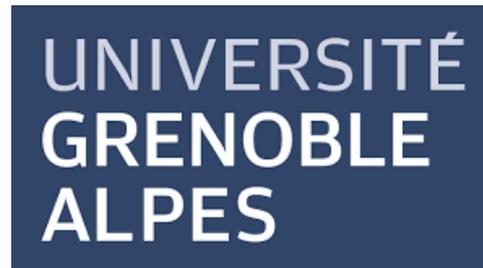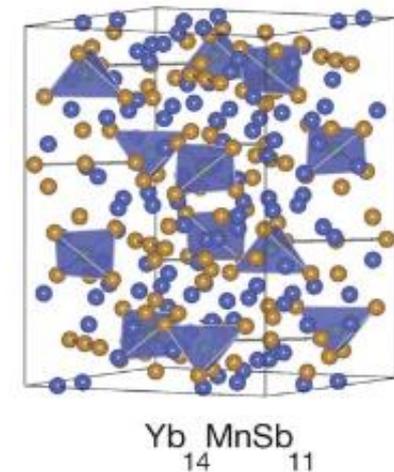# Lattice dynamics and thermal conductivity in complex metallic alloys

Pierre-François Lory
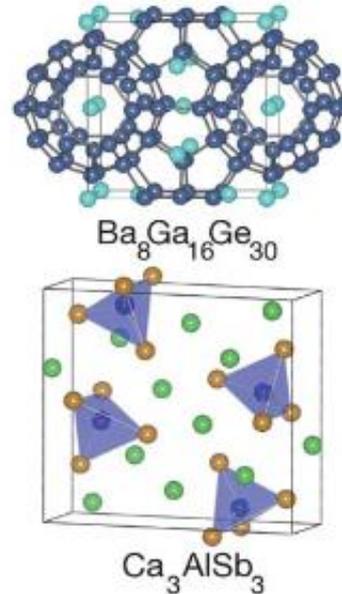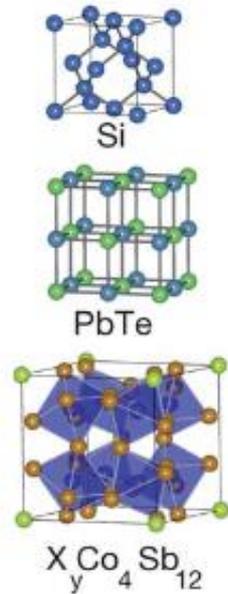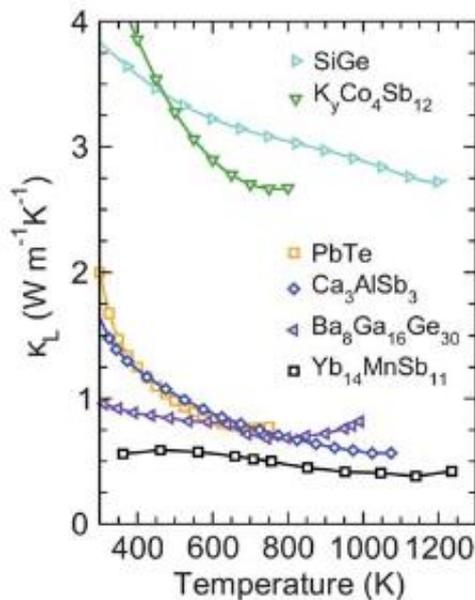
Presentation is based on my PhD work at Institute Laue-Langevin and SIMAP

Grenoble, FRANCE

Thermal conductivity (1 W/m.K) ↔ Clathrates & Quasicrystals

- Effect of structural complexity and dynamics (phonons) on thermal properties

- Various ways of reducing K_{ph} : complexity, disorder, clusters/cages,…

Toberer, E. S., Zevalkink, A., & Snyder, G. J. (2011). Phonon engineering through crystal chemistry. *Journal of Materials Chemistry*, *21*(40), 15843-15852.

1) **Introduction**

1.1) Lattice dynamic and thermal conductivity

1.2) Phonon lifetime

1.3) Inelastic Neutrons Scattering

1.4) Simulations - methods

1.5) DFT - Pair potentials

2) **Approximant o-Al$_{13}$Co$_4$**

3.1) Structure (complexity)

3.2) Lattice dynamics (phonons propagations)
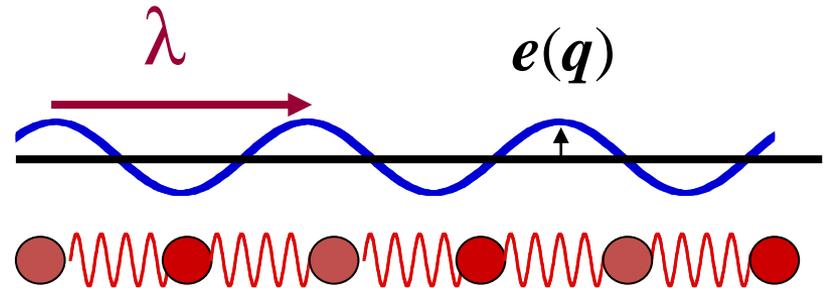
3.3) Thermal conductivity (Simulation)

3) **Conclusion & perspectives**

1) Introduction

1.1) Lattice dynamic (Phonons) and thermal conductivity

1.2) Phonon lifetime

1.3) Inelastic Neutrons Scattering

1.4) Simulations - methods

1.5) DFT - Pair potentials

- Phonon or lattice *wave:*

λ

$e(\boldsymbol{q})$

- Lattice thermal conductivity (κ^{l}_{ph}) depends on:

a) DISPERSION relation : $V_{ph}(\omega)$

b) LIFETIMES of modes : $\tau(\omega)$

$\vec{\nabla}T > 0$

Heat Flux
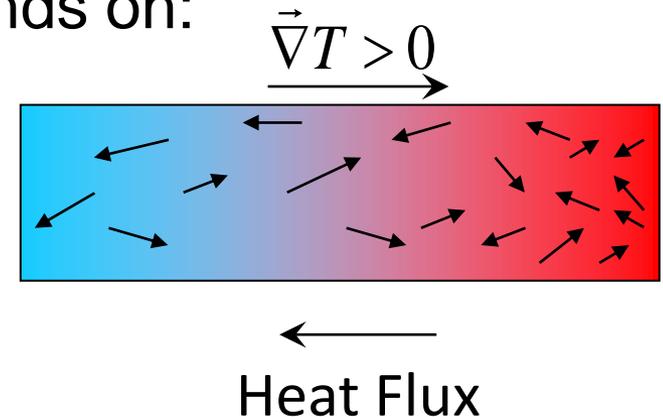
$$l_{ph}(\omega) = v_{ph}(\omega)\,\tau_{ph}(\omega)$$

$$\kappa^{l}_{ph} = \frac{1}{3}\int C_{V}(\omega)\,v_{ph}^{2}(\omega)\,\tau_{ph}(\omega)\,n(\omega)\,d\omega$$
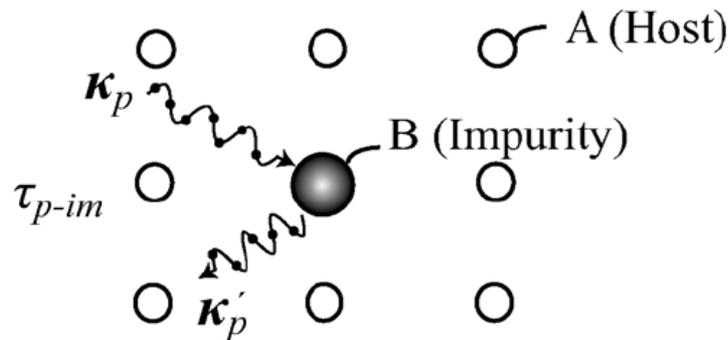
Structure (complexity, disorder) → limits thermal conductivity
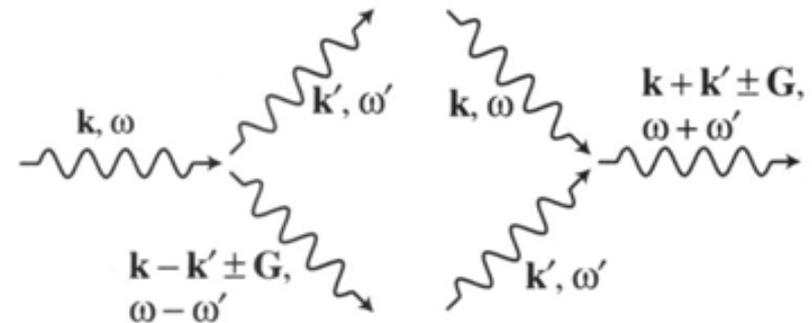
Mechanism 1:
disorder/impurity

