Anharmonic phonons in thermoelectrics and ferroelectrics studied with inelastic neutron and x-ray scattering

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https://delaire.pratt.duke.edu/

X-ray Echo Spectroscopy Workshop

Advanced Photon Source

Sep 8-10, 2016

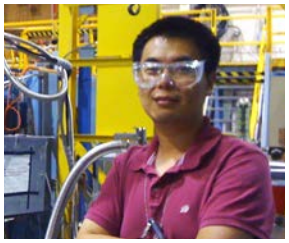
Duke UNIVERSITY

OAK RIDGE NATIONAL LABORATORY

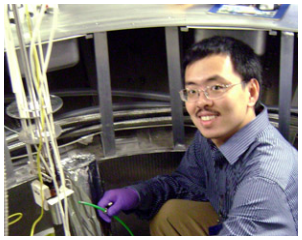
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Acknowledgements

Jie Ma
Former postdoc



Chen Li
Former postdoc



Jiawang Hong
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J. Budai, E. Specht (Scattering and ThermoPhysics Group)
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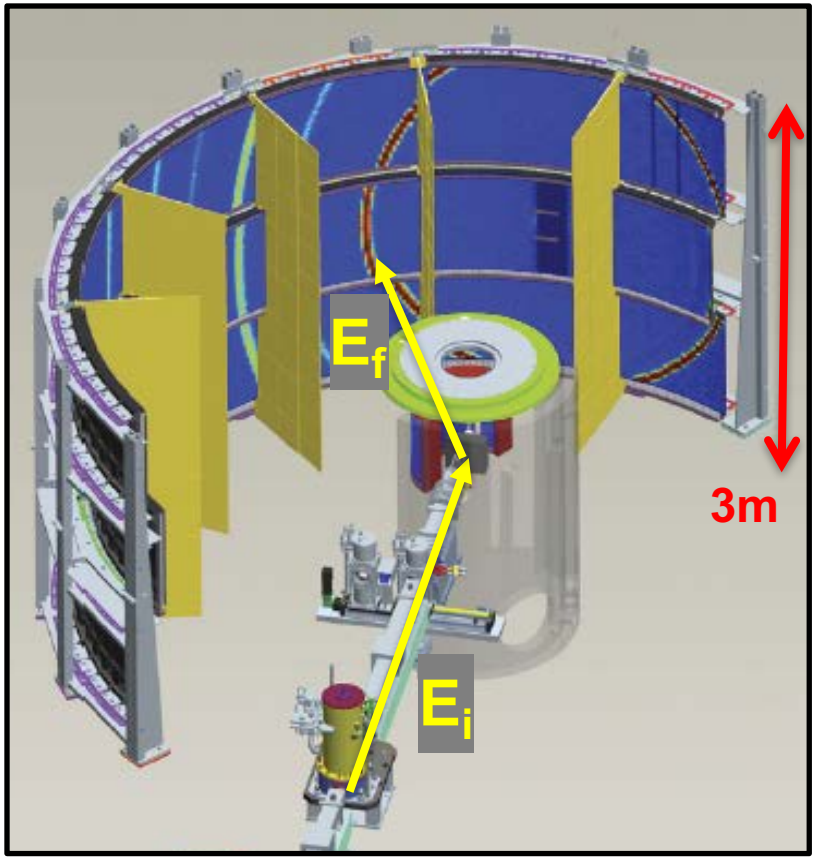
- DOE Energy Frontier Research Center (S^3TEC)
- Center for Accelerating Materials Modeling from SNS data (CAMM)

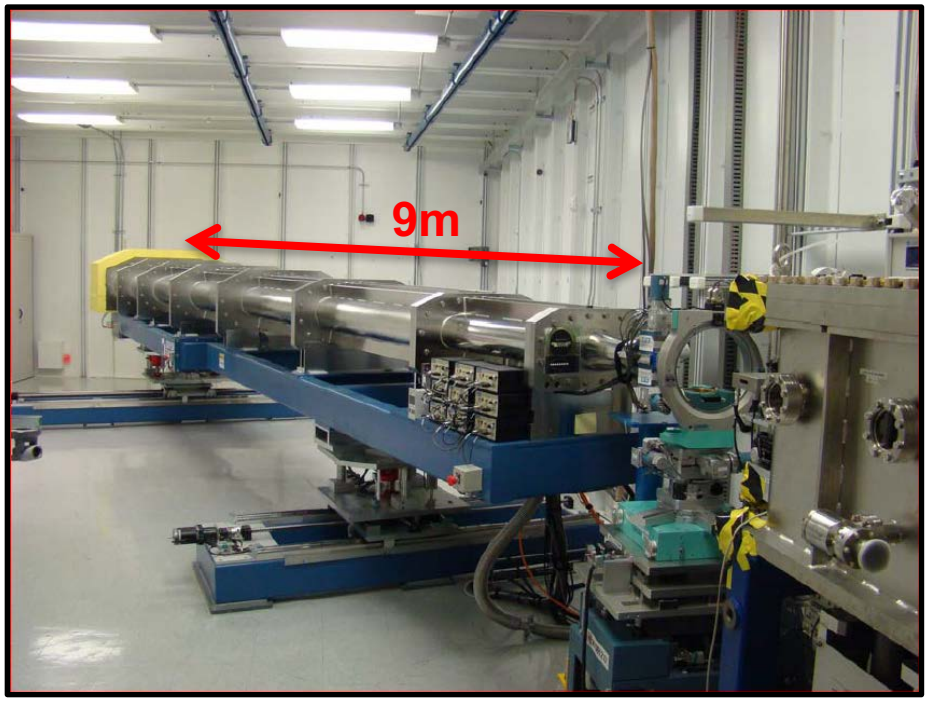
Neutron and X-ray Spectrometers

Neutron time-of-flight:



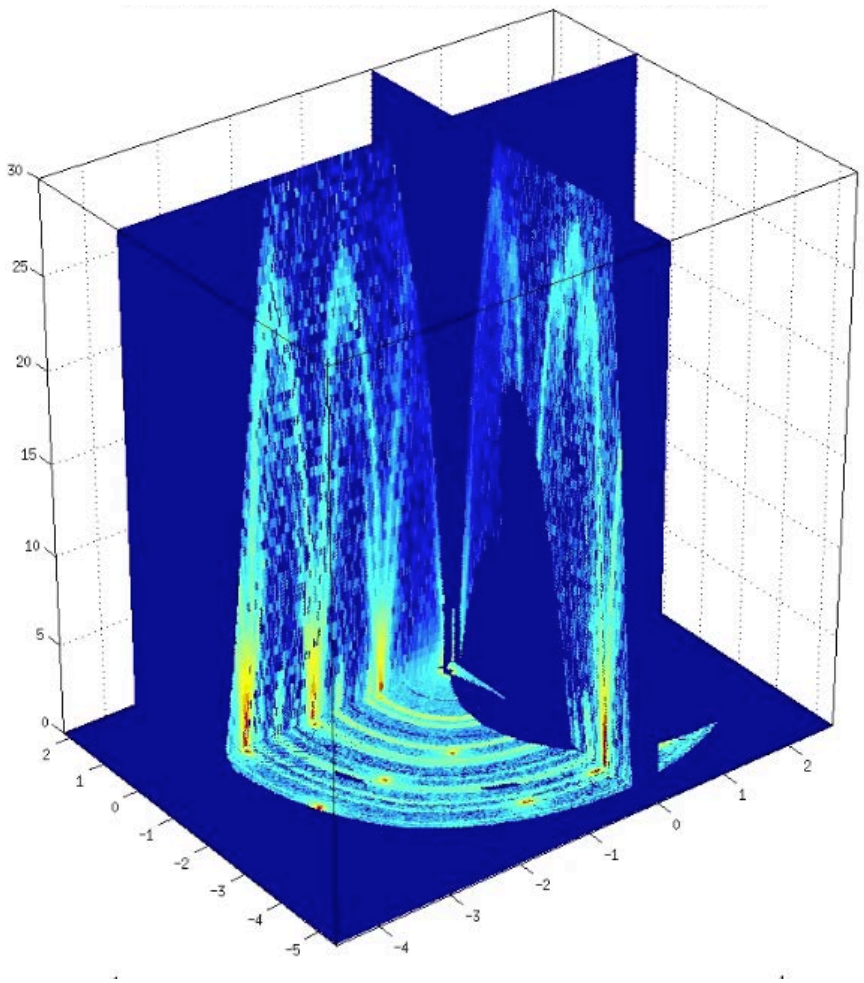
ARCS at SNS: ~10^5 pixels,
~10^4 time channels each.
beam ~ 5cm, $\Delta E/E$ ~5%

Inelastic X-ray Spectrometer:



HERIX at APS: ~10 detectors.
beam ~30 μm ; Ei = 23.7 keV
Resolution ~1.5 meV, constant with E

S(Q,E) mapping with INS



Niobium single crystal
ARCS, E_i = 50 meV, mass~10g
T = 300K

- With recent advances in time-of-flight chopper spectrometers, we can efficiently collect the entire 4-D (Q_x, Q_y, Q_z, E) space
- ARCS, CNCS, HYSPEC, SEQUOIA at SNS can provide these 4-D S(Q,E) maps

But requires large single crystals!
> several grams

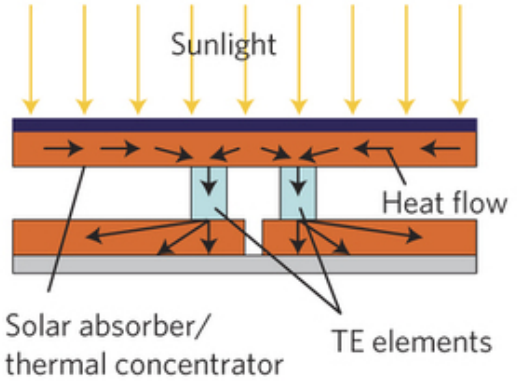
Phonon Transport in Thermoelectrics

- O. Delaire, J. Ma *et al.*, ***Nature Materials*** 10, 614 (2011)
- J. Ma*, O. Delaire*, *et al.*, ***Nature Nanotechnology*** 8, 445 (2013)
- C. Li, O. Hellman, O. Delaire *et al.*, ***Phys. Rev. Letters*** 112, 175501 (2014)
- C. Li, J. Ma, O. Delaire *et al.* ***Phys. Rev. B*** 90, 214303 (2014)
- Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, ***Nature Physics*** 11, 1063 (2015)
- Bansal, Hong, Li, May, and Delaire ***Phys. Rev. B*** 94, 054307 (2016)

Radioisotope Thermoelectric Generators

Automobile industry

Solar thermoelectrics



Thermal conductivity in thermoelectrics

- Suppress lattice thermal conductivity κ_{lat} to optimize thermoelectric efficiency:

$$zT = \frac{(\sigma S^2 T)}{(\kappa_{el} + \kappa_{lat})}$$

S: Seebeck ; σ: el. conductivity

κ: thermal conductivity

- Rationalize *microscopic origins* of κ_{lat} to gain control over phonon transport:

$$\kappa_{q,j} = \frac{1}{3} C_{q,j} v^2_{q,j} \tau_{q,j} \qquad \kappa = \sum_{q,j} \kappa_{q,j}$$

Specific heat

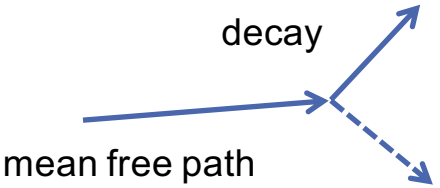
Phonon group velocities

Phonon lifetimes: many possible scattering processes combined

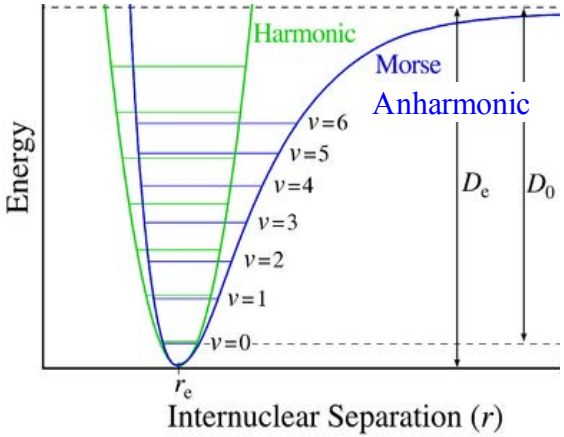
All quantities can be obtained from neutron/x-ray scattering measurements and also computed from first-principles (for moderately complex cells).

