappa\kappa'} = -K_{\kappa\kappa'}$
  - $\kappa = \kappa'$: $C_{\kappa\kappa} = -\Sigma' C_{\kappa\kappa'}$



Configuration space with
3 x N_{at} degrees of freedom

Eigenmodes of vibration

- Equation of motion :

$$M_\kappa \ddot{u}^a_{\kappa\alpha} = -\sum_{\kappa'\beta b} C^{ab}_{\kappa\alpha,\kappa'\beta} u^b_{\kappa'\beta}$$

- Solution :

$$\begin{aligned} u^a_{\kappa\alpha} &= \eta^a_{\kappa\alpha} e^{-i\omega t} \\ &= \eta^{\mathbf{k}}_{\kappa\alpha} e^{i\mathbf{k}.\mathbf{R}_a} e^{-i\omega t} \end{aligned}$$

$$\omega^2 M_\kappa \eta^{\mathbf{k}}_{\kappa\alpha} = \sum_{\kappa'\beta} \eta^{\mathbf{k}}_{\kappa'\beta} \Big(\sum_b C^{ab}_{\kappa\alpha,\kappa'\beta} e^{i\mathbf{k}.(\mathbf{R}_b - \mathbf{R}_a)} \Big)$$

$$\tilde{C}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} = \sum_b C^{0b}_{\kappa\alpha,\kappa'\beta} e^{i\mathbf{k}.\mathbf{R}_b}$$

$$\omega^2 M_\kappa \eta^{\mathbf{k}}_{\kappa\alpha} = \sum_{\kappa'\beta} \tilde{C}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} \eta^{\mathbf{k}}_{\kappa'\beta}$$

"Generalized" eigenvalue problem

Dynamical equation

$$\omega^2 M_\kappa \eta^{\mathbf{k}}_{\kappa\alpha} = \sum_{\kappa'\beta} \tilde{C}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} \eta^{\mathbf{k}}_{\kappa'\beta}$$

- If we define :

$$\begin{aligned} \tilde{D}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} &= \tilde{C}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} / \sqrt{M_\kappa M_{\kappa'}} \\ \gamma^{k}_{\kappa\alpha} &= \sqrt{M_\kappa}\eta^{k}_{\kappa\alpha} \end{aligned}$$

$$\sum_{\kappa'\beta} \tilde{D}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} \gamma^{\mathbf{k}}_{\kappa'\beta} = \omega^2 \gamma^{\mathbf{k}}_{\kappa\alpha}$$

Dynamical equation

Classical eigenvalue problem

Frequencies and eigendisplacements

ANADDB

$$\sum_{\kappa'\beta} \tilde{D}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta}\gamma^{\mathbf{k}}_{\kappa'\beta} = \omega^2\gamma^{\mathbf{k}}_{\kappa\alpha}$$

Phonon frequency

Phonon eigenvector $< \gamma^{\mathbf{k}} | \gamma^{\mathbf{k}} >= 1$

Phonon eigendisplacement $\gamma^{k}_{\kappa\alpha} = \sqrt{M_\kappa}\eta^{k}_{\kappa\alpha}$

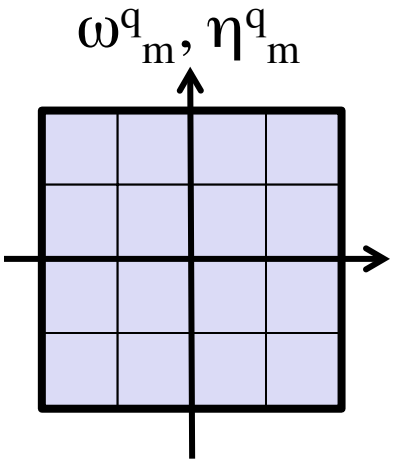
$< \eta^{\mathbf{k}} | M | \eta^{\mathbf{k}} >= 1$

Dynamical matrix

$$\tilde{D}^{\mathbf{k}}_{\kappa\alpha,\kappa'\beta} = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \frac{\partial^2 E}{\partial\eta^{\mathbf{k}}_{\kappa\alpha}\partial\eta^{\mathbf{k}}_{\kappa'\beta}}$$

