Revealing microscopic origin of ultralow lattice thermal conductivity in thermoelectric InTe using inelastic X-ray scattering technique

In the pursuit of advancing technology in fields such as thermal management in electronics, thermal barrier coatings, and thermoelectric (TE) energy conversion, materials with intrinsically low thermal conductivity play a pivotal role. Among these, TE materials require low lattice thermal conductivity (κ_L) to achieve high TE performance, as characterized by the figure of merit (zT). In this context, understanding the microscopic origin of intrinsically low κ_L is crucial for designing efficient materials. Rattlers and lone pair electrons are the two "textbook" concepts developed for understanding intrinsically low thermal conductivity. Each concept has been extensively studied and plays a fundamental role not only in the thermoelectric field but also broadly in condensed matter physics and solid state chemistry. While rattling atoms introduce localized vibration modes [1], lone pair electrons usually induce anharmonicity and lattice distortion. Recent attention has turned to materials combining both rattlers and lone pair electrons with TlSe-type compounds emerging as promising TE materials with intrinsically low κ_L. Among these compounds, the simple crystal structure of InTe exhibits a κ_L approaching the so-called glass limit (~0.3 $Wm^{-1}K^{-1}$) at high temperatures [2] despite its relatively light mass compared with Tl-related analogs, and the detailed origin of the ultralow κ_L remains unknown. In this study, we combined inelastic X-ray/neutron scattering, anharmonic phonon calculations, and quantitative chemical bonding analysis to investigate soft transverse phonons in InTe [3]. Dominated by significant In^{1+} z rattling motions, these phonons exhibit remarkable stiffening upon heating, stemming from a giant anharmonicity rooted in the strong lone pair expression tendency. This tendency, along with unstable antibonding states induced by covalency between delocalized In^{1+} $5s^2$ lone pair electrons and Te $5p$ states, contributes to the material's intrinsically low lattice thermal conductivity. Additionally, we elucidate the weak temperature-dependent lattice thermal conductivity at higher temperatures by correlating it with the observed intense stiffening of anharmonic In^{1+} z phonons and a concurrent decrease in phonon scattering strength.

InTe single crystals were grown by the vertical Bridgman method, where the phase purity was confirmed by Rietveld refinements of synchrotron powder X-ray diffraction data at 90 and 300 K collected at SPring-8 **BL44B2**. The inelastic X-ray scattering (IXS) experiments on a InTe single crystal were performed at the RIKEN Quantum NanoDynamics, SPring-8 **BL43LXU** [4,5], a cutting-edge momentum-resolved inelastic X-ray scattering spectrometer, offering unique access to very small single-crystal samples, with, in the present case, a probed sample volume of <0.1 $mm)^3$. This was particularly valuable for this study due to the small single-domain size induced by the brittle nature of InTe crystals. Si (11 11 11) backscattering was employed at an incident energy of 21.747 keV, with an instrument energy resolution of approximately 1.3 meV. To facilitate parallel data collection, a two-dimensional analyzer array was employed, allowing simultaneous measurements at 28 distinct momentum transfers. The IXS measurements were performed at 50, 100, 200, 300, 500, and 700 K.

To probe the anharmonic phonon modes in InTe, we first conducted theoretical atomic dynamics simulations by combining *ab initio* molecular dynamics

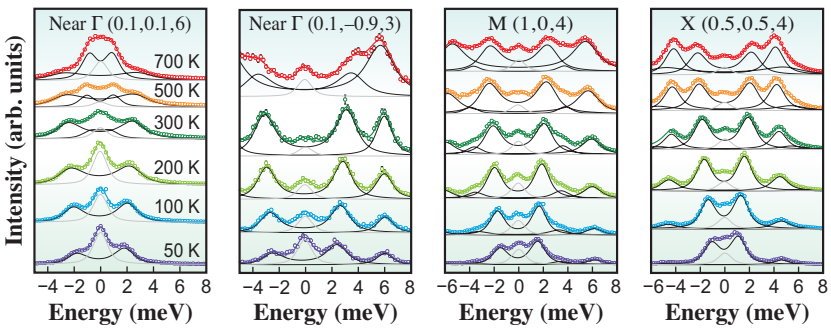

Fig. 1. The temperature dependence of the IXS spectra at Q points of near Γ (0.1,0.1,6), near Γ (0.1,–0.9,3), M (1,0,4), and X (0.5,0.5,4) for probing low-energy (In^{1+} z)-related transverse modes of near ΓO1, near ΓO2, MA1, and XA1, respectively. Open circles and lines with colors represent the IXS spectra and the fits with damped harmonic oscillators, respectively. The black (gray) lines represent the fits to the inelastic (elastic) intensity.

