Hands-on Tutorial on Phonon calculations

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- Overview
  - Introduction: How include thermal effects in theory?
  - Phonons, harmonic approximation: Theory
    - Harmonic oscillator
    - Thermodynamics (Quasi Harmonic Approximation, QHA)
    - Contributions from long wavelength phonons
  - Structure of the Earth's mantle: Applicaionts QHA
  - Extension of Quasiharmonic approximation: Decoupleed anharmonic Mode approximation (DAMA)
  - Conclusions and outlook

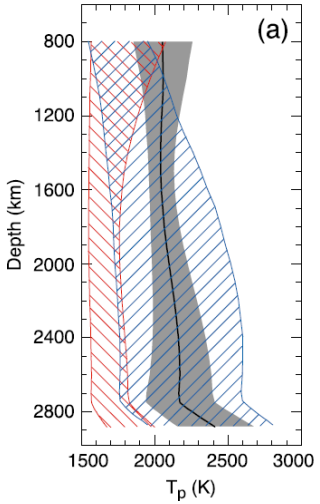
Introduction:
How include thermal effects in theory?

- Theoretical calculations often performed at T=0 K !

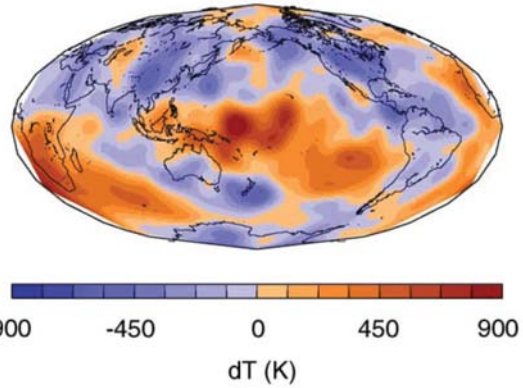
- In Earth interion minerals are commonly at *T*>0 K
- Measured wave velocities

$$d\ln V_p = \frac{\partial \ln V_p}{\partial T}\,dT + \frac{\partial \ln V_p}{\partial C}\,dC + \frac{\partial \ln V_p}{\partial F}\,dF$$

$$d\ln V_s = \frac{\partial \ln V_s}{\partial T}\,dT + \frac{\partial \ln V_s}{\partial C}\,dC + \frac{\partial \ln V_s}{\partial F}\,dF$$



- Numerical inversion $\Longrightarrow$
  - composition (*C*), temperature (*T*), fraction of partial melt (*F*)



Masters, G. et. al. (2000). In Karato, S. et al. Deep Interior: Mineral Physics and Tomography from the Atomic to the Global Scale, Washington, Am. Geophys. Union.

Deschamps, F. and Trampert, J. (2003). Phys. Earth Planet. Int., 140:277–291

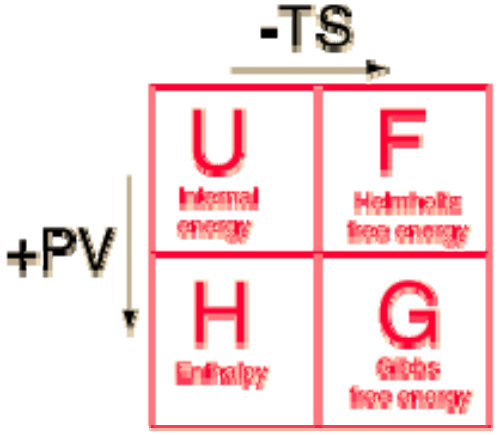
Deschamps F, Trampert J / Earth and Planetary Science Letters **222** (2004) 161–175

Background Thermodynamics

- Free energy *G(T,P)* is needed to calculate phase equilibria
- *G(T,P)* can be obtained from *F(T,V)*

$$G(P,T) = F(V,T) + P \cdot T = \underbrace{E_{0\mathrm{K}}(V)}_{=U} + E_{\mathrm{ZP}}(V) - T \cdot S(T,V) + P \cdot V$$

- $E_{0K}(V)$ can be obtained from static calculations (geometry optimization)
- $E_{ZP}(V)$ is a (small) correction, taking into account the quantum nature of the atomic cores
- $E_{ZP}(V)$-T * $S(T,V)$ can be calculated from partition function



Background
Harmonic Oscillator

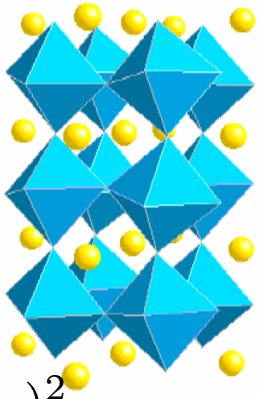
- Move 1 atom along 1 degree of freedom (N atoms, 3N-3 degrees of freedom)
- Curvature of potential energy surface determines *all* vibrational frequencies (e.g. Wu, 2008)
- (Quasi) Harmonic approximation => atoms are “connected by springs” and experience the potential

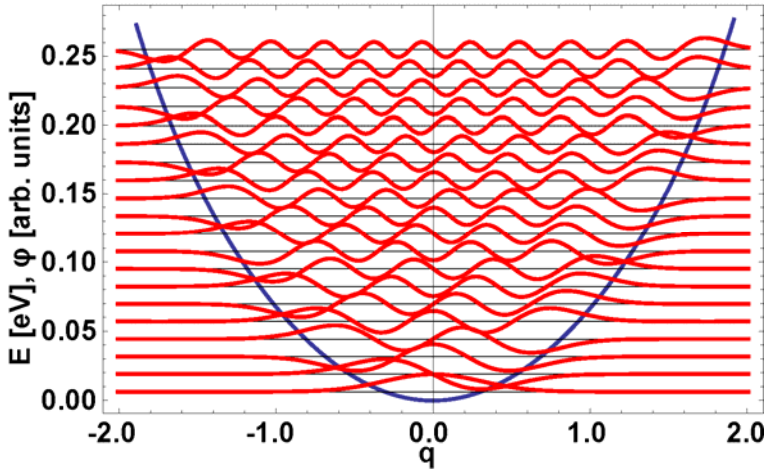
$$U = \frac{k}{2}(q_\mu)^2$$

- Energies for harmonic potential are equidistant

$$\mu \in [1, 3N-3]$$

- Indices:
  - Accounts for degree of freedom
  - J accounts for energy level
- Theory breaks down for negative curvatures of potential energy surface





$$\omega_\mu = \sqrt{\frac{1}{m_\mu}\frac{\partial^2 V(q_\mu)}{\partial q_\mu^2}}\Bigg|_{q_\mu=0}$$

$$\epsilon_\mu^j = \hbar \cdot \omega_\mu \cdot \left(\tfrac{1}{2} + j\right) \text{ and } j \in \mathbb{N}_0$$

Background Thermodynamics

- The partition function Z gives access to all thermodynamic quantities
- The free energy is the thermodynamically relavant potential at *T*>0
- Thermodynamic energy
- Heat capacity
- Elastic constant tensor

$$Z = \sum_i e^{-\frac{\epsilon_i}{k_B T}}$$

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

$$\langle E \rangle = k_B \cdot T^2 \frac{\partial \ln Z}{\partial T}$$

$$c_V = \frac{\partial \langle E \rangle}{\partial T}$$

$$c_{ij}^T(T,P) = \left[\frac{\partial^2 A}{\partial \varepsilon_i \, \partial \varepsilon_j} \right]_P$$

$$G(P,T) = F(V,T) + P \cdot T = \underbrace{E_{0\mathrm{K}}(V)}_{=U} + \underbrace{E_{\mathrm{ZP}}(V) - T \cdot S(T,V)}_{A} + P \cdot V$$