Second energy derivatives from DFPT

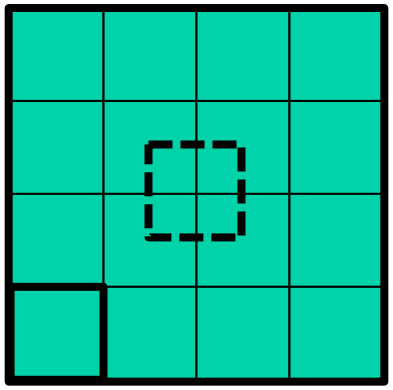
From atom to phonon basis



m-bands : $3xn_{at}$
q-points : NxNxN grid

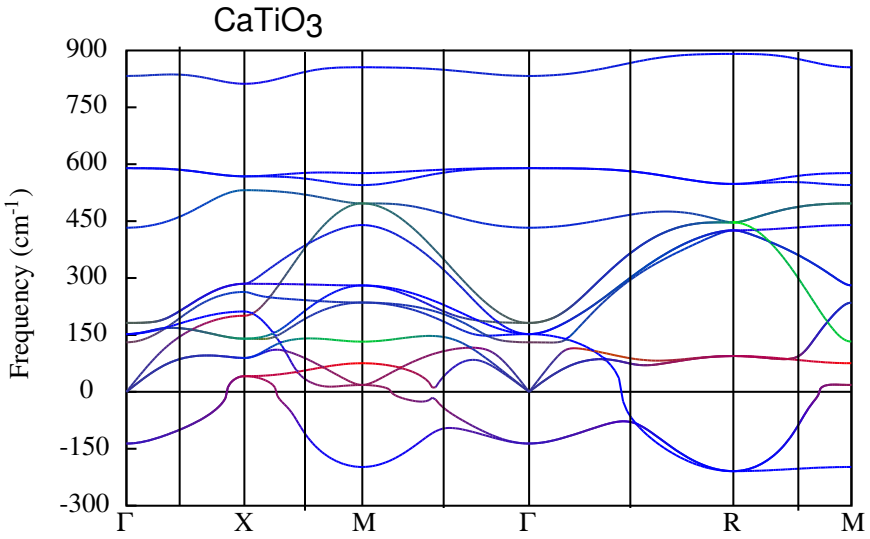
$$u^a_{\kappa\alpha} = \eta^{\mathbf{k}}_{\kappa\alpha} \cdot e^{i\mathbf{k}.\mathbf{R}_a}$$

Commensurate with



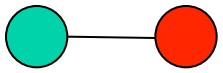
NxNxN supercell
$3xn_{at}xN^3$ degrees of freedom

Phonon modes on the N^3 grid are orthogonal to each others and form a complete basis for the atomic displacements in the N^3 supercell



From atom to phonon basis

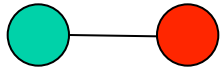
Atom basis



$u_1 = (1 \ , \ 0)$

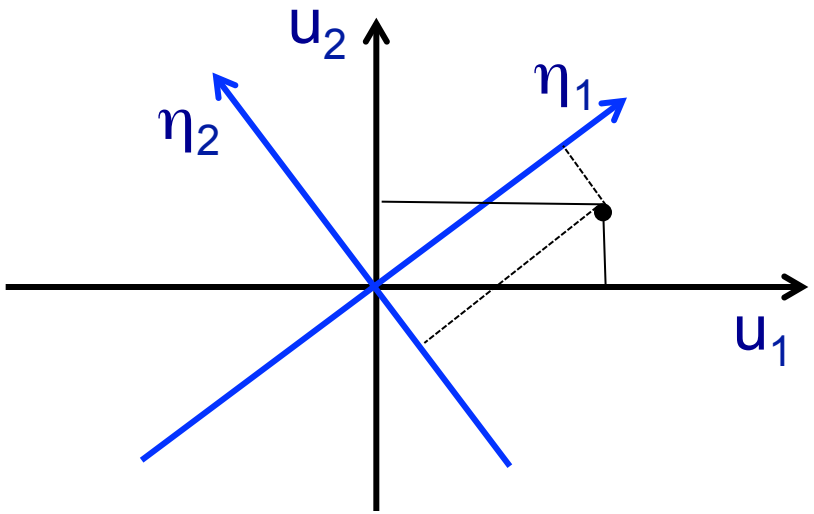
$u_2 = (0 \ , \ 1)$

Phonon basis



$\eta_1 = (1 \ , \ 1)\ \sqrt{2}/2$

$\eta_2 = (-1 \ , \ 1)\ \sqrt{2}/2$



From atom to

3xN$_{at}$ phonons form a complete basis : $u^a_{\kappa\alpha} = \sum_i q_i \, \eta^i_{\kappa\alpha}$

$$E = \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\beta}} C_{\kappa\alpha,\kappa'\beta} u_{\kappa\alpha} u_{\kappa'\beta}$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j \sum_{\substack{\kappa\alpha \\ \kappa'\beta}} C_{\kappa\alpha,\kappa'\beta} \; \eta^i_{\kappa\alpha} \; \eta^j_{\kappa'\beta}$$

