Final Technical Report

DOE award DE-SC0019252
Alexandra Zevalkink (PI), Michigan State University

and

DOE award DE-SC0019299
Olivier Delaire (co-PI), Duke University

Tuning anisotropic bonding via chemistry and pressure in layered pnictides and chalcogenides

Sponsoring Program Office:
U.S. Department of Energy, Office of Science, Basic Energy Sciences,
Materials Sciences and Engineering Division

Period covered by the report: 8/16/2018 – 8/15/2022

Executive Summary

The overarching goal of this research program, as originally delineated in the proposal "Tuning anisotropic bonding via chemistry and pressure in layered pnictides and chalcogenides" was to develop a predictive, chemistry-driven understanding of the impact of the phonon behavior on thermal properties of bulk layered materials. At finite temperatures, atomic vibrations (phonons) strongly impact the thermodynamics, thermal and electrical transport, and phase-switching properties of functional materials. In particular, soft phonon modes and strongly anharmonic potentials can have spectacular consequences, including structural phase transitions (for example in ferroelectrics and phase-change memory materials), metal-insulator transitions, and extreme thermal resistance preventing heat propagation.

Bulk materials with highly-anisotropic bonding may provide unique strategies to induce soft-phonon modes and lattice instabilities. Recently, increasingly detailed investigations of the lattice dynamics in layered materials have been made possible by the advent of first-principles phonon calculations and advanced characterization techniques based on neutron and X-ray scattering. However, due to the lack of studies in which composition and bonding character are systematically varied, there are still fundamental questions regarding the impacts of anisotropic bonding and anharmonicity on lattice stability and thermal transport. One of the major goals of this research program is therefore to address this gap by coherently tuning bonding anisotropy and anharmonicity across families of related compounds. Such approaches have revealed new strategies for exploiting structural anisotropy in quasi-1D and 2D bulk materials to obtain tailored functional properties.

This project systematically explored the lattice dynamics, phase stability, and transport properties in bulk layered materials by using both composition and applied pressure to tune the degree of bonding anisotropy and anharmonicity. To accomplish this work, we combined i) single-crystal growth of key material systems with tunable anisotropy, ii) in-situ high-temperature/high-pressure characterization of structure and phonons to probe bonding anisotropy and anharmonicity, including state-of-the-art inelastic X-ray scattering (IXS) and inelastic neutron scattering (INS), and iii) first-principles simulations leveraging large-scale computing to identify the fundamental origins of the observed effects, by relating atomic structure and dynamics to electronic orbital interactions. Finally, we modeled and verified the impact of the phonon behavior on thermal transport to identify new strategies for a-priori design of thermal conductivity. Our integrated collaborative approach helped to systematically unravel the effects of anisotropy and bonding anharmonicity on phonon transport, thermodynamics, and thermal properties of complex anisotropic materials.

Publications resulting from award DE-SC0019252 and DE-SC0019299

1. W. Peng, D. M. Smiadak, M. G. Boehlert, S. Mather, J. Williams, D. T. Morelli, A. Zevalkink, Lattice Hardening Due to Vacancy Diffusion in $(GeTe)_mSb_2Te_3$ Alloys*, J. Applied Physics*, 126 (5), 055106, (**2019**). https://doi.org/10.1063/1.5108659

2. T. Lanigan-Atkins, S. Yang, J. L. Niedziela, D. Bansal, A. F. May, A. A. Puretzky, J.Y.Y. Lin, D. Pajerowski, T. Hong, S. Chi, G. Ehlers, and O.Delaire. "Extended anharmonic collapse of phonon dispersions in SnS and SnSe", *Nature Communications* 11 (1), 1-9 (**2020**). https://doi.org/10.1038/s41467-020-18121-4

