

Impact of noble-gas filler atoms on the lattice thermal conductivity of CoSb₃ skutterudites: first-principles modelling

Jianqin Tang¹ and Jonathan M. Skelton^{1*}

¹ Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

* Corresponding author. E-Mail: jonathan.skelton@manchester.ac.uk.

Abstract

We present a systematic first-principles modelling study of the structural dynamics and thermal transport in the CoSb₃ skutterudites with a series of noble-gas filler atoms. A range of analysis techniques are proposed to estimate the filler rattling frequencies, to quantify the separate impacts of filling on the phonon group velocities and lifetimes, and to show how changes to the phonon spectra and interaction strengths lead to suppressed lifetimes. The fillers are found to reduce the thermal conductivity of the CoSb₃ framework by up to 15 % primarily by suppressing the group velocities of low-lying optic modes. Calculations show that the filler rattling frequencies are determined by a detailed balance of increasing atomic mass and stronger interactions with the framework, and are a good predictor of their impact on the heat transport. Lowering the rattling frequency below ~1.5 THz by selecting heavy fillers that interact weakly with the framework is predicted to produce a much larger suppression of the thermal transport, by inducing avoided crossings in the acoustic-mode dispersion and facilitating resonant scattering with a consequent large reduction in the lifetimes. Approximate rattling frequencies determined from the harmonic force constants may therefore provide a useful metric for selecting filler atoms to optimise the thermal transport in skutterudites and other cage compounds such as clathrates.

1. Introduction

Mitigating climate change by switching to sustainable sources of energy and reducing global greenhouse gas emissions is among the most pressing scientific and technological challenges of the 21st century. As renewable energy technologies such as photovoltaics mature and fossil-fuel power plants are decommissioned, an increasingly large proportion of emissions come from energy-intensive industries and the automotive and transportation sectors.[1] An internal combustion engine wastes up to 60 % of its energy as heat, and a recent estimate found that ~10 % of the greenhouse gas emissions in Europe are from heavy-duty transportation vehicles.[1] A coordinated approach to reducing emissions therefore requires technologies to improve the efficiency of existing energy-intensive processes alongside the expansion of renewable energy.

Thermoelectric generators (TEGs), which make use of the Seebeck effect in a thermoelectric material to extract energy from a temperature gradient and recover some of the otherwise wasted heat as electrical energy, are among the front-running technologies to meet this challenge. TEGs are solid-state devices with no moving parts, and can be deployed at scales from wireless sensors, to vehicle exhausts, to industrial plants, and possibly even as primary renewable power sources.[1] The large amount of global energy wasted as heat means that even modestly efficient TEGs could have a large impact on climate change - for example, a typical nuclear power plant loses ~60 % of its energy as waste heat, and a mere 5-10 % recovery would provide enough additional power for tens of thousands of homes.

The efficiency of a thermoelectric material is typically described using the dimensionless figure of merit ZT :[2]

$$ZT = \frac{S^2 \sigma T}{\kappa_{\text{latt}} + \kappa_{\text{el}}} \quad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, the product $S^2 \sigma$ is the power factor, and κ_{latt} and κ_{el} are the lattice (phonon) and electronic contributions to the thermal conductivity. S , σ and κ_{el} depend on the electronic structure and the carrier concentration, and are interdependent such that the ZT at a target operating temperature is typically maximised in heavily-doped semiconductors. The bulk of the κ_{latt} in semiconductors is from heat transport through phonons. This is largely independent of the electronic structure, and can be minimised to improve the ZT using a variety of strategies spanning chemical doping and alloying, to including nanoscale phase impurities, to mesoscale structuring.[2]

The majority of the current flagship TEs are heavy p-block chalcogenides including PbTe, SnSe and the current industry standard Bi₂Te₃. [1] These systems have in common narrow bandgaps and favourable electronic transport, together with large intrinsic phonon anharmonicity leading to low κ_{latt} . [2,3] However, the constituent elements are rare and/or environmentally hazardous, which prohibits the large-scale adoption of TEGs based on these materials.

The desire for crystalline-like electron transport and amorphous- (glass)-like heat transport is encapsulated by the “phonon glass electron crystal” (PGEC) concept originally put forward by Slack.[4] Among the most widely-studied PGEC materials are the skutterudites and the inorganic clathrates,[5–9] which are “cage” compounds with large intrinsic cavities that can incorporate loosely-bound guest ions to act as phonon-scattering centres while electronic transport occurs through the crystalline host framework.

Skutterudite itself is the mineral CoAs_3 , but the structure is adopted by a range of compositions with the formula M_4X_{12} , where M is a transition metal and X is a pnictogen such as P, As, or Sb. CoSb_3 has attracted the most attention as a potential high-performance TE due to its large Seebeck coefficient.[10–12] Pristine CoSb_3 has a low ZT of just 0.05 at 723 K[12] due its high κ_{latt} , which can reach $10 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature in single crystals.[10,11] However, CoSb_3 is chemically very flexible and is amenable both to doping the host framework, e.g. with transition metals[13,14] and chalcogenides,[14] and to filling the cavities with atoms including alkali and alkaline earth metals,[15,16] Group III elements,[17] chalcogens,[18] halogens,[19] transition metals[20] and rare-earth elements.[21,22]. This extraordinary flexibility has led to the experimental synthesis of a wide variety of compounds including examples doped at the Co and Sb sites, incorporating up to seven filler atoms, and with concomitant doping and filling. Some compositions with notable improvements to the ZT include $\text{Ni}_{0.3}\text{Co}_{3.7}\text{Sb}_{12}$ ($ZT = 0.52$ at 773 K),[23] $\text{Na}_{0.48}\text{Co}_3\text{Sb}_{12}$ ($ZT = 1.25$ at 800 K),[16] $\text{Sr}_{0.16}\text{Yb}_{0.03}\text{Co}_4\text{Sb}_{11.82}$ ($ZT = 1.32$ at 850 K),[24] $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.04}\text{Co}_4\text{Sb}_{12}$ ($ZT = 1.7$ at 850 K),[25] $\text{Yb}_{0.2}\text{Ba}_{0.1}\text{Al}_{0.1}\text{Ga}_{0.1}\text{In}_{0.1}\text{La}_{0.05}\text{Eu}_{0.05}\text{Co}_4\text{Sb}_{12}$ ($ZT = 1.2$ at 800 K),[26] and $\text{Ce}_{0.12}\text{Fe}_{0.71}\text{Co}_{3.29}\text{Sb}_{12}$ ($ZT = 0.8$ at 750 K).[27]

First-principles modelling of the structural dynamics and thermal transport, typically using density-functional theory (DFT), has been instrumental in understanding the intrinsically low κ_{latt} of flagship thermoelectric and other highly-anharmonic materials,[28–32] and has also been applied to identify novel candidate TEs.[33–35] Despite a large body of experimental work on the skutterudites, there are comparatively few modelling studies on the phonon thermal transport.[36–40] Such studies could provide valuable insight into the underlying microscopic mechanisms by which doping and filling reduce the κ_{latt} and direct future work to identify and optimise novel high-performance skutterudite TEs.

In this study, we present a systematic set of calculations on CoSb_3 and $\text{XCo}_8\text{Sb}_{24}$ skutterudites filled with the noble gases $\text{X} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}$ and Xe and explore how the size and mass of the chemically-inert filler atoms impact the thermal conductivity. We propose and apply a variety of analysis techniques to elucidate the microscopic mechanisms by which the fillers suppress the heat transport through the host framework, and show that an approximate rattling frequency, determined from the atomic mass and harmonic force constants, is a good predictor of the effect of a filler on the κ_{latt} . The general conclusions and modelling techniques from this study are readily applicable to other filled skutterudites, and can help to improve our fundamental understanding of the heat transport in cage compounds and identify promising research directions towards future high-performance TEs.

2. Computational Modelling

Calculations were performed using pseudopotential plane-wave density-functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP) code.[41] Calculations on pristine CoSb₃ were performed using the 32-atom conventional cell, while calculations on filled models were performed by placing a single filler ion X = He, Ne, Ar, Kr and Xe at centre of one of the two cavities at (0.5, 0.5, 0.5). The filled models have the composition XCo₈Sb₂₄, corresponding to a filling fraction of 50 %.

The electronic structure was modelled using a plane-wave basis with a 500 eV kinetic-energy cutoff and Γ -centered Monkhorst-Pack **k**-point meshes[42] with $4 \times 4 \times 4$ subdivisions. These values were determined from explicit testing to converge the total energy to < 0.1 meV atom⁻¹ and the external pressure to < 1 kbar (0.1 GPa). Electron exchange and correlation were modelled using the PBEsol generalised-gradient approximation (GGA) functional,[43] with a Hubbard *U* correction of $U_{\text{eff}} = 5$ eV applied to the Co 3d states using the rotationally-invariant Dudarev model.[44] Some additional tests were performed including the semi-empirical DFT-D3 dispersion correction.[45] Projector augmented-wave (PAW) pseudopotentials[46,47] were used to model the ion cores, with the following valence electron configurations: Co - 3p⁶4s²3d⁷, Sb - 5s²5p³, He - 1s², Ne - 2s²2p⁶, Ar - 3s²3p⁶, Kr - 4s²4p⁶, and Xe - 5s²5p⁶. Tolerances of 10⁻⁸ eV and 10⁻² eV Å⁻¹ were applied to the electronic wavefunctions and atomic forces during electronic structure solution and geometry optimisation, respectively. The PAW projection was performed in reciprocal space, non-spherical contributions to the gradient correction were included inside the PAW spheres, and the precision of the charge-density grids was automatically set to avoid aliasing errors.

Lattice-dynamics and thermal-conductivity calculations were performed using the Phonopy and Phono3py packages.[48,49] The second- and third-order interatomic force constants (IFCs) were determined using the supercell finite-displacement method[50] with displacement step sizes of 10⁻² and 3×10^{-2} Å respectively. The second-order IFCs were determined in $2 \times 2 \times 2$ supercells with 256/264 atoms, while the third-order IFCs were calculated in the base cells with 32/33 atoms. During the single-point force calculations an auxiliary charge-density grid with 8× the number of grid points was used to evaluate the forces, and the **k**-point sampling for the 256/264-atom supercells was reduced proportionately to $2 \times 2 \times 2$.

During post-processing, phonon density of states (DoS) curves $g(f)$ were computed by interpolating the frequencies onto a uniform Γ -centered grid with $48 \times 48 \times 48$ subdivisions and applying a Gaussian broadening with $\sigma = 0.032$ THz, corresponding to a full-width at half-maximum of 2.5 cm⁻¹. Atom-projected DoS (PDoS) curves were computed on $24 \times 24 \times 24$ grids. For pristine CoSb₃ a transformation matrix was used to project to the primitive cell, and the grids were increased to $60 \times 60 \times 60$ and $30 \times 30 \times 30$, respectively, to account for the 2× larger Brillouin zone. The dispersion of undoped CoSb₃ was obtained by evaluating the frequencies along paths through the high-symmetry wavevectors in the $Im\bar{3}$ Brillouin zone. The dispersions of the filled models were referenced to the CoSb₃ primitive cell using the band-unfolding approach of Allen *et al.*[51] When calculating the thermal conductivity, the phonon Brillouin zones were sampled with $9 \times 9 \times 9$ meshes, and selected analyses were performed using smaller $7 \times 7 \times 7$ meshes. Additional data on the thermal-

conductivity calculations, including a comparison of supercell sizes, an assessment of the numerical quality of the calculated force constants, and selection of appropriate sampling meshes, is given in Section 1 of the ESI.

3. Results and Discussion

a. Pristine CoSb₃

CoSb₃ is cubic with the $Im\bar{3}$ spacegroup. The 32-atom conventional unit cell (Fig. 1a) consists of eight corner-sharing CoSb₆ octahedra surrounding large cavities located at the corners and centre of the cell (Fig. 1b). The optimised lattice constant of $a_0 = 8.952$ Å obtained using PBEsol + U is within 1 % of typical experimental measurements of 9.035-9.039 Å.[11,52–54]

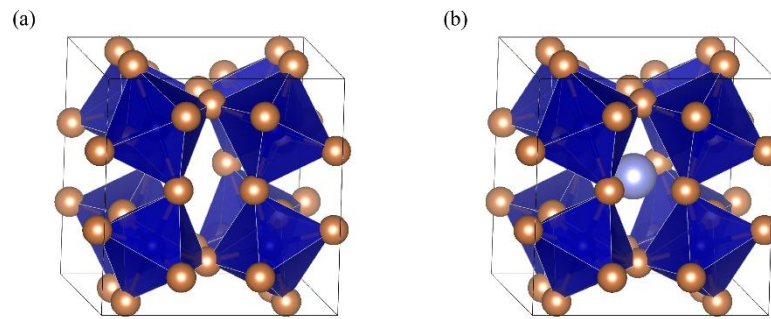


Figure 1 (a) Conventional unit cell of CoSb₃ comprising a network of corner-sharing CoSb₆ octahedra (dark blue/brown) surrounding cavities centred at (0, 0, 0) and (0.5, 0.5, 0.5). (b) Representative XCo₈Sb₂₄ filled model with the filler atom X in the central cavity (pale blue). These images were prepared using the VESTA software.[55]

The calculated phonon dispersion and atom-projected density of states of CoSb₃ are shown in Fig. 2. The 16 atoms in the primitive cell produce $3N = 48$ branches at each phonon wavevector. The three acoustic modes span a frequency range of ~2.5 THz. The 48 modes can be partitioned into low- and high-frequency groups in a 3:1 ratio, separated by a “phonon bandgap”. The lower-frequency group extends up to ~6 THz, while the upper-frequency group spans from ~7-8.5 THz. With reference to the atom-projected DoS, these bands can be assigned as predominantly vibrations involving Sb and Co motion respectively. Our results are a good match to experimental data[52,54,56,57] and to other modelling studies.[39]

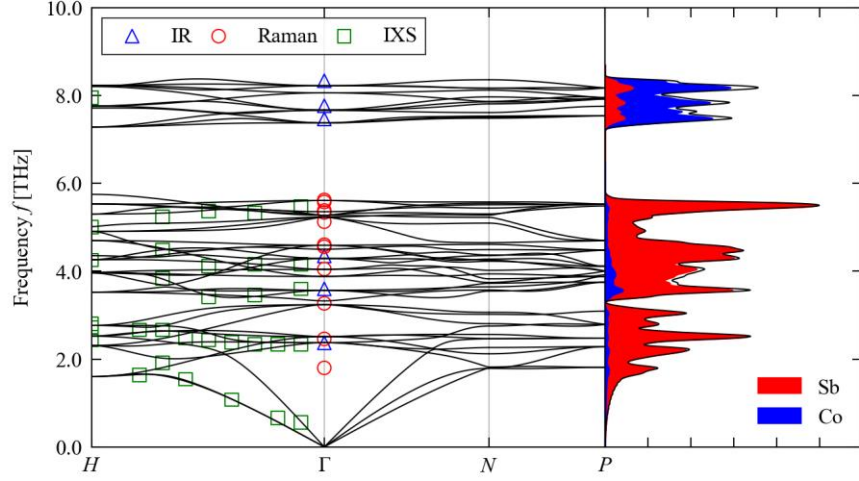


Figure 2 Calculated phonon dispersion and density of states $g(f)$ of CoSb_3 . The projections of the $g(f)$ onto the Co and Sb atoms is shown by the blue and red shaded curves respectively. Experimental measurements of the Γ -point phonon frequencies from infrared (IR)[52] and Raman spectroscopy[56,57] and measurements of the frequencies along the $\Gamma \rightarrow \text{H}$ segment of the dispersion from inelastic X-ray scattering (IXS)[54] are overlaid on the dispersion for comparison.

The lattice thermal conductivity κ_{latt} as a function of temperature, calculated using the single-mode relaxation-time approximation (RTA) model, is shown in Fig. 3. The diagonal elements κ_{xx} , κ_{yy} and κ_{zz} of the 3×3 κ_{latt} tensor correspond to the transport along the principal Cartesian directions. In a cubic system, the diagonal elements are equal, so for simplicity we discuss the scalar diagonal average $\kappa_{\text{latt}} = \frac{1}{3} \text{Tr}[\kappa_{\text{latt}}]$. The calculations are an excellent match to measurements on single crystals with modest doping levels,[10,11] and the predicted 9.98 and 4.91 $\text{W m}^{-1} \text{K}^{-1}$ at $T = 300$ and 600 K, respectively, agree quantitatively with the experimental measurements of 10 $\text{W m}^{-1} \text{K}^{-1}$ and 5-5.5 $\text{W m}^{-1} \text{K}^{-1}$ in Ref. [11]. The calculations and measurements diverge beyond 600 K due to a plateau in the measured κ_{latt} , which may be due to the neglect of higher-order anharmonic effects and/or thermal expansion in the RTA, or to other thermal effects such as the onset of oxidation or decomposition.[58]

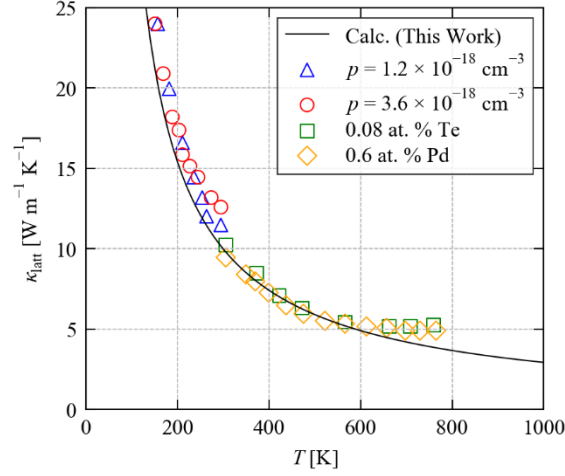


Figure 3 Calculated temperature dependence of the lattice thermal conductivity κ_{latt} of CoSb₃. The experimental measurements from Refs. [10] and [11] are overlaid for comparison.

Within the RTA κ_{latt} is computed as a sum over phonon modes λ according to:

$$\kappa_{\text{latt}} = \frac{1}{N} \sum_{\lambda} \kappa_{\lambda} = \frac{1}{NV_0} \sum_{\lambda} C_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} \tau_{\lambda} \quad (2)$$

where C_{λ} is the modal volumetric heat capacity, $\mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda}$ is the outer product of the group velocity \mathbf{v}_{λ} , τ_{λ} is the lifetime, N is the number of phonon wavevectors \mathbf{q} included in the summation, and V_0 is the volume of the unit cell. The product $\mathbf{v}_{\lambda} \tau_{\lambda}$ is the phonon mean-free path Λ_{λ} (MFP), which appears in an alternative form of Eq. 2. The C_{λ} and $\mathbf{v}_{\lambda} = \partial \omega_{\lambda} / \partial \mathbf{q}_{\lambda}$ ($\omega_{\lambda} = 2\pi f_{\lambda}$) are calculated within the harmonic approximation, while the τ_{λ} are calculated using a perturbative correction to model phonon-phonon interactions. A detailed overview of this method is given in Ref. [49] and in the following section.

Accumulating the κ_{λ} as a function of frequency and comparing the result to the phonon DoS shows how modes in different frequency ranges contribute to the overall κ_{latt} (Fig. 4). At 300 K, modes up to 2.5 THz contribute $\sim 80\%$ to the κ_{latt} , with the remaining 20 % accumulated up to ~ 6 THz. The majority of the thermal transport is therefore through the acoustic modes, the remainder is through the lower-frequency Sb-based optic modes, and the contribution of the high-frequency Co-based modes is negligible (c.f. Fig. 2). Analysis of the κ_{latt} at 600 K yields similar conclusions but with a marked reduction in the κ_{λ} across the frequency spectrum.

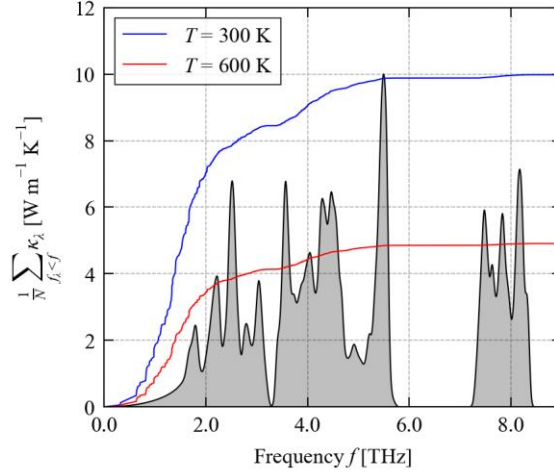


Figure 4 Accumulation of the modal thermal conductivity κ_{λ} of CoSb₃ as a function of frequency at $T = 300$ (blue) and 600 K (red). The phonon density of states $g(\nu)$ is overlaid as a filled black/grey curve for comparison.

Further insight into the nature of the $\tau\kappa_{\text{latt}}$ can be obtained from the frequency spectra of the modal terms in Eq. 2 and the mean-free paths Λ_{λ} (Fig. 5). We consider the group velocity/mean free path norms $|\mathbf{v}_{\lambda}|/|\Lambda_{\lambda}|$ and the diagonal averages of the $\boldsymbol{\kappa}_{\lambda}$ and $\mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda}$ tensors, i.e. $\frac{1}{3}\text{Tr}[\boldsymbol{\kappa}_{\lambda}]$ and $\frac{1}{3}\text{Tr}[\mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda}]$, which we denote v_{λ} , Λ_{λ} , κ_{λ} , and v_{λ}^2 . The κ_{λ} range from 10^{-5} to $1 \text{ W m}^{-1} \text{ K}^{-1}$ and are a maximum for the low-frequency acoustic modes as expected. The C_{λ} are a shallow function of frequency and vary by $\sim 30\%$ from $7.4\text{--}9.6 \times 10^{-5} \text{ eV}$ over the 9 THz range of the phonon spectrum. The v_{λ} and v_{λ}^2 span 3 and 6 orders of magnitude, respectively, and the group velocities reach up to $\sim 5,000 \text{ ms}^{-1}$. At 300 K the τ_{λ} decrease from $\sim 200 \text{ ps}$ at low frequencies to $< 10 \text{ ps}$ for the high-frequency Co-based optic modes. The large κ_{λ} of the acoustic modes thus arises from their high v_{λ} and long τ_{λ} , while the negligible contribution of the high-frequency optic modes is due to their low v_{λ} and a short τ_{λ} . The Λ_{λ} approach microns for the acoustic modes but reduce steadily with frequency so that the MFPs of the high-frequency optic modes are on the order of nm. The lifetimes are substantially lowered at 600 K with a corresponding reduction in the MFPs (see Figure S2.1).