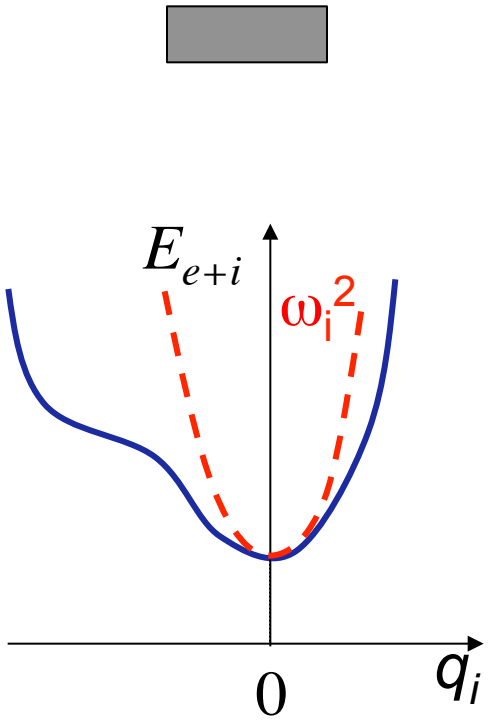
$$= \frac{1}{2} \sum_{ij} q_i \, q_j \sum_{\kappa\alpha} \eta^i_{\kappa\alpha} \sum_{\kappa'\beta} C_{\kappa\alpha,\kappa'\beta} \eta^j_{\kappa'\beta}$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j \sum_{\kappa\alpha} \eta^i_{\kappa\alpha} M_\kappa \eta^j_{\kappa\alpha} \omega_j^2$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j \, \omega_j^2 \delta_{ij}$$

$$= \frac{1}{2} \sum_i \omega_i^2 q_i^2$$

Finite crystal



Change of basis

$3xN_{at}$ phonons form a complete basis : $u^{a}_{\kappa\alpha} = \sum_{i} q_i \, \eta^{i}_{\kappa\alpha}$

$$E_{e+i} = \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\beta}} C_{\kappa\alpha,\kappa'\beta} u_{\kappa\alpha} u_{\kappa'\beta}$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j \sum_{\substack{\kappa\alpha \\ \kappa'\beta}} C_{\kappa\alpha,\kappa'\beta} \; \eta^{i}_{\kappa\alpha} \; \eta^{j}_{\kappa'\beta}$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j$$

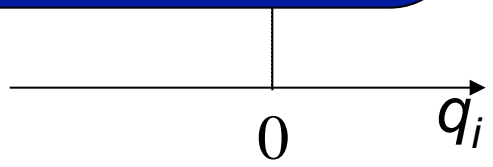
$$= \frac{1}{2} \sum_{ij} q_i \, q_j$$

$$= \frac{1}{2} \sum_{ij} q_i \, q_j \, \omega$$

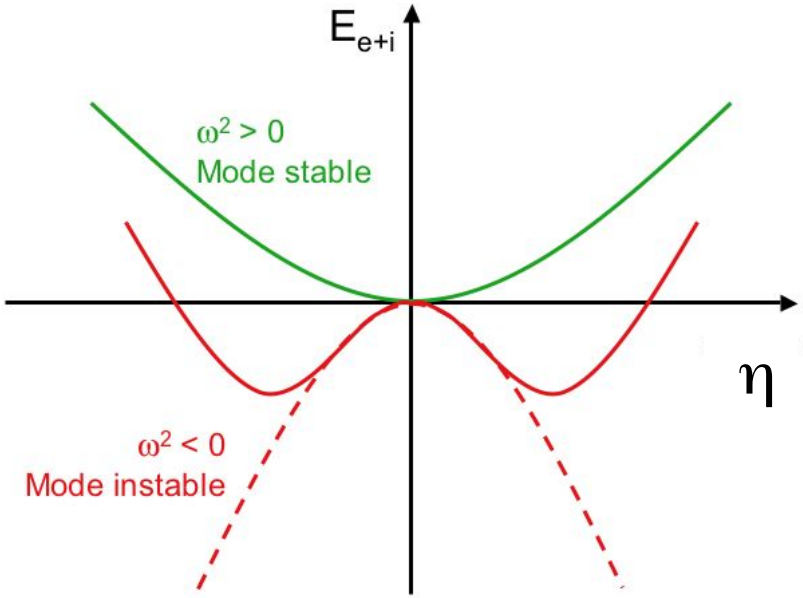
$$= \frac{1}{2} \sum_{i} \omega_i^2 q_i^2$$

Finite crystal

1. Crystal = a collection of independent harmonic oscillators ➔ phonons
2. ω^2 = curvature of E_{e+i} along a given phonon direction.