3. J. Ding, J. L. Niedziela, D. Bansal, J. Wang, X. He, A. F. May, G. Ehlers, D. L. Abernathy, A. Said, A. Alatas, Y. Ren, G. Arya, and O. Delaire, "Anharmonic lattice dynamics and superionic transition in $AgCrSe_2$", *PNAS* 117 (8) 3930-3937 (**2020**). https://doi.org/10.1073/pnas.1913916117

4. J. L. Niedziela, D. Bansal, J. Ding, T. Lanigan-Atkins, C. Li, A. F. May, H. Wang, J. Y. Y. Lin, D. L. Abernathy, G. Ehlers, A. Huq, D. Parshall, J. W. Lynn, and O. Delaire, "Controlling phonon lifetimes via sublattice disordering in $AgBiSe_2$", *Phys. Rev. Materials* 4, 105402 (**2020**). https://doi.org/10.1103/PhysRevMaterials.4.105402

5. X. Tan, J. Ding, H. Luo, O. Delaire, J. Yang, Z. Zhou, J. Lan, Y. Lin, C. Nan, "High thermoelectric performance of $AgSb_{1-x}Pb_xSe_2$ prepared by fast non-equilibrium synthesis", *ACS Applied Materials & Interfaces*, 12, 37, 41333–41341 (**2020**). https://doi.org/10.1021/acsami.0c10508

6. A. Balodhi, K. Chang, K. T. Stevens, S. K. Chakrapani, S. M. Ennaceur, A, Migliori, A. Zevalkink, "Determination of single crystal elastic moduli of KTb_3F_{10} by resonant ultrasound spectroscopy", *J. Applied Physics*, 128, 165104 (**2020**). https://doi.org/10.1063/5.0024723

7. Z. Ye, W. Peng, F. Wang, A. Balodhi, R. Basnet, J. Hu, A. Zevalkink, J Wang, "Quasi-layered Crystal Structure Coupled with Point Defects Leading to Ultralow Lattice Thermal Conductivity in n-Type $Cu_{2.83}Bi_{10}Se_{16}$", *ACS Applied Energy Materials* 4 (10), 11325-11335, (**2021**). https://doi.org/10.1021/acsaem.1c02154

8. A. J. E. Rettie, J. Ding, X. Zhou, M. J. Johnson, C. D. Malliakas, N. C. Osti, D. Y. Chung, R. Osborn, O. Delaire, S. Rosenkranz, M. G. Kanatzidis, "A two-dimensional type I superionic conductor", Nature Materials 20, 1683–1688 (**2021**). https://doi.org/10.1038/s41563-021-01053-9

9. J. Ding, T. Lanigan-Atkins, M. Calderon-Cueva, A. Banerjee, D. L. Abernathy, A. Said, A. Zevalkink, and O. Delaire, "Soft anharmonic phonons and origin of ultralow thermal conductivity in Mg_3Sb_2 and Mg_3Bi_2", *Science Advances* 7:eabg1449 (**2021**). https://doi.org/10.1126/sciadv.abg1449

10. T. Lanigan-Atkins*, X. He*, M. J. Krogstad, D. M. Pajerowski, D. L. Abernathy, Guangyong NMN Xu, Zhijun Xu, D.-Y. Chung, M. G. Kanatzidis, S. Rosenkranz, R. Osborn, and O. Delaire, "Two-dimensional overdamped fluctuations of soft perovskite lattice in $CsPbBr_3$", *Nature Materials* 20, 977–983 (**2021**), https://doi.org/10.1038/s41563-021-00947-y

11. M. Calderón-Cueva, W. Peng, S. M. Clarke, J. Ding, B. L. Brugman, G. Levental, A. Balodhi, M. Rylko, O. Delaire, J. P. S. Walsh, S. M. Dorfman, and A. Zevalkink

"Anisotropic Structural Collapse of Mg_3Sb_2 and Mg_3Bi_2 at High Pressure", *Chemistry of Materials* 33, 2, 567–573 (**2021**) https://dx.doi.org/10.1021/acs.chemmater.0c03678

