

Anharmonic materials properties from first principles with and without MD

BAM Seminar, Berlin, 7 Dec 2022

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2) NOMAD laboratory at the FHI, Berlin

Motivation

Materials properties **change with temperature**

DFT is a 0K theory → need approaches to **introduce temperature** = nuclear motion

Examples:

Phase stability

Thermal transport

Response to light and neutrons

Outline

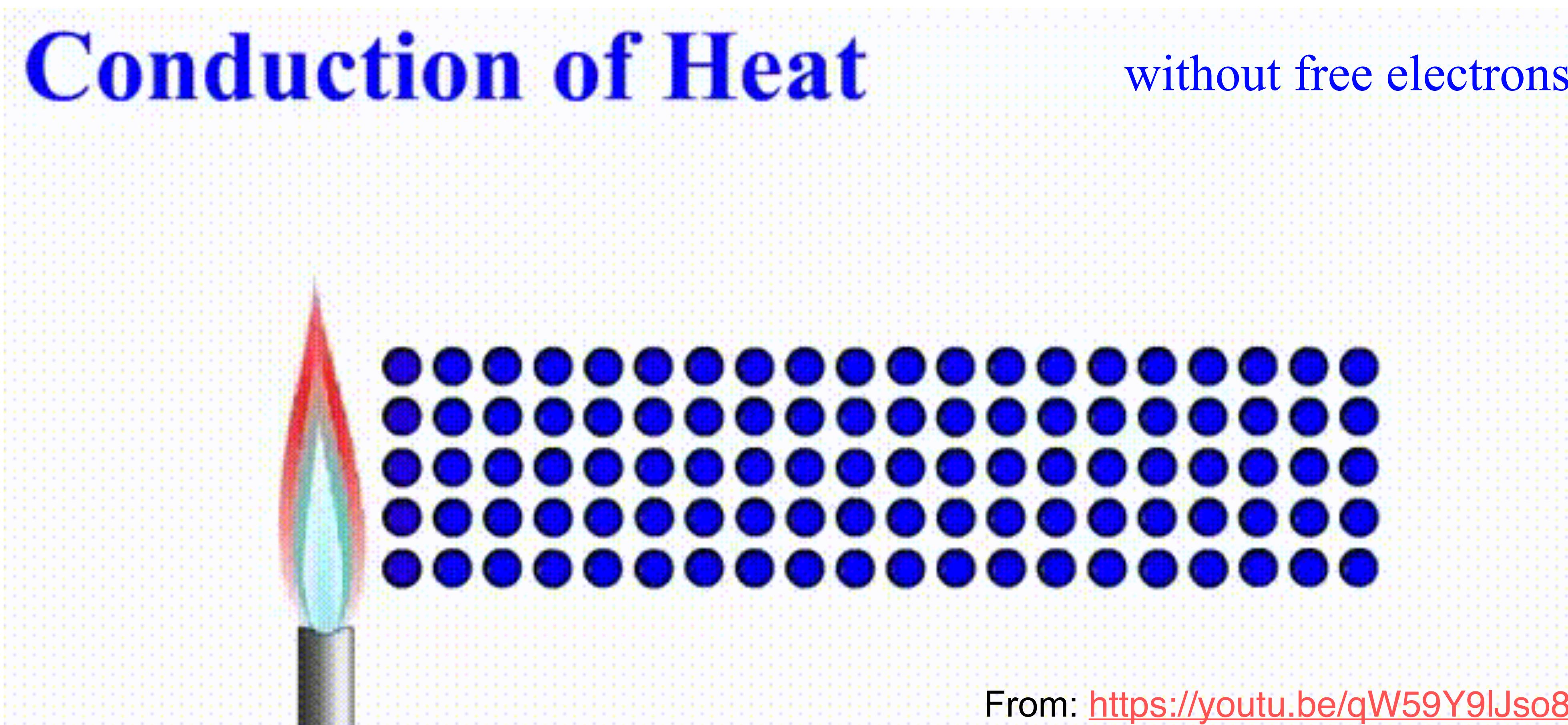
Introduction: Anharmonicity and thermal transport

Part 1: *ab initio* Green-Kubo simulations and search for thermal insulators

Part 2: Anharmonic properties fast: Temperature Dependent Effective Potentials

Application: High-pressure synthesis of Lanthanum Hydride compounds

Thermal transport: Intuition



Thermal transport: Fourier's law and unit

$$\text{Heat flux} \longrightarrow \mathbf{J} = -\kappa \nabla T \longleftarrow \text{Temperature gradient}$$

\uparrow

Thermal conductivity

Thermal transport: Fourier's law and unit

$$\text{Heat flux} \longrightarrow J = -\kappa \nabla T \longleftarrow \text{Temperature gradient}$$

Thermal conductivity

$$\text{Unit} \longrightarrow [\kappa] = \frac{\text{W}}{\text{mK}}$$

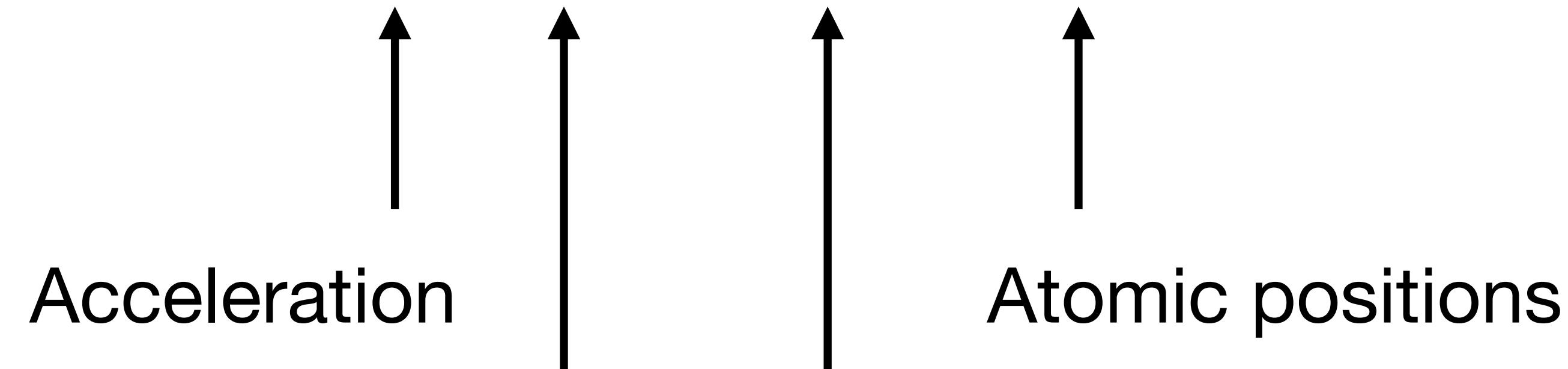
← Watt
← Meter * Kelvin

The diagram illustrates the relationship between heat flux, temperature gradient, and thermal conductivity. At the top, 'Heat flux' is shown as an arrow pointing to the left, and 'Temperature gradient' is shown as an arrow pointing to the right, separated by the equation $J = -\kappa \nabla T$. A vertical arrow points upwards from the bottom equation to the word 'Thermal conductivity'. Below this, the 'Unit' is given as $[\kappa] = \frac{\text{W}}{\text{mK}}$. To the right of this equation, two arrows point to the right, labeled 'Watt' and 'Meter * Kelvin', indicating the components of the unit.

Nuclear dynamics and harmonic approximation

Potential energy V determines dynamical properties of materials:

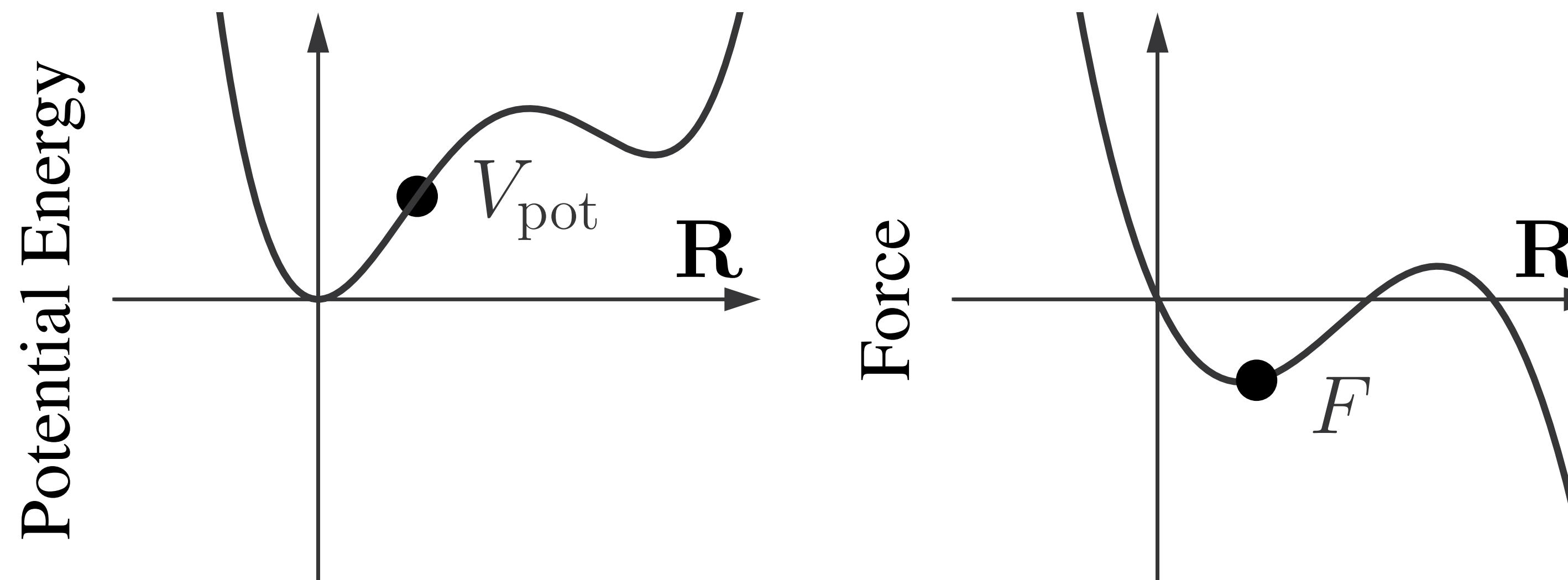
$$M\ddot{\mathbf{R}} = \mathbf{F} = - \nabla V_{\text{pot}}(\mathbf{R})$$



Nuclear dynamics and harmonic approximation

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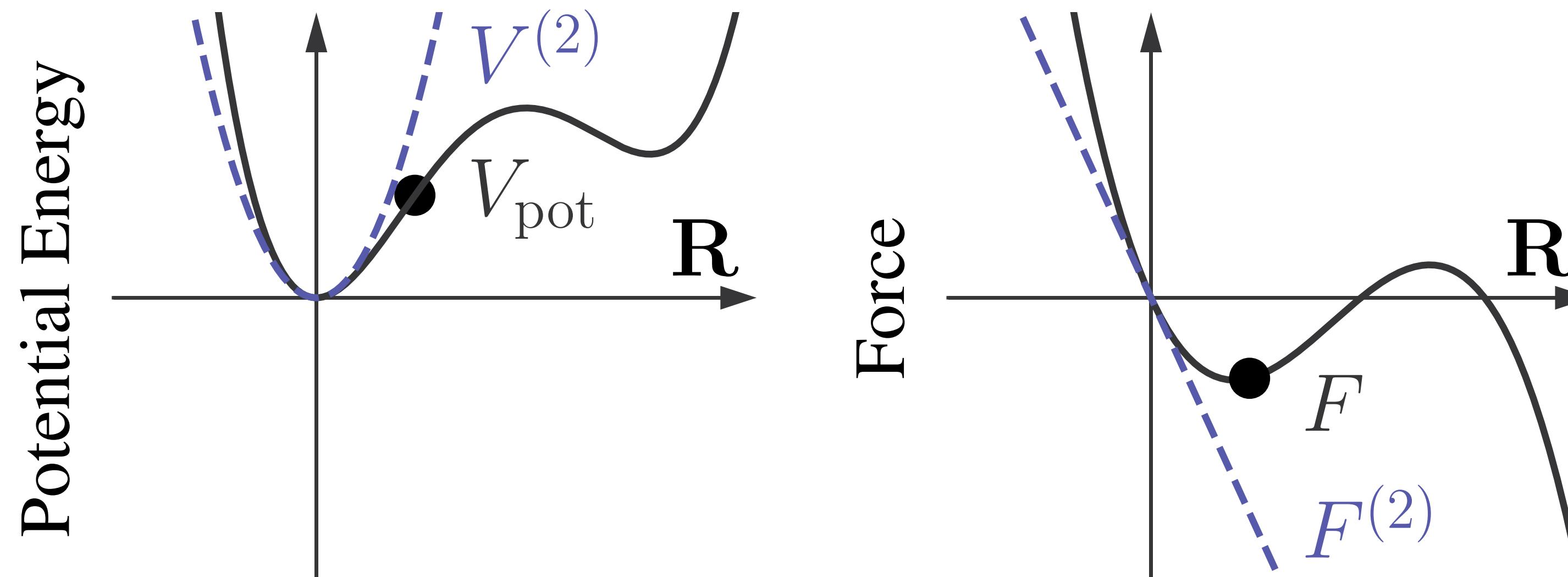
1D toy potential-energy surface

[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Nuclear dynamics and harmonic approximation

Potential energy V determines dynamical properties of materials:

$$M\ddot{\mathbf{R}} = \mathbf{F} = -\nabla V_{\text{pot}}(\mathbf{R}) \approx \mathbf{F}^{(2)}$$



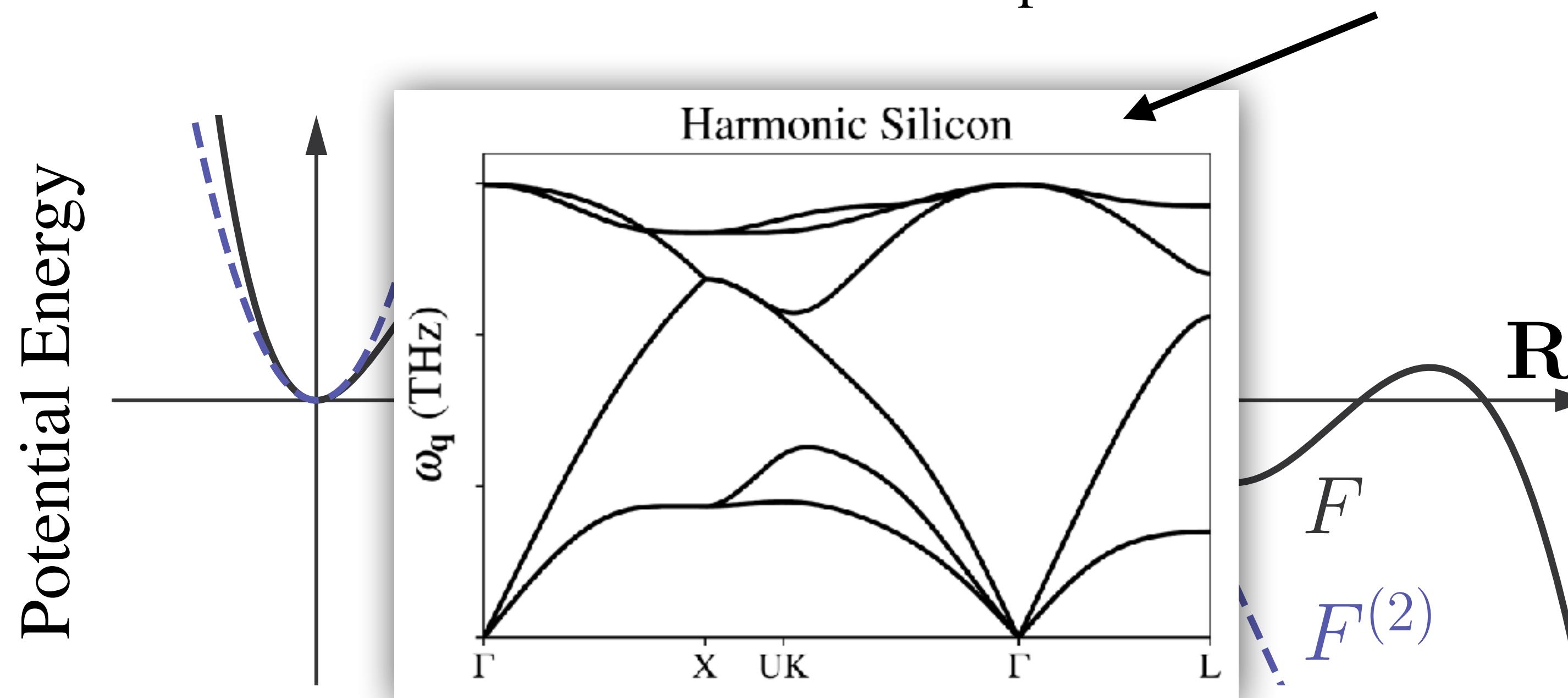
Harmonic approximation $V^{(2)} \rightarrow$ Analytical solution: **phonons**

[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Nuclear dynamics and harmonic approximation

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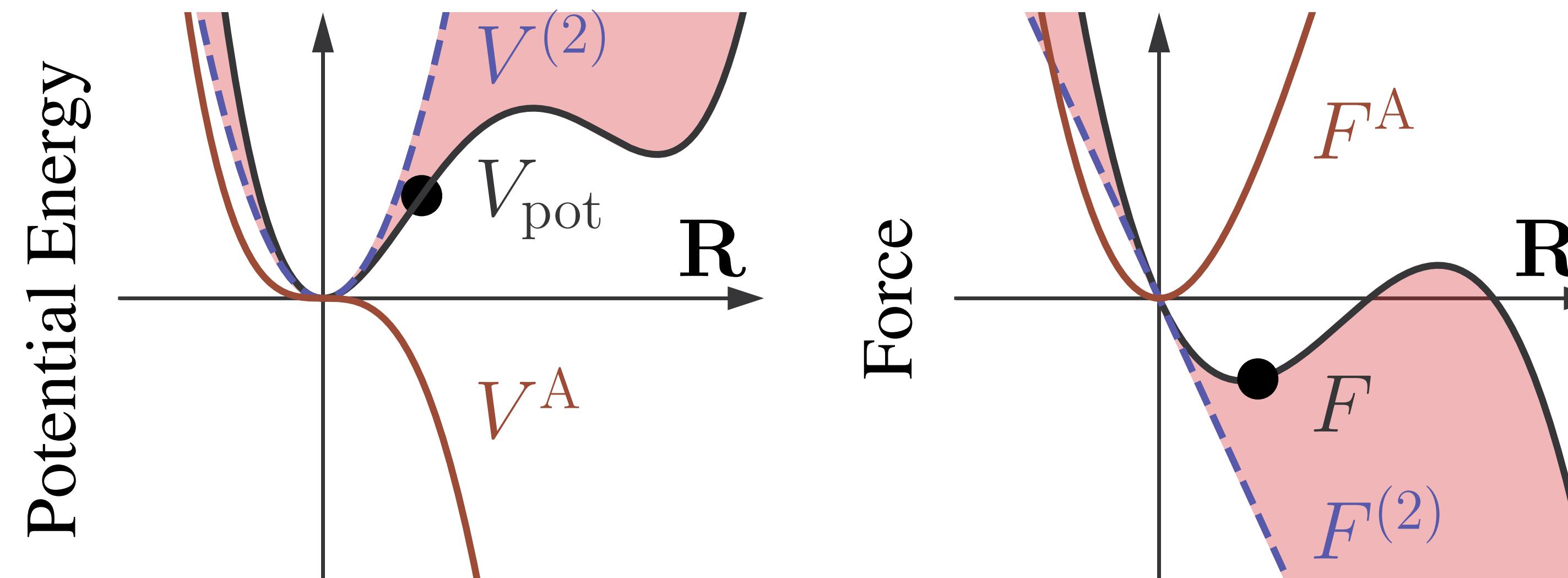
Harmonic approximation $V^{(2)} \rightarrow$ Analytical solution: **phonons** $\implies \kappa = \infty!$

[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Nuclear dynamics and harmonic approximation

Potential energy V determines dynamical properties of materials:

$$M\ddot{\mathbf{R}} = \mathbf{F} = -\nabla V_{\text{pot}}(\mathbf{R}) \approx \mathbf{F}^{(2)} + \mathbf{F}^A$$



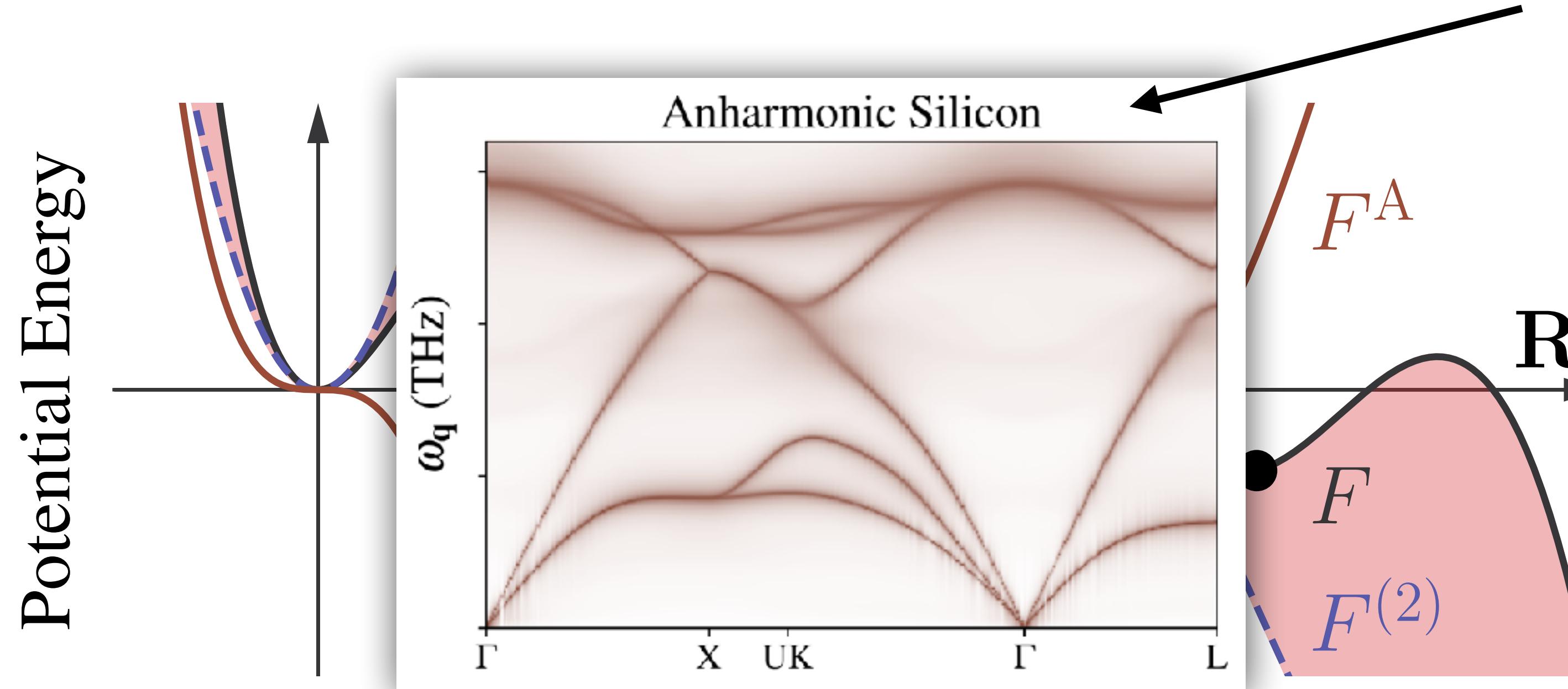
Reality: Anharmonic contributions V^A

[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Nuclear dynamics and harmonic approximation

Potential energy V determines dynamical properties of materials:

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Reality: **Anharmonic** contributions $V^A \implies \kappa < \infty$

[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

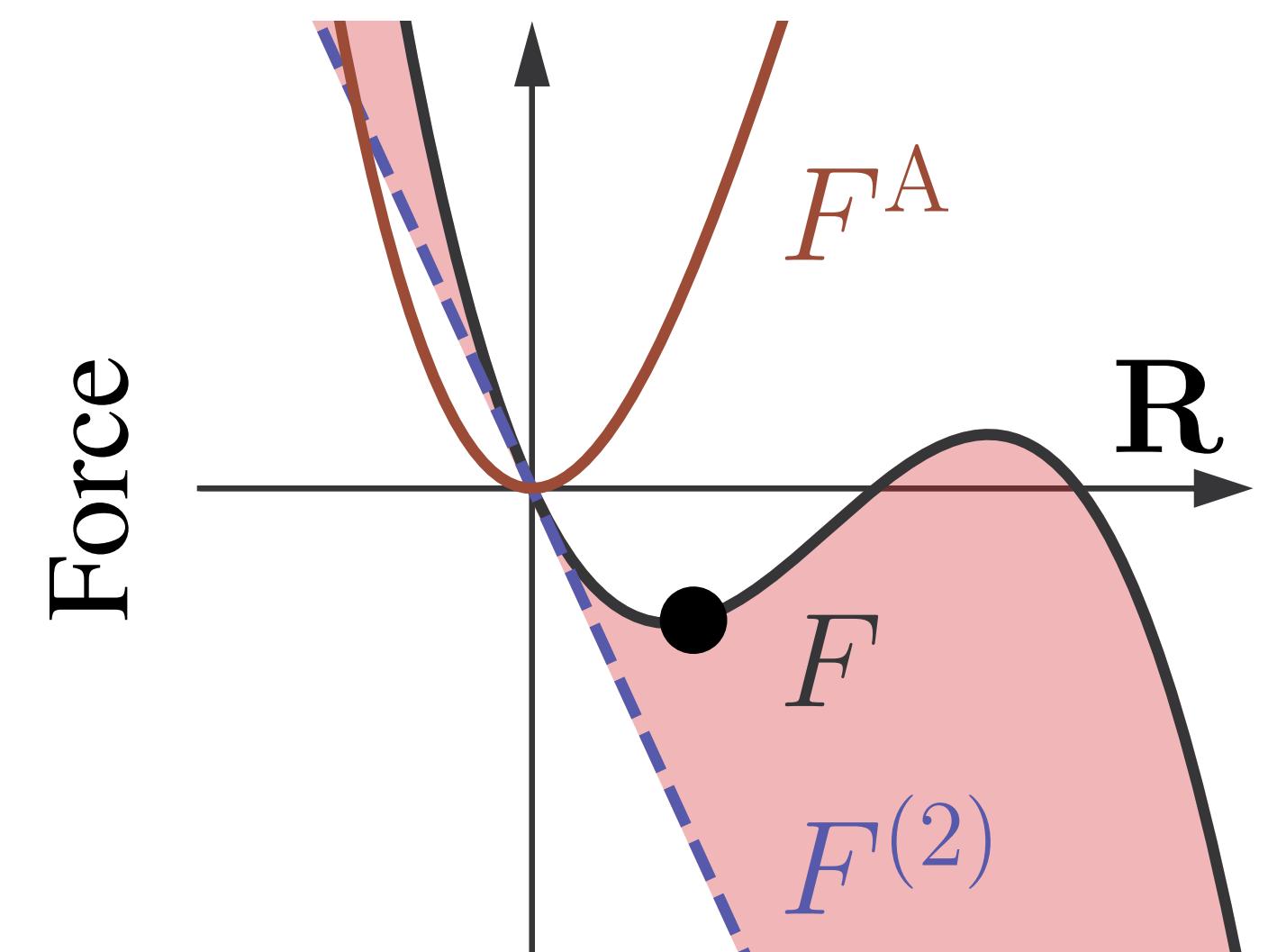
Nuclear dynamics and harmonic approximation

Potential energy V determines dynamical properties of materials:

$$M\ddot{\mathbf{R}} = \mathbf{F} = -\nabla V_{\text{pot}}(\mathbf{R}) \approx \mathbf{F}^{(2)} + \mathbf{F}^A$$

Anharmonicity measure $\sigma^A[1]$:

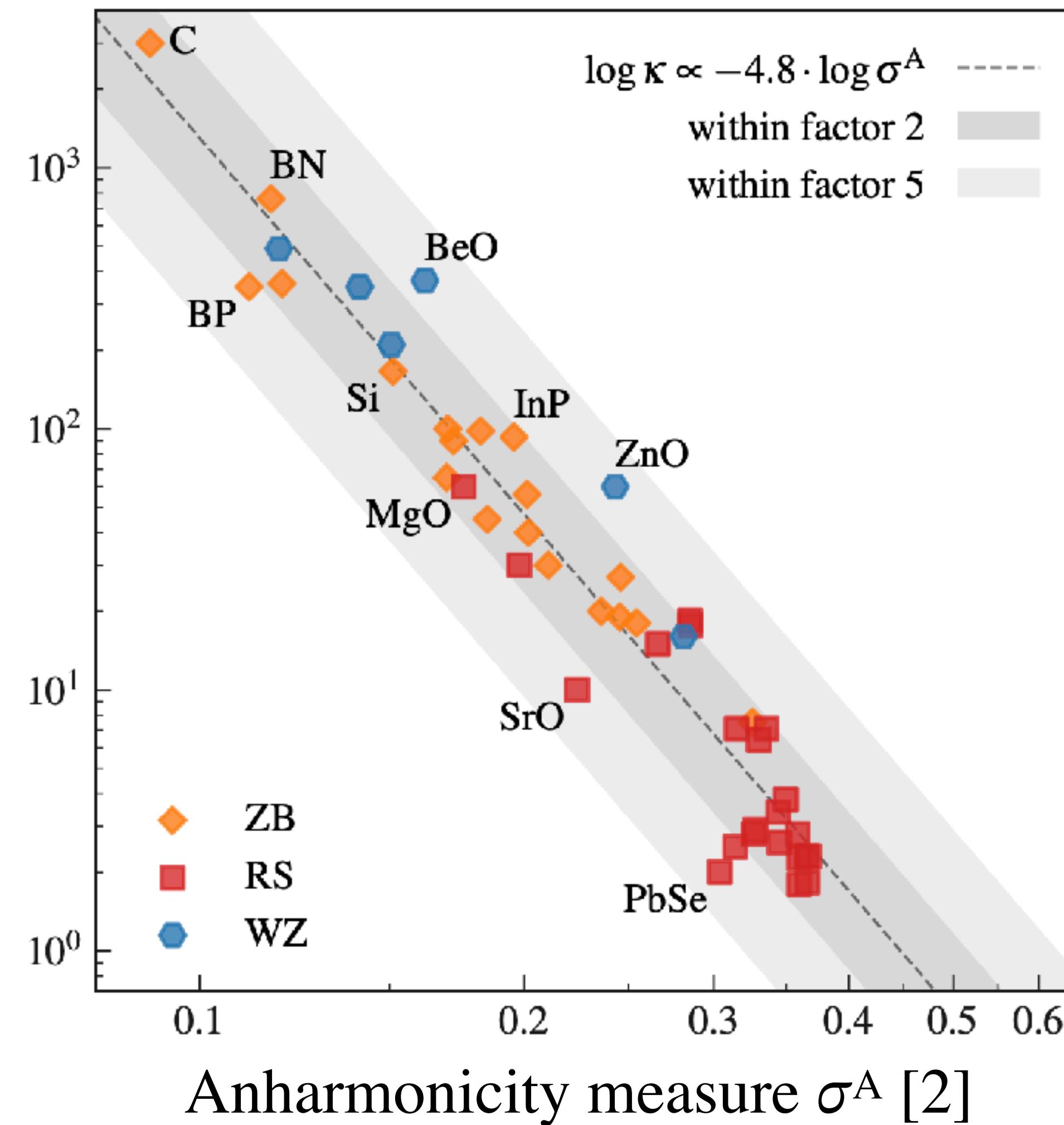
$$\sigma^A(T) = \frac{|\mathbf{F}^A|}{|\mathbf{F}|}$$



[1] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

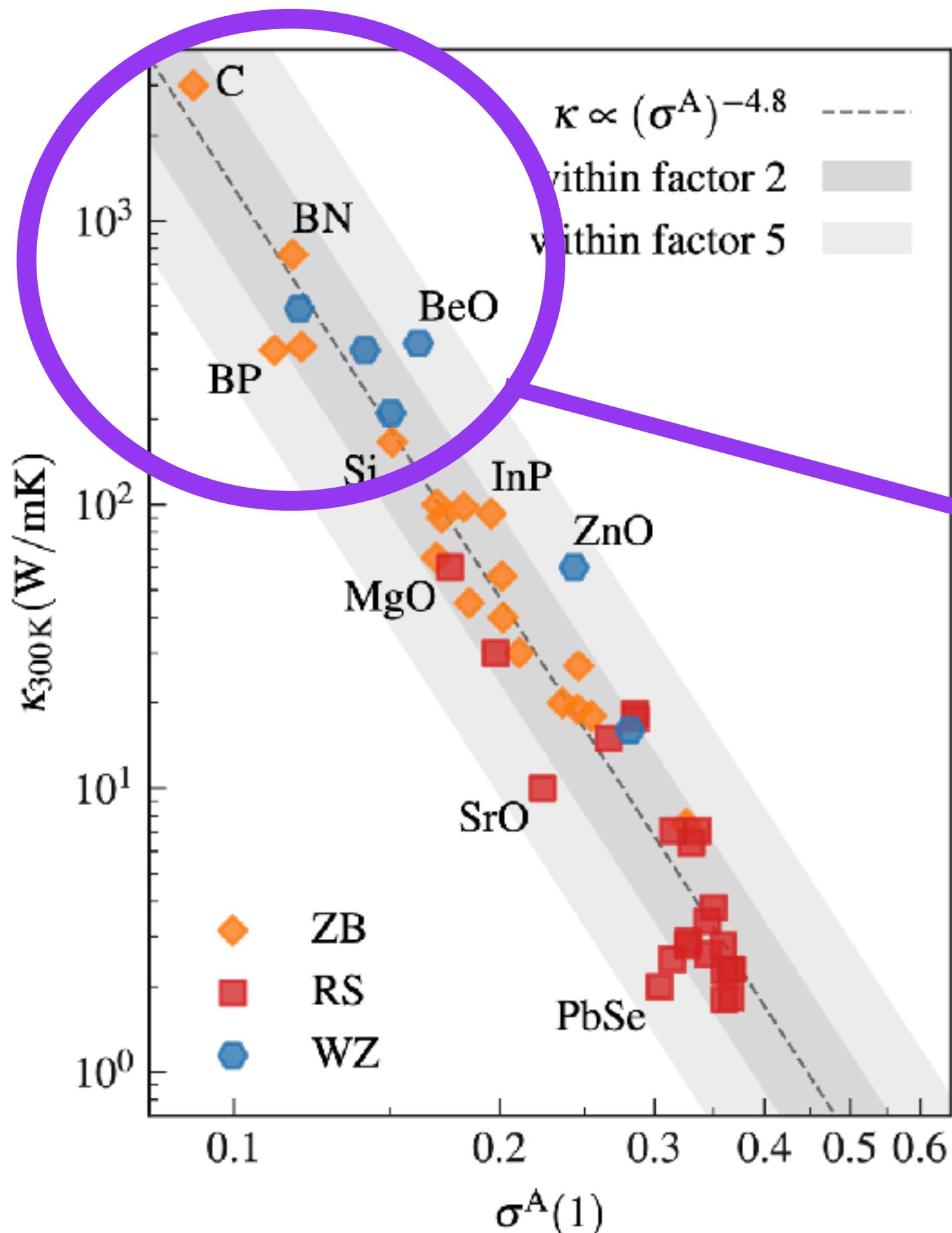
Thermal conductivity and anharmonicity

Experimental
thermal conductivities
at 300 K [1]



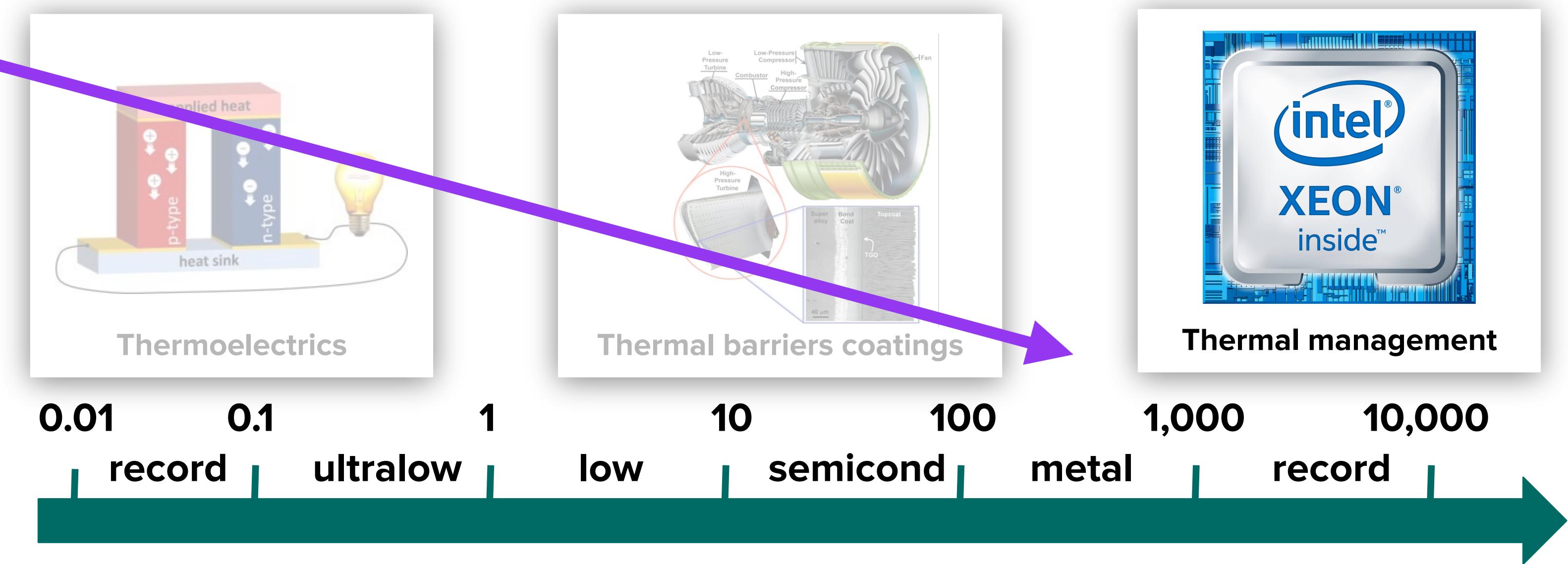
- [1] D. Morelli, G. Slack in *High Lattice Thermal Conductivity Solids*, Springer 2006
[2] FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Thermal conductivity and anharmonicity



