Anomalous suppressed thermal conductivity in $CuInTe_2$ under pressure

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Paper Presentation

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Contents

Introduction and Motivation

- We are all familiar with thermoelectricity and its benefits

Figure of merit: $$zT = \frac{S^2\sigma}{\kappa} T$$

- For good zT, need high S, σ, and low κ $(= \kappa_{el} + \kappa_{ph})$
- Unfortunately, if $\boldsymbol{\sigma}$ ↑, **then** $\boldsymbol{\kappa_{el}}$ ↑ (Wiedemann-Franz law)

- Ways to improve zT:
  1) lower κ_{ph}- nano structuring, defect engineering, alloying, etc.
  2) Increase pressure to increase σ

- **Pressure** ↑ ⇒ $\boldsymbol{\sigma}$ ↑ due to changes in electronic band structures, but also $\boldsymbol{\kappa_{ph}}$ ↑ (Liebfried-Schlomann theory)
- But for $CuInTe_2$, a different trend was observed experimentally for κ_{ph} which made it perfect for TE applications with a zT of 1.1 @ 300K under normal conditions which increased almost 5 times upon application of pressure

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Computational Details

- LDA exchange correlation functional
- Kinetic energy cutoff: 600 eV
- Self Convergence criterion: 10-6 eV
- Relaxation criterion: 1 meV/A
- 8 x 8 x 2 MP k-grid

PhonoPy

2 x 2 x 1 supercell for computing force constants

shengBTE

13 x 13 x 13 q-grid for obtaining scattering rates via Boltzmann Transport Equation

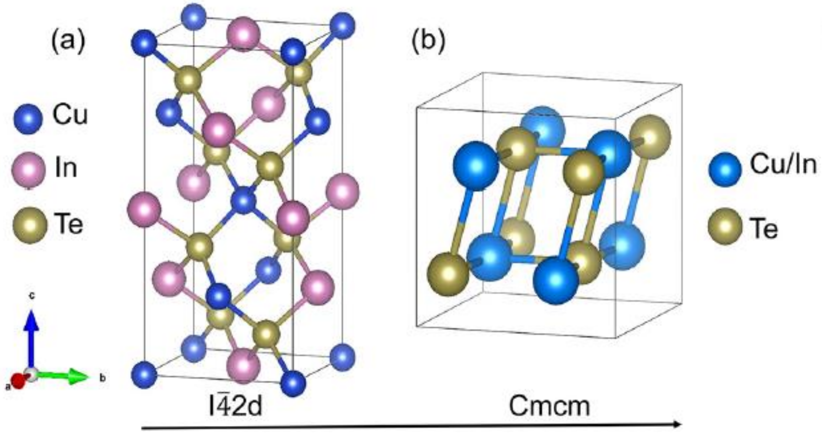
Structure of $CuInTe_2$

Belongs to a diamond-like crystal system at atmospheric pressure

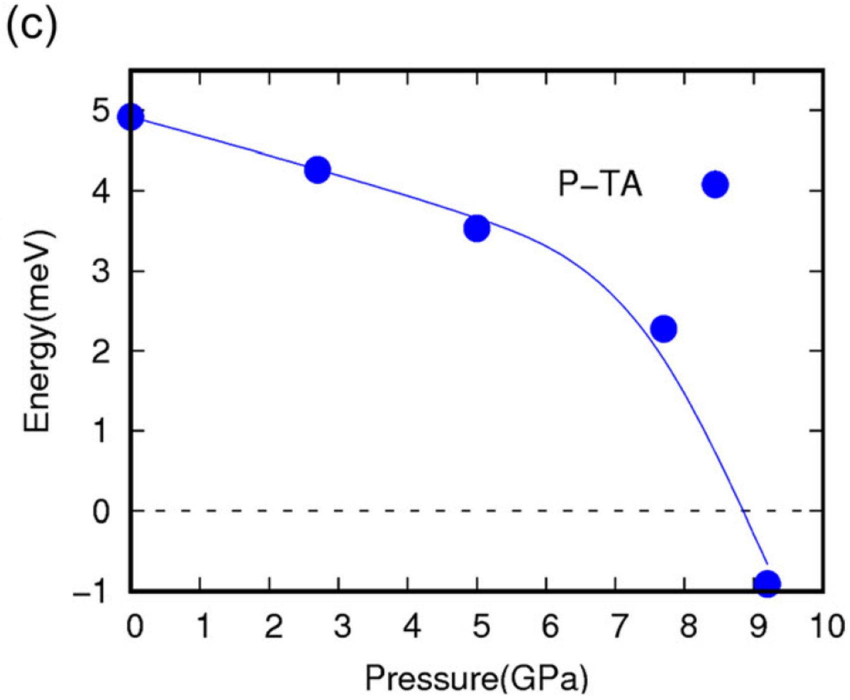
Table S1 Lattice constant and the bond length (d) of the conventional cell in comparison with the experimental results[34].

