

This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>)

Uncovering design principles for amorphous-like heat conduction using two-channel lattice dynamics

Riley Hanus^{1,2*}, Janine George³, Max Wood², Alexander Bonkowski³, Yongqiang Cheng⁴, Douglas L. Abernathy⁴, Michael E. Manley¹, Geoffroy Hautier³, G. Jeffrey Snyder², and Raphaël P. Hermann^{1*}

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

²Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA.

³Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Chemin des Étoiles 8, Louvain-la-Neuve 1348, Belgium.

⁴Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

*Corresponding authors: hanusriley@gmail.com, hermannrp@ornl.gov

ABSTRACT

The physics of heat conduction puts practical limits on many technological fields such as energy production, storage, and conversion. It is now widely appreciated that the phonon-gas model does not describe the full vibrational spectrum in amorphous materials, since this picture likely breaks down at higher frequencies. A two-channel heat conduction model, which uses harmonic vibrational states and lattice dynamics as a basis, has recently been shown to capture both crystal-like (phonon-gas channel) and amorphous-like (diffuson channel) heat conduction. While materials design principles for the phonon-gas channel are well established, similar understanding and control of the diffuson channel is lacking. In this work, in order to uncover design principles for the diffuson channel, we study structurally-complex crystalline $\text{Yb}_{14}(\text{Mn,Mg})\text{Sb}_{11}$, a champion thermoelectric material above 800 K, experimentally using inelastic neutron scattering and computationally using the two-channel lattice dynamical approach. Our results show that the diffuson channel indeed dominates in $\text{Yb}_{14}\text{MnSb}_{11}$ above 300 K. More importantly, we demonstrate a method for the rational design of amorphous-like heat conduction by considering the energetic proximity phonon modes and modifying them through chemical means. We show that increasing (decreasing) the mass on the Sb-site decreases (increases) the energy of these modes such that there is greater (smaller) overlap with Yb-dominated modes resulting in a higher (lower) thermal conductivity. This design strategy is exactly opposite of what is expected when the phonon-gas channel and/or common analytical models for the diffuson channel are considered, since in both cases an increase in atomic mass commonly leads to a decrease in thermal conductivity. This work demonstrates how two-channel lattice dynamics can not only quantitatively predict the relative importance of the phonon-gas and diffuson channels, but also lead to rational design strategies in materials where the diffuson channel is important.

Introduction

The flow of heat through solids is a topic of wide-spread technological importance. In simple crystals the thermal conductivity (κ) can be well understood within the phonon-gas model (PGM)¹. However, for amorphous materials^{2–4}, defective crystals⁵, anharmonic crystals⁶, hybrid perovskites⁷, and — as we show here — Zintl-type phases with complex crystal structures, the PGM is incomplete. Two-channel lattice dynamics simulations, which has been developed by Simoncelli *et al.*⁶ and Isaeva *et al.*⁴ and is applied in this work, has emerged as an effective way to quantitatively capture both crystal-like and amorphous-like thermal transport in solids.^{8,9} The thermal conductivity of all solids spans roughly five orders of magnitude (Figure 1a). The PGM tends to dominate in crystalline-like heat conductors and, in general, can explain the top two to three orders of magnitude. However, there is far less understanding of the detailed physics governing

heat conduction in amorphous-like heat conductors which tend to occupy the bottom two to three orders of magnitude. To build intuition regarding amorphous-like heat conduction we study the vibrational and thermal properties of crystalline $\text{Yb}_{14}MSb_{11}$ ($M = \text{Mn}$ or Mg) which has a very complex crystal structure containing 104 atoms in its primitive unit cell (Figure 2a). It is a champion p-type material system for high temperature thermoelectric energy conversion and is well studied experimentally and computationally^{10–14}. $\text{Yb}_{14}MSb_{11}$ has a κ below that of amorphous fused silica even though it is indeed a crystal. Additionally, its temperature dependence of κ above room temperature is relatively flat, similar to that of amorphous materials, rather than $\kappa_{\text{vib}} \propto T^{-1}$ which is characteristic of the PGM (crystalline-like). From this case study emerges a simple physical picture for heat conduction which enables the design of materials that exhibit crystalline-like conduction, amorphous-like conduction, as well as materials transitioning between the two extremes.