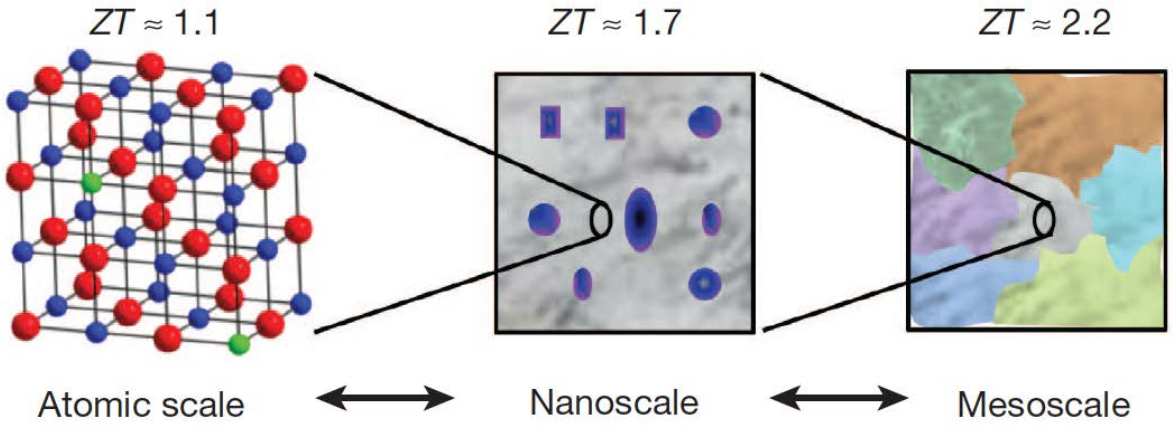
Phonons and Thermal Transport

- Perfect harmonic crystal would have *infinite thermal conductivity…*
- Phonons in real materials have finite lifetimes and mean-free-paths
- Phonon-phonon scattering from anharmonicity
- Other phonon scattering mechanisms: electron-phonon, spin-phonon, defects, nanostructure, mesoscale.



$$\Lambda_{q,j} = v_{q,j}\,\tau_{q,j}$$

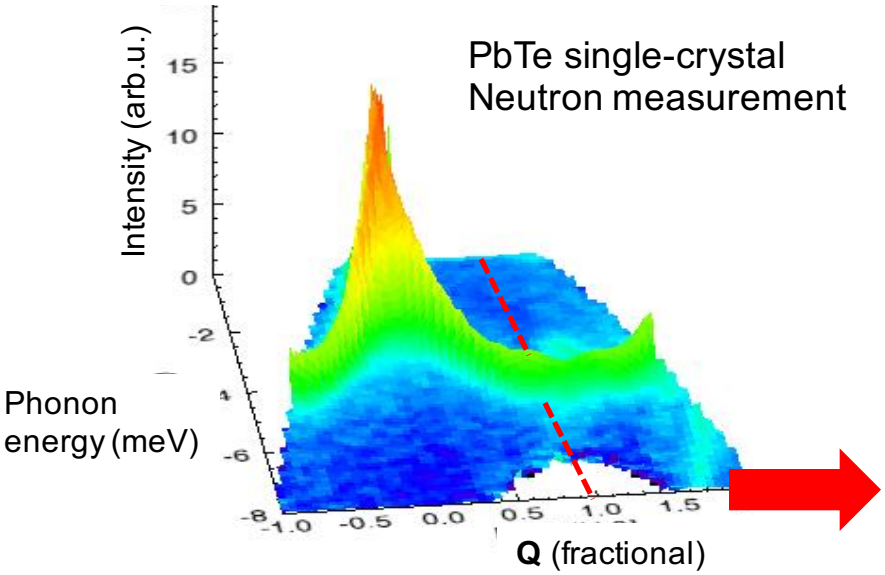




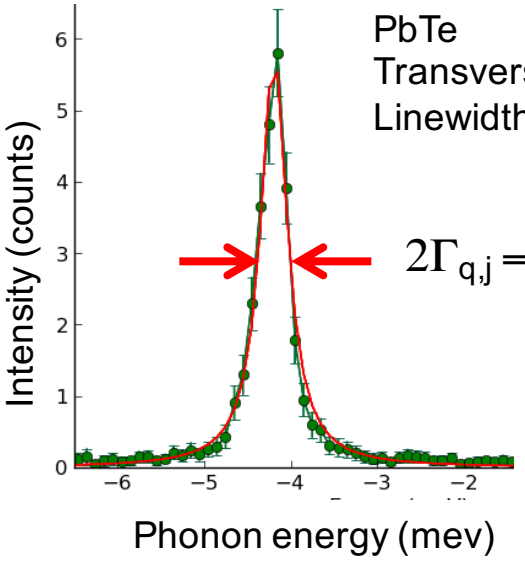
Biswas *et al.* Nature 489, 414 (2012)

Thermal conductivity and INS measurements of phonon linewidths

INS / IXS measures **dynamical structure factor,** $S(\mathbf{Q},E)$ providing details of dispersions and linewidths:



PbTe single-crystal
Neutron measurement



PbTe
Transverse-acoustic phonon
Linewidth:

$2\Gamma_{q,j} = 1/\tau_{q,j}$

Estimate thermal conductivity from INS

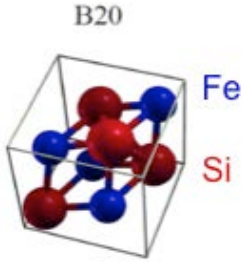
$$\kappa = \sum_{q,j} \kappa_{q,j} = \frac{1}{3} \sum_{q,j} C_{q,j} v_{q,j}^2 \tau_{q,j}$$

Matthiessen's rule:

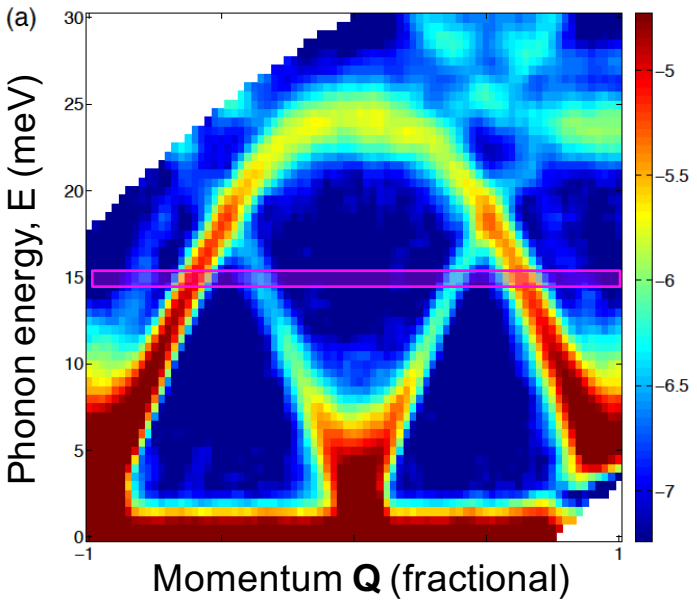
$$\tau_{tot}^{-1} = \tau_{anh}^{-1} + \tau_{el-ph}^{-1} + \tau_{defect}^{-1} + \tau_{boundary}^{-1} + \ldots$$

First-principles modeling of S(Q,E)

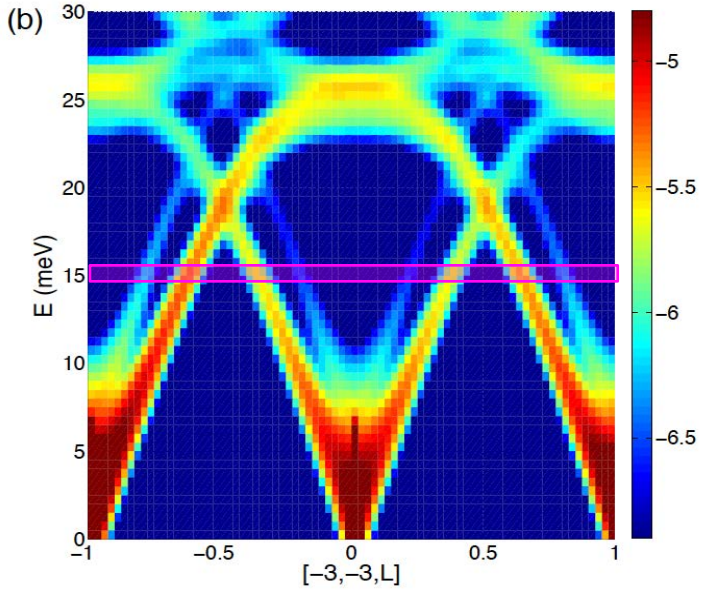
Example: S(**Q**,E) in FeSi single-crystal

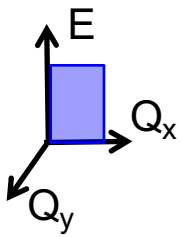


FeSi: neutron scattering

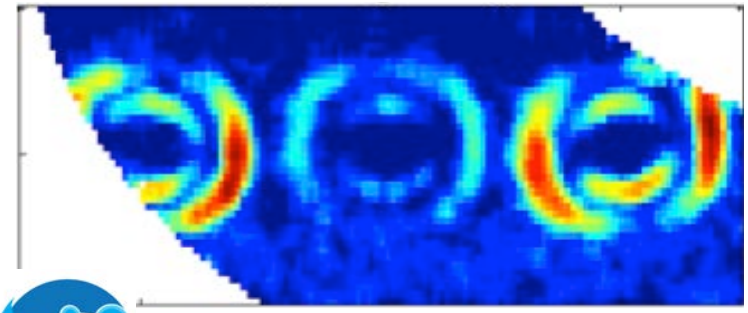


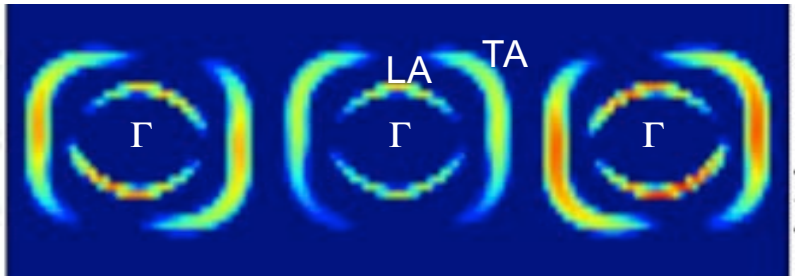
FeSi: DFT simulation

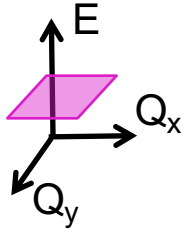




Measured intensities reflect phonon polarization vectors:





