

Anharmonic effects in thermoelectric and 2D materials

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Supervised by Aitor Bergara and Ion Errea

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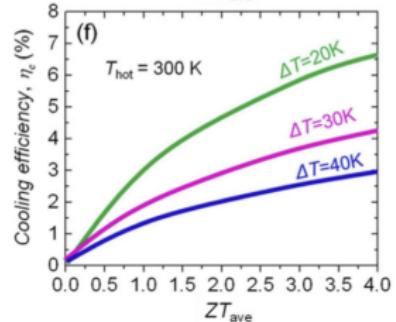
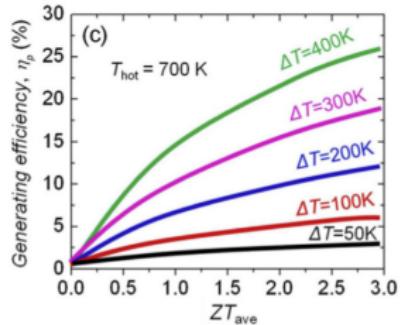
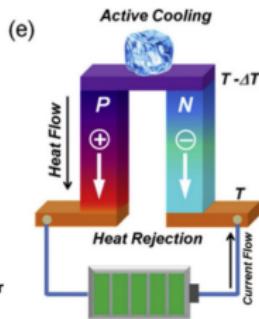
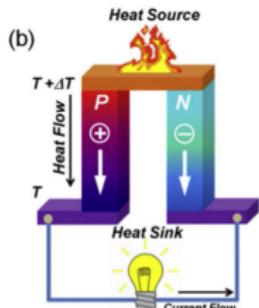


Outline

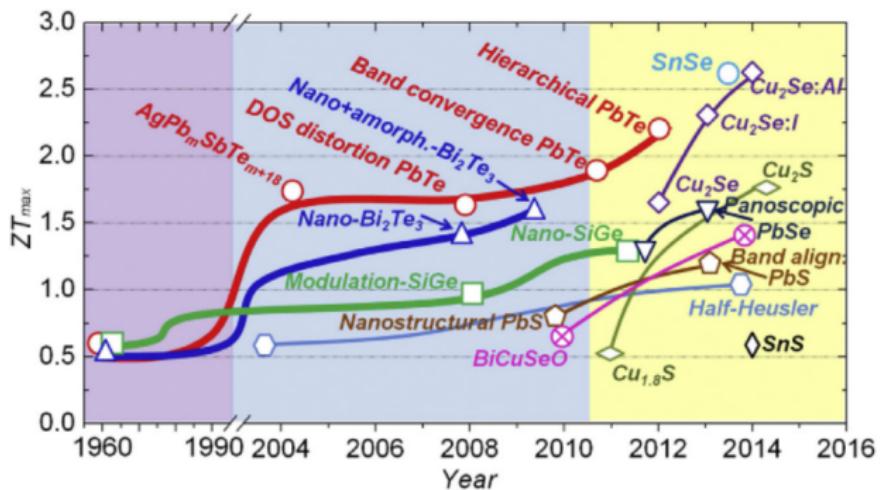
- Introduction
- Theoretical framework
- Part 1: Thermoelectric monochalcogenides
- Part 2: 2D materials
- Conclusions

Introduction

$$ZT = \frac{S^2 \sigma T}{\kappa}, \quad S = -\frac{\Delta V}{\Delta T}$$



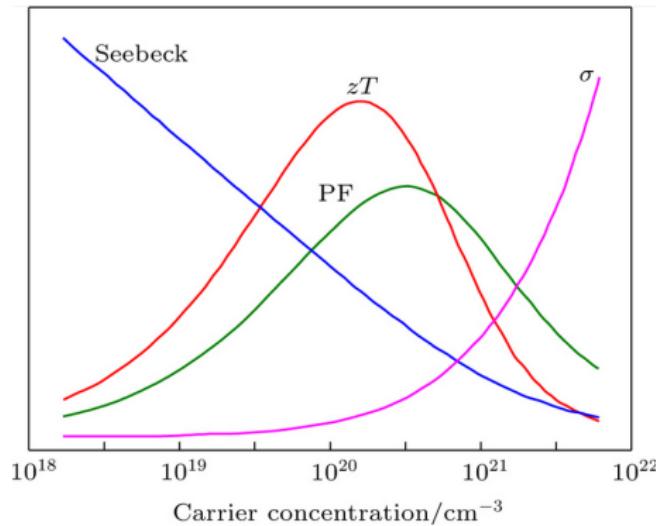
Introduction



- ZT_{max} low and in narrow temperature ranges
- Very limited technological applications.

X. Zhang, L-D. Zhao / Journal of Materomics 1 (2015) 92-105

Introduction



- The physical magnitudes that define ZT are correlated
- How to overcome:
 - Doping + nanostructuring
 - Proximity to phase transitions
 - ...

Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals

Li-Dong Zhao¹, Shih-Han Lo², Yongsheng Zhang², Hui Sun³, Gangjian Tan¹, Ctarad Uher³, C. Wolverton², Vinayak P. Dravid² & Mercouri G. Kanatzidis¹

The thermoelectric effect enables direct and reversible conversion between thermal and electrical energy, and provides a viable route for power generation from waste heat. The efficiency of thermoelectric materials is dictated by the dimensionless figure of merit, ZT (where Z is the figure of merit and T is absolute temperature), which governs the Carnot efficiency for heat conversion. Enhancements above the generally high threshold value of 2.5 have important implications for commercial deployment^{1–3}, especially for compounds free of Pb and Te. Here we report an unprecedented ZT of 2.6 ± 0.3 at 923 K, realized in SnSe single crystals measured along the b axis of the room-temperature orthorhombic unit cell. This material also shows a high ZT of 2.3 ± 0.3 along the c axis but a significantly reduced ZT of 0.8 ± 0.2 along the a axis. We attribute the remarkably high ZT along the b axis to the intrinsically ultralow lattice thermal conductivity in SnSe. The layered structure of SnSe derives from a distorted rock-salt structure, and features anomalously high Grüneisen parameters, which reflect the anharmonic and anisotropic bonding. We attribute the exceptionally low lattice thermal conductivity ($0.23 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ at 973 K) in SnSe to the anharmonicity. These findings highlight alternative strategies to nanostructuring for achieving high thermoelectric performance.

power factor (along the b axis), but, even more surprisingly, we observe that the thermal conductivity of SnSe is intrinsically ultralow ($<0.25 \text{ W m}^{-1} \text{ K}^{-1}$ at $>800 \text{ K}$), resulting in $ZT = 2.62$ at 923 K along the b axis and 2.3 along the c axis; these represent the highest ZT values reported so far for any thermoelectric system. Along the a direction, however, ZT is significantly lower, ~ 0.8 . Here, it should be noted that SnSe along the b axis shows a room-temperature $ZT = 0.12$, which is comparable to the room-temperature value of 0.15 reported earlier¹⁹. SnSe, however, reveals high ZT values near and above the transition temperature of 750 K at which the structure converts from $Pnma$ to $Cmcm$ ^{20–22}. Such ultrahigh ZT along two principal directions and the observed crystallographic and ZT anisotropy prompted us to investigate the scientific underpinning of these intriguing results.

SnSe adopts a layered orthorhombic crystal structure at room temperature, which can be derived from a three-dimensional distortion of the NaCl structure. The perspective views of the room-temperature SnSe crystal structure along the a , b , and c axial directions are shown in Fig. 1a–d. There are two-atom-thick SnSe slabs (along the b – c plane) with strong Sn–Se bonding within the plane of the slabs, which are then linked with weaker Sn–Se bonding along the a direction²⁰. The structure contains highly distorted SnSe_2 coordination polyhedra, which have

- The best thermoelectric material so far: Intrinsic semiconductor with low lattice thermal conductivity ($\kappa = \kappa_{el} + \kappa_l$)

Introduction

1	H																									2	He								
3	Li	4	Be																																
11	Na	12	Mg																																
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	*		72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	+		104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Uub	113	Uut	114	Uuq	115	Uup	116	Uuh	117	Uus	118	Uuo

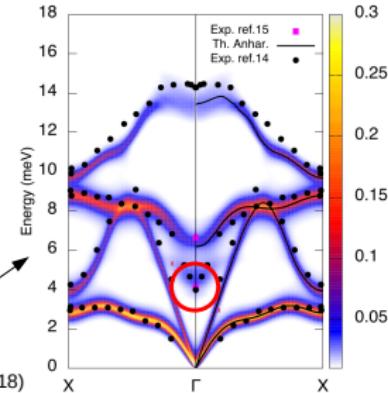
Chalcogenides

Monochalcogenides: PbTe, SnTe, GeTe, SnS...

Low lattice thermal conductivity

They show strongly anharmonic features:

- Lattice instabilities in the harmonic phonons
- Ferroelectric transitions
- Incipient ferroelectricity
- Special features in the phonon spectral function



G. A. Ribeiro et al. Physical Review B 97, 014306 (2018)

Theoretical framework

- Ionic Hamiltonian

$$H = T + V(\mathbf{R})$$

where $\mathbf{R} = \mathbf{R}_0 + \mathbf{u}$.

- Assuming that $V(\mathbf{R})$ is well reproduced by a quadratic potential in the range of \mathbf{u} , Taylor expand the potential

$$V(\mathbf{R}) \simeq V(\mathbf{R}_0) + \frac{1}{2} \sum_{ab} \phi_{ab} u_a u_b + O(u^3)$$

where $\phi_{ab} = \partial^2 V / \partial u_a \partial u_b|_0$.