Imaginary phonon frequencies



- Imaginary phonon frequencies ($\omega^2<0$) are associated to structural instabilities.
- η provides the direction to follow in order to reach the lower symmetry phase

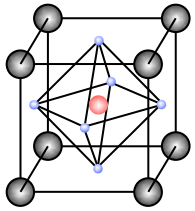
Projection on phonon modes

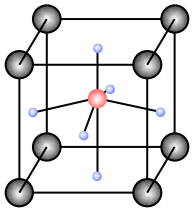
Motivation

- In crystals showing a displacive phase transition (like mode ABO_3 perovskites), the low symmetry phase appears as a small distortion of a (eventually hypothetical) high-symmetry reference.

- It is possible to analyse the atomic distortion in the low symmetry phase by projecting on the phonon of the high-symmetry phase and get many insight on the phase transition

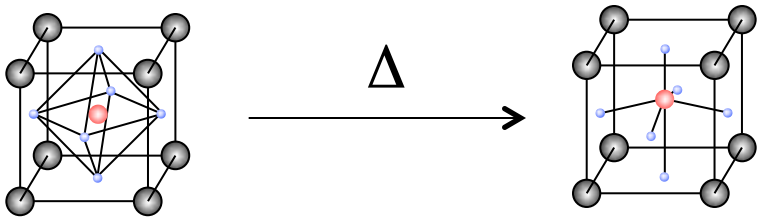
Cubic reference





Distorted phase

Mode-by-mode decomposition



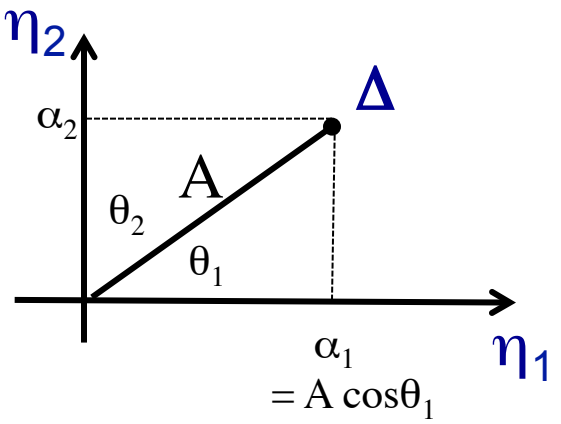
Compute distortion vector Δ :

- in reduced coordinates
- fixing CM

Mode contribution :

$$\Delta = \sum_i \alpha_i \eta_i = A \sum_i \cos\theta_i \ \eta_i$$

$$\left\langle \eta_j \middle| M \middle| \Delta \right\rangle = \sum_i \alpha_i \left\langle \eta_j \middle| M \middle| \eta_i \right\rangle = \alpha_j = A\cos\theta_j$$



Typically we can report :

- The amplitude of each mode: α_i
- The distortion amplitude : A
- The relative mode contribution : cos θ_i
-

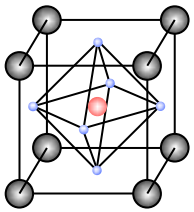
$$\left\langle \Delta \middle| M \middle| \Delta \right\rangle = \sum_i \alpha_i^2 = A^2$$

$$\sum_i \alpha_i^2 = A^2$$

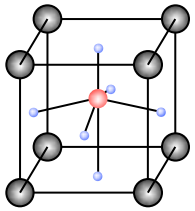
$$\sum_i \left(\cos\theta_i\right)^2 = 1$$