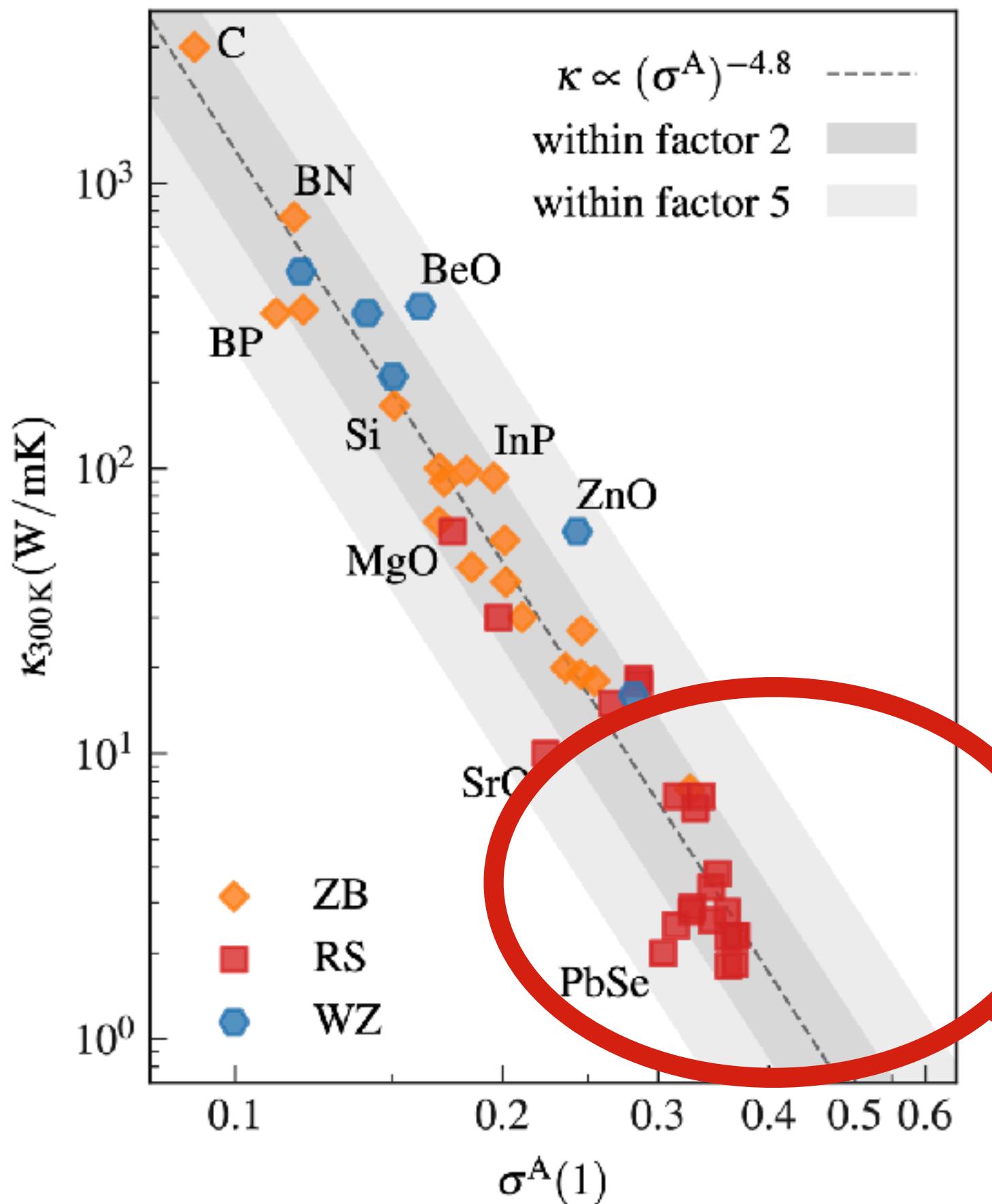
$\sigma^A << 0.2$:
Harmonic
high κ

Applications:



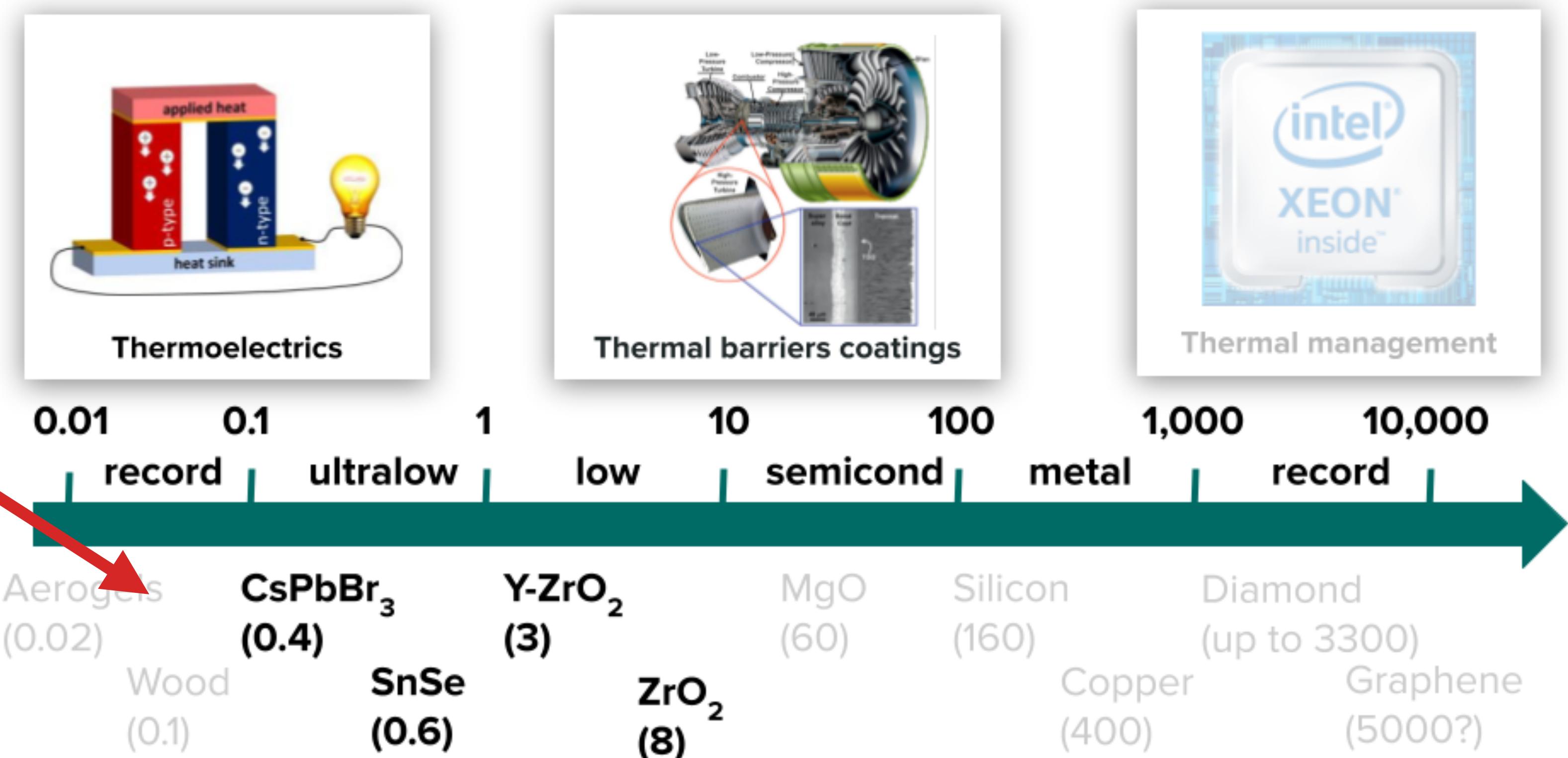
12

Thermal conductivity and anharmonicity



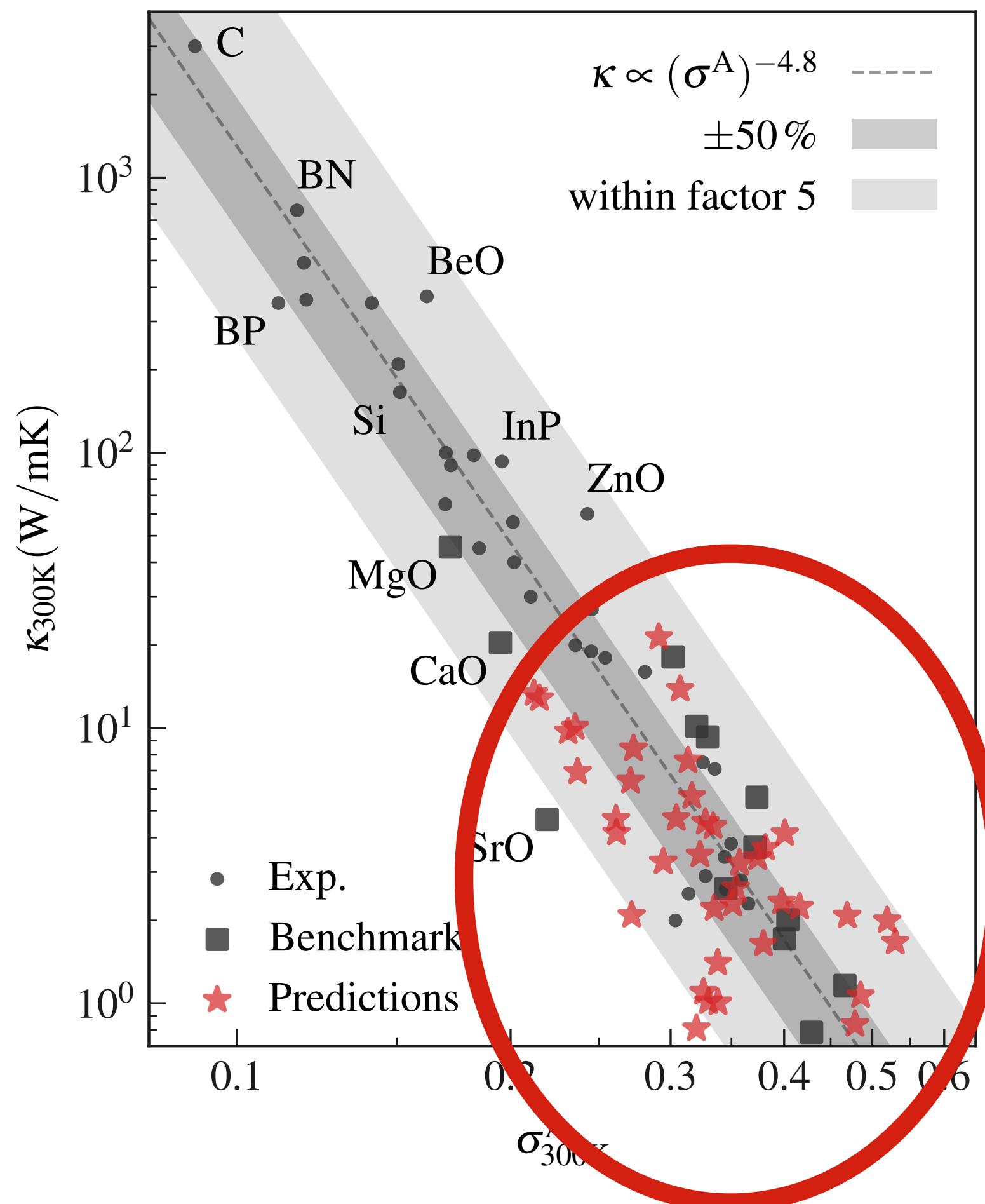
$\sigma^A > 0.2$:
Anharmonic
low κ

Applications:



Part 1: Search for thermal insulators

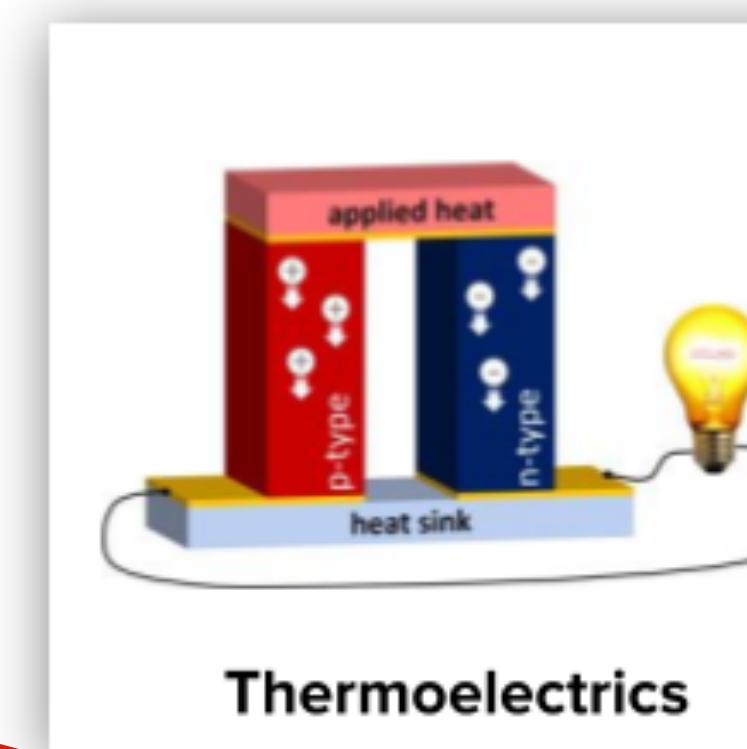
Our interest: Find new thermal insulators



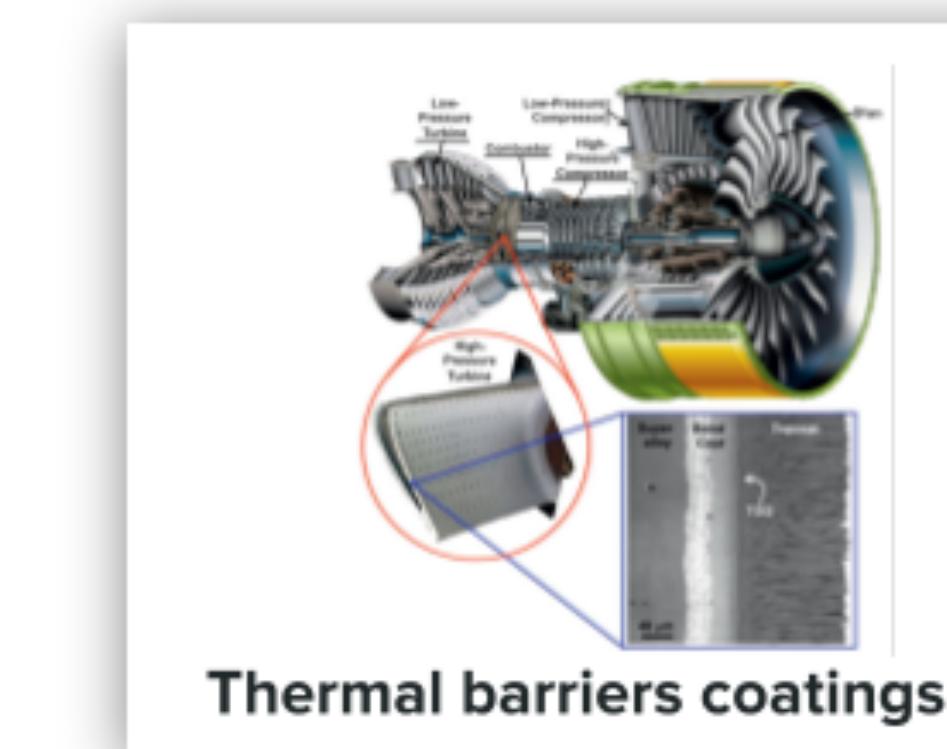
σ^A is cheap to compute:
High-throughput screening

→ T. A. R. Purcell et al., Arxiv 2204.12968 (2022)

Applications:



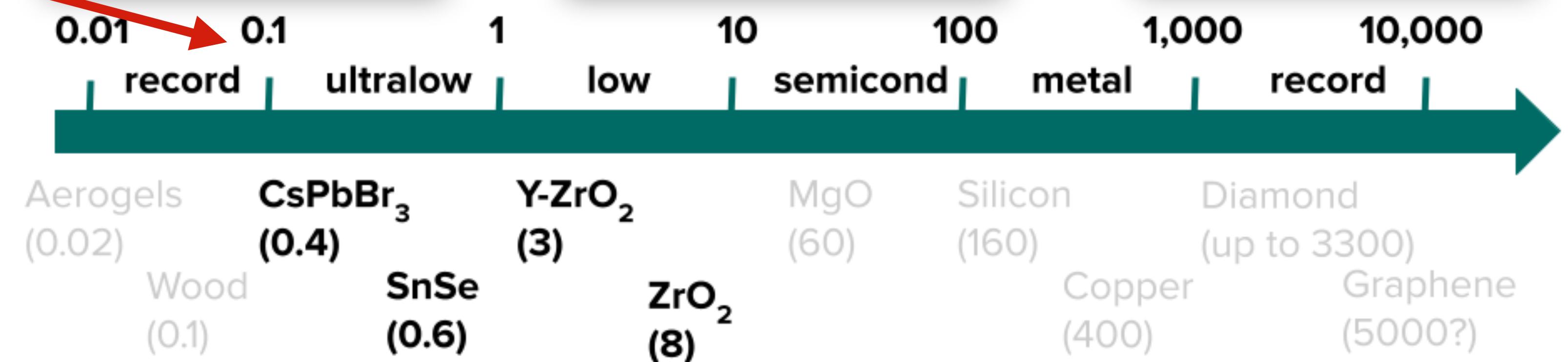
Thermoelectrics



Thermal barriers coatings



Thermal management



FK, T.A.R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020)

Green-Kubo Theory [1, 2]

Thermal conductivity

$$\kappa(T) = \frac{1}{3T^2V} \lim_{t \rightarrow \infty} \int_0^t d\tau \underbrace{\langle \mathbf{J}(\tau) \cdot \mathbf{J}(0) \rangle}_T$$

Temperature

Canonical ensemble average

Heat Flux
Autocorrelation
Function

[1] M. Green, J. Chem. Phys. **20**, 8 (1957)

[2] R. Kubo, M. Yokota, S. Nakajima, J. Phys. Soc. Jpn. **12**, 11 (1957)

Ab initio Green-Kubo Method [1]



Ab initio conductive heat flux [1]

$$\mathbf{J}(t) = \sum_I \boldsymbol{\sigma}_I(t) \cdot \dot{\mathbf{R}}_I(t)$$

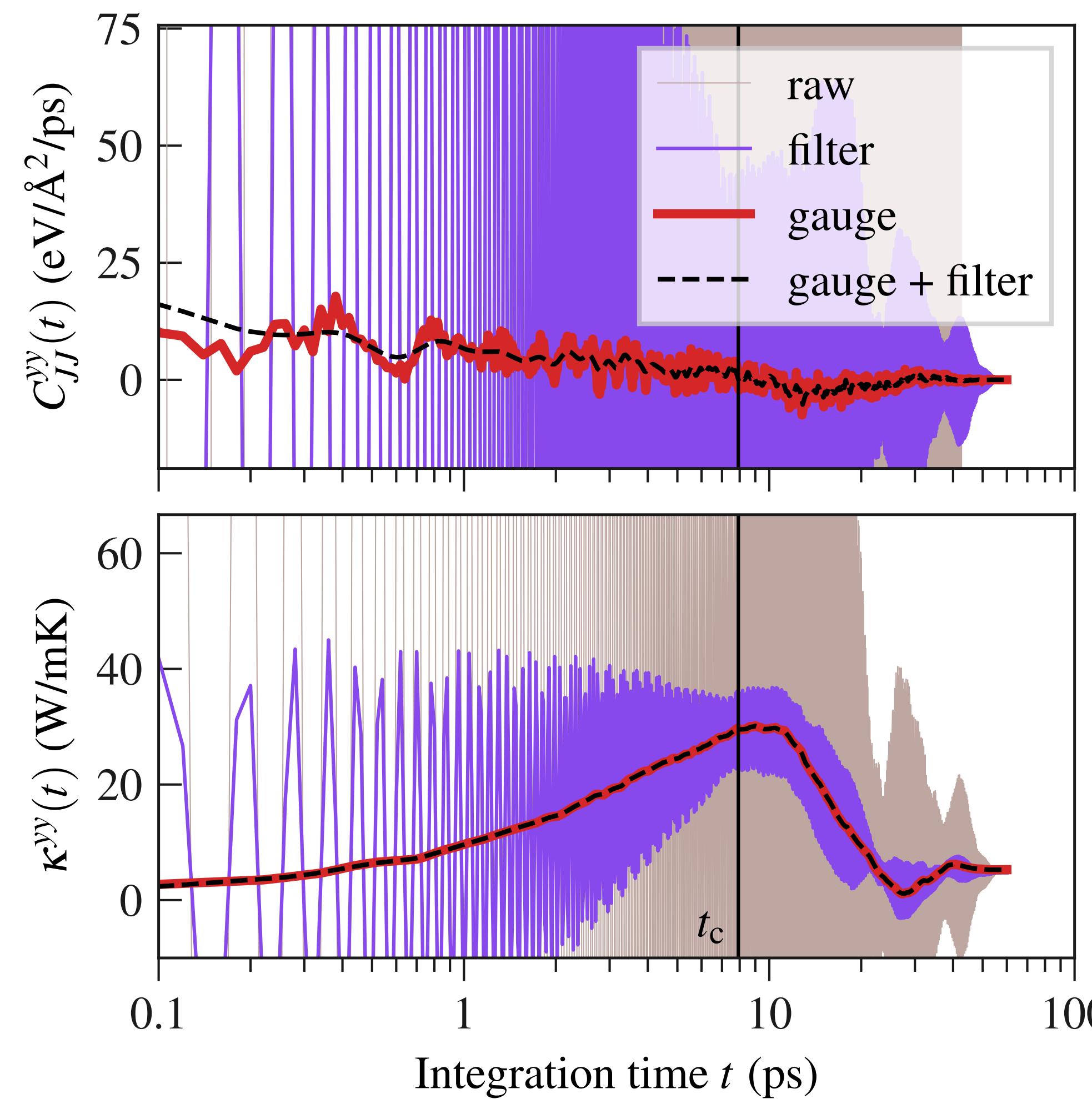
Ab initio atomic virials [2]

Atomic velocities
during
molecular dynamics simulations

[1] C. Carbogno, R. Ramprasad, M. Scheffler, *PRL* **118**, 175901 (2017)

[2] F. Knuth *et al.*, *CPC* **190**, 33 (2015), V. Blum *et al.*, *CPC* **180**, 2175 (2009)

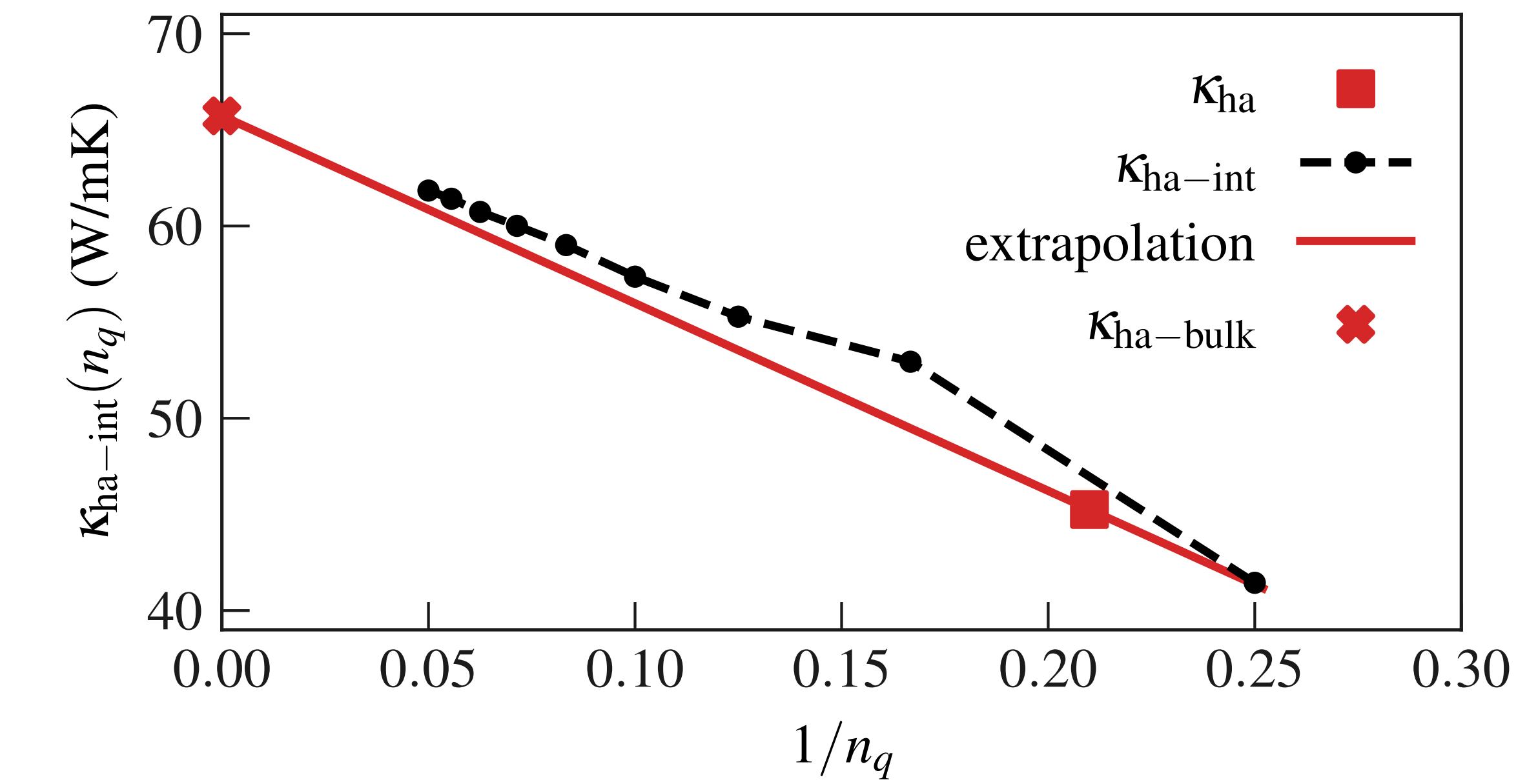
Finite time and size effects in *ab initio* molecular dynamics [2]



Implemented in FHI-vibes [3]



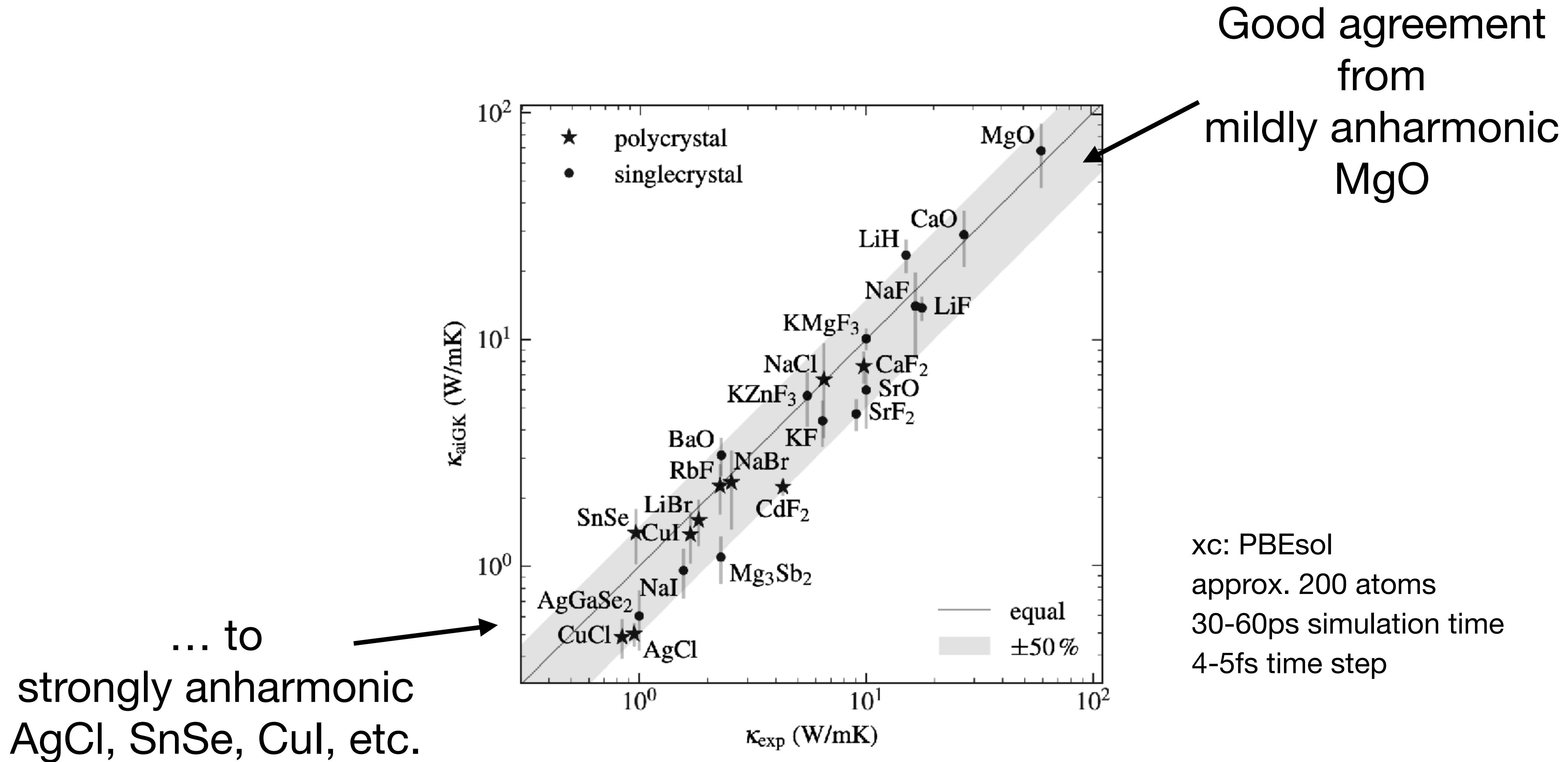
JOSS 10.21105/joss.02671



[2] FK, M. Scheffler, C. Carbogno, Arxiv 2209.01139

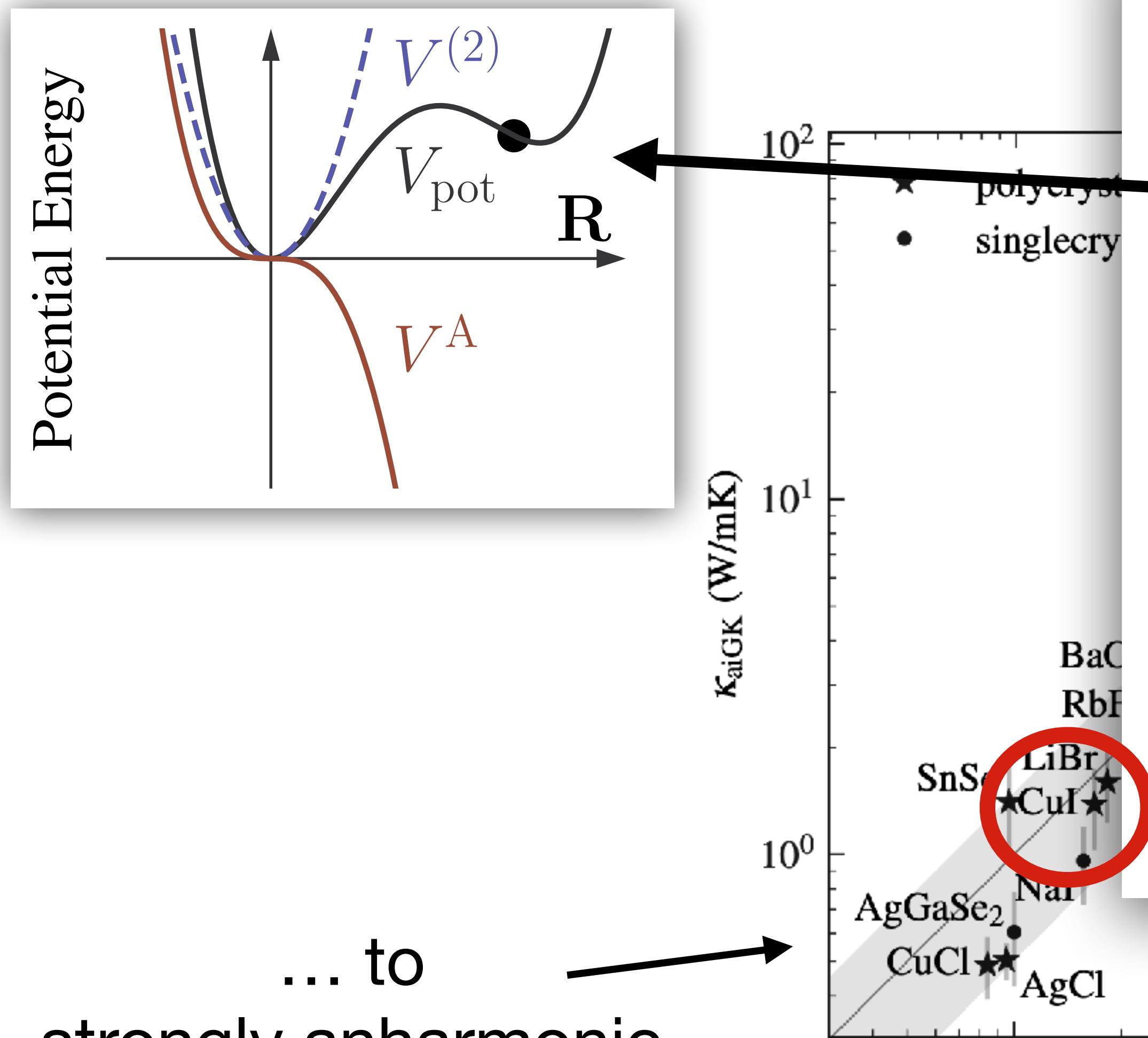
[3] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, JOSS 5, 2671 (2020)

Ab initio Green-Kubo: Benchmark [4]

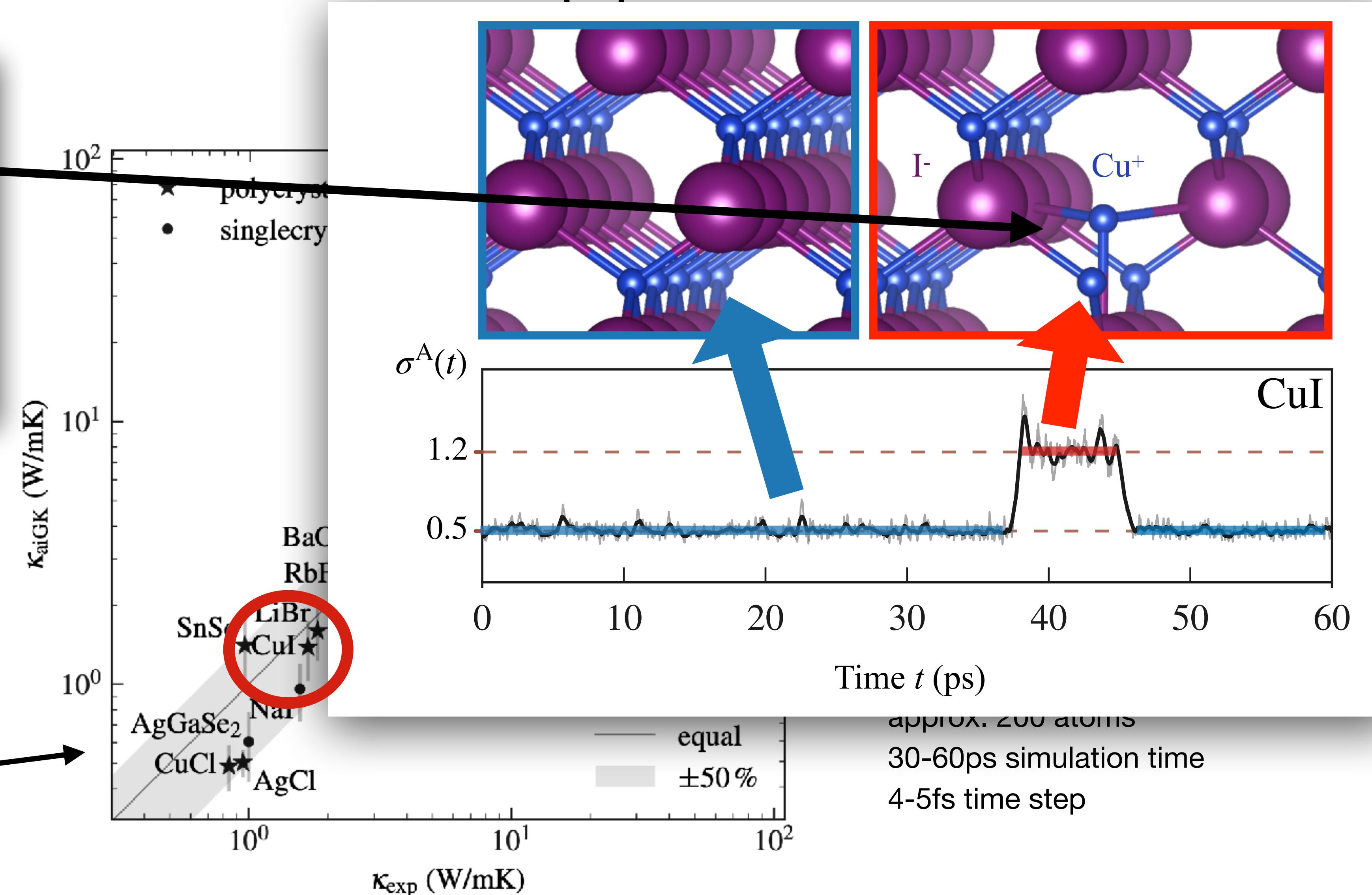


[4] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, Arxiv 2209.01139

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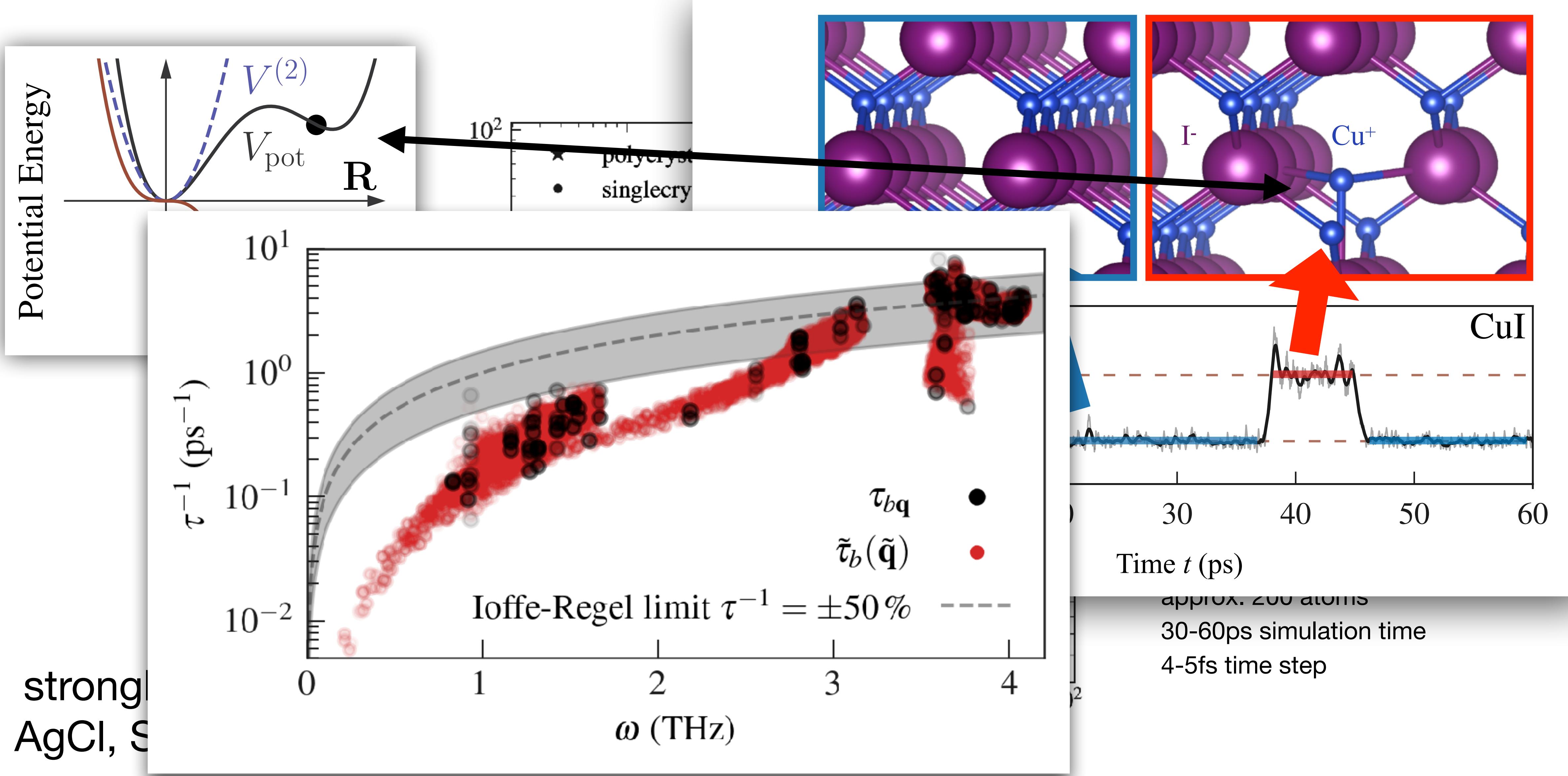


... to
strongly anharmonic
AgCl, **SnSe**, **CuI**, etc.