- T independent

Mechanism 2:
3 phonons

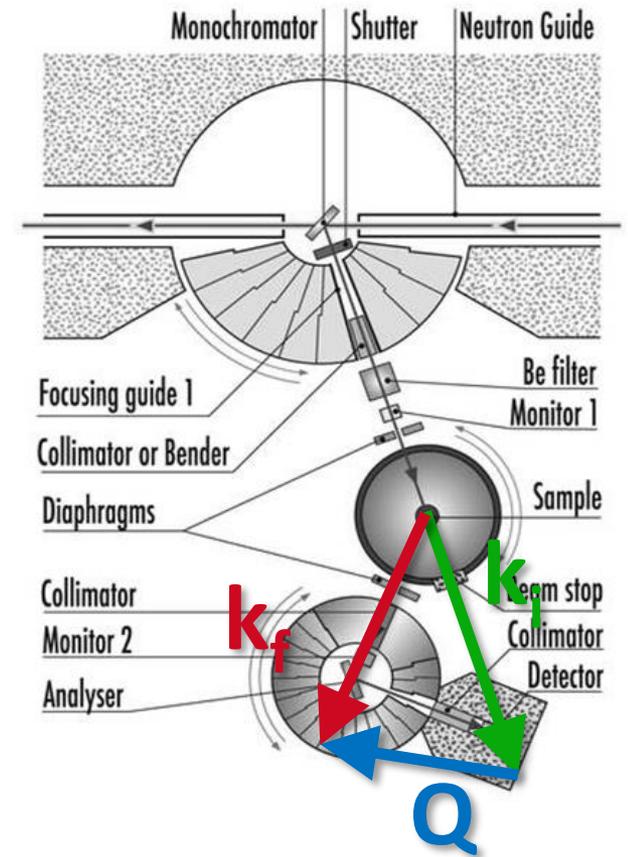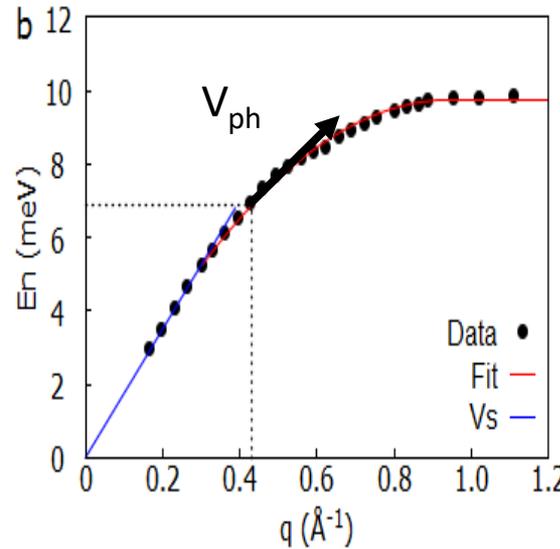- Due to anharmonicity

- T dependent, $\kappa_{ph} \sim 1/T$

(b) Phonon-Impurity (B) Scattering

- Width $\mathbf{\Gamma} \rightarrow$ Phonon lifetime τ

- E(q): dispersion $\rightarrow \mathbf{V_{ph}}$

$$\tau(\omega) = \frac{2\hbar}{\Gamma(E)_{FWHM}}$$
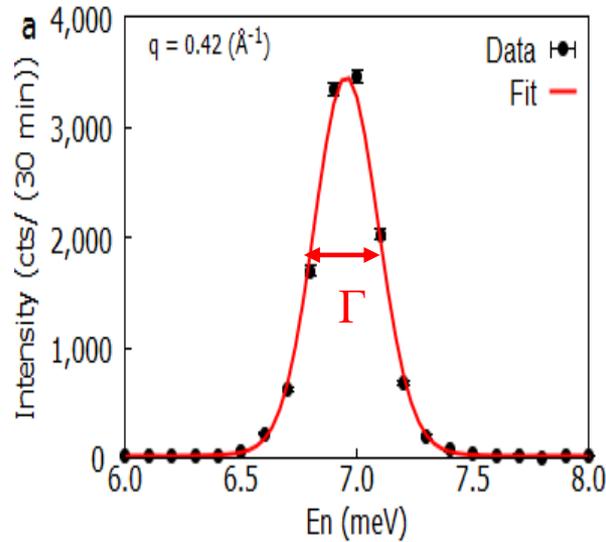
1.4) Simulations - methods

Goal : **Calculate Phonon and Thermal conductivity**
1) Normal modes - Harmonic approximation
2) Molecular Dynamics - includes Anharmonic terms

| Normal modes	Molecular Dynamic (MD)
T = 0 K (optimized structure)	80 K < T
Normal modes / phonons	Trajectories of atoms
Supercell (~10 Å) or < 800 atoms	Superbox (~10 Å to few nm) or 10^6 atoms
Quantum effects	Classic approximation
Calcul S(Q,ω) ∀ q point	**Calcul S(Q,ω) ∀ q point commensurate with the superbox**

- DFT $N_{atoms} < 800$
- Pair Potentials : to describe interactions of the Al-TM
- "Force Matching" method from M. Mihalkovic and *al.*[2]

$$V(r) = \frac{C_1}{r^{\eta 1}} + \frac{C_2}{r^{\eta 2}} \cos(k_* r + \phi_*)$$
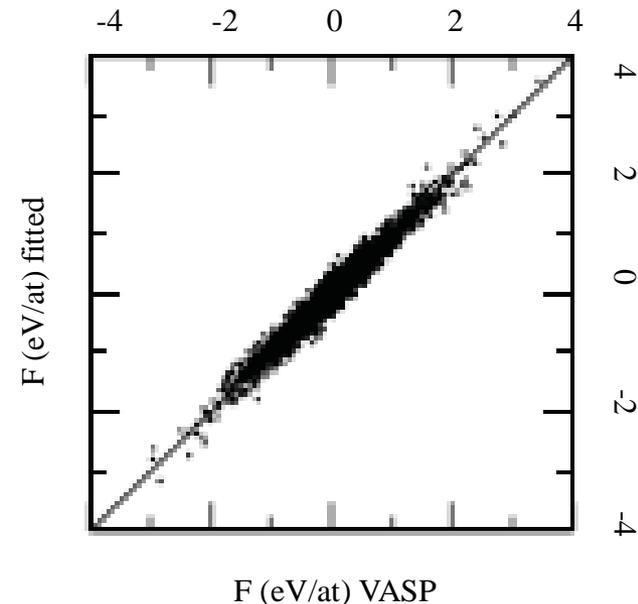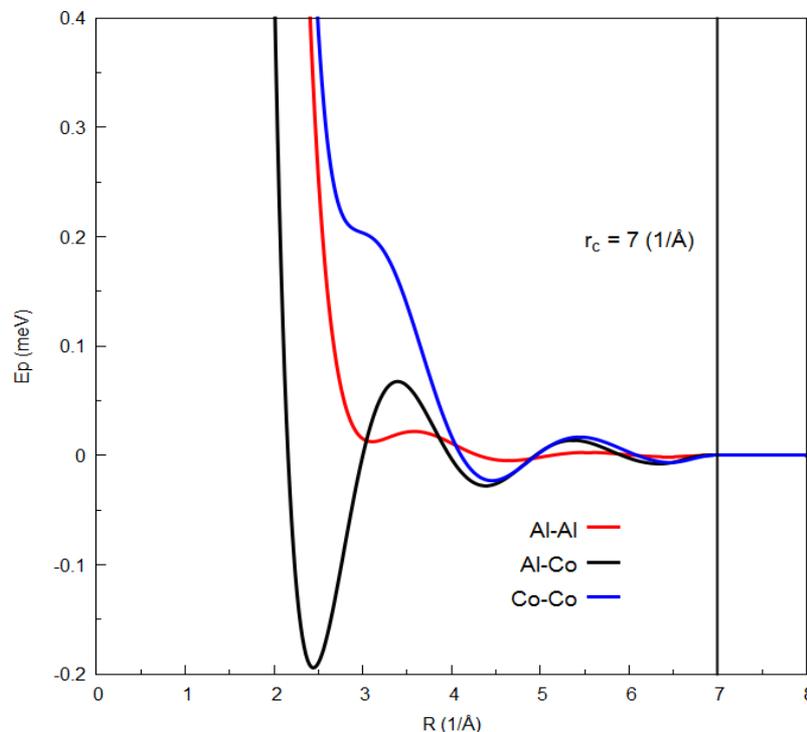
- **Use with MD simulations**