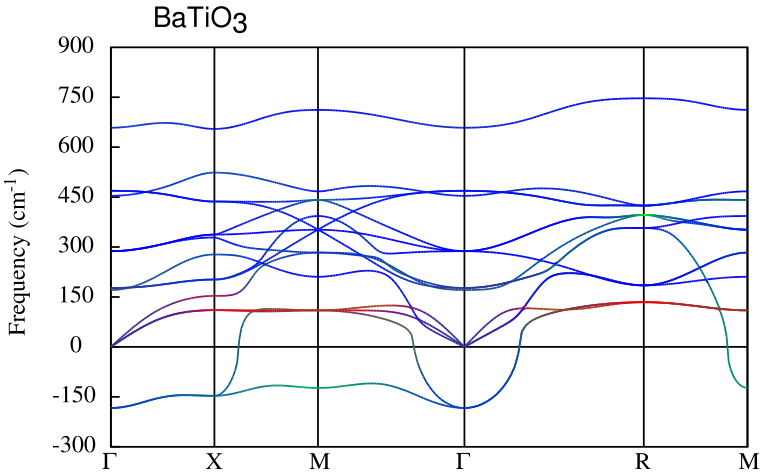
Ferroelectric distortion $BaTiO_3$

Paraelectric



Ferroelectric





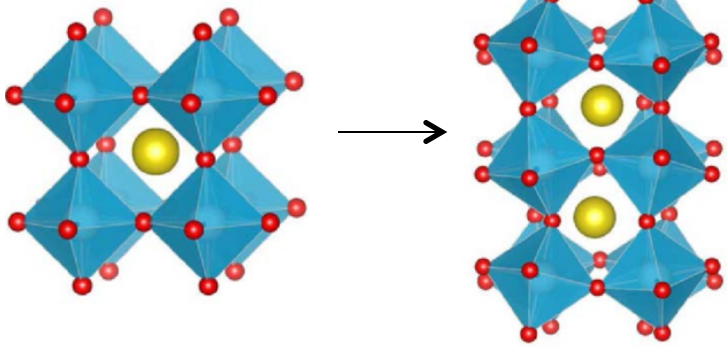
	$P4mm$	$Amm2$	$R3m$
		$BaTiO_3$	
$\|\boldsymbol{\tau}\|$	0.188	0.209	0.214
$F_{1u}(TO_1)$	0.993	0.975	0.971
$F_{1u}(TO_2)$	0.110	0.087	0.129
$F_{1u}(TO_3)$	0.032	0.194	0.228
		$CaTiO_3$	
$\|\boldsymbol{\tau}\|$	0.601	0.478	0.435
$F_{1u}(TO_1)$	0.985	0.970	0.970
$F_{1u}(TO_2)$	−0.171	−0.203	−0.199
$F_{1u}(TO_3)$	0.033	0.129	−0.143
		$CaZrO_3$	
$\|\boldsymbol{\tau}\|$	0.903	0.886	0.868
$F_{1u}(TO_1)$	0.976	0.910	0.897
$F_{1u}(TO_2)$	−0.060	0.202	−0.208
$F_{1u}(TO_3)$	−0.067	−0.336	−0.197

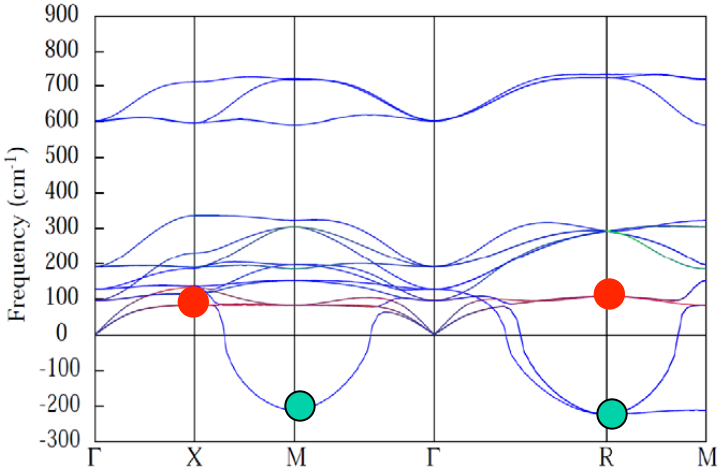
Strong domination of the unstable mode

Antiferrodistortive distortion $SrRuO_3$

Cubic

Orthorhombic





			Oxygen rotations		Anti-polar motions		Other oxygen motions	
Rotations	Symmetry	Space group number	R_4^+	M_3^+	X_5^+	R_5^+	M_2^+	M_4^+
$a^0a^0c^-$	$I4/mcm$	140	0.73	—	—	—	—	—
$a^0a^0c^+$	$P4/mbm$	127	—	0.71	—	—	—	—
$a^0b^-b^-$	$Imma$	74	0.80	—	—	0.08	—	—
$a^0b^+b^+$	$I4/mmm$	139	—	1.05	—	—	—	0.09
$a^0b^+c^-$	$Cmcm$	63	0.85	0.81	0.20	0.03	—	0.04
$a^-b^+a^-$	$Pnma$	62	1.00	0.77	0.35	0.06	0.00	—
$a^+a^+c^-$	$P4(2)/nmc$	137	1.15	1.18	0.30	—	—	0.07

The unstable modes are dominant BUT other stable modes appear due to anharmonic couplings !