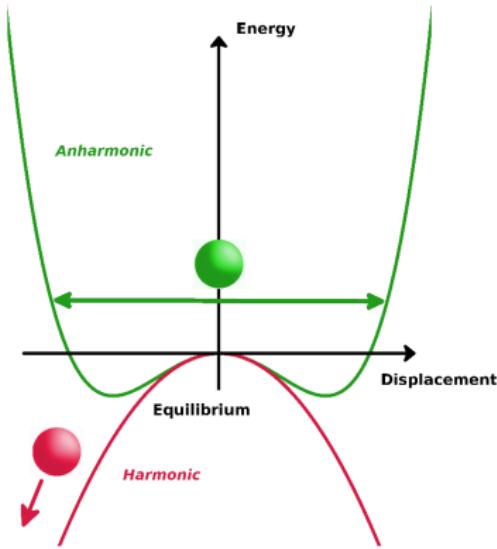
$$V^{harm}(\mathbf{R}) = V(\mathbf{R}_0) + \frac{1}{2} \sum_{ab} \phi_{ab} u_a u_b$$

- This Hamiltonian (Harmonic Hamiltonian) can be solved exactly.
- It provides well defined phonon quasiparticles

$$\sum_b \phi_{ab} \epsilon_\mu^b = M \omega_\mu^2 \epsilon_\mu^a$$

Anharmonic theory: SSCHA

- Harmonic approximation:
 - It does not work in monochalcogenides because they show harmonic instabilities.
- Perturbative approaches are not an option.
 - They are built on top of the harmonic theory.
- We apply a variational non-perturbative approach with anharmonic terms to infinite order: Stochastic self-consistent harmonic approximation (SSCHA)



Theoretical framework

- SCHA is a method for approximating the vibrational free energy of a crystal.

$$F_H = \text{tr}(\rho_H H) + \frac{1}{k_B T} \text{tr}(\rho_H \ln \rho_H)$$

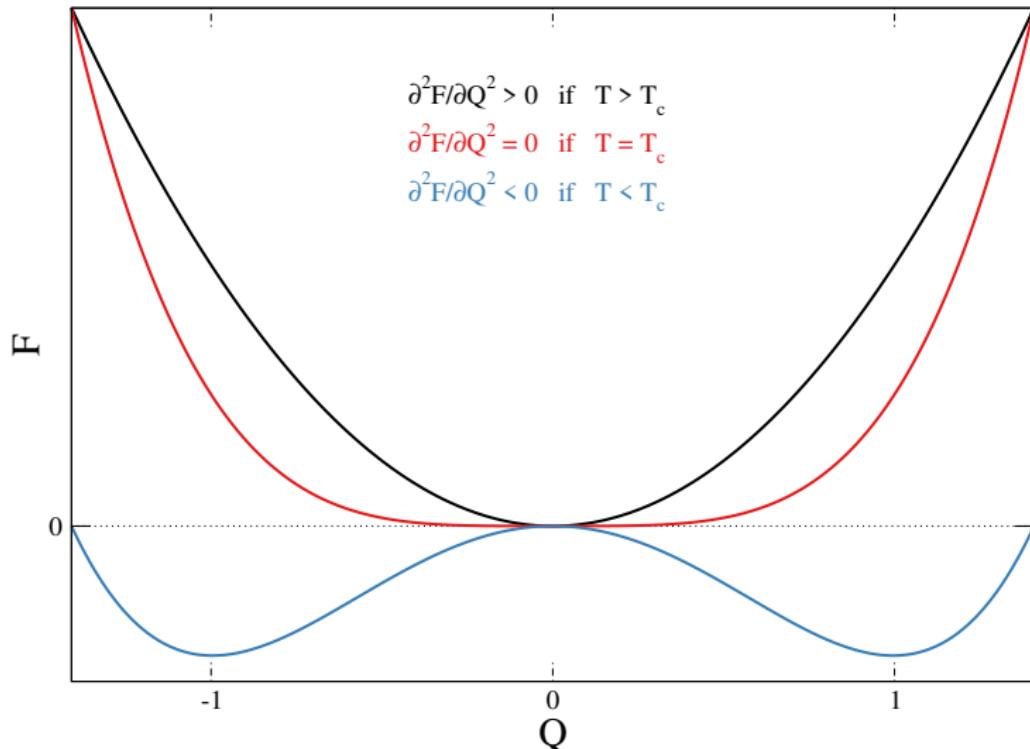
$$\mathcal{F}_H[\mathcal{H}] = \text{tr}(\rho_{\mathcal{H}} H) + \frac{1}{k_B T} \text{tr}(\rho_{\mathcal{H}} \ln \rho_{\mathcal{H}}) = F_{\mathcal{H}} + \langle V - \mathcal{V} \rangle_{\rho_{\mathcal{H}}}$$

$$F_H \leq \mathcal{F}_H[\mathcal{H}]$$

- We take a harmonic trial density matrix $\rho_{\mathcal{H}} \equiv \rho_{\mathcal{H}}(\Phi, \mathcal{R})$. Variables Φ (SCHA/auxiliary phonons) and \mathcal{R} atomic centroids.
- The SCHA provides the harmonic density matrix that minimizes the free energy.

Theoretical framework

- Landau Theory of second-order phase transitions



Theoretical framework

- The free energy is a well defined quantity within the SCHA.
- For a given temperature, experimentally measured phonon frequencies will be centered in the phonon frequencies defined by $\partial^2 \mathcal{F} / \partial \mathbf{R}^2$.

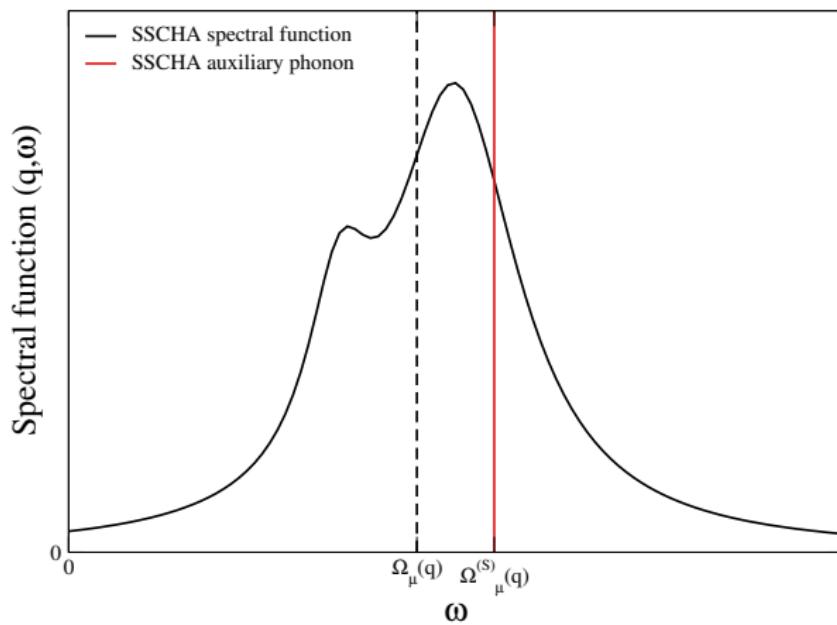
$$\frac{\partial^2 \mathcal{F}}{\partial \mathbf{R} \partial \mathbf{R}} = \Phi + {}^{(3)}\Phi \Lambda [1 - {}^{(4)}\Phi \Lambda]^{-1} {}^{(3)}\Phi$$

- ${}^{(3)}\Phi = \left\langle \frac{\partial^3 V}{\partial \mathbf{R}^3} \right\rangle_{\rho_H}$, ${}^{(4)}\Phi = \left\langle \frac{\partial^4 V}{\partial \mathbf{R}^4} \right\rangle_{\rho_H}$, and $\Lambda \equiv \Lambda(\Phi)$.

Theoretical framework

- The static theory can be expanded by a dynamical ansatz.

$$\sigma(\mathbf{q}, \omega) = \frac{1}{\pi} \times \sum_{\mu} \frac{-\omega Im\Pi_{\mu}(\mathbf{q}, \omega)}{(\omega^2 - \Omega_{\mu}^{(S)2}(\mathbf{q}) - Re\Pi_{\mu}(\mathbf{q}, \omega))^2 + (Im\Pi_{\mu}(\mathbf{q}, \omega))^2}$$

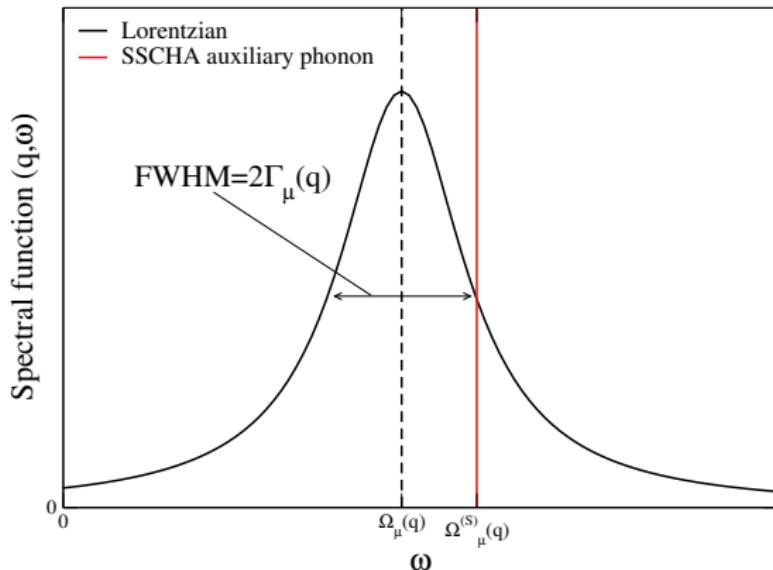


Theoretical framework

$$\mathcal{Z}_\mu(\mathbf{q}, \omega) = \sqrt{\Omega_\mu^{(S)2}(\mathbf{q}) + \Pi_\mu(\mathbf{q}, \omega + i0^+)}$$

$$\Omega_\mu(\mathbf{q}) = \text{Re} \mathcal{Z}_\mu(\mathbf{q}, \Omega_\mu^{(S)}(\mathbf{q})),$$

$$\Gamma_\mu(\mathbf{q}) = -\text{Im} \mathcal{Z}_\mu(\mathbf{q}, \Omega_\mu^{(S)}(\mathbf{q}))$$