12. J. Wang, J. Ding, O. Delaire, G. Arya, "Atomistic mechanisms underlying non-Arrhenius ion transport in superionic conductor $AgCrSe_2$", *ACS Applied Energy Materials*, 4, 7, 7157 (**2021**). https://doi.org/10.1021/acsaem.1c01237

13. M. Beekman, A. J. Karttunen, W. Wong-Ng, M. Zhang, Y.-S. Chen, C. Posadas, A. Jarymowycz, E. Cruse, W. Peng, A. Zevalkink, J. A. Kaduk, and G. S. Nolas, Thermal and mechanical properties of the clathrate-II $Na_{24}Si_{136}$, *Phys. Rev. B* 105, 214114 (**2022**). https://doi.org/10.1103/PhysRevB.105.214114

14. M. K. Gupta, J. Ding, D. Bansal, D. L. Abernathy, G. Ehlers, N. C. Osti, W. G. Zeier, O. Delaire, "Strongly Anharmonic Phonons and Their Role in Superionic Diffusion and Ultralow Thermal Conductivity of Cu_7PSe_6", *Advanced Energy Materials* 12, 2200596 (**2022**). https://doi.org/10.1002/aenm.202200596

15. A. Balodhi, J. Torres, R. Juneja, K. B. Chang, A. Brady, S. K. Chakrapani, L. R. Lindsay, Raphael P. Hermann, and Alexandra Zevalkink, Determination of single-crystal elastic moduli of $LiREF_4$ (RE=Y, Gd, and Tb) by resonant ultrasound spectroscopy, *Journal of Applied Physics* 132, 175110 (**2022**). https://doi.org/10.1063/5.0109940

16. W. Isotta, W. Peng, A. Balodhi, A. Zevalkink, "Elastic moduli: a tool for understanding chemical bonding and thermal transport in thermoelectric materials", *Submitted* (**2022**)

17. E., Michael Toriyama, R. Shupp, J. Snyder, A. Zevalkink, Effect of Sn oxides on the thermal conductivity of polycrystalline SnSe, *Submitted* (**2022**)

18. M. Calderón-Cueva, E. Isotta, M. Rylko, B. Mukherjee, P. Scardi, Alexandra Zevalkink, "Influence of crystal structure and composition on thermal conductivity of GeSe-$AgBiSe_2$ Alloys", *Submitted* (**2022**)

Other Products from award DE-SC0019252 and DE-SC0019299

During the course of this award, the PI's and personnel supported by the award (postdoctoral scholars and graduate students) have delivered more than 40 contributed and invited presentations at national and international meetings on work supported by this award. These include the March Meeting of the American Physical Society (APS), the American Conference on Neutron Scattering (ACNS), and the Materials Research Society (MRS) Meeting, the North American Solid State Chemistry Conference (NASSCC), and the TMS meeting.

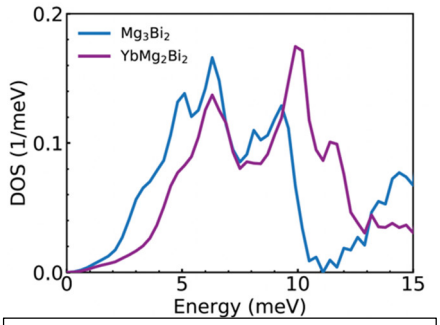
Personnel funded by DE-SC0019252 at Michigan State University

Over the course of this award the project PI (Alexandra Zevalkink), two post-doctoral researchers, two doctoral students, one M.S. student, and two undergraduate researchers were supported in part

or in full by these DOE funds. Both postdoctoral researchers are currently continuing their postdoctoral work at other US institutions in research areas related to thermal transport and phonon dynamics. One of the graduate students and the M.S. student are now working as research scientists in the US semiconductor industry, and the other graduate student plans to pursue postdoctoral work in high-pressure chemistry.