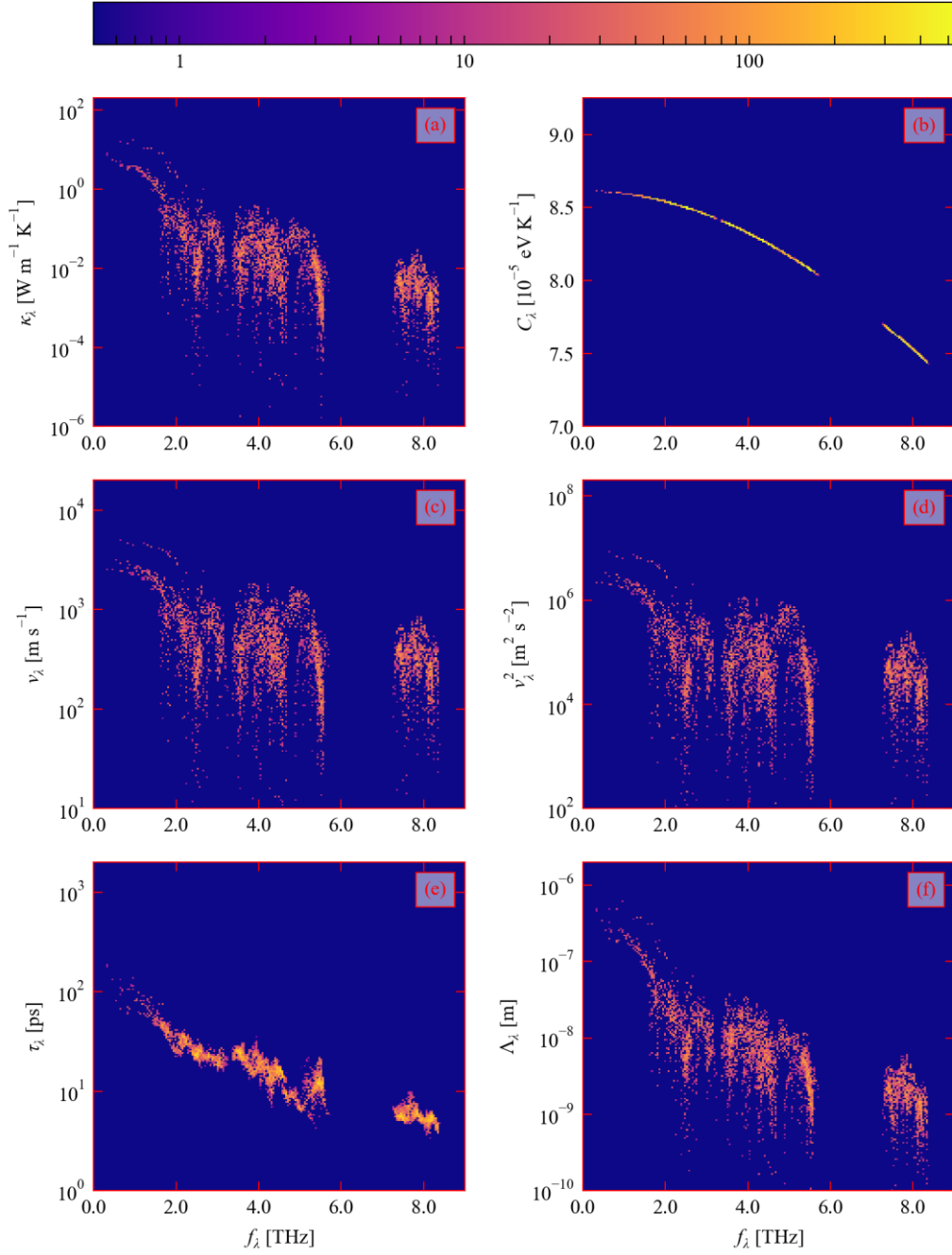


Figure 5 Frequency spectra of the modal terms in Eq. 2 at $T = 300$ K, *viz.* the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

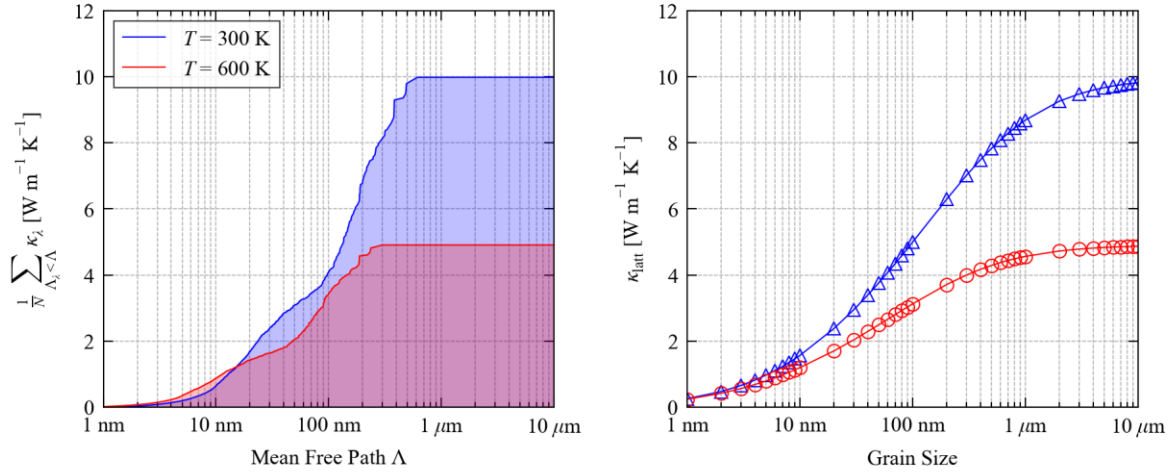


Figure 6 (a) Accumulation of the thermal conductivity κ_{latt} of CoSb_3 as a function of the phonon mean-free path $\Lambda_\lambda = v_\lambda \tau_\lambda$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

It is also of interest to analyse how the κ_{latt} accumulates with the phonon MFPs (Fig. 6a). At 300 K, around 10% of the κ_{latt} is through modes with $\Lambda_\lambda < 10$ nm, a further 30% is through modes with $\Lambda_\lambda < 100$ nm, and 60% is through modes with MFPs up to $1\ \mu\text{m}$. At 600 K the MFPs are suppressed due to the reduced lifetimes, and modes with Λ_λ from 10 - 100 nm account for $\sim 70\%$ of the κ_{latt} . The effect limiting the transport through modes with long MFPs can be investigated by using a boundary-scattering model to mimic a finite grain size (Fig. 6b). This indicates that nanostructuring can potentially yield a substantial reduction in the κ_{latt} , in keeping with its widespread use as a strategy for optimising thermoelectric performance.[2]

This analysis also highlights the sensitivity of experimental measurements to sample preparation methods. While our calculated bulk κ_{latt} agree very well with experimental measurements on single crystals, they are 25 - 30% higher than measurements on annealed powders.[12]. According to the calculations in Fig. 6b, this reduction could be obtained with a grain size of ~ 200 nm, which is not unreasonable given that the samples in Ref. [12] were calculated to be 89% of the theoretical density with an Sb/Co ratio of 2.65 .

b. CoSb₃ with noble gas fillers

The lattice constants of the five filled models, *viz.* $\text{HeCo}_8\text{Sb}_{24}$, $\text{NeCo}_8\text{Sb}_{24}$, $\text{ArCo}_8\text{Sb}_{24}$, $\text{KrCo}_8\text{Sb}_{24}$ and $\text{XeCo}_8\text{Sb}_{24}$, are listed in Table 1. Filling with Ne-Xe results in a small expansion of the lattice, increasing in proportion with the atomic radii of the fillers, and the maximum 0.64% expansion with Xe suggests the cavity is large enough to accommodate all five atoms. Geometry optimisations including the DFT-D3 dispersion correction produced lattice constants around 0.75% smaller with the same overall trend, suggesting that a dispersion correction is not required for these systems (Table S2.1).

	a_0 [Å]	Δa_0 [%]	r_X [pm]
CoSb ₃	8.952	-	-
HeCo ₈ Sb ₂₄	8.952	0.00	31
NeCo ₈ Sb ₂₄	8.960	0.09	38
ArCo ₈ Sb ₂₄	8.975	0.26	71
KrCo ₈ Sb ₂₄	8.987	0.39	88
XeCo ₈ Sb ₂₄	9.010	0.64	108

Table 1 Optimised lattice constants of CoSb₃ and XCo₈Sb₂₄ with X = He, Ne, Ar, Kr and Xe. The second column gives the % difference in the lattice constants of the filled models to pristine CoSb₃, and the third column lists the atomic radii r_X of the filler atoms for comparison.

The unfolded band dispersions and DoS curves of the filled models are shown in Fig. 7. In the “rattler” model of filled cage compounds, the fillers introduce localised bands of modes with a narrow dispersion.[59] However, theoretical studies on BaFe₄Sb₁₂ have shown that some fillers introduce features into the PDoS over a wide range of frequencies.[36] Filling with He introduces a narrow peak at ~6 THz into the DoS, which lies in the phonon bandgap and is suggestive of “rattling” behaviour. The other four fillers introduce broader bands of modes among the lower-frequency optic modes, similar to the Ba filler in BaFe₄Sb₁₂. [36] Interestingly, modes associated with Ne appear around 4 THz in NeCo₈Sb₂₄, 4-6 THz ArCo₈Sb₂₄, and ~3.5-4 THz in the Kr- and Xe-filled systems. None of the curves show any evidence of imaginary modes, suggesting that there are no driving forces for the fillers to move off centre.

The frequencies at a wavevector \mathbf{q} are the eigenvalues obtained by constructing an diagonalising the dynamical matrix $D(\mathbf{q})$ built from 3×3 blocks according to:

$$D_{\alpha\beta}(jj', \mathbf{q}) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{l'} \Phi_{\alpha\beta}(j0, j'l') \times \exp\{i\mathbf{q} \cdot [\mathbf{r}(j'l') - \mathbf{r}(j0)]\} \quad (3)$$

where the indices j and j' denote atoms with masses m_j located at $\mathbf{r}(jl)$ in the l th unit cell, and $\Phi(j0, j'l')$ are the second-order force-constant matrices:

$$\Phi_{\alpha\beta}(j0, j'l') = \frac{\partial^2 E}{\partial r_\alpha(j0) \partial r_\beta(j'l')} = -\frac{\partial F_\beta(j'l')}{\partial r_\alpha(j0)} \quad (4)$$

If the filler atoms are modelled as moving within a rigid CoSb₃ cage, an approximate rattling frequency \tilde{f}_X can be determined by diagonalising a 3×3 dynamical matrix at $\mathbf{q} = \Gamma$ built from the “self” force constants of the filler atom, i.e. with $j = j' = X$. For the cubic crystal this yields a single unique eigenvalue. Table 2 lists for each filler atom the \tilde{f}_X determined from this analysis together with the atomic masses m_X and the Frobenius norms of the $\Phi(X0, X0)$ force constants, calculated as:

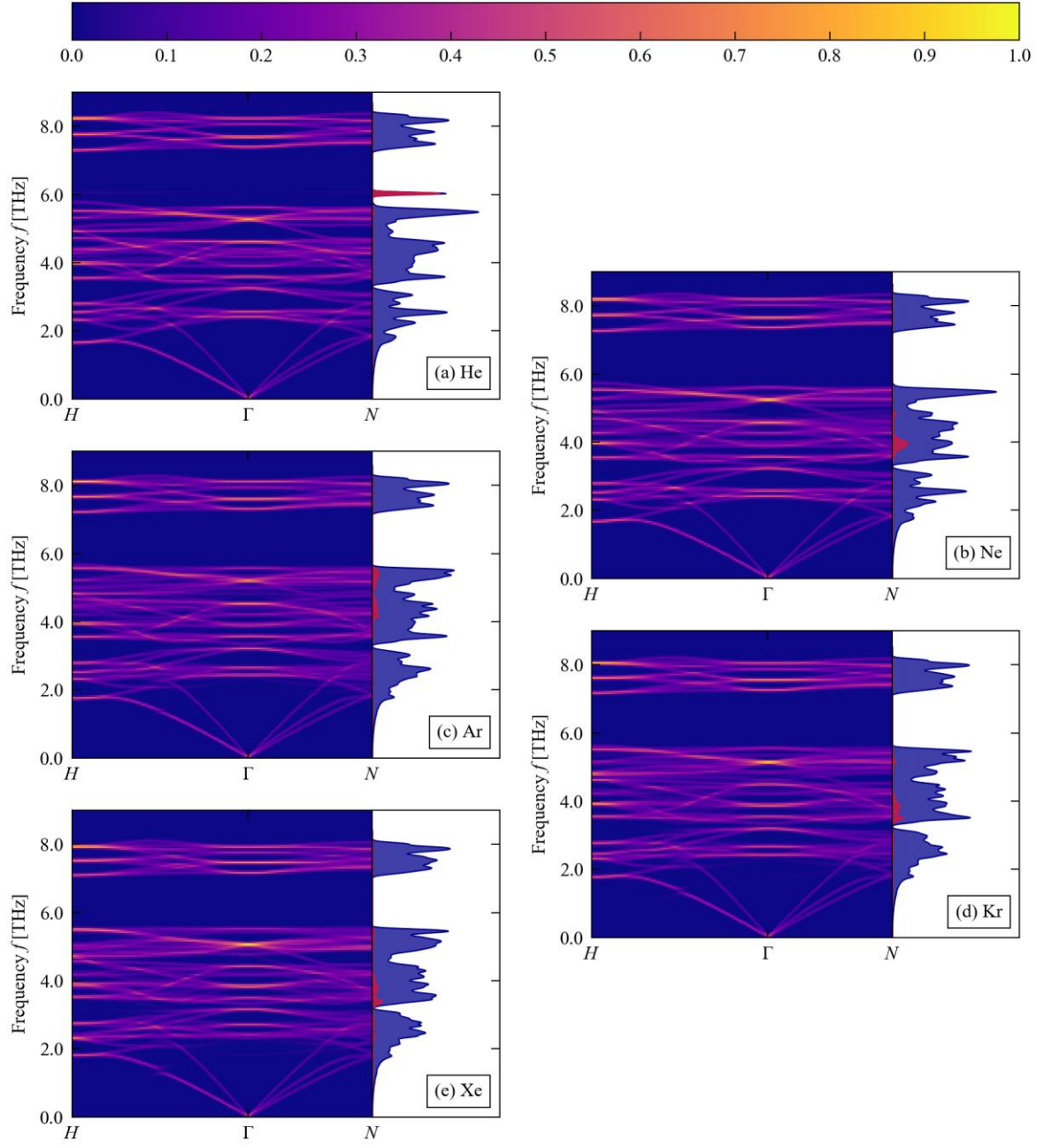


Figure 7 Unfolded band dispersions and phonon density of states $g(f)$ (DoS) of $\text{XCo}_8\text{Sb}_{24}$ with $\text{X} = \text{He}$ (a), Ne (b), Ar (c), Kr (d) and Xe (e). In each of the DoS plots the total $g(f)$ is shown in dark blue with the projection onto the filler atom X overlaid in red.

	m_X [amu]	$\ \Phi(X0, X0)\ $ [eV Å ⁻²]	\tilde{f}_X [THz]
HeCo ₈ Sb ₂₄	4.0026	1.005	5.960
NeCo ₈ Sb ₂₄	20.180	2.316	4.022
ArCo ₈ Sb ₂₄	39.948	6.410	4.745
KrCo ₈ Sb ₂₄	83.798	8.643	3.798
XeCo ₈ Sb ₂₄	131.29	12.35	3.613

Table 2 Atomic masses m_X , force-constant norms $\|\Phi(X0, X0)\|$ and approximate rattling frequencies \tilde{f}_X of the filler atoms X in the five XCo₈Sb₂₄ models. The force-constant norms and \tilde{f}_X are calculated using the procedure outlined in Eqs. 3-5.

$$\|\Phi(j0, j'l')\| = \sum_{\alpha} \sum_{\beta} |\Phi_{\alpha\beta}(j0, j'l')|^2 \quad (5)$$

This simple model predicts the centre of the filler peaks in Fig. 7 remarkably well. On going from He to Xe, the $\|\Phi(X0, X0)\|$ increase by an order of magnitude from 1.01 to 12.4 eV Å⁻², indicating that the larger filler atoms experience stronger restoring forces from the framework atoms. As per Eq. 5, a larger m_X and $\|\Phi\|$ will respectively decrease and increase \tilde{f}_X . From He to Ne, the $\|\Phi\|$ increases by a factor of two but the mass increases fivefold, resulting in a ~30 % reduction in \tilde{f}_X . On the other hand, from Ne to Ar the $\|\Phi\|$ increases by ~3× while the mass doubles, increasing the \tilde{f}_X . From Ar to Kr and Xe, the mass increases faster than the $\|\Phi\|$ and the rattling frequency falls from 4.75 to 3.80 and 3.61 THz.

Comparison of the unfolded dispersions to that of CoSb₃ (c.f. Figs. 2 and 7; see also Figs. S2.2-S2.6) shows the heavier filler atoms have a progressively larger effect on the vibrations of the host framework. In HeCo₈Sb₂₄, the spectrum is largely unchanged save for the localised branch in the phonon bandgap. From NeCo₈Sb₂₄ to XeCo₈Sb₂₄ the frequencies of the acoustic and low-lying optic modes up to ~2.5 THz are raised, with the largest increases towards the *H* wavevector, while the higher-energy optic modes are downshifted. This “depression” of optic modes may be indicative of a reduction in the group velocities, which is another mechanism by which fillers can suppress the thermal conductivity of cage compounds,[59] albeit usually when the rattling frequency falls among the acoustic modes and introduces avoided crossings into the dispersion.[38,60,61] In this case, the higher rattling frequencies of the noble gas fillers would mainly affect the optic modes, and the density of phonon branches make it difficult to identify any avoided crossings.

When placed in the centre of the cavity, as shown in Fig. 1b, the first, second and third neighbours of the filler atoms are 12 Sb atoms, 8 Co atoms, and a further 24 Sb atoms. The corresponding $\|\Phi\|$ increase by an order of magnitude from He to Xe, from 1.78×10^{-1} , 1.78×10^{-2} and 4.66×10^{-3} eV Å⁻² in HeCo₈Sb₂₄ to 1.63 , 2.32×10^{-1} and 4.88×10^{-2} eV Å⁻² in XeCo₈Sb₂₄ (Table S2.2). The stronger interactions between the larger/heavier filler atoms and the host framework explains the increasingly prominent frequency shifts in the unfolded dispersions. The $\|\Phi\|$ for the nearest-neighbour Co-Sb and Sb-Sb interactions in pristine CoSb₃ are 4.40 and 5.02 eV Å⁻², respectively, so the first-neighbour Kr-Sb and Xe-Sb interactions are of comparable strength to the bonding in the host framework.

The calculated thermal-conductivity curves for the five models (Fig. 8a) show that filling produces a modest reduction in κ_{latt} compared to pristine CoSb₃ with somewhat intricate trend among the five fillers. A comparison of values at 300 and 600 K (Table 3, Table S2.3) show that the κ_{latt} fall in the order of Ar \approx He > Ne \approx Kr > Xe, with reductions of 8-9, 11-12 and 15 % compared to CoSb₃. This correlates with the \tilde{f}_X : He and Ar have the highest \tilde{f}_X and produce the smallest reduction in κ_{latt} . Ne and Kr have similar \tilde{f}_X and produce similar reductions, and Xe has the lowest \tilde{f}_X and has the largest effect on κ_{latt} . However, it is clear that the effect of the fillers on the κ_{latt} is dependent both on the mass and how strongly they interact with the framework.

The two mechanisms by which filler atoms in cage compounds suppress the heat transport are resonant scattering, which reduces the lifetimes of framework modes close in frequency to localised “rattling” modes, and reducing the group velocities.[59] Calculations suggest that these are not mutually exclusive, as the changes to the phonon spectrum that reduce the v_λ can introduce new phonon-scattering channels that reduce the τ_λ of modes over a broader spectrum of frequencies.[38] The small differences in the κ_{latt} of the filled models makes it difficult to draw quantitative conclusions by inspecting the spectra of modal properties (Figs. S2.7-S2.11.) We therefore developed an analysis following the constant relaxation-time approximation (CRTA) approach commonly used in electronic-structure modelling and computed a quantity $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ defined as:

$$\kappa_{\text{latt}}/\tau^{\text{CRTA}} \approx \frac{1}{NV_0} \sum_{\lambda} \frac{\kappa_{\lambda}}{\tau_{\lambda}} \approx \frac{1}{NV_0} \sum_{\lambda} C_{\lambda} v_{\lambda} \otimes v_{\lambda} \quad (6)$$

where τ^{CRTA} is an effective phonon lifetime (relaxation time) and the other terms are defined as in Eq. 2. Both $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ and τ^{CRTA} are temperature dependent due to the temperature dependence of the C_{λ} and τ_{λ} . For cubic systems the diagonal elements of κ_{latt} are equal and the off-diagonal elements are negligible, so it is possible to choose a single τ^{CRTA} at each temperature such that the separation in Eq. 6 is exact. We discuss the scalar averages κ_{latt} and $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ in the following.

Figure 8 compares the κ_{latt} , $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ and τ^{CRTA} of pristine CoSb₃ and the five XCo₈Sb₂₄ filled models as a function of temperature. Values at 300 and 600 K listed in Tables 3 and S2.3. The $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ of the filled models are reduced by 4.6 - 13 % compared to pristine CoSb₃ and fall in a similar order to the rattling frequencies with HeCo₈Sb₂₄ > ArCo₈Sb₂₄ > NeCo₈Sb₂₄ > KrCo₈Sb₂₄ \approx XeCo₈Sb₂₄. In the RTA model, these reductions are purely due to changes in the harmonic frequency spectrum. On the other hand, the τ^{CRTA} in HeCo₈Sb₂₄ are reduced by ~5 % compared to pristine CoSb₃, whereas filling with Ne, Ar and Kr changes the lifetimes by at most 1 % and in some cases increases them, and filling with Xe decreases the τ^{CRTA} by a smaller 2.5-3 %. The changes in lifetimes may arise from changes in the frequency spectrum and in the anharmonic interactions between modes, which we return to later in the discussion.

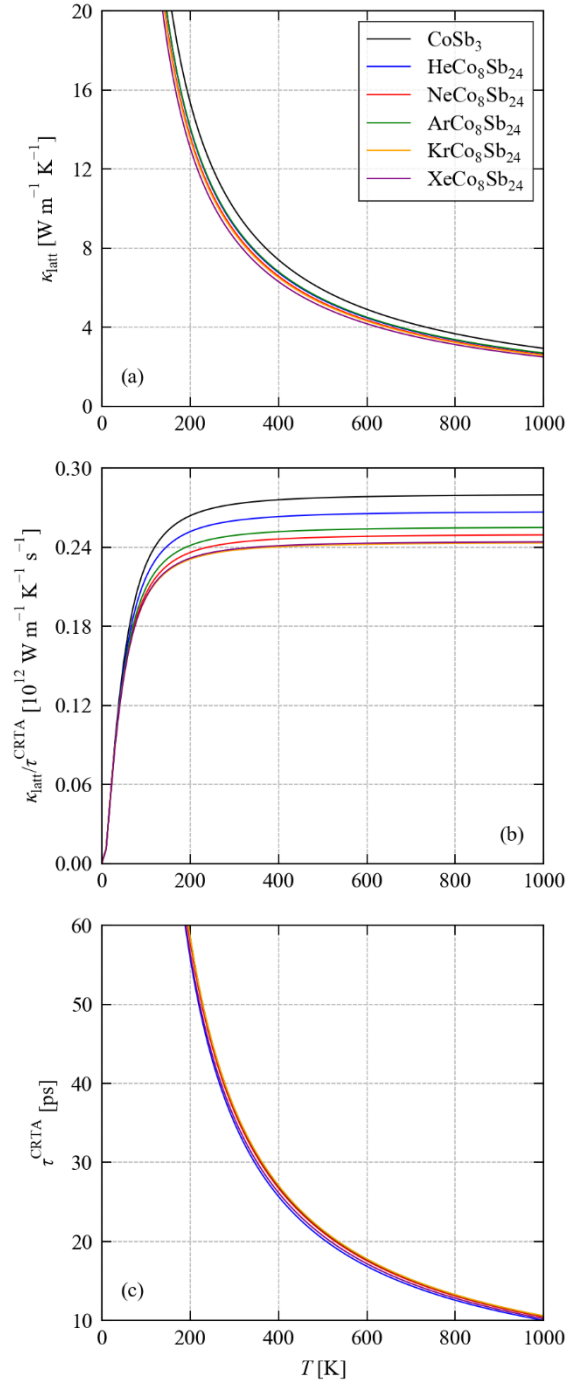


Figure 8 Analysis of the thermal conductivity of CoSb₃ and XCo₈Sb₂₄ (X = He, Ne, Ar, Kr, Xe) using the constant relaxation-time approximation (CRTA) as defined in Eq. 6. The three subplots show the thermal conductivity κ_{latt} (a), the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ (b) and the calculated τ^{CRTA} (c) as a function of temperature.