[2] M. Mihalkovic & C. L. Henley, Phys. Rev. B. 85, 9, 092- 102, (2012)
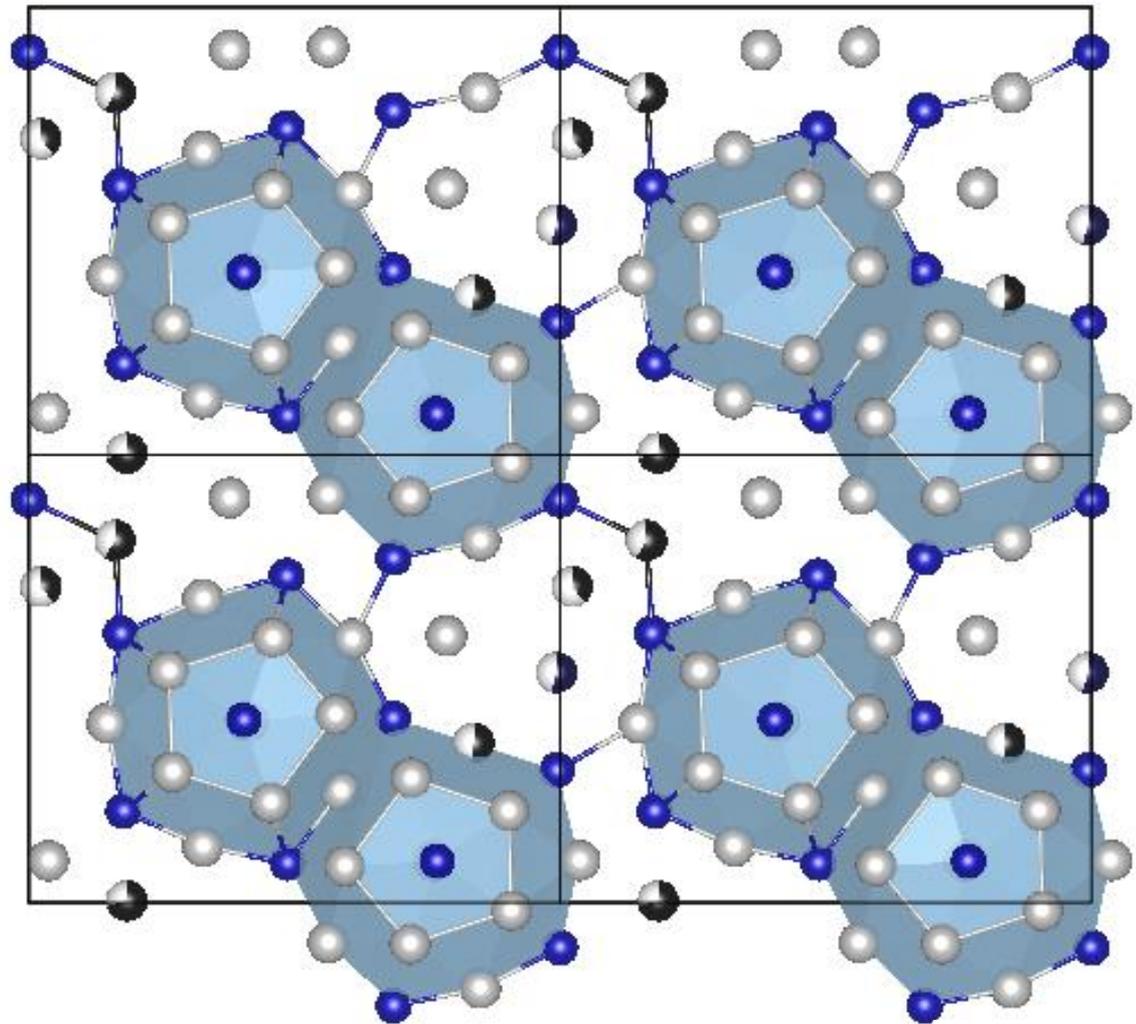
Approximant-crystal

o-$Al_{13}Co_4$

2.1) Structure of approximant o-$Al_{13}Co_4$

2.2) Lattice Dynamics
(experiment and simulation)

2.3) Thermal conductivity model

- Local structure: cluster (4.6 Å)

- [100] periodic and [010] and [001], pseudo-quasiperiodic

- Unit cell: orthorhombic (a = 8.15 Å, b = 12.34 Å, c = 14.45 Å)

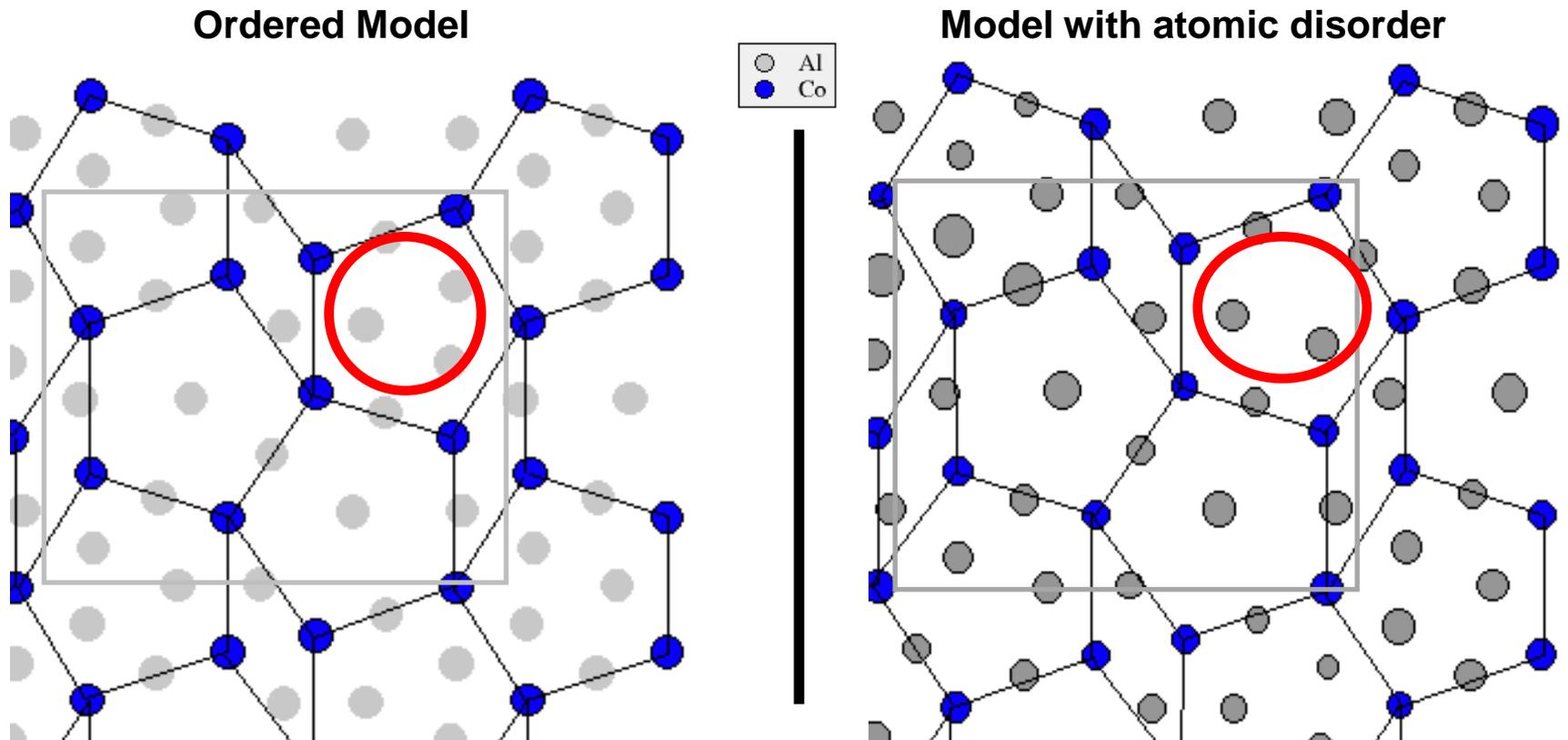|	
○	Al
●	Co

Picture of the (b,c) plane, it is the pseudo quasiperiodic plane

- Model 1: SC(1×1×1): 102 atoms
  ORDERED MODEL [1994]
- Model 2, 1 atom/site : SC(3×2×2): *1205 atoms or 100 atoms unit cell* ATOMIC DISORDER [2015]