Background
Phonons

- In solid, the lowest energy excitations are collective vibrations of atoms: phonons

$$\Phi = \begin{bmatrix} \frac{d^2E}{dq_1\,dq_1} & \cdots \\ \cdots & \frac{d^2E}{dq_\mu\,dq_\nu} \end{bmatrix}$$

- They can be obtained from force constant matrix

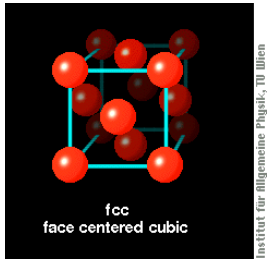
$$-\frac{dE}{dq_\mu} = F_\mu \;\Rightarrow\; \frac{d^2E}{dq_\mu\,dq_\mu} = -\frac{dF_\nu}{dq_\mu}$$

- The eigenvalues of the dynamical matrix D are eigenenergies
- The eigenvectors of the dynamica matrix D are the polarization vectors

$$D = \begin{bmatrix} \frac{1}{\sqrt{m_1 \cdot m_1}} \frac{d^2E}{dq_1\,dq_1} & \cdots \\ \cdots & \frac{1}{\sqrt{m_\mu \cdot m_\nu}} \frac{d^2E}{dq_\mu\,dq_\nu} \end{bmatrix}$$

Example
Dynamical matrix

- Dynamical matrix
  - In carthesian coordinates



$$D = -\frac{1}{\sqrt{m_\mu \cdot m_\nu}} \frac{dF_\nu}{dq_\mu} = \begin{pmatrix} -6. & 0. & 0. & 0.2 & 0.4 & 0. \\ 0. & -6. & 0. & 0.4 & 0.2 & 0. \\ 0. & 0. & -6. & 0. & 0. & 0. \\ 0.2 & 0.4 & 0. & -6. & 0. & 0. \\ 0.4 & 0.2 & 0. & 0. & -6. & 0. \\ 0. & 0. & 0. & 0. & 0. & -6 \end{pmatrix}$$

- Polarization vector
  - Collective modes

$$\varepsilon = \begin{bmatrix} 0.5 \\ 0.5 \\ 0 \\ -0.5 \\ -0.5 \\ 0 \end{bmatrix} \qquad \varepsilon_i = \begin{pmatrix} 0.5 & 0.5 & 0 & 0 & 0.5 & 0.5 \\ 0.5 & -0.5 & 0 & 0 & -0.5 & 0.5 \\ 0 & 0 & 1. & 0 & 0 & 0 \\ -0.5 & 0.5 & 0 & 0 & -0.5 & 0.5 \\ -0.5 & -0.5 & 0 & 0 & 0.5 & 0.5 \\ 0 & 0 & 0 & 1. & 0 & 0 \end{pmatrix}$$

- Eigenvalue

$$D = \begin{pmatrix} 6.6 & 0. & 0. & 0. & 0. & 0. \\ 0. & 6.2 & 0. & 0. & 0. & 0. \\ 0. & 0. & 6. & 0. & 0. & 0. \\ 0. & 0. & 0. & 6. & 0. & 0. \\ 0. & 0. & 0. & 0. & 5.8 & 0. \\ 0. & 0. & 0. & 0. & 0. & 5.4 \end{pmatrix}$$

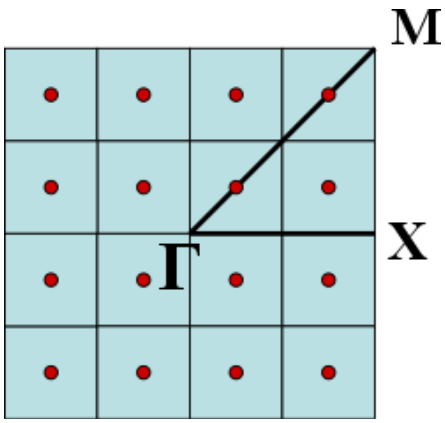
Background
Contribution of long wave-length phonons

- Free energy of solid

$$A = U + \sum_{\mu} \underbrace{\frac{1}{2}\hbar\omega_\mu + k_B T \ln\left(1 - e^{-\frac{\hbar\omega_\mu}{k_B T}}\right)}_{f(\omega_\mu)}$$

- Contribution from long wave-length phonons are important

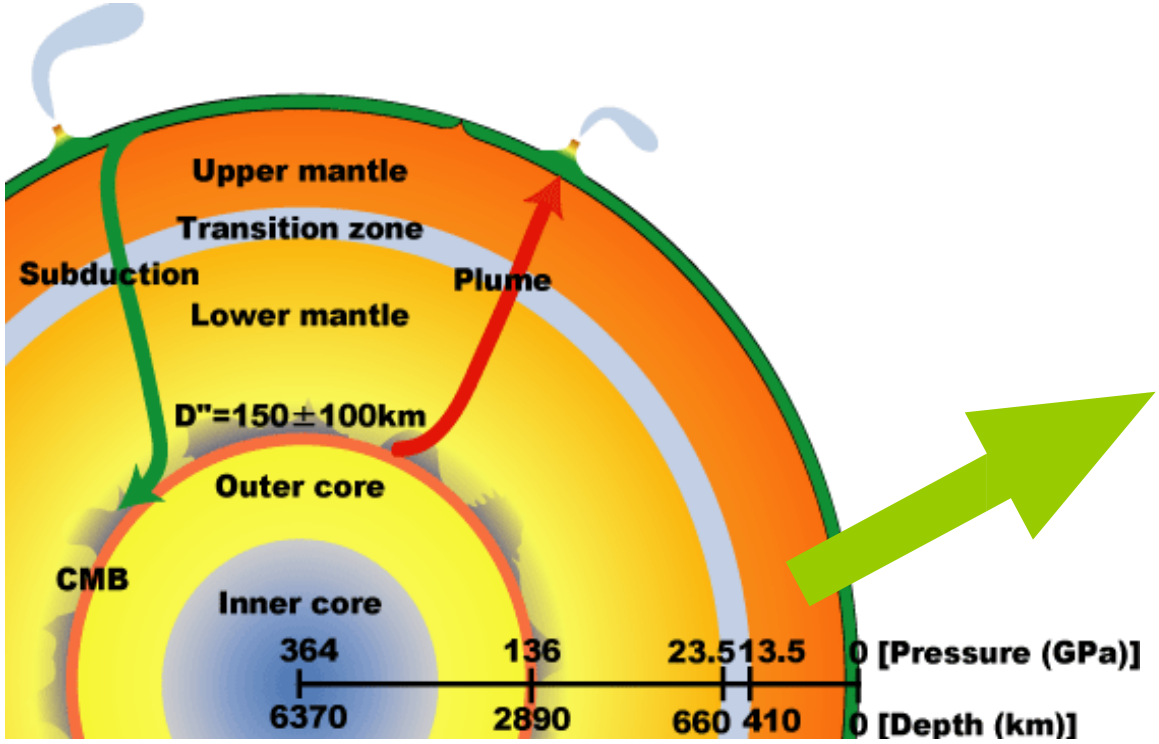
- Avoid large supercells through summation over Brillouin Zone
  - In small cell determine force constants
  - Recompute Dynamical matrix at several long wave-length phonons
  - Sum up contributions using multiplicty w_ν