	$\bar{\kappa}_{\text{latt}}$ [W m ⁻¹ K ⁻¹]	Δ [%]	$\bar{\kappa}_{\text{latt}}/\tau^{\text{CRTA}}$ [10 ¹² W m ⁻¹ K ⁻¹ s ⁻¹]	Δ [%]	τ^{CRTA} [ps]	Δ [%]	\tilde{P} [10 ⁻¹² eV ²]	Δ [%]	$\bar{\tau}_\lambda$ [ps]	\bar{P}_λ [10 ⁻¹² eV ²]
CoSb ₃	9.98	-	0.273	-	36.6	-	0.394	-	16.97	6.00
HeCo ₈ Sb ₂₄	9.11	-8.71	0.260	-4.62	35.0	-4.30	0.399	1.35	16.46	5.65
NeCo ₈ Sb ₂₄	8.86	-11.20	0.243	-10.73	36.4	-0.52	0.388	-1.35	16.62	5.46
ArCo ₈ Sb ₂₄	9.17	-8.12	0.249	-8.71	36.8	0.65	0.391	-0.71	16.30	5.35
KrCo ₈ Sb ₂₄	8.77	-12.15	0.238	-12.84	36.9	0.79	0.387	-1.65	16.38	5.27
XeCo ₈ Sb ₂₄	8.49	-14.90	0.239	-12.52	35.6	-2.72	0.386	-2.03	15.79	5.18

Table 3 Calculated lattice thermal conductivity κ_{latt} , $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$, τ^{CRTA} and \tilde{P} at $T = 300$ K for the CoSb₃ and XCo₈Sb₂₄ (X = He, Ne, Ar, Kr) models examined in this work. The quantities $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ and τ^{CRTA} are defined in Eq. 6, and the \tilde{P} are defined in the text. The percentage change in the parameters relative to pristine CoSb₃ are shown for comparison. The rightmost two columns list the averaged lifetimes and interaction strengths $\bar{\tau}_\lambda/\bar{P}_\lambda$ for comparison to the τ^{CRTA} and \tilde{P} respectively.

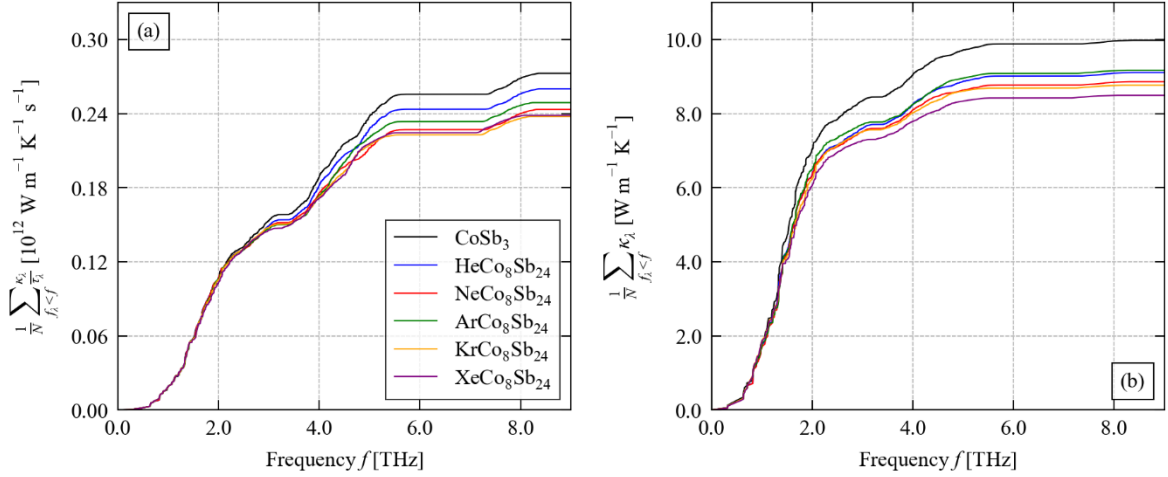


Figure 9 Accumulation of the $\kappa_\lambda/\tau_\lambda$ (a) and κ_λ (b) as a function of frequency at $T = 300$ K for pristine CoSb₃ and filled XCo₈Sb₂₄ models with $X = \text{He, Ne, Ar, Kr and Xe}$.

The differing impacts on the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ and τ^{CRTA} combine to produce the trend in κ_{latt} noted above. In HeCo₈Sb₂₄, the ~4-5 % reduction in both parameters combine to reduce the κ_{latt} by 8-9 % compared to pristine CoSb₃. In ArCo₈Sb₂₄, the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ are reduced by a larger 8-9 % but the τ^{CRTA} are mostly unchanged, resulting in a κ_{latt} higher than HeCo₈Sb₂₄ but lower than pristine CoSb₃. Filling with Ne and Kr reduces the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ by ~11-12 % while changing the τ^{CRTA} by 0.5-1 %, producing a similar overall κ_{latt} . In XeCo₈Sb₂₄, the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ and τ^{CRTA} are reduced by ~12.5 and 2.5 %, respectively, giving the smallest κ_{latt} of the five filled materials.

As for κ_λ , the $\kappa_\lambda/\tau_\lambda$ in the summand in Eq. 6 can be accumulated as a function of frequency (Fig. 9, Fig. S2.12). This shows that the largest change in the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$ on filling occurs in the optic modes between ~2.5-6 THz. Comparing accumulations of $\kappa_\lambda/\tau_\lambda$ and κ_λ , as in Fig. 4, shows a small reduction in heat transport through the acoustic modes between 1-2.5 THz and the larger difference in the optic modes reflected in the $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$. Taking these analyses together, the five fillers primarily suppress the heat transport in CoSb₃ by reducing the group velocity and lifetimes of the optic modes. Since the affected modes only account for ~20 % of the κ_{latt} , this explains why even the heaviest Xe filler produces only a 15 % reduction.

Since the CRTA method is not usually used for κ_{latt} calculations, it is interesting to see how the τ^{CRTA} compare to the actual τ_λ . In these calculations, the τ^{CRTA} at 300 and 600 K are around twice the average mode lifetime $\bar{\tau}_\lambda$ (Table 3, Table S2.3), which is not surprising given the order of magnitude variation in τ_λ with frequency in Fig. 5. The τ^{CRTA} do reflect the average order of magnitude of the τ_λ , and might serve as a useful metric to compare between systems.

To investigate the small effects of filling on the phonon lifetimes, we follow the analysis outlined in Ref. [49]. In the RTA, the τ_λ are calculated as the inverse of the phonon linewidths Γ_λ :

$$\tau_\lambda = \frac{1}{2\Gamma_\lambda} \quad (7)$$

Γ_λ are calculated from the imaginary part of the phonon self energy by summing over interactions between triplets of modes λ , λ' and λ'' :

$$\Gamma_\lambda = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 \times \{(n_{\lambda'} + n_{\lambda''} + 1)\delta(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''}) + (n_{\lambda'} - n_{\lambda''})[\delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega_\lambda - \omega_{\lambda'} + \omega_{\lambda''})]\} \quad (8)$$

where $\Phi_{-\lambda\lambda'\lambda''}$ are the three-phonon interaction strengths, ω_λ are the angular frequencies and n_λ are the phonon occupation numbers from the Bose-Einstein distribution:

$$n_\lambda = \frac{1}{\exp(\hbar\omega_\lambda/k_B T) - 1} \quad (9)$$

The $\Phi_{\lambda\lambda'\lambda''}$ are calculated from the expression:

$$\begin{aligned} \Phi_{\lambda\lambda'\lambda''} = & \frac{1}{\sqrt{N}} \frac{1}{3!} \sum_{jj'j''} \sum_{\alpha\beta\gamma} W_{\lambda,\alpha}(j) W_{\lambda',\beta}(j') W_{\lambda'',\gamma}(j'') \sqrt{\frac{\hbar}{2m_j\omega_\lambda}} \sqrt{\frac{\hbar}{2m_{j'}\omega_{\lambda'}}} \sqrt{\frac{\hbar}{2m_{j''}\omega_{\lambda''}}} \\ & \times \sum_{l'l''} \Phi_{\alpha\beta\gamma}(j0, j'l', j''l'') \times \exp\{i\mathbf{q}_{\lambda'} \cdot [\mathbf{r}(j'l') - \mathbf{r}(j0)]\} \\ & \times \exp\{i\mathbf{q}_{\lambda''} \cdot [\mathbf{r}(j''l'') - \mathbf{r}(j0)]\} \times \exp\{i(\mathbf{q}_\lambda + \mathbf{q}_{\lambda'} + \mathbf{q}_{\lambda''}) \cdot \mathbf{r}(j0)\} \\ & \times \Delta(\mathbf{q}_\lambda + \mathbf{q}_{\lambda'} + \mathbf{q}_{\lambda''}) \end{aligned} \quad (10)$$

where W_λ are the phonon mode eigenvectors (displacement patterns), the indices j , j' and j'' denote atoms with masses m_j located at $\mathbf{r}(jl)$ in the l th unit cell, and $\Phi(j0, j'l', j''l'')$ are the third-order force-constant matrices:

$$\Phi_{\alpha\beta\gamma}(j0, j'l', j''l'') = \frac{\partial^3 E}{\partial r_\alpha(j0) \partial r_\beta(j'l') \partial r_\gamma(j''l'')} \quad (11)$$

The functions δ and Δ in Eqs. 8 and 10 enforce conservation of energy and crystal momentum, respectively.

Eq. 8 encompasses two types of scattering processes, *viz.* collisions, where $\lambda + \lambda \rightarrow \lambda' + \lambda'' \rightarrow \lambda''$ or $\lambda + \lambda'' \rightarrow \lambda'$, and decays, where $\lambda \rightarrow \lambda' + \lambda''$. These are sometimes referred to in the literature as absorption and emission processes. Broad linewidths Γ_λ , i.e. short τ_λ , arise from strong $\Phi_{\lambda\lambda'\lambda''}$ and/or a high density of energy-conserving collision and decay pathways. Both factors can lead to short mode lifetimes - for example,

the picosecond lifetimes in the hybrid perovskite (CH₃NH₃)PbI₃ have been attributed to strong $\Phi_{\lambda\lambda'\lambda''}$, [31,32] whereas the low predicted κ_{latt} in Bi₂Sn₂O₇ has been ascribed to a high density of scattering channels. [35] Another subtlety of note is that the phonon frequencies ω_λ and phonon-phonon interaction strengths $\Phi_{-\lambda\lambda'\lambda''}$ are temperature independent in the RTA model, and thus the strong temperature dependence of the τ_λ and τ^{CRTA} in Figs. 5 and 8 is due entirely to the changes in the n_λ .

The $\Phi_{-\lambda\lambda'\lambda''}$ can be averaged over the $(3n_a)^2$ pairs of interacting modes to obtain a phonon-phonon interaction strength P_λ for each mode:

$$P_\lambda = \frac{1}{(3n_a)^2} \sum_{\lambda'\lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 \quad (12)$$

An approximate linewidth $\tilde{\Gamma}_\lambda$ can then be defined as the product of the P_λ and a weighted two-phonon joint density of states (w-JDoS) function $N_2(\mathbf{q}, \omega)$ counting the number of energy- and momentum-conserving scattering channels based on the spectrum of phonon frequencies:

$$\tilde{\Gamma}_\lambda = \frac{18\pi}{\hbar^2} P_\lambda N_2(\mathbf{q}_\lambda, \omega_\lambda) \quad (13)$$

The $N_2(\mathbf{q}, \omega)$ are defined as follows and are the sum of separate w-JDoS functions for collision and decay processes, which we denote Class 1 and Class 2, respectively, following Ref. [49]:

$$N_2(\mathbf{q}, \omega) = N_2^{(1)}(\mathbf{q}, \omega) + N_2^{(2)}(\mathbf{q}, \omega) \quad (14)$$

$$N_2^{(1)}(\mathbf{q}, \omega) = \frac{1}{N} \sum_{\lambda'\lambda''} \Delta(-\mathbf{q} + \mathbf{q}_{\lambda'} + \mathbf{q}_{\lambda''}) \times (n_{\lambda'} - n_{\lambda''}) [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})] \quad (15)$$

$$N_2^{(2)}(\mathbf{q}, \omega) = \frac{1}{N} \sum_{\lambda'\lambda''} \Delta(-\mathbf{q} + \mathbf{q}_{\lambda'} + \mathbf{q}_{\lambda''}) \times (n_{\lambda'} + n_{\lambda''} + 1) \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}) \quad (16)$$

In a similar manner to how the CRTA analysis enables quantification the impact of the fillers on the group velocities and lifetimes to be quantified, finding a constant value \tilde{P} such that setting the P_λ in Eq. 13 to $P_\lambda = \tilde{P}$ recovers the κ_{latt} provides a means to quantify the impact of changes to the interaction strengths on the thermal transport.

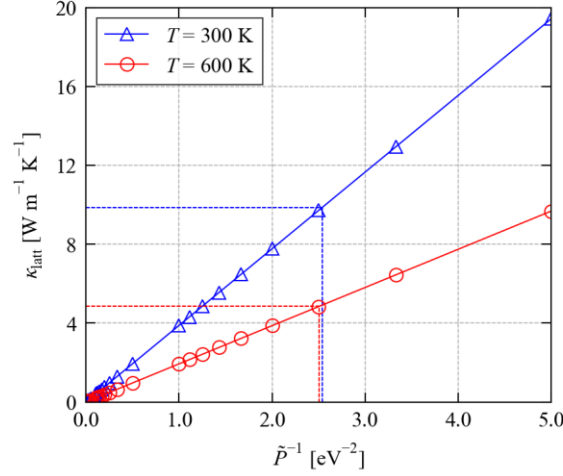


Figure 10 Dependence of the κ_{latt} of pristine CoSb₃ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{latt} at the two temperatures.

Based on Eqs. 7 and 13, the κ_{latt} vary inversely with \tilde{P} . Fig. 10 plots the κ_{latt} of CoSb₃ at 300 and 600 K as a function of \tilde{P}^{-1} . The calculated κ_{latt} is recovered for $\tilde{P} = 3.94 \times 10^{-13}$ and 3.99×10^{-13} at the two temperatures, which are both roughly an order of magnitude smaller than the average P_{λ} (Table 3, Table S2.3). The P_{λ} vary by over an order of magnitude with frequency (Figs. S2.13-S2.18), so as for the τ^{CRTA} we would expect the \tilde{P} to be weighted towards the modes that make the larger contributions to the κ_{latt} . While the $\Phi_{\lambda\lambda'\lambda''}$ in Eq. 10, and, by extension, the P_{λ} and \tilde{P} , are temperature independent, the differing values at 300 and 600 K indicate it is not strictly possible to the $\Phi_{\lambda\lambda'\lambda''}$ with a single value and exactly reproduce the κ_{latt} over a wide range of temperatures. However, the values differ by only 1.3 %, so this model to work remarkably well, and the \tilde{P} might therefore also be a useful parameter for comparing materials.

Similar analyses to Fig. 10 were performed for the five filled materials (Figs. S2.19-S2.23), and the corresponding \tilde{P} at 300 and 600 K are listed in Table 3 and Table S2.3. Taking into account the prefactor of $1/(3n_a)^2$ in Eq. 12, there are three possible scenarios: (1) if there are no interactions between the filler and framework modes - i.e. the corresponding $\Phi_{\lambda\lambda'\lambda''}$ are zero - the P_{λ} would be scaled by $32^2/33^2 = 0.94$; (2) if the interactions between the filler and framework modes are of comparable strength to those between the framework modes, the P_{λ} would be unchanged; and (3) if the filler and framework modes interact more strongly than the framework modes, the P_{λ} would increase. For HeCo₁₂Sb₂₄, the \tilde{P} are increased by ~1.3 % compared to pristine CoSb₃, indicating a strong interaction between the He and framework modes. For Ne-Xe the values are reduced by 0.5-2 %, indicating that the interactions between the filler and framework modes are not negligible, but are weaker than the interactions among framework modes. This contrast provides a natural explanation for why filling with He leads to a larger reduction in the τ^{CRTA} than the other four noble gases. The weaker

interaction strengths for the heavier fillers is also consistent with modelling studies on $\text{YbFe}_4\text{Sb}_{12}$, which found that the third-order (anharmonic) interactions involving Yb were relatively weak.[38]

We also examined the effect of the filler atoms on numbers of scattering channels by comparing the $N_2(\mathbf{q}, \omega)$ defined in Eqs. 14-16 averaged over wavevectors \mathbf{q} , i.e.:

$$\bar{N}_2(\omega) = \bar{N}_2^{(1)}(\omega) + \bar{N}_2^{(2)}(\omega) = \frac{1}{N} \sum_{\mathbf{q}} N_2^{(1)}(\mathbf{q}, \omega) + \frac{1}{N} \sum_{\mathbf{q}} N_2^{(2)}(\mathbf{q}, \omega) \quad (17)$$

As shown in Fig. 11a, collisions are the dominant process below 2 THz, while decay channels become available from ~2 THz, and the $\bar{N}_2^{(1)}(\omega)$ and $\bar{N}_2^{(2)}(\omega)$ are comparable around 4 THz. The number of collision pathways falls to zero from ~6-8 THz, and decay processes dominate at higher frequencies. The five filled models show significant changes in the number of collision channels over the 2-6 THz region where the largest reduction in the κ_{latt} is observed (c.f. Fig. 9), while $\text{KrCo}_8\text{Sb}_{24}$ and $\text{XeCo}_8\text{Sb}_{24}$ also show an number of decay channels from 4-6 THz. Similar differences are seen at 600 K (see Figure S2.24), but both w-JDoS functions are scaled by a factor of two due to the larger phonon occupation numbers.

Combining these observations with the changes in the P_λ , we conclude that He reduces the phonon lifetimes through a relatively strong interaction between the filler and framework modes and an increase in the number of collision channels, while the heavier fillers modulate the number of collision and, to a lesser extent, decay channels, leading to the intricate variation in the lifetimes seen in the CRTA analysis.

c. Discussion

The calculations on the five $\text{XCo}_8\text{Sb}_{24}$ models show that the fillers can reduce the κ_{latt} of pristine CoSb_3 by up to 15 % by limiting the thermal transport through the low-lying optic modes from 2.5-6 THz, by reducing the mode group velocities and, for some fillers, suppressing the phonon lifetimes. Although this reduction is nowhere near as substantial as seen in some filled skutterudites, nanostructuring could be used to reduce the heat transport through the acoustic modes - calculations similar to those in Fig. 6 for the filled models suggest that, for example, nanostructuring to 100 nm could reduce the room-temperature κ_{latt} of the filled models by ~50 % in addition to the smaller reductions compared to pristine CoSb_3 (Figs. S2.25-2.29). Alternatively, fillers of a similar chemical nature to the heavier noble gases could be combined with a second filler to suppress both acoustic- and optic-mode transport - this strategy of introducing two fillers with different rattling frequencies has proven successful in experiments.[62]

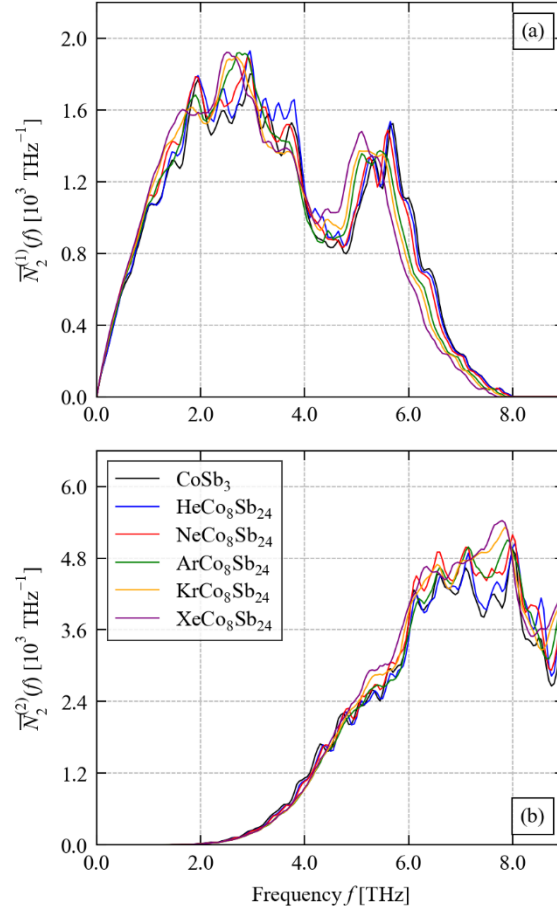


Figure 11 Averaged weighted two-phonon joint density of states (w-JDoS) functions $\bar{N}_2^{(1)}(\omega)$ (a) and $\bar{N}_2^{(2)}(\omega)$ (b) for collision and decay processes, respectively, for CoSb₃ and XCo₈Sb₂₄ with X = He, Ne, Ar, Kr and Xe at $T = 300$ K. The two w-JDoS functions are defined in Eqs. 14-17.

Given that ~80 % of the heat transport in CoSb₃ is through the acoustic modes, the resonant-scattering and avoided-crossing mechanisms both predict that lowering the rattling frequency below 2.5 THz would produce a larger reduction in κ_{latt} . This is not possible with the five fillers studied here because the heavier noble gases interact more strongly with the framework. We can, however, perform a “thought experiment” to decouple the mass and interaction strength by changing the mass of the fillers while keeping the second- and third-order force constants fixed, and vice versa.