Theoretical framework

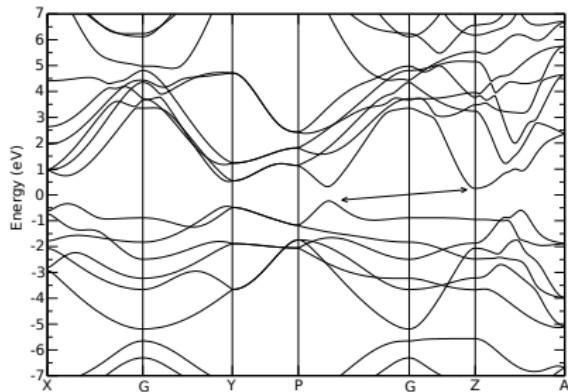
- The Lorentzian definition of phonons provides a straightforward way of calculating the lattice thermal conductivity

$$\kappa_I = \frac{1}{N_{\mathbf{q}} \Omega_{cell} k_B T^2} \sum_{\mathbf{q}\mu} v_\mu(\mathbf{q})^2 \omega_\mu(\mathbf{q})^2 n_B(\omega_\mu(\mathbf{q})) [n_B(\omega_\mu(\mathbf{q})) + 1] \tau_\mu(\mathbf{q}).$$

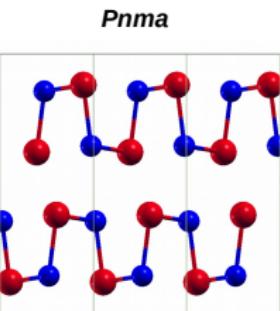
Summary:

- Anharmonic free energy
- Phase transition temperature
- Anharmonic phonons
- Lattice thermal conductivity

SnSe

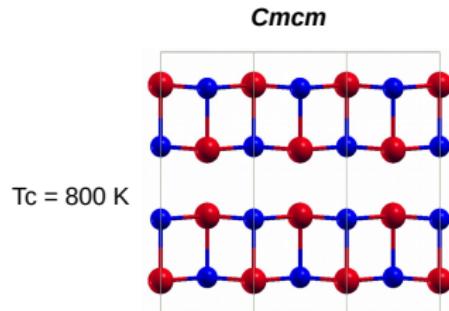


Low T, low symmetry



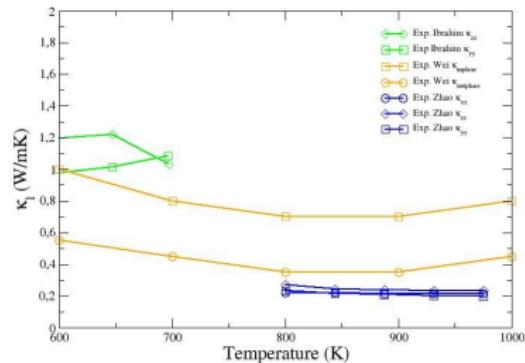
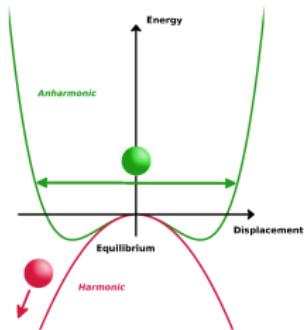
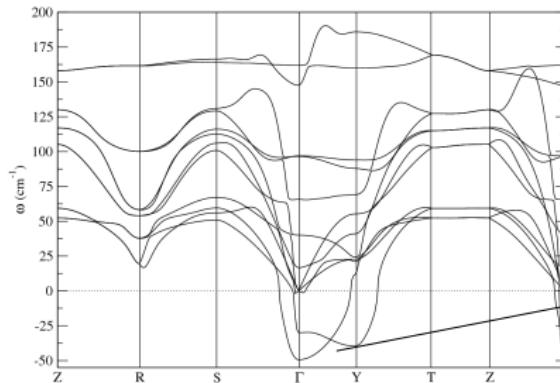
- Anisotropic crystal structure
- Narrow gap semiconductor
- Structural phase transition

High T, high symmetry



$T_c = 800 \text{ K}$

SnSe

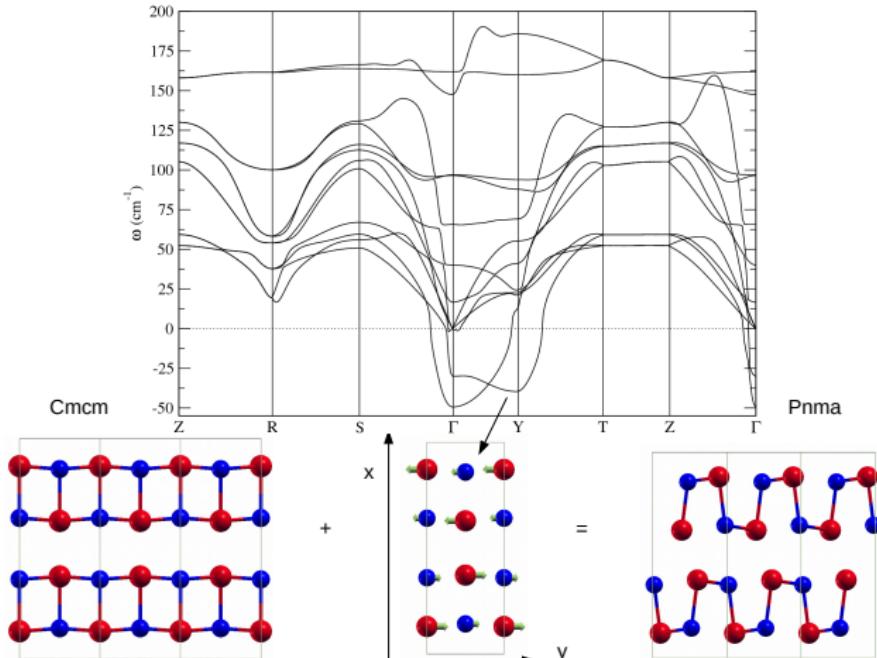


- Lattice instabilities in the harmonic approximation
- Ultralow thermal conductivity
- Experimental discrepancy
 - Value
 - Anisotropy

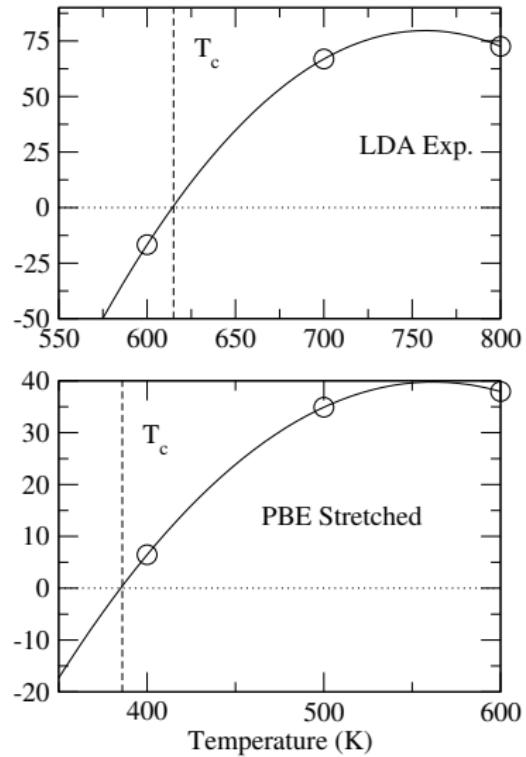
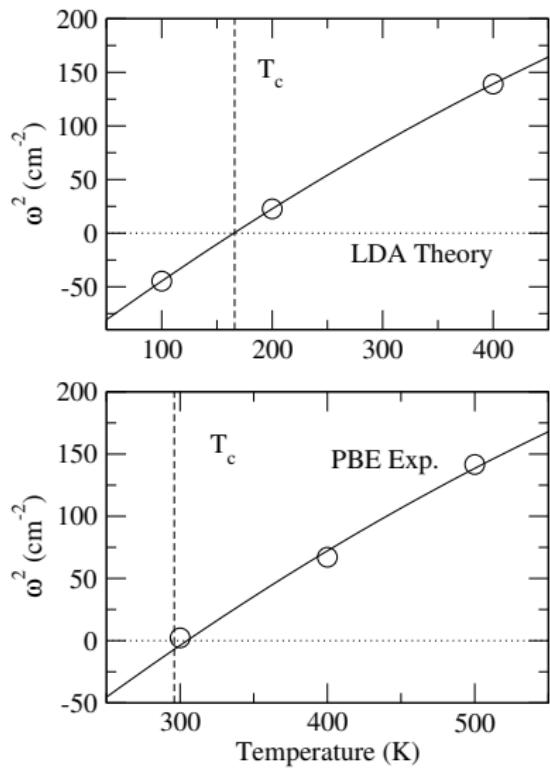
L.-D. Zhao et al. Nature 508, 373 (2014)