	a=b(Å)	c(Å)	d(Cu-Te) (Å)	d(In-Te) (Å)
experiment	6.19	12.41	2.59	2.78
0 GPa	6.13	12.28	2.52	2.79
7.7 GPa	5.92	11.83	2.43	2.70

Experiments show $CuInTe_2$ undergoes phase transition at a pressure of 6.9 GPa



Phonon dispersion calculations reveal that the transverse acoustic (TA) mode at the high-symmetry P point starts to soften with increasing pressure and becomes –ve at around 8.7 GPa



To analyse the pressure effect before phase transition, the authors calculate phonon dispersions and thermal-k at **0 GPa** and **7.7 GPa**

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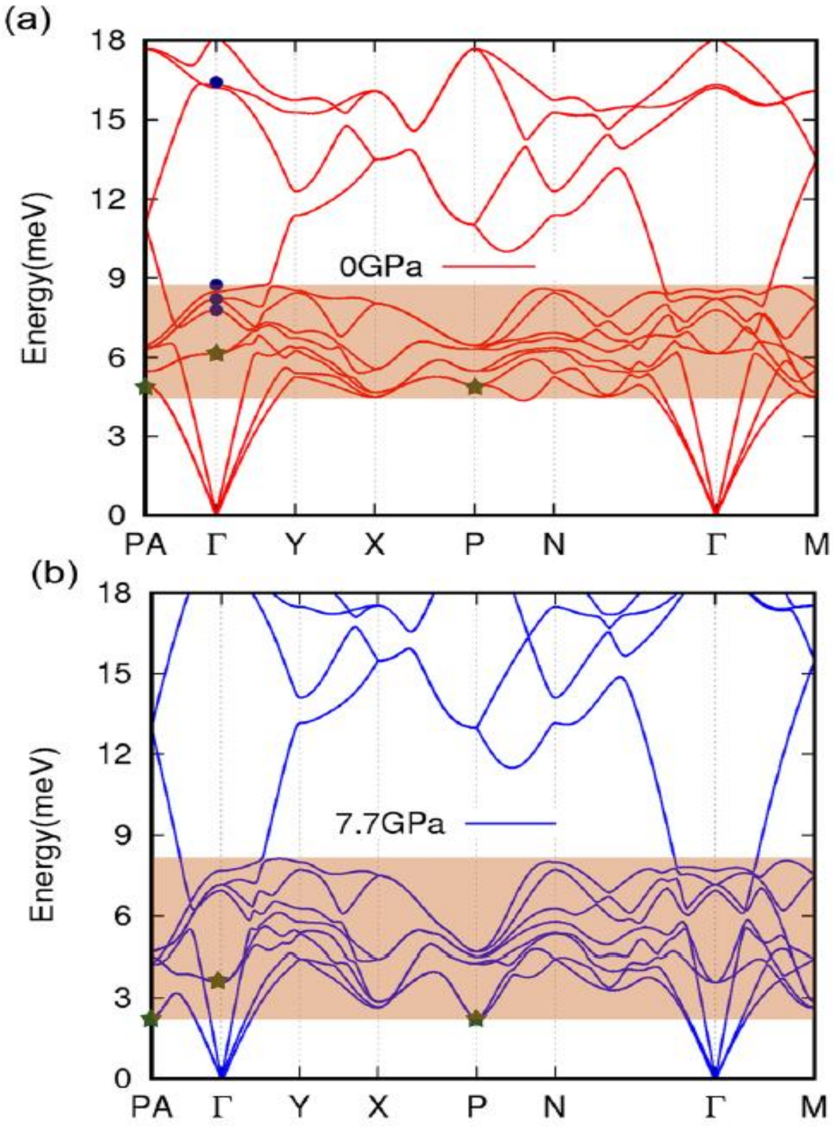
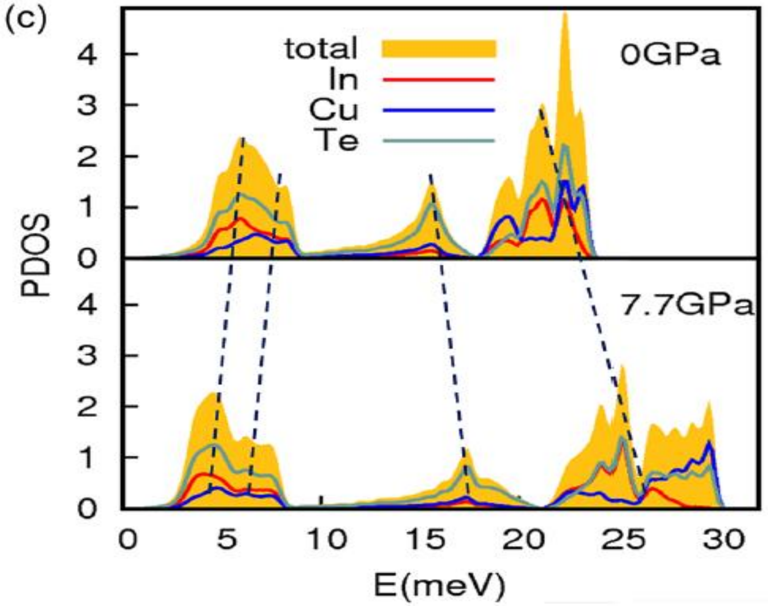
Phonon Dispersions