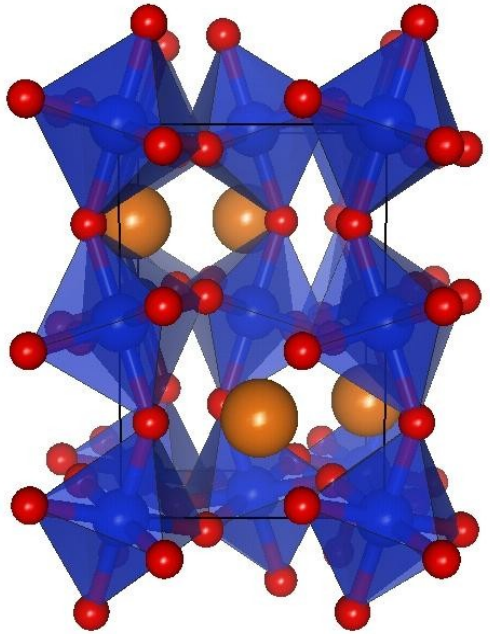


$$A \rightarrow U + \sum_{\nu << 3N-3} w_\nu \cdot f(\omega_\nu)$$

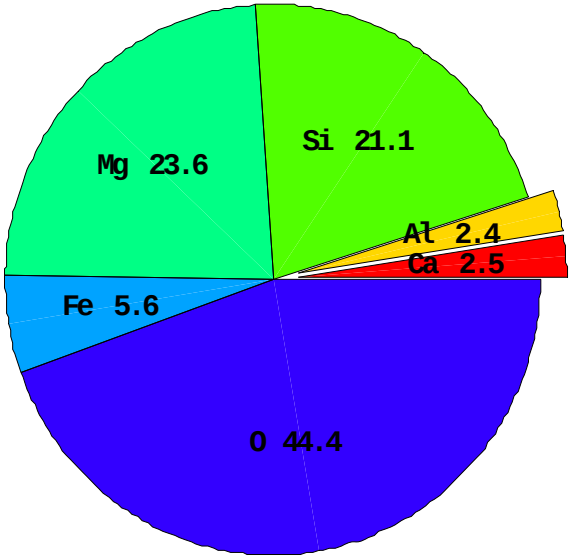
Composition of the Earth‘s (lower) mantle

- $MgSiO_3$: most abundant constituent in the Earth’s lower mantle
- Orthorhombic distorted perovskite structure (*Pbnm*)
- Its stability is important for understanding deep mantle (D” layer)





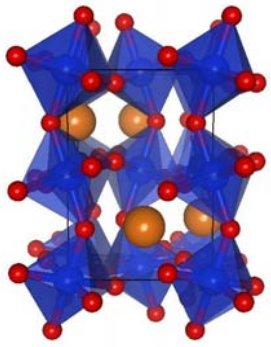
Lower mantle composition

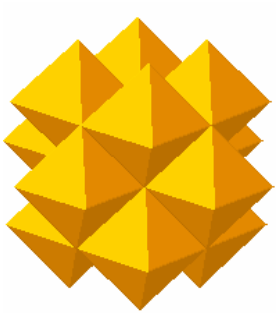


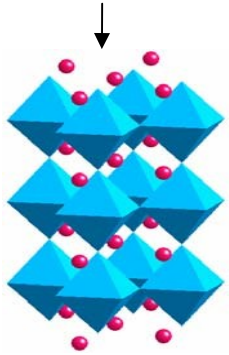
Lower mantle:

- 53 vol.% of the Earth
- 75 wt.% - $MgSiO_3$ (post)-perovskite
- 18 wt.% - (Mg,Fe)O magnesiowüstite
- 7 wt.% - $CaSiO_3$ perovskite