SnSe

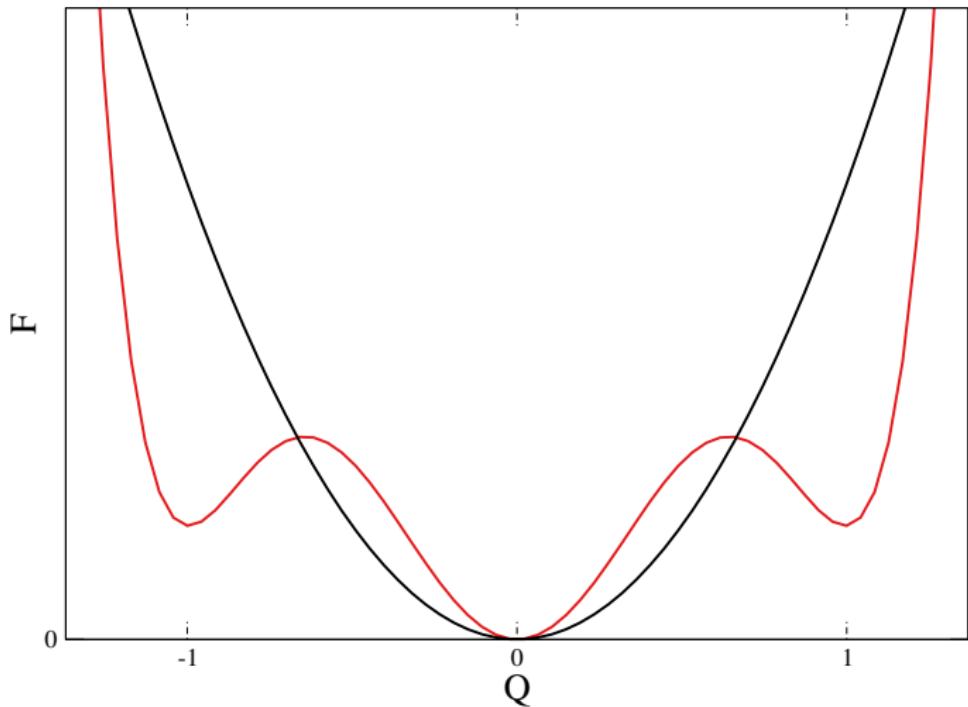
$$\frac{\partial^2 F}{\partial Q^2} \propto \omega_{Y_1}^2(T), \quad \frac{\partial^2 F}{\partial \mathcal{R} \partial \mathcal{R}} = \Phi + \overset{(3)}{\Phi} W \overset{(3)}{\Phi}, \quad \overset{(3)}{\Phi} = \left\langle \frac{\partial^3 V}{\partial \mathcal{R}^3} \right\rangle$$



SnSe

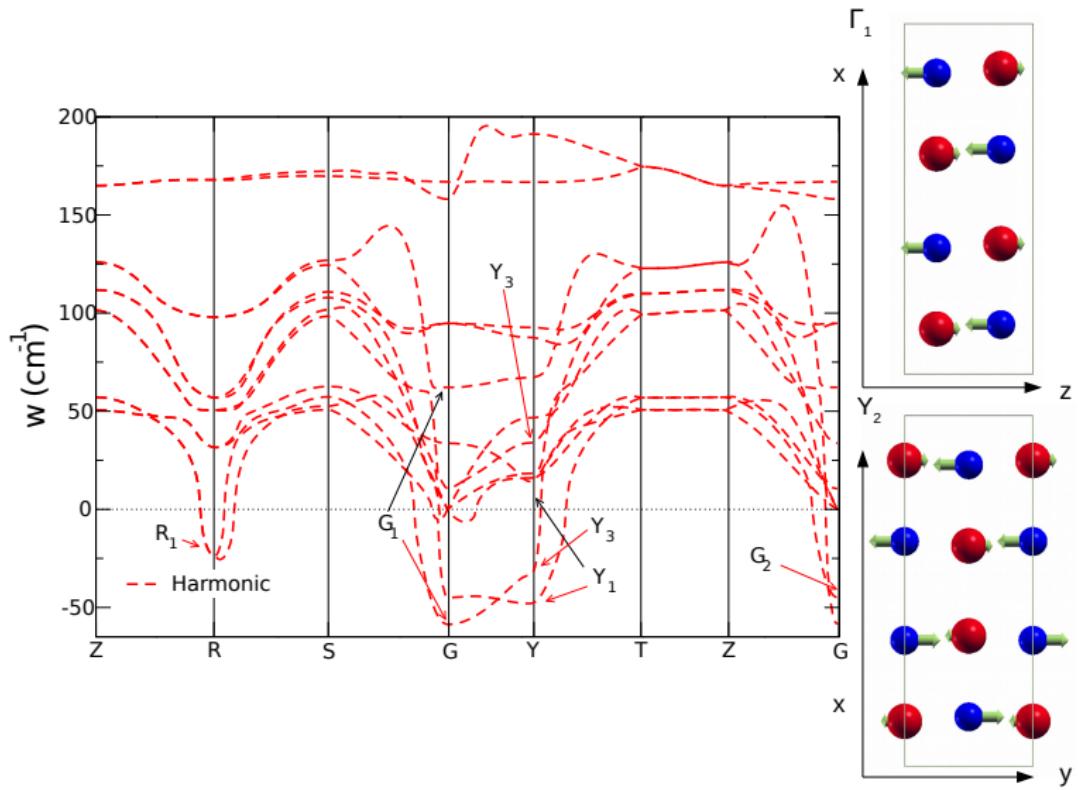


SnSe

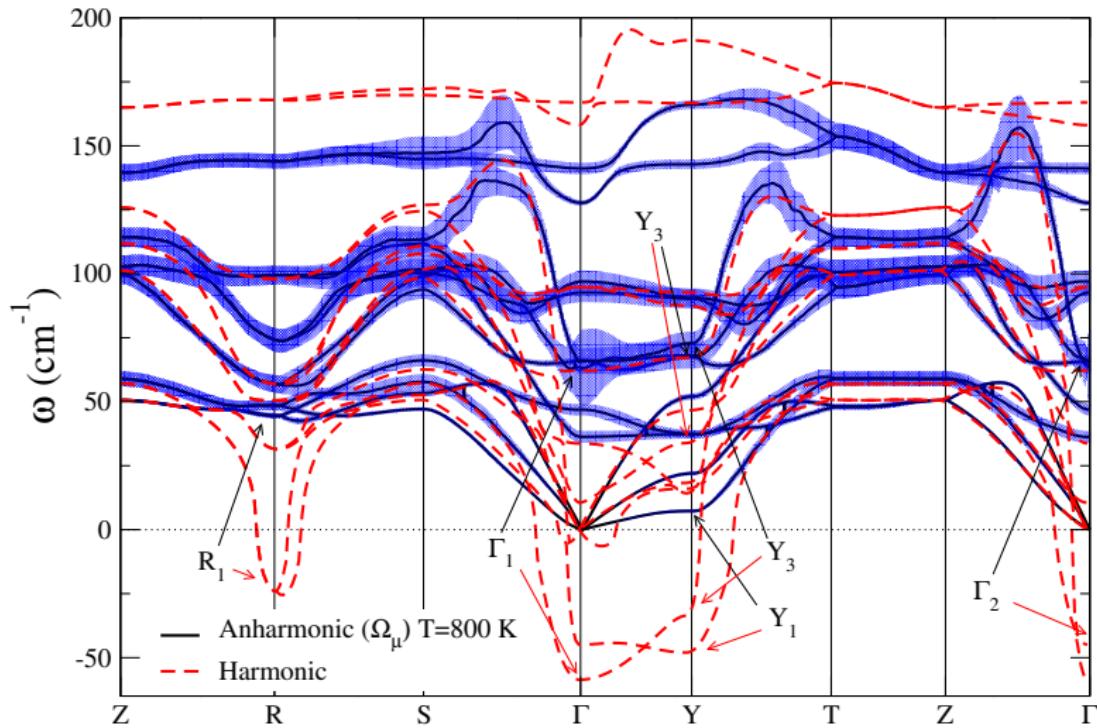


- We discard the first-order phase transition.

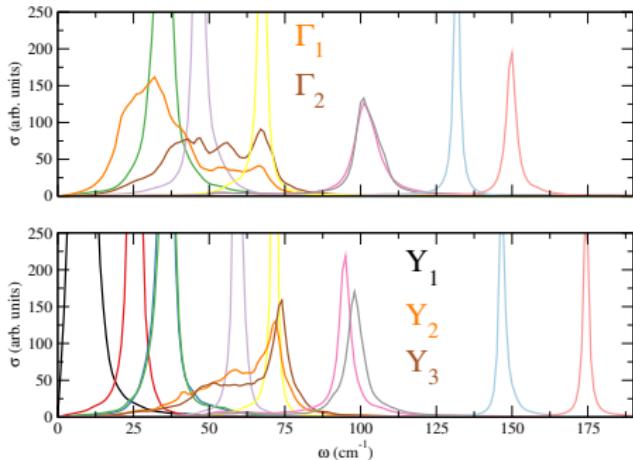
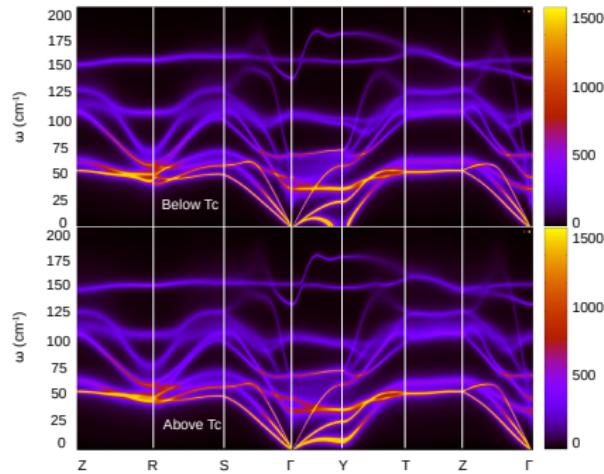
SnSe



SnSe



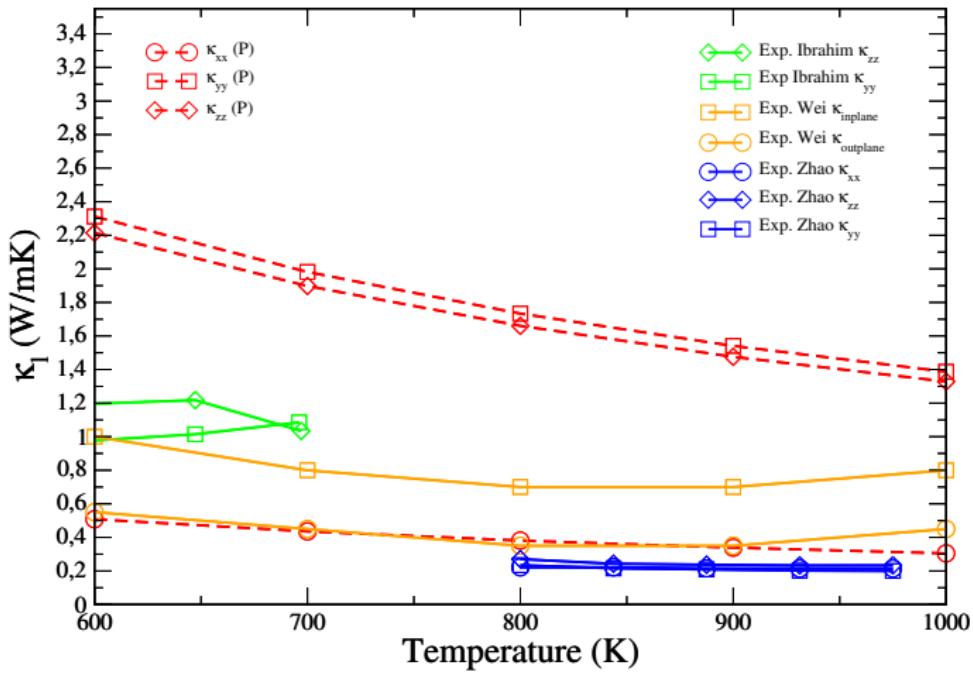
SnSe



- The phase transition is measurable in INS experiments.
- There are modes that strongly deviate from the Lorentzian limit.