- The acoustic phonons and first 6 optical phonons soften in the entire BZ upon increasing pressure except for LA which hardens around Γ. The other branches harden (no anomaly there)
- The low energy phonon bandwidth increases from 4.5 meV at 0 GPa to 6 meV at 7.7 Gpa
- This is also reflected in the phonon-dos



Phonons below 10 meV soften whereas the highest phonon frequency increases from 23.4 to 29.9 meV upon increasing pressure
The DoS peak around 6 meV decreases to 4 meV and the shoulder around 8 meV broadens

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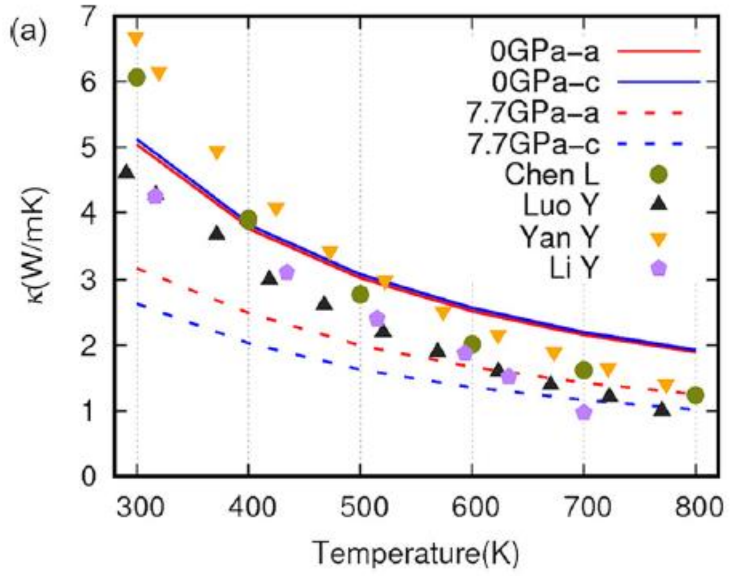
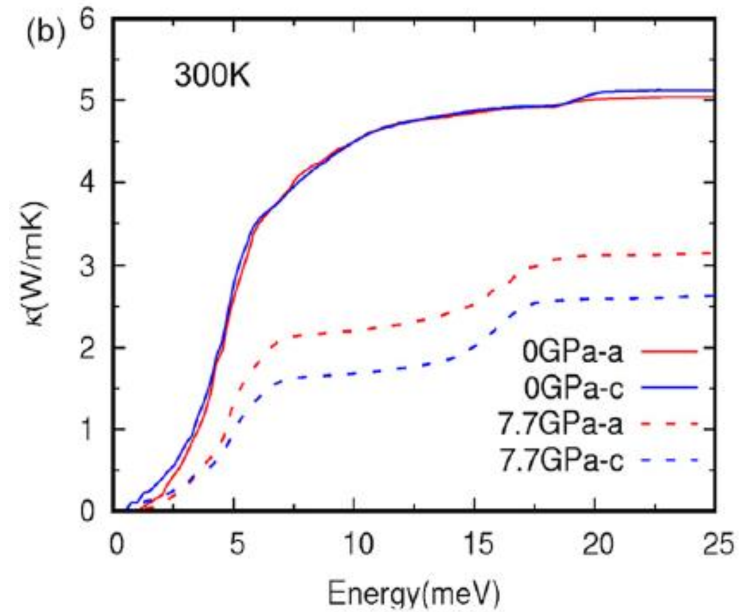
Thermal Conductivity