Fig. 12 shows how the rattling frequency and room-temperature κ_{latt} vary for each filler as the mass m_X is varied from He to Xe. The frequencies vary inversely as $\sqrt{m_X}$ and fall below 2.5 THz when the mass of the weakly-interacting He filler is increased to m_{Ar} , m_{Kr} and m_{Xe} , or when the mass of Ne is increased to m_{Kr} and m_{Xe} . The changes in κ_{latt} in Fig. 12b show two distinct effects. For higher \tilde{f}_X , the κ_{latt} follow a general decreasing trend with m_X to the maximum ~15 % reduction with XeCo₈Sb₂₄. Once \tilde{f}_X falls below a certain threshold, which from these tests appears to be around 1.5 THz, i.e. well within the acoustic bands, there is a large drop in the κ_{latt} .

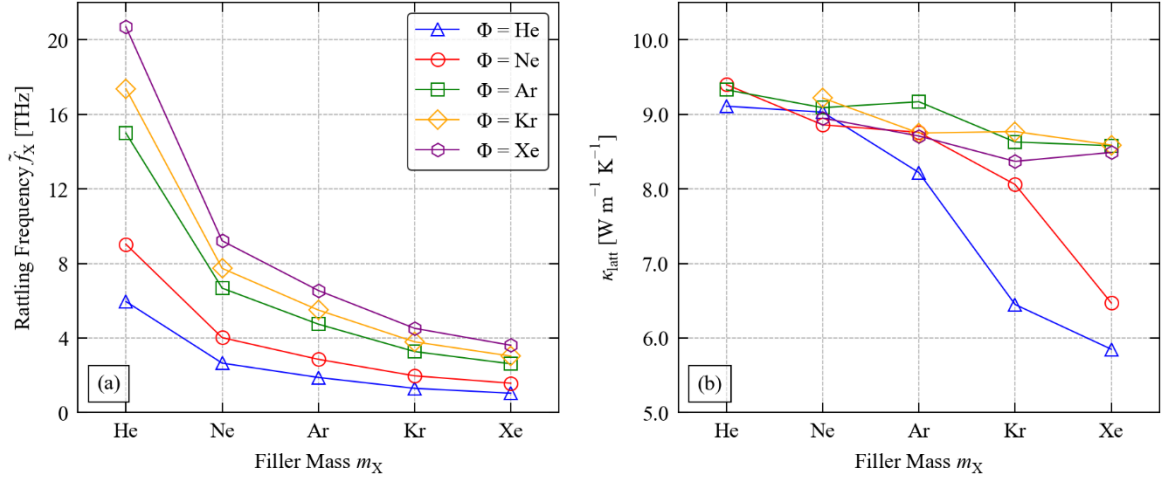


Figure 12 Variation in the approximate filler rattling frequency \tilde{f}_X and 300 K lattice thermal conductivity κ_{latt} with the filler mass m_X for fixed second- and third-order force constants Φ .

The He and Ne calculations show that when the filler modes fall among the acoustic modes the κ_{latt} can be reduced by up to 40 % compared to pristine CoSb_3 . Using the CRTA analysis, we find that for He this is due to a 10-15 % reduction in the group velocities and a 20-30 % reduction in the lifetimes, while for Ne it is due to a 20 % reduction in the v_λ and a 15 % reduction in the τ_λ (Figs. S2.30/S2.31). Comparison of the unfolded band structures and projected DoS curves of $\text{HeCo}_8\text{Sb}_{24}$ as the mass of the He atom is increased show that rattling frequencies within the acoustic bands lead to localised modes with narrow dispersion (Figs. S2.32-S2.35). Although there is some evidence of avoided crossings where the acoustic and filler modes cross, the CRTA analysis points to a minor effect on the group velocities, which suggests the reduced lifetimes are mainly due to resonant scattering with the filler modes.

We also note that lowering the masses of Kr and Xe, with the strongest filler-framework interactions, to that of He gives an unphysically large κ_{latt} . This combination results in rattling frequencies of 17.4 and 20.7 THz, which are both so far outside the frequency range of the CoSb_3 spectrum that there are probably very few energy-conserving scattering channels to limit their modal κ_λ .

This analysis clearly shows, as per the “rattler” model of cage compounds, that the largest reductions in κ_{latt} are obtained with heavy fillers that interact weakly with the framework. The mass is a known parameter, and the interaction strength, as we have shown, can be determined approximately from the second-order (harmonic) force constants, providing an efficient means to screen potential fillers theoretically.

4. Conclusions

In summary, we have used first-principles modelling to investigate the structural dynamics and thermal transport in pristine CoSb_3 and filled $\text{XC}_8\text{Sb}_{24}$ containing a series of noble gas atoms. This “toy model” provides a useful baseline to explore how the size and mass of filler atoms and their interaction with the host framework impact on the thermal transport.

The relaxation-time approximation provides a quantitative description of the thermal transport in CoSb₃ and highlights how synergistic nanostructuring could be used as an additional means to control the thermal conductivity in these materials.

The rattling frequencies of the noble gas atoms are determined through a detailed balance of their atomic mass and how strongly they interact with the host framework, which both increase from He to Xe. The heavier filler atoms suppress the heat transport through the low-lying optic modes, which accounts for ~20 % of the total κ_{latt} in pristine CoSb₃, primarily by reducing the group velocity. The effect of the fillers on the phonon lifetimes depends intricately on changes in the phonon-phonon interaction strengths and changes in the number of energy-conserving scattering pathways for modes in different parts of the phonon spectrum. The heavier noble gases show comparatively weak phonon-phonon interactions, and their effect on the phonon lifetimes occurs mainly through the latter.

We have also proposed various analyses that can be used to gain better insight into the impact of the fillers atoms on the thermal transport. Of particular note are the constant relaxation-time model to quantitatively attribute changes in κ_{latt} to changes in the phonon mode group velocities and lifetimes, and the approximate model for phonon linewidths to attribute changes in lifetimes to changes in the phonon-phonon interaction strengths and the numbers of scattering pathways. These tools may prove useful both to better understand and to compare the impact of filler atoms on the heat transport in skutterudites and other cage compounds.

Finally, we have shown that approximate rattling frequencies, determined from the harmonic force constants, appear to be a useful predictor of the κ_{latt} in the filled skutterudites. In particular, rattling frequencies in the range of the acoustic modes, obtained by heavy fillers that interact weakly with the CoSb₃ framework, are predicted to lead to the largest suppression of the thermal transport. Identifying descriptors to predict the interaction strength between the fillers and the framework (e.g. charge, electronegativity, and polarizability) is therefore likely to be a useful step towards the rational selection of fillers for controlling the heat transport in cage compounds.

5. Acknowledgements

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6. Data-Access Statement

Data from the modelling studies in this work including optimised structures, calculated force constants and phonon spectra, and raw data from the thermal-conductivity calculations are available to download from an online repository at [\[URL to be added on acceptance\]](#). Data not available as supporting information or from the

repository may be obtained from the authors on request. Some of the codes used to analyse the modelling data are available from the GitHub repository at: <https://github.com/skelton-group/Phono3py-Power-Tools>.

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Impact of noble-gas filler atoms on the lattice thermal conductivity of CoSb₃ skutterudites: first-principles modelling

Electronic supporting information

Jianqin Tang¹ and Jonathan M. Skelton^{1*}

¹ Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

* Corresponding author. E-Mail: jonathan.skelton@manchester.ac.uk.

1. Computational modelling

a. Supercell size for determining the second- and third-order interatomic force constants

To verify the suitability of our chosen supercell for computing the second-order interatomic force constants (IFCs), we compared phonon dispersion and density of states (DoS) curves for CoSb₃ obtained from IFCs computed in $2 \times 2 \times 2$ expansions of the primitive and conventional cells containing 128 and 256 atoms respectively. The technical parameters listed in the text were used for the calculations on the primitive cell, with $4 \times 4 \times 4$ and $2 \times 2 \times 2$ **k**-point meshes used for the base cell and supercell expansion. As shown in Figure S1.1, the results are practically superimposable.

To verify the suitability of the base CoSb₃ conventional cell for computing the third-order IFCs, we also calculated third-order IFCs in the base primitive cell with 16 atoms and a $2 \times 2 \times 2$ expansion with 128 atoms. As shown in Figures S1.2 and Table S1, the thermal conductivity calculated using the conventional-cell model is ~10 % larger than the primitive-cell model with the small third-order supercell, but is within 1 % of the model using the larger 128-atom third-order supercell.

These tests therefore suggest that the conventional-cell model is an appropriate balance between accuracy and cost, and is particularly convenient for these calculations given that it makes it possible to model filled CoSb₃ with a reasonable filling fraction.

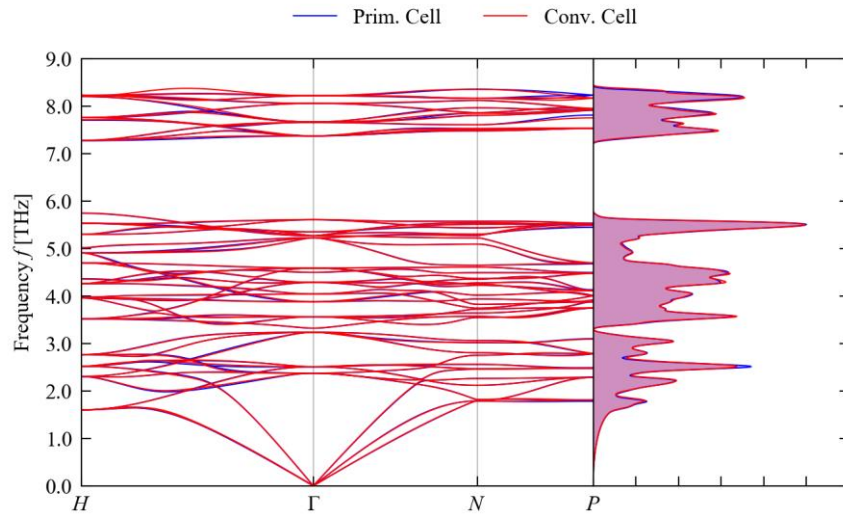


Figure S1.1 Comparison of the phonon dispersion and density of states $g(f)$ (DoS) of pristine CoSb₃ calculated using force constants obtained in $2 \times 2 \times 2$ supercell expansions of the primitive (blue) and conventional cells (red) with 128 and 256 atoms, respectively.

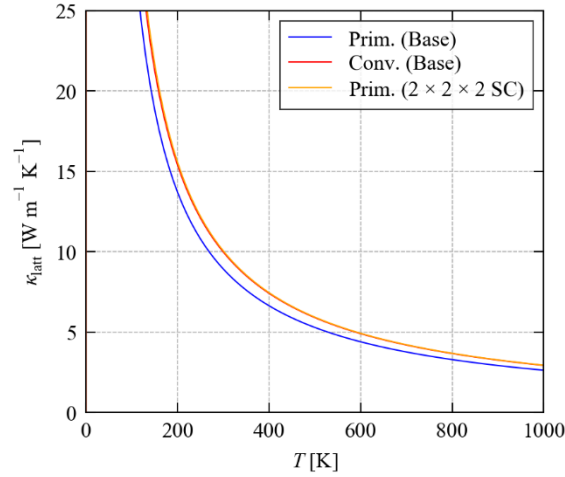


Figure S1.2 Lattice thermal-conductivity κ_{latt} of pristine CoSb_3 as a function of temperature calculated using three models: (1) the primitive cell with the 2nd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion and the 3rd-order IFCs evaluated in the base cell (blue); (2) the conventional cell (red); and (3) the primitive cell with the 2nd- and 3rd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion (orange). The κ_{latt} of the conventional cell model was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} , while the κ_{latt} of the primitive cell models was computed on $11 \times 11 \times 11$ grids with $\sim 2\times$ as many wavevectors in proportion to their $2\times$ larger Brillouin zones.

b. Numerical quality of the interatomic force constants

A good proxy for the numerical quantity of the calculated force constants is to compare thermal-conductivity calculations performed with and without applying symmetrisation to the force constants. Figures S1.3-S1.10 compare thermal-conductivity curves for all the pristine CoSb_3 and filled $\text{XCo}_8\text{Sb}_{24}$ models considered in this work computed with and without force-constant symmetrisation, and values at 300 and 600 K are compared in Table S1.2. We find a maximum absolute difference of 1.05 % in the two sets of values, which indicates that the calculated force constants have a low level of numerical noise.

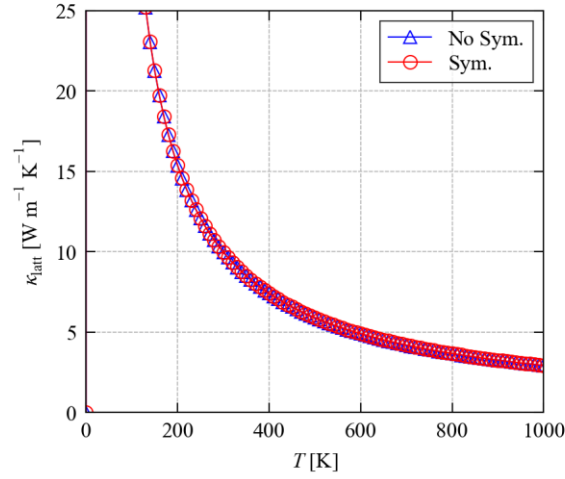


Figure S1.3 Lattice thermal-conductivity κ_{latt} of pristine CoSb₃ calculated with (red) and without (blue) force-constant symmetrisation (conventional cell model). In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

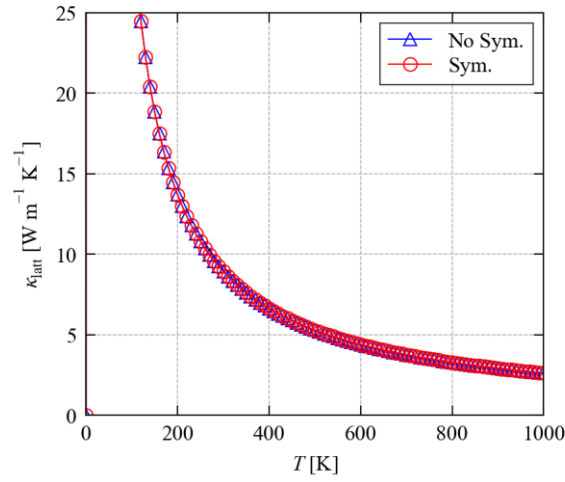


Figure S1.4 Lattice thermal-conductivity κ_{latt} of pristine CoSb₃ calculated with (red) and without (blue) force-constant symmetrisation (primitive cell model with 2nd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion and 3rd-order IFCs evaluated in the base cell). In both cases the κ_{latt} was computed from modal properties evaluated on an $11 \times 11 \times 11$ grid of phonon wavevectors \mathbf{q} .

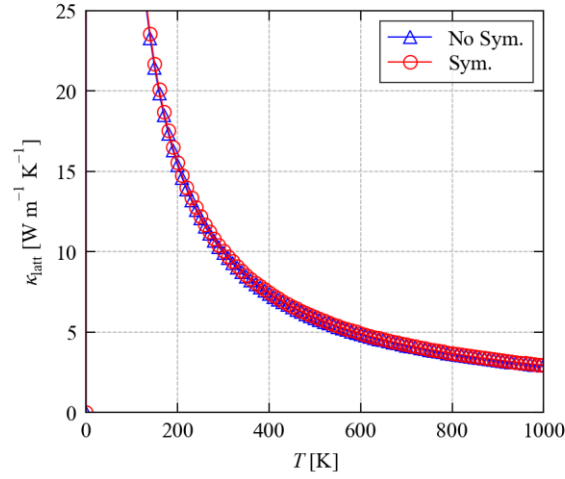


Figure S1.5 Lattice thermal-conductivity κ_{latt} of pristine CoSb₃ calculated with (red) and without (blue) force-constant symmetrisation (primitive cell model with 2nd- and 3rd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion). In both cases the κ_{latt} was computed from modal properties evaluated on an $11 \times 11 \times 11$ grid of phonon wavevectors \mathbf{q} .

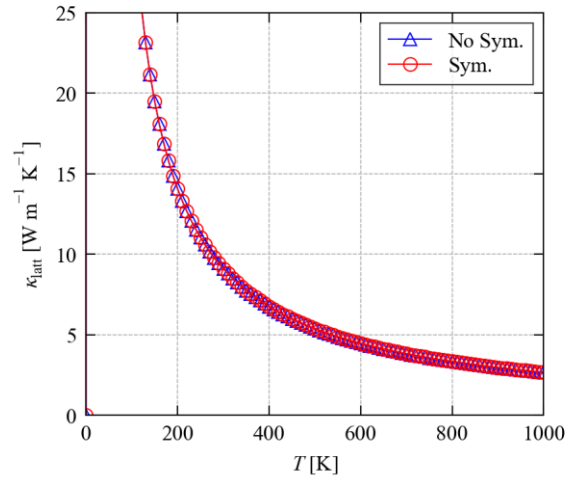


Figure S1.6 Lattice thermal-conductivity κ_{latt} of HeCo₈Sb₂₄ calculated with (red) and without (blue) force-constant symmetrisation. In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

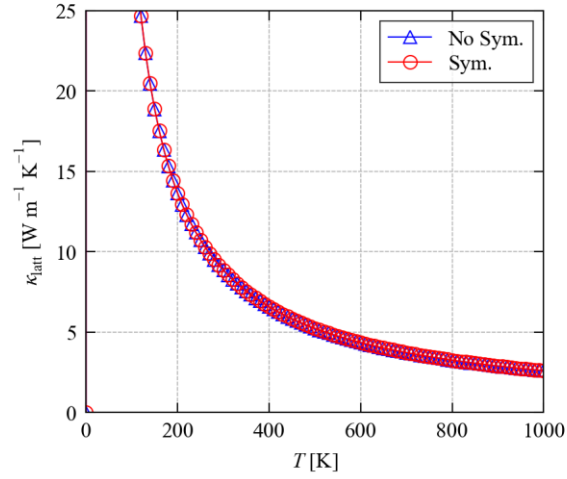


Figure S1.7 Lattice thermal-conductivity κ_{latt} of $\text{NeCo}_8\text{Sb}_{24}$ calculated with (red) and without (blue) force-constant symmetrisation. In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

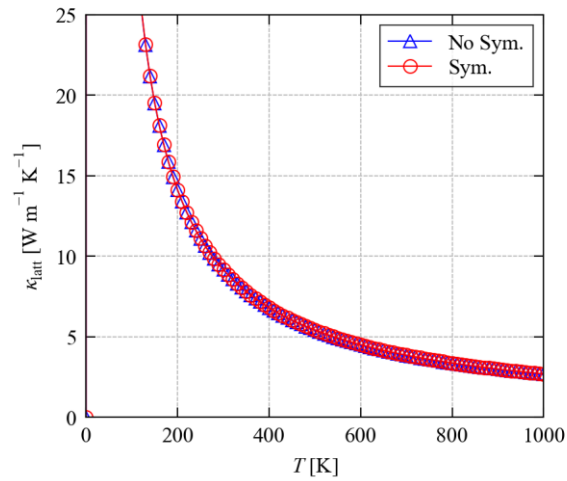


Figure S1.8 Lattice thermal-conductivity κ_{latt} of $\text{ArCo}_8\text{Sb}_{24}$ calculated with (red) and without (blue) force-constant symmetrisation. In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

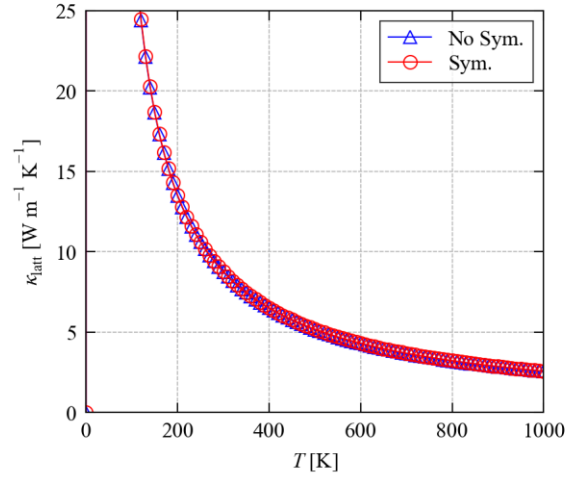


Figure S1.9 Lattice thermal-conductivity κ_{latt} of $\text{KrCo}_8\text{Sb}_{24}$ calculated with (red) and without (blue) force-constant symmetrisation. In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

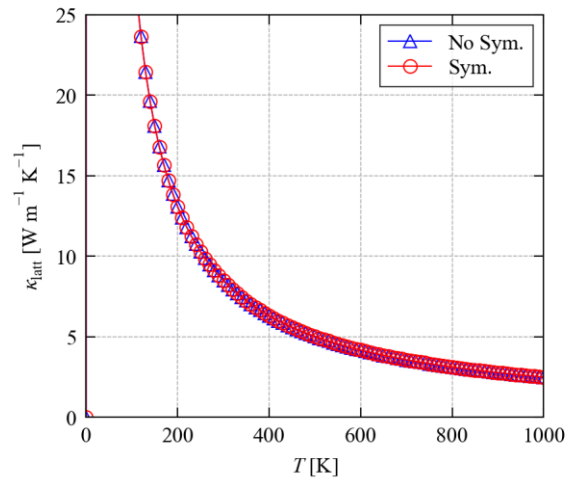


Figure S1.10 Lattice thermal-conductivity κ_{latt} of $\text{XeCo}_8\text{Sb}_{24}$ calculated with (red) and without (blue) force-constant symmetrisation. In both cases the κ_{latt} was computed from modal properties evaluated on a $9 \times 9 \times 9$ grid of phonon wavevectors \mathbf{q} .

Cell	IFC Supercell		Sampling Mesh	$T = 300$ K		$T = 600$ K	
	2 nd -order	3 rd -order		κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]	κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]
Conv.	$2 \times 2 \times 2$	Base	$9 \times 9 \times 9$	9.981	-	4.909	-
Prim.	$2 \times 2 \times 2$	Base	$11 \times 11 \times 11$	8.927	-10.6	4.402	-10.3
Prim.	$2 \times 2 \times 2$	$2 \times 2 \times 2$	$11 \times 11 \times 11$	10.054	0.73	4.931	0.45

Table S1.1 Comparison of the calculated lattice thermal conductivity κ_{latt} of CoSb₃ at $T = 300$ and 600 K obtained using three different models, viz. (1) 2nd- and 3rd-order IFCs computed in a $2 \times 2 \times 2$ expansion and a single unit of the 32-atom conventional cell, (2) 2nd- and 3rd-order IFCs computed in a $2 \times 2 \times 2$ expansion and a single unit of the 16-atom primitive cell; and (3) 2nd- and 3rd-order IFCs computed in a $2 \times 2 \times 2$ expansion of the 16-atom primitive cell. The κ_{latt} for the three models were evaluated using the sampling meshes indicated.