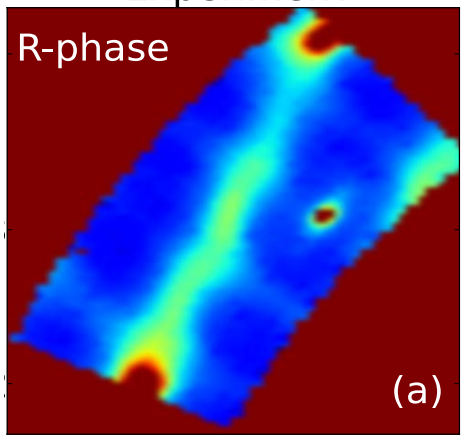


PNAS 2011, PRB 2013, PRB 2015

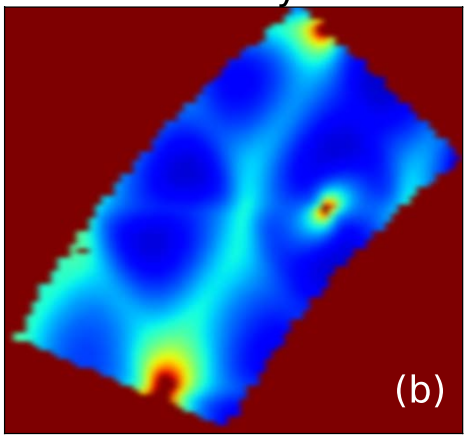
Thermal diffuse scattering DFT modeling

APS: VO_2 T-dependent

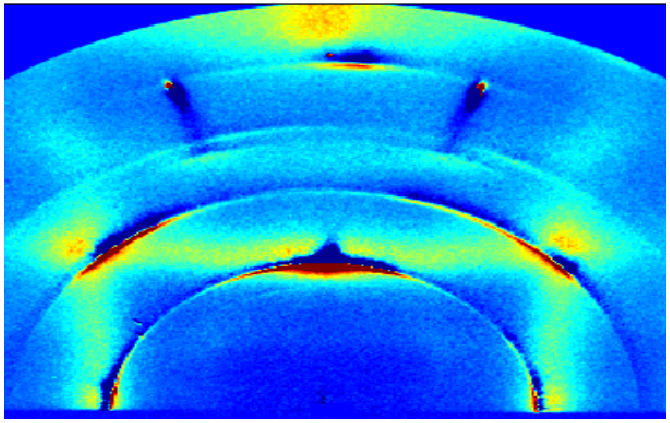
Experiment

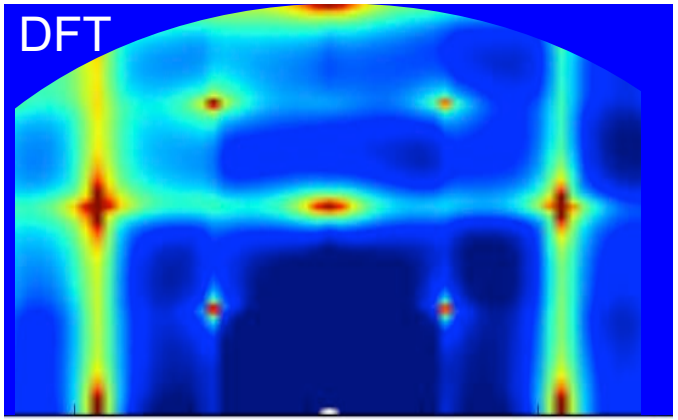


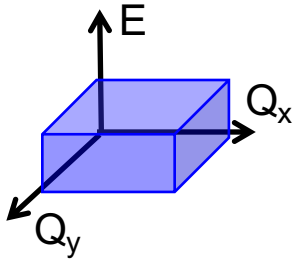
Theory



PbTe, SSRL
with D. Reis' group, Stanford/SLAC



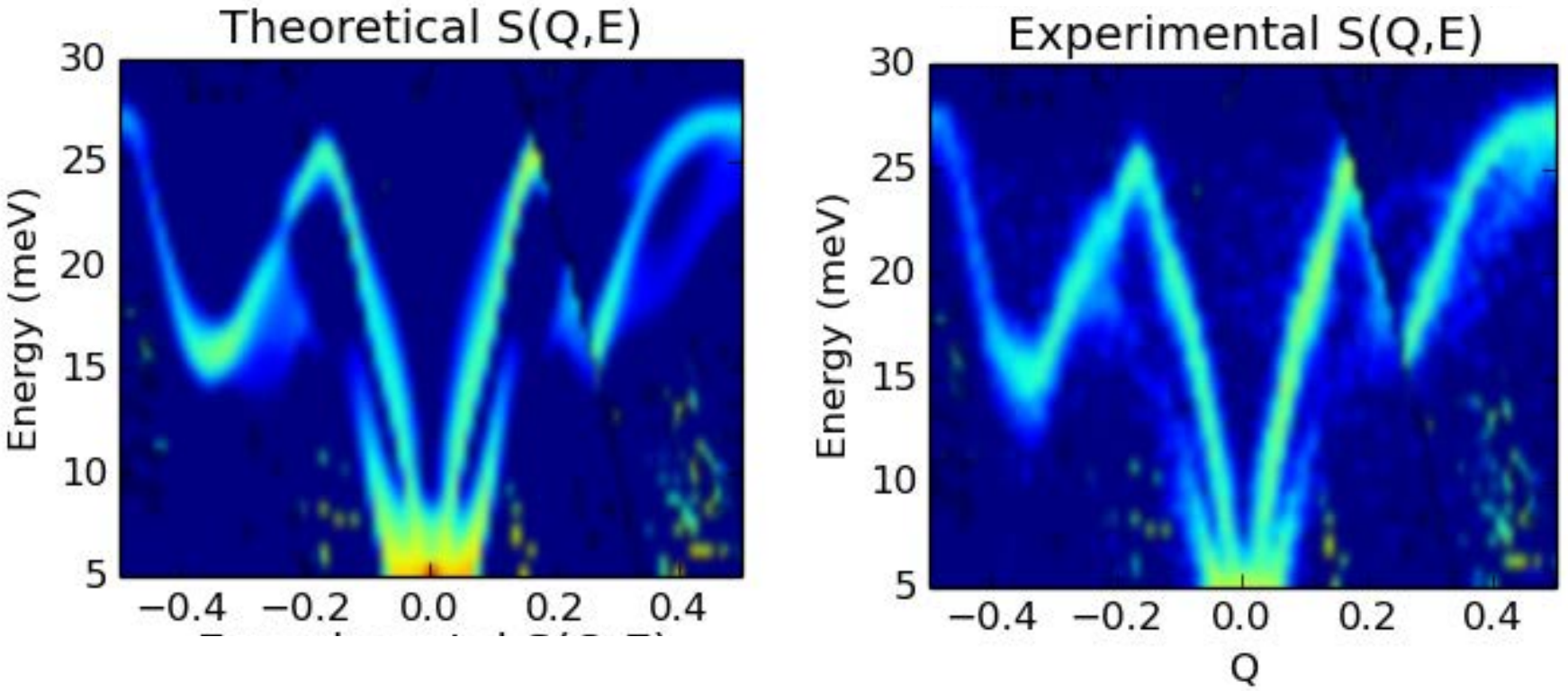




Budai*, Hong*, Manley, Specht, Li, Tischler, Abernathy, Said, Leu, Boatner, McQueeney, and Delaire, "Metallization of vanadium dioxide driven by large phonon entropy." Nature 515, 535 (2014)

S(Q,E) Modeling: Comparison Between Experiment and Simulations: niobium

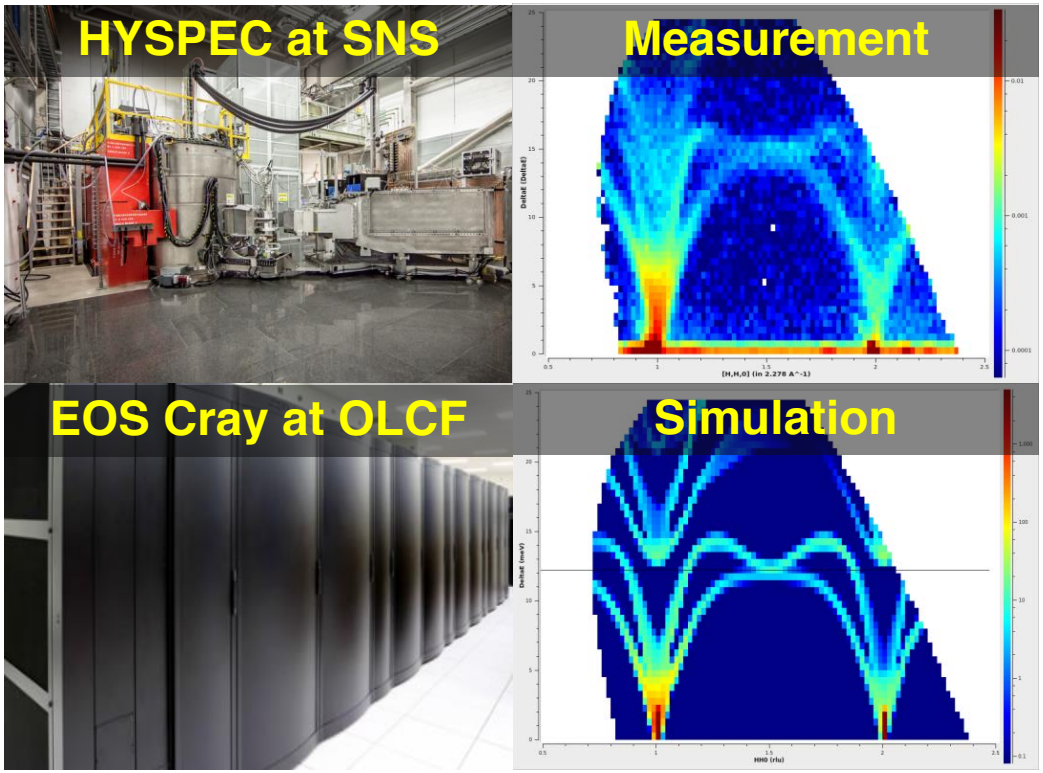
(DFT + optimization)



Bao, Archibald, Bansal, Delaire J. Comp. Physics, 315 (2016)

(our *Simphonies* software is available from GitHub)

CAMM supports concurrent inelastic neutron scattering measurements and first-principles modeling of anharmonic phonons



O. Delaire, J. Hong, H. Cao, A. Savici, B. Winn, L. Boatner, G. Shipman, manuscript in preparation

- Study of ferroelectric instabilities in $SrTiO_3$
- Measurements on HYSPEC using live data streaming (top)
- Dedicated access to Cray XC30 EOS cluster at Oak Ridge Leadership Computing Facility (11,000 cores)
- Full scale ab-initio molecular dynamics simulations on experiment timescale allowing real time decisions

CADES Compute & Data Environment for Science

http://camm.ornl.gov

Effort supported by Center for Accelerating Materials Modeling.

PbTe: strong phonon anharmonicity near ferroelectric instability

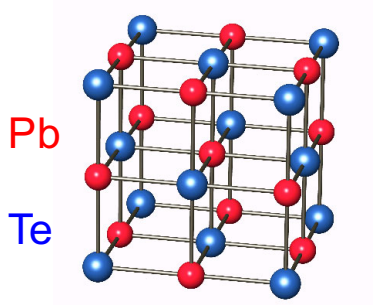
Delaire, Ma *et al.*, ***Nature Materials*** 10, 614 (2011)

Li, Hellman, Delaire *et al.*, ***Phys. Rev. Lett.*** 112, 175501 (2014)

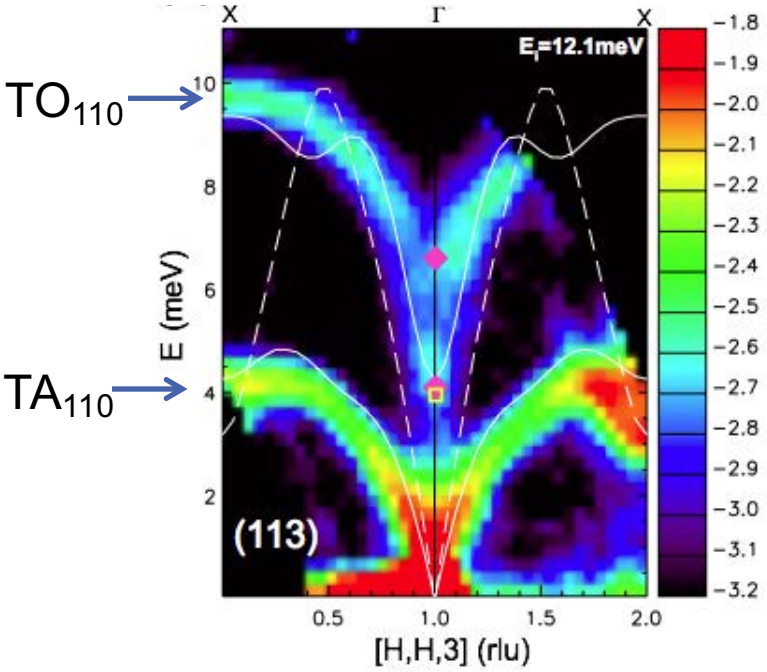
Li, Ma, Delaire *et al.* ***Phys. Rev. B*** 90, 214303 (2014)

Anharmonicity in rocksalt PbTe

- Large figure-of-merit ZT_{max}~ 2 (Pei Nature 2011, Biswas Nature 2012)
- Low thermal conductivity κ_{lat}=2 W/m/K at 300K
- ***Strongly anharmonic transverse-optic (TO) mode ("soft mode").***
- **5x suppression in κ_{lat}** from ***optic-acoustic scattering*** (Shiga PRB 2012, Tian PRB 2012)

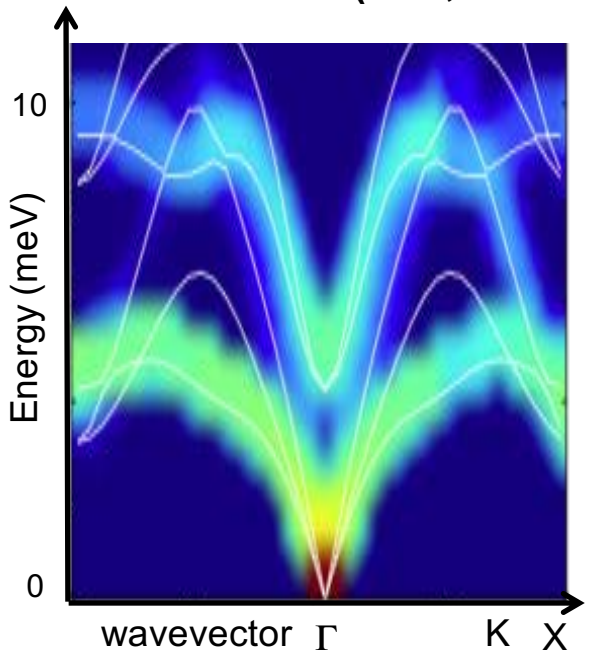


PbTe experiment (INS)



CNCS @ SNS (12meV)

PbTe calculation (DFT, harmonic)



Delaire, Ma *et al.*, Nature Materials 2011

Time-resolved thermal diffuse scattering: LCLS measurements on PbTe

Photoinduced suppression of the ferroelectric instability in PbTe
Jiang *et al.* Nature Commun. 2016 (collaboration with D. Reis)

- **No evidence for off-centering/dipoles in diffuse scattering**

>>> Does not support conclusions of Bozin, Billinge *et al.*, "Entropically Stabilized Local Dipole Formation in Lead Chalcogenides", Science (2010)

- **Diffuse scattering entirely from phonons (THz timescale)**

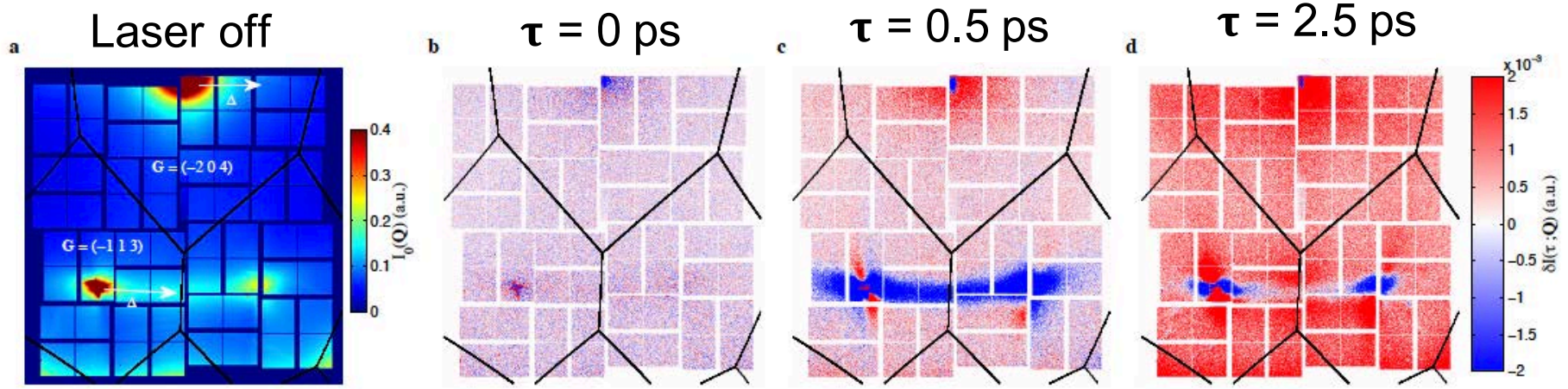


Figure 1 | Femtosecond x-ray diffuse scattering from PbTe. a, Reference scattering from PbTe prior to photoexcita-

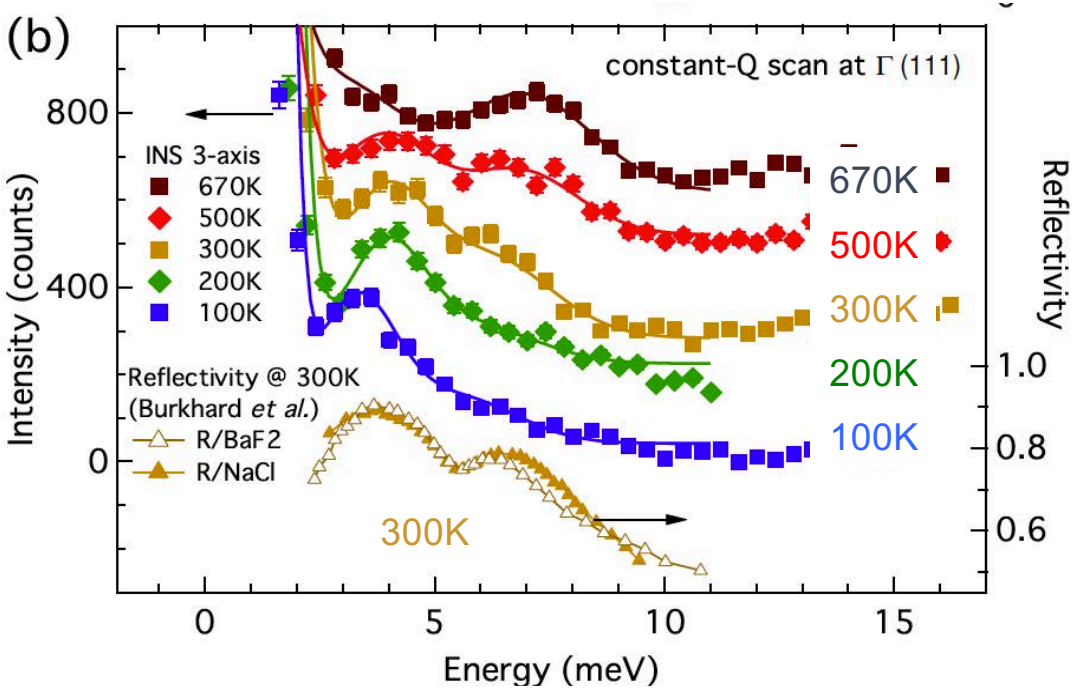
PbTe single-crystal time-resolved pump-probe TDS on LCLS / XPP

T-dependence of TO phonon in PbTe

Deviates strongly from quasi-harmonic behavior:

- Broad TO (ferroelectric) mode at Γ, stiffens with increasing T.
- Double-peak structure, with strong T-dependence.