Ordered Model

Model with atomic disorder

Approximant-crystal
o-Al$_{13}$Co$_4$

2.1) Structure of approximant o-Al$_{13}$Co$_4$

2.2) Lattice Dynamics (experiment and simulation)
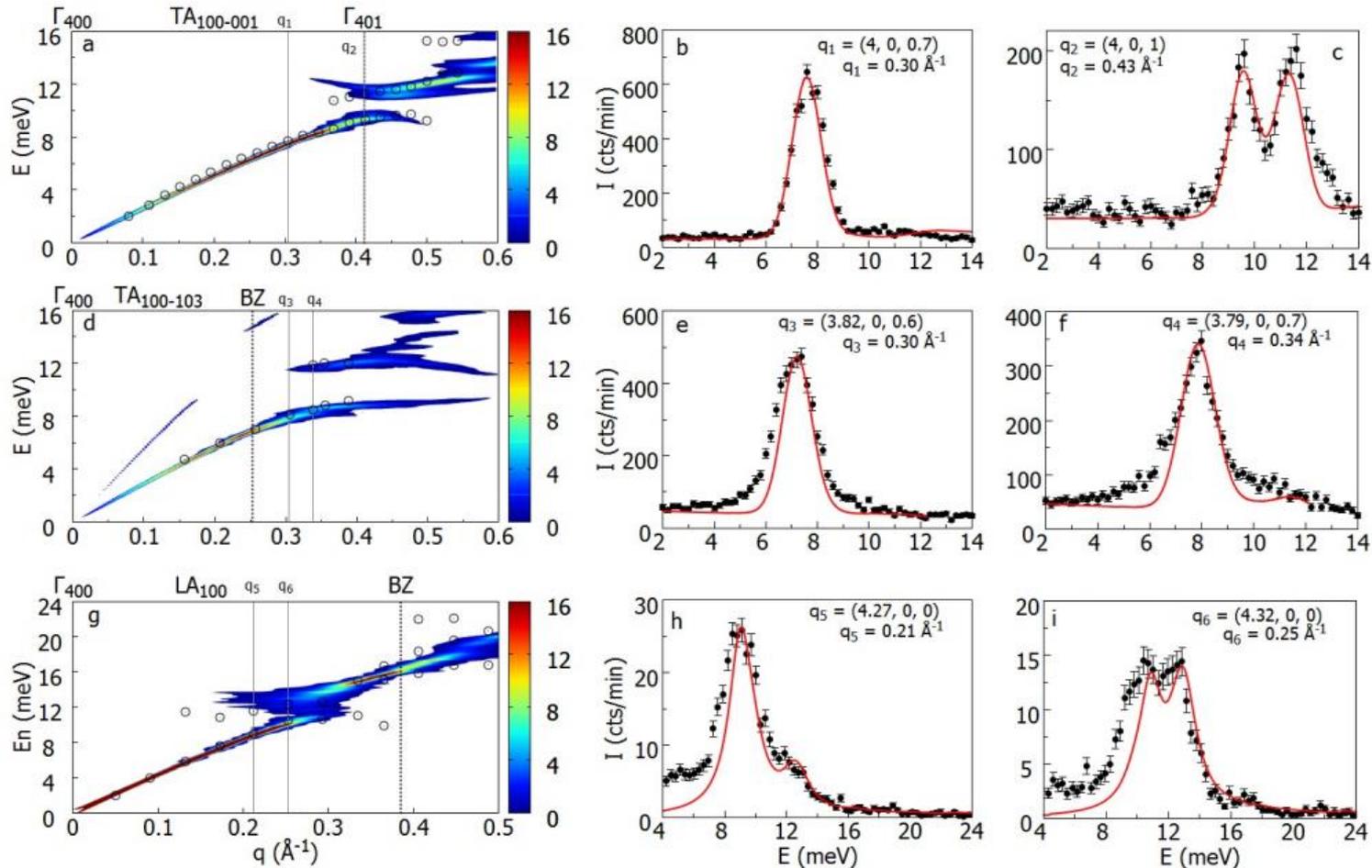Method 1 : Harmonic approximation
Method 2 : Classical MD

2.3) Thermal conductivity model
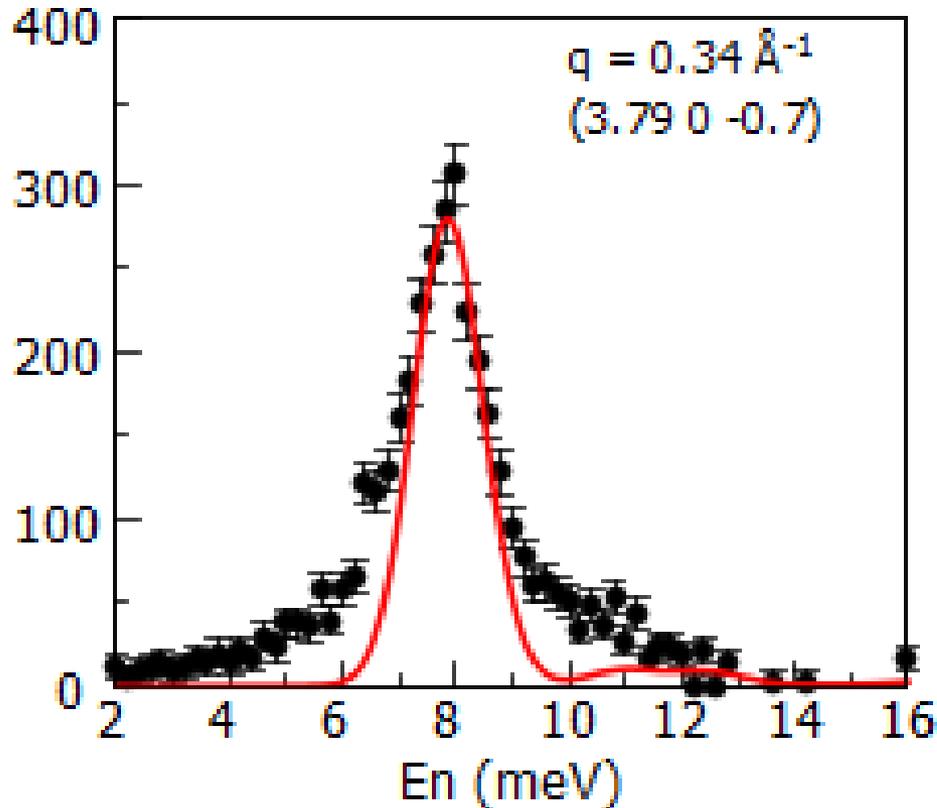
Experiment (INS, dots)

Harmonic simulation (red lines)