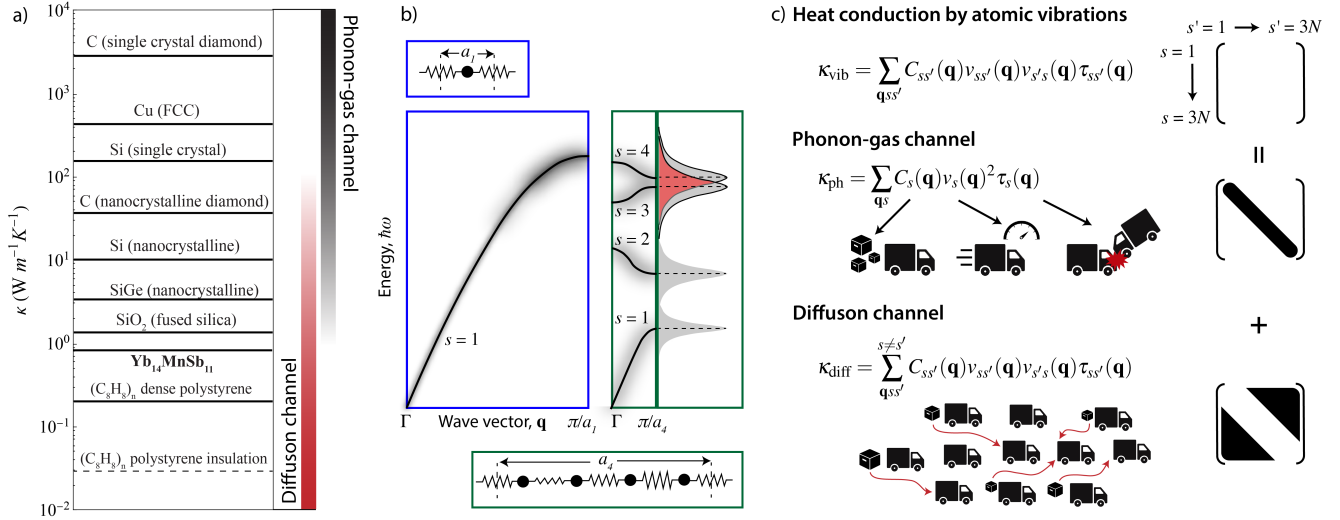


Figure 1. a) Overall range of thermal conductivity in solids spanning approximately 5 orders of magnitude. The top 2 to 3 orders of magnitude (above $\kappa_{\text{vib}} \approx 50$ W/mK) are well described by the phonon-gas model, exhibiting crystalline-like heat conduction. The phonon-gas model alone is insufficient for materials in the bottom 2 to 3 orders of magnitude. b) A one dimensional illustration of band folding when the unit cell is increased in size by, for example, modulating the interatomic force constants. The overlap of broadened modes enables heat conduction through the diffuson channel and is highlighted in red. c) The thermal conductivity viewed as a matrix with rows and columns designating the phonon branch index (s and s'). The phonon-gas channel is simply the sum of the diagonal components of this matrix. The diffuson-channel is the sum of off-diagonal components. Heat conducting through these two channels have very different physical interpretations which, as described in the text, the trucks illustrations help conceptualize.

We analyze the vibrational and thermal properties of Yb₁₄MSb₁₁ within a two-channel lattice dynamical (LD) approach

$$\kappa_{\text{vib}} = \sum_{\mathbf{q}ss'} C_{ss'}(\mathbf{q}) v_{ss'}(\mathbf{q}) v_{s's}(\mathbf{q}) \tau_{ss'}(\mathbf{q}). \quad (1)$$

Here, we follow the work of Hardy¹⁵, Allen *et al.*¹⁶, Simoncelli *et al.*⁶, Isavea *et al.*⁴, and Luo *et al.*⁸ and we consider not only the phonon-gas channel ($s = s'$, where s is the phonon branch index), but also heat conduction through the coupling of eigenstates with the same phonon wavevector $\mathbf{q}$ (i.e. between $\mathbf{q}s$ and $\mathbf{q}s'$) which we call the diffuson channel.

In principle coupling between eigenstates with different $\mathbf{q}$ -vector should be possible (i.e. between $\mathbf{q}s$ and $\mathbf{q}'s'$), but has not been considered to date and is also neglected here. Any mechanism that limits phonon lifetime or spatial extent will lead to a $\mathbf{q}$ -broadening, which is inseparable from the more commonly considered energy broadening. It is unclear at the moment how important coupling between $\mathbf{q}$ -vectors will be. We can say that approaching the amorphous limit, we expect $\mathbf{q}s$ to $\mathbf{q}s'$ coupling to be sufficient for capturing the diffuson channel since the Brillouin zone effectively collapses to a single $\mathbf{q}$ -point. As for Yb₁₄(Mn, Mg)Sb₁₁, we expect $\mathbf{q}$ to $\mathbf{q}'$ coupling to be relatively less important than in simpler crystals (larger Brillouin zones) with similarly low thermal conductivity that have been considered using two-channel lattice dynamics, such as CsPbBr₃⁶.

Each term in the thermal conductivity (Eq. 1) is represented by its appropriate matrix, and they are defined in Computational methods section. $C_{ss'}(\mathbf{q})$ is the heat capacity matrix; $v_{ss'}(\mathbf{q})$ is the velocity matrix; and $\tau_{ss'}(\mathbf{q})$ is the lifetime matrix. The diagonal and off-diagonal components of these matrices have distinctly different physical interpretations. A schematic of this formalism is shown in Figure 1c.

The diagonal components of this matrix ($s = s'$) designate the commonly used phonon-gas model

$$\kappa_{\text{ph}} = \sum_{\mathbf{q}s} C_s(\mathbf{q}) v_s(\mathbf{q})^2 \tau_s(\mathbf{q}), \quad (2)$$

where each of the matrices reduce to the common phonon property, i.e. the heat capacity $C_s(\mathbf{q}) = C_{ss}(\mathbf{q})$ (dropping the redundant branch index subscript), the phonon group velocity $v_s(\mathbf{q}) = v_{ss}(\mathbf{q})$, and the phonon relaxation time $\tau_s(\mathbf{q}) = \tau_{ss}(\mathbf{q})$.