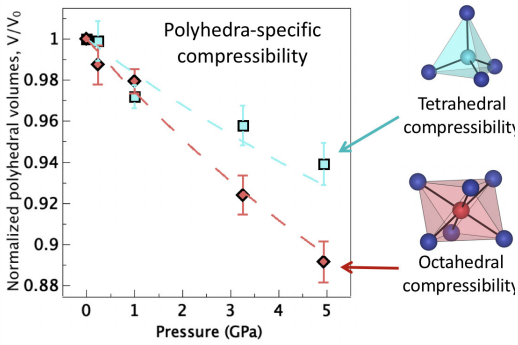
Review of Technical Achievements

Phonons and origin of ultralow thermal conductivity in Mg_3Pn_2: Mg_3Sb_2 and Mg_3Bi_2 exhibit an anomalously low thermal conductivity, comparable to those of much heavier compounds PbTe or Bi_2Te_3. Contrary to common mass-trend expectations, replacing Mg with much heavier Ca or Yb yields a threefold increase in thermal conductivity in ternary $CaMg_2Sb_2$ and $YbMg_2Bi_2$. We performed a comprehensive analysis of phonons in the series AMg_2X_2 (A = Mg, Ca, Yb, X = Bi, Sb) based on inelastic neutron and x-ray scattering, complemented with first-principles simulations, and showed for the first time that the anomalously low lattice thermal conductivity of Mg_3X_2 has an inherent phononic origin. We uncovered a large phonon softening and flattening of low-energy transverse acoustic phonons in Mg_3Bi_2 and Mg_3Sb_2 compared to the ternary analogues (A = Ca, Yb). Our first-principles simulations revealed how this is traced to a weak Mg-X chemical bond, which softens low-energy transverse acoustic phonons. While the suppression in group velocity reduces κ_{lat} by a modest 20%, the soft anharmonic dispersion enables a threefold increase in phonon scattering primarily by enhancing the scattering phase-space. These findings rationalize the microscopic origins of the outstanding thermal properties of AMg_2X_2 compounds, and provide fundamental insights on means to control thermal transport properties, by manipulating phonon scattering without the traditional reliance on heavy elements or disorder. This work was published in Science Advances [9].



Low-energy phonon density of states of Mg_3Bi_2 and $YbMg_2Bi_2$ measured with neutron scattering.

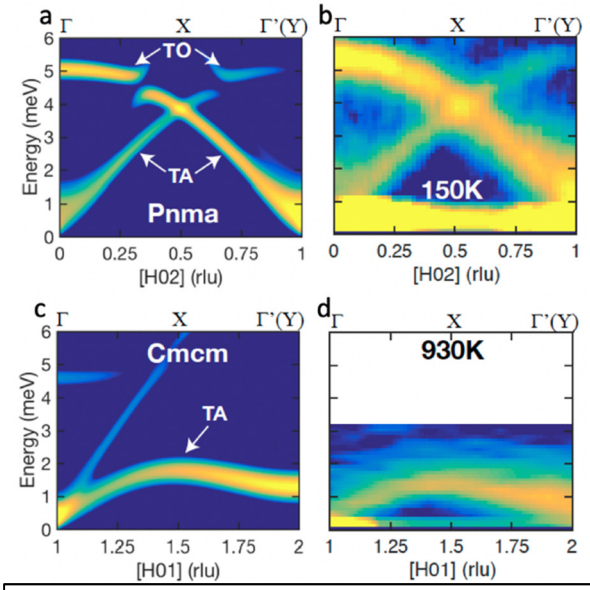
Investigation of Mg_3Pn_2 at high-pressures: In this study, in-situ high-pressure synchrotron x-ray diffraction was used to investigate the structure and bonding in Mg_3Sb_2 and Mg_3Bi_2 at pressures up to 50 GPa. Our results confirmed prior predictions of isotropic in-plane and out-of-plane compressibility but revealed large disparities between the bond strength of the two distinct Mg sites. Using single crystal diffraction, we showed that the octahedral Mg-Sb bonds are significantly more compressible than the tetrahedral Mg-Sb bonds in Mg_3Sb_2, which lends support to arguments that the weaker octahedral Mg bonds are responsible for the anomalous thermal properties of Mg_3Sb_2 and Mg_3Bi_2. Further, we reported the discovery of a displacive and reversible phase transition in both Mg_3Sb_2 and Mg_3Bi_2 above 7.8 GPa and 4.0 GPa, respectively. The