PbTe TO mode spectra at Γ



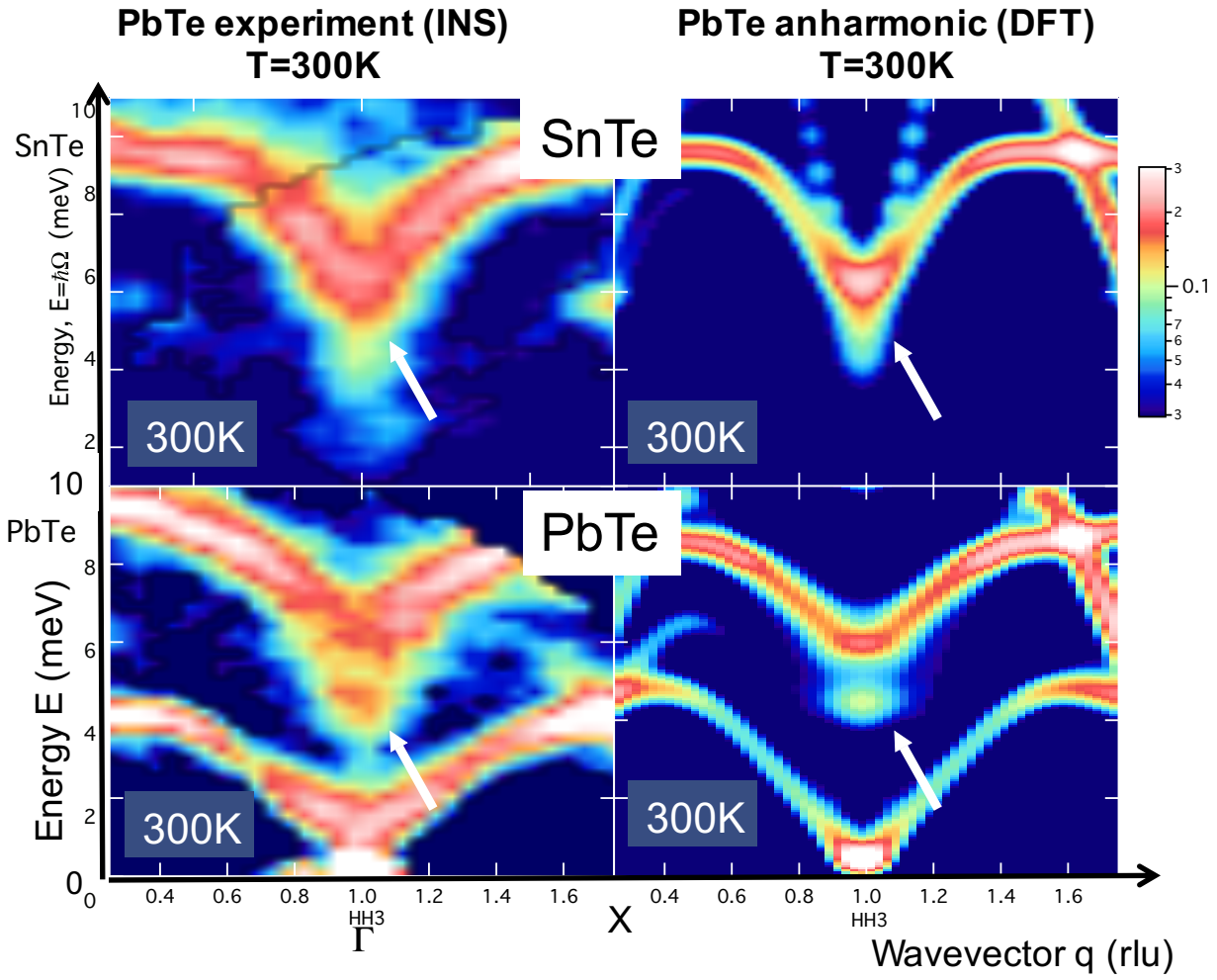
HB3 @ HFIR (thermal 3-axis)

Delaire, Ma *et al.*, Nature Materials **10**, 614 (2011)

Confirmed by Jensen *et al.* PRB **86**, 085313 (2012)

Anharmonic phonon spectral functions

- **Ab-initio MD + TDEP reproduces strong anharmonic effects**
- $\chi''(Q,E)$ computed from anharmonic phonon self-energy $\Sigma_q(E)$
- Reproduce TO phonon splitting in PbTe, by including anharmonicity



Phys. Rev. Letters 112, 175501 (2014)
Phys. Rev. B 90, 214303 (2014)

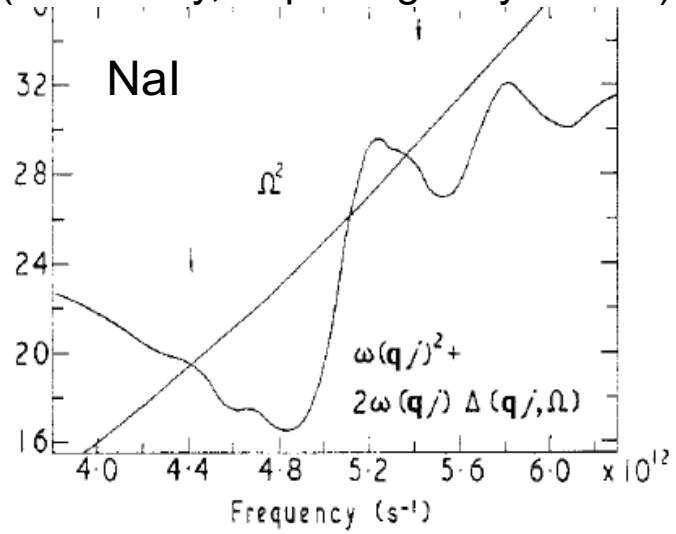
Neutron spectra as probes of many-body effects

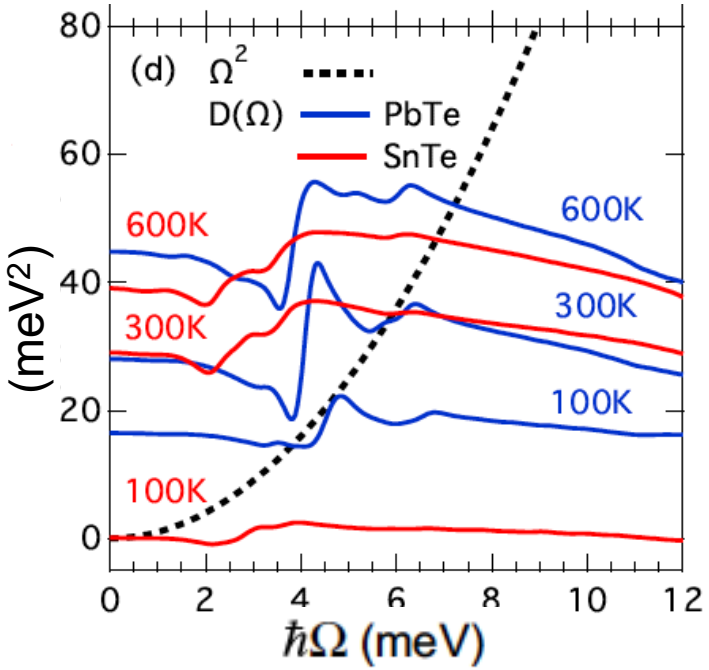
- Dynamical susceptibility:

$$\chi''_{\mathbf{q}j}(\Omega) = |F(\mathbf{Q},\Omega)|^2 \times \frac{2\omega_{\mathbf{q}j}\Gamma_{\mathbf{q}j}(\Omega)}{\{\Omega^2 - \omega^2_{\mathbf{q}j} - 2\omega_{\mathbf{q}j}\Delta_{\mathbf{q}j}(\Omega)\}^2 + 4\omega^2_{\mathbf{q}j}\Gamma_{\mathbf{q}j}(\Omega)^2}$$

- Look for minima in {…}
- Multiple crossings lead to multiple peaks in the INS spectra for $\chi_q''(E)$
- $\Delta_{q,j}(\Omega)$ obtained from anharmonic interatomic force-constants.

(R. Cowley, Rep. Prog. Phys. 1968)





Phonon "nesting" increases phase-space for acoustic-optic scattering of TO mode

Imaginary part of self-energy (damping):

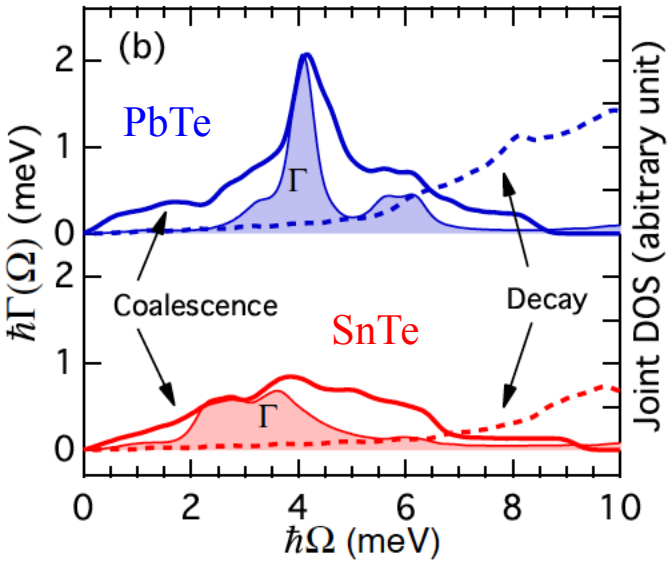
$$\Gamma_{\mathbf{q}j}(\Omega) = \frac{18}{\hbar^2} \sum_{\mathbf{q}_1 \mathbf{q}_2 j_1 j_2} \left| V_3 \begin{pmatrix} \mathbf{q}\, \mathbf{q}_1\, \mathbf{q}_2 \\ j\, j_1\, j_2 \end{pmatrix} \right|^2 \times$$

$$\Big((n_1 + n_2 + 1)\left[\delta_{\omega_1+\omega_2-\Omega} - \delta_{\omega_1+\omega_2+\Omega}\right] + (n_2 - n_1)\left[\delta_{\omega_1-\omega_2-\Omega} - \delta_{\omega_1-\omega_2+\Omega}\right] \Big) ,$$

3-phonon interaction strength (transition probability)

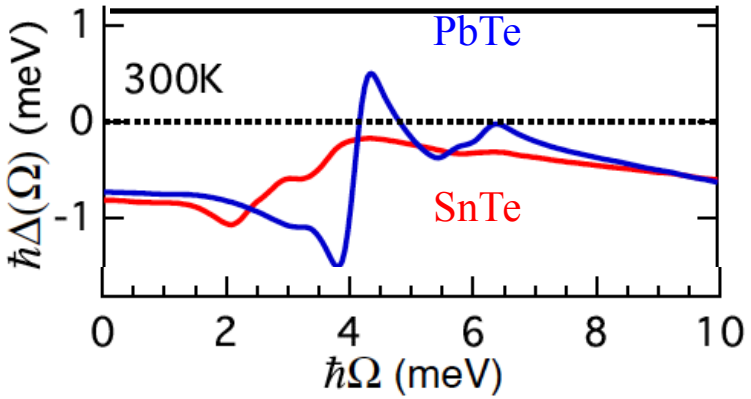
Kinematic constraints for conserving energy and momentum (phase space size ~ joint DOS)

Real and imaginary parts of self-energy related by Kramers-Kronig (Hilbert) transformation:



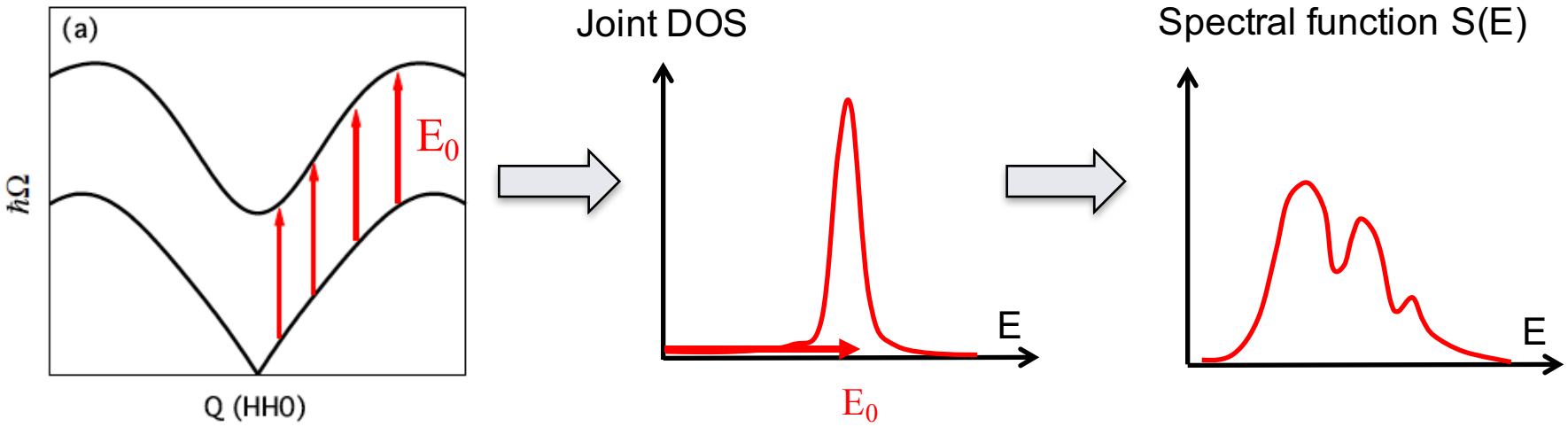
$\mathcal{H}$

$\mathcal{H}[\delta(x)] = 1/x$



Phonon "nesting" increases phase-space for acoustic-optic scattering of TO mode

- Phase-space size amplifies effect of anharmonic potential
- Nesting of phonon dispersions:



➔ *screen/engineer materials for favorable dispersions*

SnSe: bonding instability, phase transition and anharmonicity

Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, ***Nature Physics*** 11, 1063 (2015)

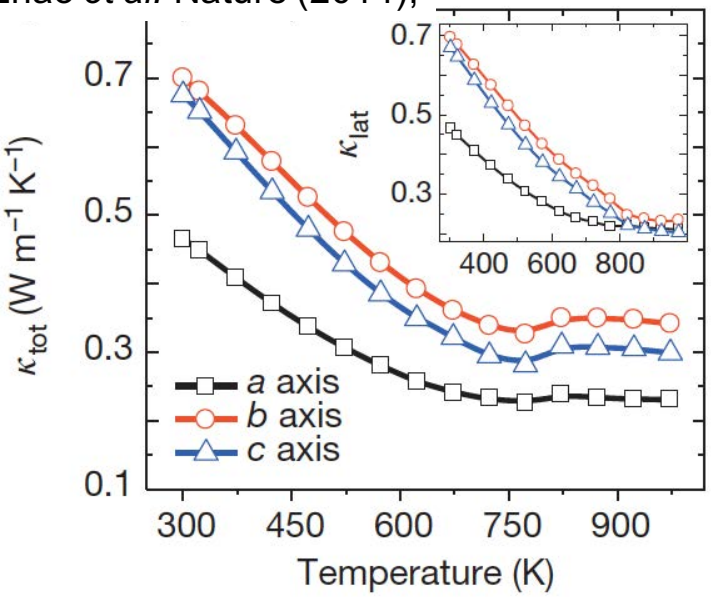
Bansal, Hong, Li, May, and Delaire ***Phys. Rev. B*** 94, 054307 (2016)

Hong and Delaire, arxiv:1604.07077

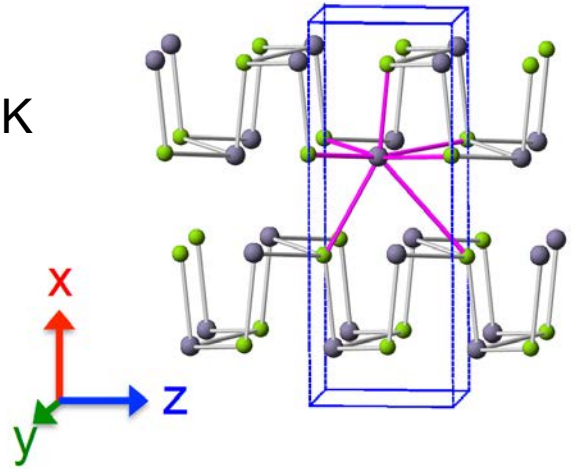
SnSe: anisotropy and phase transition

- Very high zT ~ 2.5 and very low thermal conductivity $\kappa_{lat} < 1\ Wm^{-1}K^{-1}$
- Strongly anisotropic,
- Structural phase transition at ~805K

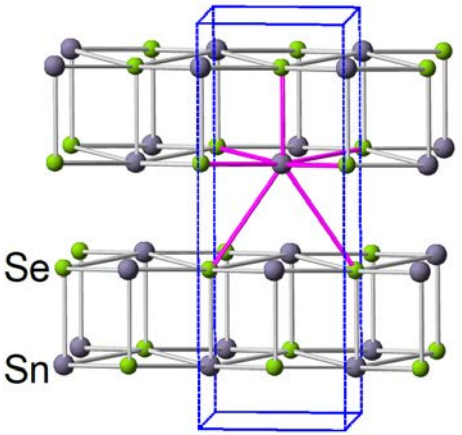
Zhao *et al.* Nature (2014),



Pnma
T<805K



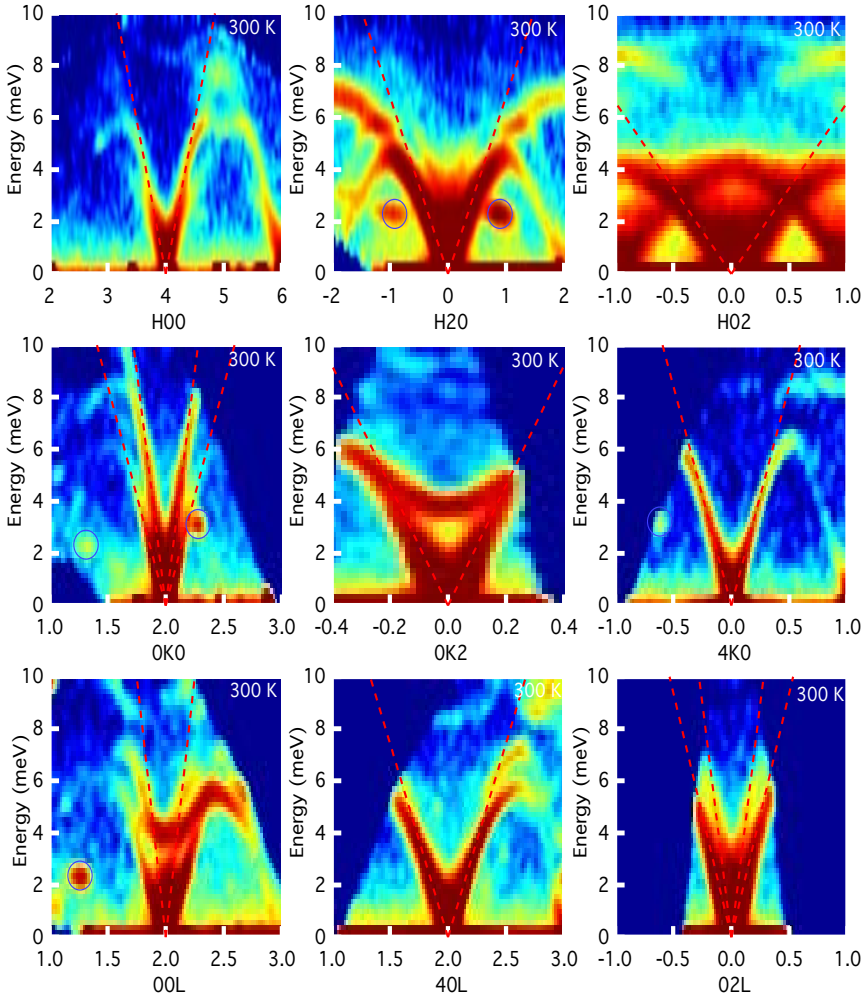
Cmcm
T>805K

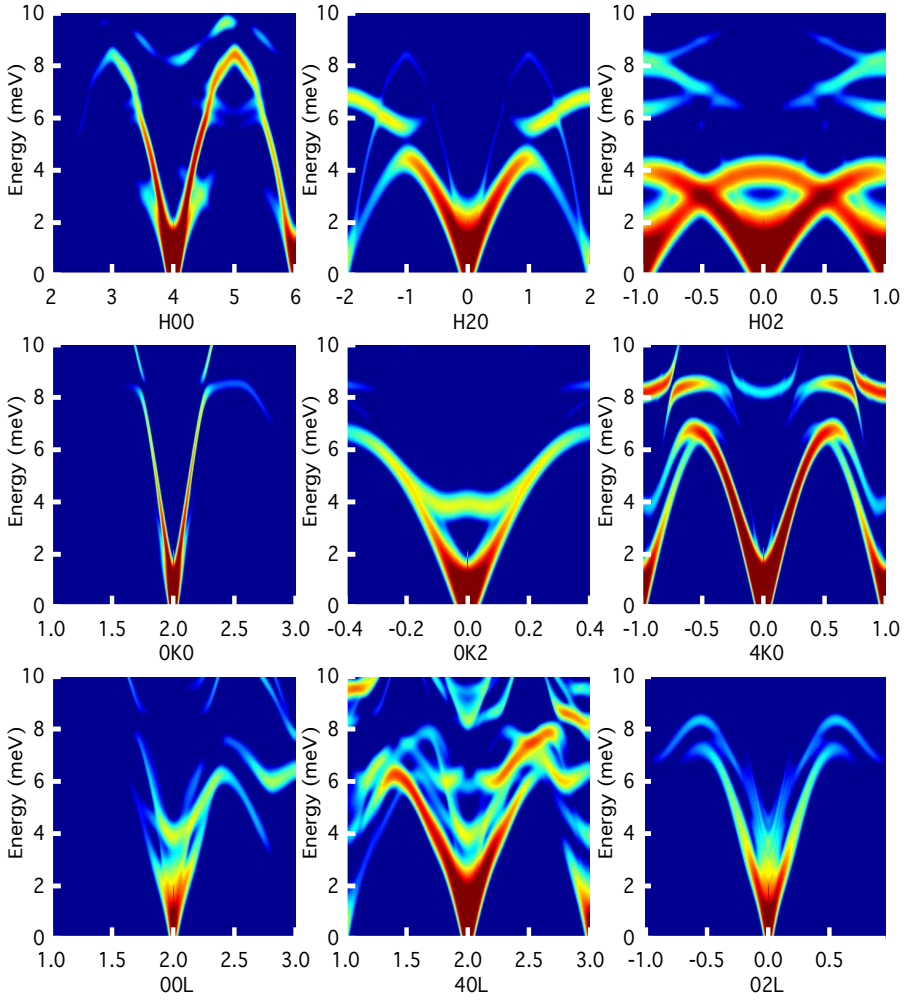


Zhao *et al.* Nature (2014), Zhao *et al.* Science (2016),
Chen *et al*. J. Mater. Chem. 2014, Carrete *et al.* APL (2014)

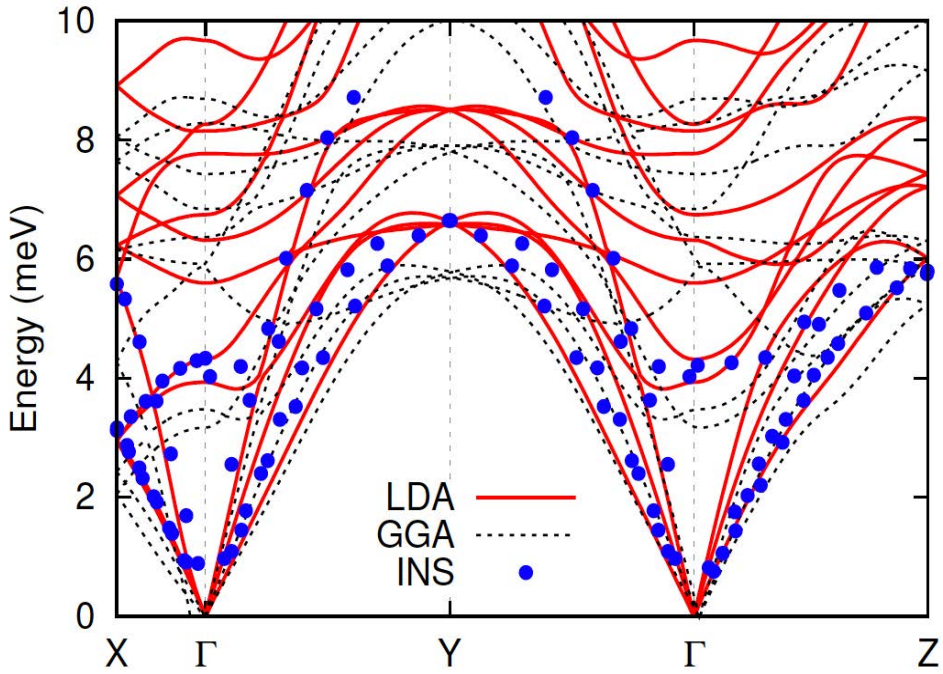
Neutron scattering

First-principles simulations





Important to preserve information about the polarization vectors

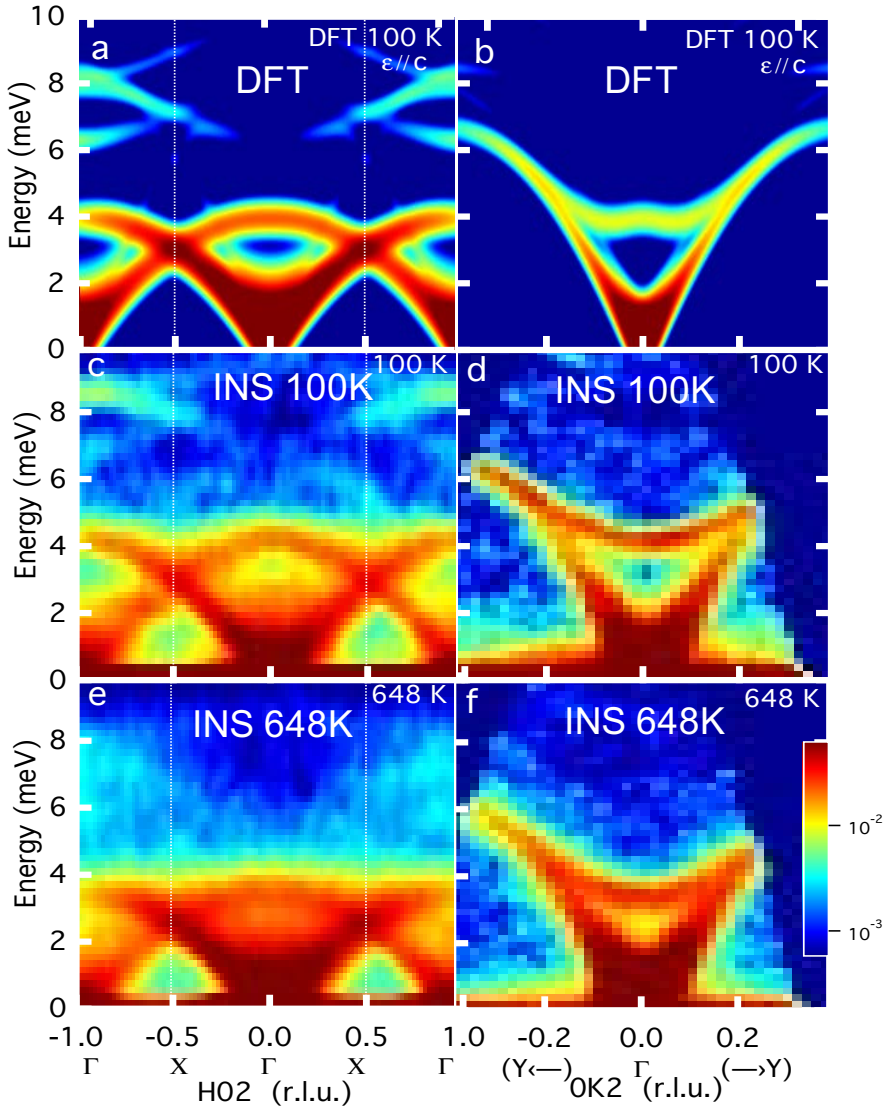


LDA more accurate than GGA (PBE)

FIG. 2. ons with either LDA or GGA exchange-correlation functionals (relaxed unit cells), compared with experimental INS data at 300 K.