Not suitable for harmonic approximation

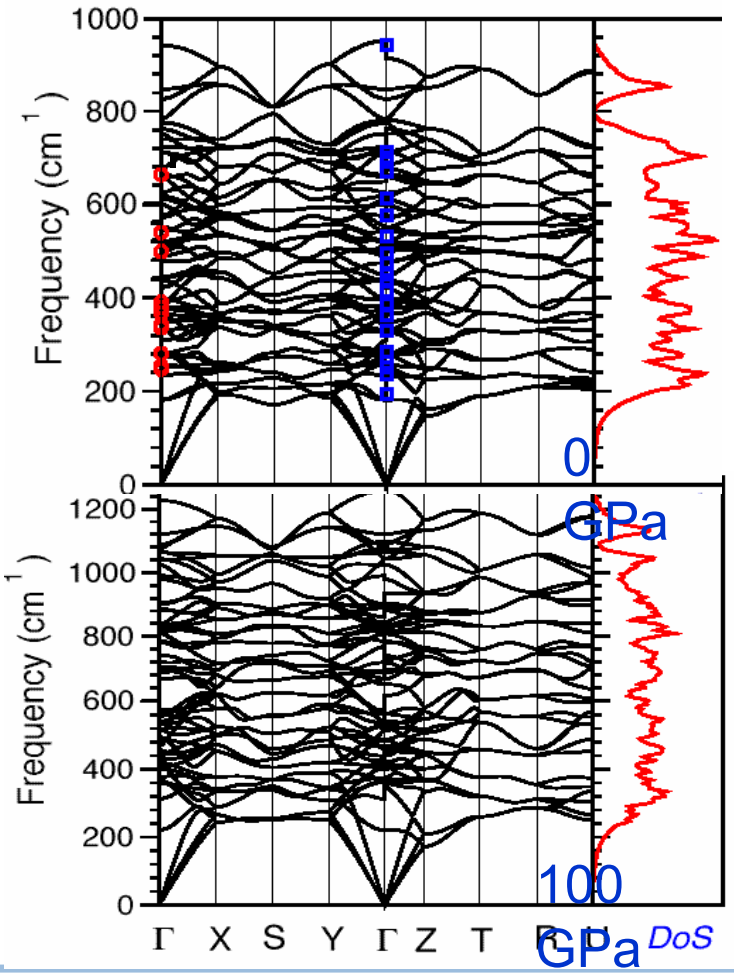


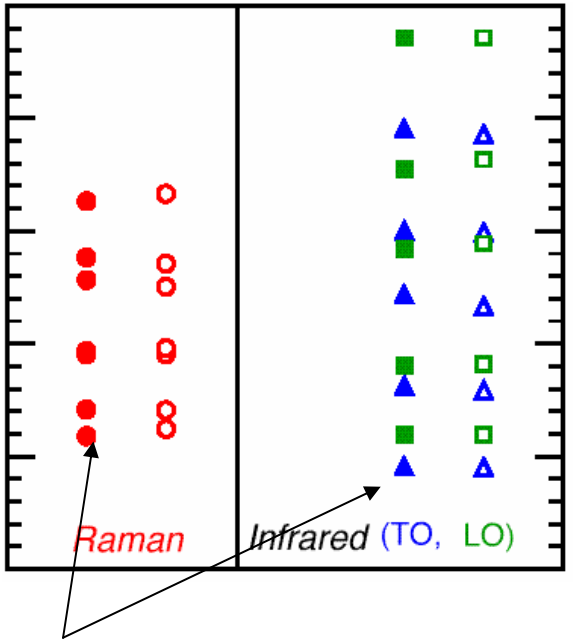


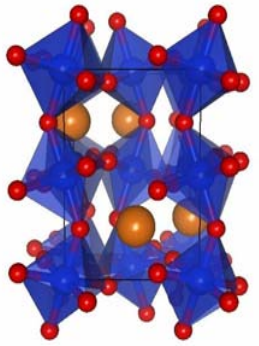


$(Mg_{(1-x-z)},Fe_x, Al_z)(Si_{(1-y)},Al_y)O_3$	$(Mg_x,Fe_{(1-x)})O$	$CaSiO_3$

Phonon dispersion of $MgSiO_3$ perovskite



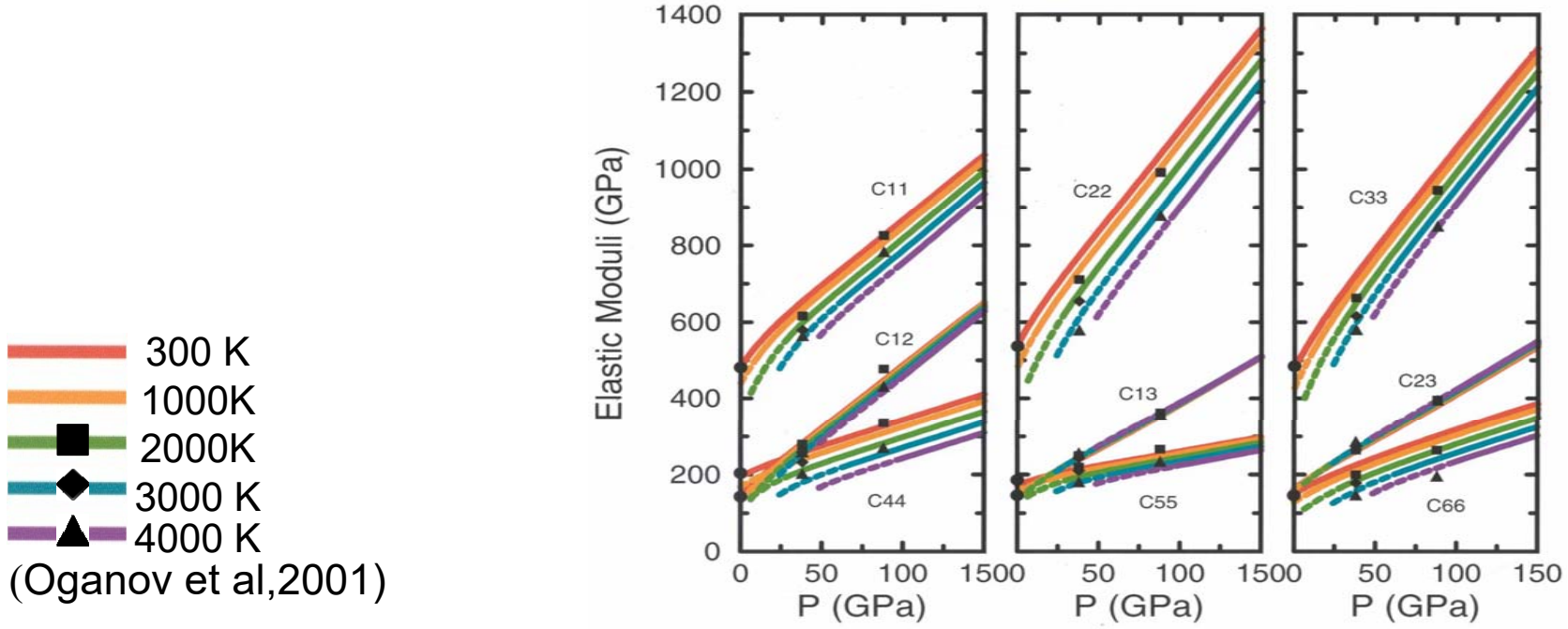




Theory: Karki, Wentzcovitch, de Gironcoli, Baroni (2000) PRB 62, 14750
Exp: Raman (Durben and Wolf, 1992)
Infrared (Lu et al. 1994)

Temperature dependent elastic constants MgSiO3 perovskite

$$c_{ij}^{T}(T,P) = \left[\frac{\partial^2 A}{\partial\varepsilon_i\,\partial\varepsilon_j}\right]_P$$



(Oganov et al,2001)

Wentzcovitch, Karki, Cococciono, de Gironcoli (2004) Phys. Rev. Lett.

Hands-on Tutorial on Phonon calculations

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- Conclusions
  - Harmonic theory treats vibrations as if they did not interact
  - System is equivalent to a collection of independent harmonic oscillators
  - Energies used to compute partition function Z and the free energy, A(T).
  - Through the free energy all properties are accessible
  - DAMA allows to calculate the free energy even for materials with dynamic instabilities
  - Dynamic instabilities are common in high temperature phases
  - Good agreement between QHA (and DAMA) and experiment, e.g. for phase transition cryolite

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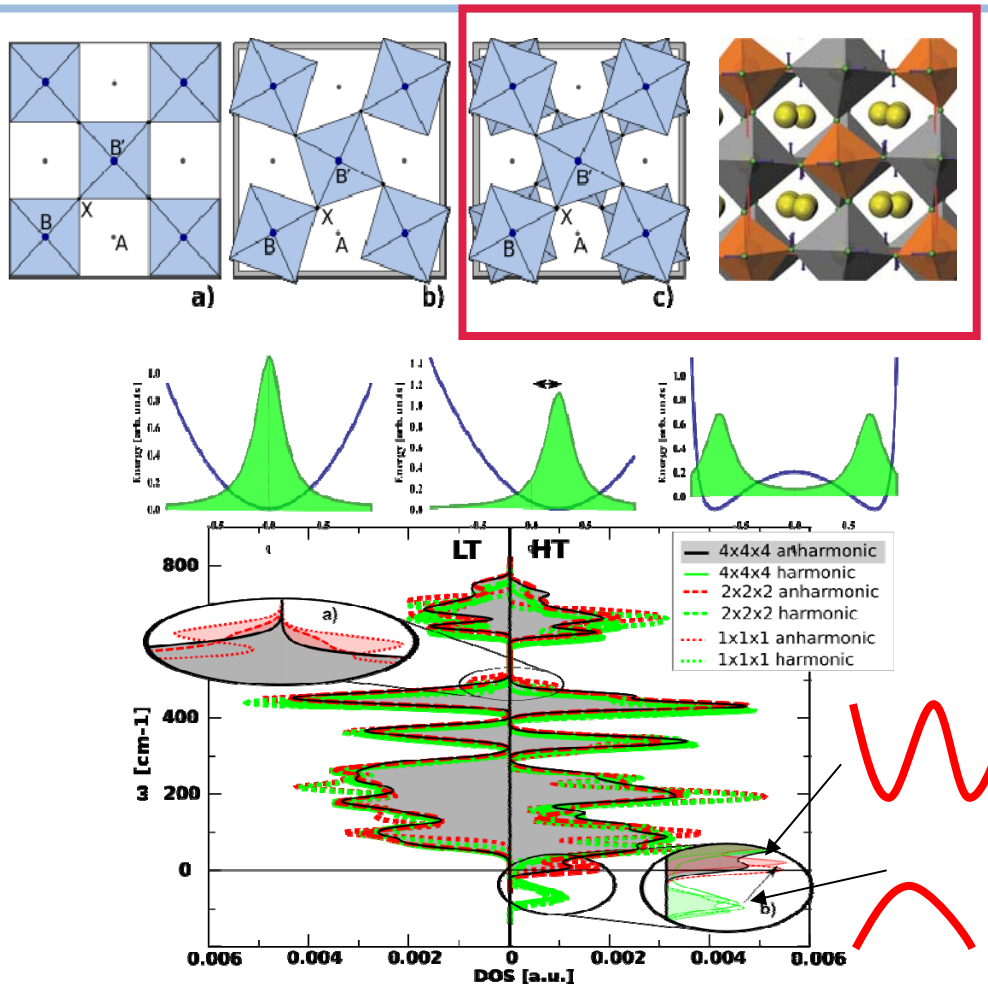
DAMA: extension of the harmonic approximation to materials with negative curvature of the potential energy surface