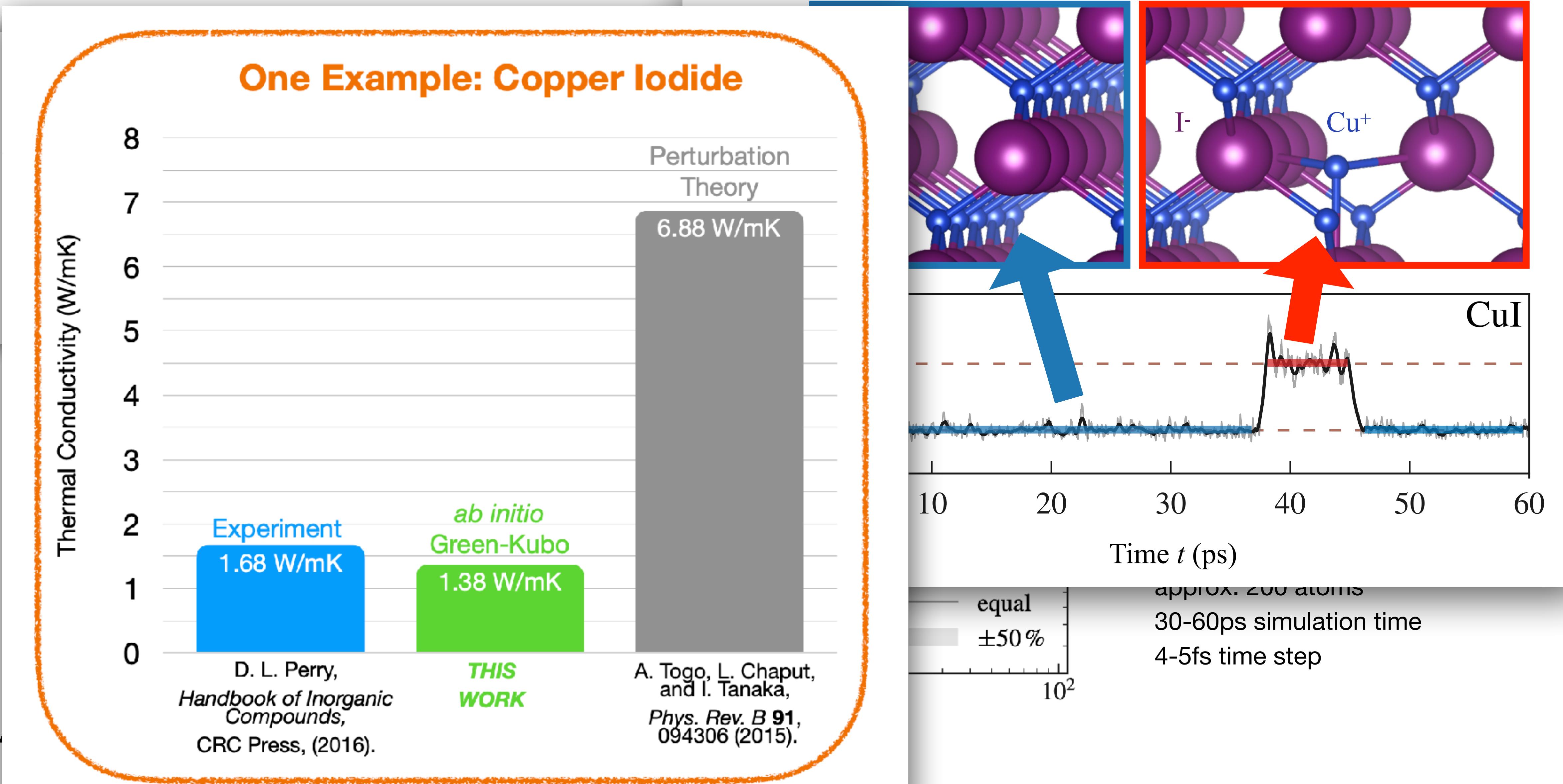
[4] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, Arxiv 2209.12720

Ab initio Green-Kubo: Benchmark [4]

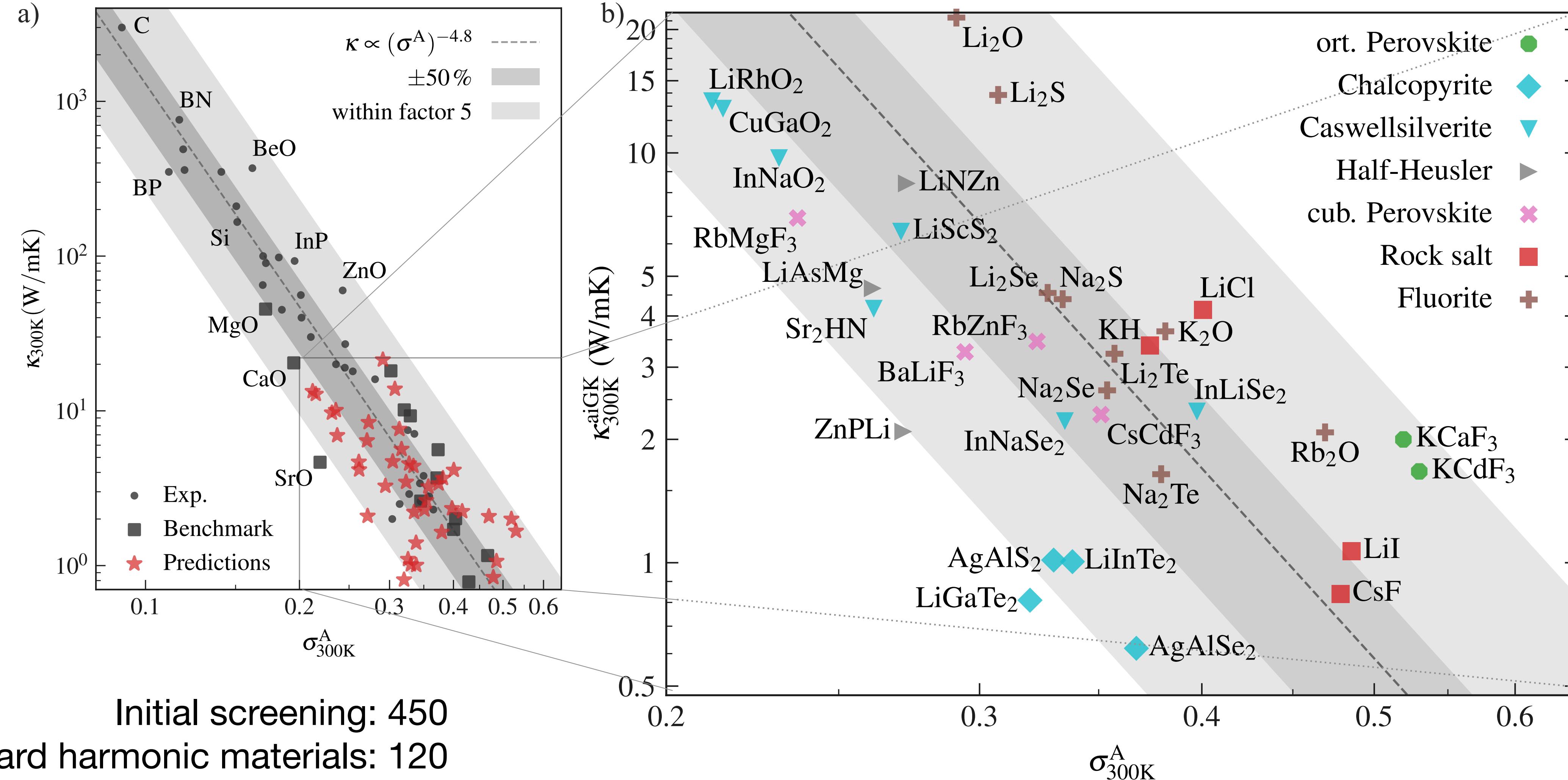


[4] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, Arxiv 2209.12720

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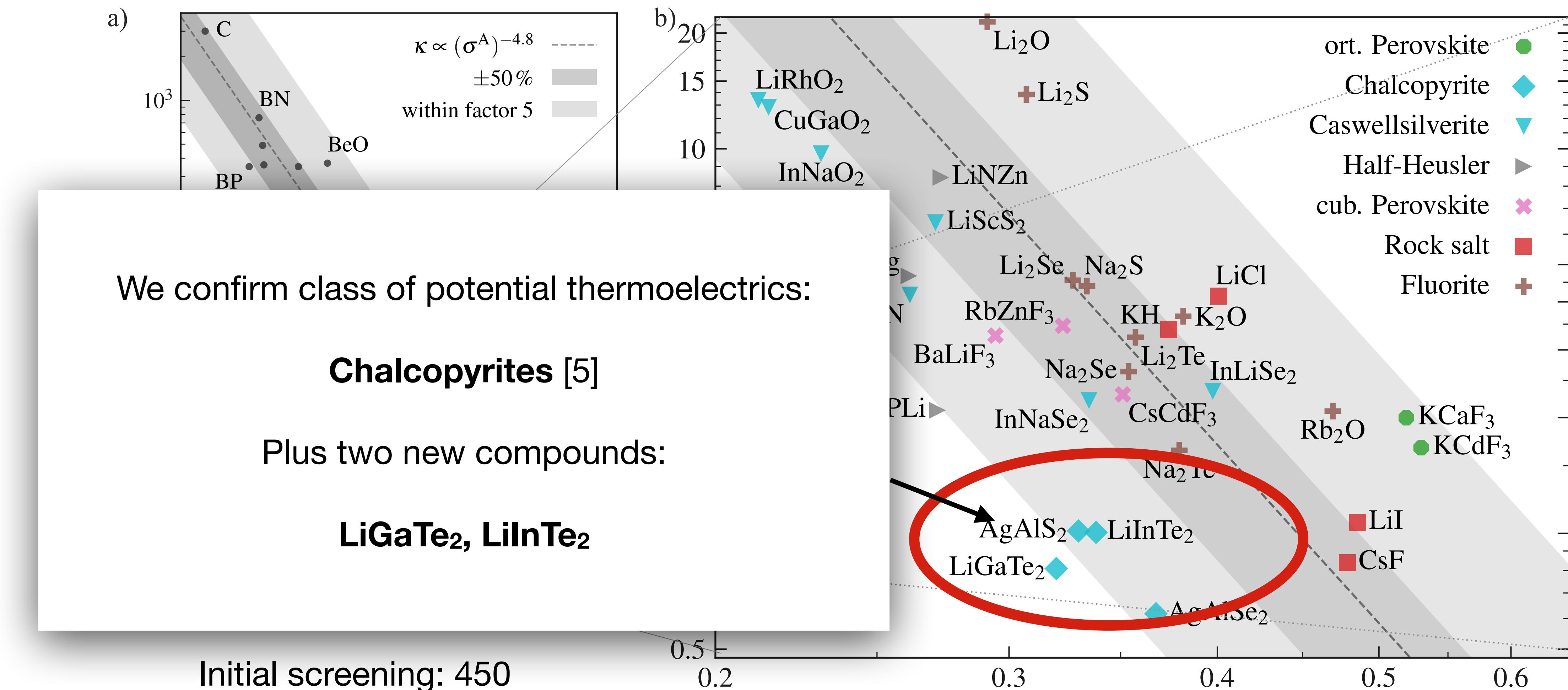


Ab initio Green-Kubo: Predicted materials [4]



[4] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, Arxiv 2209.12720

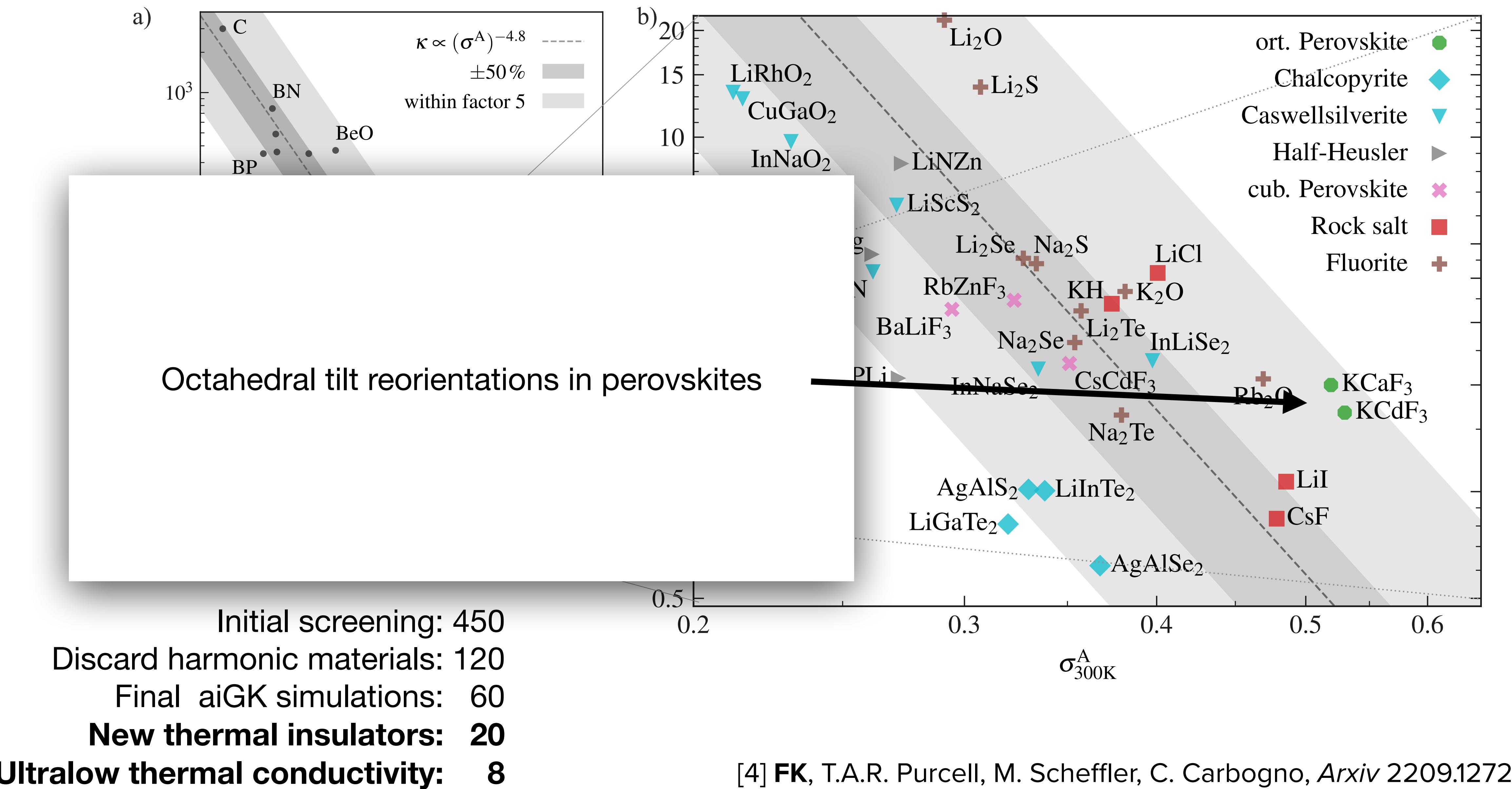
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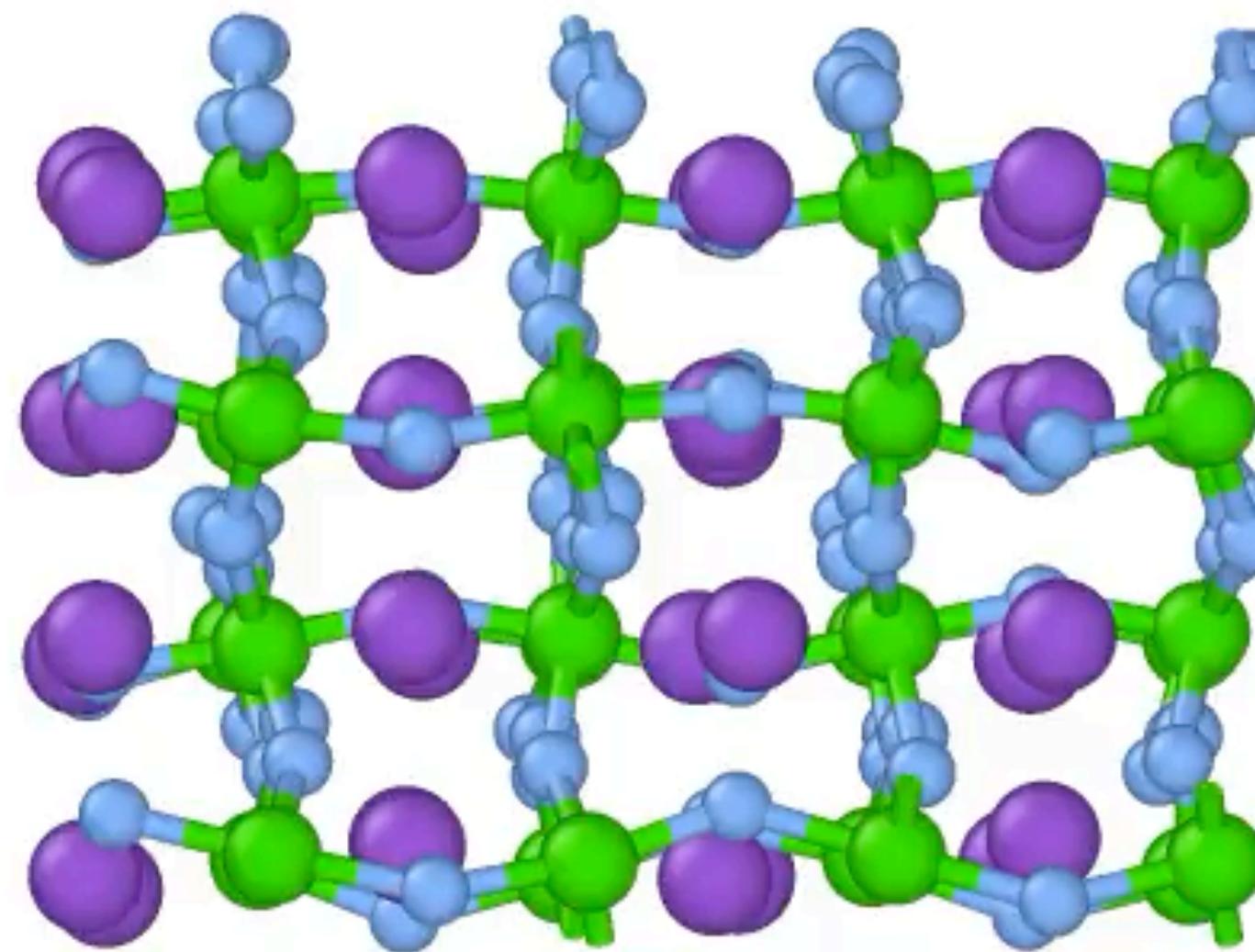
[5] J. J. Plata, et al., Chem. Mater. **34**, 2833 (2022)

Ab initio Green-Kubo: More dynamical disorder

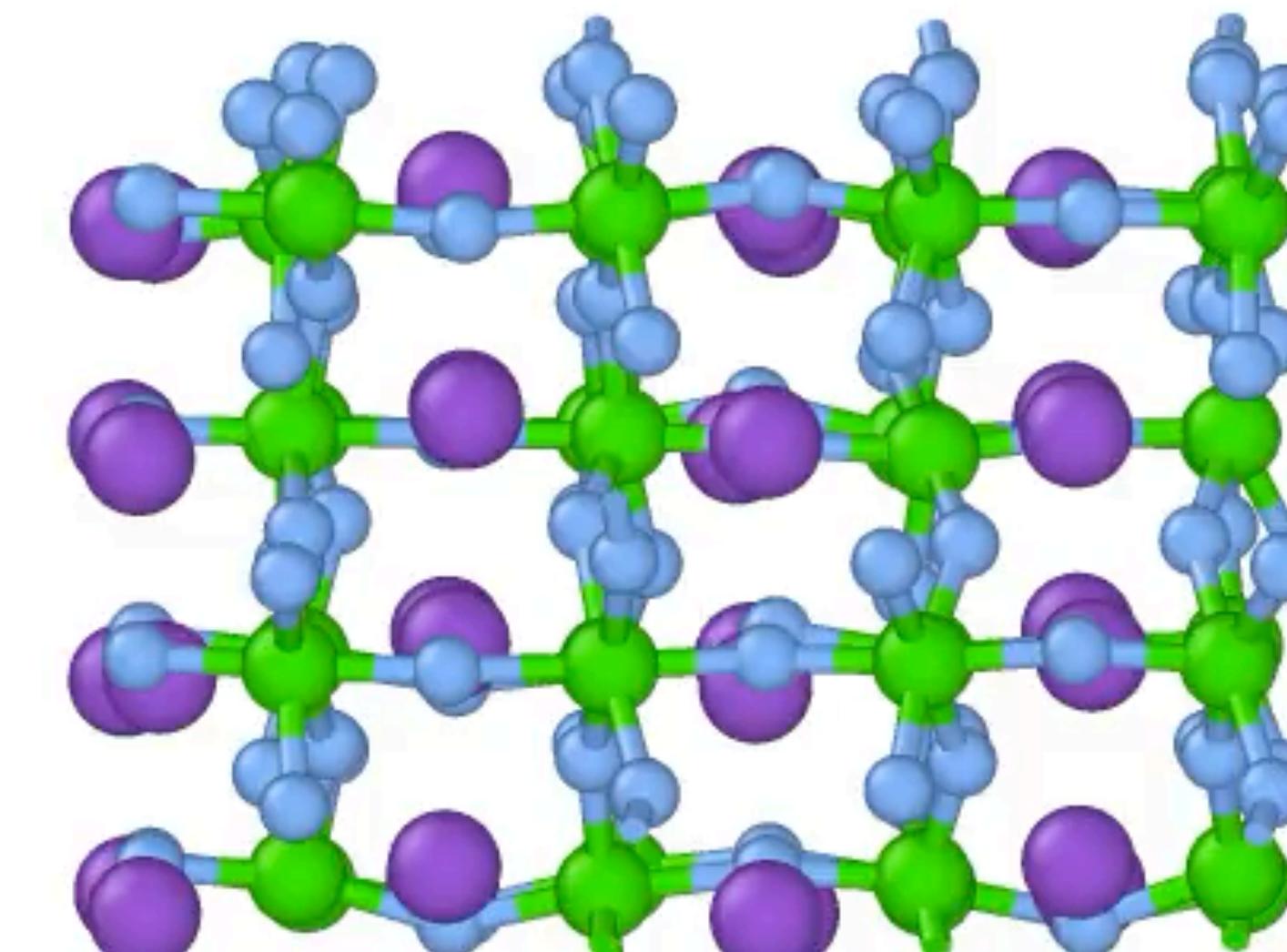


Ab initio Green-Kubo: More dynamical disorder

A



Viewed along a axis



Viewed along b axis

15.000ps

flokno.me/video1

Ab initio Green-Kubo study: Summary

Ab initio Green-Kubo allows for accurate predictions

in strongly-anharmonic thermal insulators

Correlation between anharmonicity and thermal conductivity holds

but weakens as materials become more complex

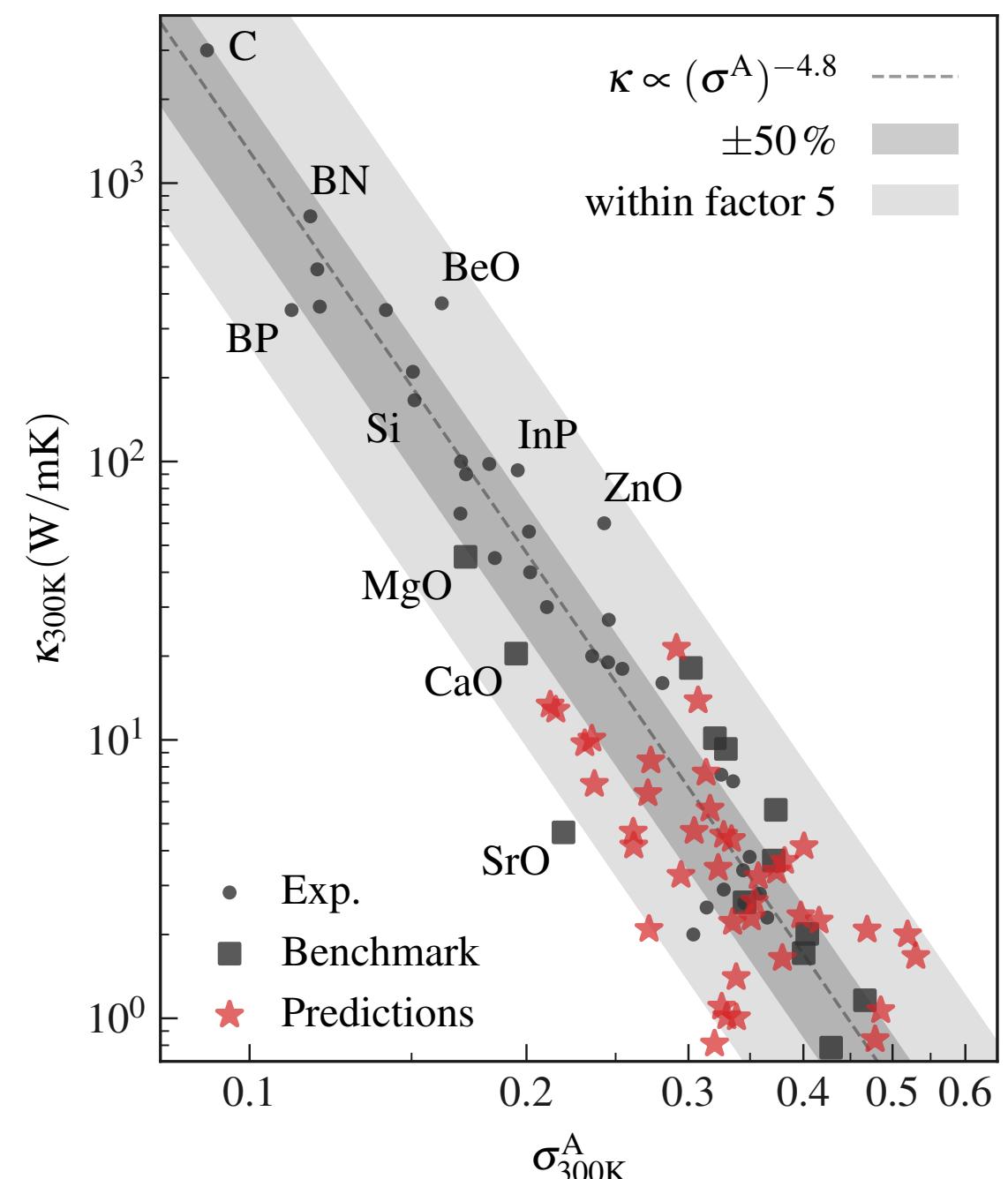
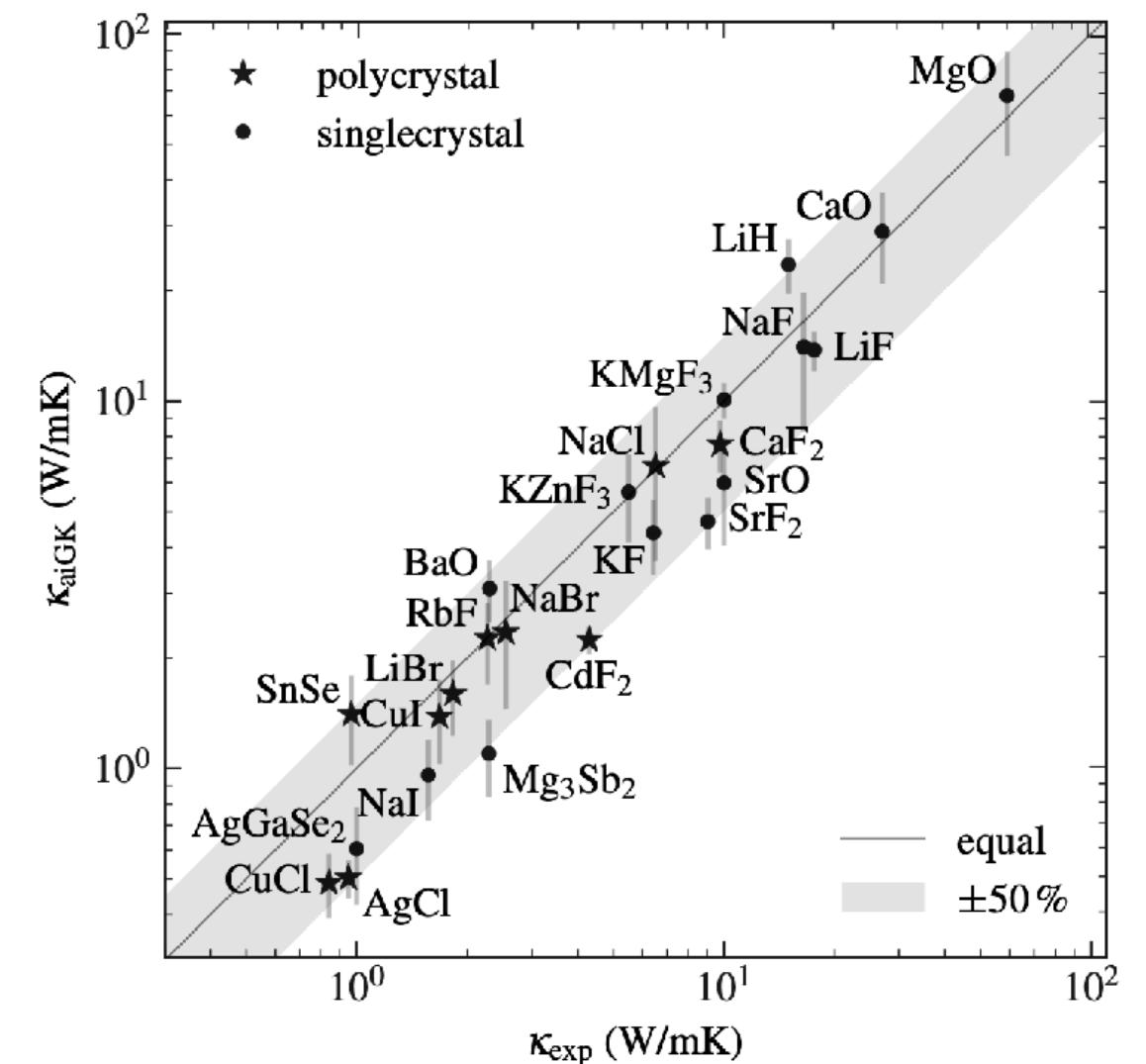
Dynamical disorder effects like metastable defects can

occur in these compounds → important for modeling

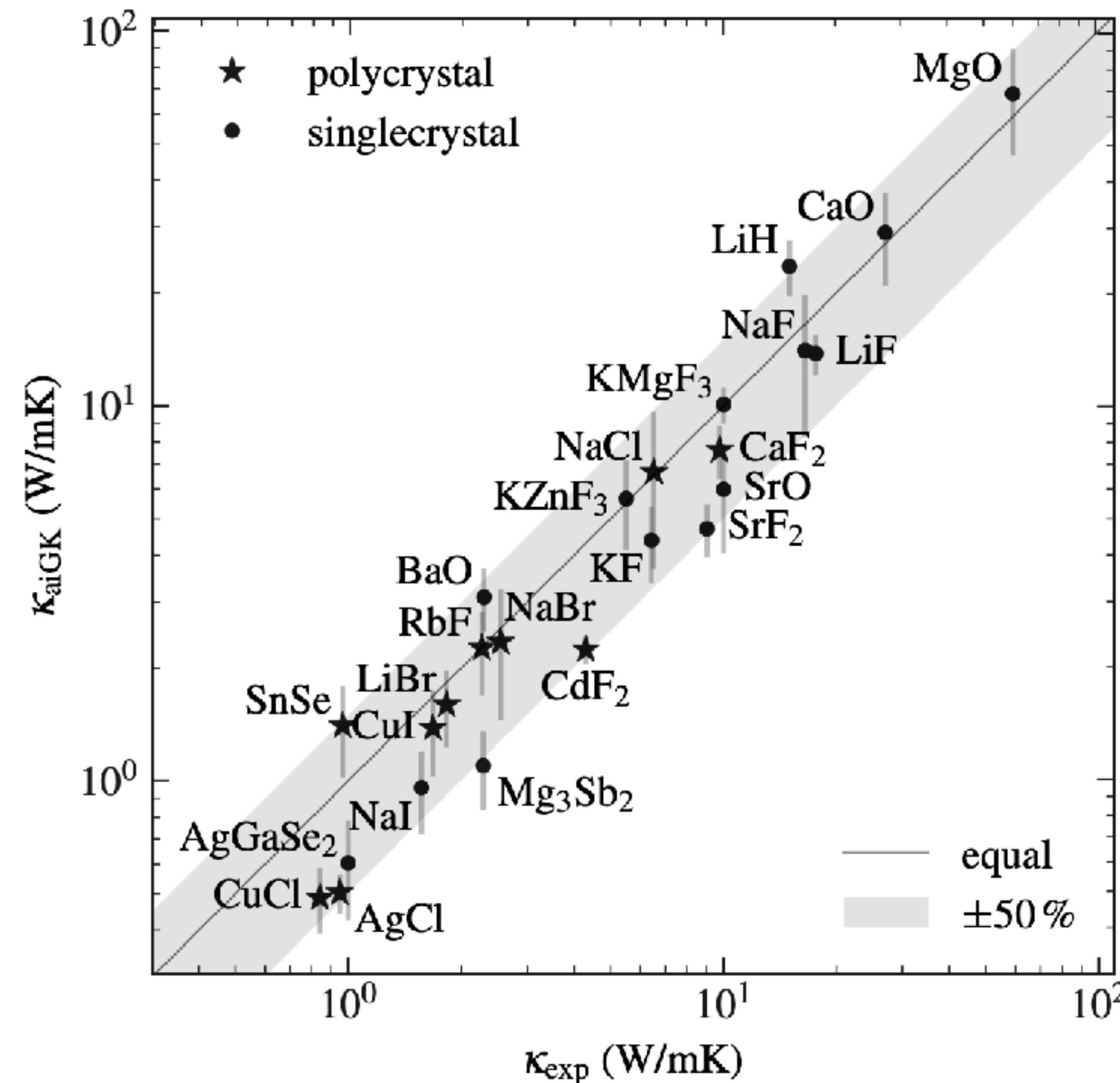
[1] FK, M. Scheffler, C. Carbogno, Arxiv 2209.01139

[2] FK, T.A.R. Purcell, M. Scheffler, C. Carbogno, Arxiv 2209.12720

[3] T. A. R. Purcell *et al.*, Arxiv 2204.12968 (2022)



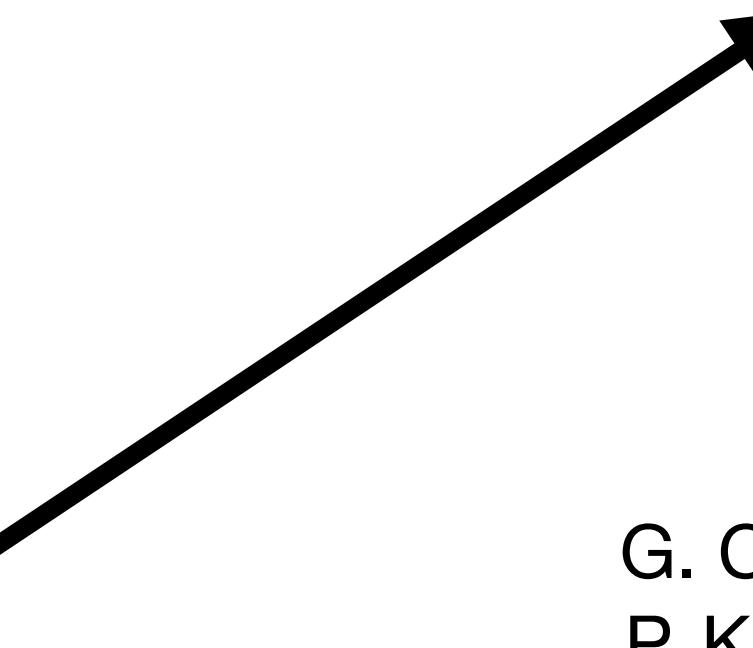
Outlook: Can we reduce the cost?