$a^-b^+a^-$ $\quad$ $Pnma$ $\quad$ 62 $\quad$ $Q(R_4^+)Q(M_3^+)Q(X_5^+) + Q(R_4^+)Q(M_2^+)Q(X_5^+) + Q(R_5^+)Q(M_3^+)Q(X_5^+)\ldots$

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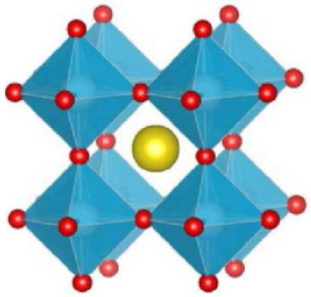
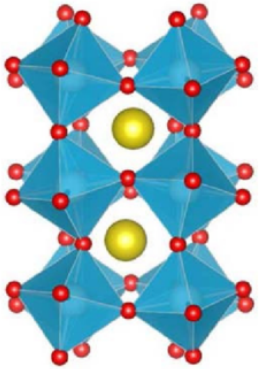
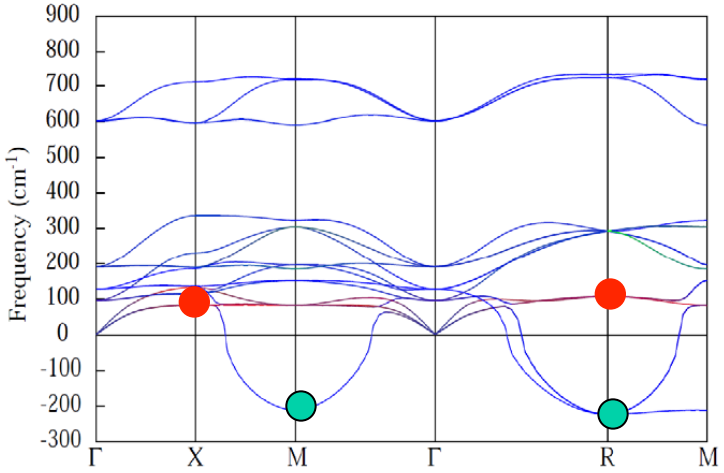
Antiferrodistortive distortion $SrRuO_3$

Cubic



Orthorhombic





Rotations	Symmetry	Space group number
$a^0a^0c^-$	$I4/mcm$	140
$a^0a^0c^+$	$P4/mbm$	127
$a^0b^-b^-$	$Imma$	74
$a^0b^+b^+$	$I4/mmm$	139
$a^0b^+c^-$	$Cmcm$	63
$a^-b^+a^-$	$Pnma$	62
$a^+a^+c^-$	$P4(2)/nmc$	137

$$E = \frac{1}{2}A_1Q_M^2 + \frac{1}{4}B_1Q_M^4 + \frac{1}{2}A_2Q_R^2 + \frac{1}{4}B_2Q_R^4 + C_{12}Q_R^2Q_M^2 + \frac{1}{2}A_3Q_X^2 - \lambda Q_MQ_RQ_X + \ldots$$

The unstable modes are dom
stable modes appear due to

$a^-b^+a^-$	$Pnma$	62	$Q(R_4^+)Q(M_3^+)Q(X_5^+) + Q(R_4^+)Q(M_2^+)Q(X_5^+) + Q(R_5^+)Q(M_3^+)Q(X_5^+)\ldots$