	Sampling Mesh	$T = 300$ K			$T = 600$ K		
		κ_{latt} [W m ⁻¹ K ⁻¹]		Δ [%]	κ_{latt} [W m ⁻¹ K ⁻¹]		Δ [%]
		No Sym.	Sym.		No Sym.	Sym.	
CoSb ₃ (Conv.)	$9 \times 9 \times 9$	9.974	9.981	0.08	4.905	4.909	0.08
CoSb ₃ (Prim.)	$11 \times 11 \times 11$	8.929	8.927	-0.02	4.403	4.402	-0.02
CoSb ₃ (Prim. - $2 \times 2 \times 2$ SC)	$11 \times 11 \times 11$	9.950	10.054	1.04	4.881	4.931	1.02
HeCo ₈ Sb ₂₄	$9 \times 9 \times 9$	9.110	9.112	0.02	4.476	4.476	0.01
NeCo ₈ Sb ₂₄	$9 \times 9 \times 9$	8.852	8.864	0.13	4.355	4.360	0.13
ArCo ₈ Sb ₂₄	$9 \times 9 \times 9$	9.160	9.171	0.12	4.506	4.512	0.12
KrCo ₈ Sb ₂₄	$9 \times 9 \times 9$	8.744	8.768	0.28	4.300	4.312	0.28
XeCo ₈ Sb ₂₄	$9 \times 9 \times 9$	8.503	8.494	-0.10	4.183	4.179	-0.10

Table S1.2 Comparison of the calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for the pristine CoSb₃ and filled XCo₈Sb₂₄ models considered in this work, obtained with and without force-constant symmetrisation using the sampling meshes indicated.

c. Brillouin-zone sampling meshes for the thermal-conductivity calculations

Using the single-mode relaxation-time approximation, the macroscopic thermal conductivity κ_{latt} is calculated as a sum of modal contributions evaluated on a regular grid of wavevectors sampling the phonon Brillouin zone (Eq. 2 in the text). Appropriate sampling meshes for each of the models investigated in this work were determined by explicit convergence testing to be $9 \times 9 \times 9$ for the pristine and filled models based on the CoSb₃ conventional cell and $11 \times 11 \times 11$ for the pristine model based on the primitive cell.

Figs. S1.11-S1.18 plot for each of the models the thermal conductivity as a function of temperature obtained using a series of sampling meshes. Tables S1.3-S1.10 compare κ_{latt} values at $T = 300$ and 600 K on each of the meshes tested to the chosen converged meshes. We note in passing that for most of the models sampling meshes with an odd number of subdivisions appear to converge faster than “even” meshes, which we attribute to a flattening of the acoustic mode dispersion close to the zone boundary (c.f. Fig. 2 in the text).

Finally, a smaller $7 \times 7 \times 7$ mesh was used to compare the two-phonon joint density of states (w-JDoS) functions and averaged phonon-phonon interaction strengths for the pristine and filled models based on the CoSb₃ conventional cell, and to investigate the effect of varying the atomic mass of the noble gas atoms in the filled models. The thermal conductivities calculated using these reduced meshes are within 1-5 % of those obtained using the $9 \times 9 \times 9$ meshes, and the approximately twofold reduction in the number of grid points makes the post processing much less computationally intensive.

Sampling Mesh	$T = 300$ K		$T = 600$ K	
	κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]	κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]
$2 \times 2 \times 2$	4.135	-58.6	2.036	-58.5
$3 \times 3 \times 3$	8.316	-16.7	4.097	-16.5
$4 \times 4 \times 4$	9.071	-9.12	4.463	-9.09
$5 \times 5 \times 5$	9.692	-2.90	4.769	-2.86
$6 \times 6 \times 6$	9.549	-4.33	4.699	-4.27
$7 \times 7 \times 7$	9.872	-1.10	4.857	-1.06
$8 \times 8 \times 8$	9.853	-1.29	4.847	-1.26
$9 \times 9 \times 9$	9.981	0.00	4.909	0.00

Table S1.3 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for pristine CoSb₃ obtained with the series of sampling meshes shown in Fig. 1.11 (conventional cell model).

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.000	-100.00	-4.402	-100.00
$3 \times 3 \times 3$	6.054	-32.18	-1.407	-31.95
$4 \times 4 \times 4$	8.118	-9.06	-0.392	-8.90
$5 \times 5 \times 5$	8.467	-5.15	-0.222	-5.05
$6 \times 6 \times 6$	8.433	-5.53	-0.244	-5.53
$7 \times 7 \times 7$	8.797	-1.45	-0.061	-1.39
$8 \times 8 \times 8$	8.803	-1.38	-0.059	-1.34
$9 \times 9 \times 9$	8.818	-1.22	-0.053	-1.21
$10 \times 10 \times 10$	8.734	-2.16	-0.095	-2.17
$11 \times 11 \times 11$	8.927	0.00	0.000	0.00

Table S1.4 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for pristine CoSb_3 obtained with the series of sampling meshes shown in Fig. 1.12 (primitive cell model with 2nd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion and 3rd-order IFCs evaluated in the base cell).

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.000	-100.00	0.000	-100.00
$3 \times 3 \times 3$	6.241	-37.93	3.085	-37.43
$4 \times 4 \times 4$	8.650	-13.96	4.267	-13.47
$5 \times 5 \times 5$	9.109	-9.40	4.483	-9.08
$6 \times 6 \times 6$	9.337	-7.13	4.587	-6.97
$7 \times 7 \times 7$	9.847	-2.06	4.838	-1.89
$8 \times 8 \times 8$	9.781	-2.71	4.805	-2.57
$9 \times 9 \times 9$	9.873	-1.80	4.845	-1.75
$10 \times 10 \times 10$	9.823	-2.29	4.818	-2.29
$11 \times 11 \times 11$	10.054	0.00	4.931	0.00

Table S1.5 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for pristine CoSb_3 obtained with the series of sampling meshes shown in Fig. 1.13 (primitive cell model with 2nd- and 3rd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion).

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.157	-98.28	0.077	-98.27
$3 \times 3 \times 3$	7.757	-14.86	3.818	-14.70
$4 \times 4 \times 4$	6.422	-29.51	3.153	-29.56
$5 \times 5 \times 5$	8.825	-3.15	4.336	-3.12
$6 \times 6 \times 6$	7.746	-14.99	3.807	-14.95
$7 \times 7 \times 7$	9.018	-1.03	4.432	-0.99
$8 \times 8 \times 8$	8.082	-11.30	3.970	-11.31
$9 \times 9 \times 9$	9.112	0.00	4.476	0.00

Table S1.6 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for $\text{HeCo}_8\text{Sb}_{32}$ obtained with the series of Brillouin-zone sampling meshes shown in Fig. 1.14.

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.000	-100.00	0.000	-100.00
$3 \times 3 \times 3$	7.395	-16.57	3.644	-16.44
$4 \times 4 \times 4$	6.451	-27.22	3.173	-27.23
$5 \times 5 \times 5$	8.631	-2.63	4.247	-2.59
$6 \times 6 \times 6$	7.581	-14.47	3.730	-14.45
$7 \times 7 \times 7$	8.523	-3.85	4.194	-3.81
$8 \times 8 \times 8$	7.774	-12.29	3.824	-12.30
$9 \times 9 \times 9$	8.864	0.00	4.360	0.00

Table S1.7 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for $\text{NeCo}_8\text{Sb}_{32}$ obtained with the series of Brillouin-zone sampling meshes shown in Fig. 1.15.

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.000	-100.00	0.000	-100.00
$3 \times 3 \times 3$	8.317	-9.31	4.096	-9.20
$4 \times 4 \times 4$	6.803	-25.82	3.346	-25.84
$5 \times 5 \times 5$	8.981	-2.08	4.419	-2.05
$6 \times 6 \times 6$	7.888	-13.99	3.880	-13.99
$7 \times 7 \times 7$	8.807	-3.98	4.334	-3.95
$8 \times 8 \times 8$	8.209	-10.49	4.038	-10.50
$9 \times 9 \times 9$	9.171	0.00	4.512	0.00

Table S1.8 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for $\text{ArCo}_8\text{Sb}_{32}$ obtained with the series of Brillouin-zone sampling meshes shown in Fig. 1.16.

Sampling Mesh	$T = 300 \text{ K}$		$T = 600 \text{ K}$	
	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$	$\kappa_{\text{latt}} [\text{W m}^{-1} \text{K}^{-1}]$	$\Delta [\%]$
$2 \times 2 \times 2$	0.000	-100.00	0.000	-100.00
$3 \times 3 \times 3$	7.847	-10.51	3.865	-10.36
$4 \times 4 \times 4$	6.324	-27.87	3.110	-27.86
$5 \times 5 \times 5$	8.330	-5.00	4.097	-4.99
$6 \times 6 \times 6$	7.787	-11.19	3.830	-11.17
$7 \times 7 \times 7$	8.360	-4.66	4.113	-4.61
$8 \times 8 \times 8$	7.924	-9.63	3.896	-9.64
$9 \times 9 \times 9$	8.768	0.00	4.312	0.00

Table S1.9 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for $\text{KrCo}_8\text{Sb}_{32}$ obtained with the series of Brillouin-zone sampling meshes shown in Fig. 1.17.

Sampling Mesh	$T = 300$ K		$T = 600$ K	
	κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]	κ_{latt} [W m ⁻¹ K ⁻¹]	Δ [%]
$2 \times 2 \times 2$	0.000	-100.00	0.000	-100.00
$3 \times 3 \times 3$	7.588	-10.67	3.738	-10.55
$4 \times 4 \times 4$	6.332	-25.46	3.114	-25.48
$5 \times 5 \times 5$	8.005	-5.76	3.939	-5.75
$6 \times 6 \times 6$	7.586	-10.70	3.732	-10.69
$7 \times 7 \times 7$	8.087	-4.80	3.980	-4.76
$8 \times 8 \times 8$	7.813	-8.03	3.843	-8.04
$9 \times 9 \times 9$	8.494	0.00	4.179	0.00

Table S1.10 Calculated lattice thermal conductivity κ_{latt} at $T = 300$ and 600 K for $\text{XeCo}_8\text{Sb}_{32}$ obtained with the series of Brillouin-zone sampling meshes shown in Fig. 1.18.

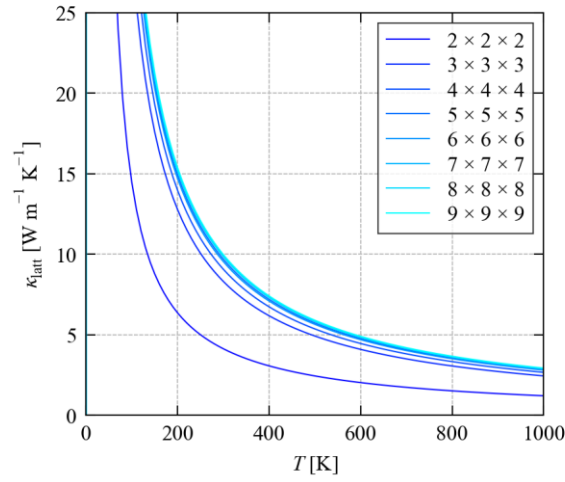


Figure S1.11 Lattice thermal-conductivity κ_{latt} of pristine CoSb_3 calculated with a series of Brillouin-zone sampling meshes (conventional cell model).

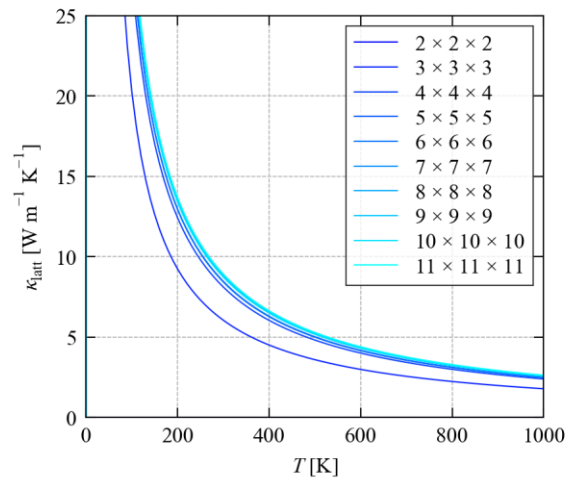


Figure S1.12 Lattice thermal-conductivity κ_{latt} of pristine CoSb_3 calculated with a series of Brillouin-zone sampling meshes (primitive cell model with 2nd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion and 3rd-order IFCs evaluated in the base cell).

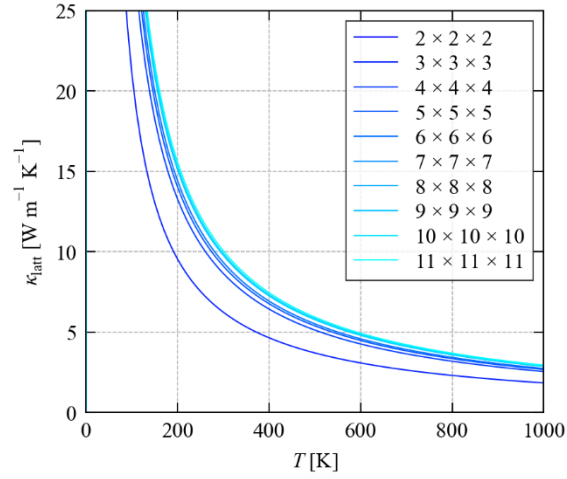


Figure S1.13 Lattice thermal-conductivity κ_{latt} of pristine CoSb_3 calculated with a series of Brillouin-zone sampling meshes (primitive cell model with 2nd- and 3rd-order IFCs computed using a $2 \times 2 \times 2$ supercell expansion).

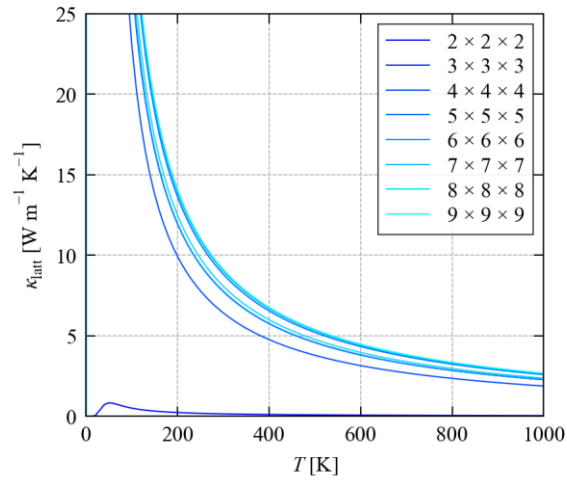


Figure S1.14 Lattice thermal-conductivity κ_{latt} of $\text{HeCo}_8\text{Sb}_{24}$ calculated with a series of Brillouin-zone sampling meshes.

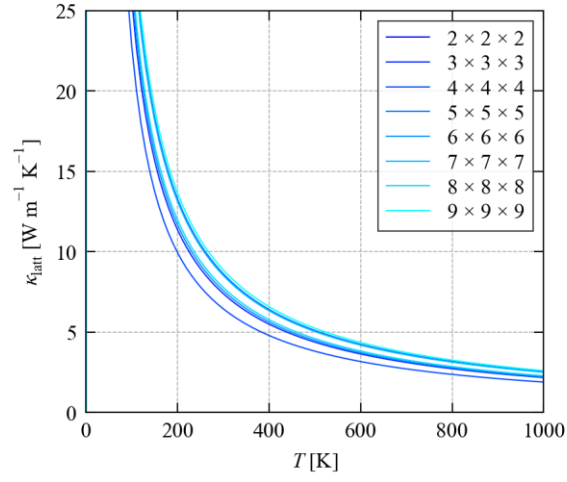


Figure S1.15 Lattice thermal-conductivity κ_{latt} of $\text{NeCo}_8\text{Sb}_{24}$ calculated with a series of Brillouin-zone sampling meshes.

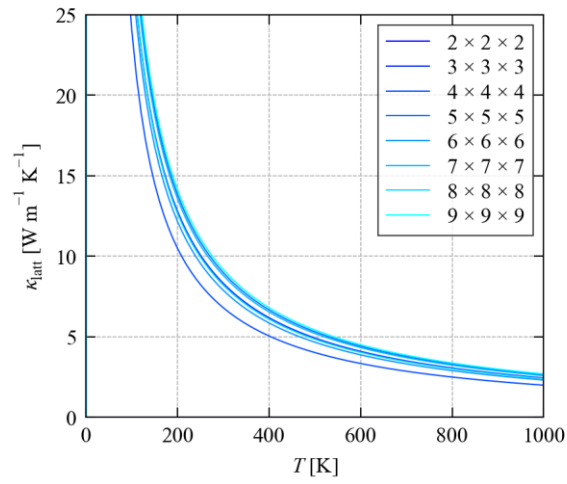


Figure S1.16 Lattice thermal-conductivity κ_{latt} of $\text{ArCo}_8\text{Sb}_{24}$ calculated with a series of Brillouin-zone sampling meshes.

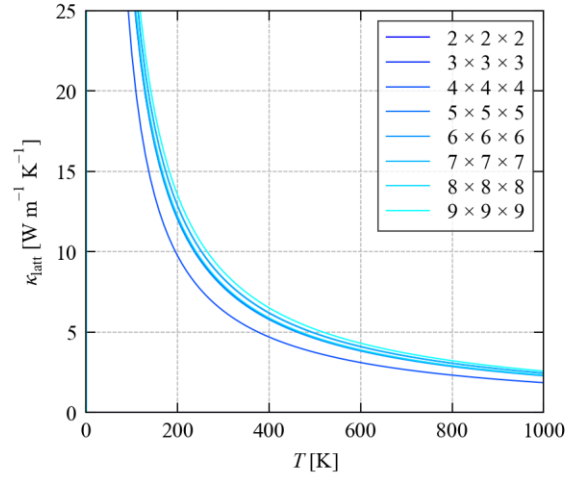


Figure S1.17 Lattice thermal-conductivity κ_{latt} of $\text{KrCo}_8\text{Sb}_{24}$ calculated with a series of Brillouin-zone sampling meshes.

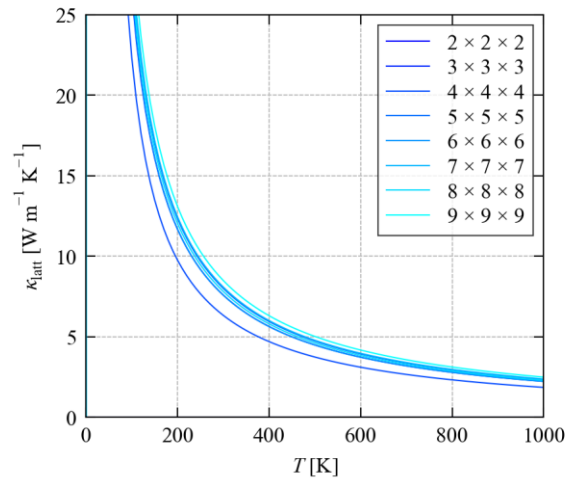


Figure S1.18 Lattice thermal-conductivity κ_{latt} of $\text{XeCo}_8\text{Sb}_{24}$ calculated with a series of Brillouin-zone sampling meshes.

3. Results and Discussion

a. Pristine CoSb₃

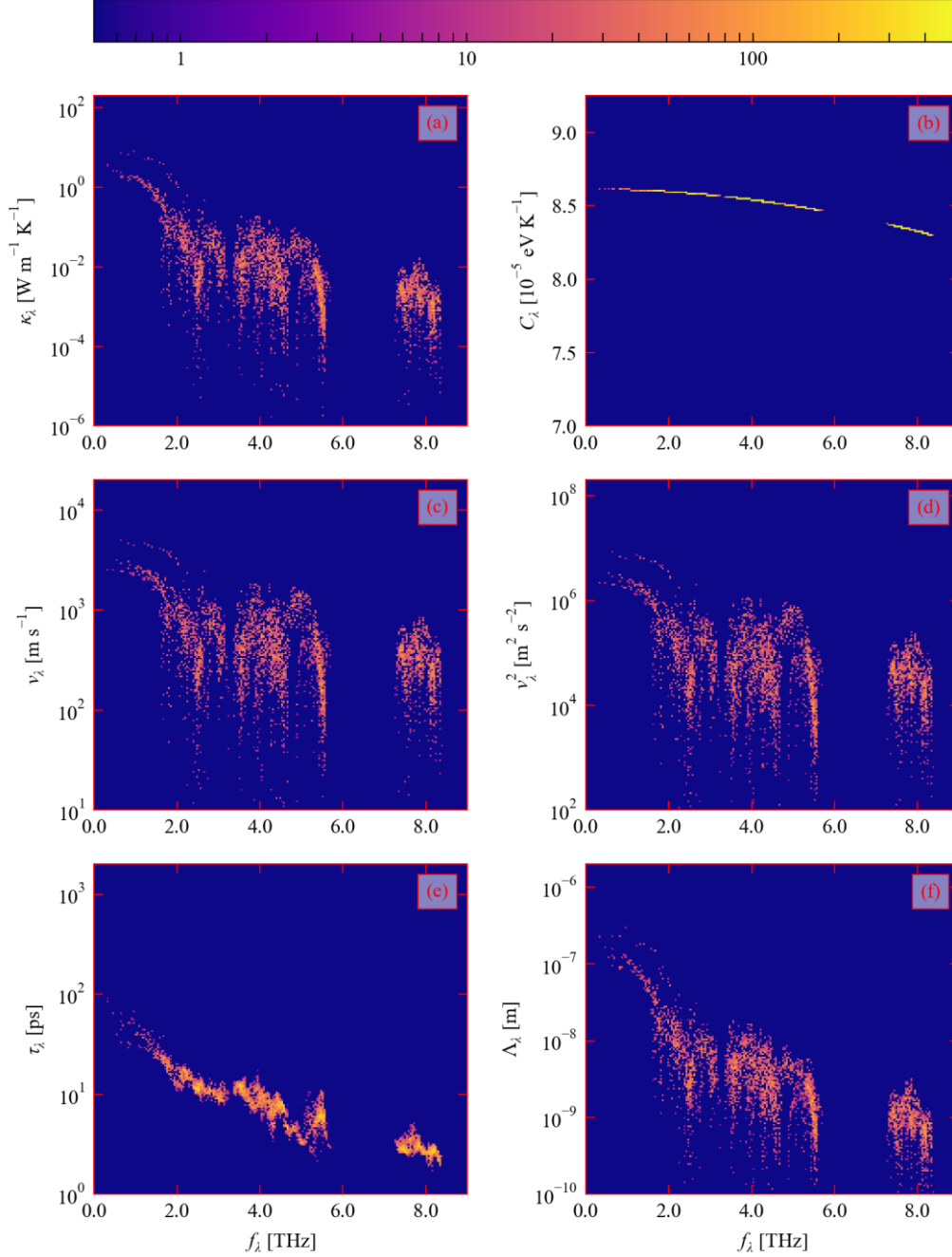


Figure S2.1 Frequency spectra of the modal terms in Eq. 2 in the text for pristine CoSb₃ at $T = 600$ K, *viz.* the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale. The y-axis limits are set to the same as Fig. 5 in the text for easy comparison between the two sets of data.

b. CoSb₃ with noble gas fillers

	a_0 [Å]		Δ [%]
	PBesol	PBesol + D3	
CoSb ₃	8.952	8.885	-0.75
HeCo ₈ Sb ₂₄	8.952	8.886	-0.73
NeCo ₈ Sb ₂₄	8.960	8.892	-0.76
ArCo ₈ Sb ₂₄	8.975	8.909	-0.74
KrCo ₈ Sb ₂₄	8.987	8.922	-0.73
XeCo ₈ Sb ₂₄	9.010	8.943	-0.74

Table S2.1 Optimise lattice constants of pristine CoSb₃ and filled XCo₈Sb₂₄ with X = He, Ne, Ar, Kr and Xe obtained with the PBesol functional with and without the DFT-D3 dispersion correction. The right-hand column shows the % differences for comparison.