Octahedral Mg–Sb bonds are significantly more compressible than the tetrahedral Mg–Sb bonds in Mg_3Sb_2

transition to the high-pressure structure involves a highly anisotropic volume collapse, in which the out-of-plane axis compresses significantly more than the in-plane axes. Single crystal diffraction at high pressure was used to solve the monoclinic high-pressure structure ($C2/m$), which is a distorted variant of the ambient-pressure structure containing four unique Mg coordination environments. This work was published in Chemistry of Materials [11].

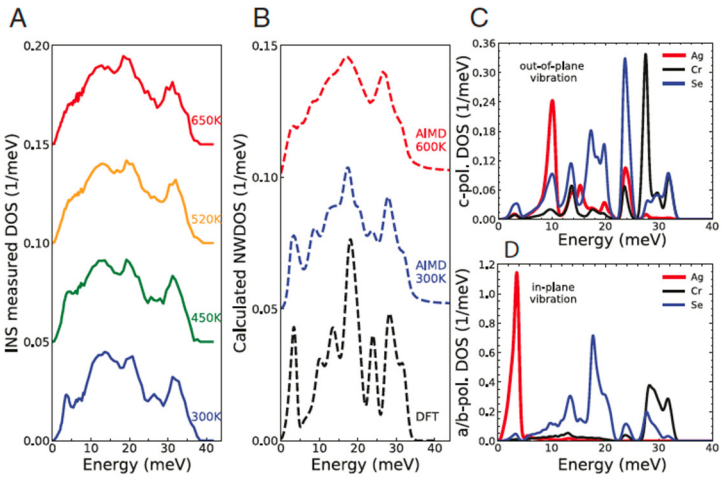
Anisotropic bonding, phonon anharmonicity and ultralow thermal conductivity in SnS: The lattice dynamics and high-temperature structural transition in SnS and SnSe were investigated via inelastic neutron scattering, high-resolution Raman spectroscopy and first-principles simulations. The results revealed a spectacular, extreme softening and reconstruction of an entire manifold of low-energy acoustic and optic branches across a structural transition, reflecting strong directionality in bonding strength and anharmonicity. Further, our results solved a prior controversy by revealing the soft-mode mechanism of the phase transition that impacts thermal transport and thermoelectric efficiency. Our simulations of anharmonic phonon renormalization captured these striking effects, showing that the large phonon shifts directly affect the thermal conductivity by altering both the phonon scattering phase space and the group velocities. These results provide a new level of microscopic understanding of phase stability and thermal transport in technologically important materials, providing further insights on ways to control phonon propagation in thermoelectrics, photovoltaics, and other materials requiring thermal management. The results were published in Nature Communications [2].



Phonon dispersions of the *Pnma* low-temperature phase (a,b) and *Cmcm* high-temperature phase (c,d) of thermoelectric compound SnS. Panels (a,c) are first-principles simulations, and (b,d) are inelastic neutron scattering data. A strong renormalization is seen, leading to flat, low-energy dispersions at high temperature, favoring low thermal conductivity.