Ab initio: accurate but **expensive**

xc: PBEsol
approx. 200 atoms
30-60ps simulation time
4-5fs time step

Replace DFT by
Machine Learning Potentials!
(Safe factor 100-1000 computations)



Existing approaches:

G. C. Sosso, et al., Phys. Rev. B **86**, 104301 (2012)

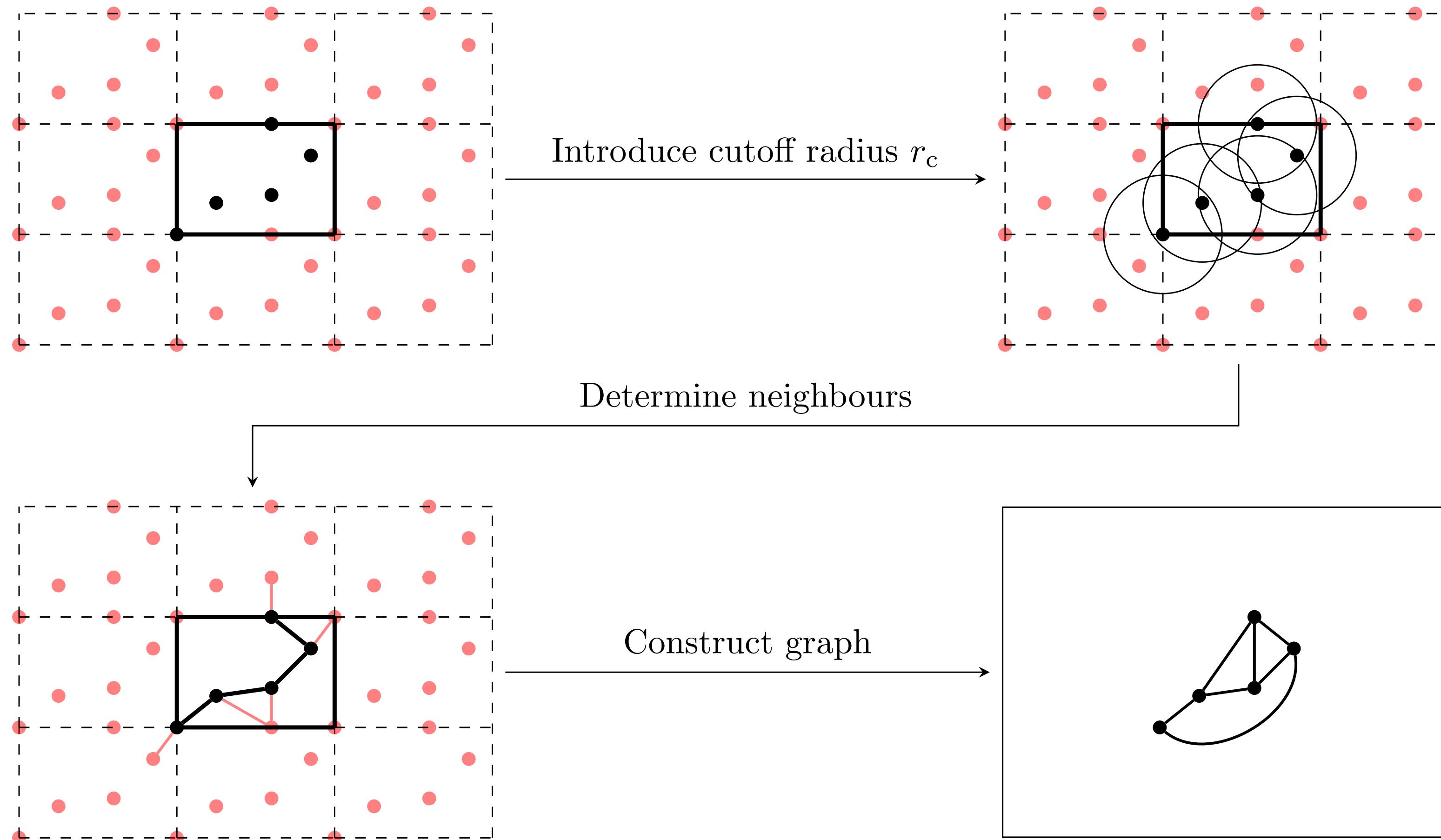
P. Korotaev et al., Phys. Rev. B **100**, 144308 (2019)

C. Mangold et al., J. Appl. Phys. **127**, 244901 (2020)

R. Li, E. Lee, and T. Luo, Mater. Today Phys. **12**, 100181 (2020)

C. Verdi et al., npj Comput. Mater. **7**, 156 (2021)

Message-Passing Graph Neural Networks (MPNN)

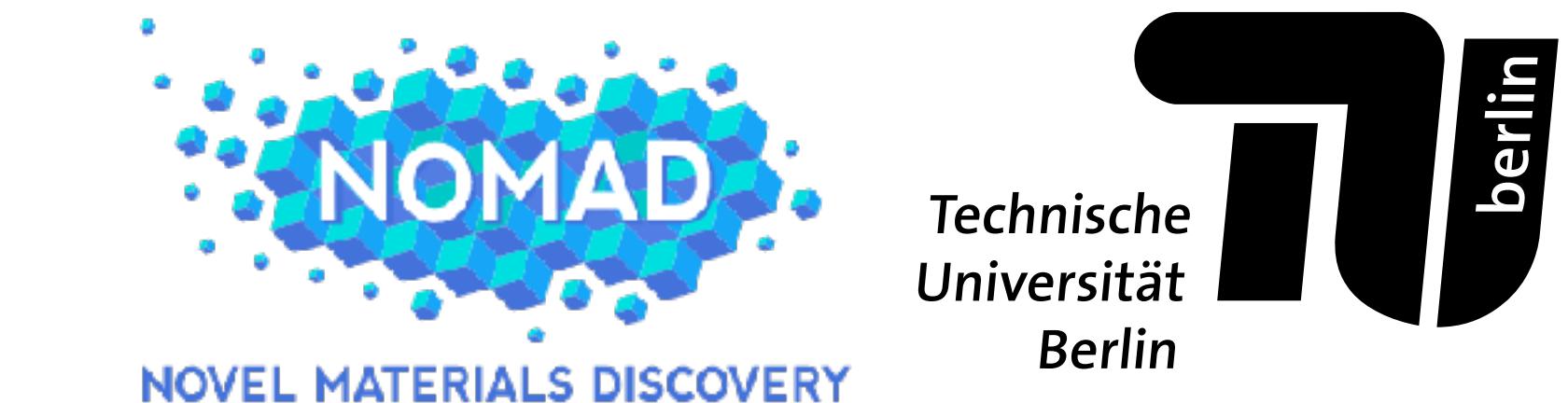
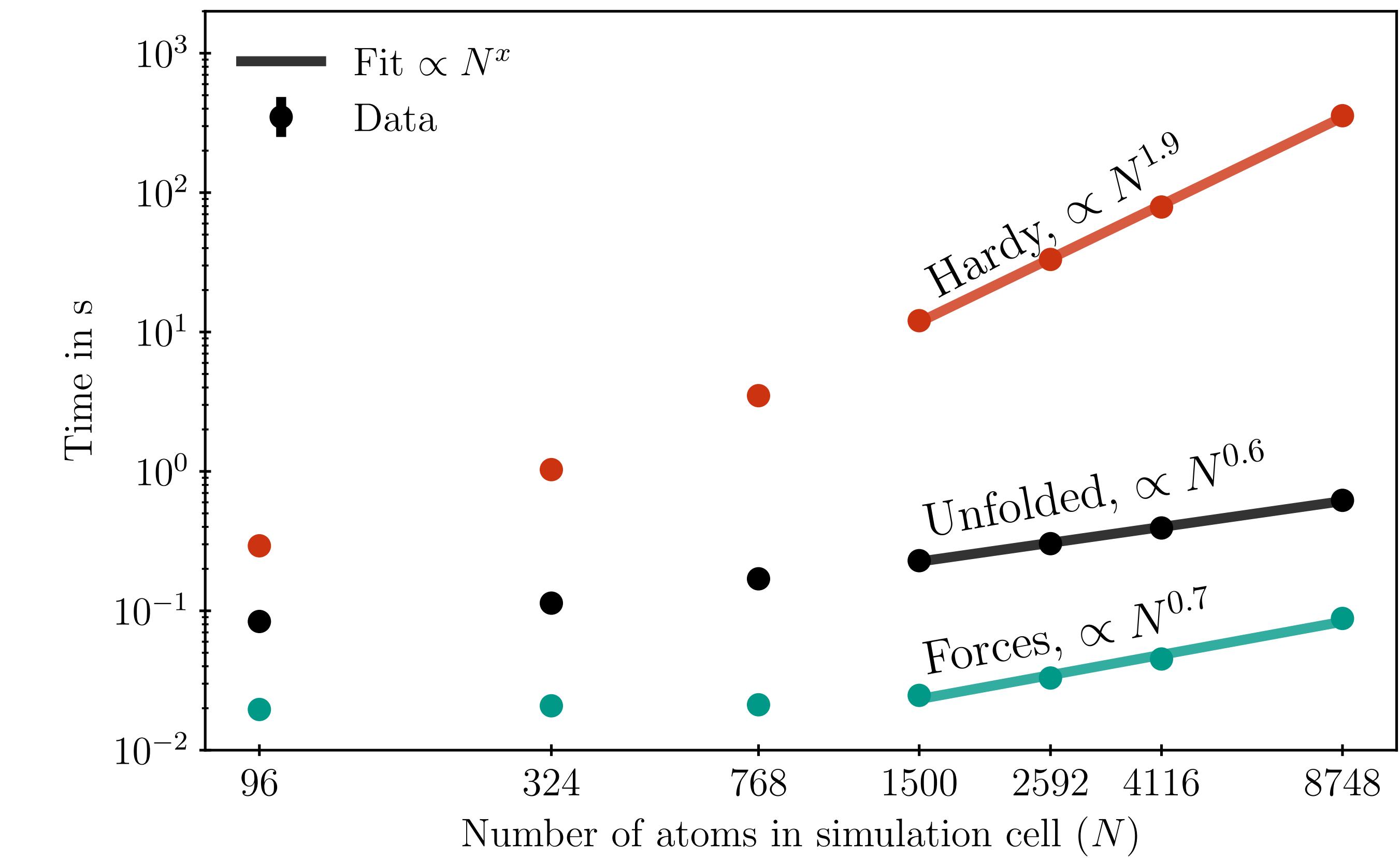
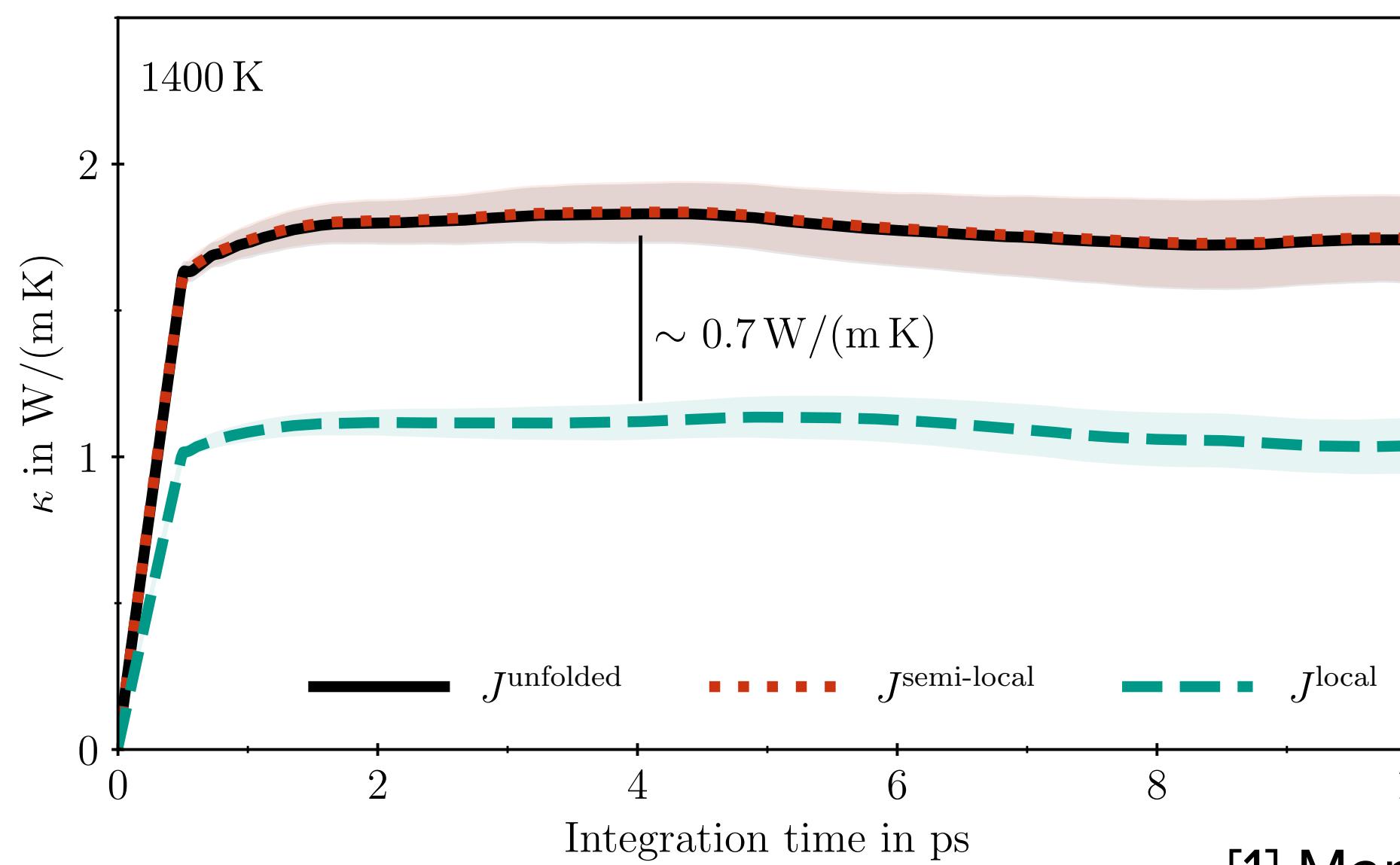
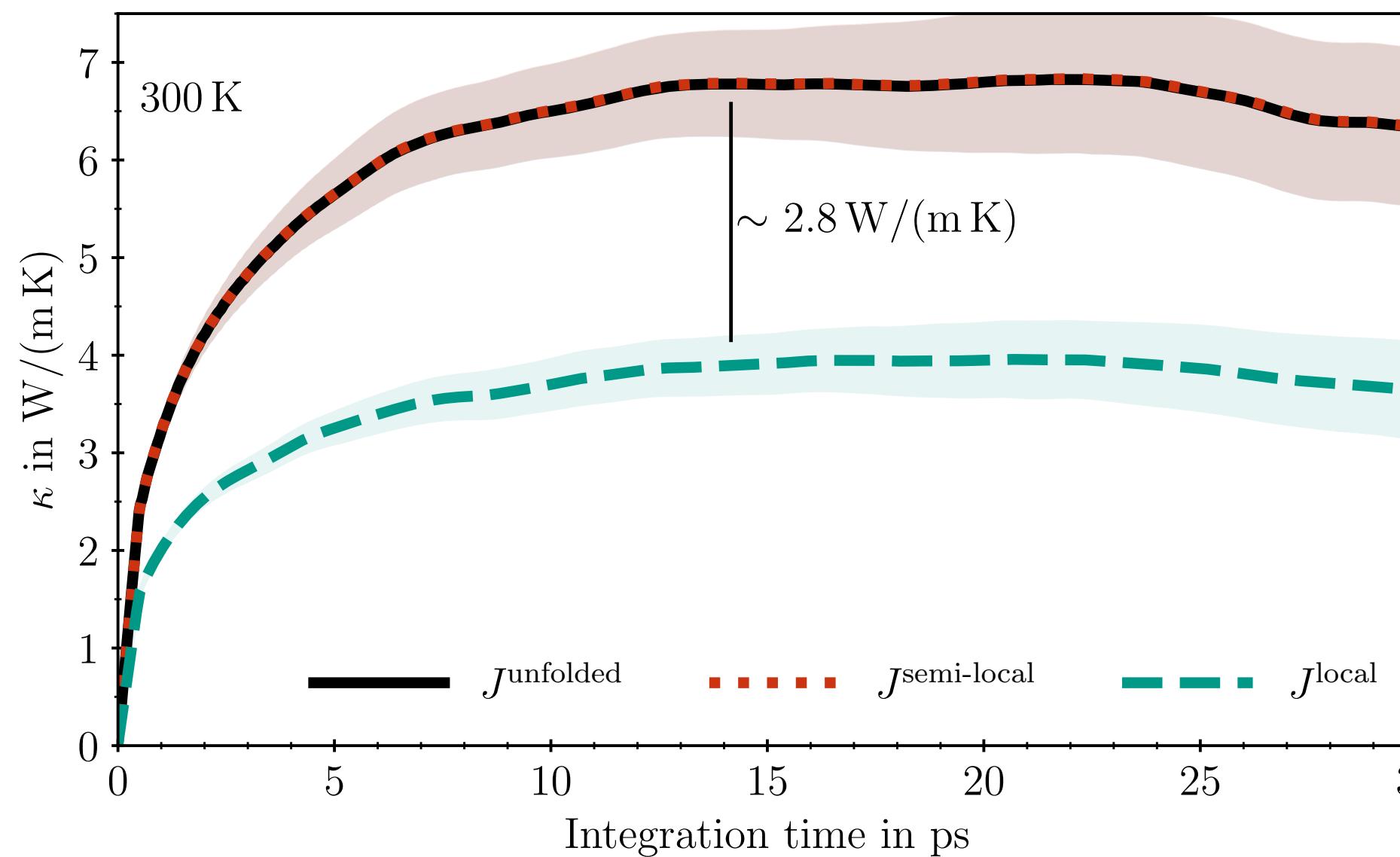


GNNs: P. W. Battaglia *et al.*, arXiv 1806.01261 (2018)

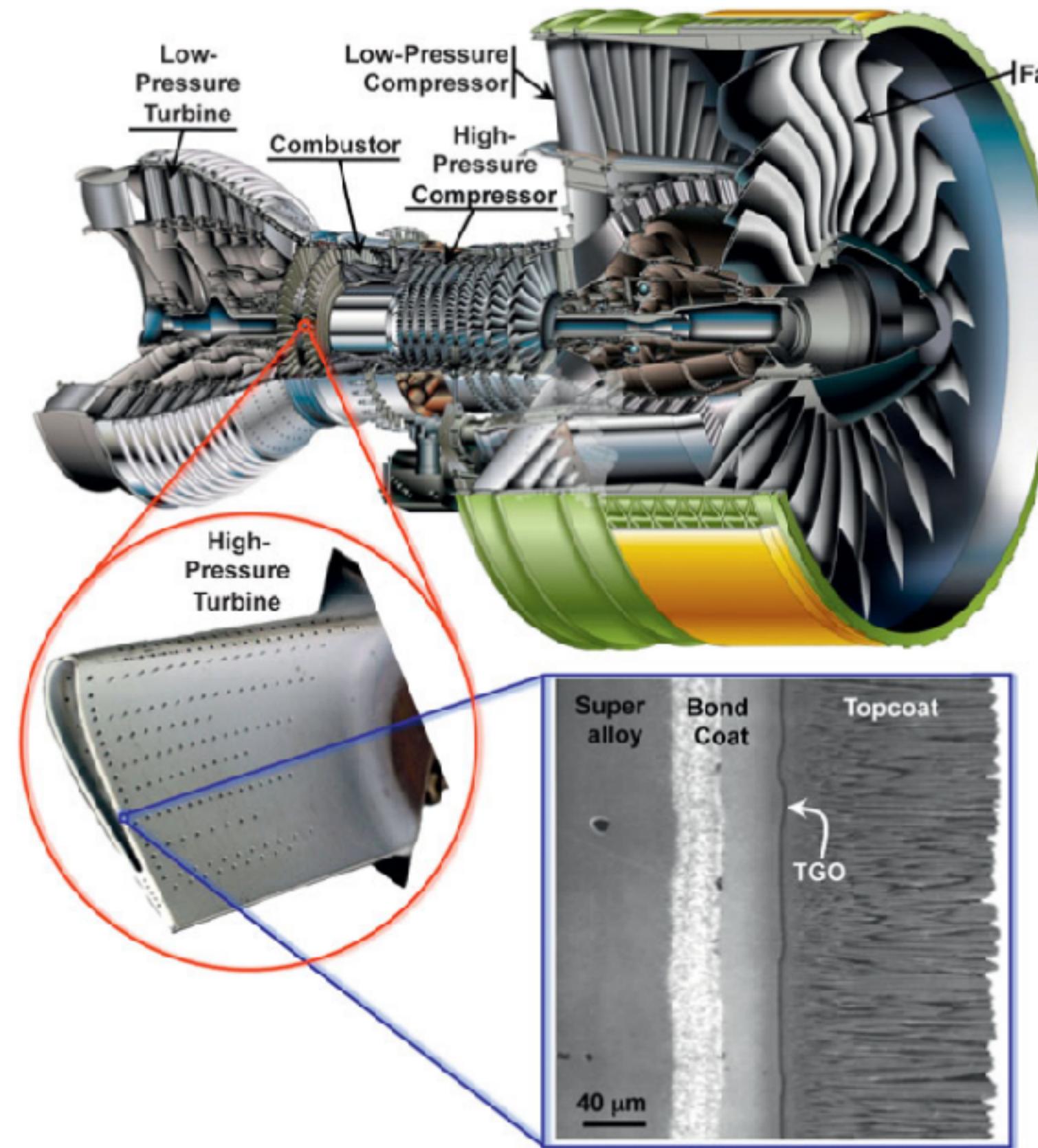
GNNs for materials: T. Xie and J.C. Grossman, Phys. Rev. Lett. **120**, 145301(2018); C. Chen *et al.*, Chem. Mater. **31**, 9 (2019); C.W. Park and C. Wolverton, Phys. Rev. Mater. **4**, 063801 (2020)

MPNNs: J. Gilmer, S.S. Schoenholz, P.F. Riley, O. Vinyals, and G.E. Dahl, in Proc. of Mach. Learn. Res., Vol. 70 (2017)

MPNN potentials require adapted heat flux formulation [1]

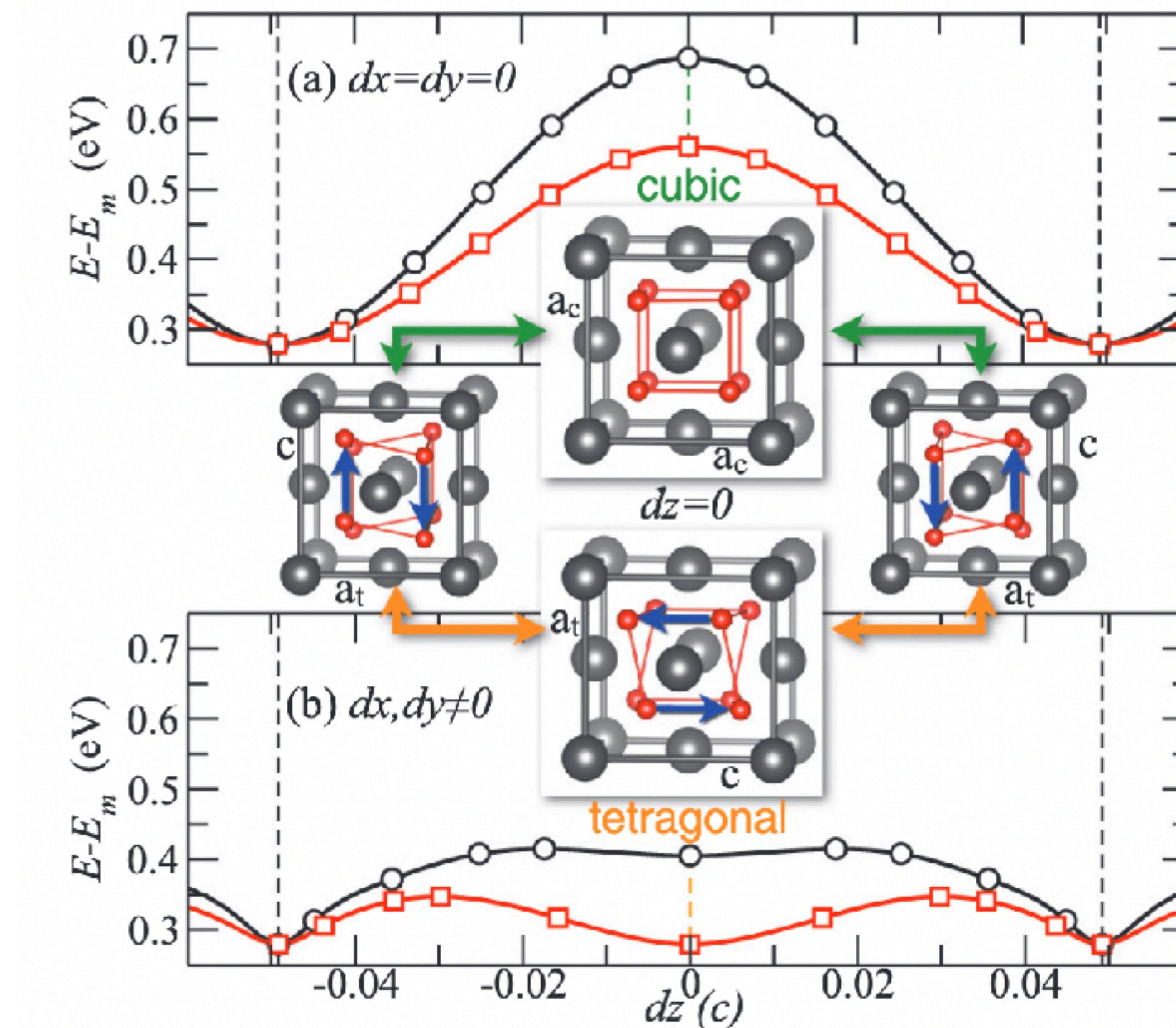


Test system: Zirconia (ZrO_2), reference material for TBCs



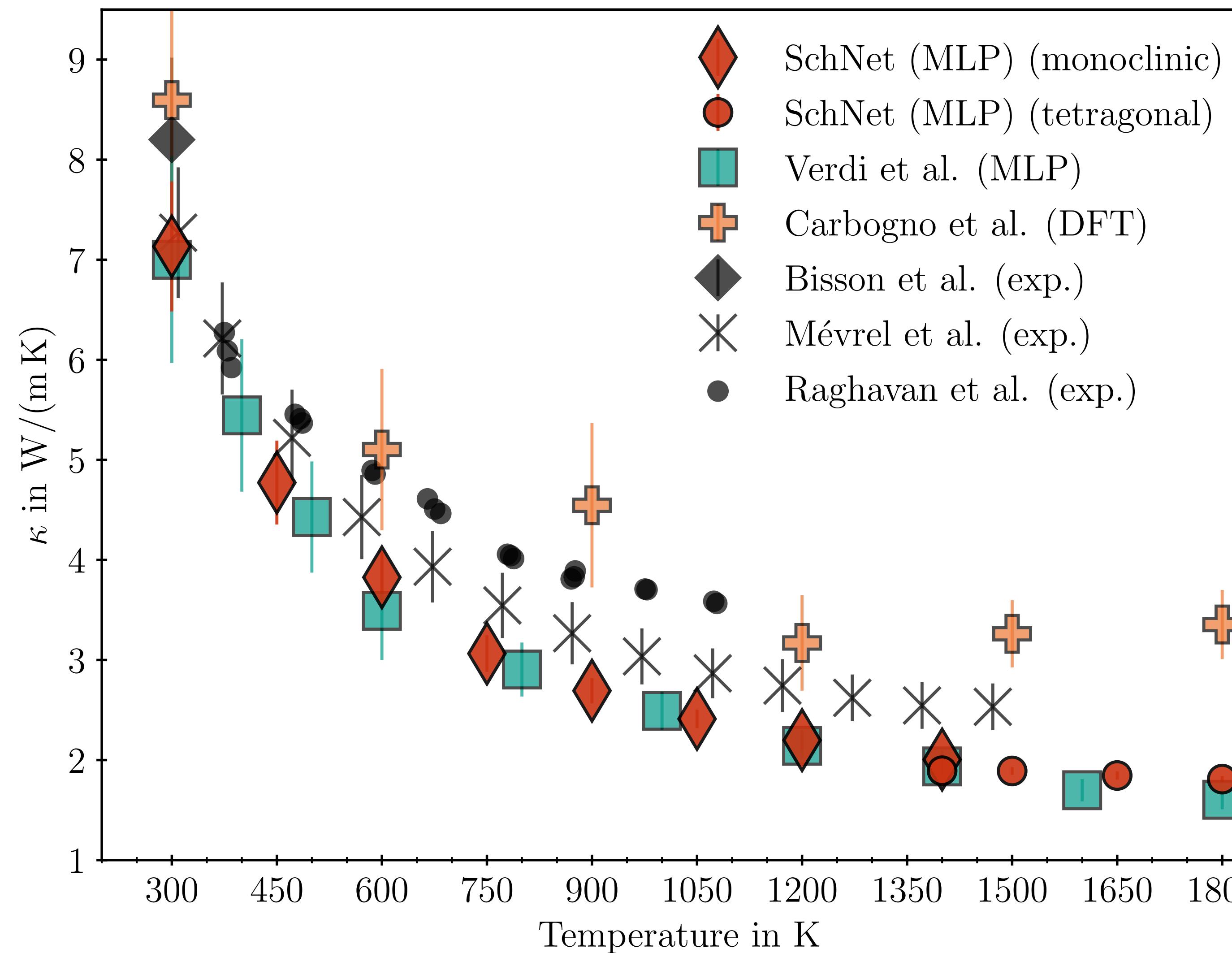
Thermal barrier coating: Y-ZrO_2

C. Carbogno *et al.*, Phys Rev B **90**, 144109 (2014)



Dynamically stabilized
cubic phase

Results [1]



C. Verdi *et al.*, *njp Comp. Mat.* **7**, 156 (2021)
C. Carbogno, *et al.*, *Phys. Rev. Lett.* **118** (2017)
J.F. Bisson *et al.*, *J. Am. Chem. Soc.* **83**, 1993 (2000)
R. Mévrel *et al.*, *J. Eur. Ceram. Soc.* **24**, 3081 (2004)
S. Raghavan *et al.*, *Scr. Mater.* **39**, 1119 (1998)

Good agreement with literature

<10000 DFT calculations

Emerging alternative for aiGK

Part 2: Dynamics without dynamics: TDEP

Igor Abrikosov

Olle Hellman

Temperature Dependent Effective Potentials

History: Description of dynamically unstable systems [1]

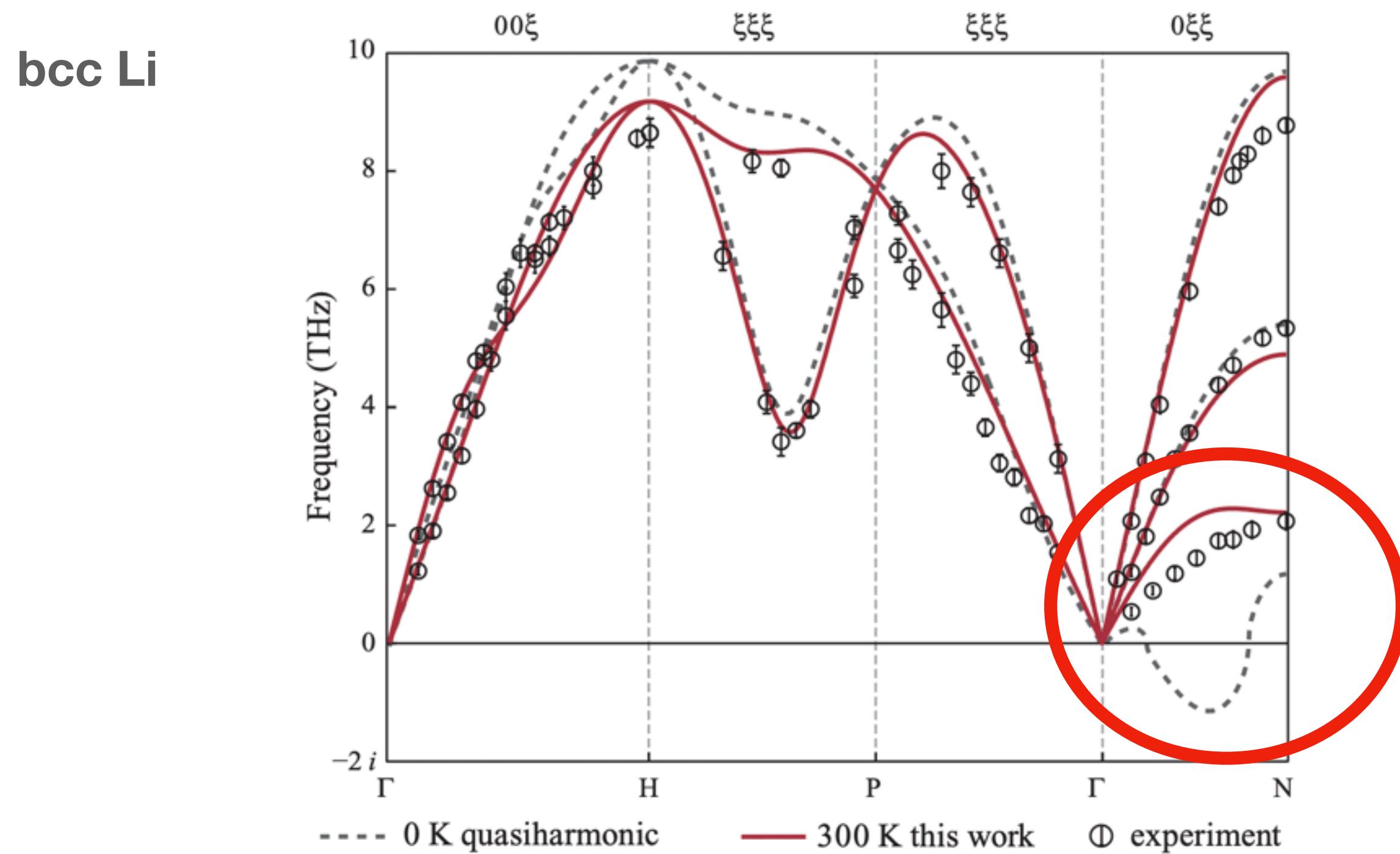


FIG. 2. (Color online) Phonon dispersion relations in bcc Li along high-symmetry directions. The symbols are experimental values (293 K),²⁹ the solid lines correspond to calculations carried out at 300 K with the method proposed in this work, and the dashed black lines correspond to the 0-K harmonic calculations.