SnSe: S(Q,E) for *c*-polarized modes

- Measured phonons with neutron scattering on single-crystals at 100K < T < 850K
- Mapped all crystallographic directions (orthorombic a≠b≠c)
- Observe strong softening with increasing temperature (up to Pnma – Cmcm phase transition)
- Especially anharmonic modes with polarizations along *c*-axis.
- Good agreement with DFT / LDA but GGA underestimates phonon frequencies.



k // [100] ***k*** // [010]

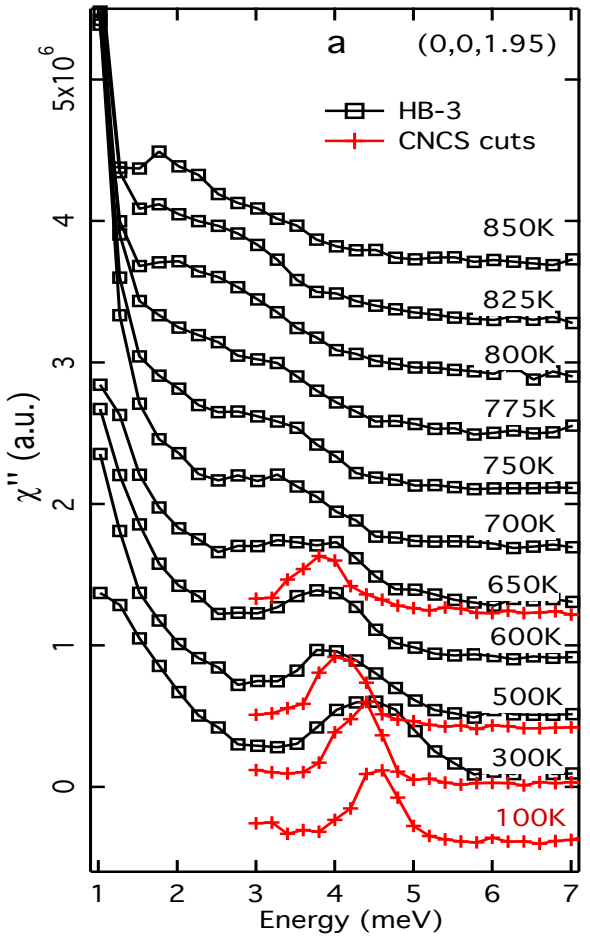
Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, Nature Physics 11, 1063 (2015)

CNCS @ SNS (12meV)

SnSe soft-mode behavior of $TO_c(\Gamma)$

- Many acoustic and optical phonons show strong temperature dependence.
- Lowest zone-center TO_c mode softens at the phase transition.
- Confirms strong anharmonicity.

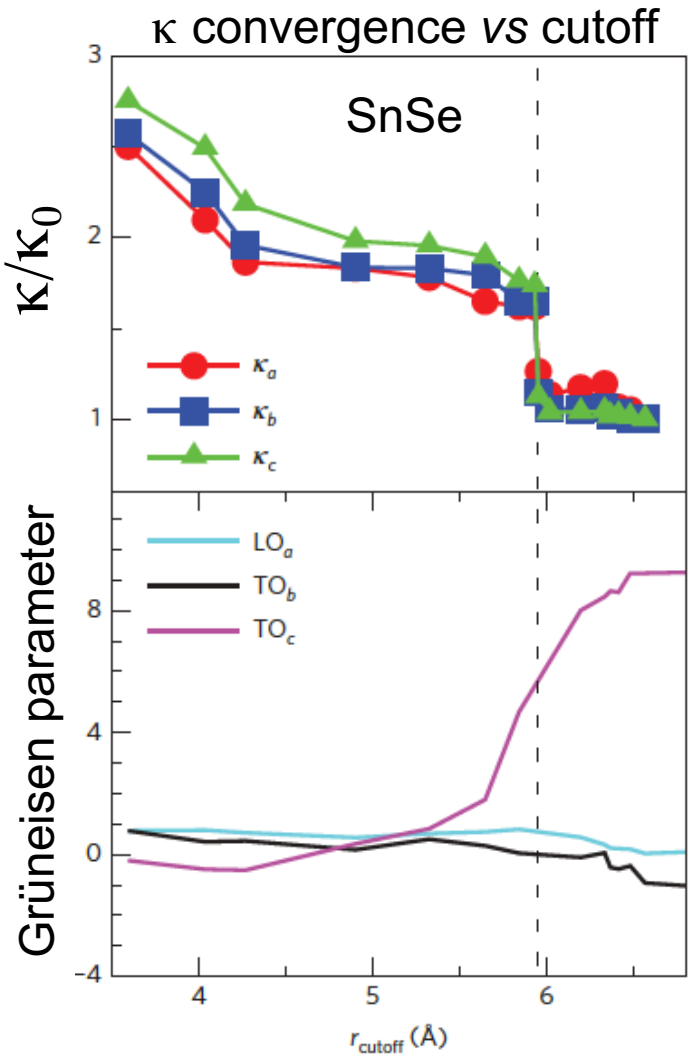
SnSe zone-center TO_c



Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, Nature Physics 11, 1063 (2015)

HB3 @ HFIR
CNCS @ SNS

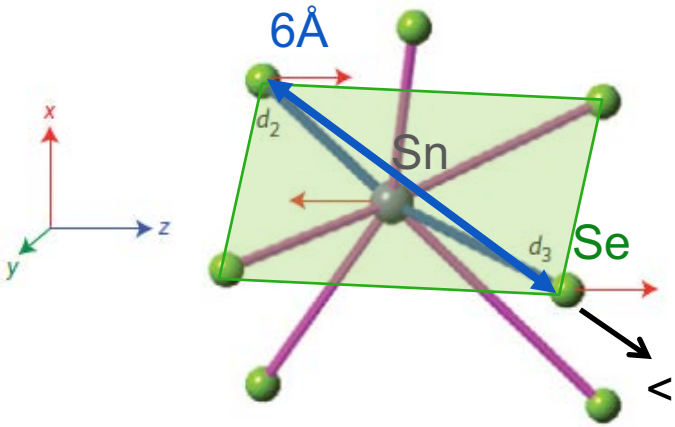
Anharmonicity and thermal transport



Cutoff radius for Ψ_3

- SnSe thermal conductivity computed from first-principles.
- Strong influence of cubic terms Ψ within Sn 1NN coordination polyhedron for triplet with Se-Se distance ~6Å

$$V = V_0 + \frac{1}{2!}\Sigma_{i,j,\alpha,\beta}\Phi_{i,j}^{\alpha,\beta}u_i^\alpha u_j^\beta + \frac{1}{3!}\Sigma_{i,j,k,\alpha,\beta,\gamma}\Psi_{i,j,k}^{\alpha,\beta,\gamma}u_i^\alpha u_j^\beta u_k^\gamma + \cdots$$



Connect with structure and bonding

Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, Nature Physics 11, 1063 (2015)

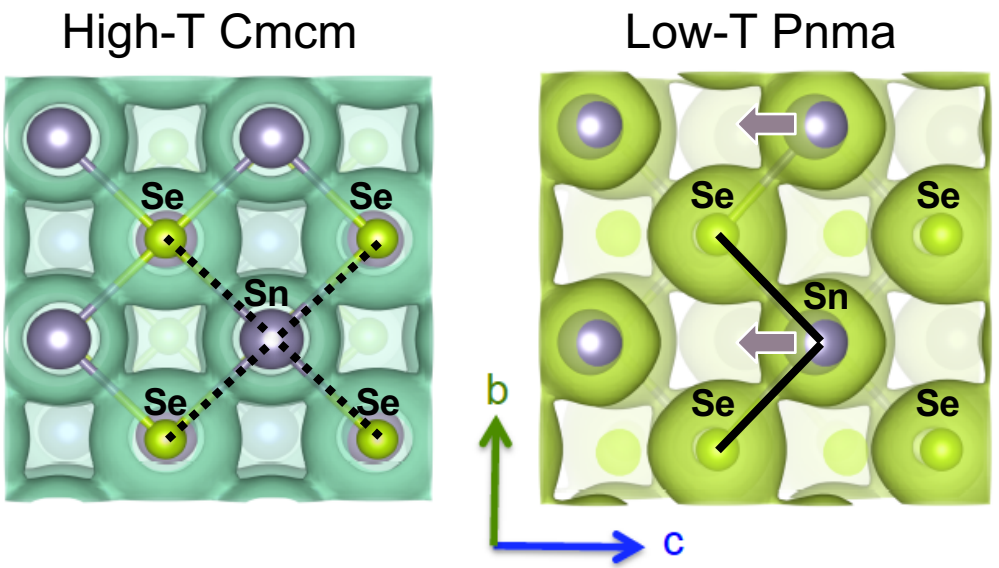
*W. Li Comput. Phys. Commun. 185, 17471758 (2014)

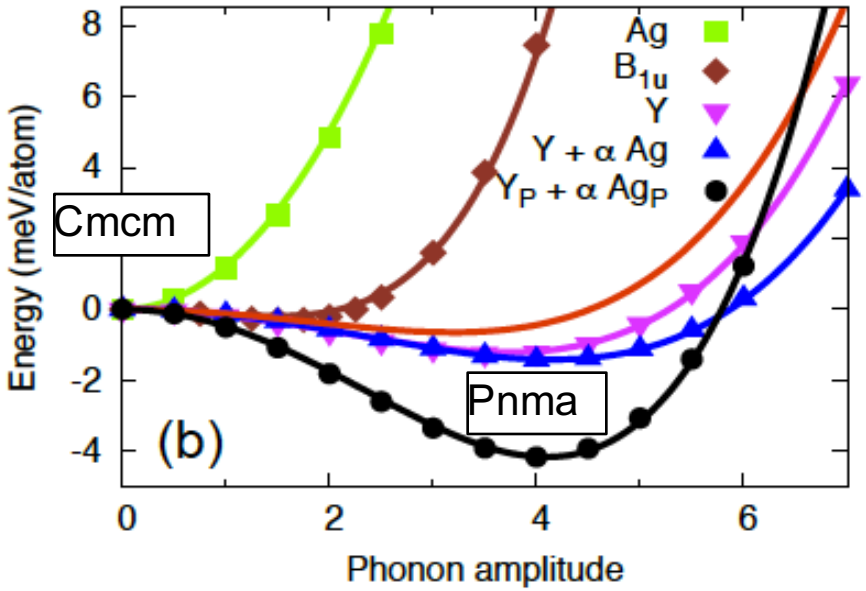
Anharmonicity from bonding instability

- Electronic instability (Jahn-Teller) of high-T Cmcm phase: Resonantly-bonded high-symmetry Cmcm phase distorts to Pnma to lower electronic energy.
- Results in double-well anharmonic potential for ions.
- **We have identified several strongly anharmonic materials near Jahn-Teller / Peierls instabilities**.

Hong and Delaire,
arxiv:1604.07077

Electron Localization Function



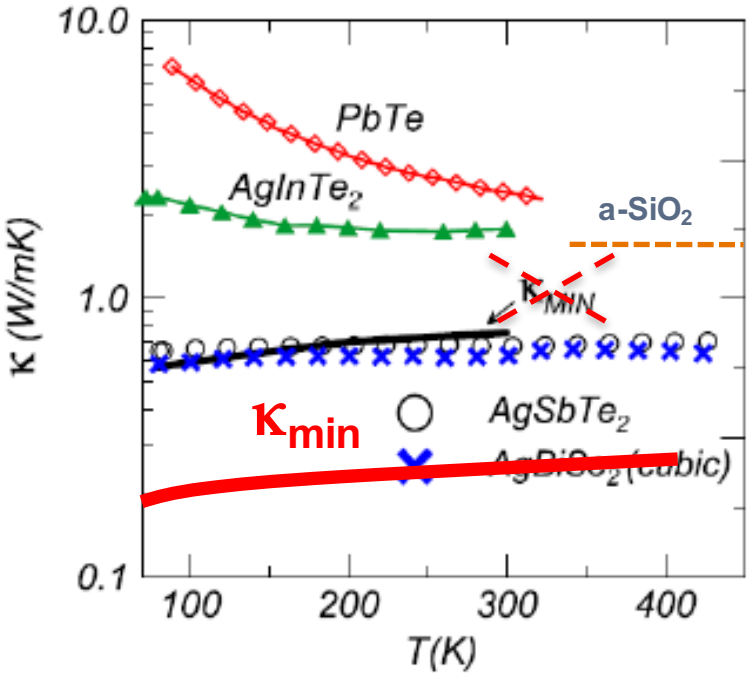


$AgSbTe_2$: importance of nanostructure

J. Ma*, O. Delaire*, *et al.*, ***Nature Nanotechnology*** 8, 445 (2013)

Ma, Delaire *et al.* ***Phys. Rev. B*** 90, 134303 (2014)

$AgSbTe_2$ *vs* PbTe: the importance of nanostructure



Why are the thermal conductivities of PbTe and $AgSbTe_2$ so different?