- In perovskites ABO_3 the (large) size of the B cation stabilizes structure
- Large B => cubic structures
- Small B => static tilt (MgSiO3)
- Intermediate B => instabilities
  - CaSiO3
  - cryolite Na_3AlF_6
- Main effect of the anharmonic treatment is stabilization of vibrational modes with imaginary frequencies.
- All the frequencies are positive in the DAMA



Phase transition in cryolite

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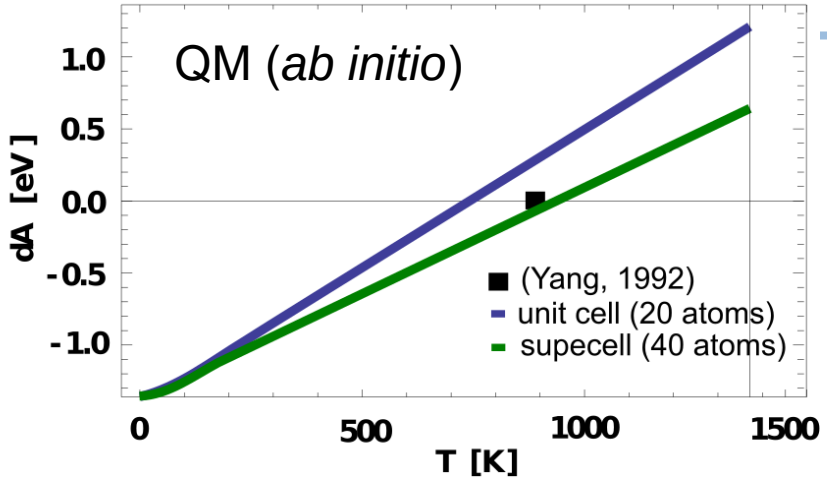
> Phase transition from the *P*21/n to the *Immm* space group at critical temperature between 710 and 950 K (experimental value 885 K, Yang, 1993)



Cell	no. q-points	Method	T_C [K]	$\widehat{T}_C$ [K]
$1 \times 1 \times 1$	1	*ab initio*	770	880
$1 \times 1 \times 2$	2	*ab initio*	950	1060
$1 \times 1 \times 1$	1	PIM	830	950
$2 \times 2 \times 2$	8	PIM	710	900
$4 \times 4 \times 4$	64	PIM	830	971

100 K ≈ 10^{-3} eV

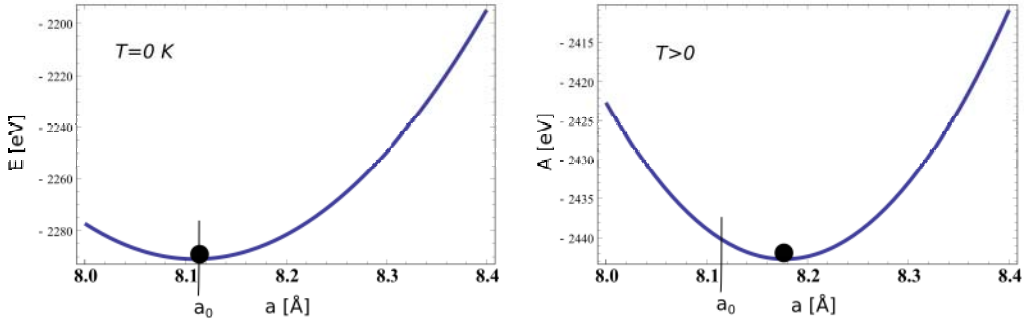
Adams, D. J. and Passerone, D. (2016) Insight into structural phase transitions from the decoupled anharmonic mode approximation, J. Phys. Cond. Matt, **28**, 305401

Yang et al. (1993) Phys. Chem. Minerals 19, 528

Foy, Madden (2006) Ionic Motion in Crystalline Cryolite, J. Phys. Chem. B, 2006, 110 (31), pp 15302–15311

The DAMA Method

- Decoupled Anharmonic Mode Approximation (DAMA)
- At T>0 the free energy is minimized (not the inner energy)

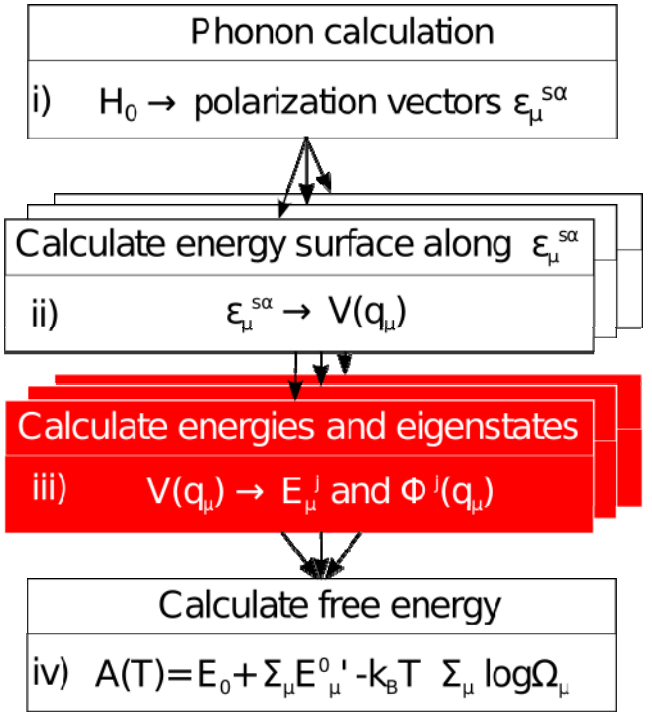


- From the derivatives of the free energy many properties can be calculated
  - e.g. the temperature (and pressure) dependent elastic constants (*eij* are infinitesimal strains)

$$c^T_{ijkl} = \frac{1}{V}\left(\frac{\partial^2 A}{\partial e_{ij}\partial e_{kl}}\right) + \frac{1}{2}p\cdot(2\pm_{ij}\pm_{kl} - \pm_{il}\pm_{jk} - \pm_{ik}\pm_{jl})$$

The DAMA Method:
If you know the Partition Function, you know all the thermal properties of the system!