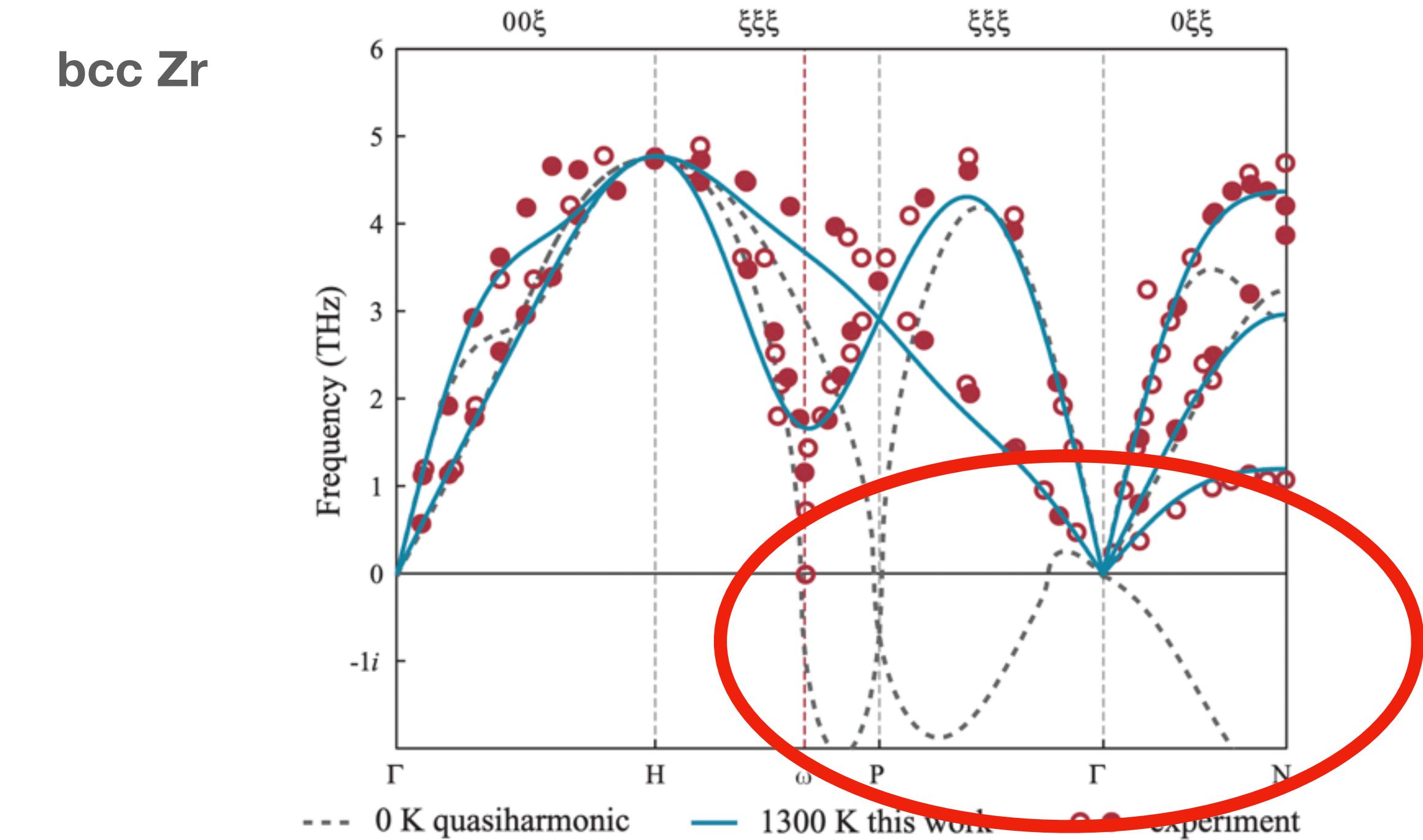


FIG. 3. (Color online) Phonon dispersion relations for bcc Zr. Solid lines correspond to calculations at 1300 K, dashed lines denote the quasiharmonic results, and symbols represent experimental values from Heiming *et al.*³⁰ (circles) and Stassis *et al.*³¹ (filled circles). The dotted vertical line is at $q = (\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$. The observed softening at this point, experimental as well as theoretical, is important for the bcc to ω phase transition.

[1] O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys Rev B **84**, 180301 (2011).

How does TDEP work?

Formally similar to Taylor expansion of potential-energy surface

$$V^{\text{DFT}}(\mathbf{R}) \approx V^{\text{TDEP}}(\mathbf{R}) = V_0^{\text{TDEP}} + V_2^{\text{TDEP}}(\mathbf{R}) + V_3^{\text{TDEP}}(\mathbf{R}) + \dots$$

$$V_2^{\text{TDEP}}(\mathbf{R} = \mathbf{R}^0 + \mathbf{U}) = \frac{1}{2} \sum_{IJ} \Phi_{I\alpha, J\beta}(\mathbf{R}^0) U_I^\alpha U_J^\beta$$

Φ, Ψ : Force constants

$$V_3^{\text{TDEP}}(\mathbf{R} = \mathbf{R}^0 + \mathbf{U}) = \frac{1}{3!} \sum_{IJK} \Psi_{I\alpha, J\beta, K\gamma}(\mathbf{R}^0) U_I^\alpha U_J^\beta U_K^\gamma ,$$

How to obtain the force constants?

Fit model forces to actual forces [1]

$$\mathbf{F}(\mathbf{R}) = - \frac{dV(\mathbf{R})}{d\mathbf{R}}$$

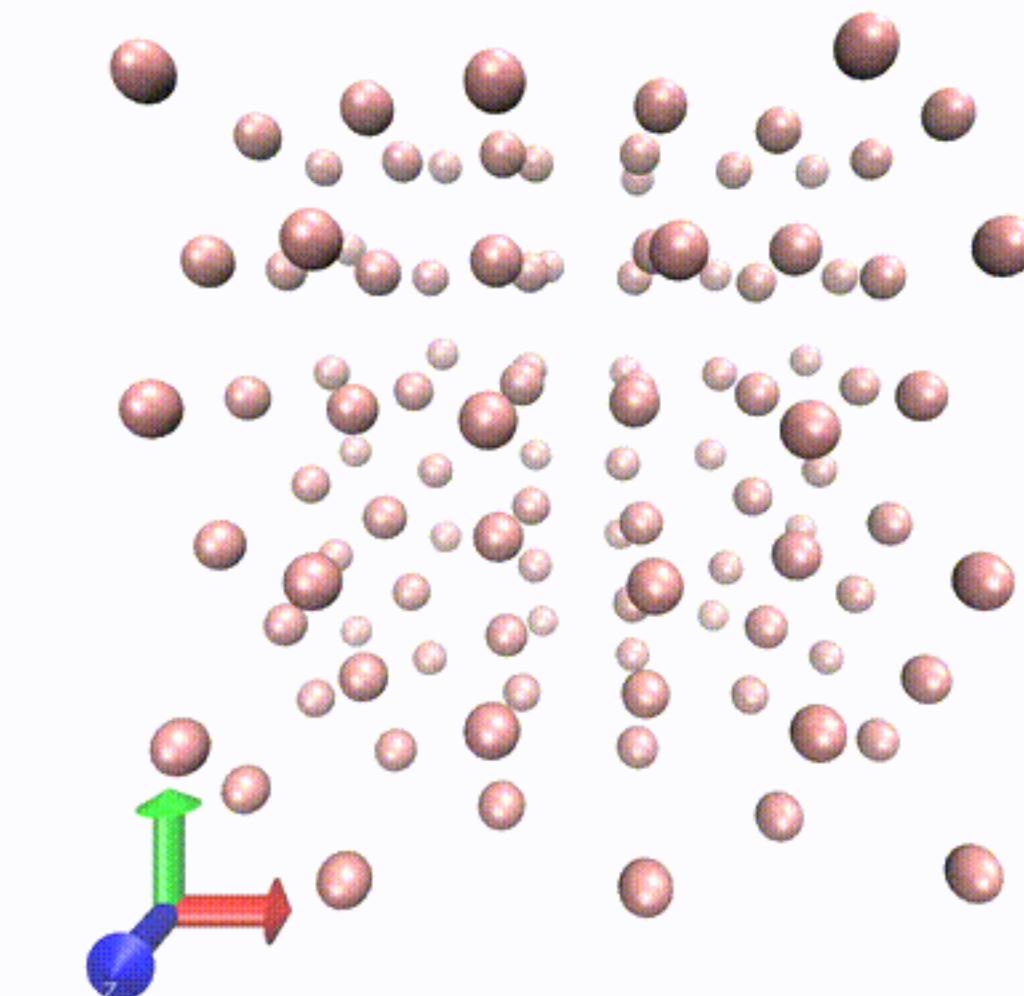
$$\Phi(T), \Psi(T) = \arg \min_{\Phi, \Psi} \left\langle \left\| \mathbf{F}^{\text{DFT}}(\mathbf{R}) - \mathbf{F}^{\text{TDEP}}(\mathbf{R}) \right\|^2 \right\rangle_T$$

[1] O. Hellman *et al.*, Phys Rev B **87**, 104111 (2013).

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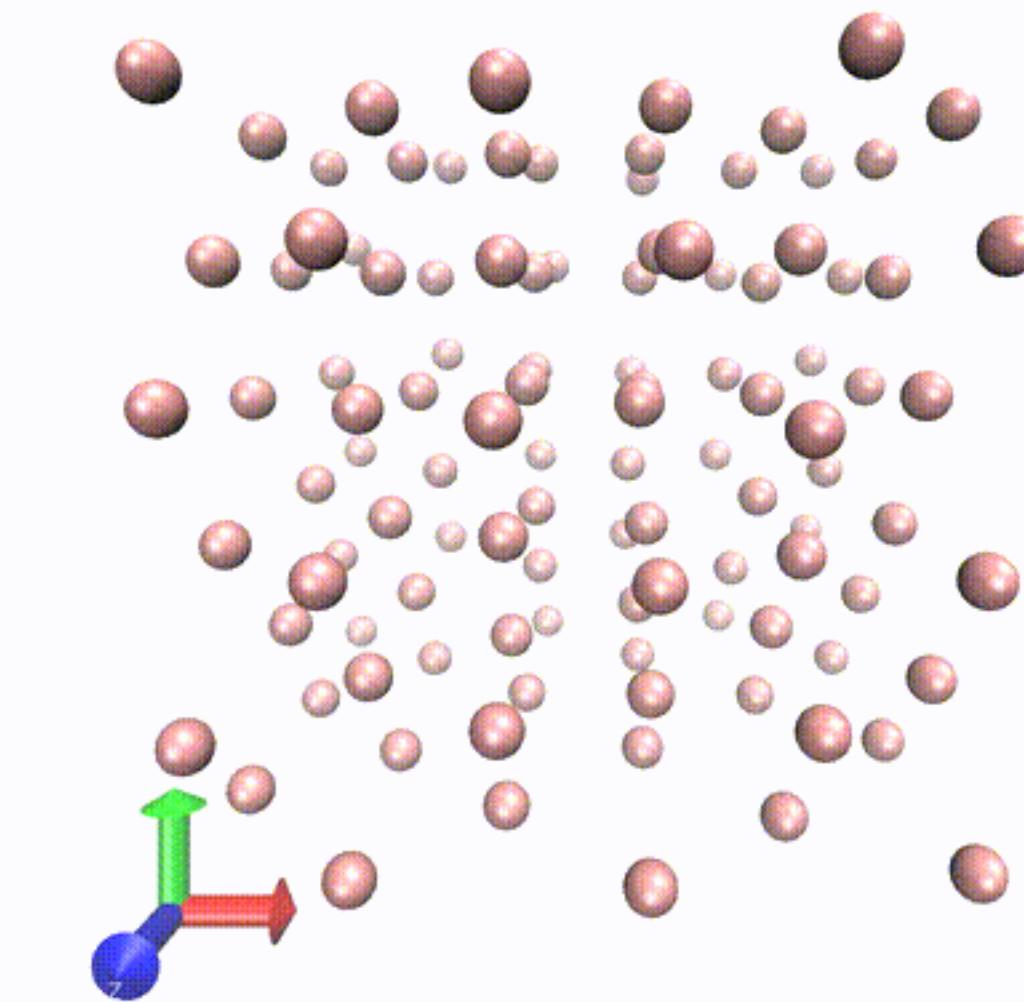
Thermodynamic sampling of positions \mathbf{R} at temperature T , e. g., MD

[1] O. Hellman *et al.*, Phys Rev B **87**, 104111 (2013).

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Least squares fit to obtain model parameters at temperature T

[1] O. Hellman *et al.*, Phys Rev B **87**, 104111 (2013).

How to do this efficient without Molecular Dynamics?

Use harmonic force constants to samples displacements [1]

$$\langle O \rangle_T = \int d\mathbf{R} e^{-\beta V(\mathbf{R})} O(\mathbf{R})$$
$$\approx \langle O \rangle_T^{(2)} = \int d\mathbf{R} e^{-\beta V_2(\mathbf{R})} O(\mathbf{R})$$
$$\Rightarrow \mathbf{U}_I(t) = \sum_q \zeta_q^t A_q \mathbf{e}_{qI}$$

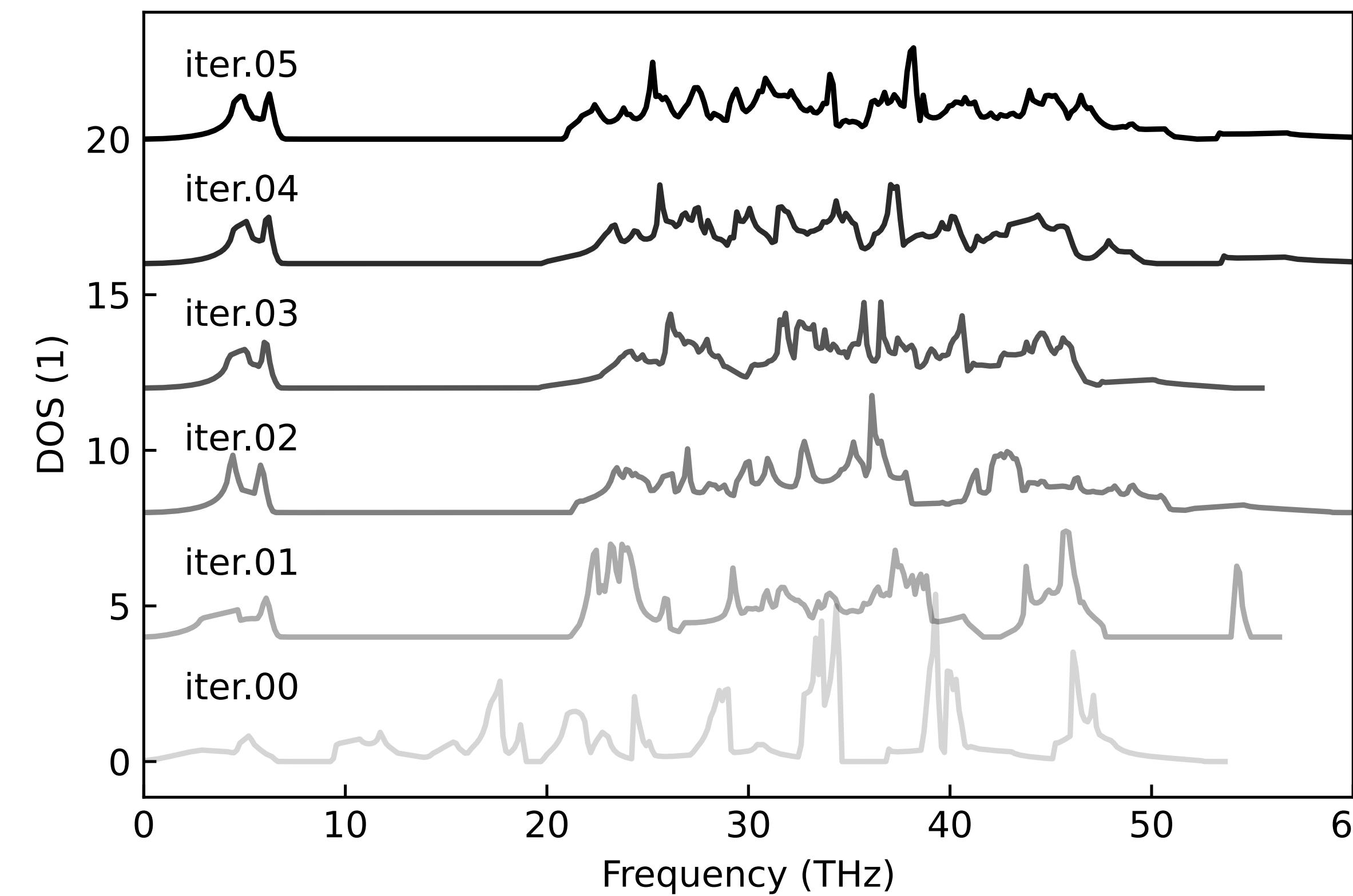
Random number Mode eigenvector
 ↓
 Mode amplitude

[1] D. West and S. K. Estreicher, Phys Rev Lett **96**, 115504 (2006).

How to do this efficient without Molecular Dynamics?

Solve self-consistently → rapid convergence with <1000 DFT calculations [1]

High-pressure LaH₁₀ phonon density of states:



[1] N. Shulumba, O. Hellman, and A. J. Minnich, Phys Rev Lett **119**, 185901 (2017).

Now we have model Hamiltonians, what can we do with them?

Best model Hamiltonian for Lattice Dynamics

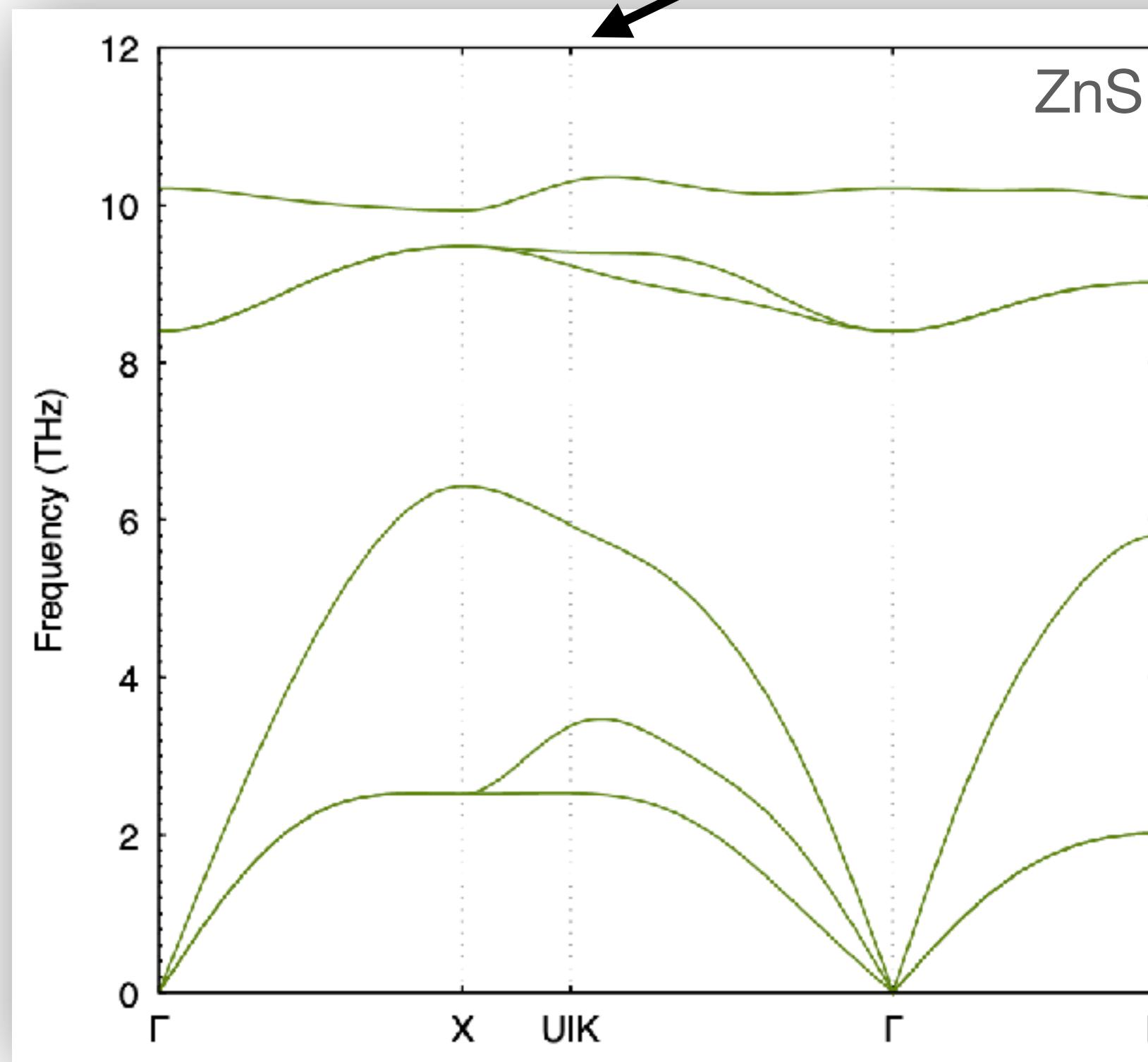
Including anharmonic materials

$$V^{\text{TDEP}}(\mathbf{R}) = V_0^{\text{TDEP}} + \frac{1}{2} \sum_{IJ} \Phi_{I\alpha, J\beta}(\mathbf{R}^0) U_I^\alpha U_J^\beta + \frac{1}{3!} \sum_{IJK} \Psi_{I\alpha, J\beta, K\gamma}(\mathbf{R}^0) U_I^\alpha U_J^\beta U_K^\gamma ,$$

Best model Hamiltonian for Lattice Dynamics

Harmonic model: Phonon dispersions

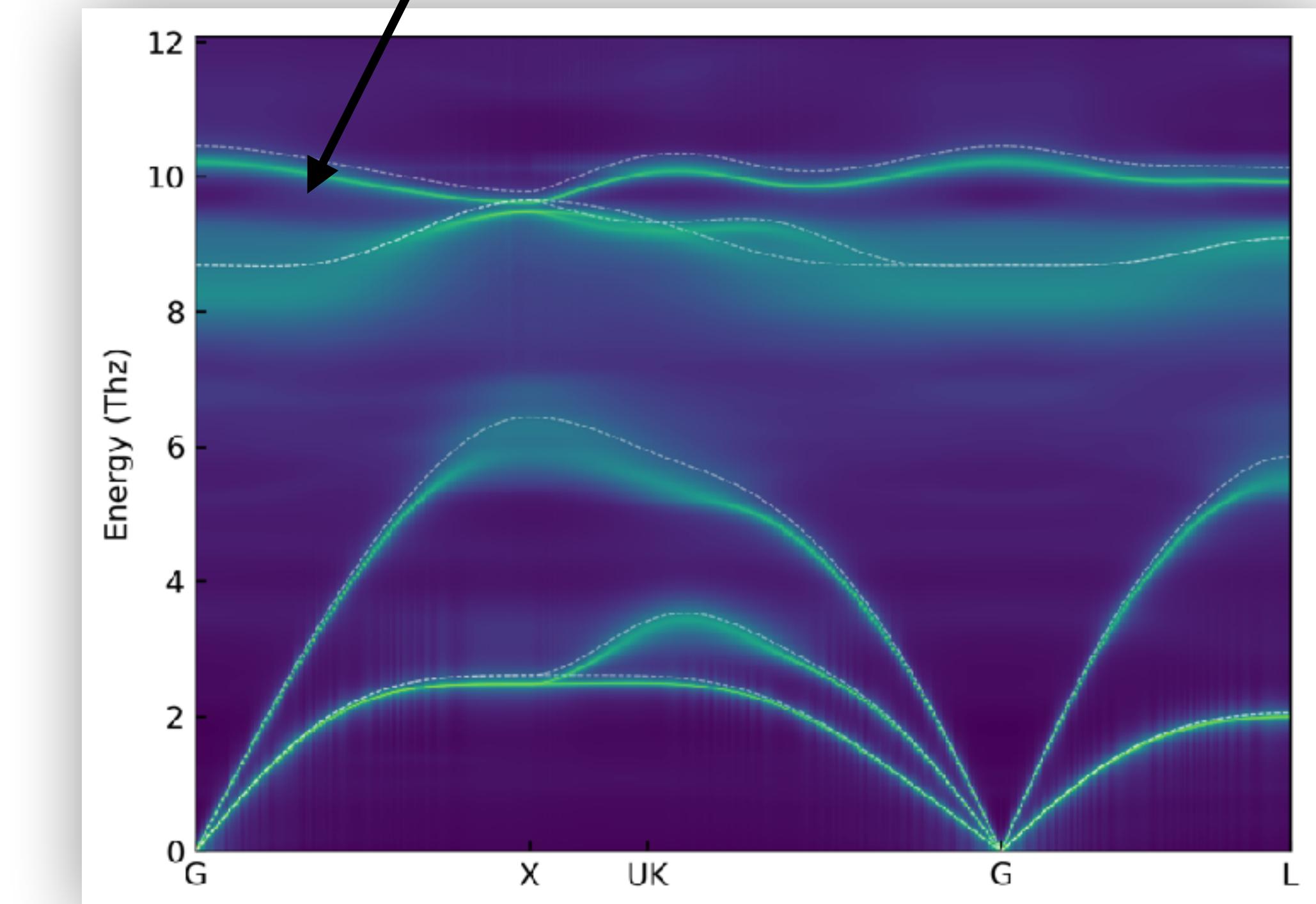
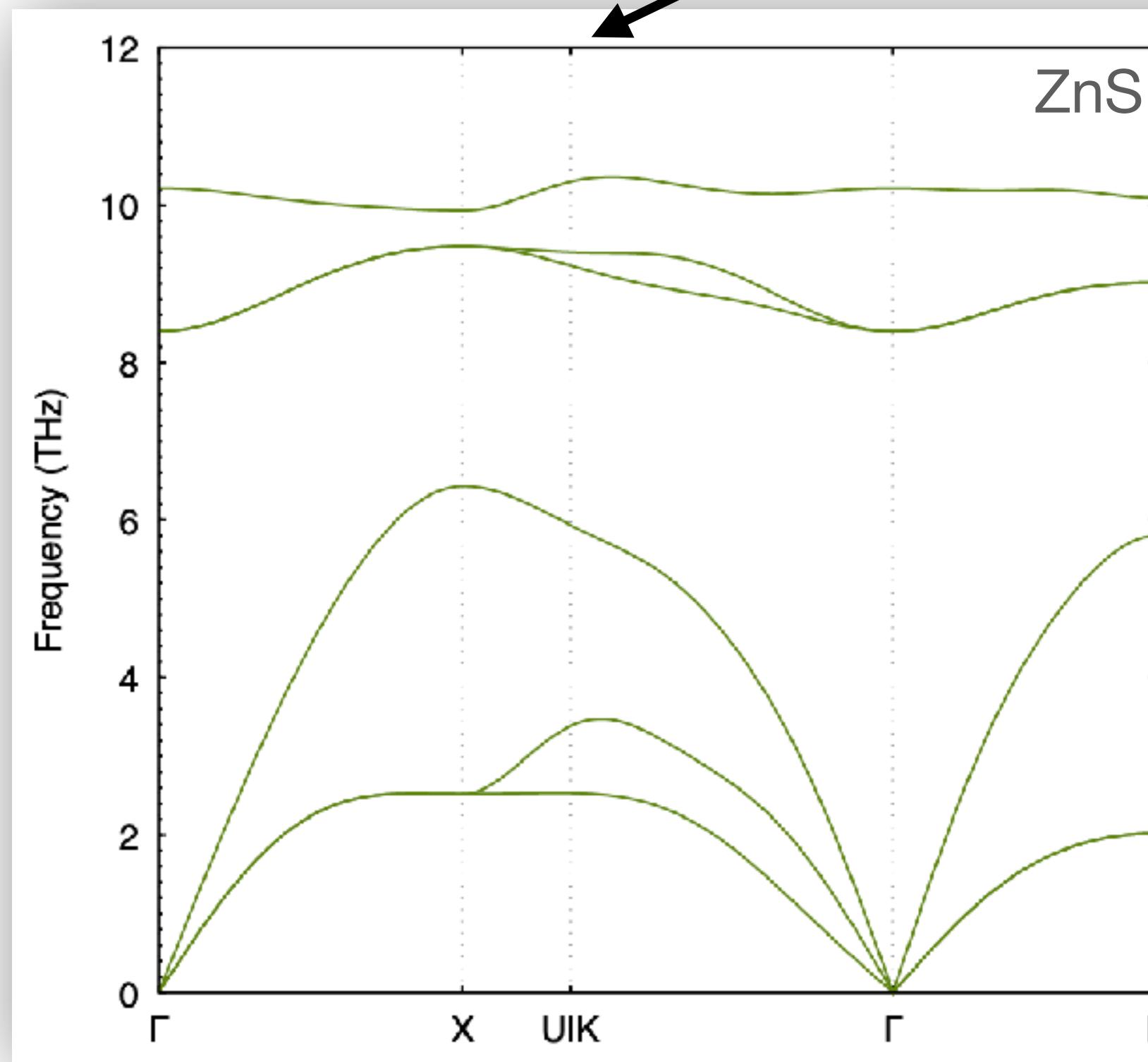
$$V^{\text{TDEP}}(\mathbf{R}) = V_0^{\text{TDEP}} + \frac{1}{2} \sum_{IJ} \Phi_{I\alpha, J\beta}(\mathbf{R}^0) U_I^\alpha U_J^\beta + \frac{1}{3!} \sum_{IJK} \Psi_{I\alpha, J\beta, K\gamma}(\mathbf{R}^0) U_I^\alpha U_J^\beta U_K^\gamma ,$$



Best model Hamiltonian for Lattice Dynamics

Anharmonicity: Spectral functions, lifetimes, etc.

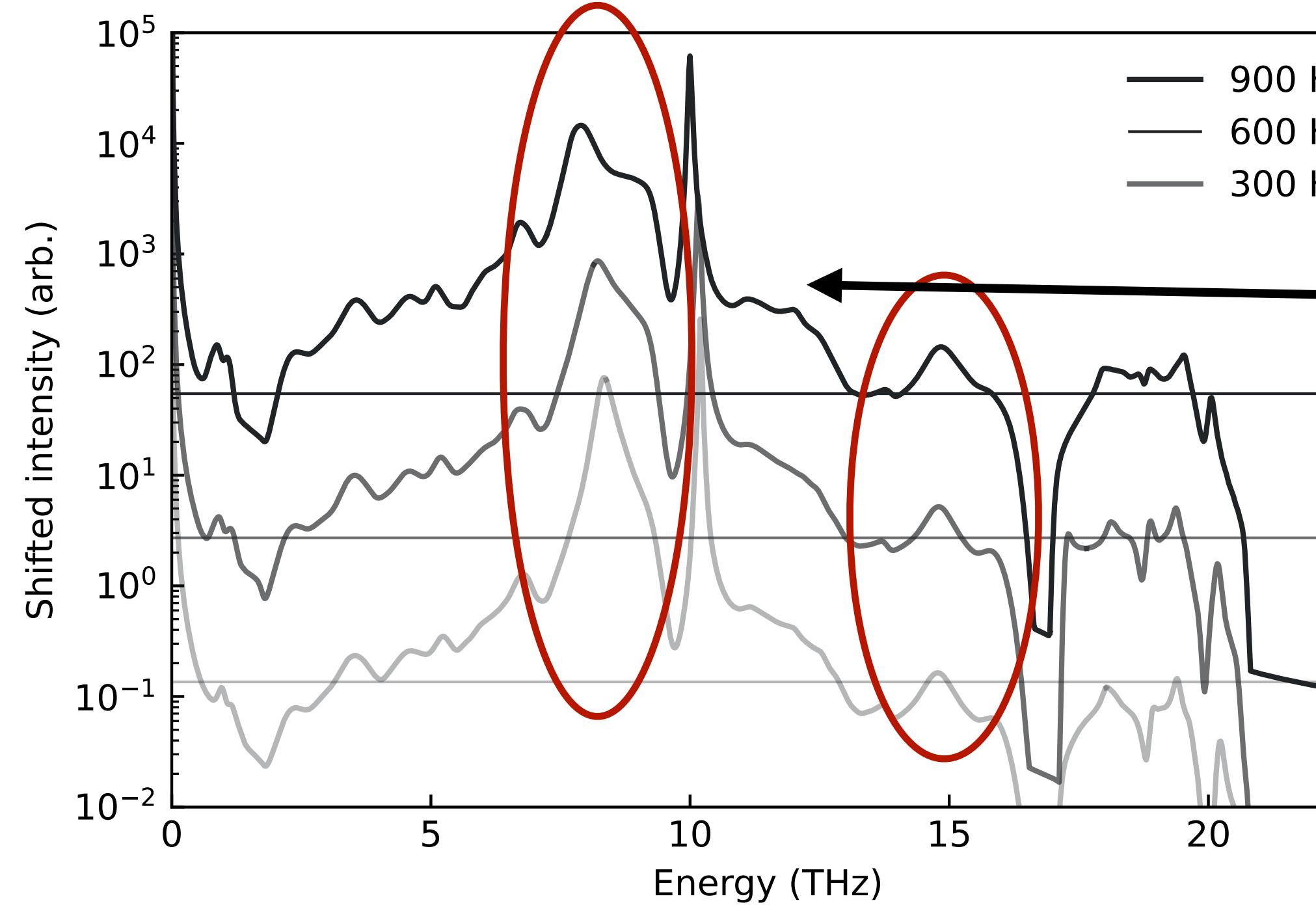
$$V^{\text{TDEP}}(\mathbf{R}) = V_0^{\text{TDEP}} + \frac{1}{2} \sum_{IJ} \Phi_{I\alpha, J\beta}(\mathbf{R}^0) U_I^\alpha U_J^\beta + \frac{1}{3!} \sum_{IJK} \Psi_{I\alpha, J\beta, K\gamma}(\mathbf{R}^0) U_I^\alpha U_J^\beta U_K^\gamma ,$$



Best model Hamiltonian for Lattice Dynamics

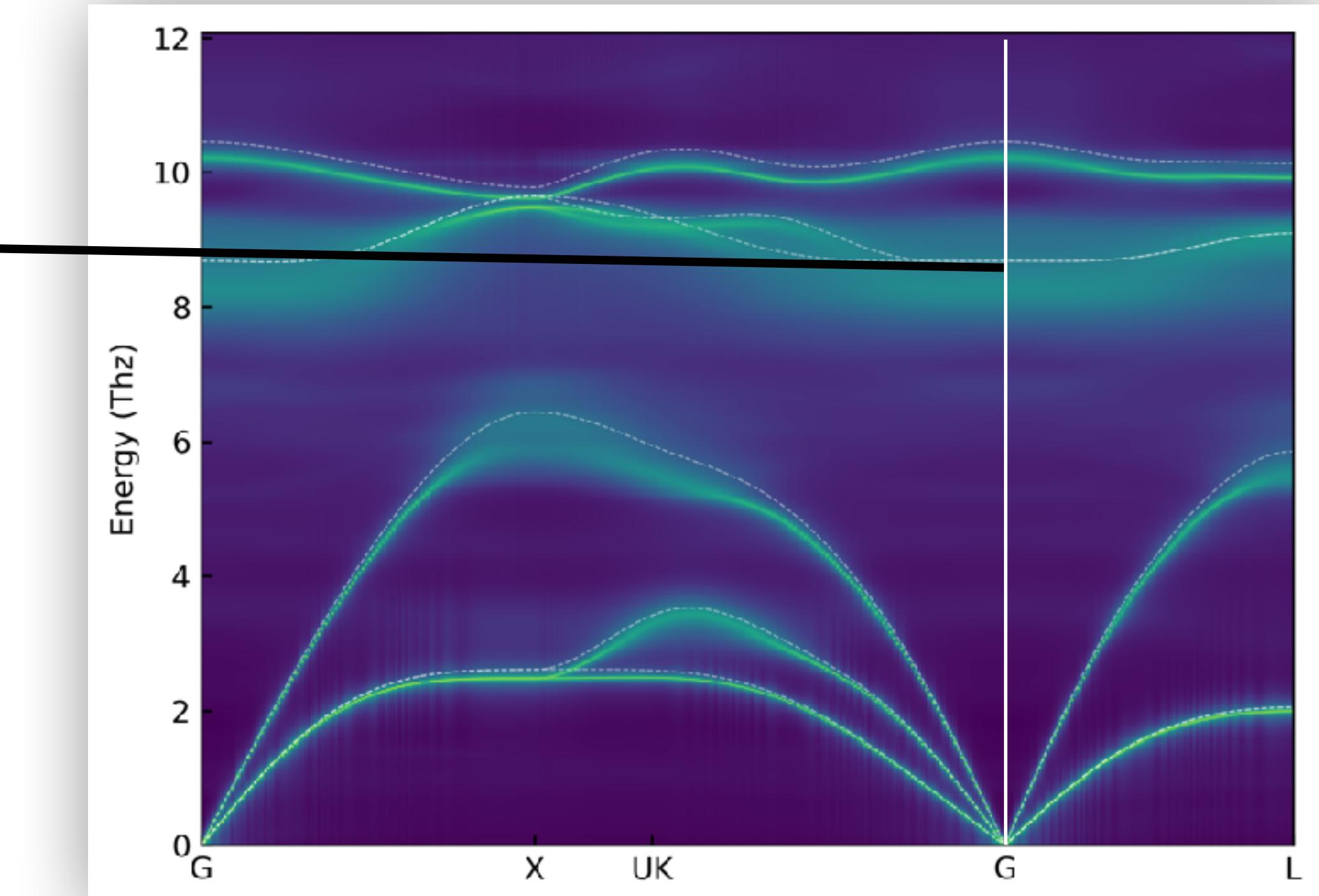
Insight into spectral properties, e.g., for Neutron scattering experiments

$$V^{\text{TDEP}}(\mathbf{R}) = V_0^{\text{TDEP}} + \frac{1}{2} \sum_{IJ} \Phi_{I\alpha, J\beta}(\mathbf{R}^0) U_I^\alpha U_J^\beta + \frac{1}{3!} \sum_{IJK} \Psi_{I\alpha, J\beta, K\gamma}(\mathbf{R}^0) U_I^\alpha U_J^\beta U_K^\gamma ,$$



→ non-Lorentzian lineshapes [1]

[1] Y. Shen, et al., Phys Rev B **103**, 134302 (2021).