"Ioffe-Regel limit"
= *minimum* lattice thermal conductivity

(mean-free-paths of phonons cannot be smaller than interatomic distance)

Morelli *et al.* PRL 2008

Ma*, Delaire* *et al.* Nature Nanotechnology 2013

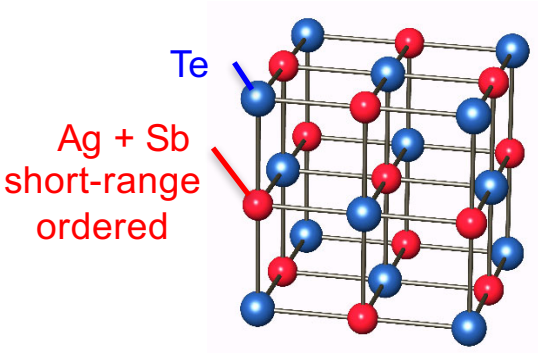
$AgSbTe_2$: glass-like κ_{lat}, but not minimum

- Estimate thermal conductivity from INS data:

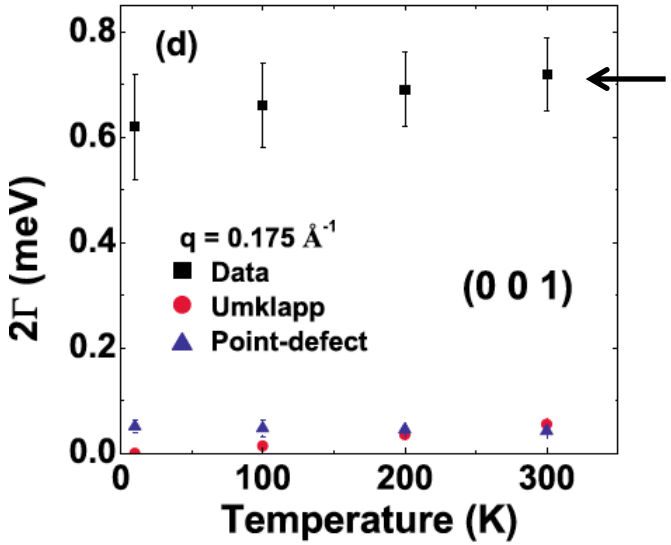
  Transport: κ_{lat} = **0.7 $Wm^{-1}K^{-1}$** at 300K

  From INS: κ_{lat} = **0.8 ± 0.15 $Wm^{-1}K^{-1}$** at 300K

- INS shows broad linewidths (but not fully damped), independent of temperature: *structural scattering*



➔ INS provides *microscopic view on thermal transport.*



← Linewidth independent of T (INS)

↓

Anharmonicity **not** dominant for T<300K (≠ Morreli's conjecture)

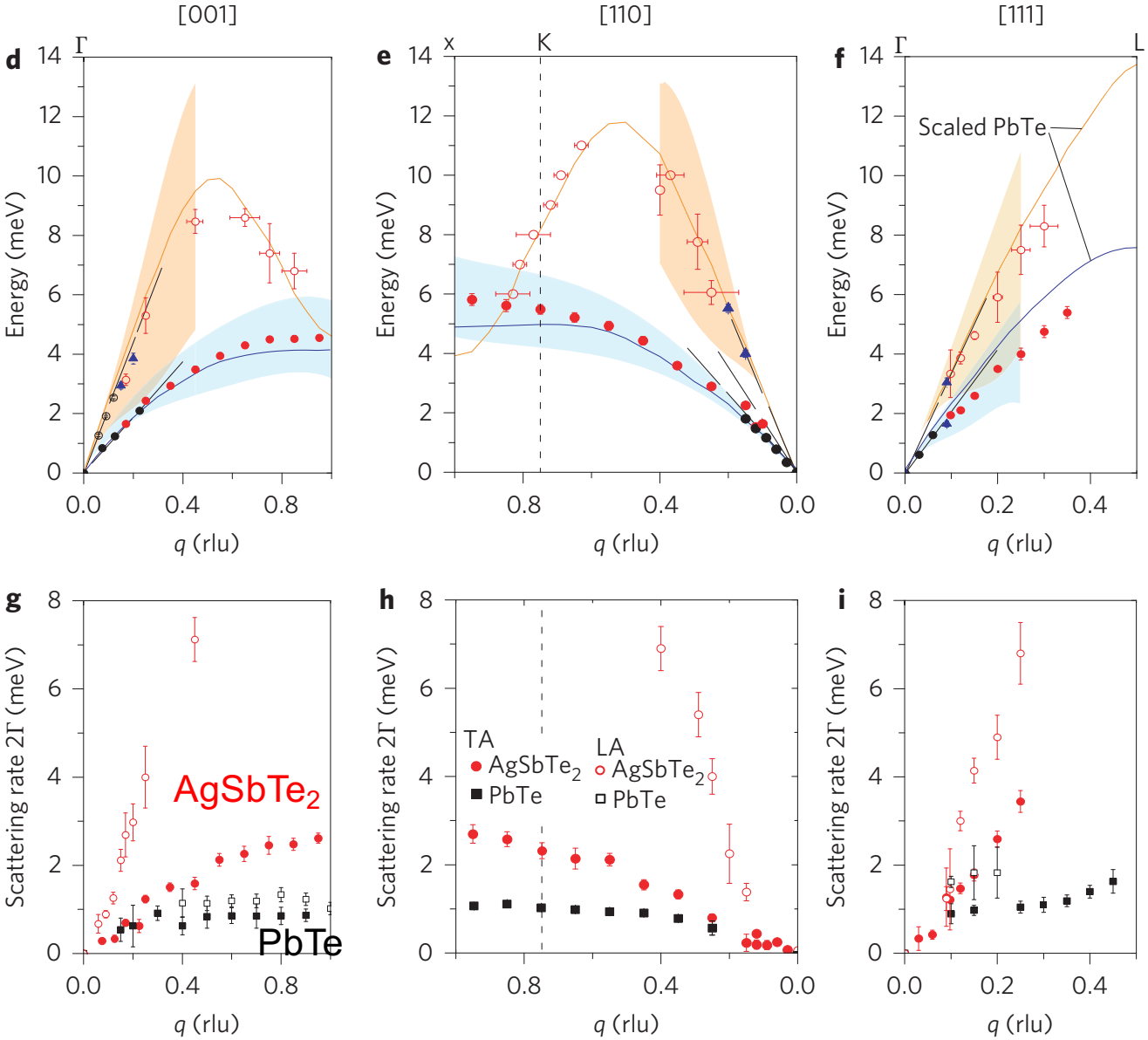
Ma*, Delaire* *et al.* Nature Nanotechnology 2013

$AgSbTe_2$ phonon dispersions and lifetimes

Mapped dispersions in $AgSbTe_2$ (INS):

dispersions similar to PbTe (scaled by $M^{½}$).

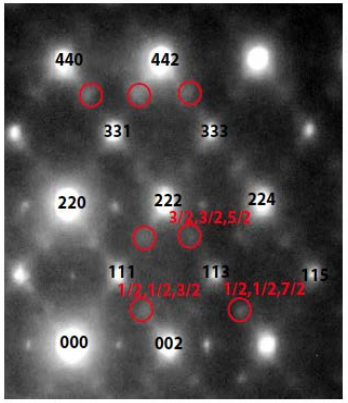
Scattering rates are much larger in $AgSbTe_2$ *than in PbTe.*



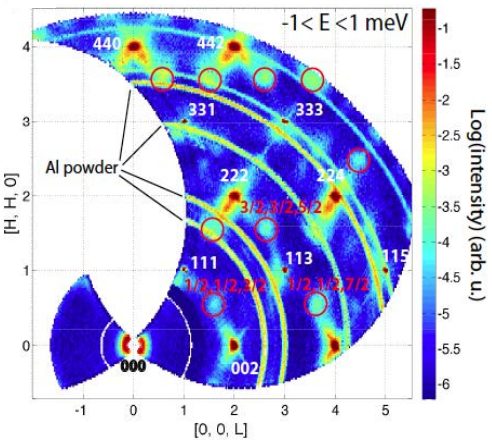
Diffraction reveals nano-scale ordering

- Short-range ordering of Ag/Sb seen with neutrons, x-rays, and TEM, agreement with DFT prediction (Barabash PRL 2008).
- Superlattice half-integer peaks (cation ordering), rods along <111>, and lobes.
- Ordering correlation length ξ~3nm. Nanoscale ordering twins distort lattice.

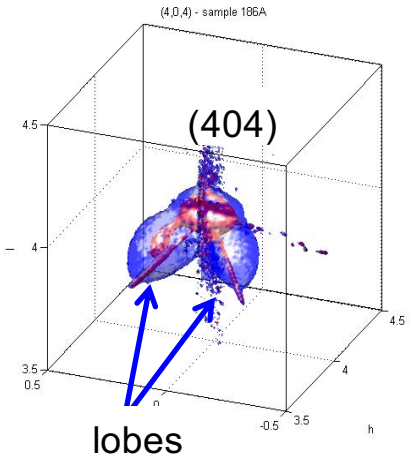
TEM diffraction:
diffuse + superlattice
(1,-1,0) reciprocal plane

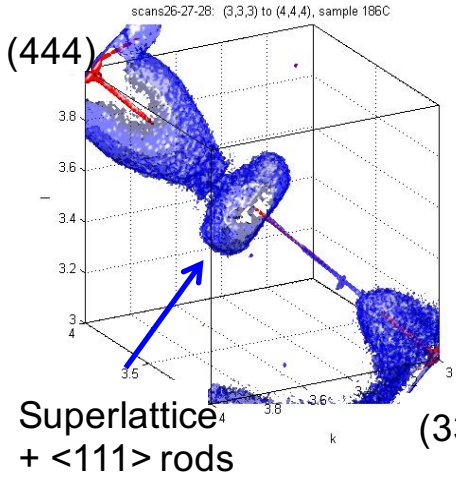


Neutron elastic scattering:
diffuse + superlattice
(1,-1,0) reciprocal plane



X-ray diffuse scattering (APS 33BM):
superlattice + lobes + <111> rods



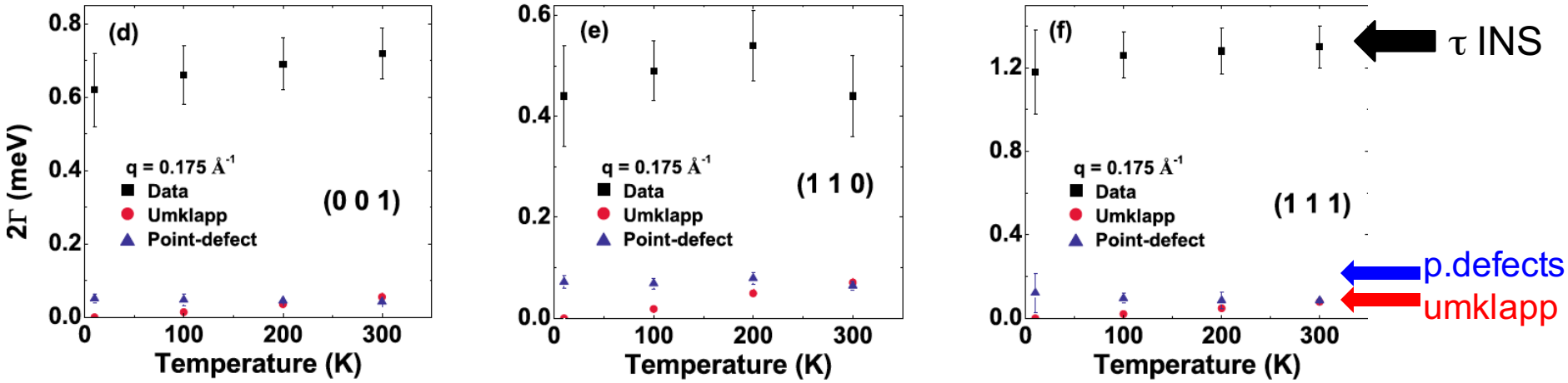


Ma, Delaire *et al.* Nature Nano 2013

Ma, Delaire *et al.* PRB 2014

Temperature dependence of linewidths

- Phonon linewidths (scattering rates) **constant** with temperature ≠ anharmonic.
- Measured widths much larger than umklapp or point-defect contributions.