U. Aseginolaza et al. PRL 122, 075901 (2019)

SnSe



L.D. Zhao et al. Nature 508, 373 (2014), Ibrahim et al. Appl. Phys. Lett. 110, 032103 (2017),

U. Aseginolaza et al. PRL 122, 075901 (2019)

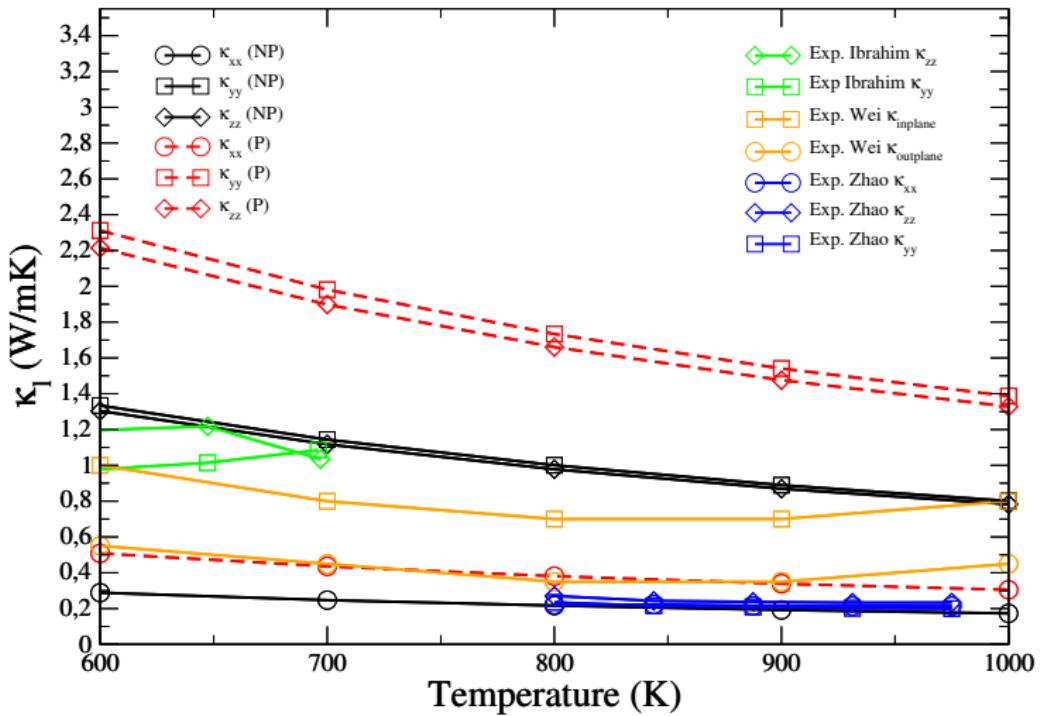
- Perturbative

$$\left[\frac{\partial^3 V}{\partial \mathbf{R}^3} \right]_0$$

- Non-perturbative

$$\left\langle \frac{\partial^3 V}{\partial \mathbf{R}^3} \right\rangle_{\rho_{\mathcal{H}}}$$

SnSe

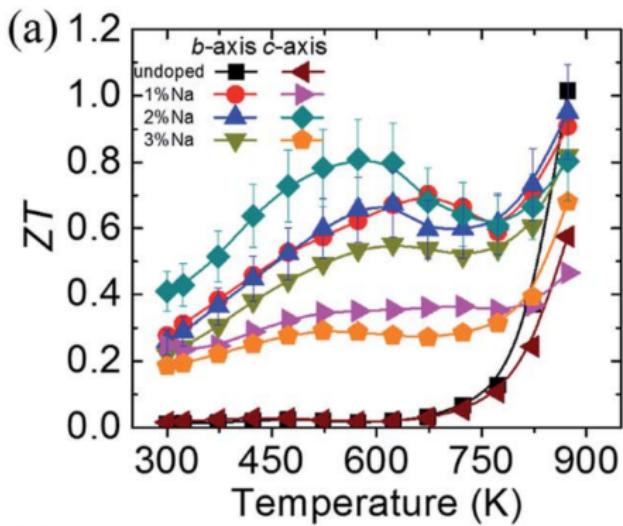
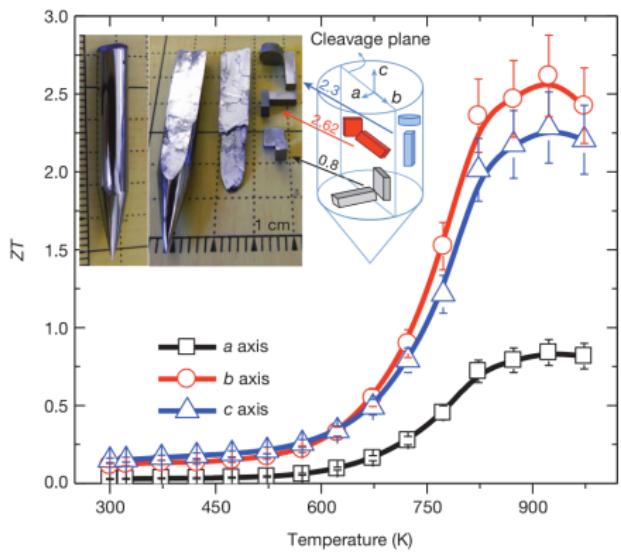


L.D. Zhao et al. Nature 508, 373 (2014), Ibrahim et al. Appl. Phys. Lett. 110, 032103 (2017),

U. Aseginolaza et al. PRL 122, 075901 (2019)

SnSe and SnS

Left: SnSe, Right: SnS



- They look very similar thermoelectric materials.

SnSe and SnS

$$ZT = \frac{P_F T}{\kappa}, \quad P_F = S^2 \sigma$$

$$\sigma(T, \mu) = e^2 \int_{-\infty}^{\infty} d\varepsilon \left[-\frac{\partial f(T, \mu, \varepsilon)}{\partial \epsilon} \right] \Sigma(\varepsilon),$$

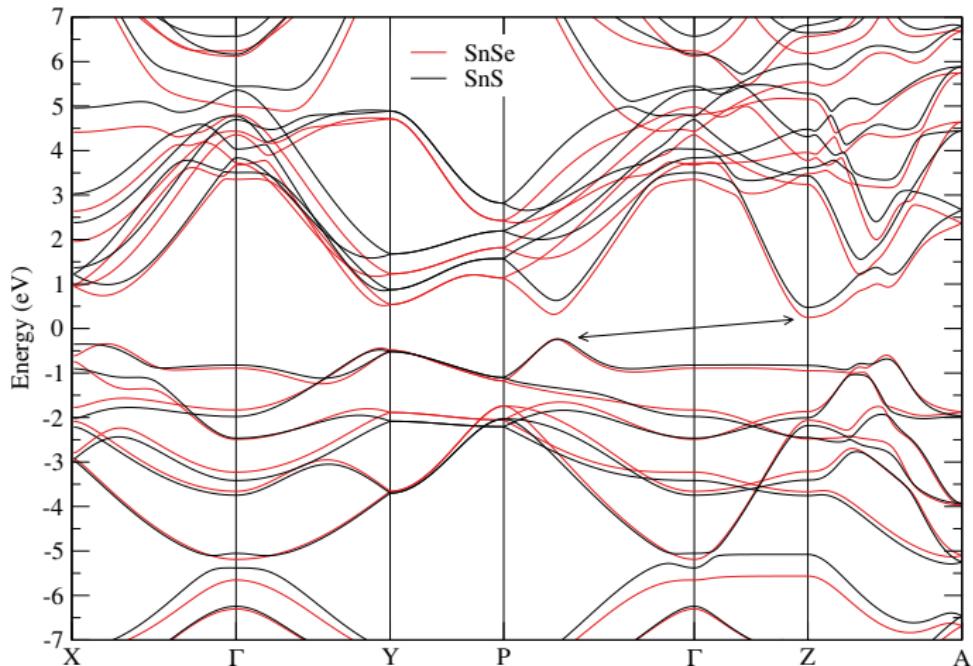
$$S(T, \mu) = \frac{e}{T \sigma(T, \mu)} \int_{-\infty}^{\infty} d\varepsilon \left[-\frac{\partial f(T, \mu, \varepsilon)}{\partial \epsilon} \right] \Sigma(\varepsilon)(\varepsilon - \mu),$$

$$\Sigma(\varepsilon) = \frac{1}{\Omega N_{\mathbf{k}}} \sum_{n\mathbf{k}} \tau_{n\mathbf{k}}^e |\mathbf{v}_{n\mathbf{k}}|^2 \delta(\varepsilon - \varepsilon_{n\mathbf{k}}),$$