- Expression for free energy $$A = \underbrace{U_0(V)}_{\text{inner Energy (at } T\text{=0 K)}} - \underbrace{k_B \cdot T \log(Z(V,T))}_{\text{temperature effects}} + \underbrace{p \cdot V}_{\text{pressure effects}}$$
- Calculate partition Function $$Z = \sum_{\mu} \Omega_\mu \text{ and } \Omega_\mu = \sum_{k} e^{-\frac{\epsilon_{\mu,k}}{k_B \cdot T}}$$
- Decoupled Anharmonic Mode Approximation (DAMA)
  - Optimization of atomic positions
  - Rotation of coordinates eliminate coupling between vibrational modes up to order 2 (Normal-Modes)
  - Along these modes vibrational spectra are calculated
  - All energies are inserted into partition fuction



Techniques to approximate hamiltonian

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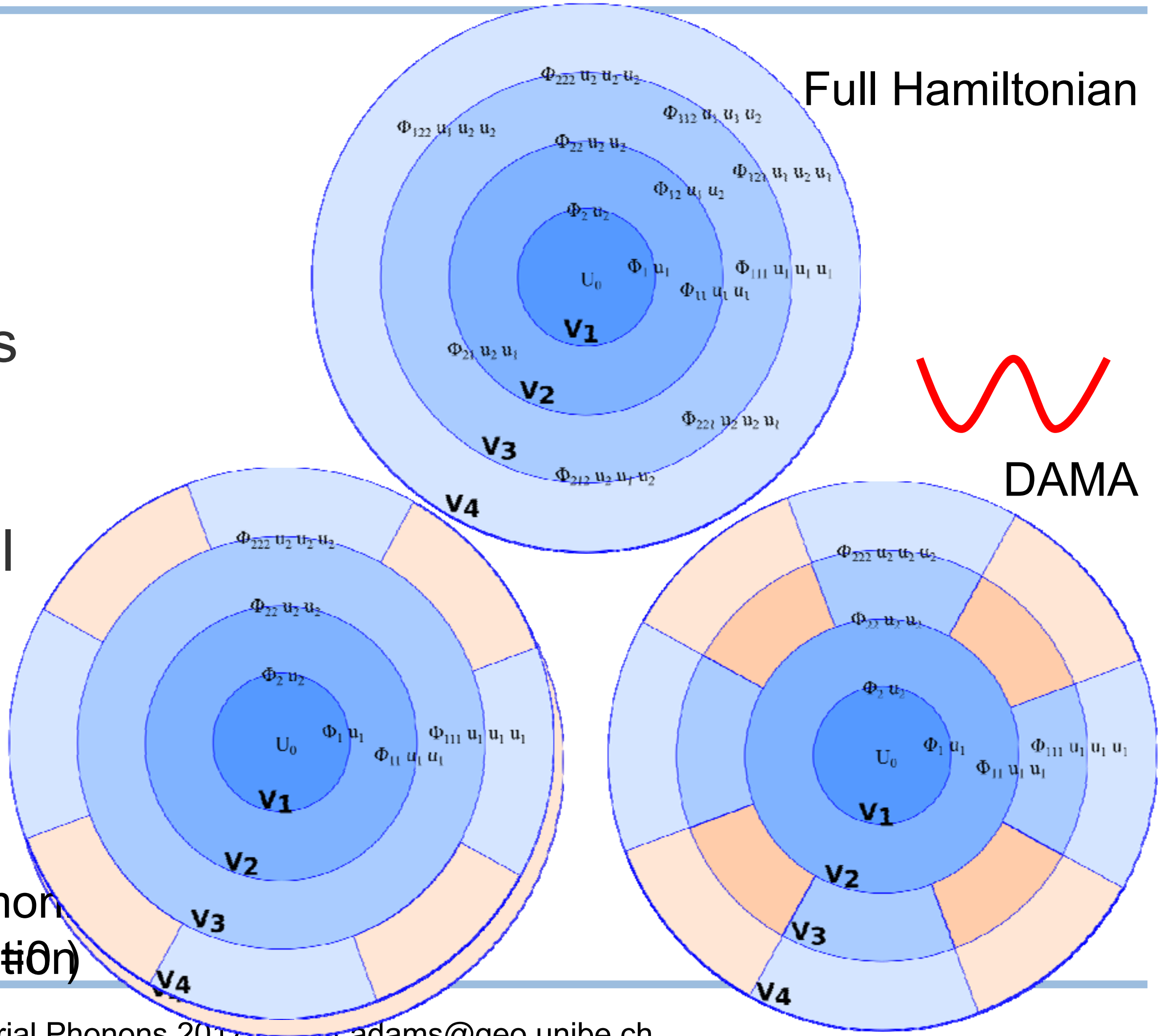
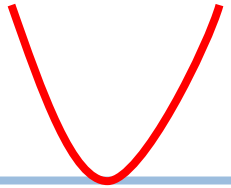
- Optimization of structures eliminates terms of order 1
- Rotation of structural coordinates eliminates off-diagonal terms of order 2
- DAMA keeps diagonal terms to *infinite order*
- DAMA profites from uncoupling keeping high order terms



Thermal average: $\Phi_{211}=0$ Quasiharmonic approximation
No polarization coupling ($\Phi_{123}=0$)

The DAMA Method, Comparison to the Quasiharmonic approximation (QHA)



- Curvatures of potential energy surface determines all vibrational frequencies (e.g. Wu, 2008)

$$\omega_\mu = \sqrt{\frac{1}{m_\mu}\frac{\partial^2 V(q_\mu)}{\partial q_\mu^2}}\Big|_{q_\mu=0}$$

- Energies for harmonic potential are equidistant

$$E_\mu^j = \hbar \cdot \omega_\mu \cdot \left(\tfrac{1}{2} + j\right) \text{ and } j \in \mathbb{N}^0$$

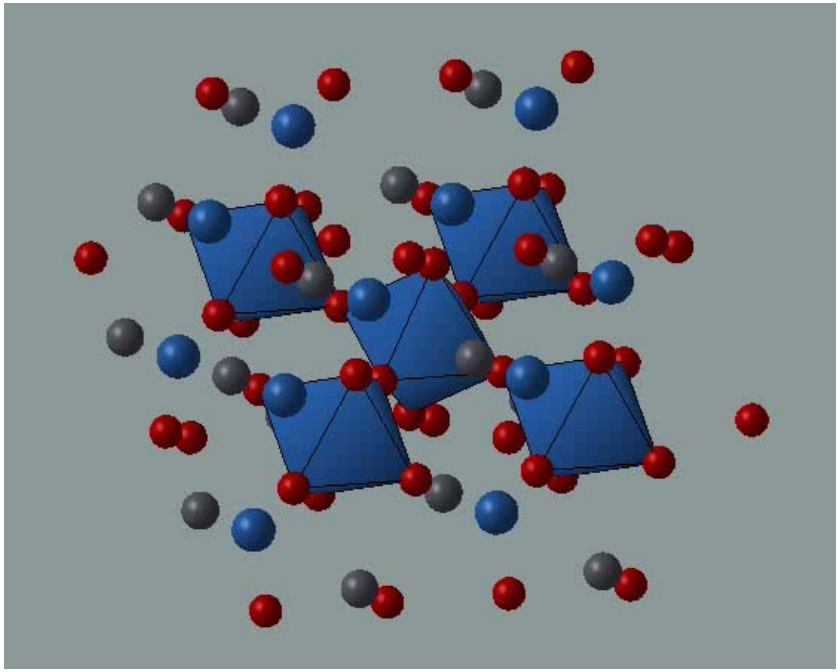
- Energies give rise to geometric series, which can be summed

$$A(T) = E_0 + \tfrac{1}{2}\sum_\mu E_\mu^0 + k_B T \sum_\mu \log\left[1 - \exp(-\hbar\omega_\mu / k_B T)\right]$$