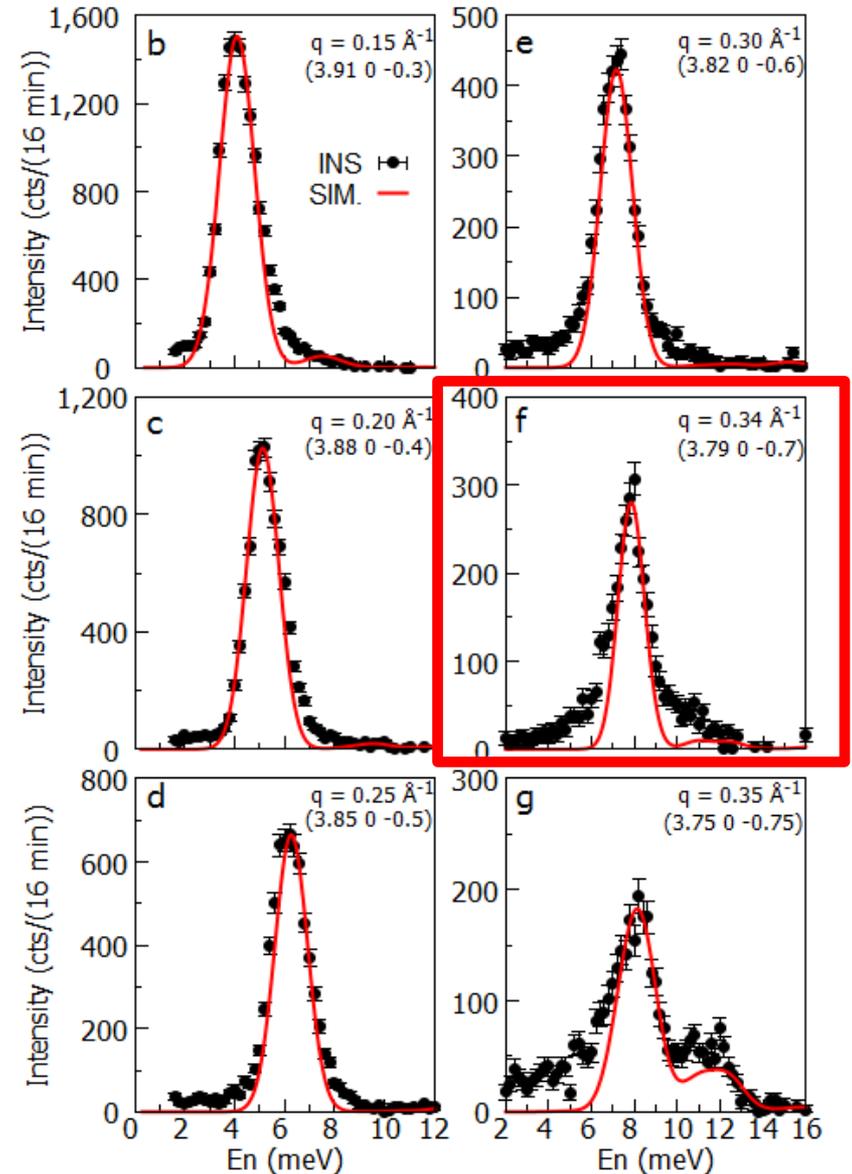**SIMULATION ⊗ RESOLUTION**

GOOD AGREEMENT
experiment-simulation
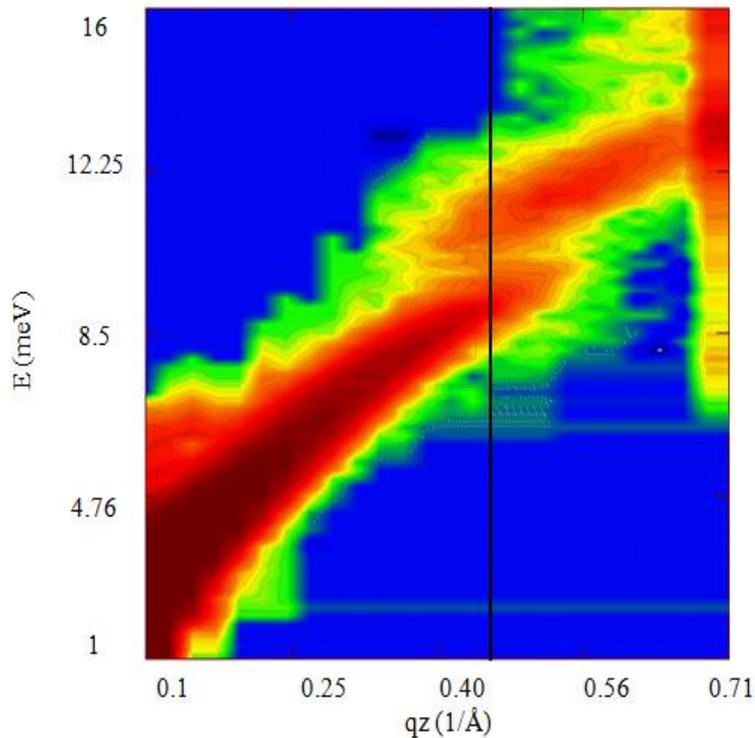
Experiment (INS, dots)
Harmonic simulation (red lines)

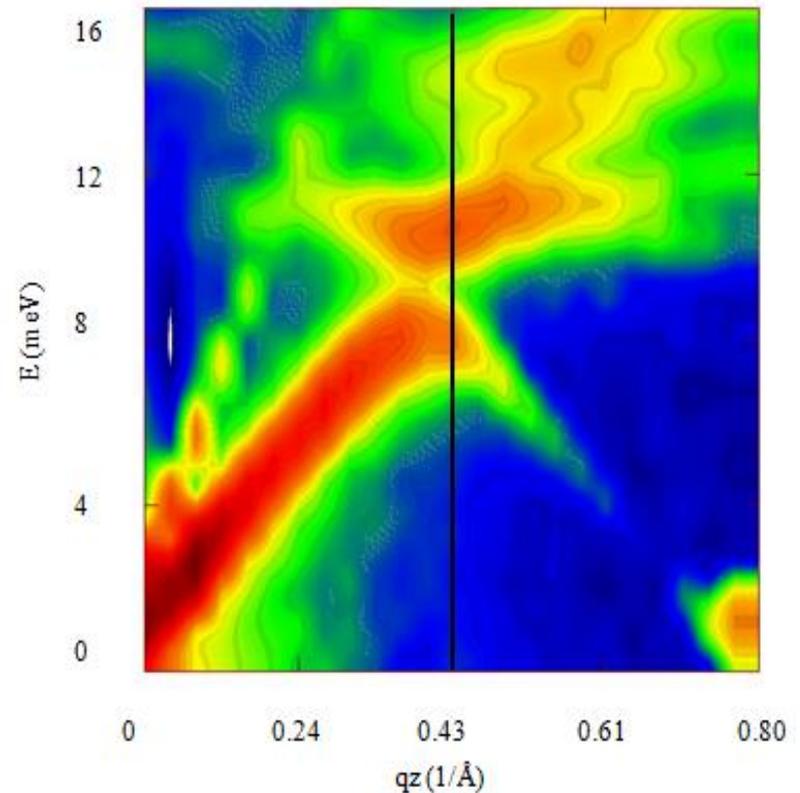Experiment: PHONON DHO at q=0,34 Å^{-1}

$\Gamma_E = 0.5$ meV $\approx$ $\tau = 2.63$ ps

Lattice dynamics:

Experiment and

Molecular dynamics simulations (LAMMPS + data analysis with nMoldyn
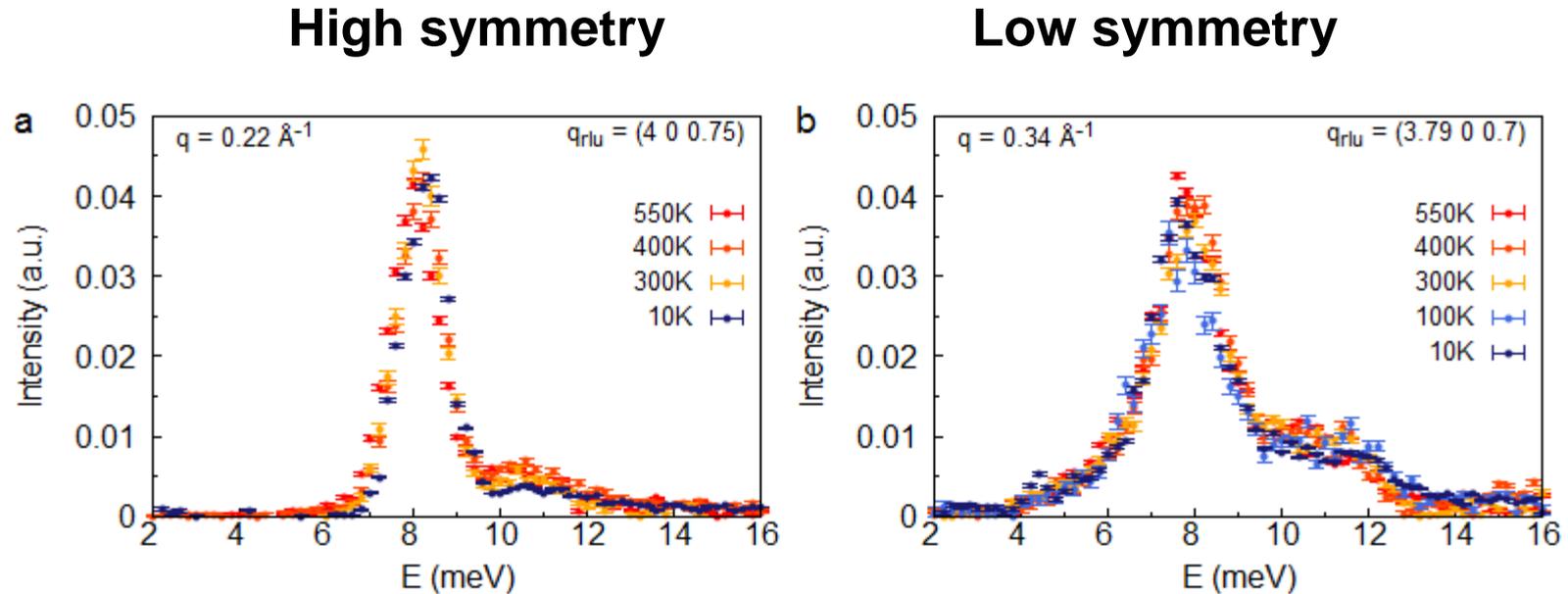
Inelastic Neutron Scattering
(IN22)

Molecular simulation
(LAMMPS and nMoldyn)

- MD simulation reproduce very well the phonon dispersion mapping (high symmetric direction)
- MD mapping has been convoluted by the instrumental resolution (Gaussian function)