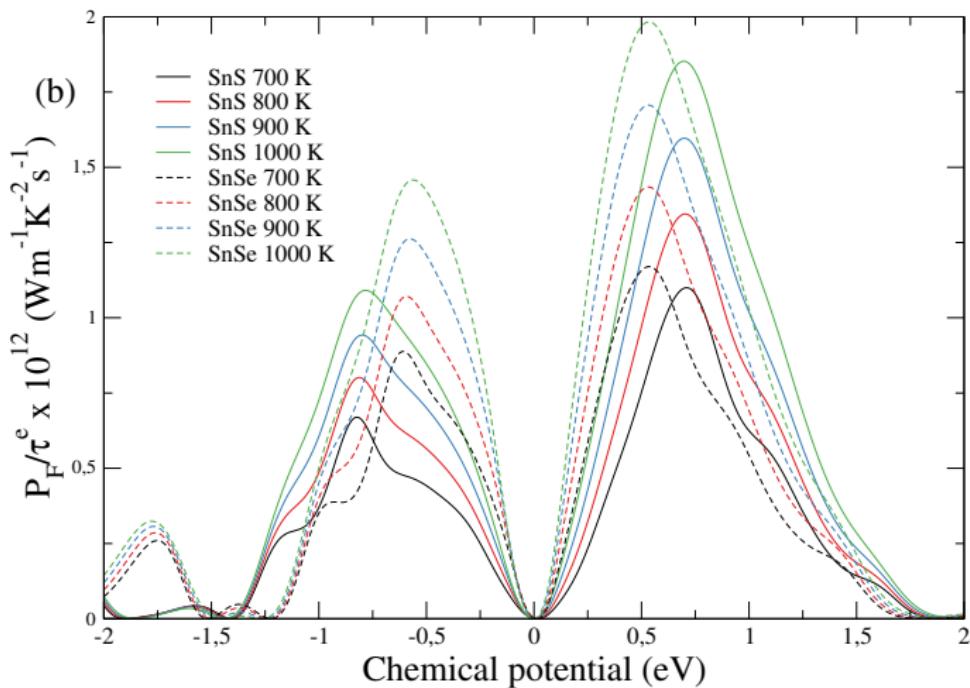
- We use the Boltztrap software package

G. K. Madsen et al. Computer Physics Communications 175, 67 (2006)

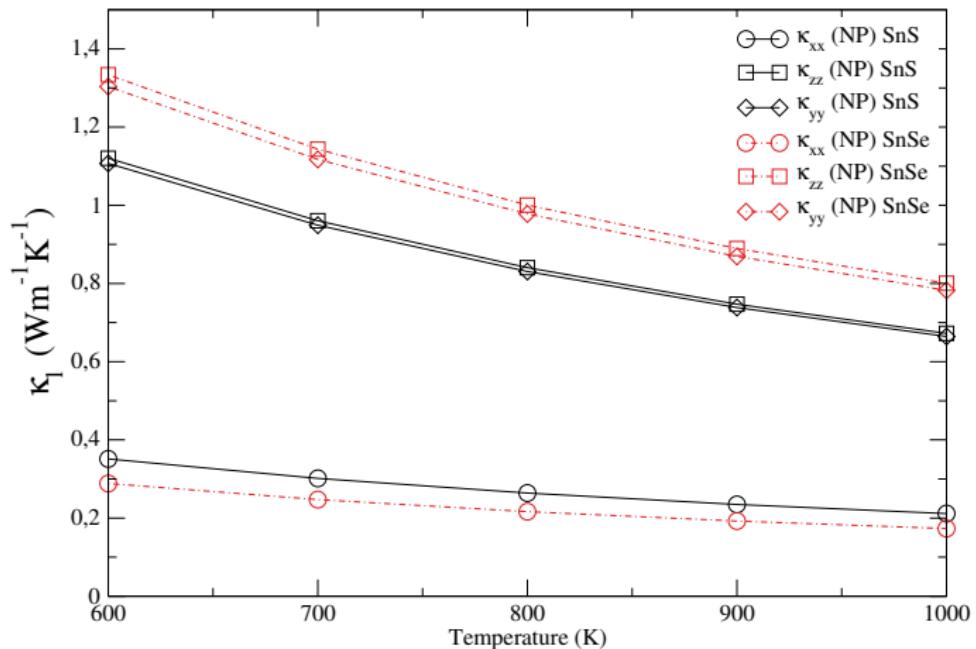
SnSe and SnS



SnSe and SnS



SnSe and SnS



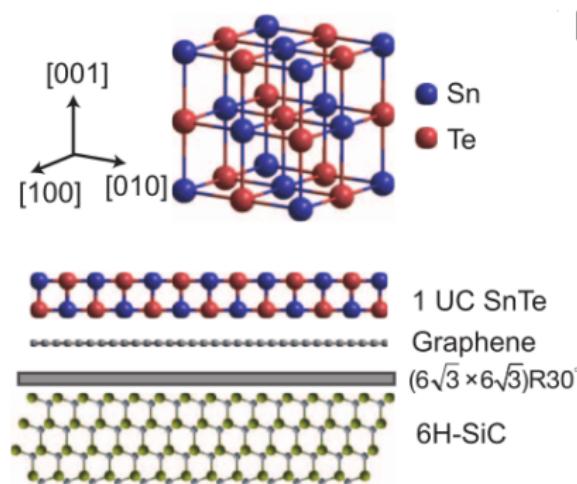
SnSe and SnS: Conclusions

- Second-order phase transitions
- Strongly anharmonic phonon spectra
- Ultralow anisotropic lattice thermal conductivity, important non-perturbative effects
- Both good thermoelectric materials

Monolayer SnSe

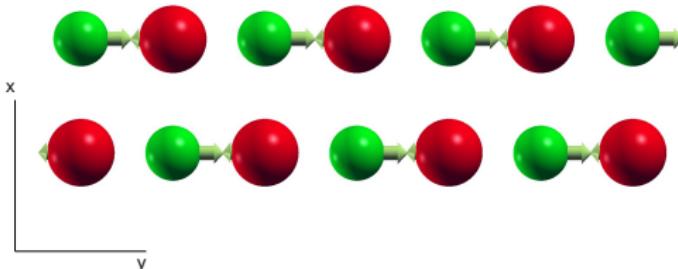
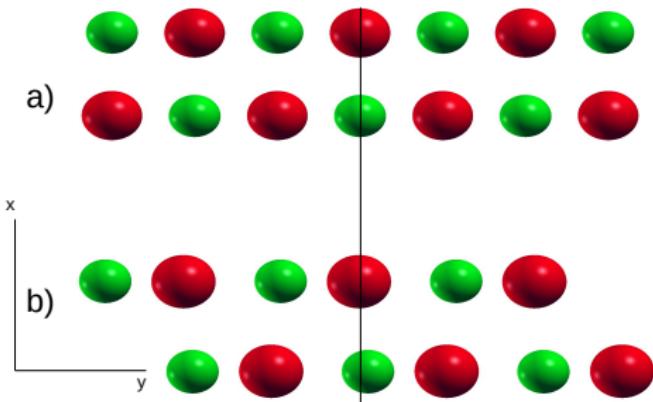
Two reasons to study monolayer SnSe:

- Theoretical calculations claim it could be an efficient thermoelectric material
- It could be an atomically thick ferroelectric material

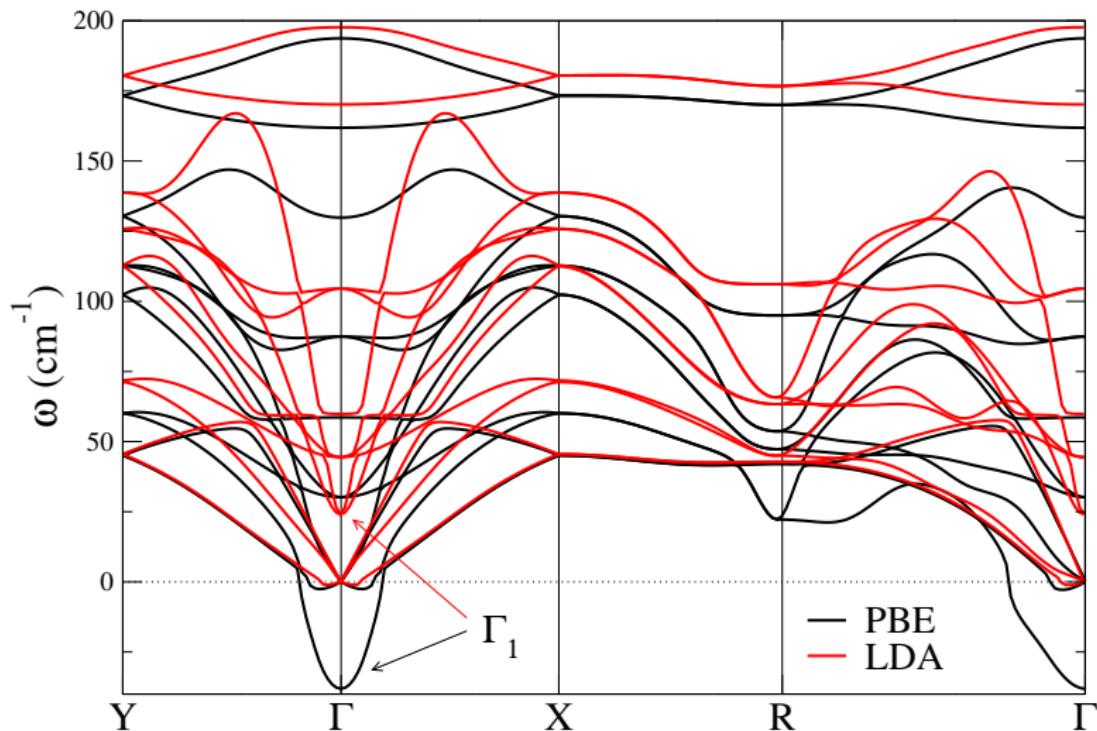


This is the case in SnTe (Kai Chang et al. Science 353, 6296 (2016))