(a) Thermal-k with temperature at 0 and 7.7 GPa

- κ_a decreases by 41% (from 5.40 to 3.18 W/mK) and κ_c decreases by 49% (from 5.15 to 2.64 W/mK) upon increasing pressure to 7.7 GPa
- Agreement between experiments and computations is poor at high temperatures as T-dependent IFCs are not considered



(b) Cumulative thermal-k at 0 and 7.7 GPa

Most of the contribution to thermal-k at both 0 and 7.7 Gpa is from acoustic and low frequency optic modes (below 15 meV)

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Why thermal-k decrease? (1)

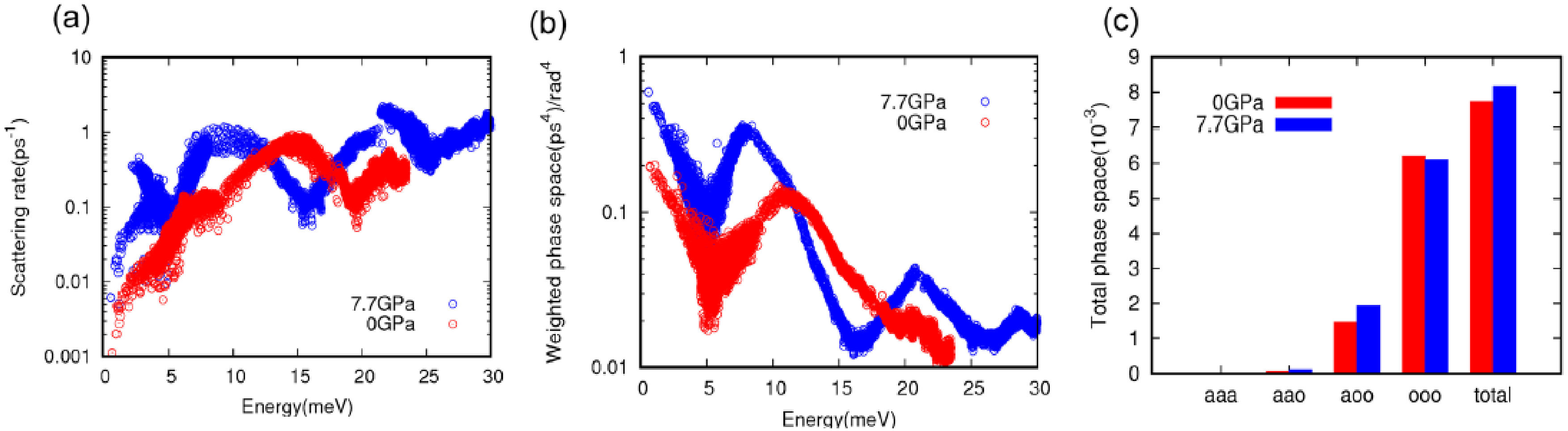
$$\kappa = \frac{1}{3}\sum_{\mathbf{q}s} C_{\mathbf{q}s} v_{\mathbf{q}s}^2 \tau_{\mathbf{q}s}$$ (Linearized BTE + RTA + Fourier's law)