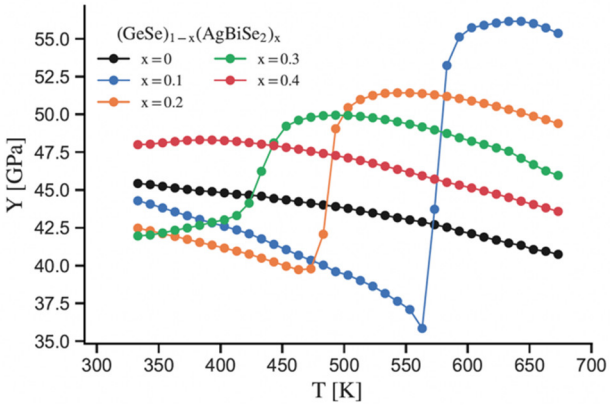
Anharmonic lattice dynamics and superionic transition in layered chalcogenide $AgCrSe_2$: Unveiling the unusual atomic dynamics in superionic conductors is critical for the design of energy conversion and storage materials, for example to rationalize their thermal transport properties in thermoelectric applications or their fast ionic conductivity in solid-state electrolytes. Intrinsically low lattice thermal conductivity (κ_{lat}) in superionic conductors is of great interest for energy conversion applications in thermoelectrics. Yet, the complex atomic dynamics leading to superionicity and ultralow thermal conductivity have remained poorly understood. We performed a comprehensive study of the lattice dynamics and superionic diffusion in AgCrSe2 from energy- and momentum-resolved neutron and X-ray scattering techniques, combined with first-principles calculations. Our results settled unresolved questions about the lattice dynamics and thermal

conduction mechanism in $AgCrSe_2$. We found that the heat-carrying long-wavelength transverse acoustic (TA) phonons coexist with the ultrafast diffusion of Ag ions in the superionic phase, while the short-wavelength nondispersive TA phonons break down. Strong scattering of phonon quasiparticles by anharmonicity and Ag disorder are the origin of intrinsically low κ_{lat}. The breakdown of short-wavelength TA phonons is directly related to the Ag diffusion, with the vibrational spectral weight associated to Ag oscillations evolving into stochastic decaying fluctuations. Furthermore, the origin of fast ionic diffusion was shown to arise from extended flat basins in the energy landscape and collective hopping behavior facilitated by strong repulsion between Ag ions. These results provide fundamental insights into the complex atomic dynamics of superionic conductors. The results were published in PNAS [3].



Phonon DOS from experiments and simulations. (A) INS powder measurements at the ARCS with Ei =20 and 80 meV to get fine resolution at the low-energy portion and the whole spectrum. Data are stitched together at 9 meV. Blue, green, orange, and red lines are measured at 300, 450, 520, and 650 K, respectively. (B) Calculated neutron-weighted DOS. Black dashed line is labeled as DFT, and AIMD at 300 and 600 K are blue and red dashed lines, respectively. (C and D) Site-projected DOS from DFT for the c-axis polarized (C) and in-plane (D) motions in the a–b plane. Ag motions mainly contribute the strong peak around 3.5 meV for the in-plane vibration and a weaker peak near 10 meV for c-axis. polarizations.

Sublattice disordering in $AgBiSe_2$: The lattice dynamics and thermal transport properties in the end compound $AgBiSe_2$ have been investigated at Duke using a combination of INS measurements, thermal transport and calorimetry measurements, and first-principles simulations. This compound undergoes a sequence of phase transitions on cooling, from a rock-salt disordered phase above 560K to a more layered rhombohedral phase at room temperature. The analysis of the neutron scattering data and modeling of the thermal transport based on DFT phonon simulations revealed a large increase in phonon scattering rates in the disordered phase. A manuscript was published in Physical Review Materials [4].