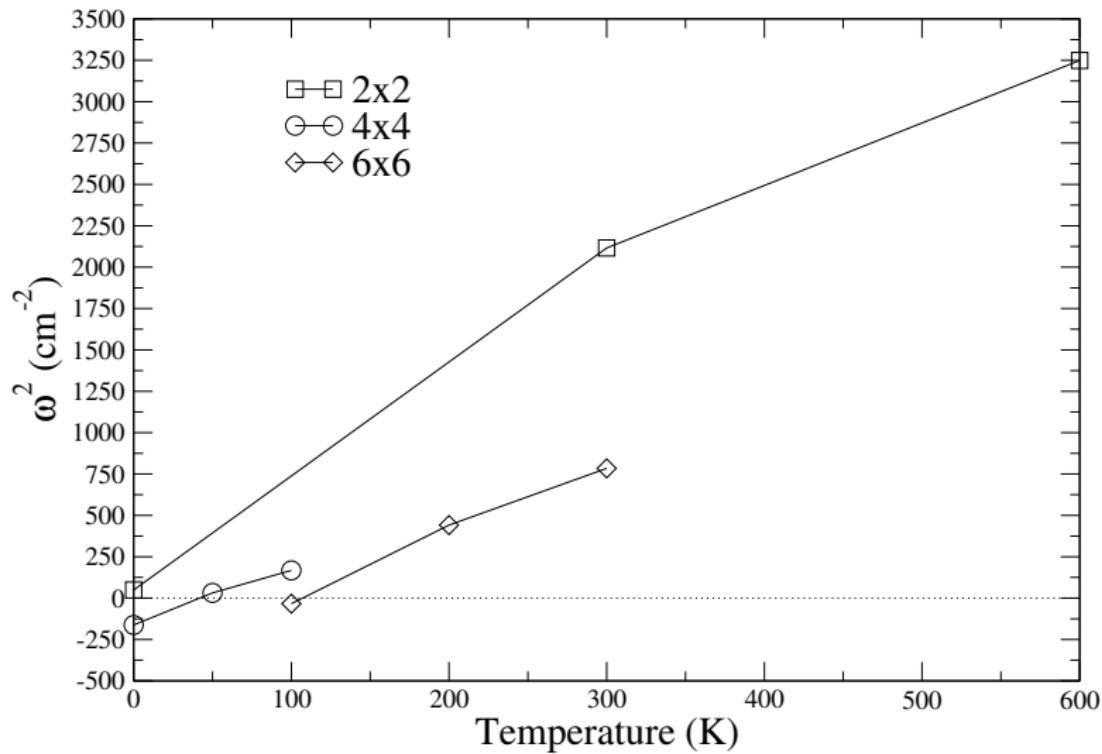
Monolayer SnSe



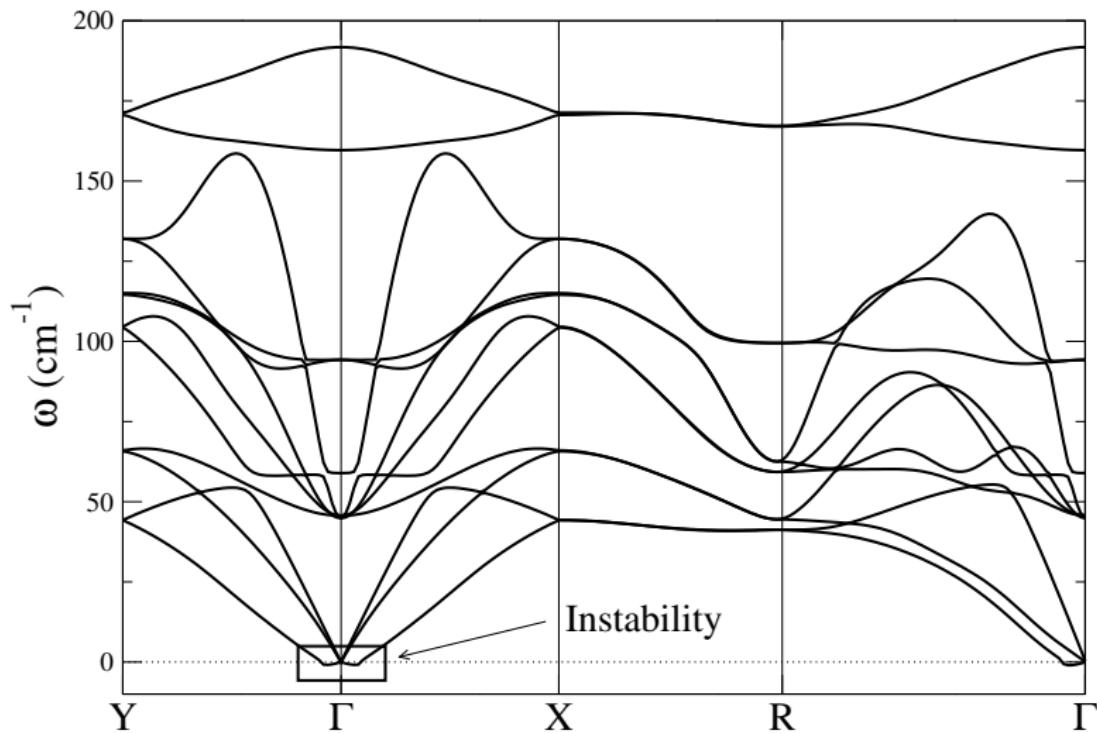
Monolayer SnSe



Monolayer SnSe



Monolayer SnSe



Monolayer SnSe

Conclusions:

- Unstable SSCHA auxiliary phonons related to the 2D symmetry of the system.

Graphene

PHYSICAL REVIEW

VOLUME 176, NUMBER 1

5 DECEMBER 1968

Crystalline Order in Two Dimensions*

N. D. Mermin[†]

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

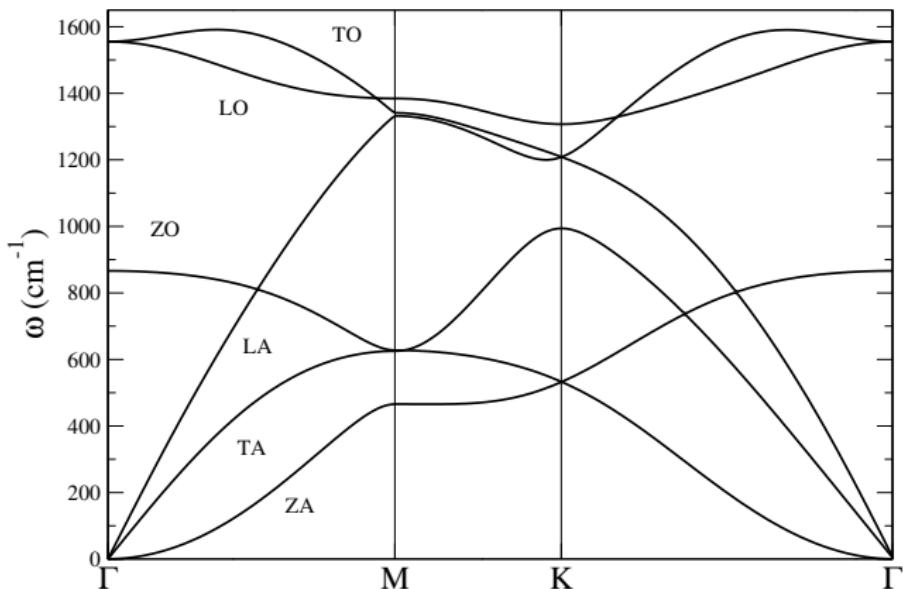
(Received 1 July 1968)

If N classical particles in two dimensions interacting through a pair potential $\Phi(\vec{r})$ are in equilibrium in a parallelogram box, it is proved that every $k \neq 0$ Fourier component of the density must vanish in the thermodynamic limit, provided that $\Phi(\vec{r}) - \lambda r^2 |\nabla^2 \Phi(\vec{r})|$ is integrable at $r = \infty$ and positive and nonintegrable at $r = 0$, both for $\lambda = 0$ and for some positive λ .

This result excludes conventional crystalline long-range order in two dimensions for power-law potentials of the Lennard-Jones type, but is inconclusive for hard-core potentials. The corresponding analysis for the quantum case is outlined. Similar results hold in one dimension.

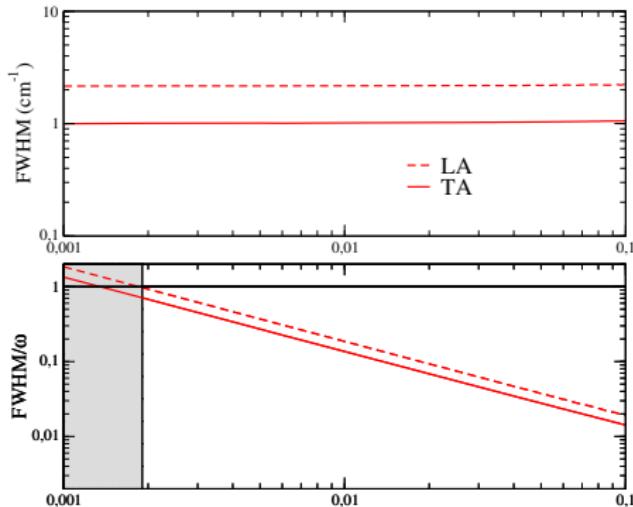
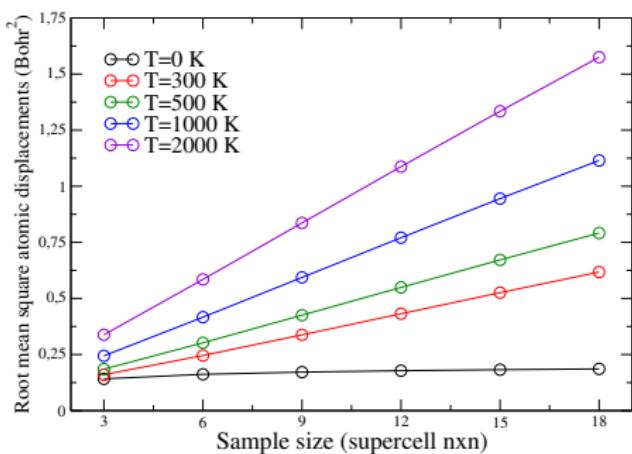
- The existence of 2D materials was not believed to be possible.
- Nowadays there is a whole branch of science exploiting their applications.