with the temperature-dependent effective potential technique (TDEP). The very large mode Grüneisen parameters as well as the highly-anharmonic frozen phonon potential energy curves reveal giant phonon anharmonicity of low-lying optical and transverse acoustic modes ΓO1, ΓO2, MA1, XA1, and ZO1 dominated by In^{1+} *z* vibrations. To experimentally elucidate these low-lying anharmonic modes, we conducted IXS measurements using carefully selected **Q** points of (0.1,0.1,6), (0.1,–0.9,3), (1,0,4), and (0.5,0.5,4). **Q** points of (0.1,0.1,6) and (0.1,–0.9,3) were used to probe the near ΓO1 and ΓO2 optical modes close to the Brillouin zone center, whereas (1,0,4) and (0.5,0.5,4) were adopted to measure the XA1 and MA1 transverse modes at the zone boundary. The IXS spectra exhibit distinct peaks described by damped harmonic oscillators (Fig. 1). The low-energy phonon dispersion at 300 K aligns well with TDEP simulations (Fig. 2(a)), considering an ideal defect-free structure.

We then explored the temperature dependence of the low-energy phonon modes. Notably, we found that phonon modes such as near ΓO1, near ΓO2, XA1, and MA1 exhibit an anomalously strong stiffening trend with increasing temperature, contrary to the typical softening observed in high-energy phonons with lattice expansion at elevated temperatures (Figs. 2(b,c)). This stiffening, consistent with the inelastic neutron scattering data, is accurately captured by TDEP simulations. The stiffening of rattling modes, commonly observed in rattling systems, is attributed to the rattler's larger thermal motion exploring steeper walls of anharmonic potential surfaces at higher temperatures. In this study, this stiffening behavior has an electronic origin, stemming from the stabilizing effect of lone-pair-induced occupied antibonding states with larger In^{1+} *z* thermal motions. Additionally, the low-energy (In^{1+} *z*)-related modes exhibit clear broadening as temperature rises, in line with significant anharmonic In^{1+} *z* thermal motions.

The momentum-resolved inelastic X-ray scattering data collected at BL43LXU in this research is remarkable as it reveals for the first time the low-energy anharmonic In^{1+} *z* rattling phonon modes as the microscopic origin of the ultralow lattice thermal conductivity in InTe. This comprehensive study not only uncovers the correlation between lone pair electrons on rattlers and lattice anharmonicity but also provides insights into the unique phonon dynamics contributing to ultralow κ_L in InTe. The covalency-driven instability of antibonding states results in highly anharmonic phonon modes, contributing to the exceptional thermal properties of InTe. The combination of experimental techniques and theoretical insights showcased in this study exemplifies a holistic approach to unraveling the complexities of materials at the atomic level, paving the way for designing efficient materials for TE application.

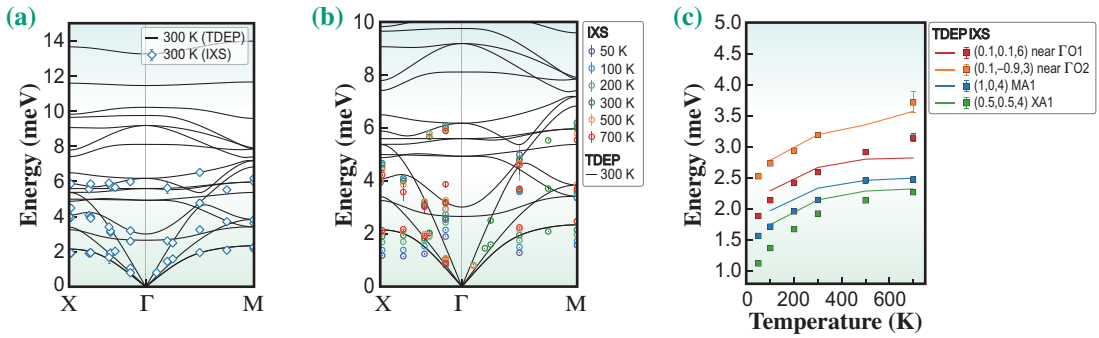

Fig. 2. (**a**) Measured low-energy phonon dispersions by IXS in comparison with the TDEP simulation of InTe at 300 K. (**b**) Measured low-energy phonon dispersions by IXS of InTe at 50, 100, 200, 300, 500, and 700 K. (**c**) Temperature dependence of phonon energies of the low-energy modes at (0.1,0.1,6), (0.1,–0.9,3), (1,0,4), and (0.5,0.5,4).

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