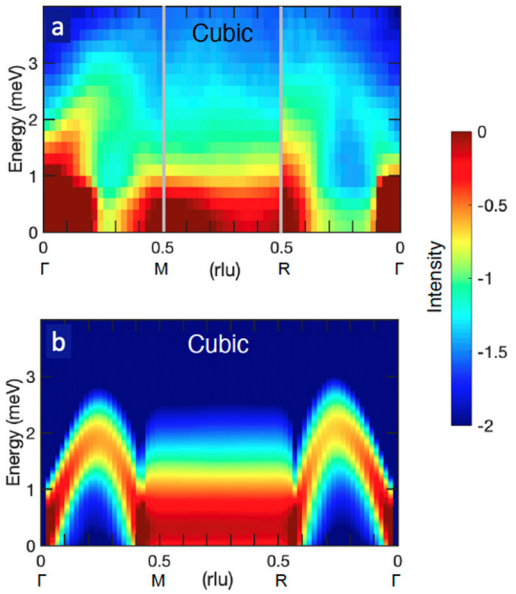


The Young's modulus increases drastically at the rhombohedral to cubic phase transition in $(GeSe)_{1-x}$-$(AgBiSe_2)_x$ alloys. Increasing the $AgBiSe_2$ content, in contrast, has only a modest effect on the moduli.

At MSU, we used a combination of resonant ultrasound spectroscopy and high temperature diffraction experiments to investigate the influence of crystal structure and composition on the lattice thermal properties of the $(GeSe)_{1-x}$-

$(AgBiSe_2)_x$ system. Within a narrow alloying region (0-40% of $AgBiSe_2$), the room-temperature crystal structure progressively transitions from an orthorhombic *Pnma*, to a rhombohedral *R3m*, to a cubic *Fm-3m* arrangement, with marked consequences on the lattice thermal conductivity. At high temperatures, the cubic rock-salt arrangement is the thermodynamically stable phase across the whole compositional range. In this work, we investigated the elastic behavior of the $(GeSe)_{1-x}$-$(AgBiSe_2)_x$ system to shed light on the respective contributions of chemistry and crystal structure to thermal transport. Within the same structure, alloying progressively reduces the lattice thermal conductivity due to point-defect phonon scattering. An anomalous increase in thermal conductivity with the transition from the rhombohedral to the cubic phase was shown to be correlated with a significant stiffening of the elastic moduli. This manuscript is currently under review. Further, to directly investigate the influence of structure type on phonon behavior in rock salt chalcogenides, single crystals in the $(GeSe)_{1-x}$-$(AgBiSe_2)_x$ system were grown at MSU using the Bridgman technique and have been used in inelastic neutron scattering measurements. Analysis of these results is ongoing.

Soft perovskite lattice in $CsPbBr_3$: Lead-halide perovskites exhibit structural instabilities and large atomic fluctuations impacting their optical and thermal properties, yet the structural and temporal correlations of their atomic motions remain poorly understood. We have resolved unusual atomic dynamics in $CsPbBr_3$ using momentum-resolved neutron and x-ray scattering measurements as a function of temperature, complemented with first-principles simulations. We performed single crystal inelastic neutron scattering (INS), probing phonons across large swaths of 4D (Q,E) space in all three phases (orthorhombic, tetragonal, cubic). INS data were compared with x-ray diffuse scattering data, both showing pervasive temperature dependent diffuse scattering rods along Brillouin zone (BZ) boundaries. These diffuse rods reveal extended over-damped fluctuations of 2D domains of Br octahedra tilts. We rationalized our observations with anharmonic fist-principles phonon simulations based on ab-initio molecular dynamics (AIMD) performed at NERSC. Our simulations capture the observations and reveal their primary origin in the weak and anharmonic interatomic potential connecting Br atoms across PbBr6 octahedra. Further, the overdamped phonon modes identified here strongly modulate the electronic band edge states and bandgap. These results provide key insights to understand the origin of both the ultralow thermal conductivity and the large amplitude vibrations coupling to the electronic structure. The results were published in Nature Materials [10].



Overdamping of phonon modes along M-R in the cubic phase of CsPbBr3. (a) INS measurements (b) first-principles simulations of anharmonic damping.