Upon increasing pressure to 7.7 Gpa

1. Heat capacity: changes from 192.83 J/mol/K to 190.08 J/mol/K
2. Group Velocity: v_{LA} along $\Gamma - M$ and $\Gamma - Y$ both, increase by 10% and v_{TA} decreases by around 10-17% along $\Gamma - Y$

These two factors cannot explain lowering of thermal-k!

3. Scattering:



- Broadened phonon bandwidth enlarges phonon scattering phase space
- The phase space at 7.7 GPa is much larger in 0-12 meV range especially around 5 meV

Scattering is enhanced at high pressure!

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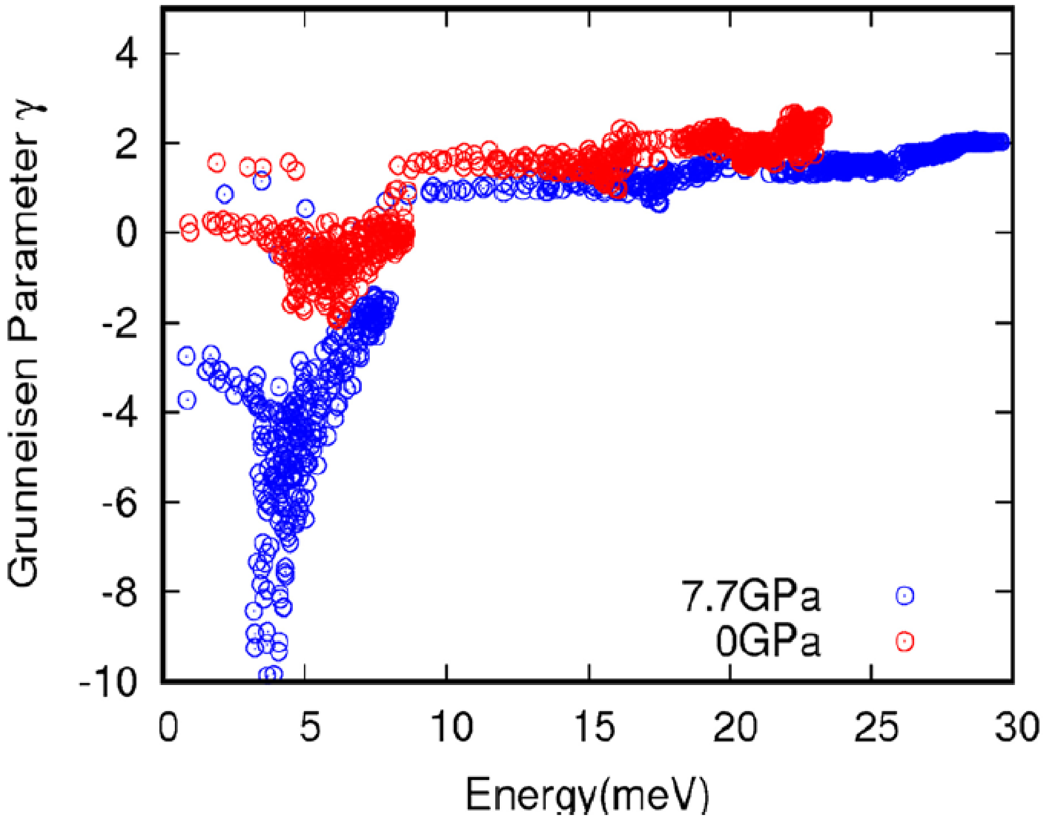
Why thermal-k decrease? (2)