S(Q,w) from MD simulations, where we observe the DHO signature from INS

High symmetry   **Low symmetry**
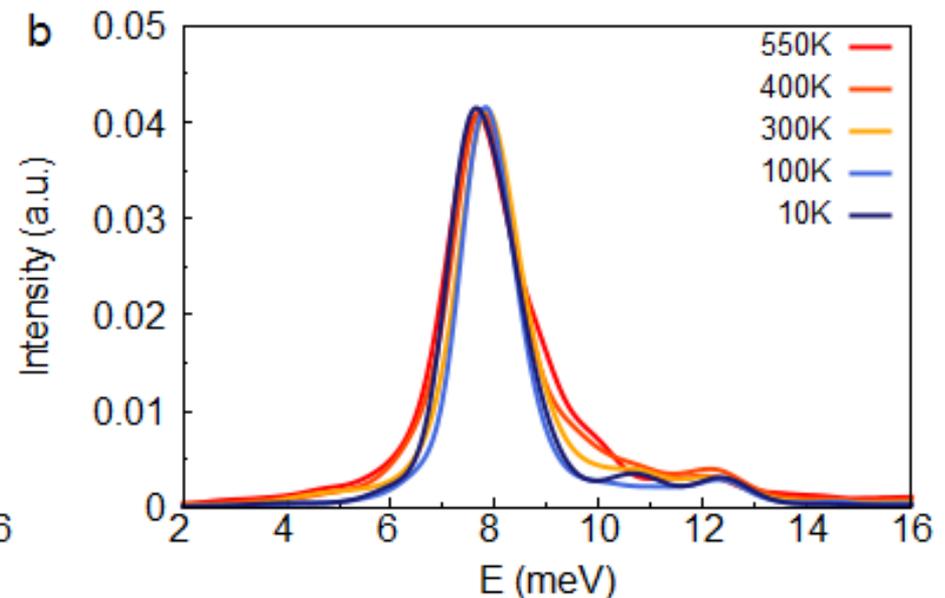

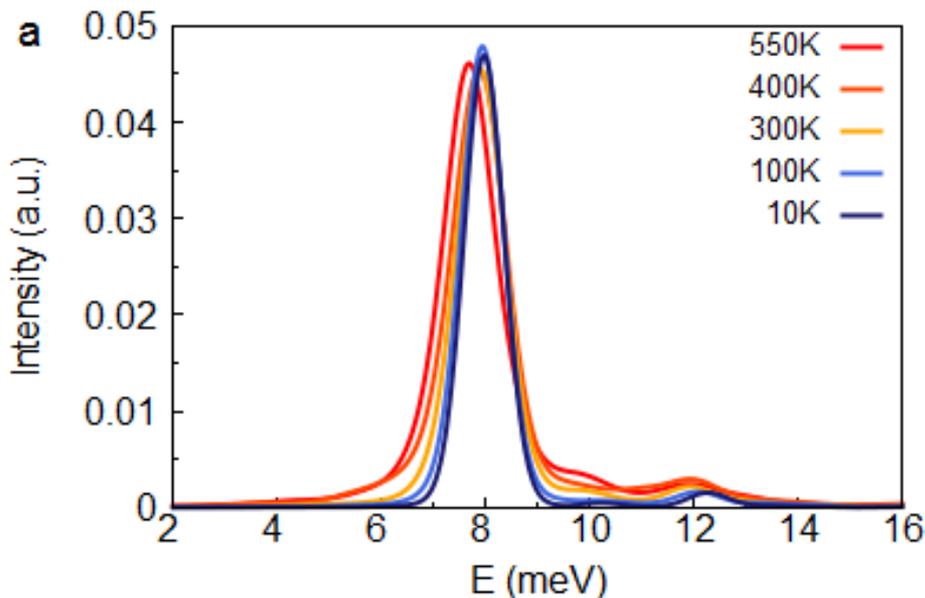- Measure in large range of temperatures [10 K to 550 K], (TAS-IN22 + cryofurnace)

- Conclusion : Γ is not dependent on the temperature

MD of S(Q,ω) low symmetry : q = 0.34 Å^{-1} (measured DHO)

Model 1: ordered   **Model 2: disordered**
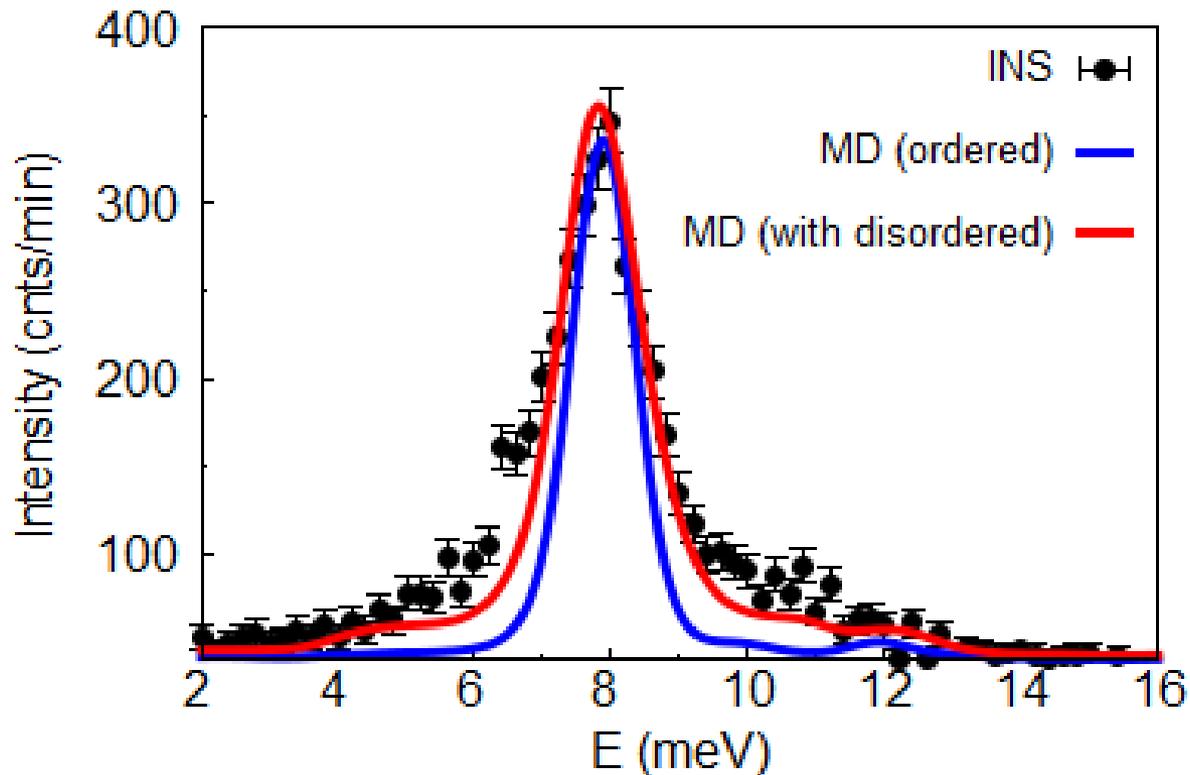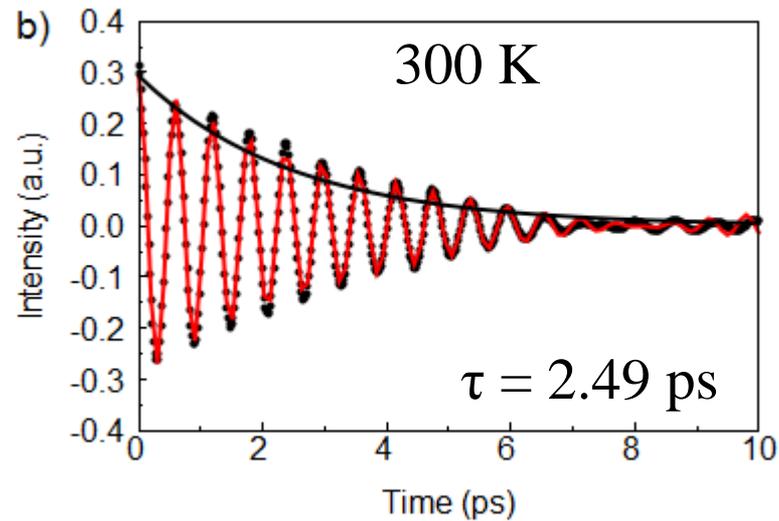

- Effect of T more important in model 1
- Weak temperature dependence
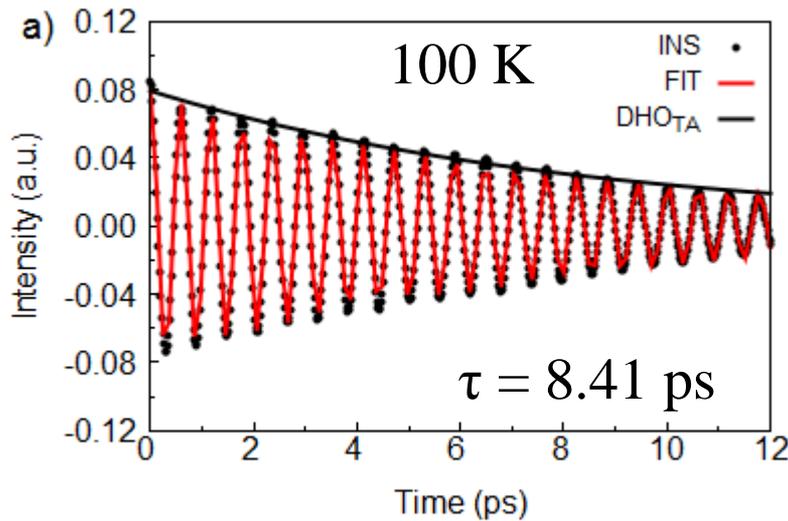
- MD with Anharmonic terms using pair potentials
- Phonon with finite lifetime → Model 2 with atomic disorder

