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

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Neutron and X-ray Spectrometers

**Neutron time-of-flight:**
- ARCS at SNS: ~10^5 pixels, ~10^4 time channels each.
- Beam ~ 5cm, ΔE/E ~5%

**Inelastic X-ray Spectrometer:**
- HERIX at APS: ~10 detectors.
- Beam ~30 μm ; E_i = 23.7 keV
- Resolution ~1.5 meV, constant with E
S(Q,E) mapping with INS

- 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

Niobium single crystal
ARCS, \(E_i = 50\) meV, mass~10g
\(T = 300K\)
Phonon Transport in Thermoelectrics

- Bansal, Hong, Li, May, and Delaire *Phys. Rev. B* 94, 054307 (2016)
Thermal conductivity in thermoelectrics

• Suppress lattice thermal conductivity $\kappa_{\text{lat}}$ to optimize thermoelectric efficiency:

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

S: Seebeck ; $\sigma$: el. conductivity
$\kappa$: thermal conductivity

• Rationalize *microscopic origins* of $\kappa_{\text{lat}}$ to gain control over phonon transport:

$$K_{q,j} = \frac{1}{3} C_{q,j} \nu_{q,j}^2 \tau_{q,j}$$

$K = \sum_{q,j} K_{q,j}$

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.

\[
\Lambda_{q,j} = v_{q,j} \tau_{q,j}
\]

Thermal conductivity and INS measurements of phonon linewidths

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

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

Matthiessen’s rule:

\[ \tau^{-1}_{tot} = \tau^{-1}_{anh} + \tau^{-1}_{el-ph} + \tau^{-1}_{defect} + \tau^{-1}_{boundary} + \ldots \]
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: VO₂ T-dependent
  - Experiment
    - R-phase
  - Theory
    - (a)

- PbTe, SSRL with D. Reis’ group, Stanford/SLAC
  - DFT
    - (b)

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

- 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

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

http://camm.ornl.gov
PbTe: strong phonon anharmonicity near ferroelectric instability

Delaire, Ma et al., *Nature Materials* 10, 614 (2011)
Li, Ma, Delaire et al. *Phys. Rev. B* 90, 214303 (2014)
Anharmonicity in rocksalt PbTe

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

Delaire, Ma et al., Nature Materials 2011

CNCS @ SNS (12meV)  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


• Diffuse scattering entirely from phonons (THz timescale)

![Image of diffuse scattering over time]

**Figure 1 | Femtosecond x-ray diffuse scattering from PbTe.** a, Reference scattering from PbTe prior to photoexcitation; b, τ = 0 ps; c, τ = 0.5 ps; d, τ = 2.5 ps

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 $\Gamma$, stiffens with increasing T.
- Double-peak structure, with strong T-dependence.

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

Neutron spectra as probes of many-body effects

- Dynamical susceptibility:
\[
\chi''_{q,j}(\Omega) = |F(Q, \Omega)|^2 \times \\
\{ \Omega^2 - \omega_{q,j}^2 - 2\omega_{q,j} \Delta_{q,j}(\Omega) \}^2 + 4\omega_{q,j}^2 \Gamma_{q,j}(\Omega)^2
\]

- Look for minima in \{\ldots\}

- Multiple crossings lead to multiple peaks in the INS spectra for \(\chi''(E)\)

- \(\Delta_{q,j}(\Omega)\) obtained from anharmonic interatomic force-constants.
Phonon “nesting” increases phase-space for acoustic-optic scattering of TO mode

Imaginary part of self-energy (damping):

\[ \Gamma_{j}(\Omega) = \frac{18}{\hbar^2} \sum_{q_1 q_2 j_1 j_2} |V_{3}(q, q_1 q_2)|^2 \times \]

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

3-phonon interaction strength (transition probability)

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

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

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


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

Important to preserve information about the polarization vectors
FIG. 2. LDA more accurate than GGA (PBE) 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 $a \neq b \neq c$)
- 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.

Li*, Hong*, May, Bansal, Ma, Hong, Chi, Ehlers, and Delaire, Nature Physics 11, 1063 (2015)
SnSe soft-mode behavior of $\text{TO}_c(\Gamma)$

- Many acoustic and optical phonons show strong temperature dependence.
- Lowest zone-center $\text{TO}_c$ mode softens at the phase transition.
- Confirms strong anharmonicity.

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

![SnSe zone-center TOc graph]
Anharmonicity and thermal transport

- SnSe thermal conductivity computed from first-principles.
- Strong influence of cubic terms $\Psi$ within Sn 1NN coordination polyhedron for triplet with Se-Se distance $\sim6\text{Å}$

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

Connect with structure and bonding

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

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
AgSbTe$_2$ : importance of nanostructure

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 $\kappa_{\text{lat}}$, but not minimum

- Estimate thermal conductivity from INS data:
  
  Transport: $\kappa_{\text{lat}} = 0.7$ Wm$^{-1}$K$^{-1}$ at 300K
  
  From INS: $\kappa_{\text{lat}} = 0.8 \pm 0.15$ Wm$^{-1}$K$^{-1}$ at 300K

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

$\rightarrow$ INS provides microscopic view on thermal transport.

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$^{1/2}$).

**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 $\xi \sim 3\text{nm}$. 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.

\[ \tau^{-1} \approx \frac{\hbar \gamma^2}{M v^2 \theta_D} \omega^2 T \exp(-\frac{\theta_D}{3T}) \]

With measured \( \omega, \theta_D, v, \) and \( \gamma=2.1 \)

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

With calculated \( k_{Sb}/k_{Ag} \sim 2 \) And 5% vacancies
Electron-phonon coupling in $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$

Lattice thermal conductivity vs Te-alloying

Valence band filling with Te substitution


20 atoms in conventional cubic cell

Structural transition (cubic>tetra) below 53K
Te-alloying in Mo$_3$Sb$_{7-x}$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.
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 $\sim 10-50 \mu$eV for longer phonon lifetimes, in materials with larger thermal conductivities $>10 \text{ W/(m.K)}$

• 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