

# Anharmonic effects in thermoelectric and 2D materials

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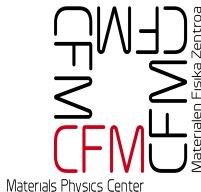
Supervised by Aitor Bergara and Ion Errea

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Materials Physics Center

Centro de Física de Materiales



Donostia International Physics Center

## ① Thermoelectric monochalcogenides (part 1)

- Bulk SnSe and SnS
- Monolayer SnSe

## ② 2D materials (part 2)

- Graphene

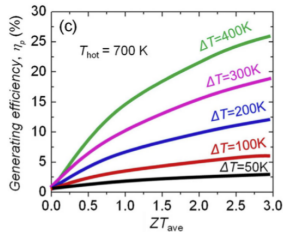
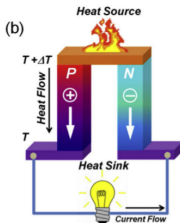
- Introduction
- Theoretical framework
- Part 1: Thermoelectric monochalcogenides
- Part 2: 2D materials
- Conclusions

# Introduction

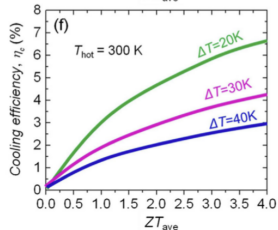
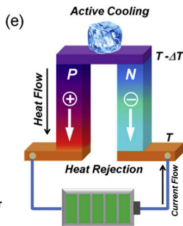
$$ZT = \frac{S^2 \sigma T}{\kappa}, \quad S = -\frac{\Delta V}{\Delta T}$$



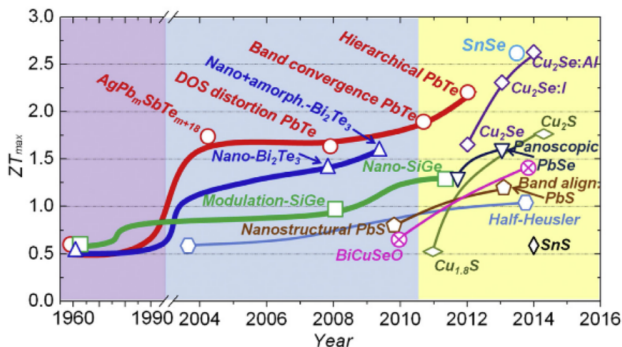
Thomas Johann Seebeck  
German (1770-1831)



Jean Charles Athanase Peltier  
French (1785-1845)



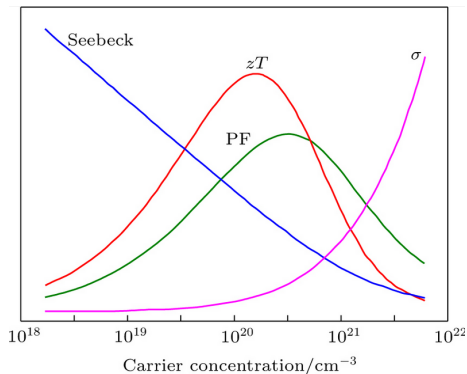
# Introduction



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

X. Zhang, L-D. Zhao / Journal of Materiomics 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 Zhao<sup>1</sup>, Shih-Han Lo<sup>2</sup>, Yongsheng Zhang<sup>2</sup>, Hui Sun<sup>3</sup>, Gangjian Tan<sup>1</sup>, Citrad Uher<sup>3</sup>, C. Wolverton<sup>2</sup>, Vinayak P. Dravid<sup>2</sup> & Mercouri G. Kanatzidis<sup>1</sup>

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<sup>1,2</sup>, especially for compounds free of Pb and Te. Here we report an unprecedented  $ZT$  of  $2.6 \pm 0.3$  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  $2.3 \pm 0.3$  along the  $c$  axis but a significantly reduced  $ZT$  of  $0.8 \pm 0.2$  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,  $\sim 0.8$ . 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 earlier<sup>19</sup>. SnSe, however, reveals high  $ZT$  values near and above the transition temperature of 750 K at which the structure converts from  $Pnma$  to  $Cmcm$ <sup>20–22</sup>. 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  $a$  direction<sup>20</sup>. The structure contains highly distorted SnSe<sub>4</sub> coordination polyhedra, which have

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

# Introduction

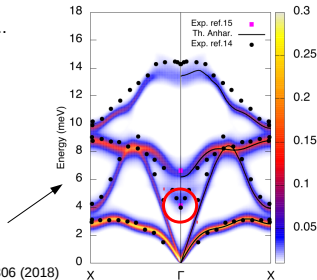
1																	2
H																	He
Chalcogenides																	
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	+	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

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

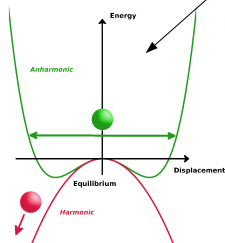
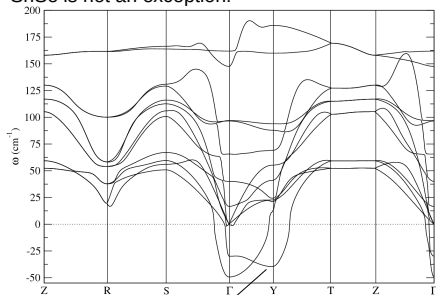