$S(Q,\omega)$ **low symmetry**: q = 0.34 Å^{-1}
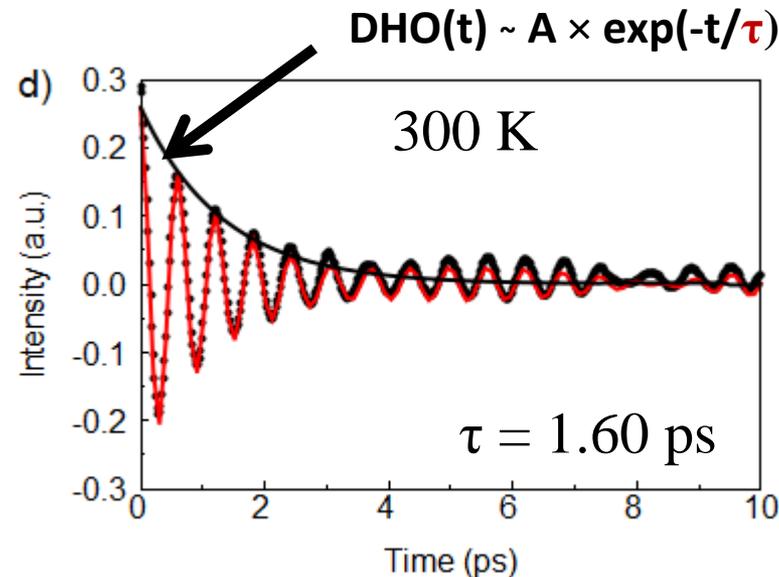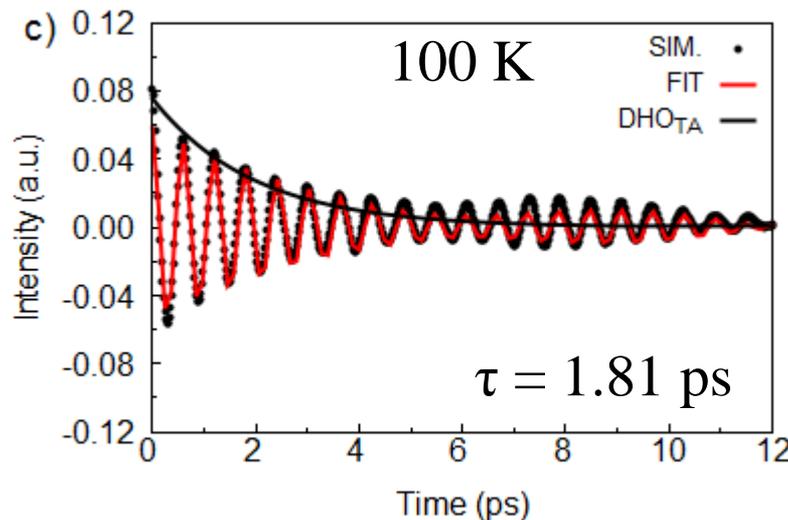
S(Q,t) from MD simulations at q = 0.34 nm^{-1}, where we observe the DHO signature in INS

Approximant-crystal
o-Al$_{13}$Co$_4$

Structure model

Potentials (PP)

Molecular Dynamics *(LAMMPS)*

Conditions
Time step : 2 fs
Total time : 10 ns

Positions, velocities
Energy and forces

Statistical method

Green-Kubo
Heat Current
$J_i(t)$

$$J_i(t) = \sum_i v_i\, E_i + \sum_{i \neq j} r_{ij}(F_{ij} \cdot v_j)$$

Ordered model: 16×8×8 supercell (131×100×114 A^3)

Disordered model: 6×6×6 supercell (146×148×173 A^3)

$$K_{ph}(T) = \frac{V}{3 k_B T^2} \int_0^t \sum_{i=x,y,z} \langle J_i(t) . J_i(0) \rangle\, dt$$

Thermal conductivity
K_{ph}

$K_{ph}(T) \sim T^{-0.5}$

$K_{ph}(T) \sim T^{-0.1}$
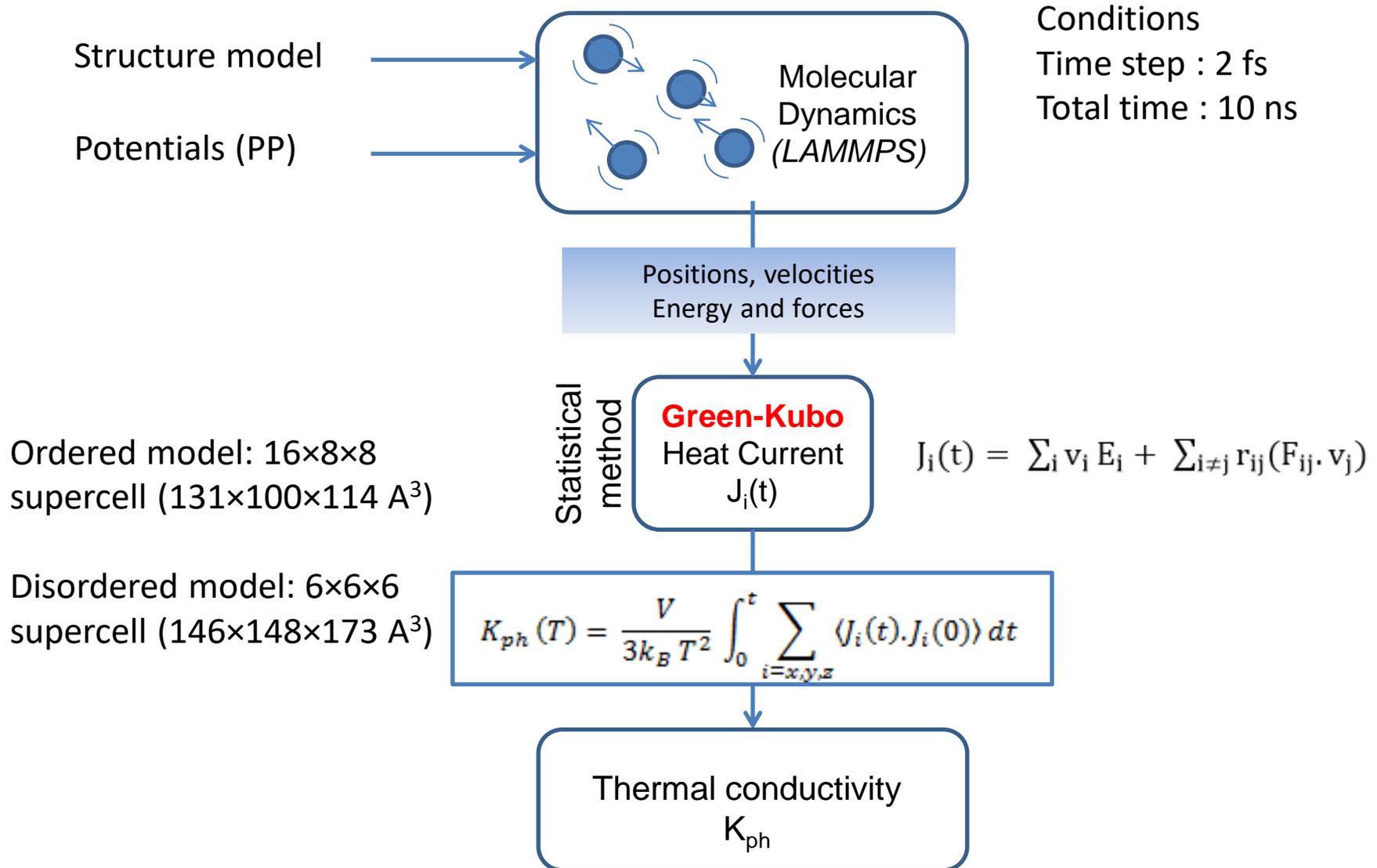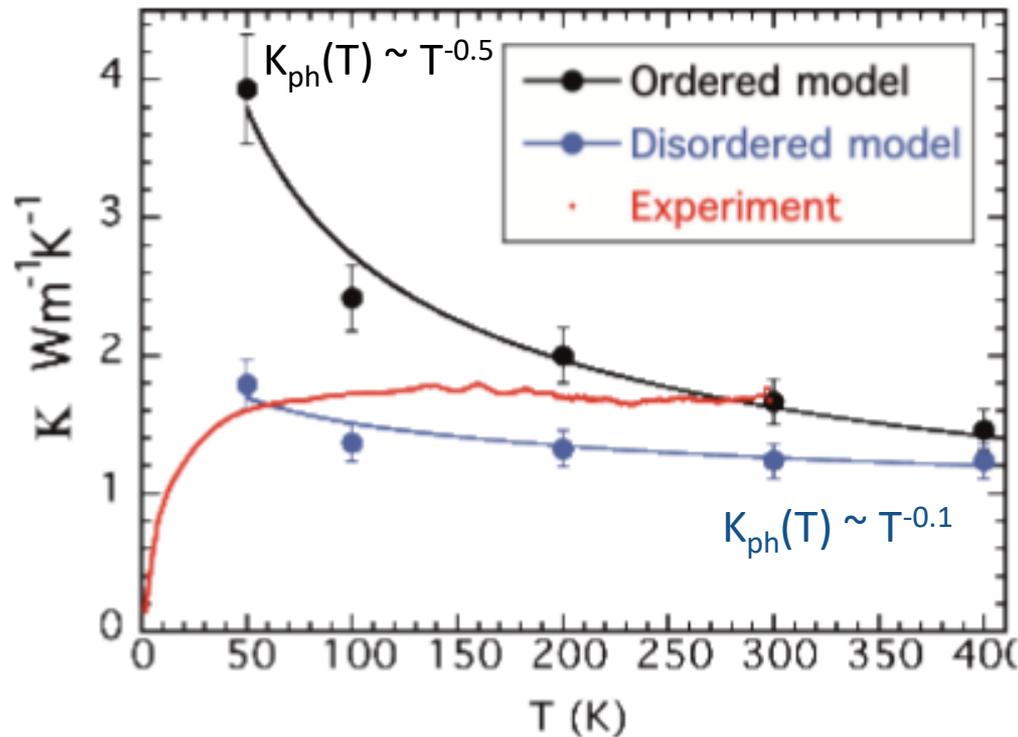
- For **K**$_{total,\textbf{ph}}$,simulations coherent with experiment
- Weak temperature dependence (disorder model)