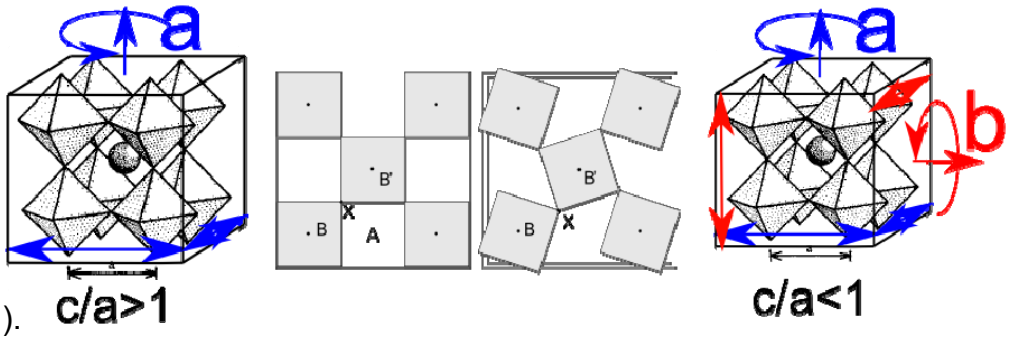
- Theory breaks down for negative curvatures of potential energy surface (i.e. QHE not valid, partition function is still valid)
- Many efforts have been made to calculate the free energy
  - Stochastic self-consistent harmonic approximation (Errea 2014)
  - Self-consistent *ab initio* lattice dynamical calculations (Souvatzis, 2008)
  - Solution of effective Hamiltonians using Monte Carlo simulations (Zhong, 1994)
  - Molecular dynamics sampling (e.g. Zhang, 2014)

Souvatzis P, Eriksson O, Katsnelson M I and Rudin S P 2008 Phys. Rev. Lett. **100** 095901
Zhong W, Vanderbilt D and Rabe K 1994 Phys. Rev. Lett. **73** 1861
Zhang D-B, Sun T and Wentzcovitch R M 2014 Phys. Rev. Lett. **112** 058501
Errea I, Calandra M and Mauri F (2014) Phys. Rev. B **89** 064302
Wu, Wentzcovitch, Umemoto et al. (2008) J. Geophys Res. **113**

Perovskites with dynamical instabilities at *T>0* K

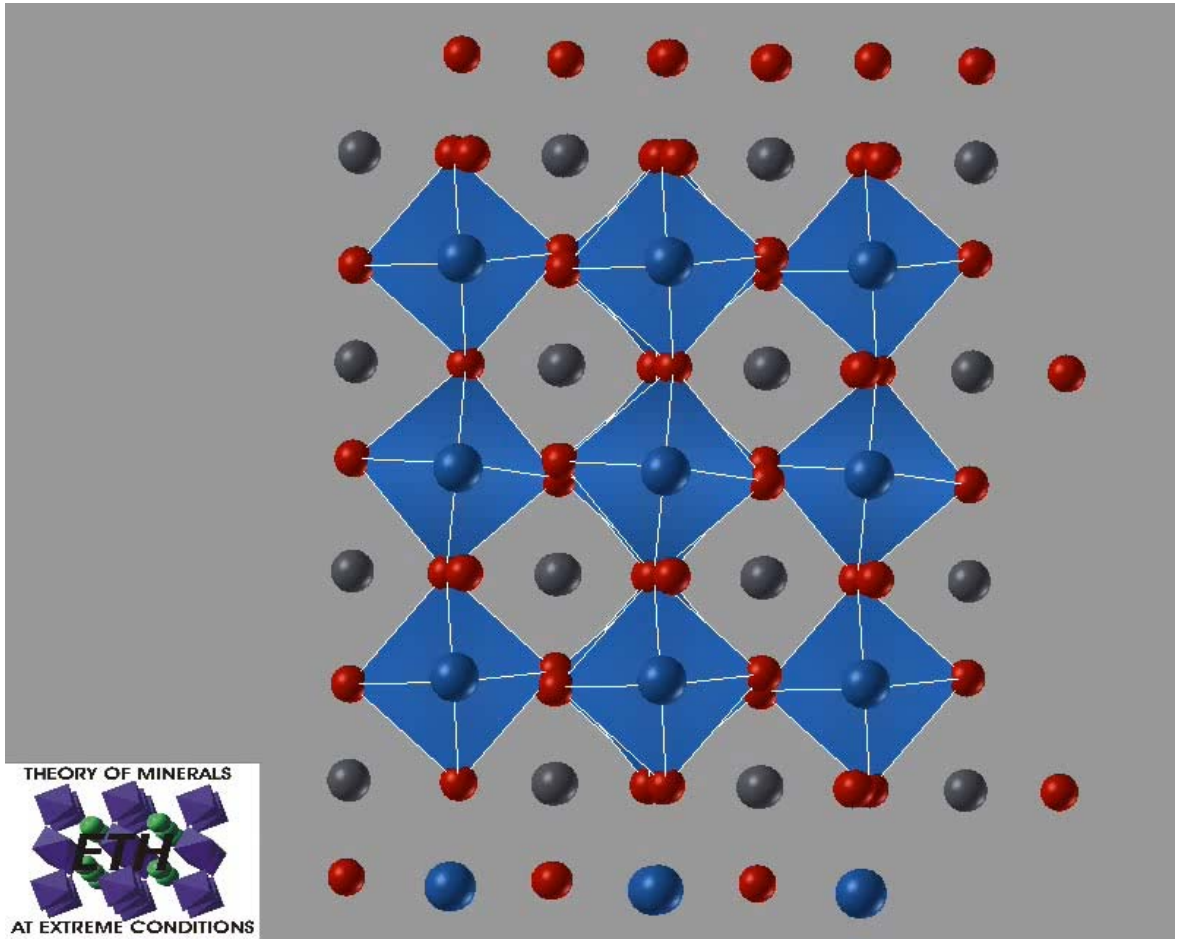


- General formula ABX3
- Octahedra rigid
- If A cation does not fill out space $\Longrightarrow$ tiltings
- Tilting can be in 3 spatial directions
- Combinations tiltings leads to *c/a*=1, *c/a*>1, *c/a*<1
- Tilting system is linked to a unique space group (Woodward 1997; Lufaso 2001)

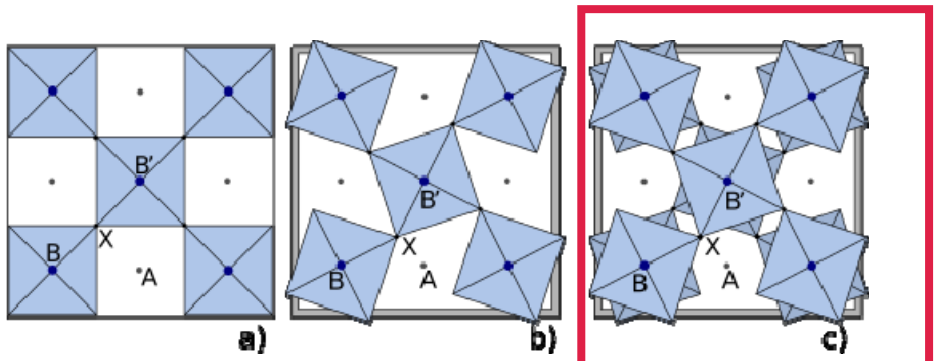


Woodward PM, Acta Cryst. B **53**, 32 (1997).
Woodward PM, Acta Cryst. B **53**, 44 (1997).
Lufaso WM and Woodward PM, Acta Cryst. B **57**, 725 (2001).