Thermal transport (again)

Thermal transport fits into the response formalism [1]

$$\kappa^{\alpha\beta} = \frac{V}{k_B T^2} \int \langle J^\alpha(0) J^\beta(t) \rangle dt$$

$$\kappa^{\alpha\beta} = \frac{V}{k_B T^2} \lim_{\omega \rightarrow 0} e^{-i\omega t} \int \langle J^\alpha(0) J^\beta(t) \rangle dt$$

→ can be traced to phonon spectral function

→ describe e.g. anharmonic materials with phase transitions

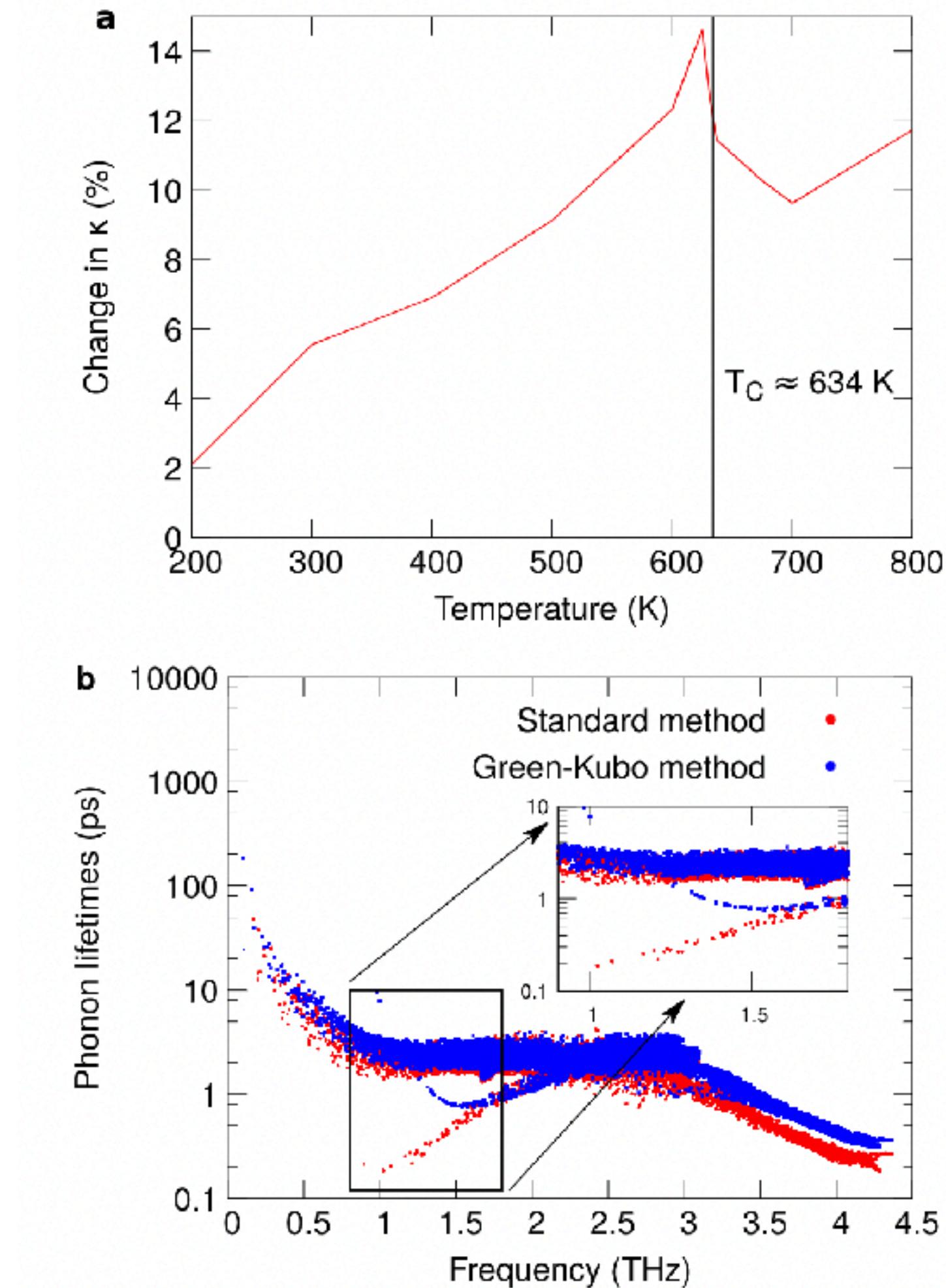


Fig. 6 Green-Kubo lattice thermal conductivity. a Difference in the calculated lattice thermal conductivity using the Green-Kubo

Higher-order Raman response [2]

Raman scattering cross section [1]

$$\sigma(\omega) \propto \sum_{\mu\nu\xi\rho} E_\mu^{\text{out}} E_\xi^{\text{out}} I_{\mu\nu,\xi\rho}(\omega) E_\nu^{\text{in}} E_\rho^{\text{in}}$$

Spectral Raman response tensor [1]

$$I_{\mu\nu,\xi\rho}(\omega) = \int dt \langle P^{\mu\nu}(t) P^{\xi\rho}(0) \rangle e^{-i\omega t}$$

Polarizability as function of displacements

$$P^{\mu\nu}(\mathbf{R}) = P_0^{\mu\nu} + \sum_{i=i\alpha} P_{1,i}^{\mu\nu} U_i + \frac{1}{2} \sum_{ij} P_{2,ij}^{\mu\nu} U_i U_j + \dots$$

$$\Rightarrow I_{\mu\nu,\xi\rho}(\omega) = I_1 + I_2 + \dots$$

First-order Raman

Second-order Raman

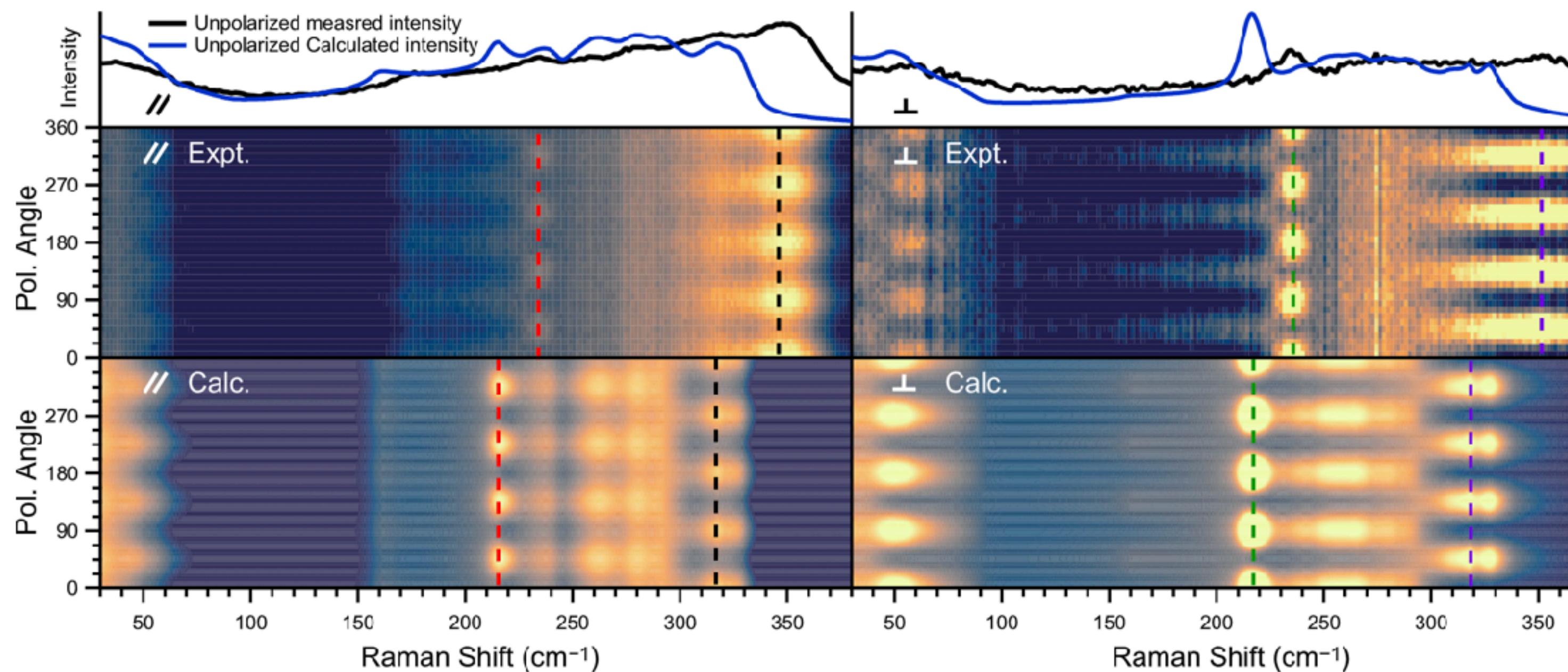
Collaboration mit Omer Yaffe (Weizmann Institute of Science):

[1] N. Benshalom *et al.*, Arxiv 2204.12528

[2] N. Benshalom *et al.*, Phys Rev Mater 6, 033607 (2022).

Higher-order Raman response [2]

Raman scattering cross section [1]



$$\sigma(\omega) \propto \sum_{\mu\nu\xi\rho} E_\mu^{\text{out}} E_\xi^{\text{out}} I_{\mu\nu,\xi\rho}(\omega) E_\nu^{\text{in}} E_\rho^{\text{in}}$$

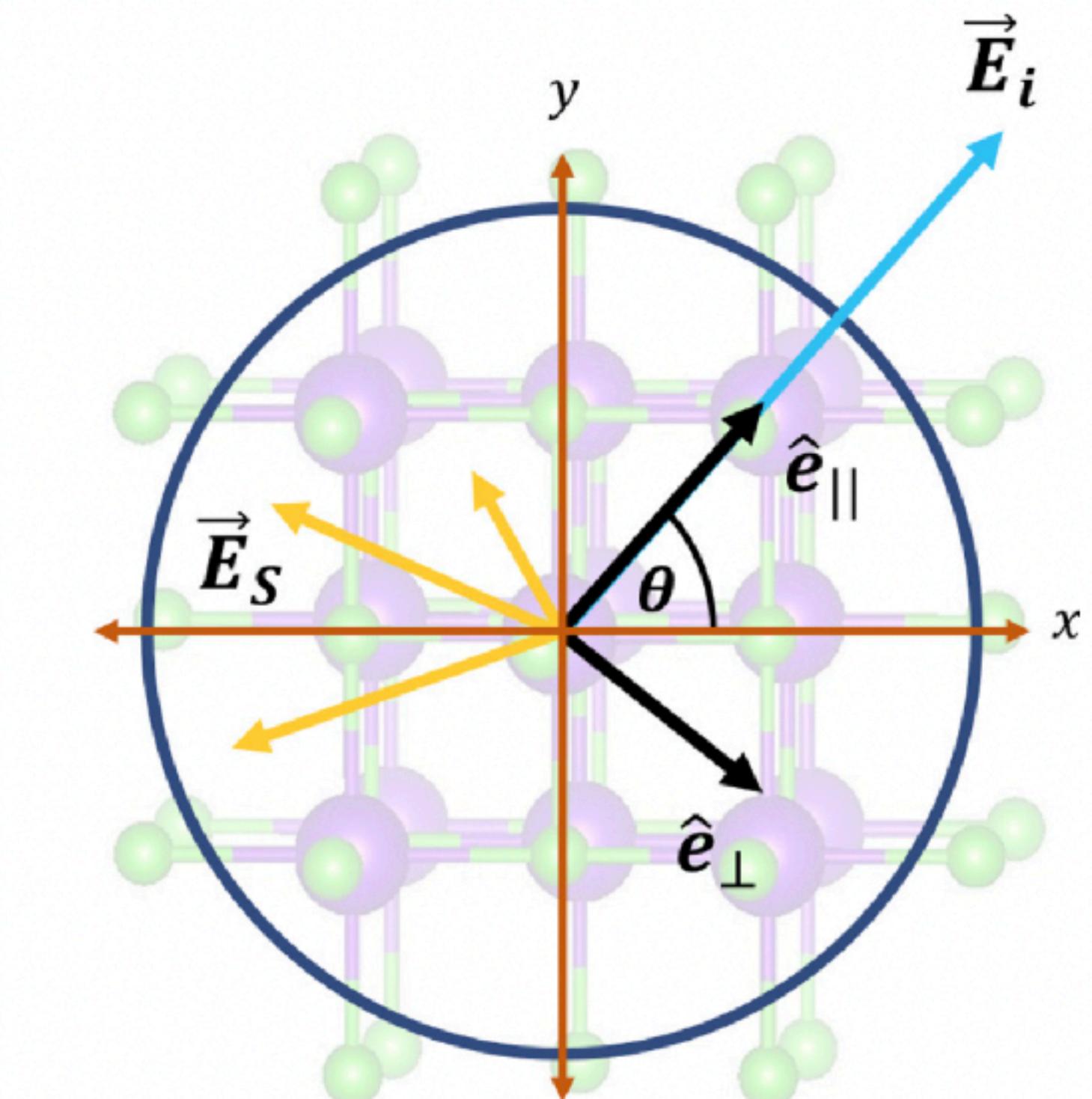


FIG. 3. NaCl Raman PO color map for measurement and TDEP simulation in 300 K. Unpolarized spectra are on top, measured spectra in

Collaboration mit Omer Yaffe (Weizmann Institute of Science):

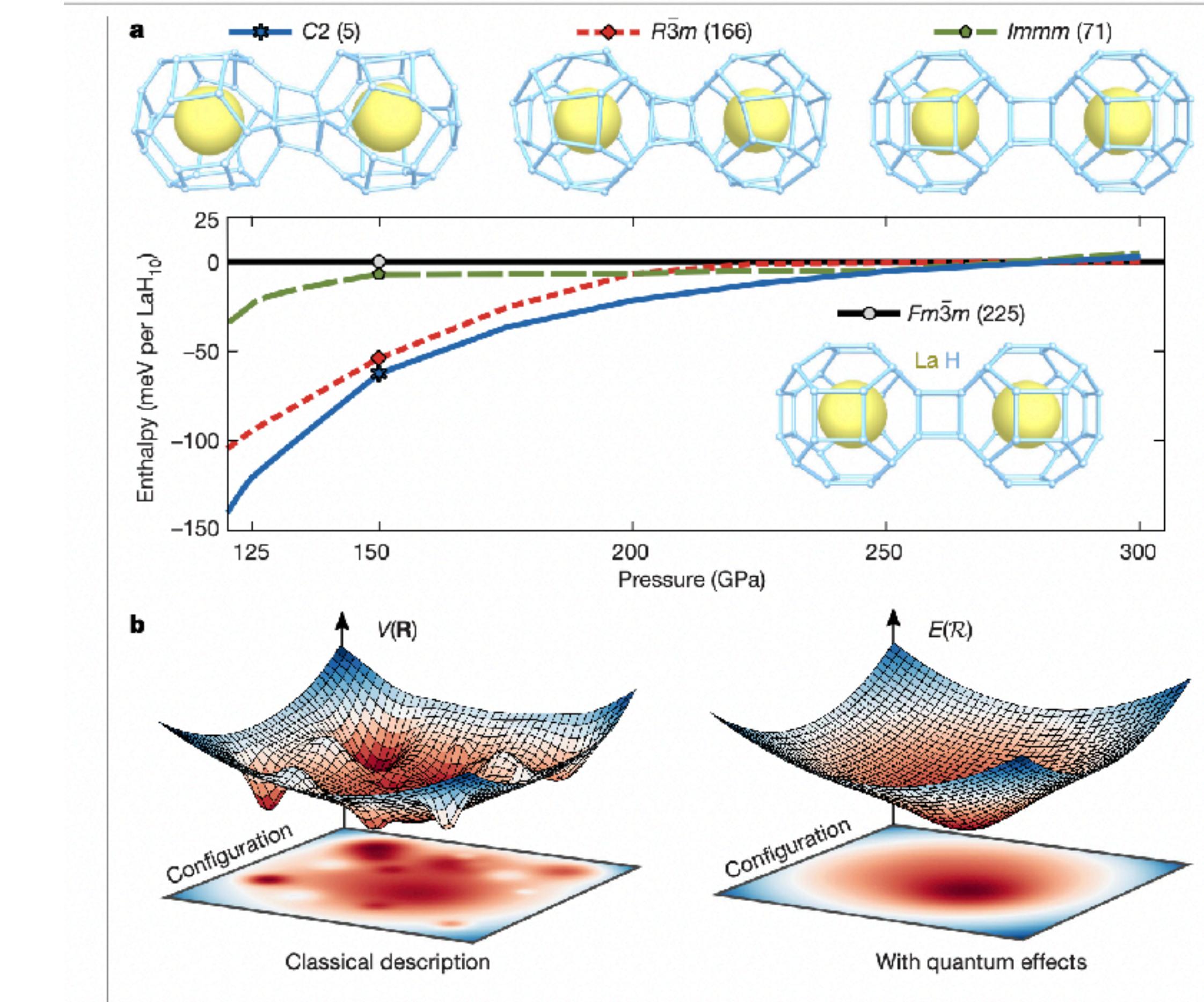
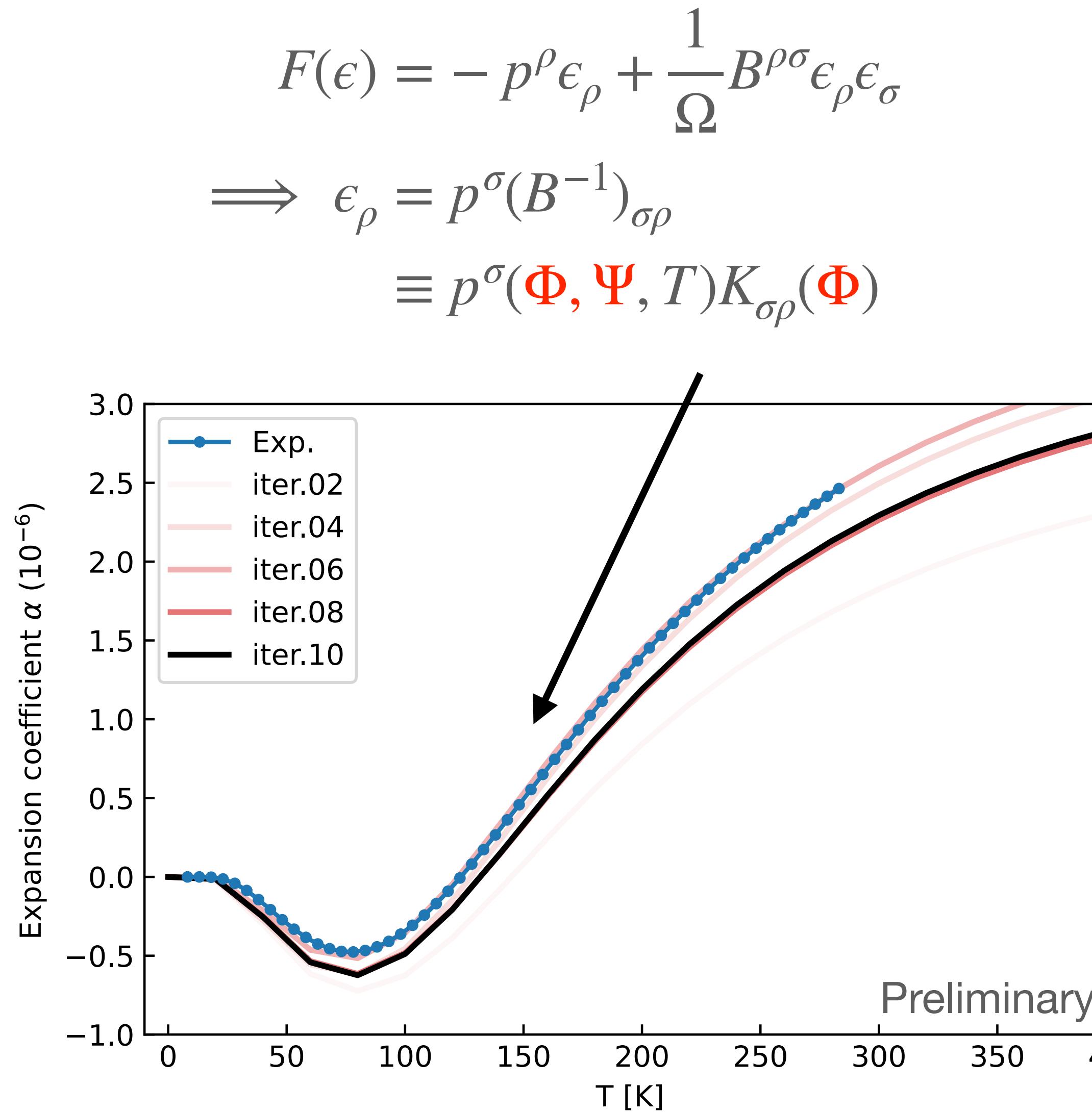
[1] N. Benshalom *et al.*, Arxiv 2204.12528

[2] N. Benshalom *et al.*, Phys Rev Mater 6, 033607 (2022).

What else can we do with this approach?

Finite-temperature, high-pressure lattice expansion

Goal: fully anisotropic pressure estimates based on TDEP Hamiltonian



From: I. Errea *et al.*, Nature 578, 66 (2020).

Motivation: LaH₁₀ a *potential* high-temperature superconductor



Zuschriften



High-Pressure Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201709970
Internationale Ausgabe: DOI: 10.1002/anie.201709970

Synthesis and Stability of Lanthanum Superhydrides

Zachary M. Geballe,* Hanyu Liu, Ajay K. Mishra, Muhtar Ahart, Maddury Somayazulu,
Yue Meng, Maria Baldini, and Russell J. Hemley

Z. M. Geballe *et al.*,
Angew Chem **130**, 696 (2018).

LETTER

<https://doi.org/10.1038/s41586-019-1201-8>

Superconductivity at 250 K in lanthanum hydride under high pressures

A. P. Drozdov^{1,7}, P. P. Kong^{1,7}, V. S. Minkov^{1,7}, S. P. Besedin^{1,7}, M. A. Kuzovnikov^{1,6,7}, S. Mozaffari², L. Balicas², F. F. Balakirev³, D. E. Graf², V. B. Prakapenka⁴, E. Greenberg⁴, D. A. Knyazev¹, M. Tkacz⁵ & M. I. Eremets^{1*}

A. P. Drozdov *et al.*, Nature **569**, 528 (2019).

Motivation: LaH₁₀ a *potential* high-temperature superconductor

PHYSICAL REVIEW LETTERS 122, 027001 (2019)

Editors' Suggestion

Featured in Physics

Evidence for Superconductivity above 260 K in Lanthanum Superhydride at Megabar Pressures

Maddury Somayazulu,^{1,*} Muhtar Ahart,¹ Ajay K. Mishra,^{2,†} Zachary M. Geballe,² Maria Baldini,^{2,§} Yue Meng,³ Viktor V. Struzhkin,² and Russell J. Hemley^{1,†}

¹*Institute for Materials Science and Department of Civil and Environmental Engineering,
The George Washington University, Washington, DC 20052, USA*

²*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*

³*HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*



(Received 23 August 2018; revised manuscript received 3 December 2018; published 14 January 2019)

Recent predictions and experimental observations of high T_c superconductivity in hydrogen-rich materials at very high pressures are driving the search for superconductivity in the vicinity of room temperature. We have developed a novel preparation technique that is optimally suited for megabar pressure syntheses of superhydrides using modulated laser heating while maintaining the integrity of sample-probe contacts for electrical transport measurements to 200 GPa. We detail the synthesis and characterization of lanthanum superhydride samples, including four-probe electrical transport measurements that display significant drops in resistivity on cooling up to 260 K and 180–200 GPa, and resistivity transitions at both lower and higher temperatures in other experiments. Additional current-voltage measurements, critical current estimates, and low-temperature x-ray diffraction are also obtained. We suggest that the transitions represent signatures of superconductivity to near room temperature in phases of lanthanum superhydride, in good agreement with density functional structure search and BCS theory calculations.

DOI: 10.1103/PhysRevLett.122.027001

Our work: try to shed some light [1]

nature communications

Article <https://doi.org/10.1038/s41467-022-34755-y>

High-pressure synthesis of seven lanthanum hydrides with a significant variability of hydrogen content

Received: 12 August 2022

Accepted: 4 November 2022

Published online: 16 November 2022

 Check for updates

Dominique Laniel  , Florian Trybel³, Bjoern Winkler⁴, Florian Knoop , Timofey Fedotenko¹, Saiana Khandarkhaeva¹, Alena Aslandukova⁵, Thomas Meier⁶, Stella Chariton⁷, Konstantin Glazyrin , Victor Milman , Vitali Prakapenka , Igor A. Abrikosov , Leonid Dubrovinsky & Natalia Dubrovinskaia 

[1] D Laniel, F Trybel, B Winkler, FK, et al., *Nat Commun* **13**, 6987 (2022)

Task for DFT: Fill La structures seen in XRD with H atoms

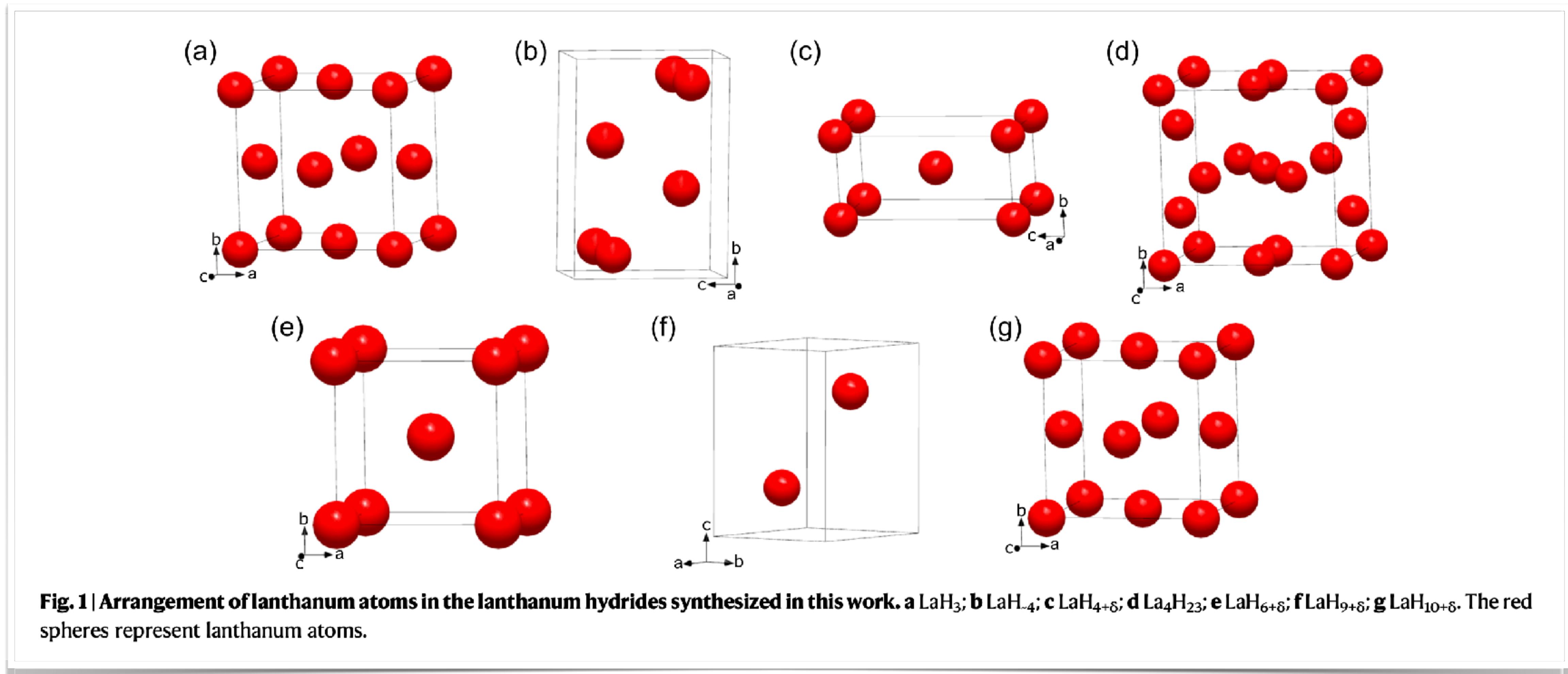


Fig. 1 | Arrangement of lanthanum atoms in the lanthanum hydrides synthesized in this work. **a** LaH_3 ; **b** LaH_4 ; **c** $\text{LaH}_{4+\delta}$; **d** La_4H_{23} ; **e** $\text{LaH}_{6+\delta}$; **f** $\text{LaH}_{9+\delta}$; **g** $\text{LaH}_{10+\delta}$. The red spheres represent lanthanum atoms.

Or: Solve a puzzle without seeing the pieces

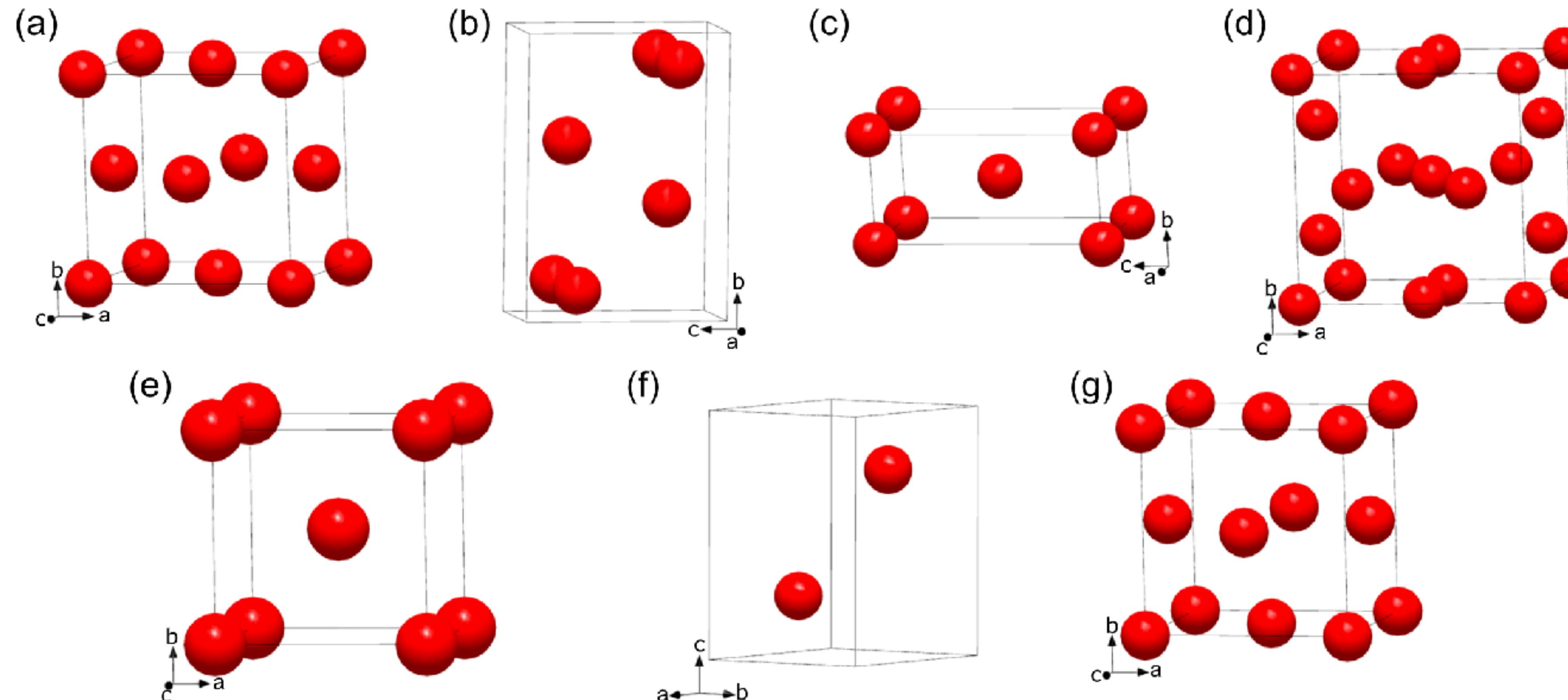


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Best candidates from structure search:

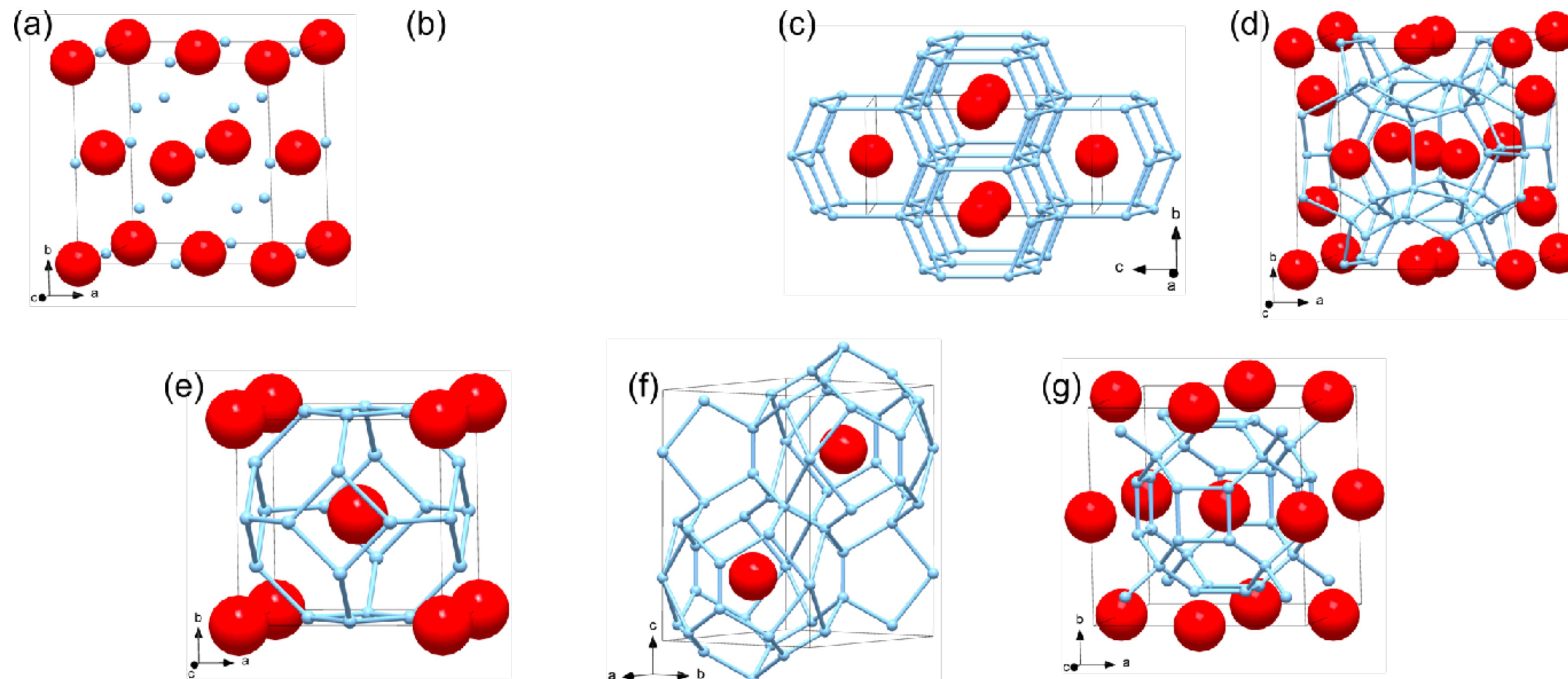
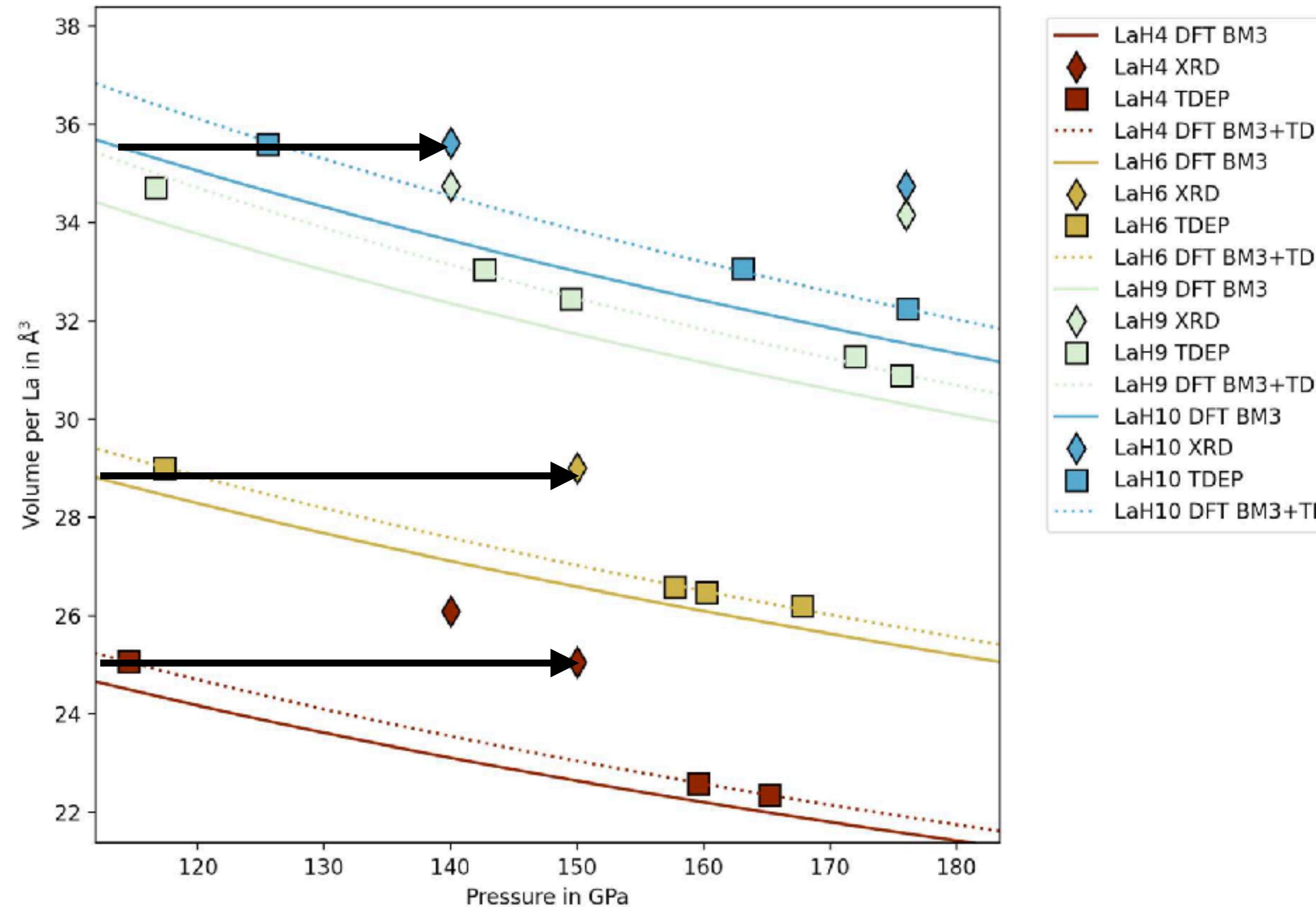


Fig. 1 | Arrangement of lanthanum atoms in the lanthanum hydrides synthesized in this work. **a** LaH_3 ; **b** LaH_4 ; **c** $\text{LaH}_{4+\delta}$; **d** La_4H_{23} ; **e** $\text{LaH}_{6+\delta}$; **f** $\text{LaH}_{9+\delta}$; **g** $\text{LaH}_{10+\delta}$. The red spheres represent lanthanum atoms.