Measure: J. Dolinšek, M. Komelj, P. Jeglič, S. Vrtnik, D. Stanić, P. Popčević, J. Ivkov, A. Smontara, Z. Jagličić, P. Gille, Yu. Grin, *Phys. Rev. B*, **79**, 184-201, (2009)

Structure → Lattice Dynamics → Thermal conductivity

For approximant-crystal o-$Al_{13}Co_4$

- Finite phonon lifetime due to disorder

- Phonon lifetime for acoustic mode : 33 ps

- Mean free path ~25 nm >>> a = 10.8 $\mathring{A}$

- Cluster structure and atomic disorder → low and weak T-dependence of thermal conductivity in o-$Al_{13}Co_4$

Perspective : Investigate the thermal properties on the Clathrate $Ba_8Ge_{40.6}Au_{5.25}$ by Classical simulation and potentials

P.-F. Lory, V. M. Giordano, P. Gille, H. Euchner, M. Mihalkovič, E. Pellegrini, M. Gonzalez, L.-P. Regnault, P. Bastie, H. Schober, S. Pailhes, M. R. Johnson, Yu. Grin, and M. de Boissieu, Phys. Rev. B **102**, 024303, (2020)

Ge

Ba₈Ge₄₀Au₆

$Ba_8Ge_{40}Au_6$

$Ba_8Ge_{40.3}Au_{5.25}$

Ge₄₆

Ge_{46}
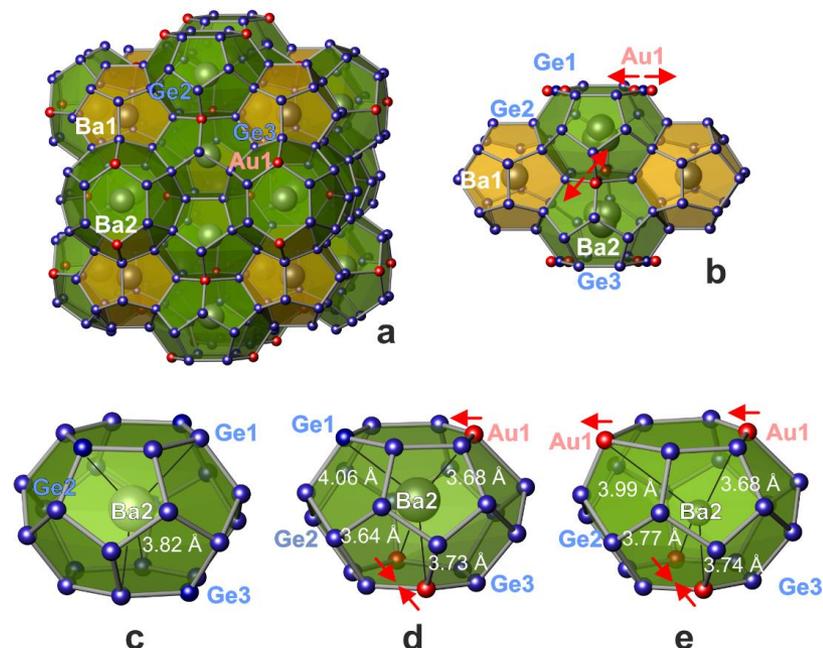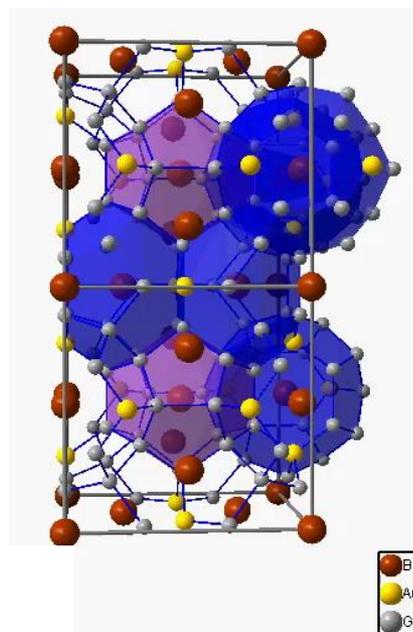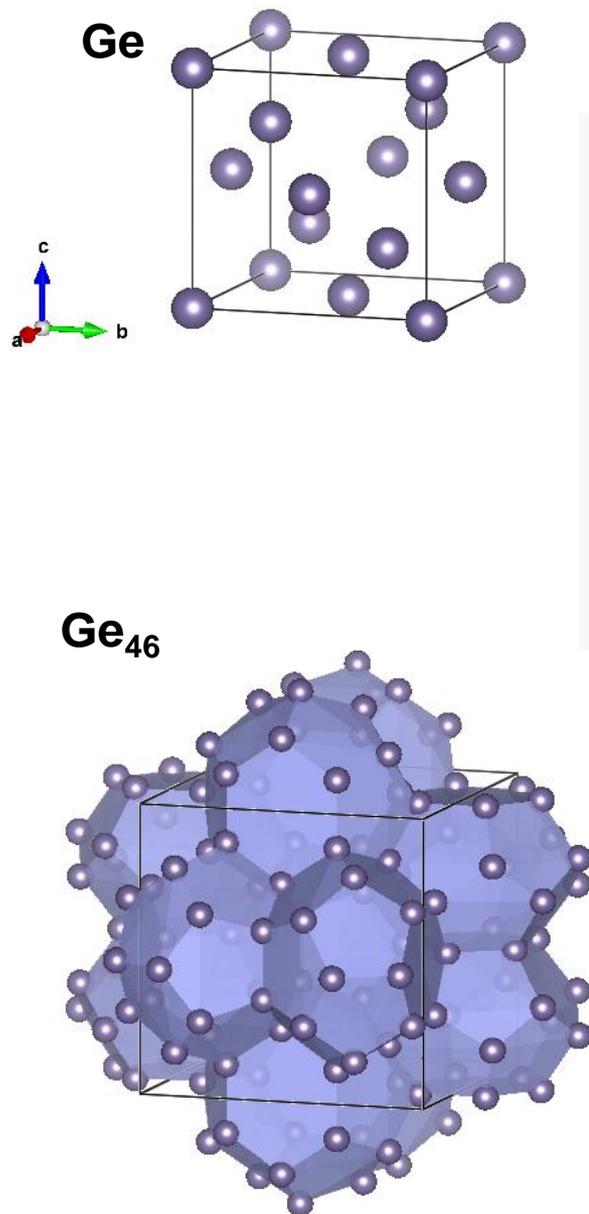
- Investigate the thermal properties on the clathrate series by Classical molecular simulation
- Compare with the experimental work (Measure $\tau_{ph} \sim [30 - 53]$ ps)

Lory, P. F., Pailhès, S., Giordano, V. M., Euchner, H., Nguyen, H. D., Ramlau, R., ... & de Boissieu, M. (2017). Direct measurement of individual phonon lifetimes in the clathrate compound Ba 7.81 Ge 40.67 Au 5.33. *Nature communications*, *8*(1), 1-10.

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Thank you for your attention