	NN 1 - 12 Sb		NN 2 - 8 Co		NN 3 - 24 Sb	
	d [Å]	$\ \Phi\ $ [eV Å ⁻²]	d [Å]	$\ \Phi\ $ [eV Å ⁻²]	d [Å]	$\ \Phi\ $ [eV Å ⁻²]
HeCo ₈ Sb ₂₄	3.312	1.70×10^{-1}	3.875	1.78×10^{-2}	5.615	4.66×10^{-3}
NeCo ₈ Sb ₂₄	3.320	3.38×10^{-1}	3.880	1.54×10^{-2}	5.621	6.67×10^{-3}
ArCo ₈ Sb ₂₄	3.342	8.50×10^{-1}	3.890	9.94×10^{-2}	5.631	2.07×10^{-2}
KrCo ₈ Sb ₂₄	3.355	1.15	3.897	1.53×10^{-1}	5.639	3.01×10^{-2}
XeCo ₈ Sb ₂₄	3.377	1.63	3.911	2.32×10^{-1}	5.655	4.88×10^{-2}

Table S2.2 Neighbour distances d between the filler atom X and the three nearest neighbours in XCo₈Sb₂₄ (X = He, Ne, Ar, Kr and Xe), together with the Frobenius norms $\|\Phi\|$ of the corresponding second-order (harmonic) force constants (see Eq. 5 in the text).

	$\bar{\kappa}_{\text{latt}}$ [W m ⁻¹ K ⁻¹]	Δ [%]	$\bar{\kappa}_{\text{latt}}/\tau^{\text{CRTA}}$ [10 ¹² W m ⁻¹ K ⁻¹ s ⁻¹]	Δ [%]	τ^{CRTA} [ps]	Δ [%]	\tilde{P} [10 ⁻¹² eV ²]	Δ [%]	$\bar{\tau}_\lambda$ [ps]	\bar{P}_λ [10 ⁻¹² eV ²]
CoSb ₃	4.91	-	0.278	-	17.6	-	0.399	-	8.31	6.00
HeCo ₈ Sb ₂₄	4.48	-8.82	0.265	-4.64	16.9	-4.38	0.404	1.30	8.06	5.65
NeCo ₈ Sb ₂₄	4.36	-11.18	0.248	-10.83	17.6	-0.39	0.393	-1.53	8.14	5.46
ArCo ₈ Sb ₂₄	4.51	-8.09	0.254	-8.81	17.8	0.79	0.395	-0.90	7.98	5.35
KrCo ₈ Sb ₂₄	4.31	-12.17	0.242	-13.02	17.8	0.98	0.391	-1.88	8.01	5.27
XeCo ₈ Sb ₂₄	4.18	-14.87	0.243	-12.71	17.2	-2.47	0.389	-2.31	7.72	5.18

Table S2.3 Calculated lattice thermal conductivity κ_{latt} , $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$, τ^{CRTA} and \tilde{P} at $T = 600$ K for the CoSb₃ and XCo₈Sb₂₄ (X = He, Ne, Ar, Kr) models examined in this work. The quantities $\kappa_{\text{latt}}/\tau^{\text{CRTA}}$, τ^{CRTA} and \tilde{P} are defined in the text. The percentage change in the parameters relative to pristine CoSb₃ are shown for comparison. The rightmost two columns list the averaged lifetimes and interaction strengths $\bar{\tau}_\lambda/\bar{P}_\lambda$ for comparison to the τ^{CRTA} and \tilde{P} respectively.

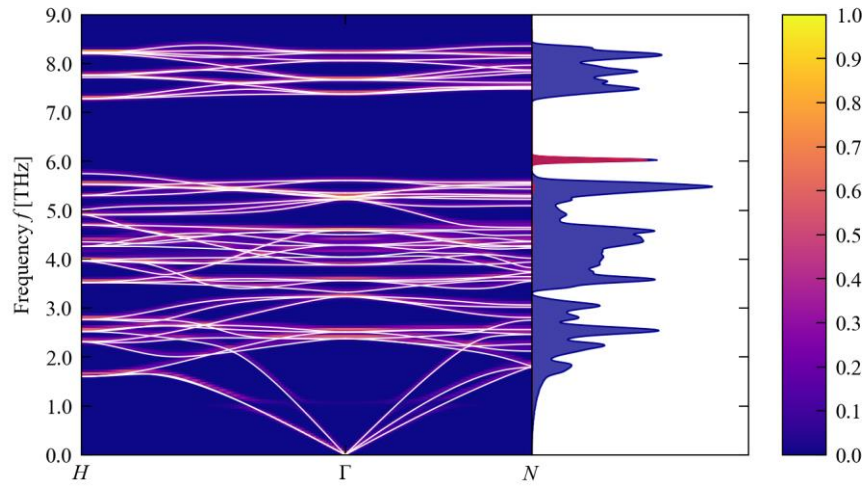


Figure S2.2 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{HeCo}_8\text{Sb}_{24}$. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the He filler is overlaid on the $g(f)$ in red.

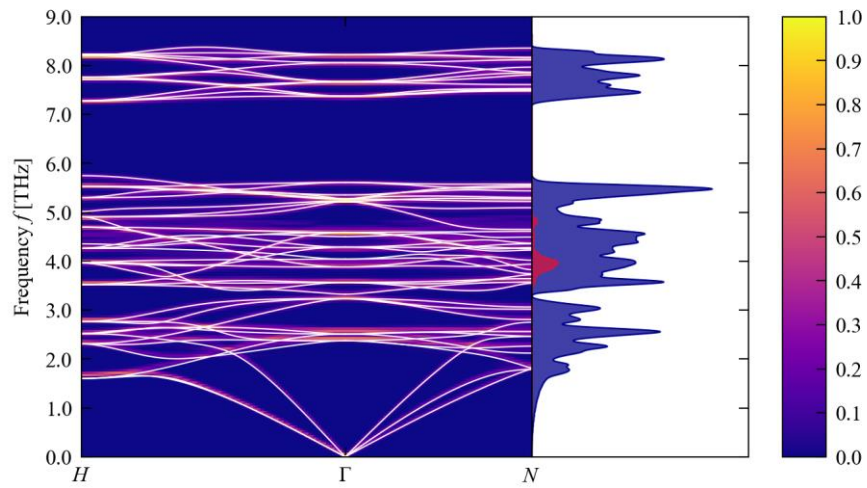


Figure S2.3 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{NeCo}_8\text{Sb}_{24}$. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the Ne filler is overlaid on the $g(f)$ in red.

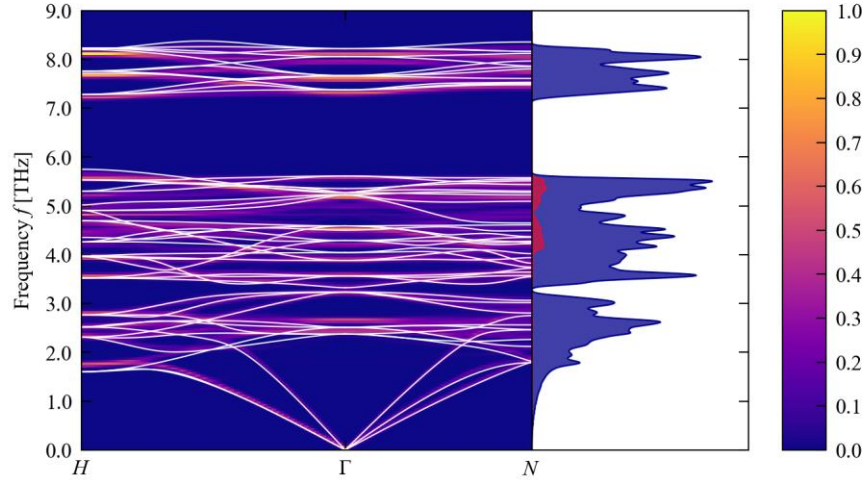


Figure S2.4 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{ArCo}_8\text{Sb}_{24}$. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the Ar filler is overlaid on the $g(f)$ in red.

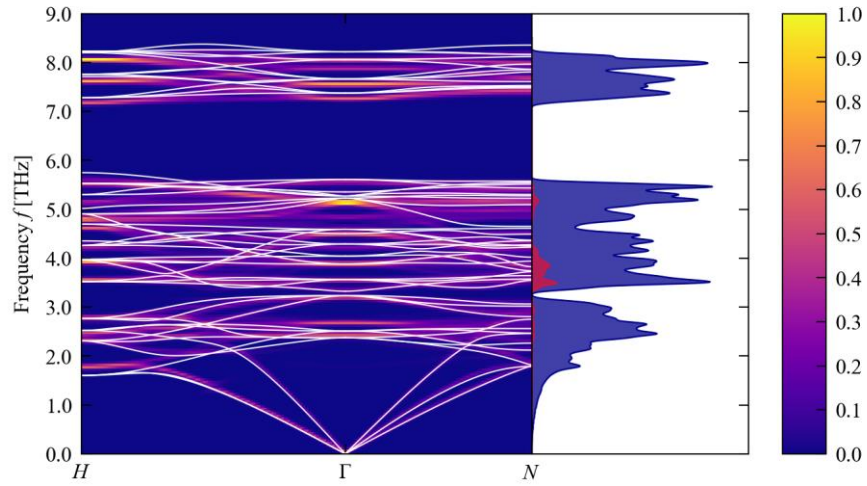


Figure S2.5 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{KrCo}_8\text{Sb}_{24}$. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the Kr filler is overlaid on the $g(f)$ in red.

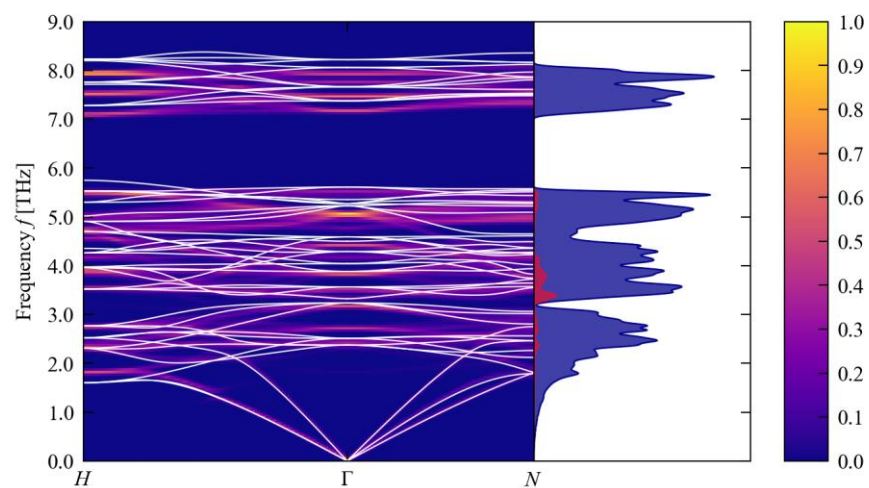


Figure S2.6 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{XeCo}_8\text{Sb}_{24}$. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the Xe filler is overlaid on the $g(f)$ in red.

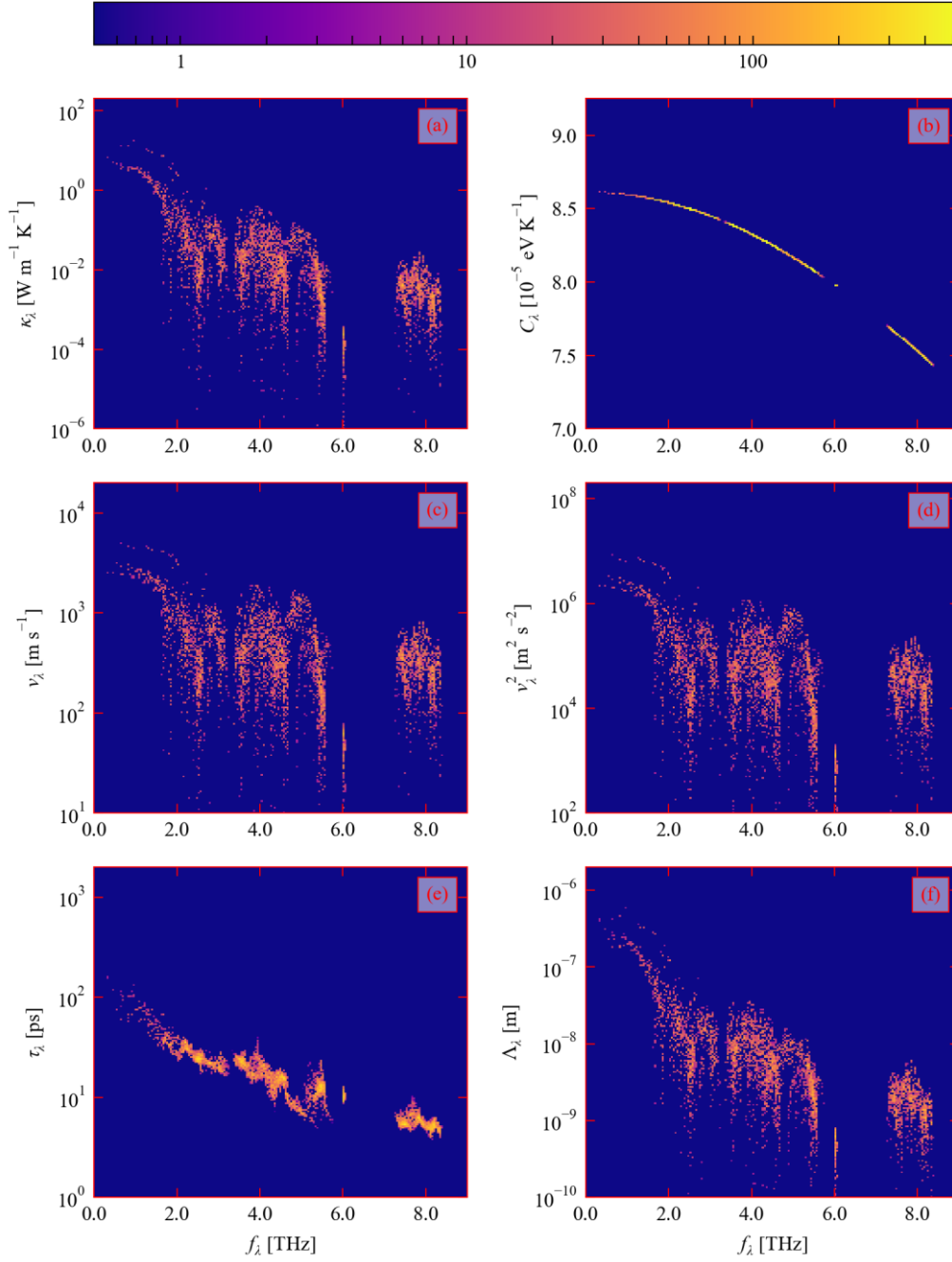


Figure S2.7 Frequency spectra of the modal terms in Eq. 2 in the text for $\text{HeCo}_8\text{Sb}_{24}$ at $T = 300$ K, *viz.* the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

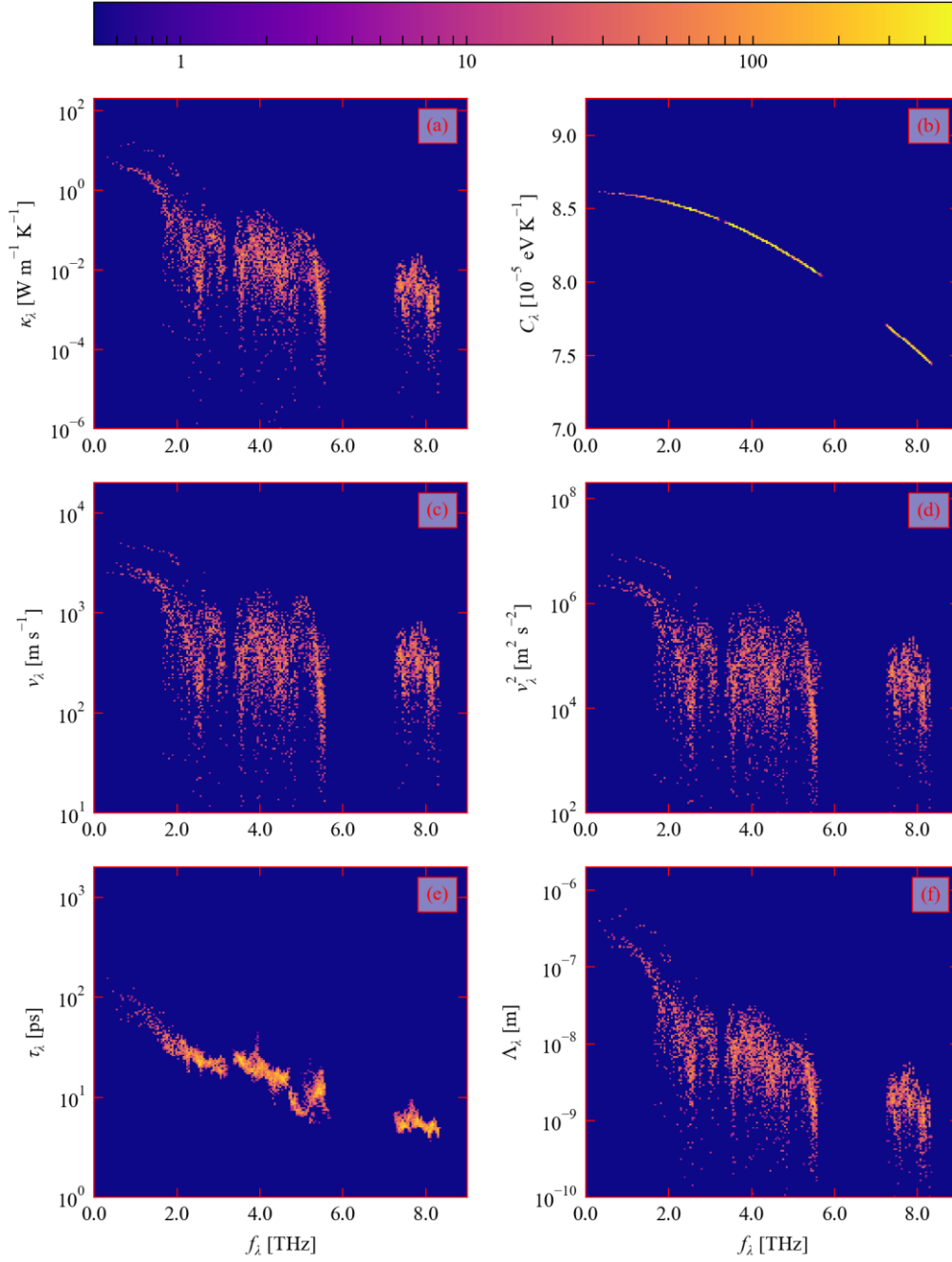


Figure S2.8 Frequency spectra of the modal terms in Eq. 2 in the text for $\text{NeCo}_8\text{Sb}_{24}$ at $T = 300$ K, viz. the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

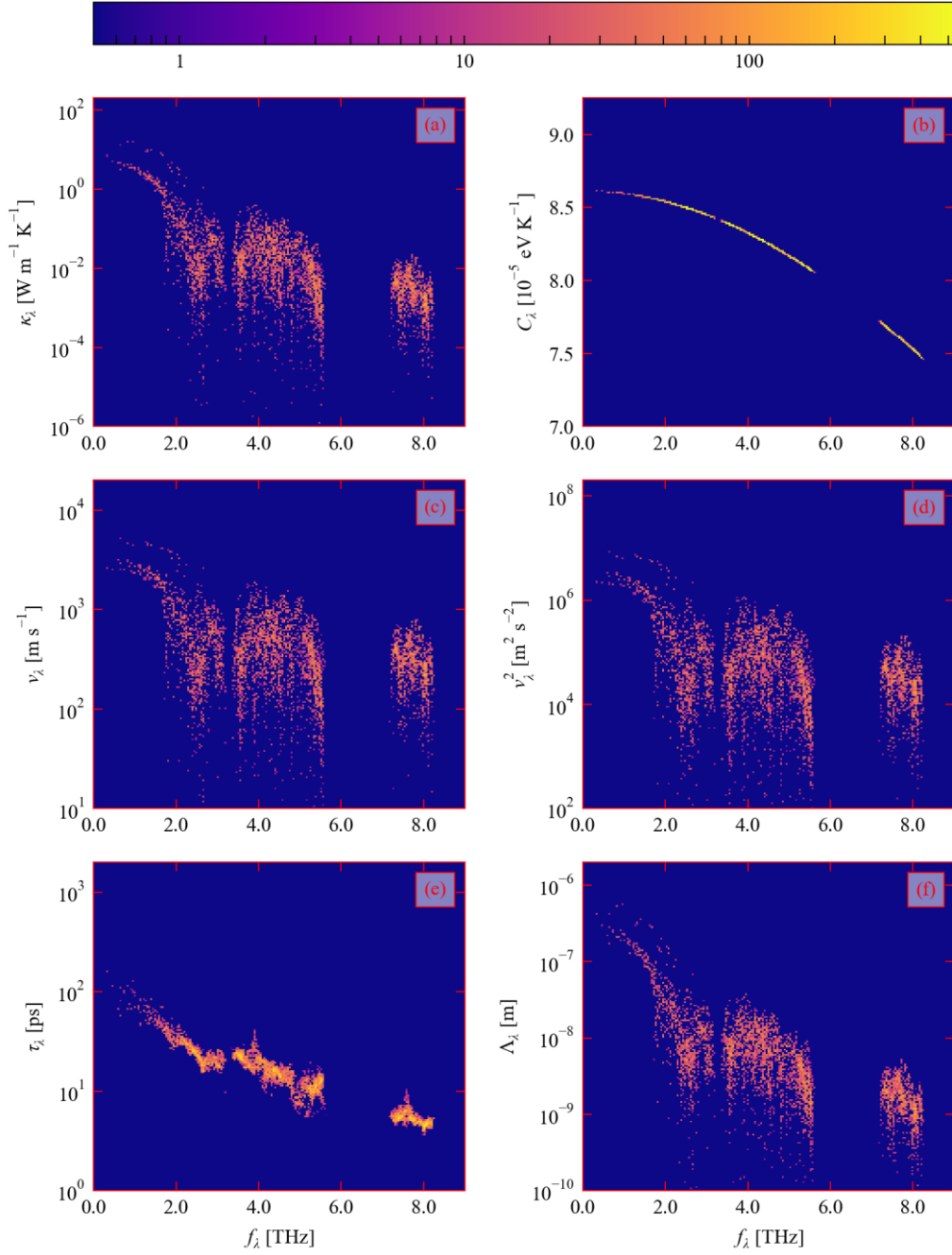


Figure S2.9 Frequency spectra of the modal terms in Eq. 2 in the text for $\text{ArCo}_8\text{Sb}_{24}$ at $T = 300$ K, viz. the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