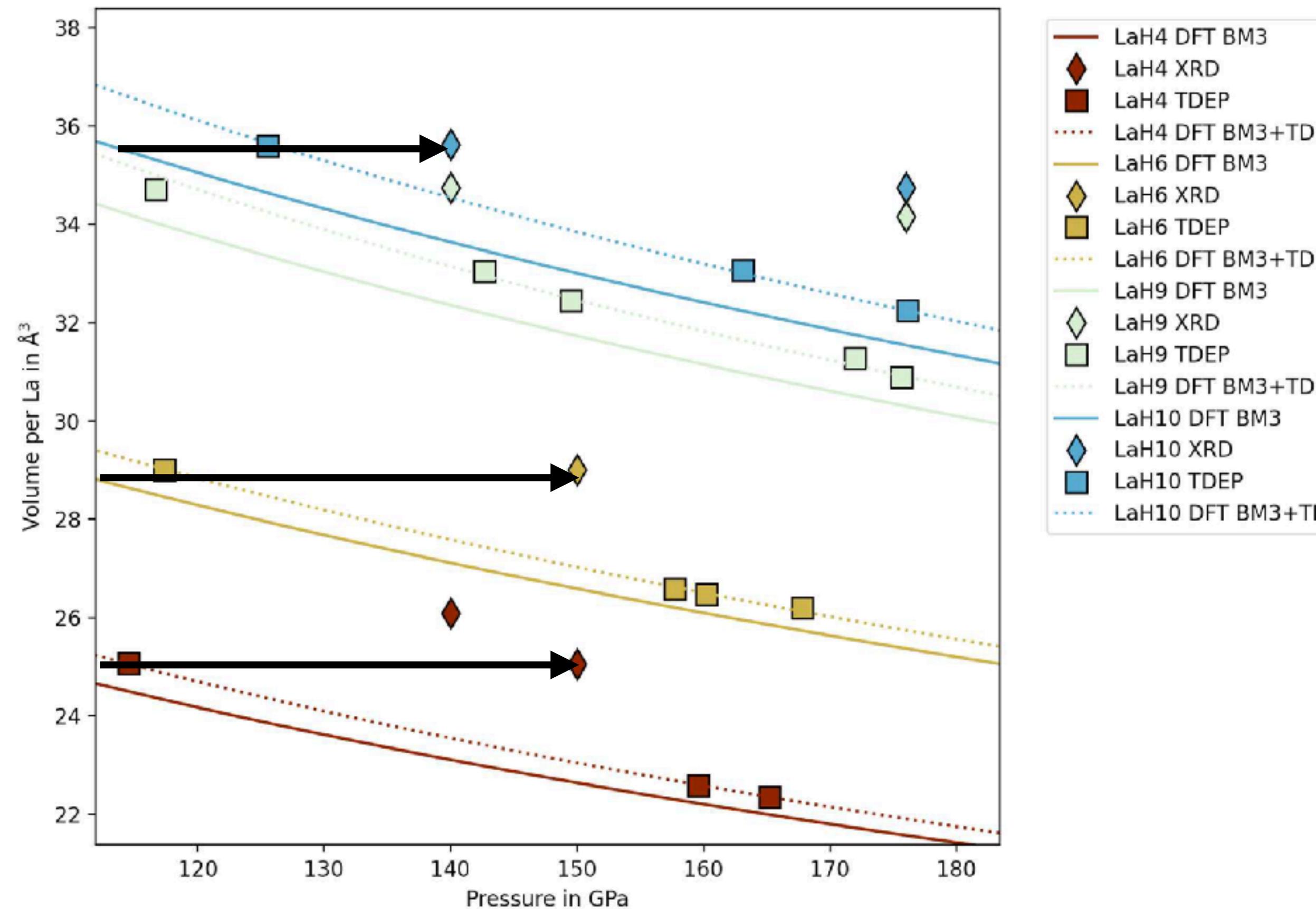
0K DFT EOS for best candidates and experiments are quite off



Sources of error:

- Experiment: $\pm 10 \text{ GPa}$
- Hydrogen mismatch?
- xc functional: $\pm 10 \text{ Gpa}$
- Static 0K calculations:
 - Zero-point motion (hydrogen)?
 - Temperature?

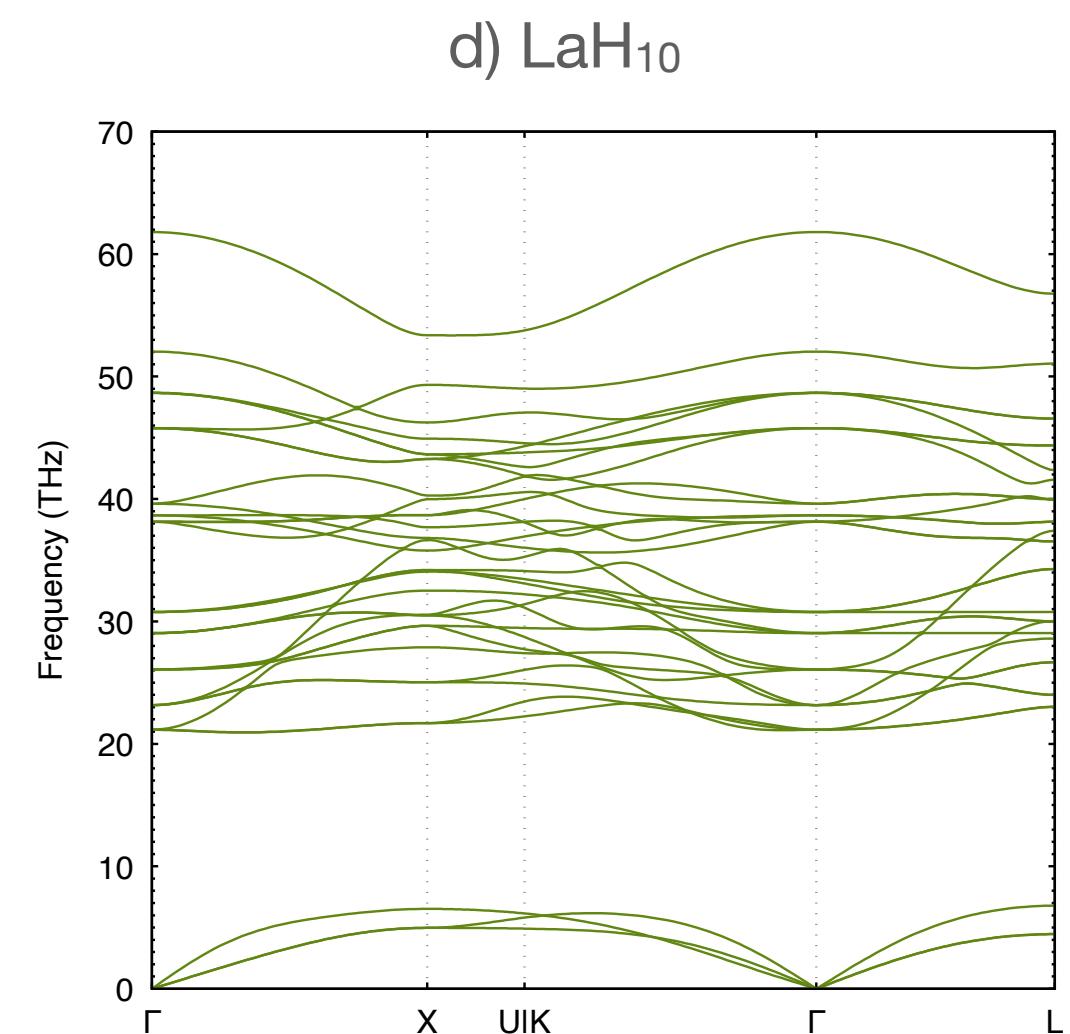
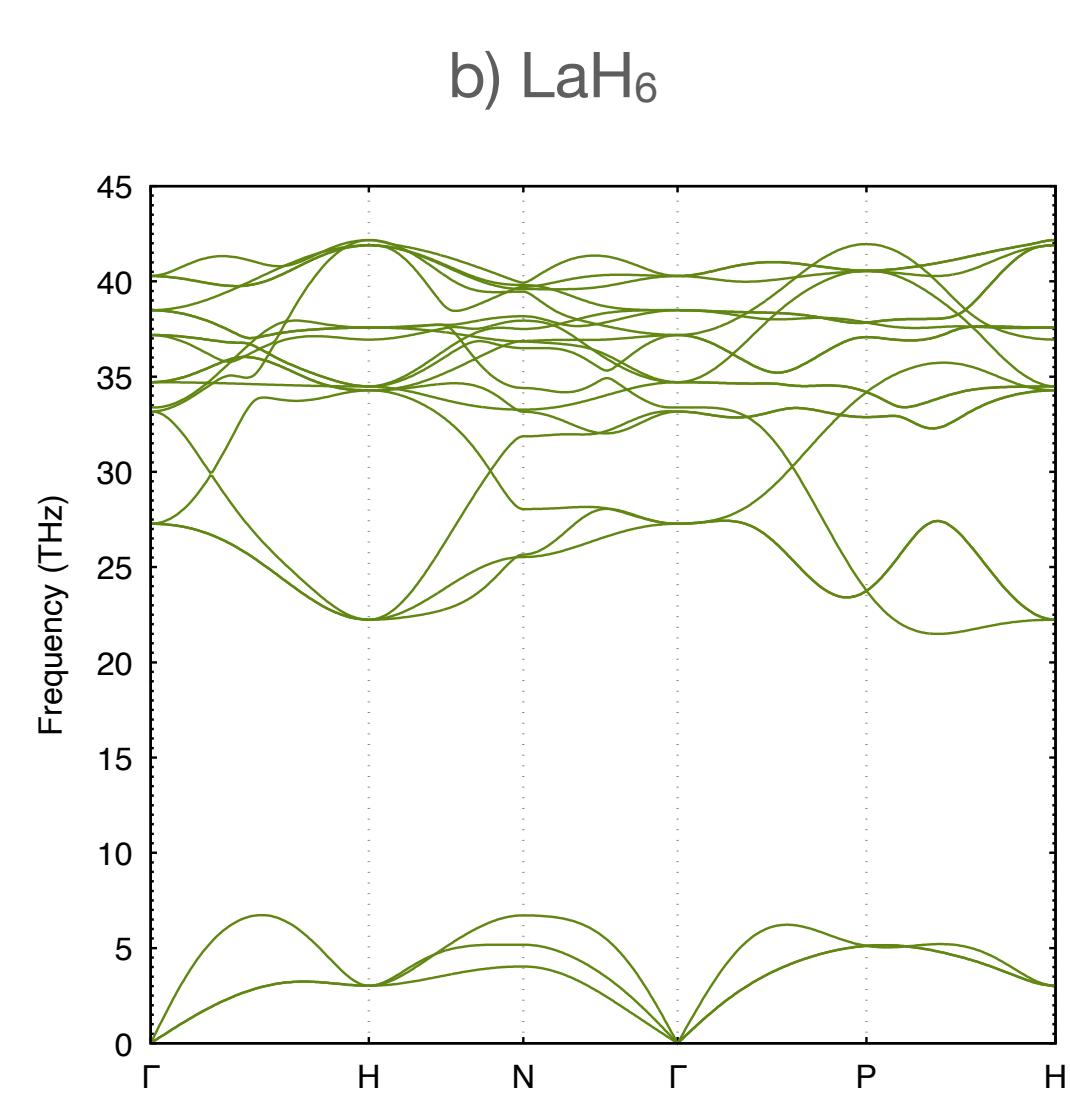
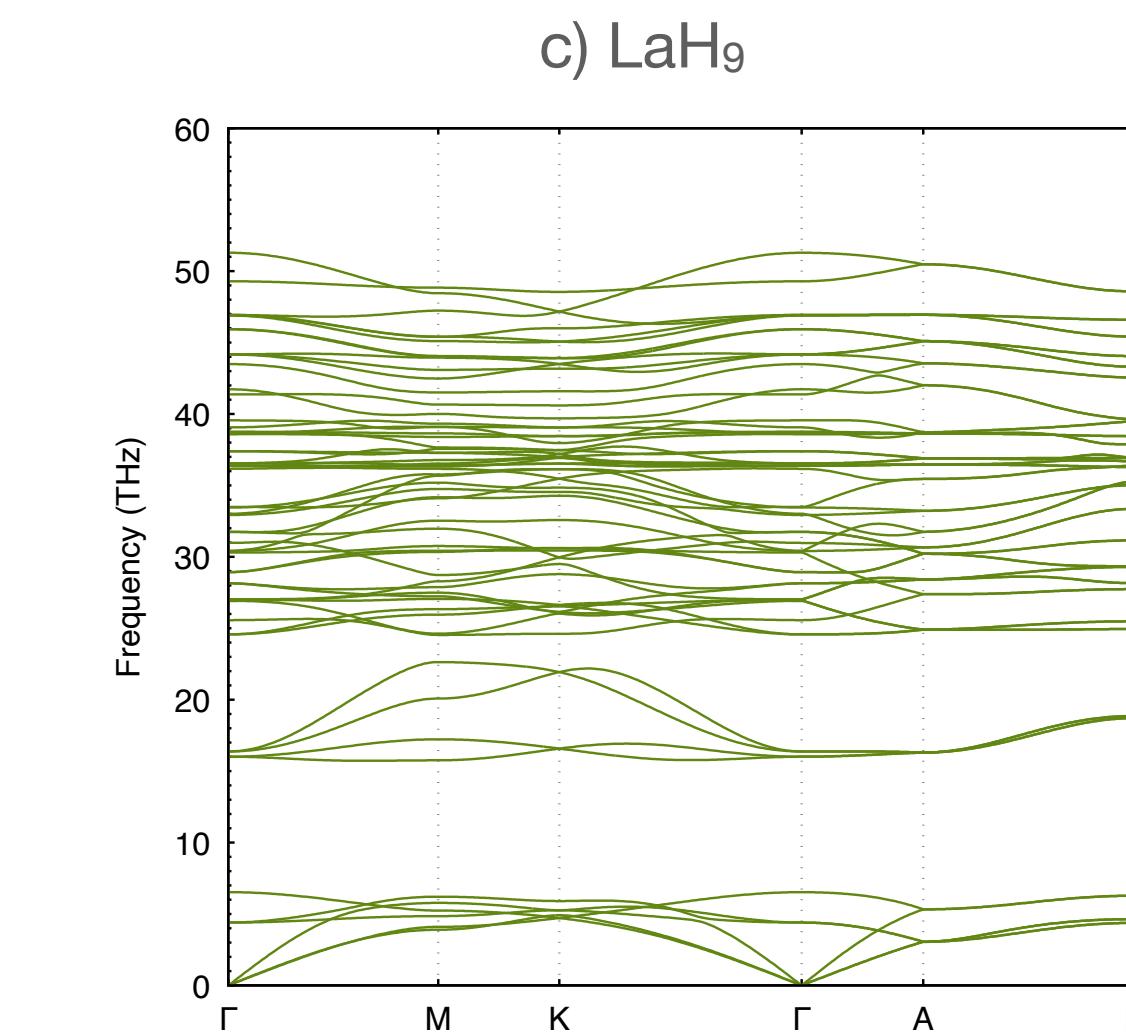
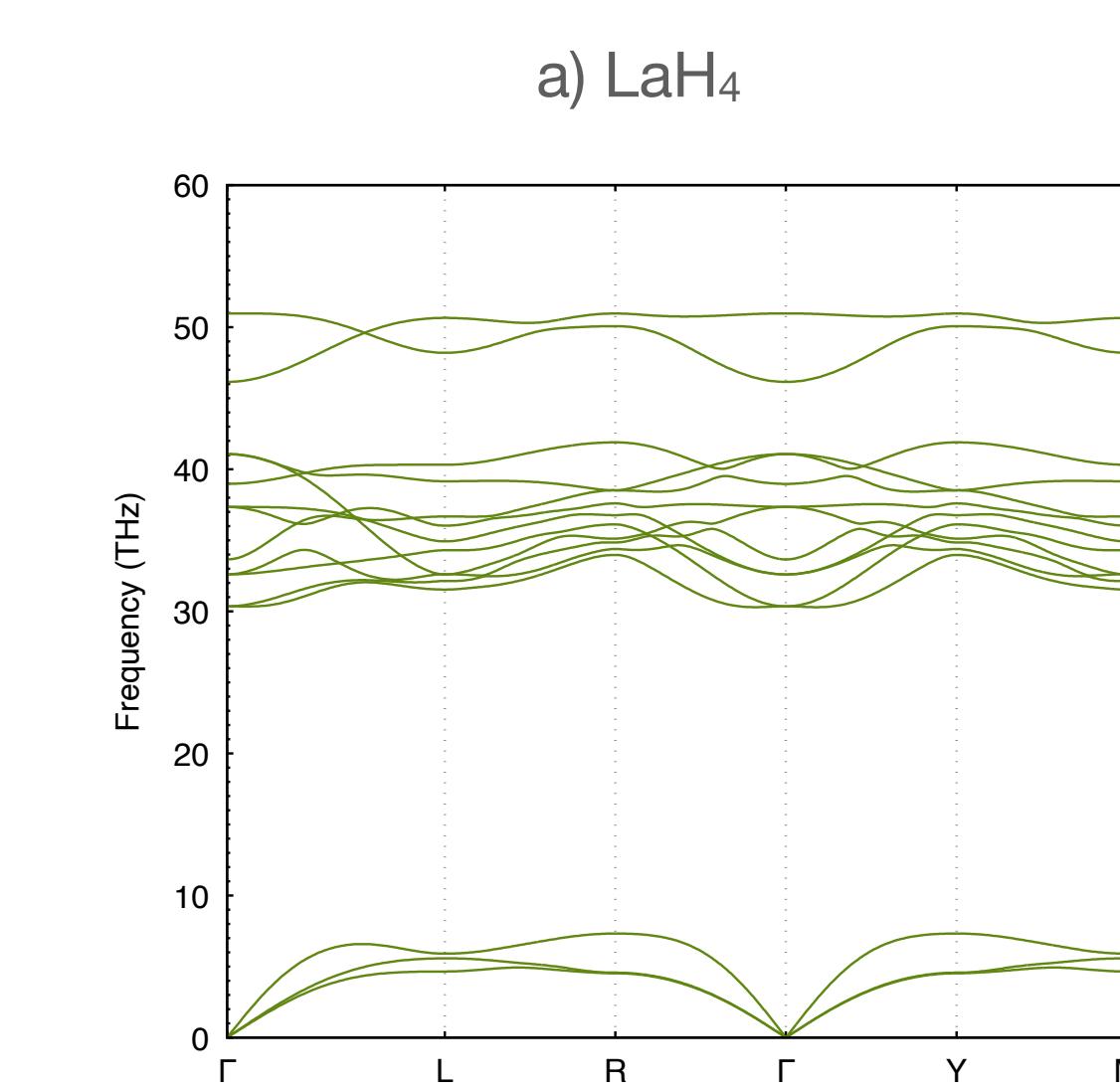
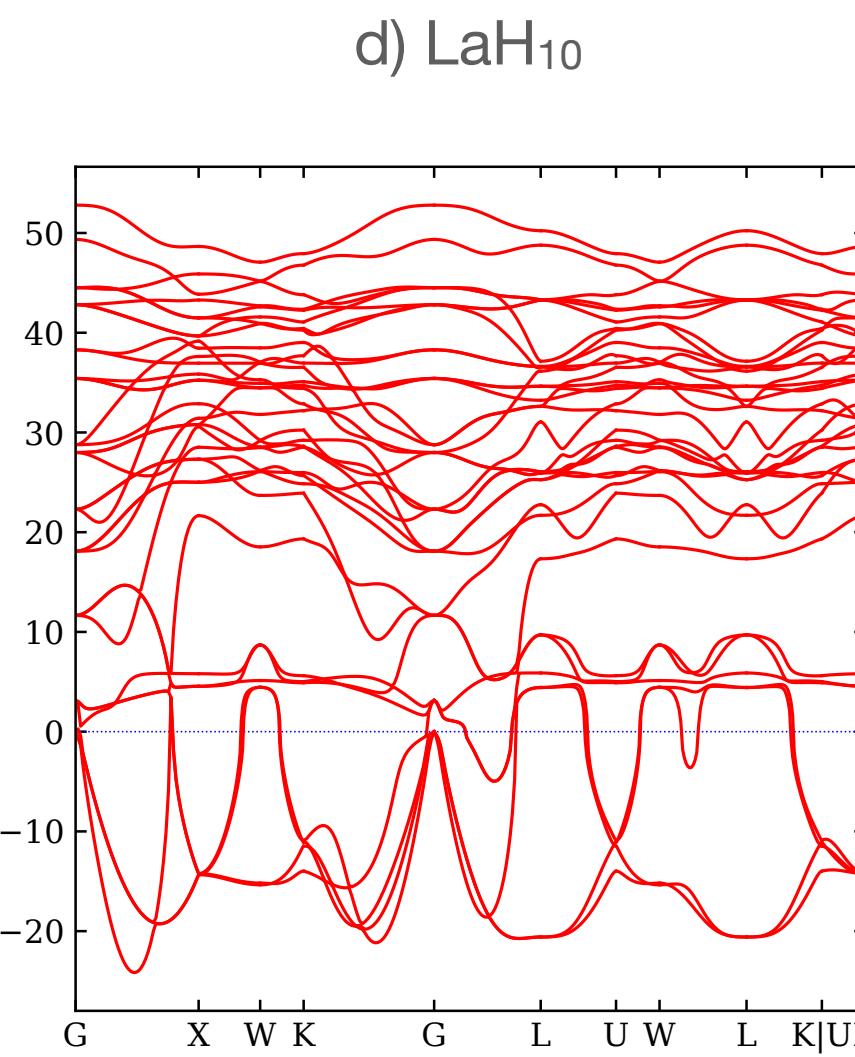
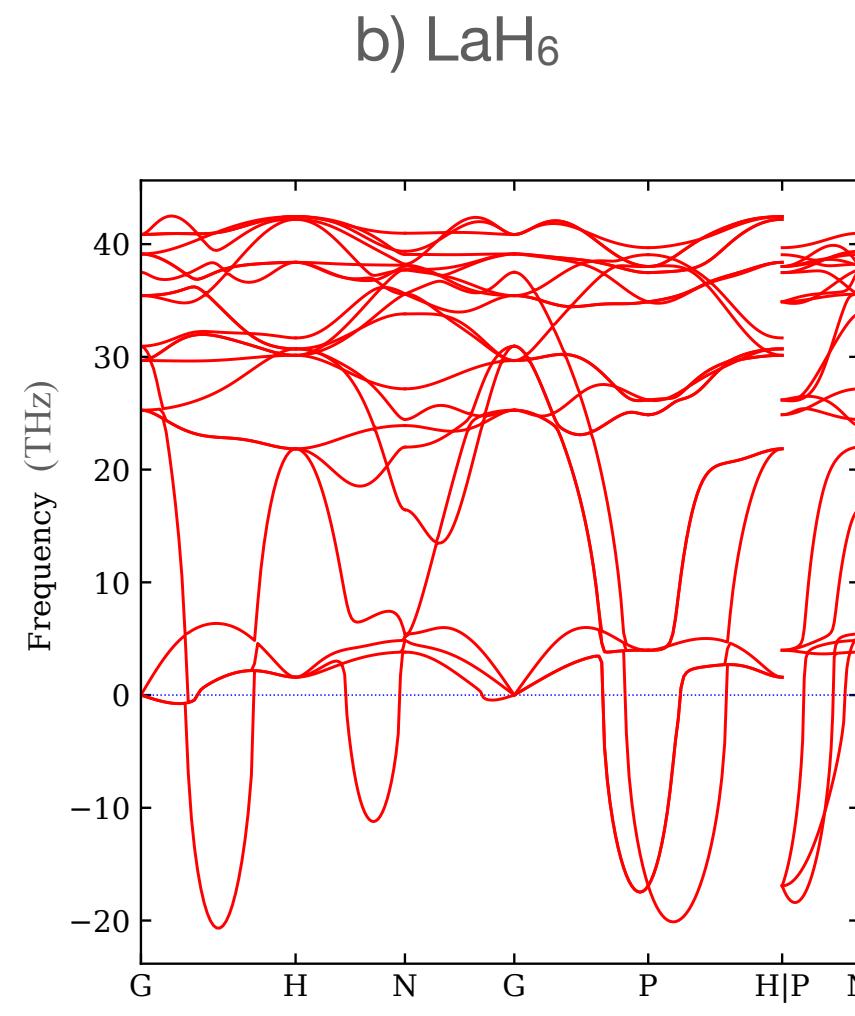
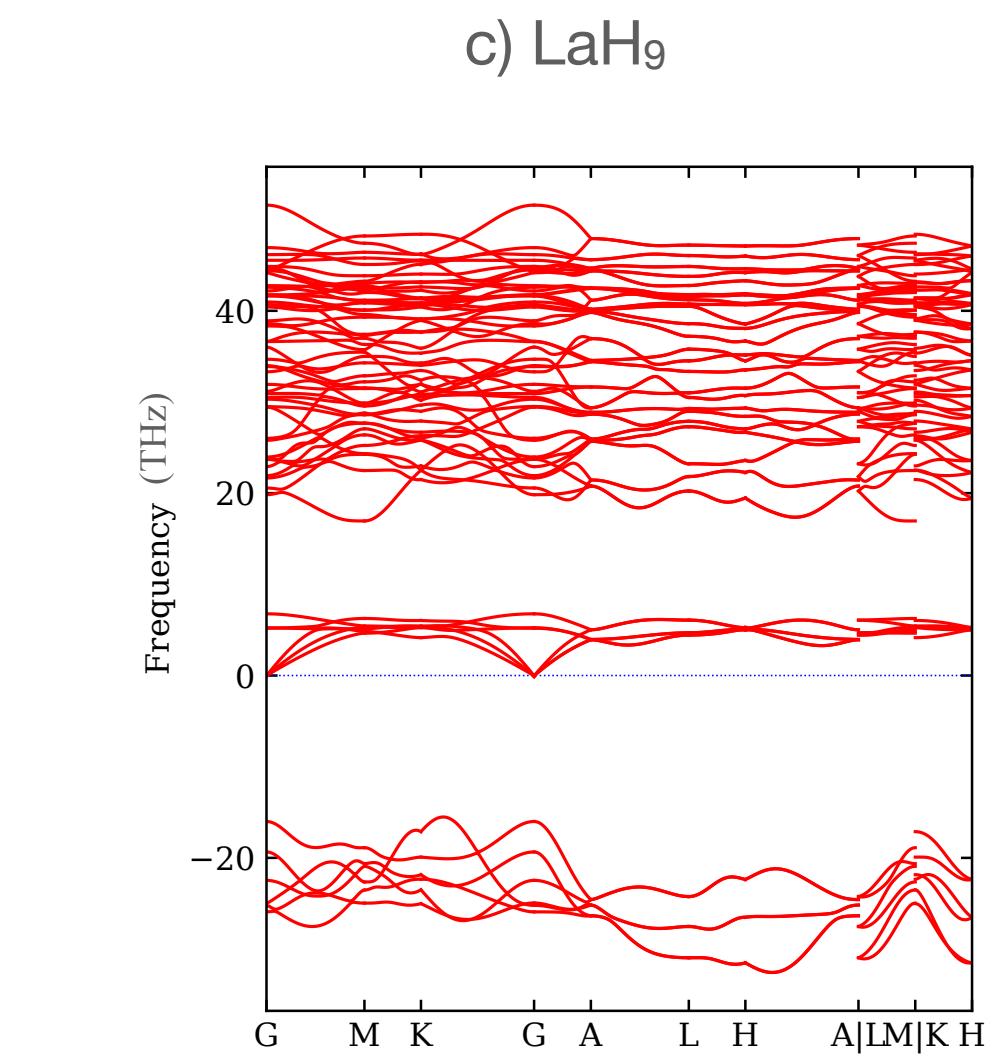
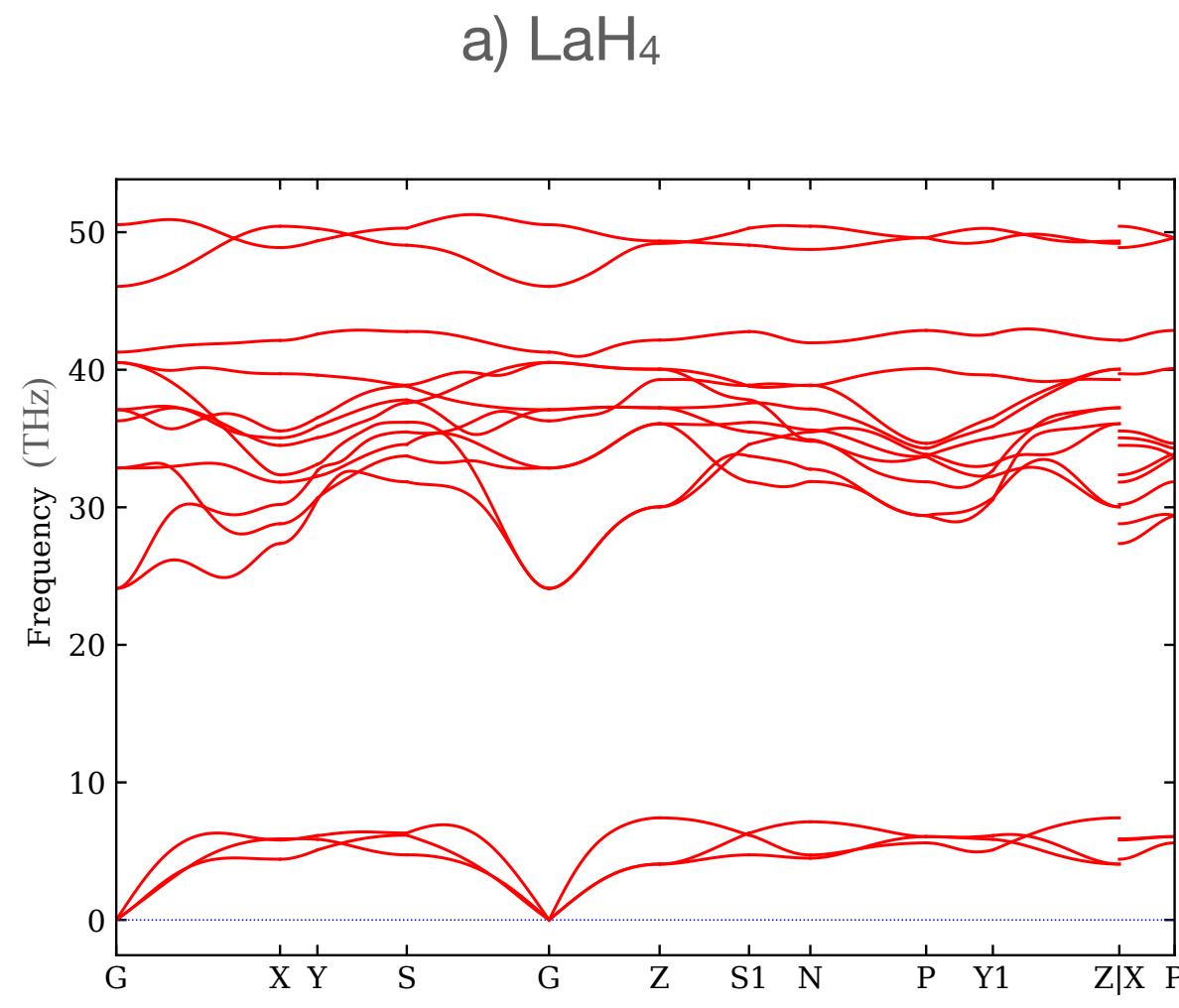
How much do we gain from thermal and quantum nuclear motion?



Sources of error:

- Experiment: $\pm 10 \text{ GPa}$
- Hydrogen mismatch?
- xc functional: $\pm 10 \text{ Gpa}$
- Static 0K calculations:
 - Zero-point motion (hydrogen!)?
 - Temperature?

Problem 1: Dynamical stability



Sup. Fig. 9: Harmonic approximation via Phonopy

Sup. Fig. 6: TDEP

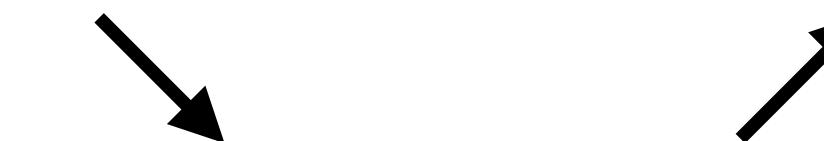
Problem 2: Estimate pressure incl. temperature and quantum statistics

Pressure (exact, classical):

$$p = -\frac{\partial F}{\partial \Omega} = -\left\langle \frac{\partial H}{\partial \Omega} \right\rangle = -\left\langle \frac{\partial V}{\partial \Omega} - \frac{2}{3\Omega} T \right\rangle$$

Approximation 1:
Sample with harmonic model

$$\left\langle \frac{\partial V}{\partial \Omega} - \frac{2}{3\Omega} T \right\rangle_V \approx \left\langle \frac{\partial V}{\partial \Omega} - \frac{2}{3\Omega} T \right\rangle_{V_2} = \left\langle \frac{\partial V}{\partial \Omega} - \frac{2}{3\Omega} V_2^2 \right\rangle_{V_2}$$



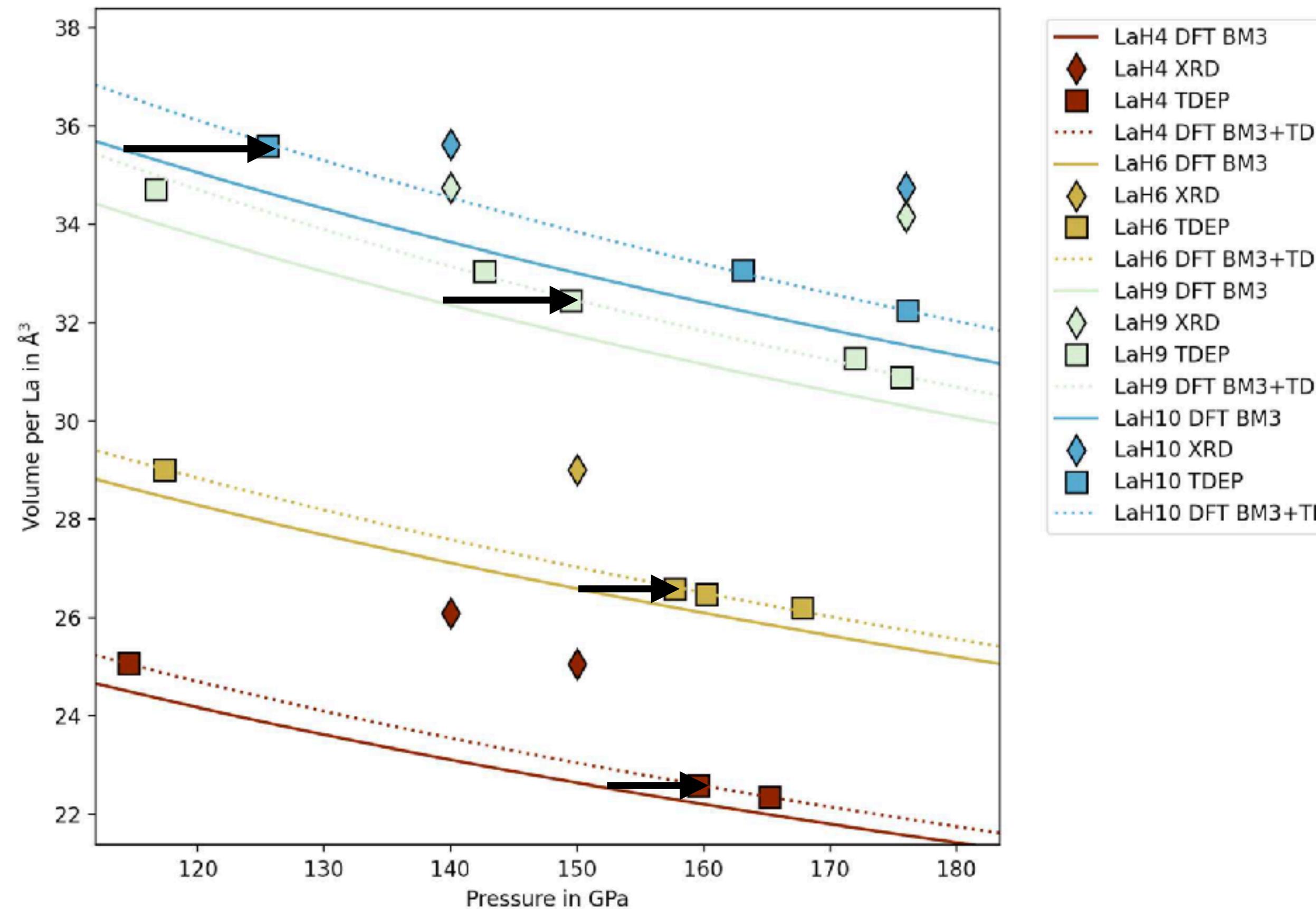
Equipartition theorem!

Approximation 2:
Use quantum distribution
To estimate nuclear quantum effects [1]

$$\begin{aligned} \langle A \rangle_{V_2} &= \frac{1}{Z} \int dR e^{-\beta \textcolor{red}{V}_2(\mathbf{R})} A(\mathbf{R}) \rightarrow \frac{1}{Z} \text{Tr} \{ \rho_\Phi A \} \\ &= \frac{1}{Z} \int dR e^{-\beta \textcolor{red}{W}_2(\mathbf{R})} A(\mathbf{R}) \end{aligned}$$

[1] R. P. Feynman and H. Kleinert, Phys Rev A 34, 5080 (1986).

Results [1]: Pressure incl. temperature and zero-point motion



Temperature + zero-point motion:

Adds ~ 1 GPa per H atom

→ good agreement with theory prediction for LaH_{10} [2]

→ still >15 GPa off

→ does not explain everything!