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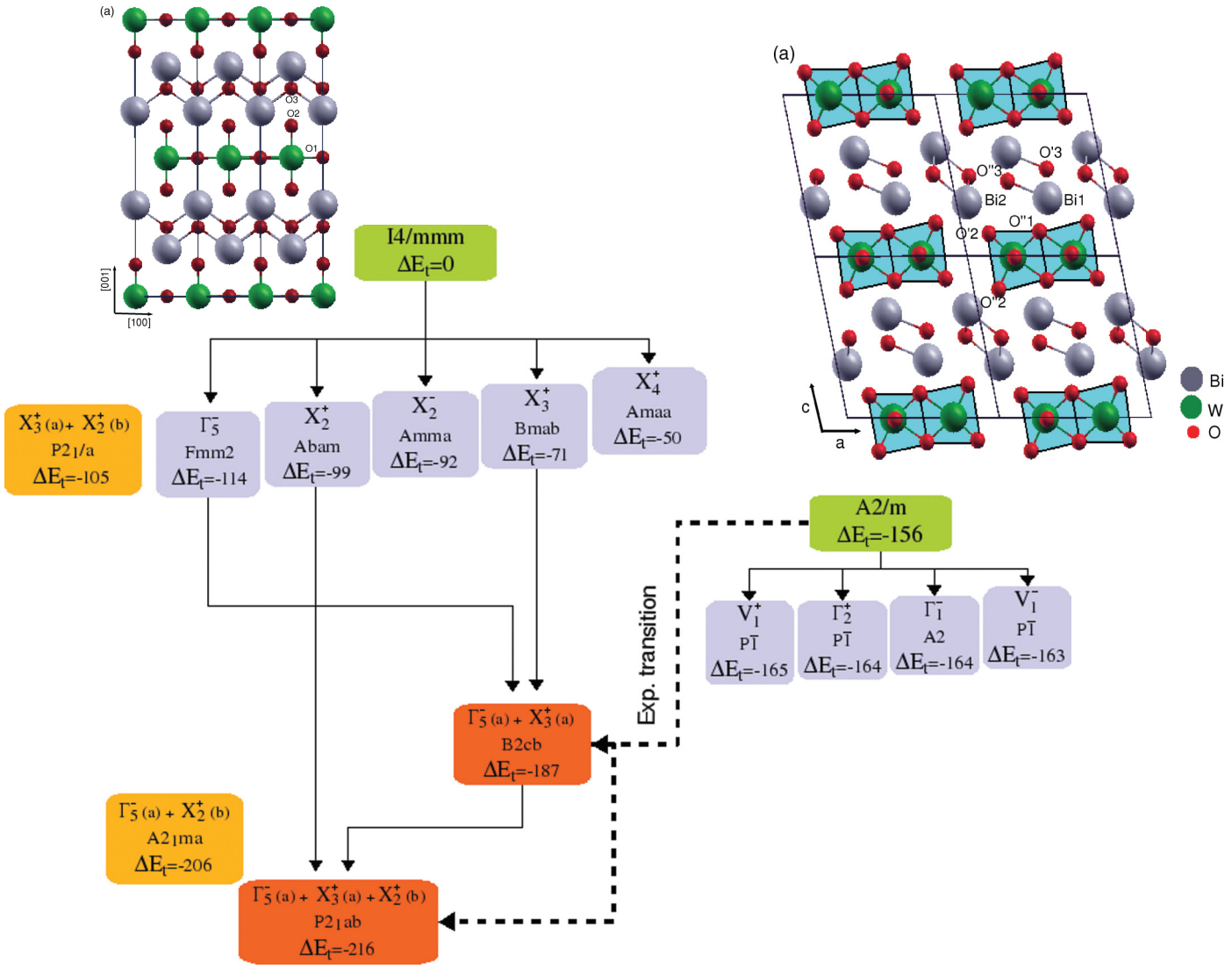
Aurivillius Bi_2WO_6



Aurivillius Bi_2WO_6

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	

Allow to follow mode amplitude evolution from one phase to another and to understand mode competition or cooperation

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

Aurivillius Bi_2WO_6

Comparison of theoretical and experimental GS structures

Atomic positions

Structure	Atom	Wyckoff	x	y	z
		$P2_1ab$			
$a = 5.30$ Å	Bi_1	$4a$	0.0109	0.4843	0.1698
(5.45)			(−0.0126	0.5113	0.1730)
	Bi_2	$4a$	0.0036	0.5074	−0.1698
$b = 5.32$ Å			(−0.0113	0.4762	0.1719)
(5.48)	W	$4a$	0.0000	0.0000	0.0000
	O'_1	$4a$	0.2318	0.6896	0.0108
$c = 16.17$ Å			(0.2679	0.6933	−0.0147)
(16.47)	O''_1	$4a$	0.3321	0.1984	−0.0109
			(0.3342	0.2220	0.0163)
	O'_2	$4a$	−0.0684	−0.0368	0.1109
			(0.0854	0.0449	0.1072)
	O''_2	$4a$	0.4428	0.4563	−0.1108
			(0.5703	0.5526	−0.1086)
	O'_3	$4a$	0.2676	0.2413	0.7515
			(0.2728	0.2508	0.7489)
	O''_3	$4a$	0.2752	0.2465	0.2516
			(0.2740	0.2326	0.2514)

Mode décomposition

Table 2. Contribution of the Phonon Modes of the Hypothetical *I*4/*mmm* Phase (Frequencies in Brackets in cm^{-1}) to the Distortion from the *I*4/*mmm* Phase to the Calculated and Experimental (300 K) $P2_1ab$ Ground State[a]

		Γ_5^-	X_2^+	X_3^+	Γ_5^-
	A	(198i)	(135i)	(104i)	(29)
calculated (present)	585	0.52	0.59	0.55	0.04
experiment (300 K)[6]	772	0.56	0.30	0.59	0.35

[a]Only the most significant contributions are retained. A is the distortion amplitude (in Bohr) and α_i the cosine director, according to the conventions and normalization conditions defined in ref 7.