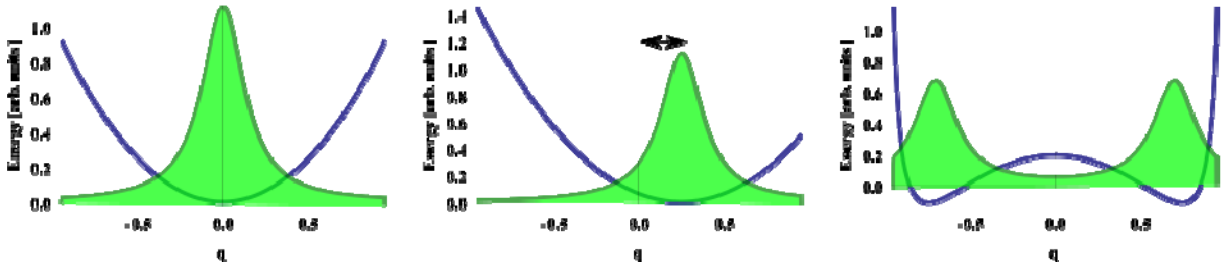
Perovskites with dynamical instabilities at *T>0* K

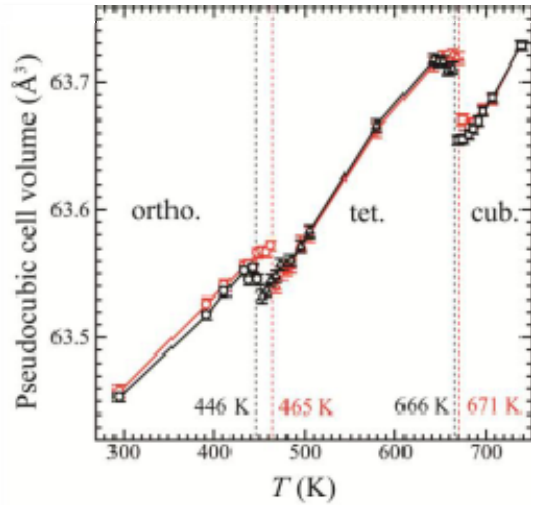


New type of perovskite structures with *dynamical* tilting



No tilt Static tilt Dynamic tilt





Volume of $Na_{0.5}K_{0.5}NbO_3$ between 300 and 700 K according to Sakakura et al.13

> Dynamical tilting can explain volume *degrease* and symmetry restorations (when temperature is *increased*)

Adams and Churakov (2017) Classification of perovskite structural types with dynamical octahedral Tilting, submitted
Sakakura, Wang et al. (2011) in IOP Conference Series: Materials Science and Engineering, Vol. 18

Indicators for dynamic tilting

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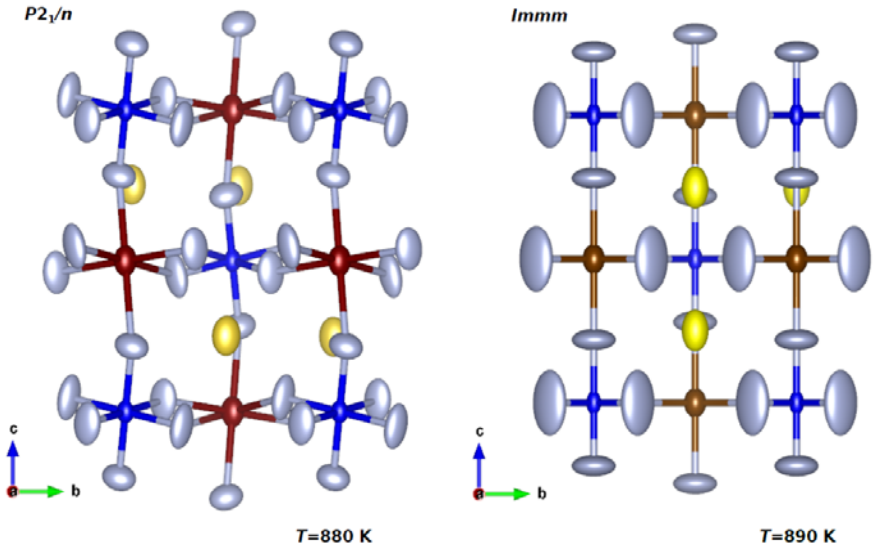
- Volume increase in the low temperature phase (corresponds to the freezing out of dynamical tilts giving rise to a larger volume of the unit cell)
- Apparent distortion of octahedra
- The observed instantaneous symmetry (e.g. from IR spectrum) does not correspond to the average symmetry.
- Experimentally observed space group of a perovskite-type structure not listed in the tables (Glazer 1972; Woodward 1997; Aleksandrov 1976).
- Proportions of the lattice parameters at odds with the ones indicated from the theory of static tilts.
- Large thermal displacement factors for B and X sites.

Woodward PM, Acta Cryst. B **53**, 32 (1997).
Aleksandrov K, Ferroelectrics 24, 801 (1976).
Glazer (A), Acta Cryst. B 28, 3384 (1972).



Vibrational ellipsoids of cryolite below and above the phase transition

- **Cryolite Na_3AlF_6:**
- Low temperature phase is $P2_1/n$ ($a^+b^-c^-$)
- high temperature Phase *Immm* would be $a^0b^+c^+$ based on static tilts
- Dynamic tilt: at least one dynamic tilt, e.g. $a^+b^0c^+$

New type of perovskite structures with *dynamical* tilting

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Tilt system	Space group	No	a	b	c
$a^-b^-c^d$	$C2/m$	12	$2a_p$	$-2c_p$	$-a_p + b_p$
$a^+b^dc^+$	$Immm$	71	$2a_p$	$2b_p$	$2c_p$
$a^db^+c^-$	$Cmcm$	63	$-2a_p$	$2c_p$	$2b_p$
$a^-b^dc^d$	$Fmmm$	69	$2a_p$	$2b_p$	$2c_p$
$a^db^+c^d$	$Cmcm$	65	$-2a_p$	$2c_p$	b_p
$a^db^-c^d$	$Fmmm$	69	$2a_p$	$2b_p$	$2c_p$
$a^+b^dc^d$	$Cmmm$	65	$2c_p$	$-2b_p$	a_p
$a^db^dc^d$	$Pmmm$	47	c_p	b_p	$-a_p$
$a^-a^-b^d$	$Imma$	74	$a_p - b_p$	$-2c_p$	$a_p + b_p$

Tilt system	Space group	No	a	b	c
$a^+a^db^+$	$Immm$	71	$2a_p$	$2b_p$	$2c_p$
$a^+a^db^d$	$Cmmm$	65	$2c_p$	$-2b_p$	a_p
$a^-a^db^d$	$Fmmm$	69	$2a_p$	$2b_p$	$2c_p$
$a^da^db^-$	$I4/mcm$	140	$-a_p - b_p$	$a_p - b_p$	$2c_p$
$a^da^db^+$	$P4/mbm$	127	$a_p + b_p$	$-a_p + b_p$	c_p
$a^da^db^d$	$P4/mmm$	123	b_p	a_p	$-c_p$
$a^-a^+a^d$	$Cmcm$	63	$-2c_p$	$2a_p$	$-2b_p$
$a^-a^-a^d$	$Imma$	74	$-2c_p$	$-a_p + b_p$	$a_p + b_p$
$a^+a^+a^d$	$I4/mmm$	139	$2a_p$	$2b_p$	$2c_p$

Adams and Churakov (2017) Classification of perovskite structural types with dynamical octahedral tilting, submitted

Application to Al: Thermal expansion

- Calculate vibrational spectrum (for different lattice constants)
- Calculate free energy *A* (interpolate A between different lattice constants)
- At given temperature minimize *A* => lattice constant
- At 500 K: a_0 = 2.0311 Å (-0.2%)

T[K]	a/a_0 DAMA	a/a_0 exp	diff [%]
500	1.	1.	0.
700	1.00574	1.00565	0.00913321
900	1.01359	1.01179	0.178006