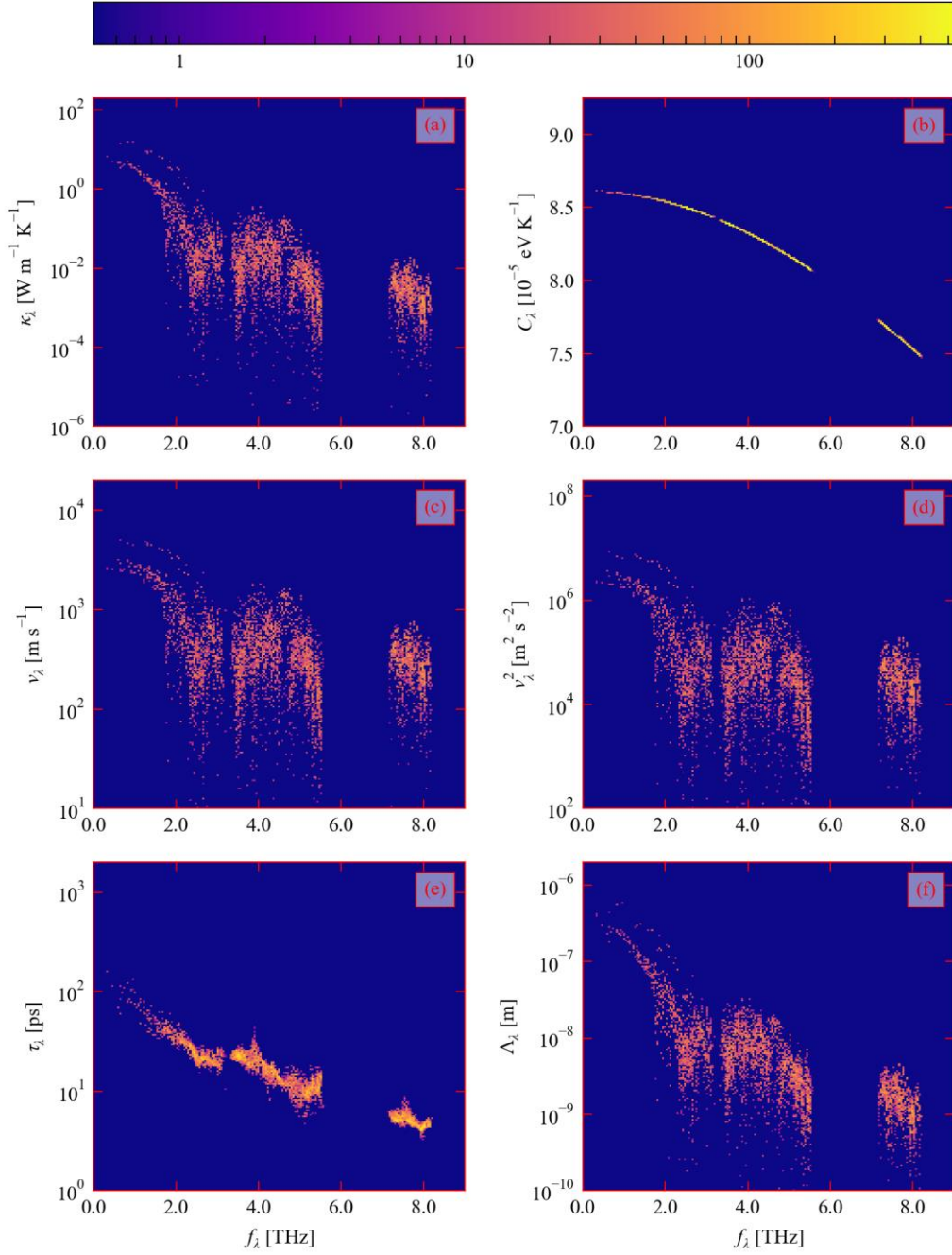


Figure S2.10 Frequency spectra of the modal terms in Eq. 2 in the text for $\text{KrCo}_8\text{Sb}_{24}$ at $T = 300$ K, viz. the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

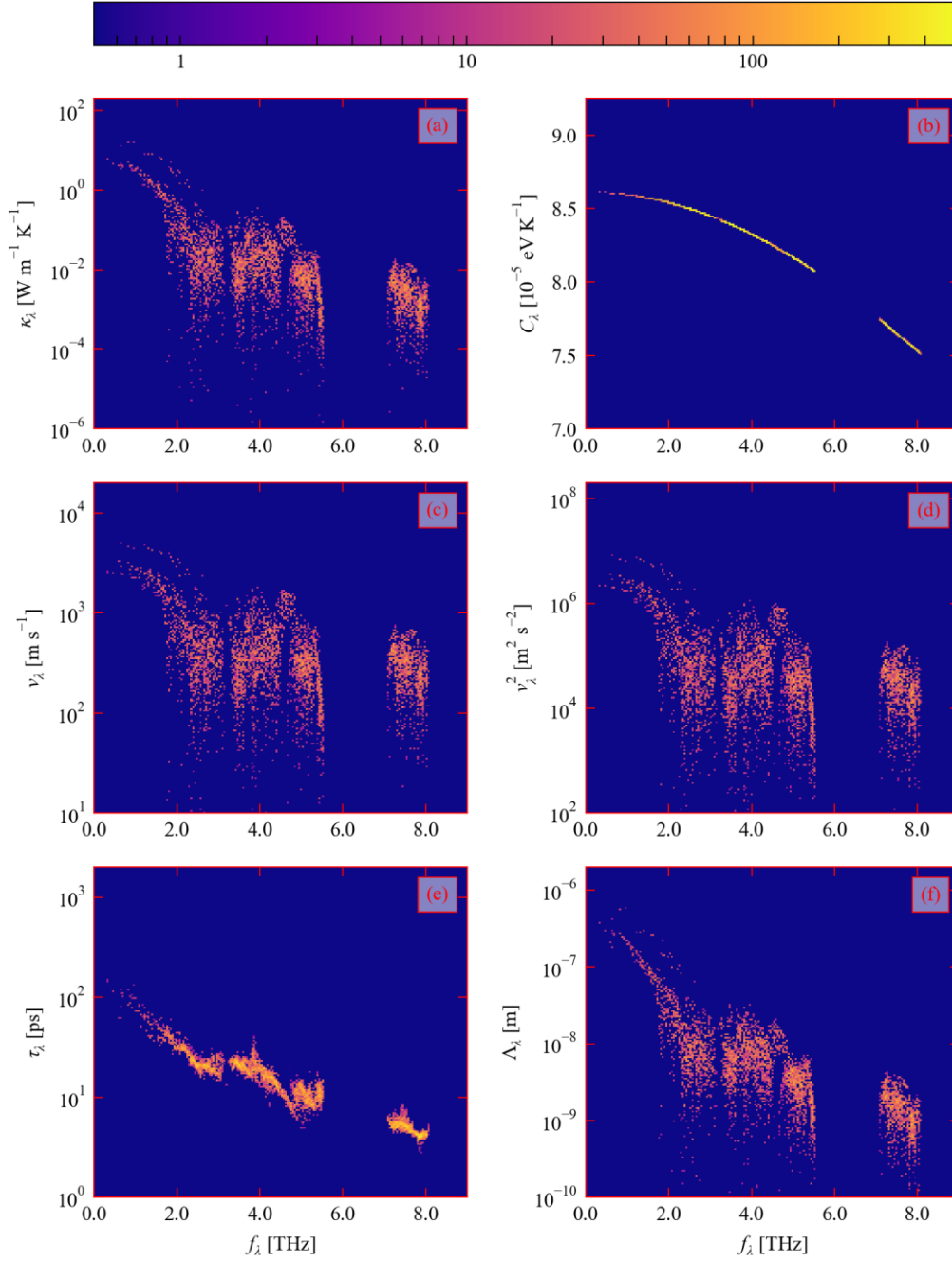


Figure S2.11 Frequency spectra of the modal terms in Eq. 2 in the text for $\text{XeCo}_8\text{Sb}_{24}$ at $T = 300$ K, viz. the thermal conductivities κ_λ (a), heat capacities C_λ (b), group velocities v_λ (c) and outer products v_λ^2 (d), and the lifetimes τ_λ (e), together with the mean-free paths $\Lambda_\lambda = v_\lambda \tau_\lambda$ (f). Note that quantities in (a) and (c)-(f) are shown on a logarithmic scale, while the C_λ in (b) are shown on a linear scale.

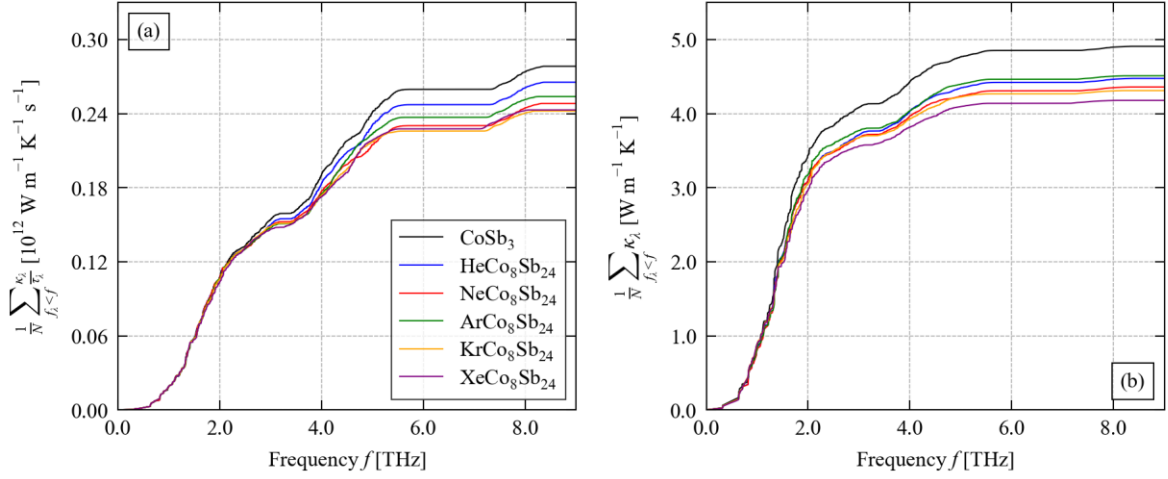


Figure S2.12 Accumulation of the $\kappa_{\lambda}/\tau_{\lambda}$ (a) and κ_{λ} (b) as a function of frequency at $T = 600$ K for pristine CoSb_3 and filled $\text{XCo}_8\text{Sb}_{24}$ models with $\text{X} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}$ and Xe .

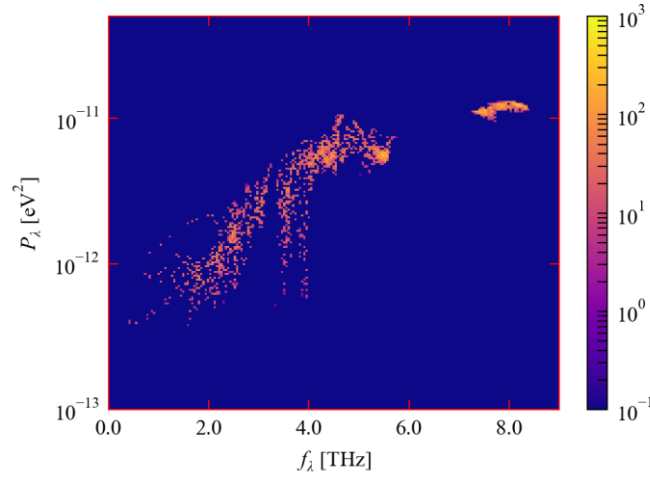


Figure S2.13 Frequency spectra of the averaged modal three-phonon interaction strengths P_{λ} of CoSb_3 as defined in Eq. 12 in the text.

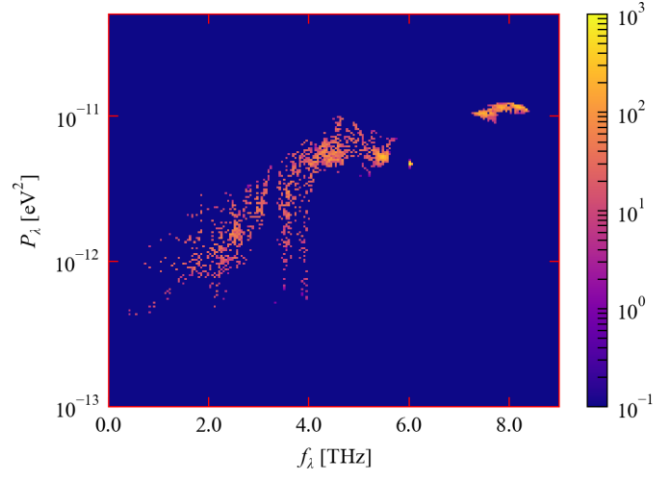


Figure S2.14 Frequency spectra of the averaged modal three-phonon interaction strengths P_λ of $\text{HeCo}_8\text{Sb}_{24}$ as defined in Eq. 12 in the text.

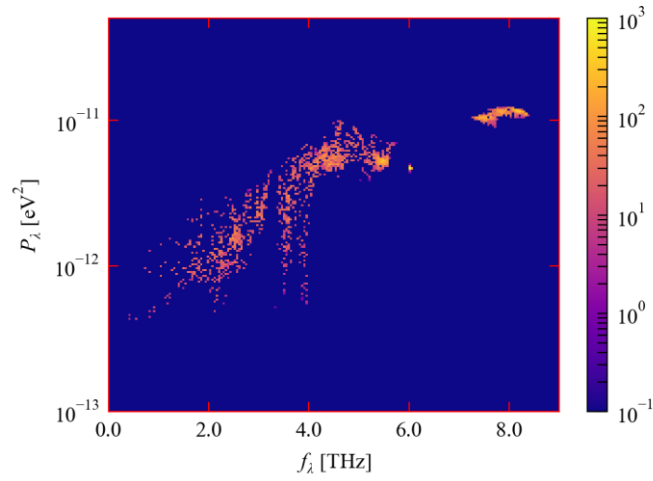


Figure S2.15 Frequency spectra of the averaged modal three-phonon interaction strengths P_λ of $\text{NeCo}_8\text{Sb}_{24}$ as defined in Eq. 12 in the text.

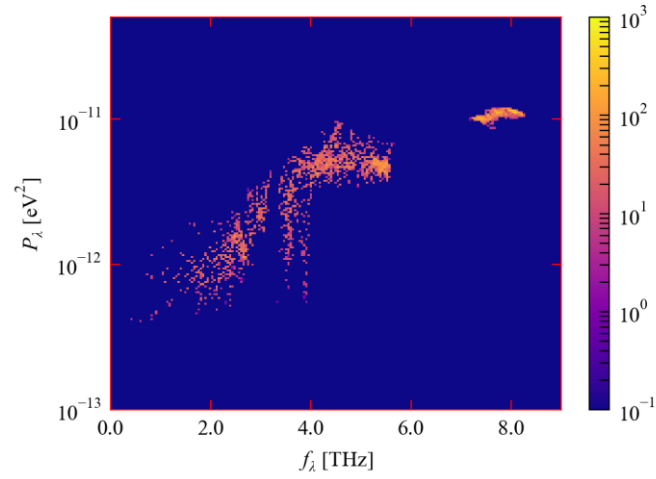


Figure S2.16 Frequency spectra of the averaged modal three-phonon interaction strengths P_λ of $\text{ArCo}_8\text{Sb}_{24}$ as defined in Eq. 12 in the text.

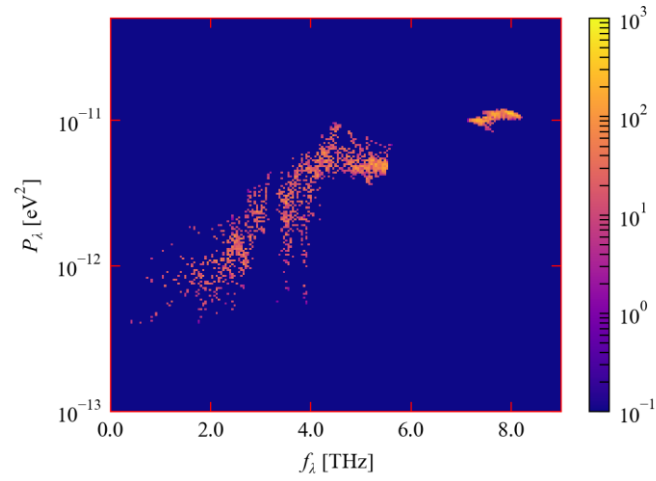


Figure S2.17 Frequency spectra of the averaged modal three-phonon interaction strengths P_λ of $\text{KrCo}_8\text{Sb}_{24}$ as defined in Eq. 12 in the text.

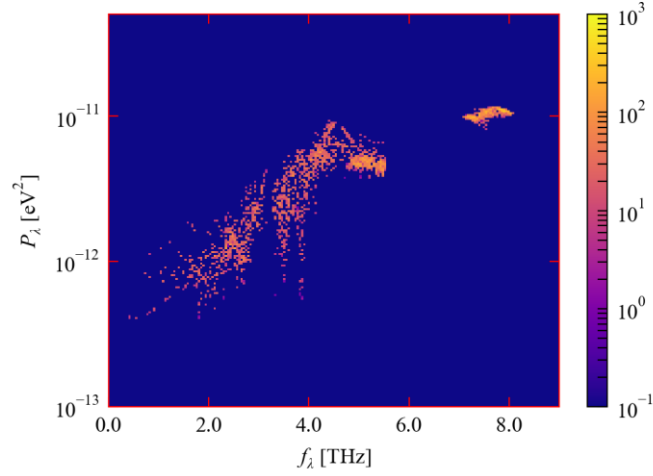


Figure S2.18 Frequency spectra of the averaged modal three-phonon interaction strengths P_λ of $\text{XeCo}_8\text{Sb}_{24}$ as defined in Eq. 12 in the text.

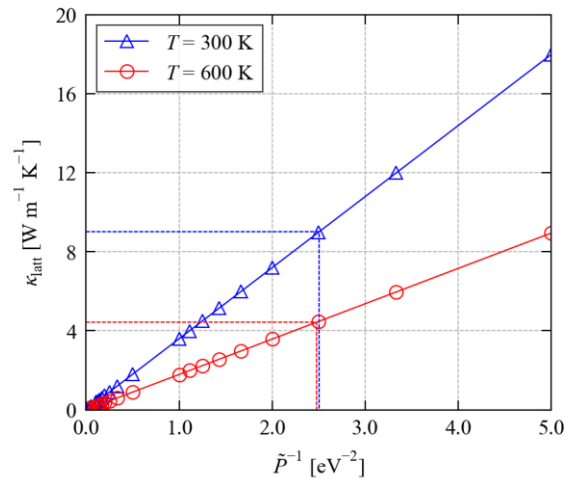


Figure S2.19 Dependence of the κ_{latt} of $\text{HeCo}_8\text{Sb}_{24}$ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{latt} at the two temperatures.

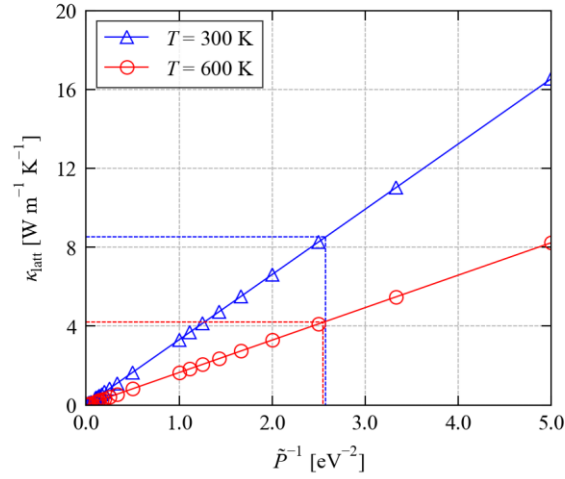


Figure S2.20 Dependence of the κ_{lat} of $\text{NeCo}_8\text{Sb}_{24}$ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{lat} at the two temperatures.

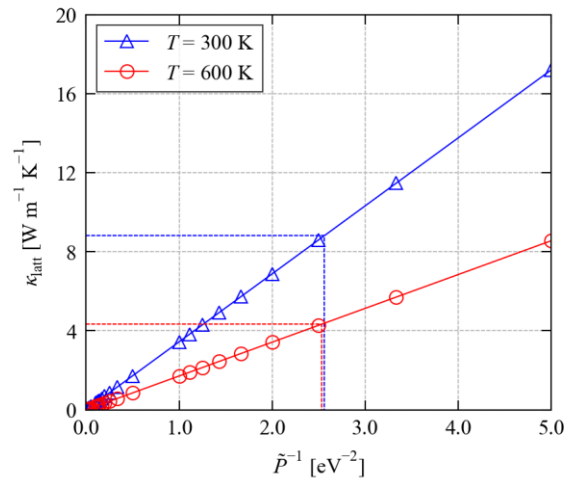


Figure S2.21 Dependence of the κ_{lat} of $\text{ArCo}_8\text{Sb}_{24}$ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{lat} at the two temperatures.

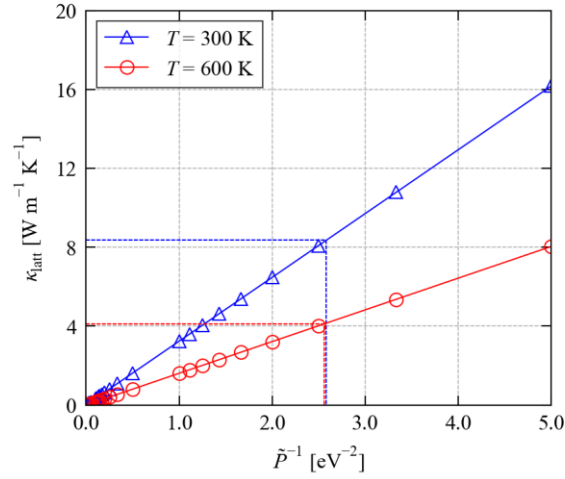


Figure S2.22 Dependence of the κ_{lat} of $\text{KrCo}_8\text{Sb}_{24}$ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{lat} at the two temperatures.

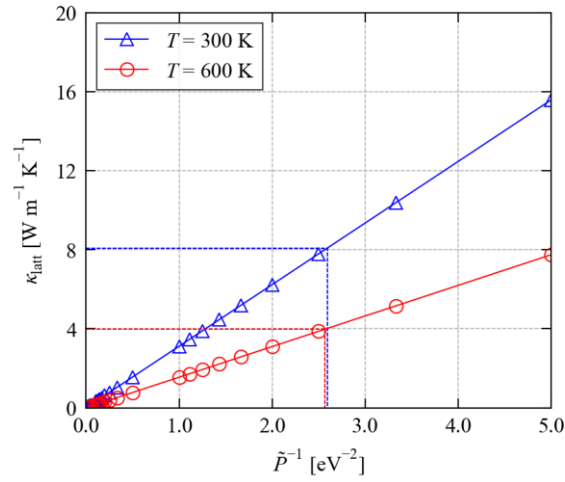


Figure S2.23 Dependence of the κ_{lat} of $\text{XeCo}_8\text{Sb}_{24}$ on the averaged three-phonon interaction strength \tilde{P} defined in the text at $T = 300$ and 600 K (blue/red). The dashed lines mark the \tilde{P} that recover the calculated κ_{lat} at the two temperatures.