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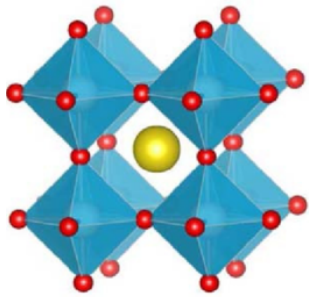
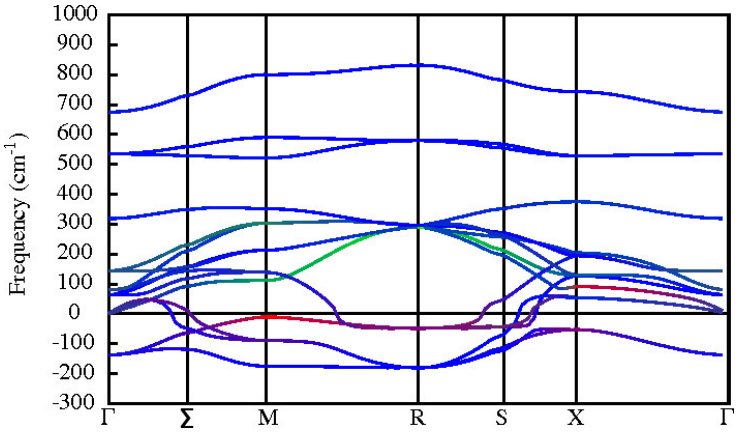
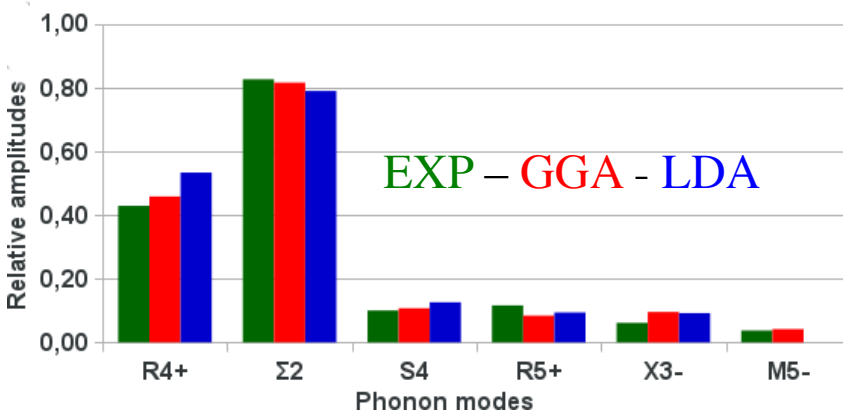
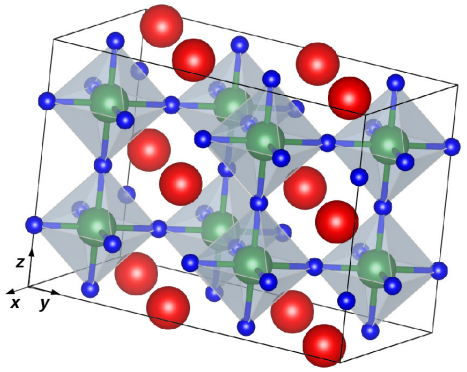
Antiferroelectric PbZrO3

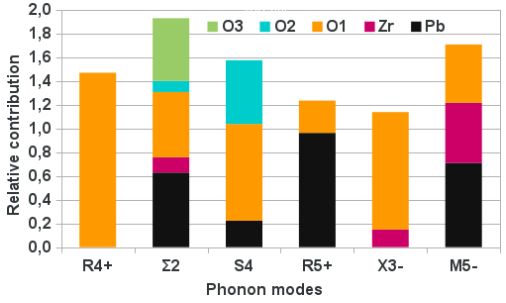




k-points		Mode	Type	ω	
				GGA-WC	LDA
Γ	$(0,0,0)$	Γ_4^-	(FE)	$137i$	$143i$
X	$(\frac{1}{2},0,0)$	X_5^+	(AP)	$52i$	$58i$
M	$(\frac{1}{2},\frac{1}{2},0)$	M_3^+	(AFD)	$175i$	$190i$
		M_5^-	(AP)	$89i$	$100i$
		M_2^-	(AP)	$10i$	$16i$
R	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	R_4^+	(AFD)	$180i$	$196i$
		R_5^+	(AP)	$48i$	$53i$
Σ	$(\frac{1}{4},\frac{1}{4},0)$	Σ_2	(AP)	$121i$	
		Σ_2	(AP)	$62i$	
S	$(\frac{1}{2},\frac{1}{4},\frac{1}{4})$	S_4	(AFD/AP)	$128i$	
		S_4	(AFD/AP)	$50i$	







qAgate

(**A**binit **G**raphical **A**nalysis **T**echnical **E**ngine)

Amongst many other functionalities :

- Condense phonon modes with given amplitudes in a REF structure (useful to look at energy wells or fit an energy expansion in terms of selected degrees of freedom).

- Provides mode-by-mode analysis of a the distortion between a REF and a distorted structure.

(a public version with documentation soon)