H atoms mismatch?

Are we looking at pure phases?

Open questions remain!

[1] D Laniel, F Trybel, B Winkler, FK, et al., *Nat Commun* **13**, 6987 (2022)

[2] I. Errea et al., *Nature* **578**, 66 (2020).

LaH is an interesting system with many open questions to be answered

TDEP allows to get many **observables** incl. temperature dependence

TDEP is **efficient**: Results shown were obtained with $\mathcal{O}(100)$ DFT calculations

Key references:

- [1] O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys Rev B **84**, 180301 (2011).
- [2] O. Hellman *et al.*, Phys Rev B **87**, 104111 (2013).
- [3] O. Hellman and I. A. Abrikosov, Phys Rev B **88**, 144301 (2013).
- [4] M. E. Manley *et al.*, Nat Commun **10**, 1928 (2019).
- [5] Đ. Dangić *et al.*, Npj Comput Mater **7**, 57 (2021).
- [6] N. Benshalom *et al.*, Phys Rev Mater **6**, 033607 (2022).
- [7] A. Cohen *et al.*, Adv Mater 2107932 (2022).
- [8] D Laniel, F Trybel, B Winkler, FK, et al., Nat Commun **13**, 6987 (2022)



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Collaborators and funding

Thermal transport

Christian Carbogno (FHI)



Matthias Scheffler (FHI)



Thomas Purcell (FHI)



Marcel Langer (FHI, TU Berlin)

Matthias Rupp (LIST)

Thank you!



TDEP

Olle Hellman (Weizmann Institute)



Swedish
Research
Council
2020-04630

Igor Abrikosov (LiU)

Sergei Simak (LiU)

Florian Trybel (LiU)

Dominique Laniel (U Edinburgh)



Conclusion

Anharmonicity and thermal transport

σ^A : quantitative measure of anharmonicity

- correlates with thermal conductivity κ
- predict thermal insulators

Ab initio Green-Kubo: accurate reference method

→ enables search for novel thermal insulators in materials space

Machine learning potentials: route towards accelerated simulations

TDEP

The fast way to anharmonic properties

More infos, reach out:

flokno.me/



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Thank you!

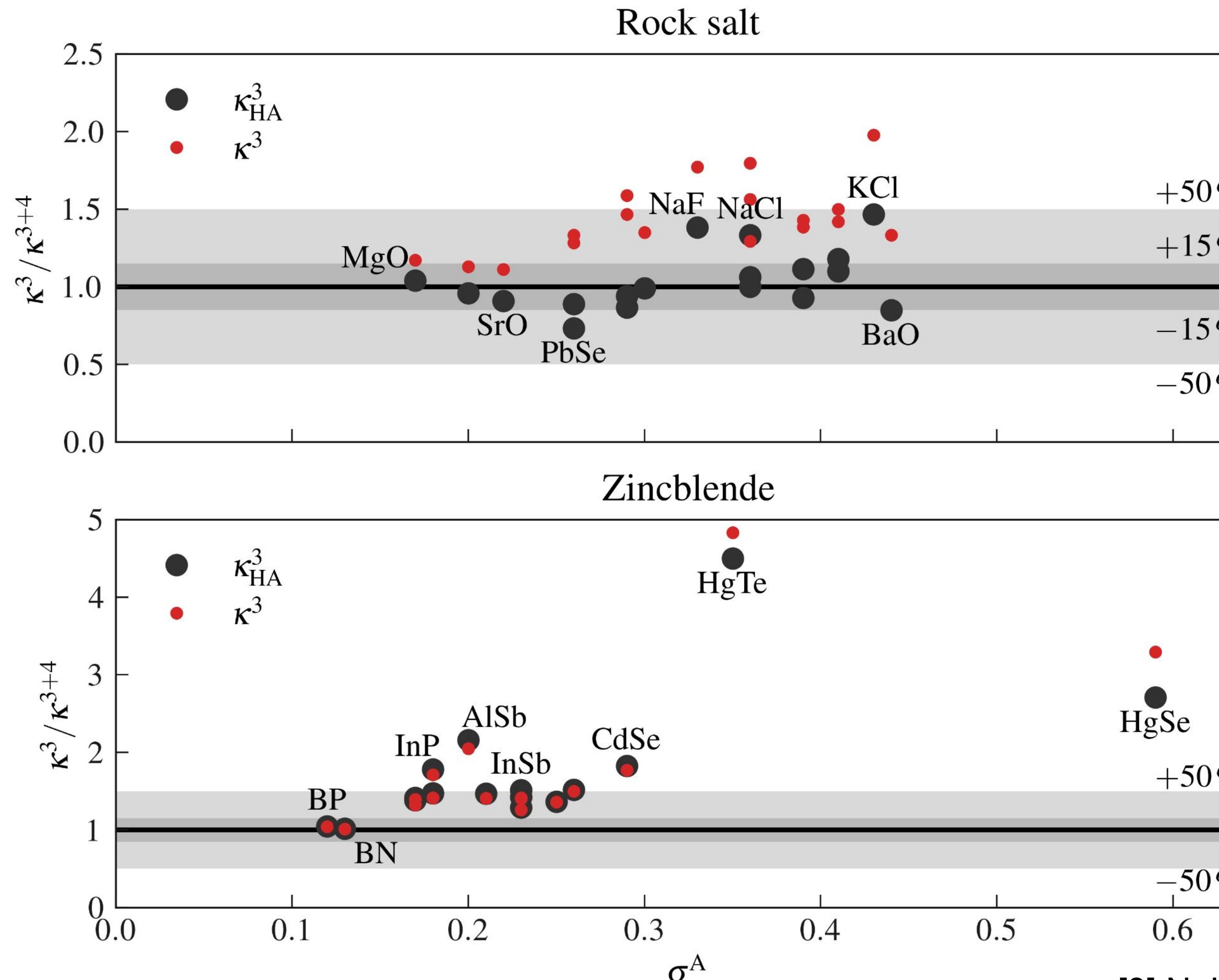


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Bonus Content

Boltzmann Transport and Anharmonicity



κ^3_{HA} : BTE with harmonic dispersion

κ^3 : BTE with renormalized dispersion

κ^{3+4} : BTE with renormalized dispersion incl. 4th-order scattering

→ values from [4]

σ^A_{OS} : Anharmonicity score introduced and computed in [0]

[0] F. Knoop et al., Phys Rev Mater 4, 083809 (2020).

[1] T. Feng and X. Ruan, Phys Rev B 93, 045202 (2016).

[2] Y. Xia, Appl Phys Lett 113, 073901 (2018).

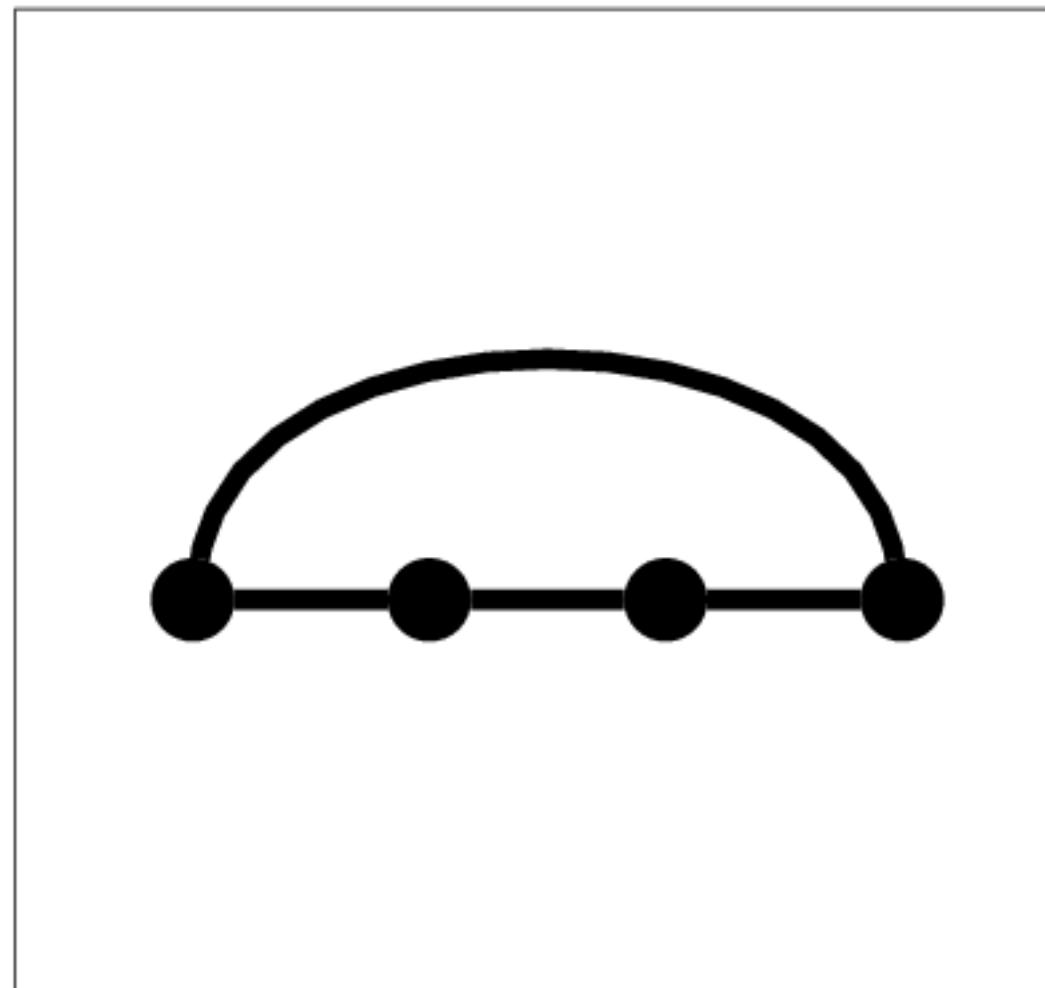
[3] N. K. Ravichandran and D. Broido, Phys Rev B 98, 085205 (2018).

[4] Y. Xia et al., Phys Rev X 10, 041029 (2020).

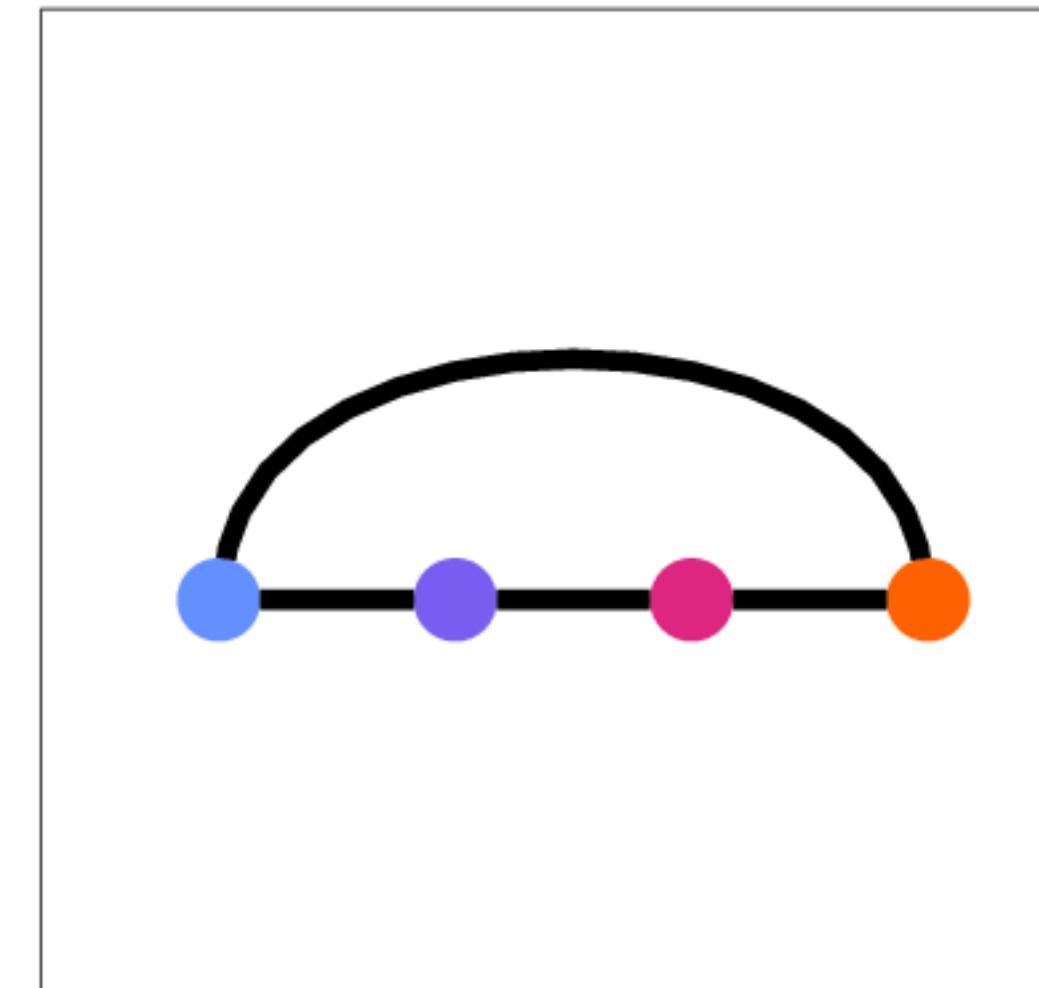
[5] N. K. Ravichandran and D. Broido, Phys Rev X 10, 021063 (2020).

Message-Passing Graph Neural Networks

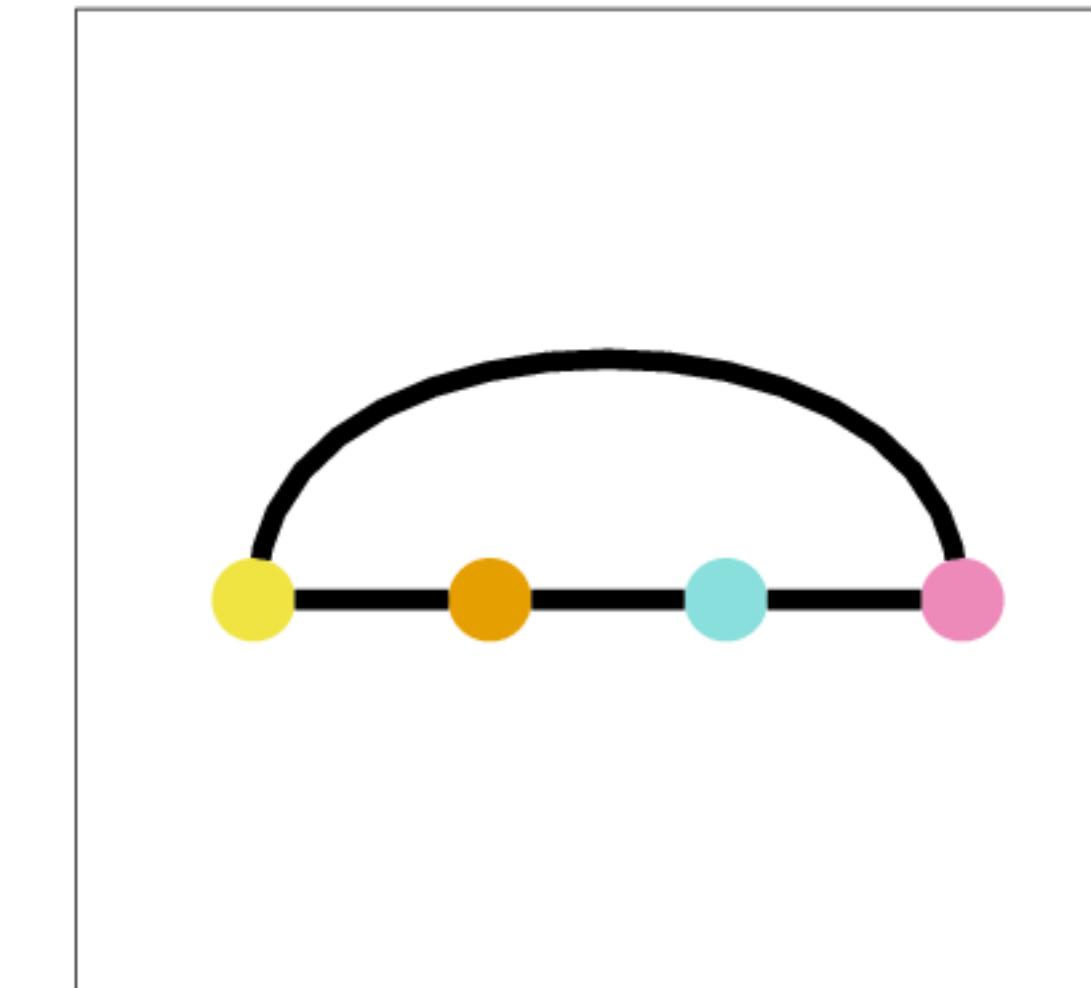
Initialisation



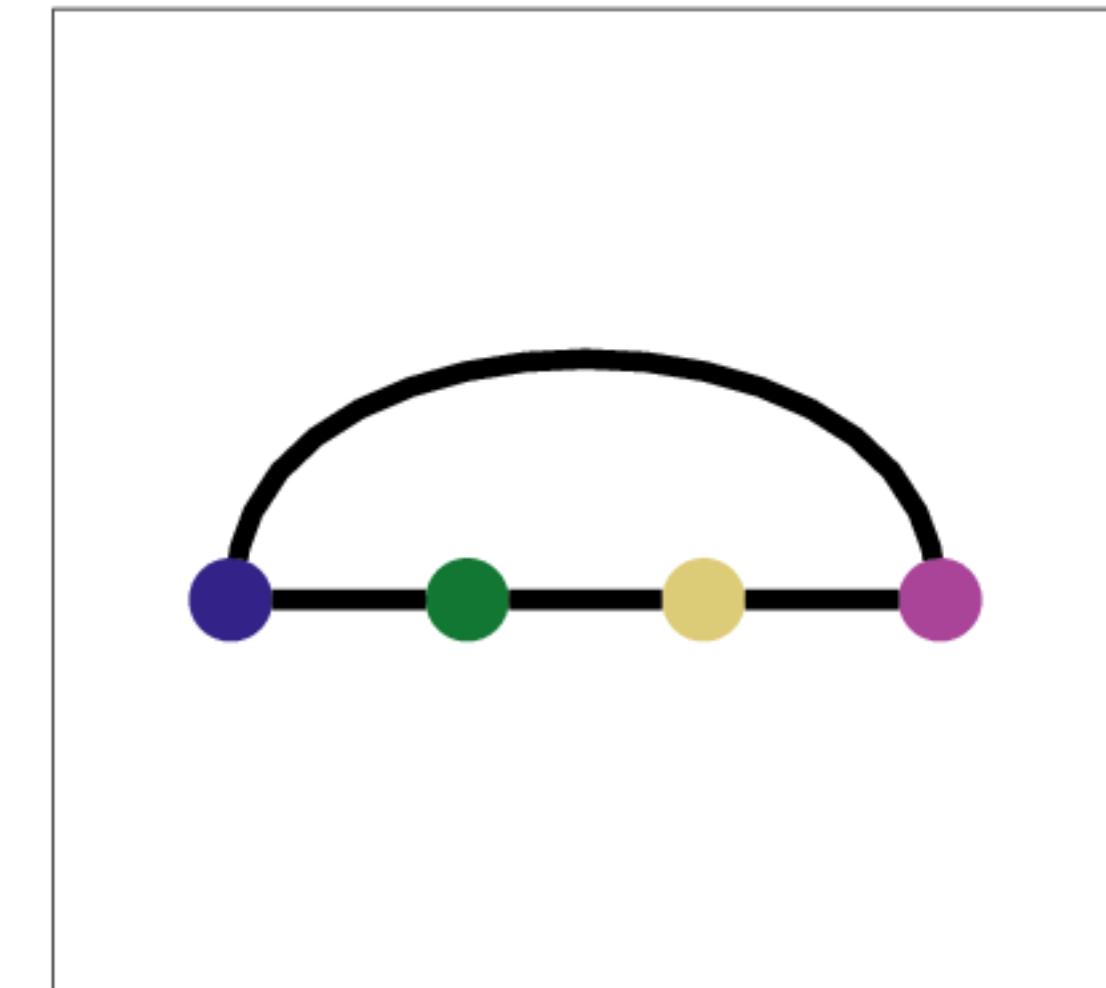
Message-passing step 1



Message-passing step 2



Readout, pooling



SchNet:

K. T. Schütt *et al.*, in *Advances in Neural Information Processing Systems 30*, Los Angeles, California (2017)
K. T. Schütt *et al.*, J. Chem. Phys. **148**, 241722 (2018)

Other MPNNs:

O. T. Unke and M. Meuwly, J. Chem. Theor. Comput. **15**, 3678 (2019)
S. Batzner *et al.*, arXiv 2101.03164 (2021)
K. T. Schütt, O.T. Unke, and M. Gastegger, arXiv 2102.03150 (2021)

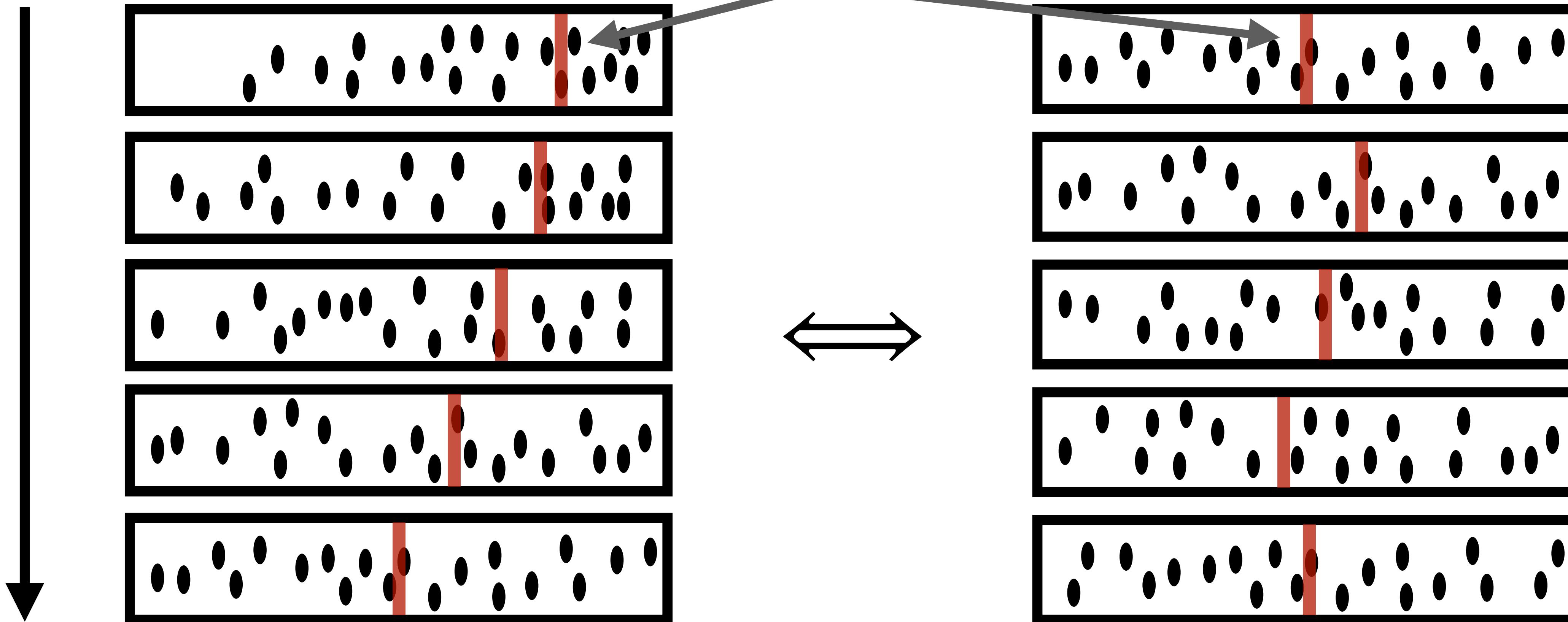
SchNet Details

- **Model architecture**
5 interaction layers, cutoff 5Å, default settings otherwise
- **Training with summed squared error of energy, forces and stress**
weights: 0.001, 0.999, 10.0
- **Early stopping with validation set**
last 20% of trajectories, patience 200
- **Learning rate reduction on plateau**
factor 0.75, patience 20, starting from 1e-4, stopping at 1e-6
- **Training time**
~3 days on 2x NVIDIA V100 (32GB)

Fluctuation dissipation theorem

Time

Energy barycenter



Relaxation to equilibrium

Fluctuation at equilibrium

L. Onsager, Phys. Rev. **37**, 4 405 (1931)

Heat flux formulation

Energy

$$E(t) = \int d^3r e(r, t)$$

Energy density

Heat flux

$$J(t) = \frac{d}{dt} \left(\int d^3r r e(r, t) \right)$$

Energy barycenter

Atomic partitioning

$$e(r) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) (U_i + T_i)$$

Potential + kinetic energy

Hardy flux

$$\Rightarrow J = \sum_{ji} \mathbf{r}_{ji} \left(\frac{\partial U_i}{\partial \mathbf{r}_j} \cdot \mathbf{v}_j \right)$$

R. J. Hardy, Phys Rev **132**, 168 (1963)
Z. Fan *et al.*, Phys. Rev. B **92** 094301 (2015)
L. Ercole *et al.*, J Low Temp Phys **185**, 79 (2016)

Motivation: LaH₁₀ a *potential* high-temperature superconductor

PHYSICAL REVIEW B 103, 134505 (2021)

Nonstandard superconductivity or no superconductivity in hydrides under high pressure

J. E. Hirsch¹ and F. Marsiglio²

¹*Department of Physics, University of California, San Diego, La Jolla, California 92093-0319, USA*

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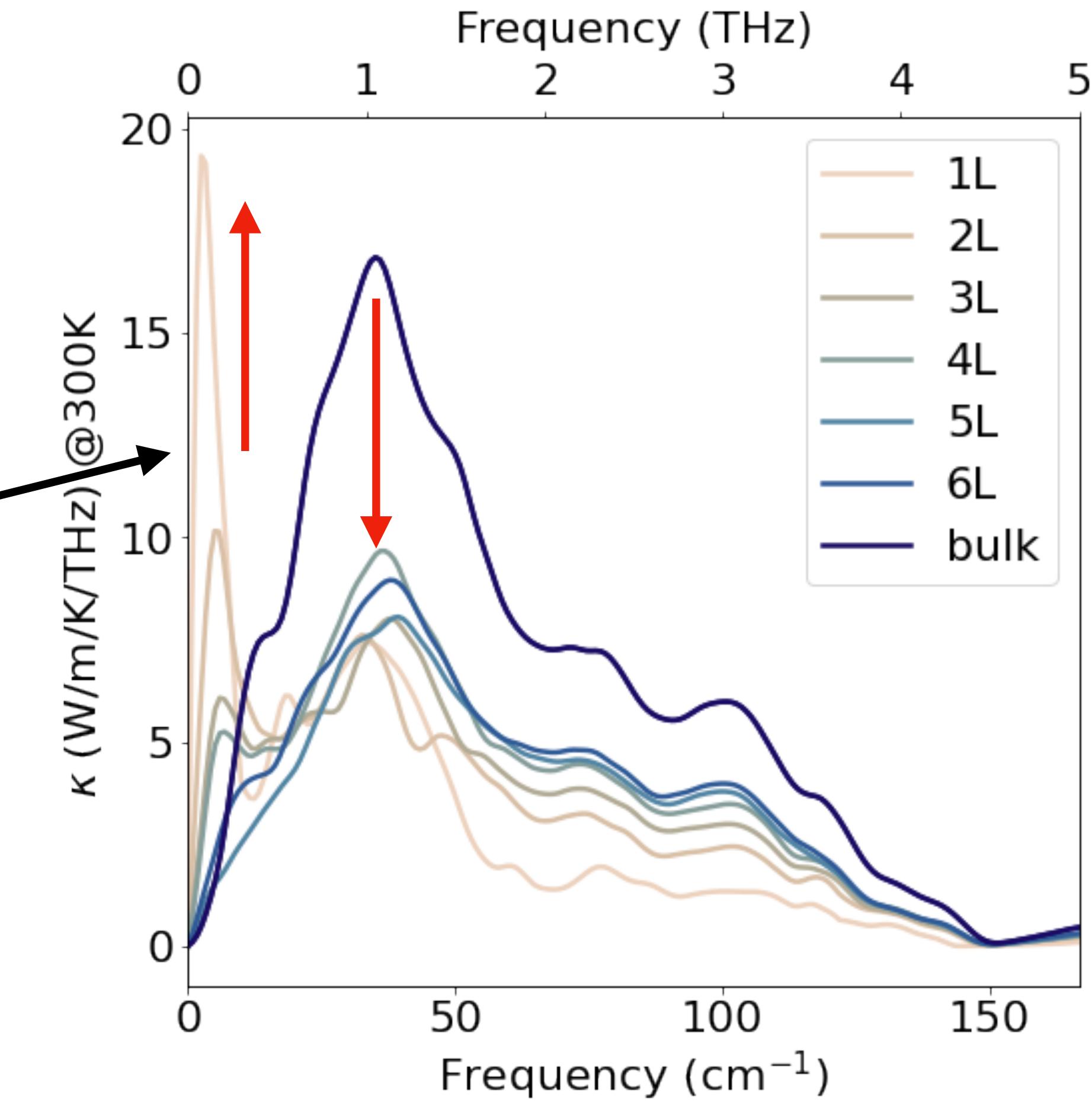
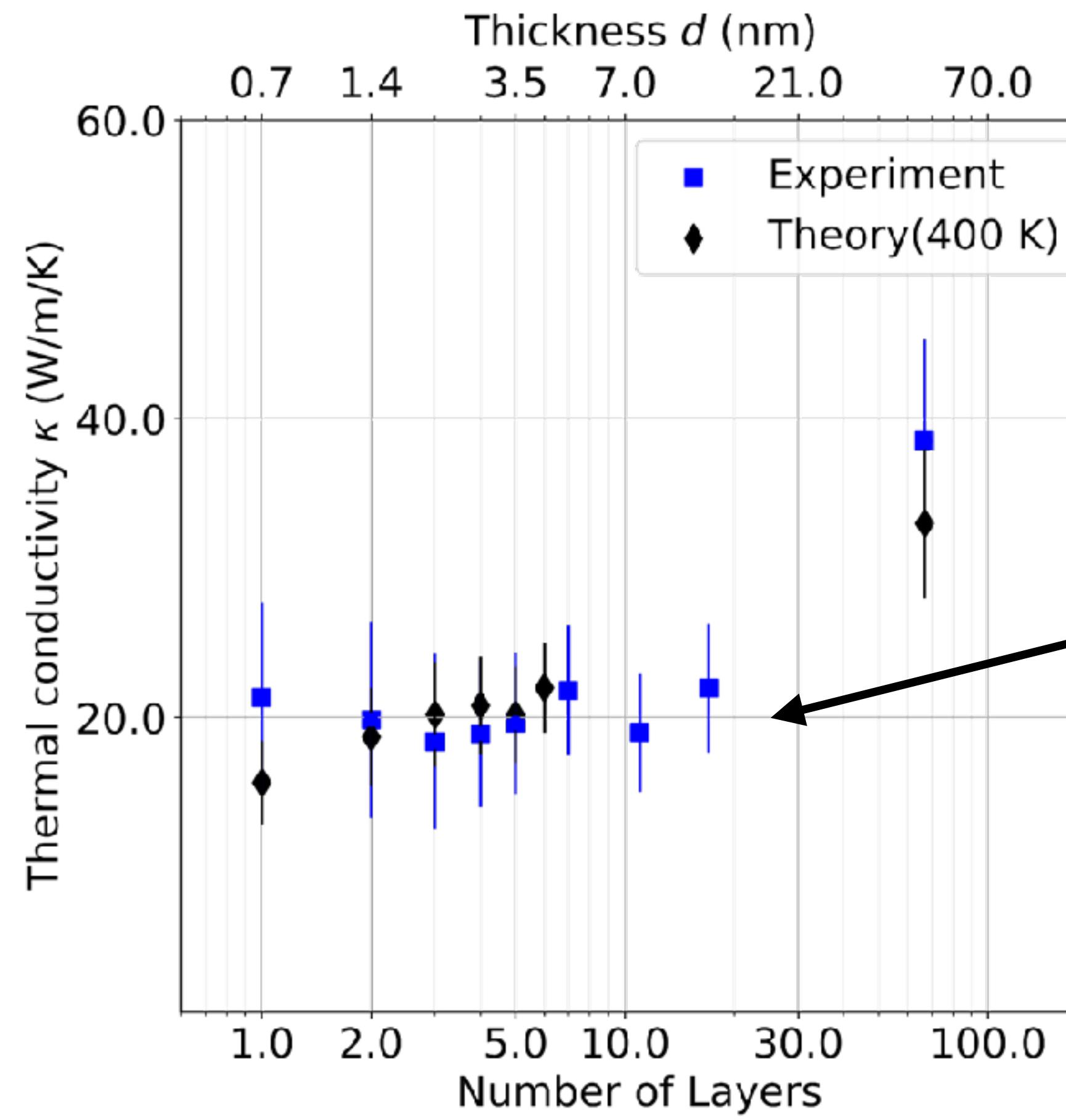
(Received 23 December 2020; accepted 23 March 2021; published 6 April 2021)

Over the past six years, superconductivity at high temperatures has been reported in a variety of hydrogen-rich compounds under high pressure. That high temperature superconductivity should exist in these materials is expected according to the conventional theory of superconductivity, as shown by detailed calculations. However, here we argue that experimental observations rule out conventional superconductivity in these materials. Our results indicate that either these materials are unconventional superconductors of a novel kind, which we term “nonstandard superconductors,” or alternatively, that they are not superconductors. If the first is true, we point out that the critical current in these materials should be several orders of magnitude larger than in standard superconductors, potentially opening up the way to important technological applications. If the second is the case, which we believe is more likely, we suggest that the signals interpreted as superconductivity are either experimental artifacts or they signal other interesting physics but not superconductivity.

DOI: [10.1103/PhysRevB.103.134505](https://doi.org/10.1103/PhysRevB.103.134505)

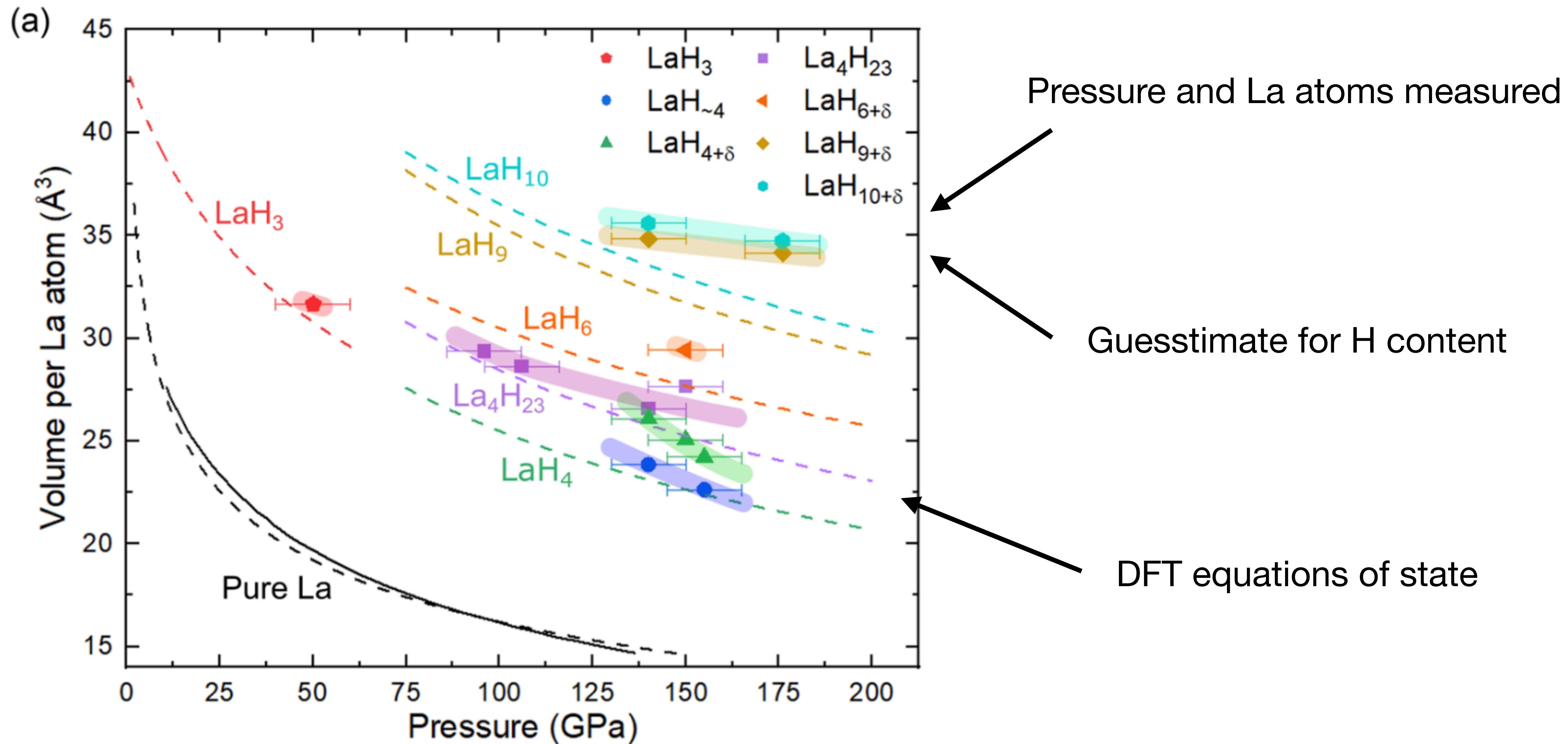
Best model Hamiltonian for Lattice Dynamics

Heat transport including 2D and layered systems like MoSe₂ [1]



Collaboration with Roberta Farris, Matthieu Verstraete, and more: [1] D. S. Reig *et al.*, Adv Mater **34**, 2108352 (2022).

DFT structure search: the ugly truth



[1] D Laniel, F Trybel, B Winkler, FK, et al., *Nat Commun* **13**, 6987 (2022)