Role of Gruneisen Parameter: $$\gamma_i = -\frac{V}{\omega_i}\frac{d\omega}{dp}$$



- According to Debye-Calleway model, the scattering rate τ^{-1} is proportional to γ^2
- Even though γ is negative for phonons with energy < 10 meV, $|\gamma|$ is higher and therefore, a higher scattering rate
- γ of the TA branch at P and PA points reaches largest value at 7.7 GPa and becomes 7 times larger than those at 0 GPa

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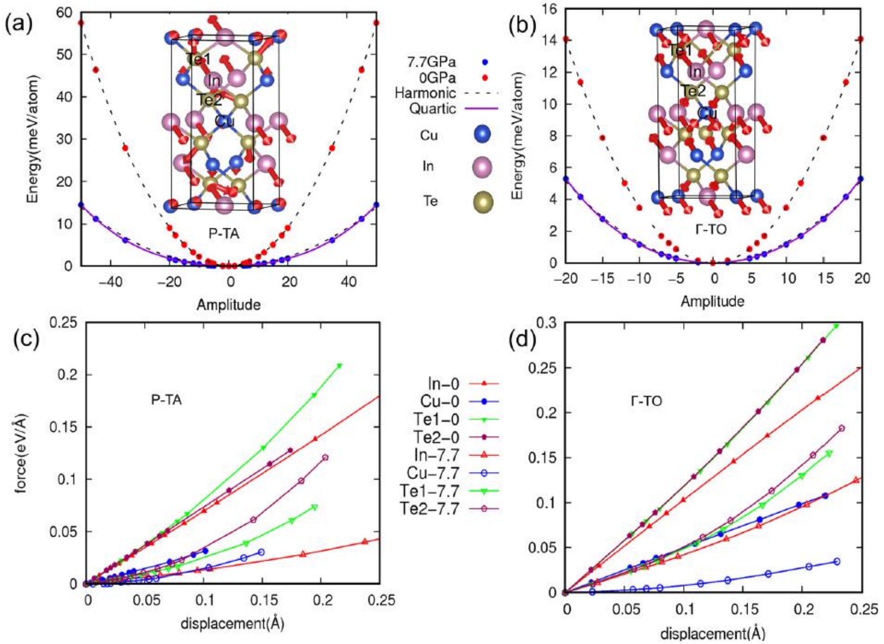
Frozen phonon potential (Displace atoms along mode eigenvectors)

Potential energies of TA and TO phonon modes at P and Γ respectively:



		P-TA			Γ-TO		
		0 GPa	7.7 GPa	Δ	0 GPa	7.7 GPa	Δ
mFC		0.07	0.03	−52%	0.07	0.03	−57%
a-mFC	In	0.70	0.12	−83%	1.03	0.41	−60%
	Cu	0.26	0.03	−88%	0.49	0.06	−88%
	Te1	0.74	0.18	−76%	1.16	0.45	−61%
	Te2	0.74	0.18	−76%	1.16	0.46	−60%

- Surprisingle P-TA and Γ-TO modes become flatter under higher pressure
- Unusual since Cu-In and In-Te bond lengths are shorter which should otherwise result in bond-stiffening and steeper potential energy surface
- Harmonic fitting of PES are good enough at both pressures indicating anharmonicity has no role to play here
- Introduced mode Force Constant (mFC) as second derivative of mode PES at equilibrium
- Extracted forces on each atom at various displacements (c and d) and computed atom based mode FC

mFCs decrease by more than half!
Some amFCs decrease upto 88%

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Conclusions

- Pressure lowers lattice thermal-k of $CuInTe_2$
- Upon increasing pressure from 0 GPa to 7.7 GPa, the thermal-k along c direction lowers by almost 49%, thus making $CuInTe_2$ an attractive TE material
- The negative relation between thermal-k and pressure is due to stronger phonon scattering rate under pressure
- Softening of acoustic phonons and low frequency optical phonons broadens the low energy phonon bandwidth which increases scattering phase space resulting in higher scattering rate

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"That's all Folks!"