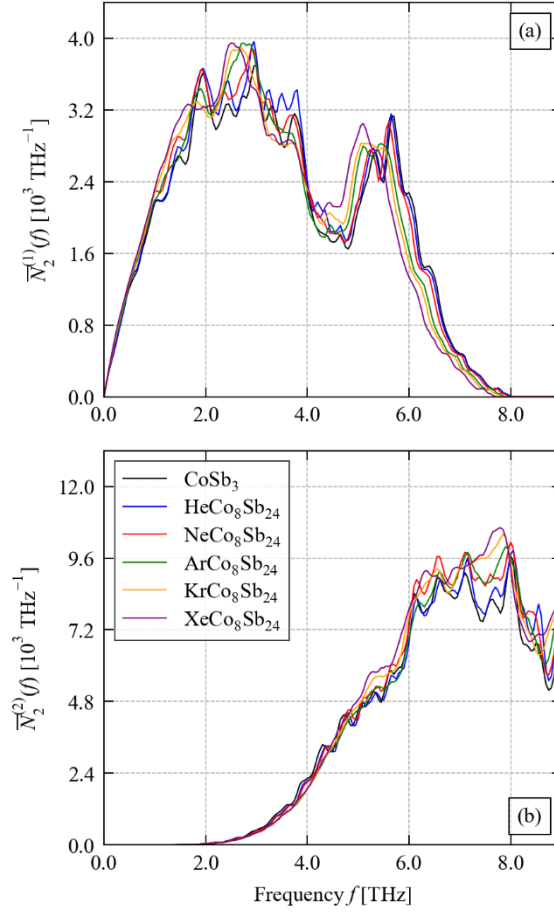


Figure S2.24 Averaged weighted two-phonon joint density of states (w-JDoS) functions $\bar{N}_2^{(1)}(\omega)$ (a) and $\bar{N}_2^{(2)}(\omega)$ (b) for collision and decay processes, respectively, for CoSb₃ and XC₀₈Sb₂₄ with X = He, Ne, Ar, Kr and Xe at $T = 600$ K. The two w-JDoS functions are defined in Eqs. 14-17 in the text.

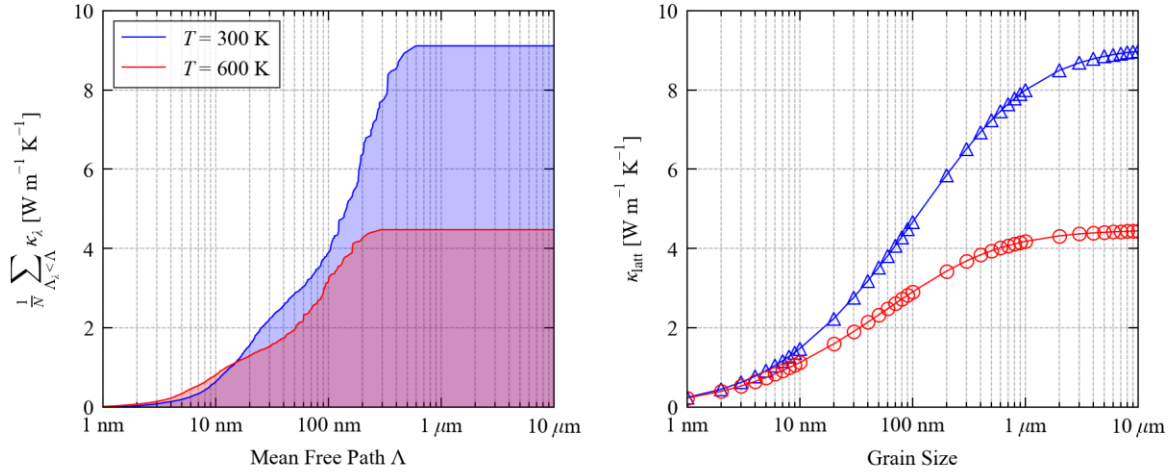


Figure S2.25 (a) Accumulation of the thermal conductivity κ_{latt} of HeCo₈Sb₂₄ as a function of the phonon mean-free path $\Lambda_{\lambda} = v_{\lambda}\tau_{\lambda}$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

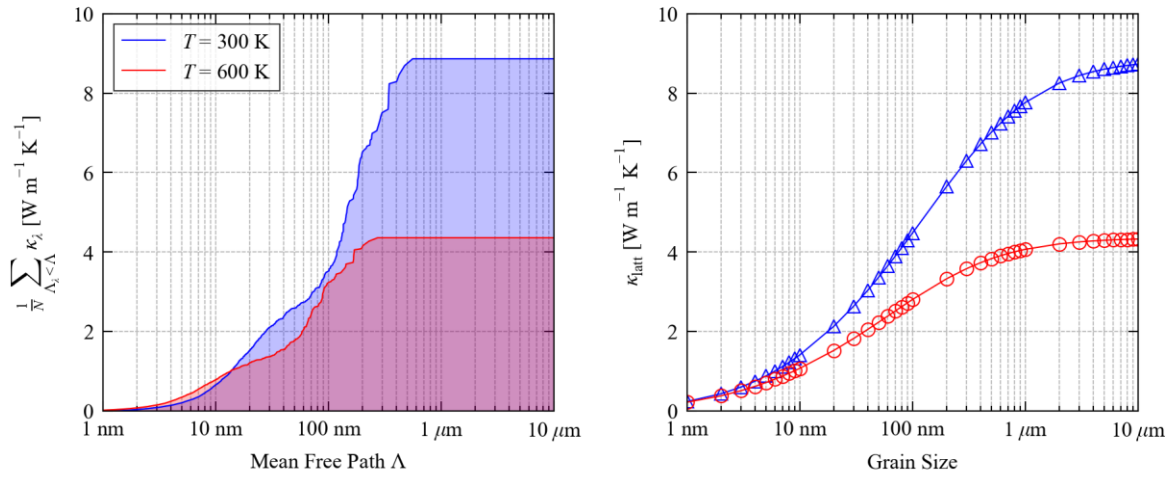


Figure S2.26 (a) Accumulation of the thermal conductivity κ_{latt} of NeCo₈Sb₂₄ as a function of the phonon mean-free path $\Lambda_{\lambda} = v_{\lambda}\tau_{\lambda}$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

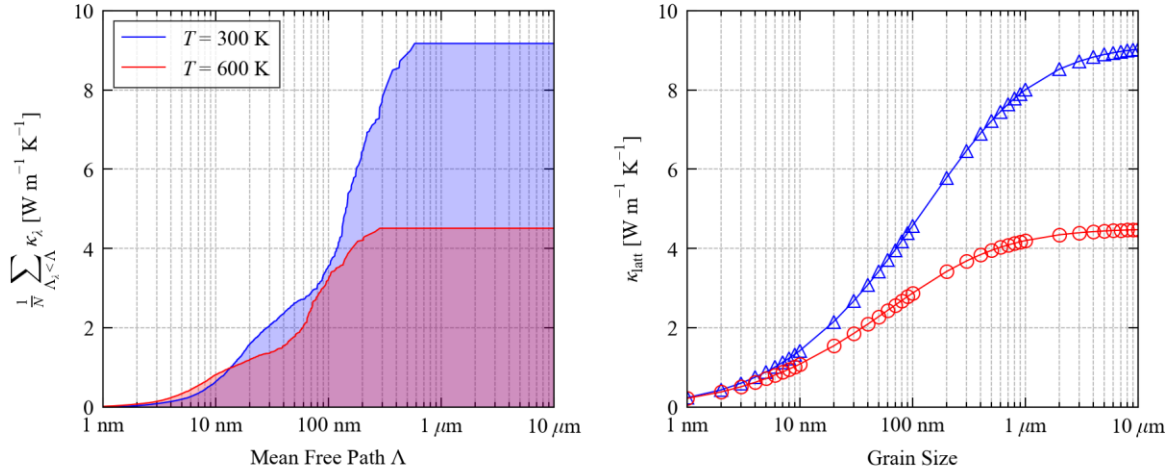


Figure S2.27 (a) Accumulation of the thermal conductivity κ_{latt} of ArCo₈Sb₂₄ as a function of the phonon mean-free path $\Lambda_{\lambda} = v_{\lambda}\tau_{\lambda}$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

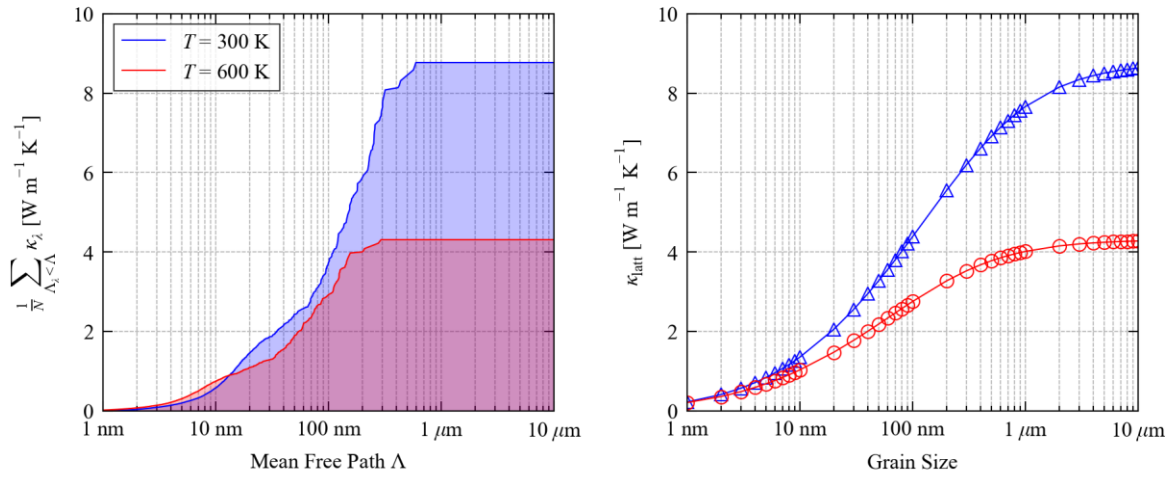


Figure S2.28 (a) Accumulation of the thermal conductivity κ_{latt} of KrCo₈Sb₂₄ as a function of the phonon mean-free path $\Lambda_{\lambda} = v_{\lambda}\tau_{\lambda}$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

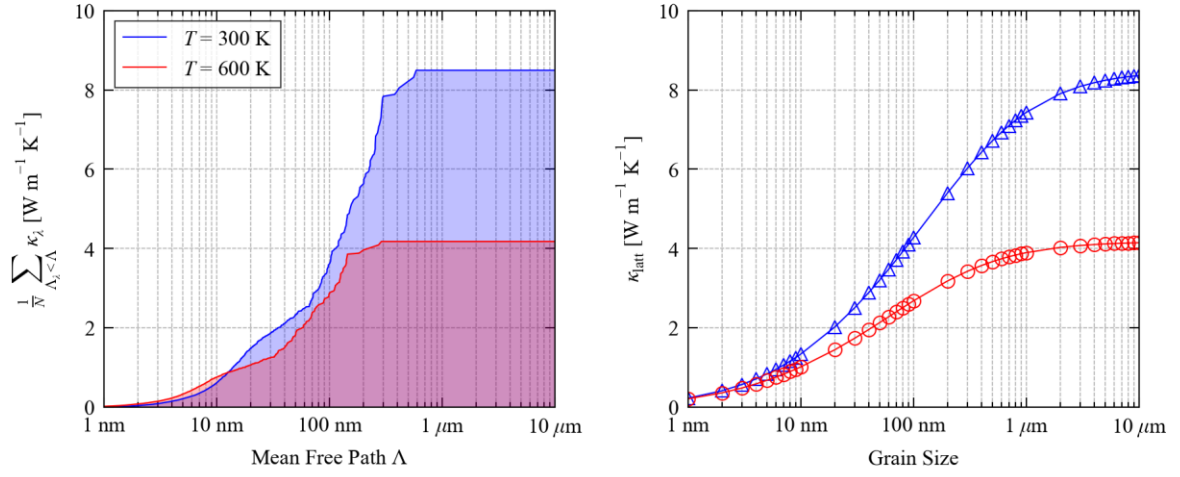


Figure S2.29 (a) Accumulation of the thermal conductivity κ_{latt} of $\text{XeCo}_8\text{Sb}_{24}$ as a function of the phonon mean-free path $\Lambda_\lambda = v_\lambda \tau_\lambda$ at $T = 300$ and 600 K (blue/red). (b) Estimated dependence of the κ_{latt} at 300 and 600 K on the crystal grain size using a boundary-scattering model.

c. Discussion

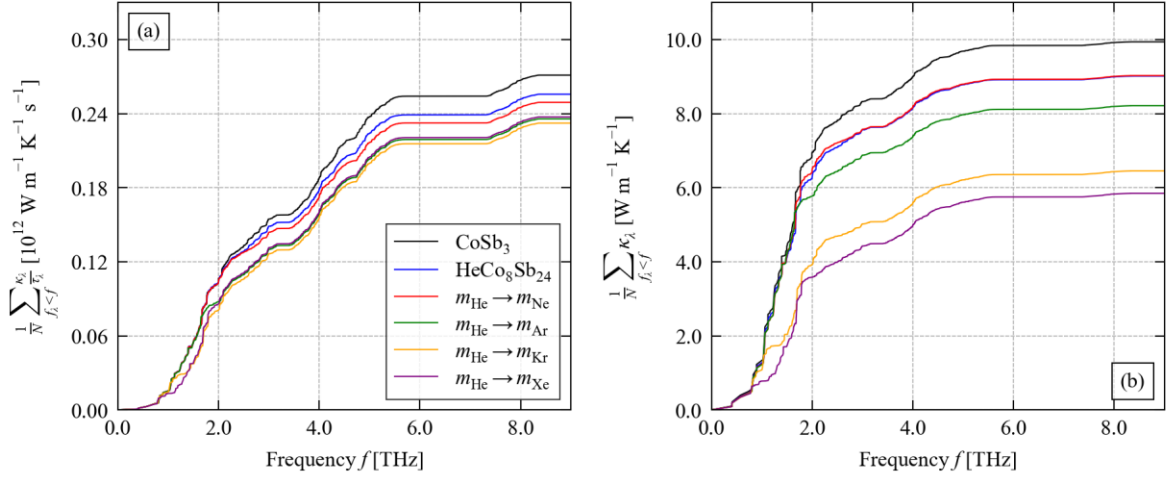


Figure S2.30 Accumulation of the $\kappa_\lambda/\tau_\lambda$ (a) and κ_λ (b) as a function of frequency at $T = 300$ K for pristine CoSb_3 , $\text{HeCo}_8\text{Sb}_{24}$ and $\text{HeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{He} changed to the masses of Ne, Ar, Kr and Xe while keeping the force constants fixed.

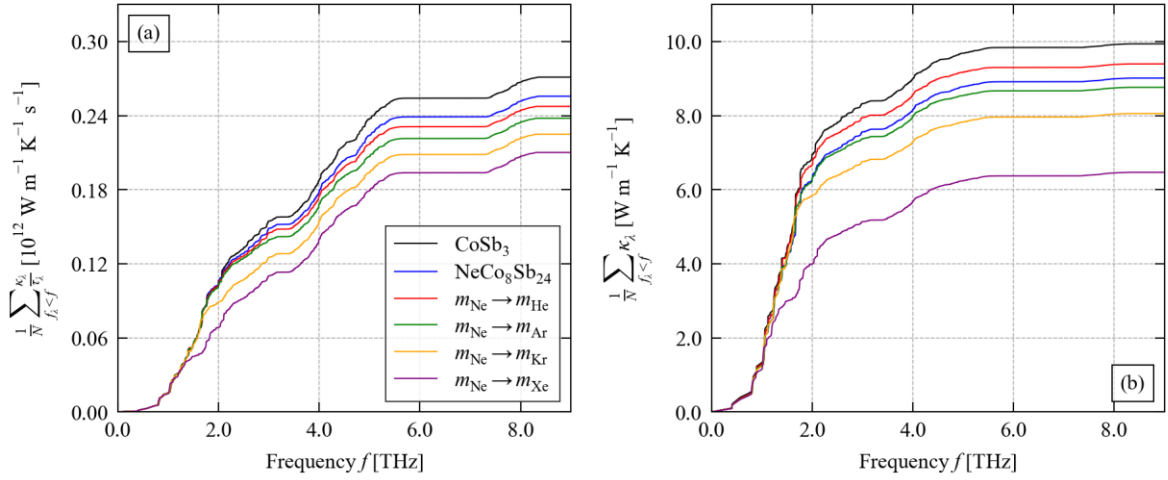


Figure S2.31 Accumulation of the $\kappa_\lambda/\tau_\lambda$ (a) and κ_λ (b) as a function of frequency at $T = 300$ K for pristine CoSb_3 , $\text{NeCo}_8\text{Sb}_{24}$ and $\text{NeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{Ne} changed to the masses of He, Ar, Kr and Xe while keeping the force constants fixed.

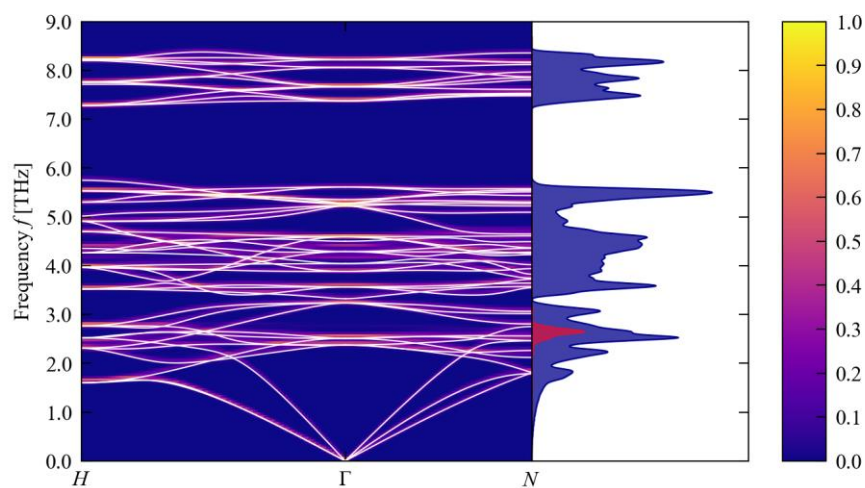


Figure S2.32 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{HeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{He} changed to the mass of Ne. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the filler is overlaid on the $g(f)$ in red.

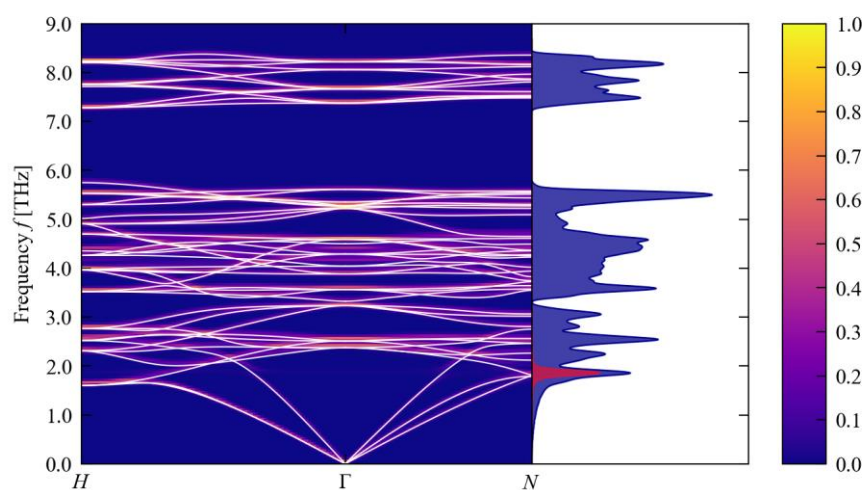


Figure S2.33 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{HeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{He} changed to the mass of Ar. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the filler is overlaid on the $g(f)$ in red.

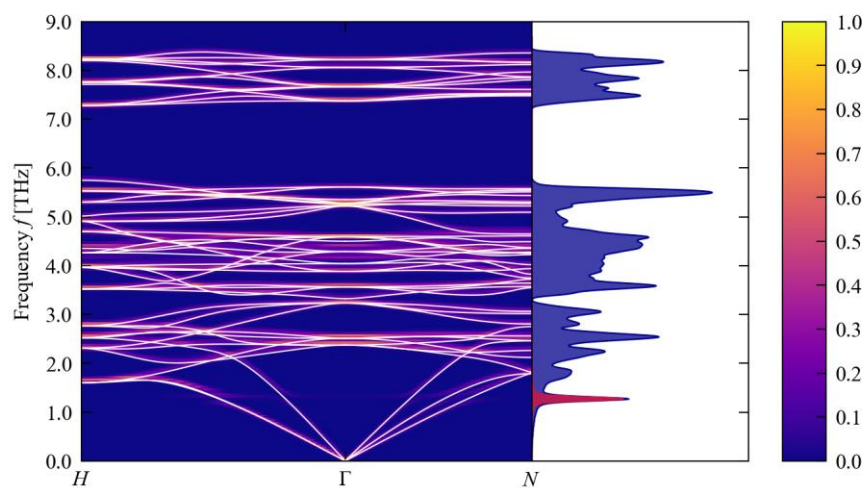


Figure S2.34 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{HeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{He} changed to the mass of Kr. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the filler is overlaid on the $g(f)$ in red.

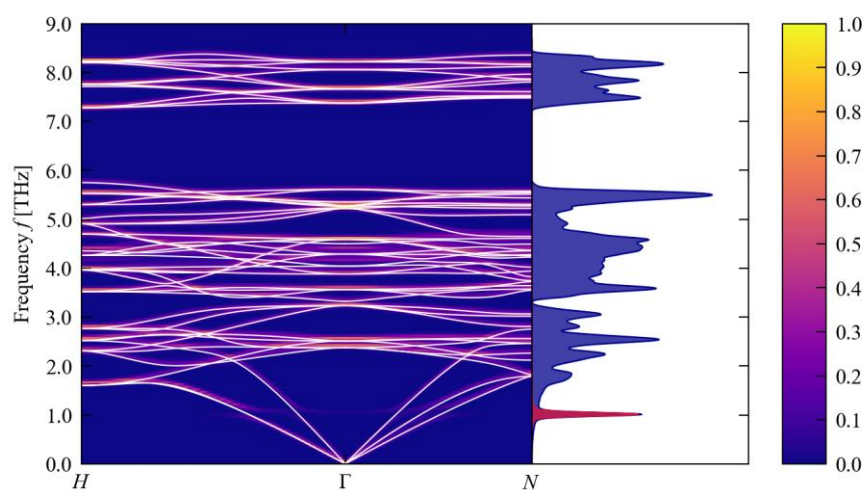


Figure S2.35 Unfolded band dispersion and phonon density of states $g(f)$ (DoS) of $\text{HeCo}_8\text{Sb}_{24}$ with the mass of the He atom m_{He} changed to the mass of Xe. The band structure of pristine CoSb_3 is overlaid on the dispersion in white, and the projection of the DoS onto the filler is overlaid on the $g(f)$ in red.