G. A. Ribeiro et al. Physical Review B 97, 014306 (2018)



# Introduction

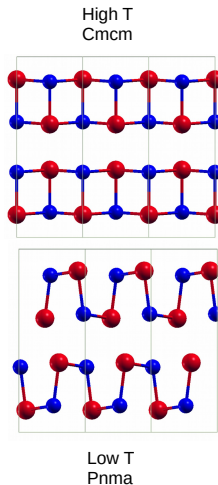
SnSe is not an exception:



LATTICE INSTABILITIES

PHASE TRANSITION

$T_c = 800 \text{ K}$



Very low lattice thermal conductivity 0.3-1.0 W/mK (800 K)

# 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

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

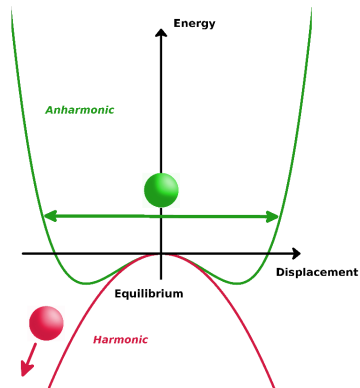
# Anharmonic theory: SSCHA

- **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.

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

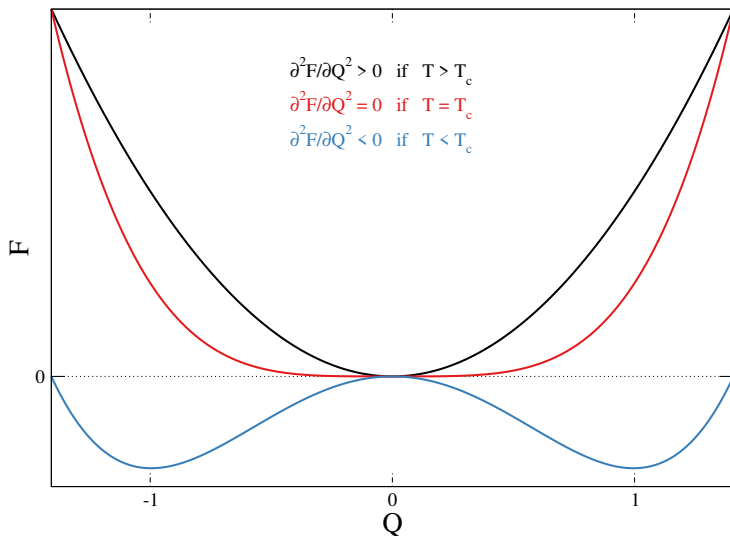
$$\mathcal{F}_H[\mathcal{H}] = \text{tr}(\rho_{\mathcal{H}} H) + \frac{1}{k_B T} \text{tr}(\rho_{\mathcal{H}} \ln \rho_{\mathcal{H}}) = F_{\mathcal{H}} + \langle V - \mathcal{V} \rangle_{\rho_{\mathcal{H}}}$$

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

- We take a harmonic trial density matrix  $\rho_{\mathcal{H}} \equiv \rho_{\mathcal{H}}(\Phi, \mathcal{R})$ . Variables  $\Phi$  (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  $\partial^2 \mathcal{F} / \partial \mathbf{R}^2$ .

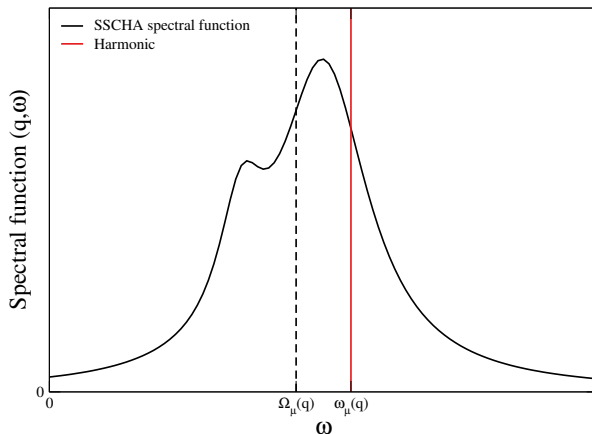
$$\frac{\partial^2 \mathcal{F}}{\partial \mathbf{R} \partial \mathbf{R}} = \mathbf{\Phi} + \mathbf{\Phi}^{(3)} \Lambda [\mathbf{1} - \mathbf{\Phi}^{(4)} \Lambda]^{-1} \mathbf{\Phi}^{(3)}$$

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

# Theoretical framework

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

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

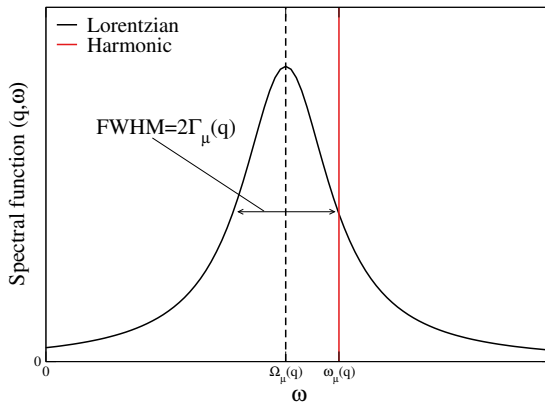


# Theoretical framework

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

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

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





# Theoretical framework

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

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

Summary:

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