Umklapp $$\tau_u^{-1} \approx \frac{\hbar\gamma^2}{Mv^2\theta_D}\omega^2 T exp(-\frac{\theta_D}{3T})$$

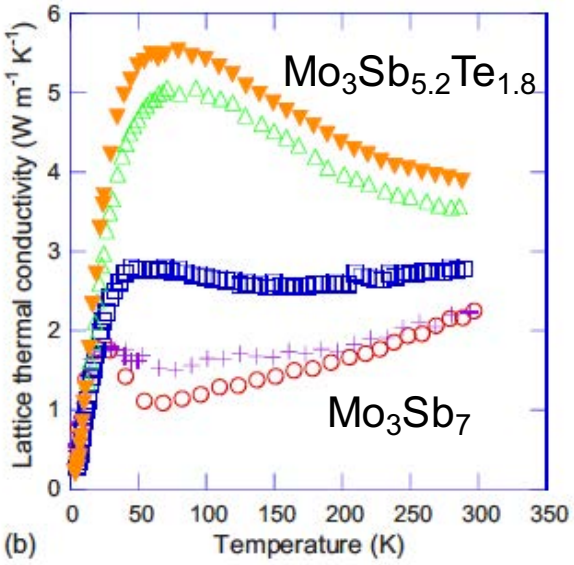
With measured ω, θ_D, v, and γ=2.1

Point-defects $$\tau_{p.d.}^{-1} = \frac{V}{4\pi v^3}\omega^4 \sum_i f_i[\frac{\bar{m}-m_i}{\bar{m}} + \frac{2(\bar{k}-k_i)}{\bar{k}}]^2$$

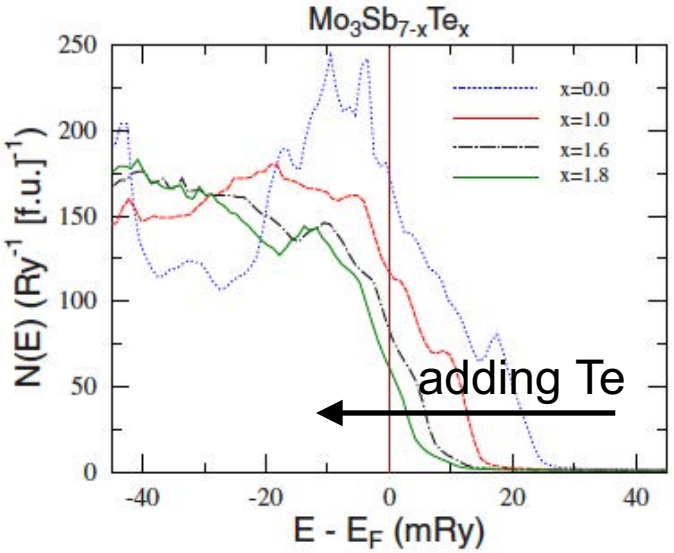
With calculated k_{Sb}/k_{Ag}~2
And 5% vacancies

Electron-phonon coupling in $Mo_3Sb_{7-x}Te_x$

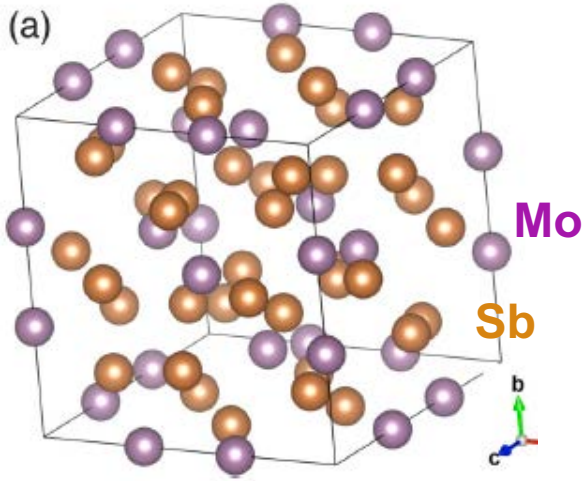
Lattice thermal conductivity vs Te-alloying



Valence band filling with Te substitution



From: Candolfi *et al.* Phys. Rev. B 79, 235108 2009



20 atoms in conventional cubic cell

Structural transition (cubic>tetra) below 53K

PHYSICAL REVIEW B **92**, 214301 (2015)

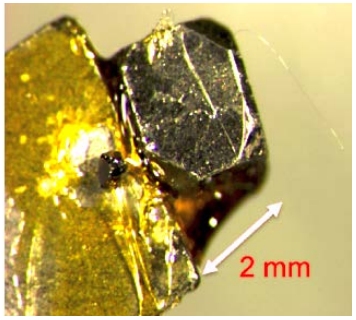
Electron-phonon coupling and thermal transport in the thermoelectric compound $Mo_3Sb_{7-x}Te_x$

Dipanshu Bansal,[1,*] Chen W. Li,[1] Ayman H. Said,[2] Douglas L. Abernathy,[3] Jiaqiang Yan,[1,4] and Olivier Delaire[1,†]

Te-alloying in $Mo_3Sb_{7-x}Te_x$ shows stiffening of phonon dispersions and DOS.

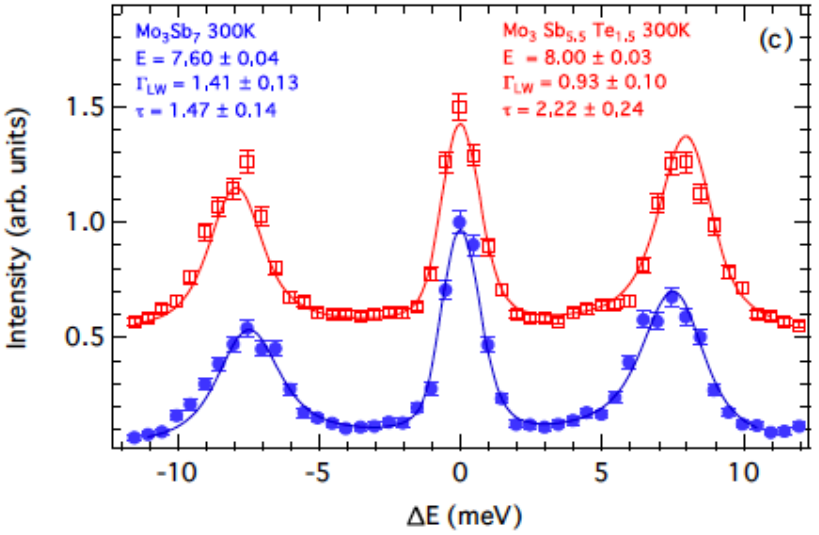
Studied with combination of IXS on small crystals (for dispersions) and INS on powders (for DOS).

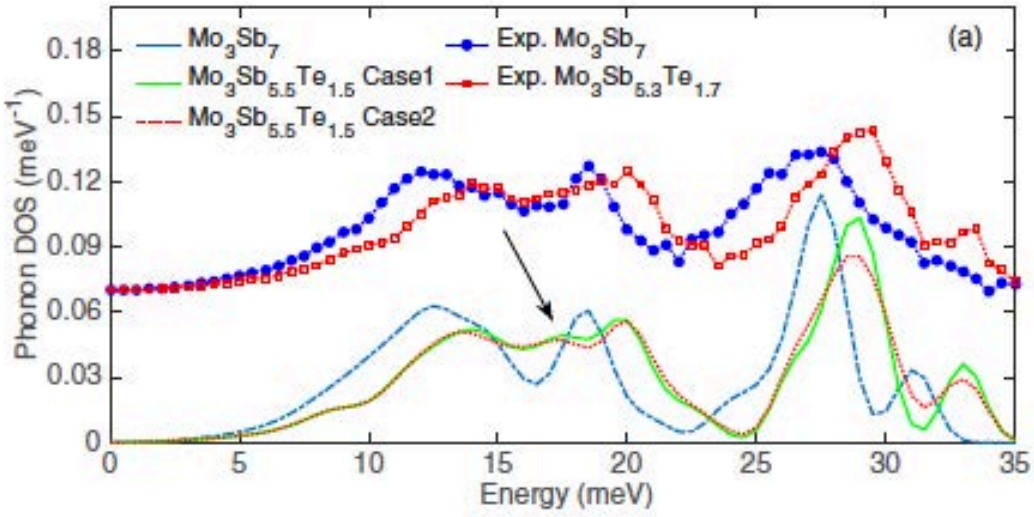
Te-alloying fills valence band and decreases electronic density, suppressing electron-phonon coupling.



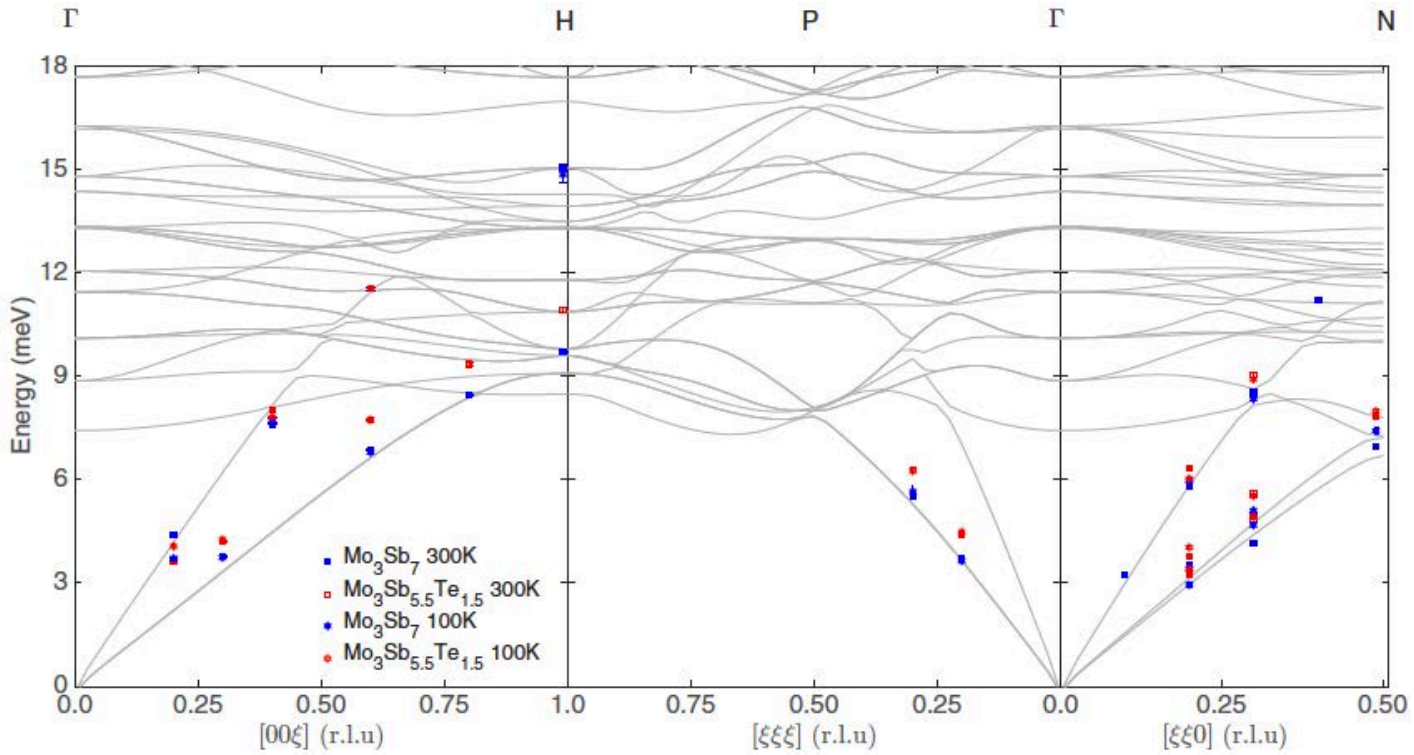
2mm crystal in reflection geometry

Measured on HERI





Comparison with DFT dispersions

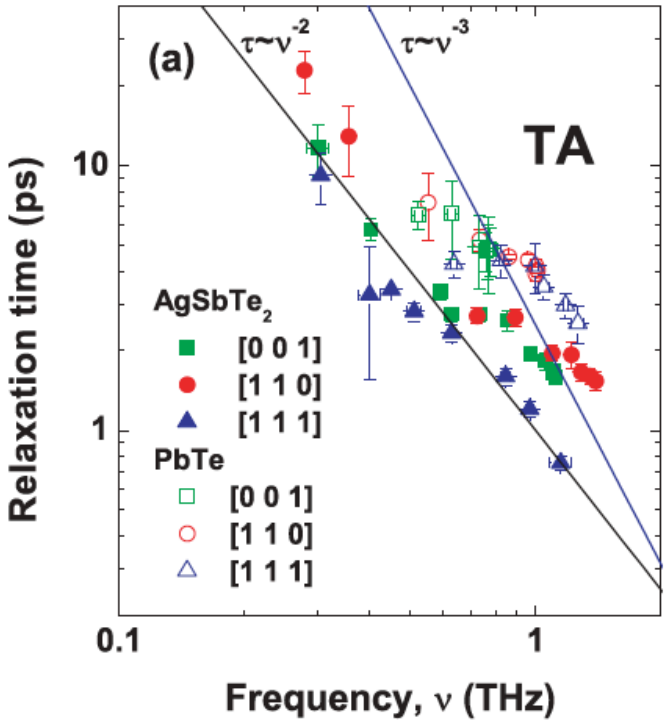


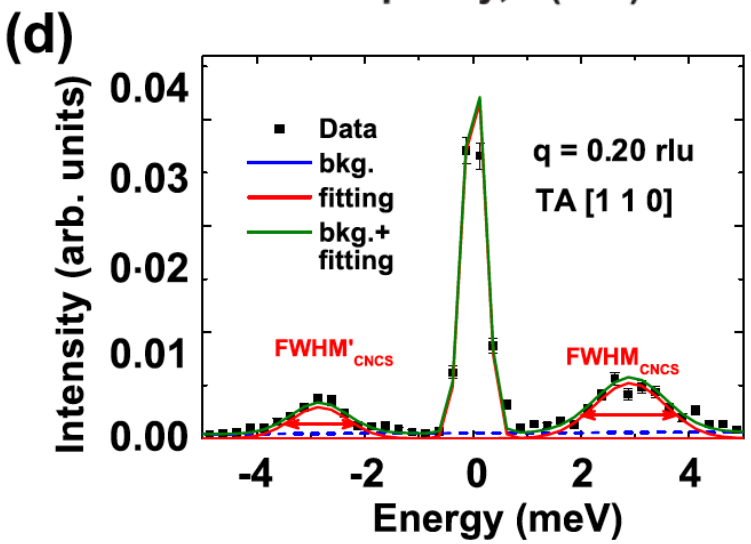
First-principles (DFT) simulations achieve good agreement with IXS

But need experimental data on linewidths to push theory:
combined anharmonicity, electron-phonon, disorder, spin-phonon scattering

Challenges ahead:

- Necessary to analyze many mode linewidths to validate theory: need automatization of resolution corrections
- Need better E-resolution ~10-50μeV for longer phonon lifetimes, in materials with larger thermal conductivities >10 W/(m.K)
- Monte-Carlo modeling of Q-E resolution and multiple scattering effects with scattering kernels including phonon relaxation (with Jiao Lin).





Conclusions

- Combined IXS / INS experiments and DFT simulations provide powerful insights.
- Opportunities to investigate phonon scattering mechanisms and push theoretical modeling.
- Strong anharmonicity near lattice instabilities in chalcogenide thermoelectrics (displacive transitions with soft-modes), electron-phonon coupling, spin-phonon coupling.
- **High-resolution and high-intensity IXS are *timely* and *needed*.**

Thank You