Graphene



- $\omega_{ZA}(|\mathbf{q}|) = \alpha|\mathbf{q}| + \beta|\mathbf{q}|^2 + \dots$
- Rotational invariance (RI) together with the 2D character of ϕ_{ab} makes the harmonic dispersion of mode ZA quadratic ($\alpha = 0$).

Graphene



- $\langle u^2 \rangle$ diverges for finite temperatures.
- Finite linewidths of LA/TA modes at decreasing momenta.
- Both properties arise due to the quadratic ZA modes.

Graphene

Hypothesis

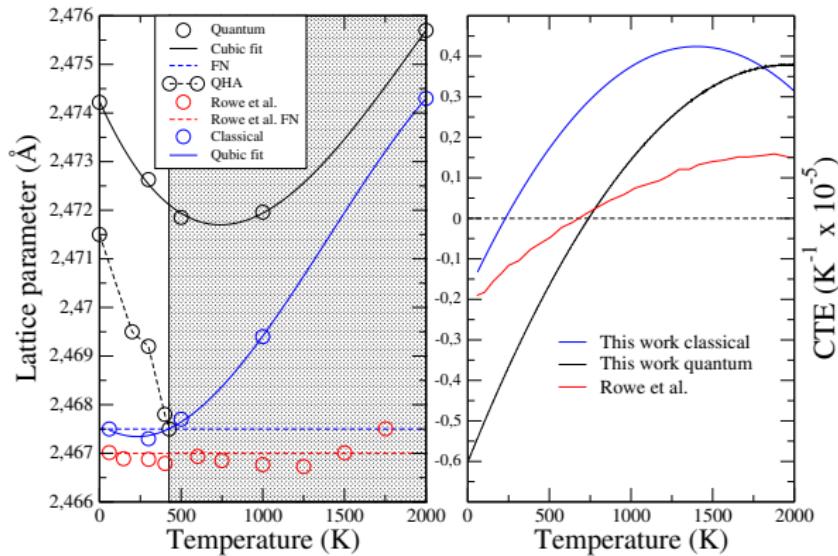
- Quadratic physical phonons are expected and compatible with the absence of divergences.

What have we done?

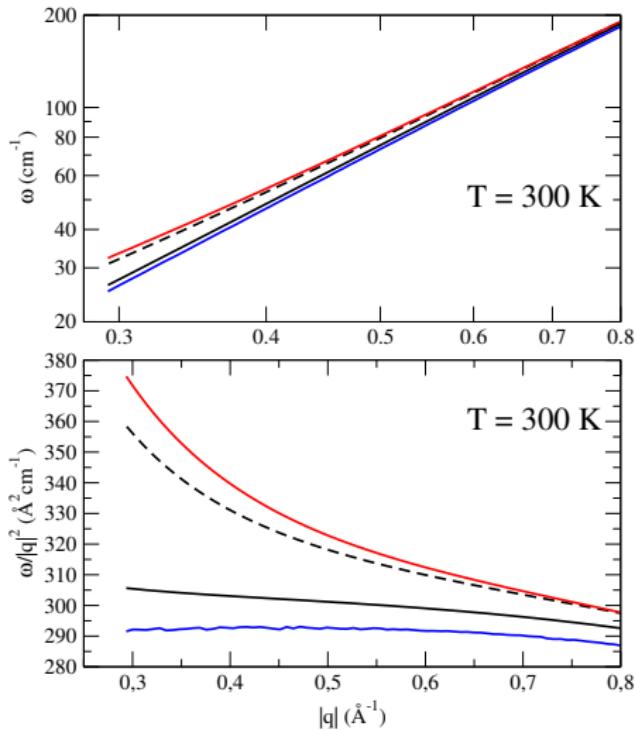
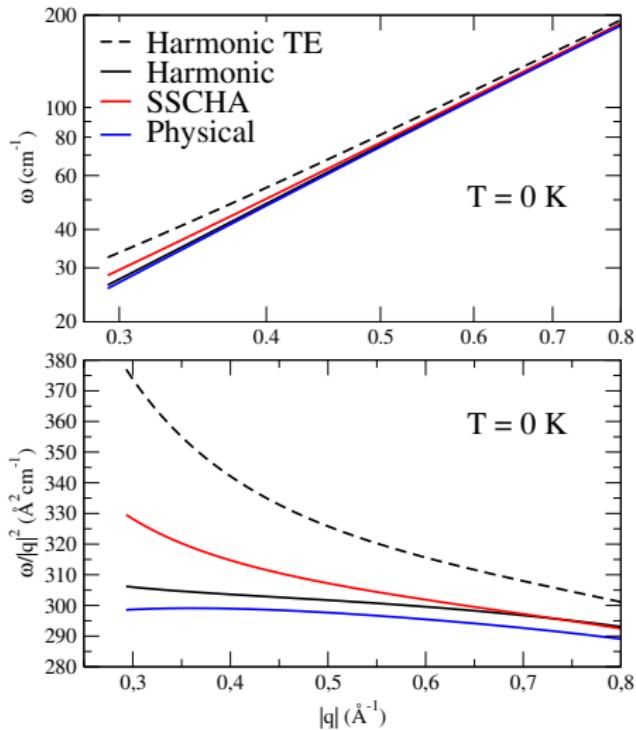
- ① Perform SCHA in an atomistic model using an empirical machine learning potential trained with DFT.
- ② Perform SCHA in a continuum membrane model Hamiltonian.
 - Provides information at much smaller momenta.

Graphene

$$P_{\alpha\beta}^{SSCHA}(\mathcal{R}, \{\mathbf{a}_i\}) = -\frac{1}{\Omega} \left. \frac{\partial \mathcal{F}_H[\mathcal{R}, \{\mathbf{a}_i\}]}{\partial \epsilon_{\alpha\beta}} \right|_{\epsilon=0}$$

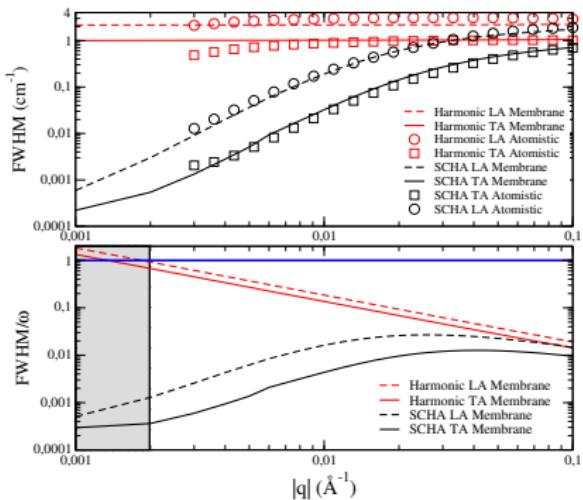
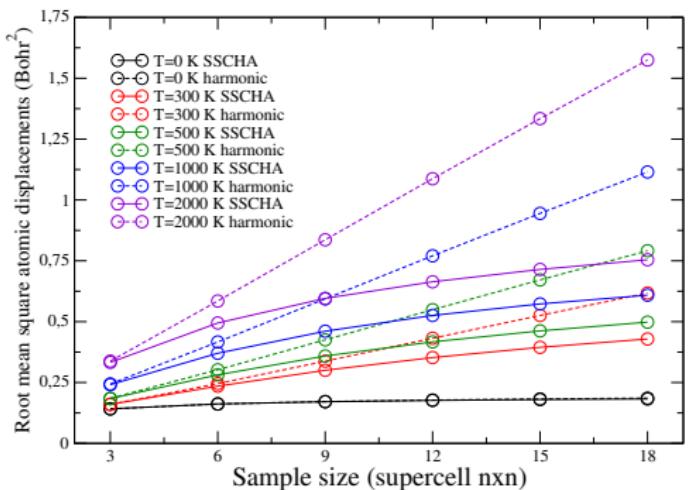


Graphene



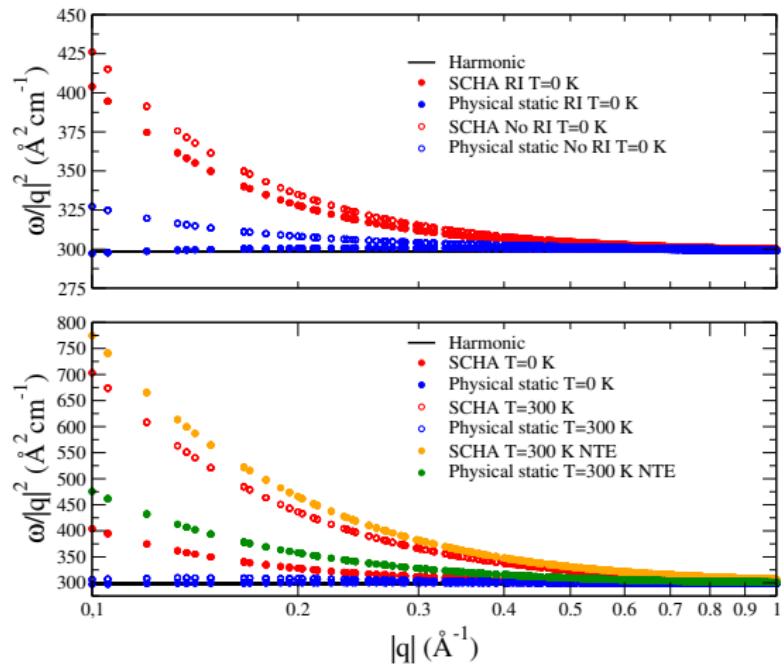
Graphene

- We calculate $\langle u^2 \rangle$ using the density matrix given by the SCHA.
- We calculate the FWHM using the SCHA phonons for the three phonon scattering phase space.



- The SCHA linearisation clearly removes the problems.

Graphene



- SCHA phonons are linear.
- Physical phonons are quadratic.

Graphene: Conclusions

- ① Atomistic and continuum results are in agreement.
- ② Anharmonicity linearises the auxiliary phonons and removes divergences in the displacements.
- ③ Physical phonons have a quadratic dispersion as expected for RI membranes.