The off-diagonal components ($s \neq s'$) we call the diffuson-channel since it is mathematically the same mechanism through which diffusons were defined^{2,17}, and represents a coupling between vibrational states which results in diffusive heat conduction

$$\kappa_{\text{diff}} = \sum_{\mathbf{q}ss'} C_{ss'}(\mathbf{q}) v_{ss'}(\mathbf{q}) v_{s's}(\mathbf{q}) \tau_{ss'}(\mathbf{q}). \quad (3)$$

Therefore, κ_{ph} and κ_{diff} simply sum together to give the total thermal conductivity due to atomic vibrations (i.e. the

lattice thermal conductivity)

$$\kappa_{\text{vib}} = \kappa_{\text{ph}} + \kappa_{\text{diff}}. \quad (4)$$

There have been several reports of two channel models for κ_{vib} where one of the additive terms is the phonon-gas model and the other is an analytical model for the amorphous/minimum thermal conductivity^{18–20}. For the amorphous thermal conductivity specifically, there have been a number of analytical models proposed^{21–24}. It seems as though these analytical (or semi-analytical) treatments have been attempting to capture the effect of the diffusion channel defined in Eq. 3.

The diffusion channel, κ_{diff} represents the diffusion of thermal energy through quasi-degenerate normal modes⁴, or normal mode mixing (also referred to as coherences⁶). Normal mode mixing and κ_{diff} can be understood through the concept of band folding which we schematically show for one dimension in Figure 1b. As the number of atoms per unit cell is increased, the bands are folded resulting in a smaller maximum $\mathbf{q}$ -vector, and more branches occupying the same $\mathbf{q}$ -space. Each phonon branch has a linewidth, which is inversely proportional to its lifetime, and may arise from the materials natural anharmonicity and/or defects. When the phonon branches are packed close enough together in energy and/or their linewidths are large enough such that the modes at the same $\mathbf{q}$ -point overlap in energy (highlighted in red in Figure 1b), normal mode mixing can occur. This is mathematically reflected by the Lorentzian form of $\tau_{ss'}(\mathbf{q})$ (Eq. 14). Given that normal mode mixing ‘can’ occur ($\tau_{ss'}(\mathbf{q}) > 0$), the velocity matrix determines whether or not it ‘will’ occur ($v_{ss'}(\mathbf{q}) > 0$). For off-diagonal components, $v_{ss'}(\mathbf{q})$ captures how strongly phonon mode $\mathbf{q}s$ and $\mathbf{q}s'$ will be coupled, based on the mode shapes (i.e. eigenvectors, polarizations).

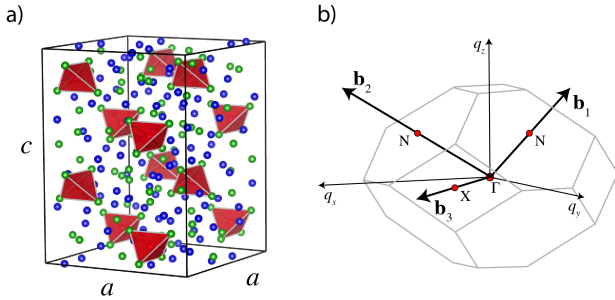


Figure 2. a) The conventional unit cell of $\text{Yb}_{14}\text{MSb}_{11}$ (208 atoms) with Yb in blue, Sb in green, and $M = \text{Mg}$ or Mn residing in the red tetrahedrons. The primitive cell contains 104 atoms (Figure S3). b) The Brillouin zone of $\text{Yb}_{14}\text{MSb}_{11}$ ($I4_1/acd$ no. 142 with $c/a > 1$).

We note that just as harmonic phonon eigenstates are used as a basis to compute the thermal conductivity in standard lattice dynamics and κ_{ph} , they are also used as a basis to compute κ_{diff} . In both cases, the real system can not be described within the harmonic approximation, and anharmonic contributions are required to obtain physical results (i.e. a finite κ_{ph}

and $\kappa_{\text{diff}} > 0$). Therefore, using precise language, κ_{ph} and κ_{diff} are defined as the thermal conductivity of harmonic phonon eigenstates which are conducting heat through the phonon-gas and diffusion channels, respectively. Modes which have a significant κ_{diff} contribution are expected to quickly lose their phonon-like, propagating plane-wave character if the true potential energy landscape was used to obtain vibrational properties.

A useful metaphor for conceptualizing the phonon-gas channel is that of trucks on a highway (Figure 1c). The truck represents the phonon mode; its cargo represents the heat capacity; its speed represents the phonon group velocity; and collisions between trucks represent phonon scattering events. If one desires an equally simplistic view of the diffusion channel, this metaphor can be extended. When the diffusion channel is important there are many trucks on the road, and presumably the majority of the trucks have a low velocity and collisions may be frequent. However, within the diffusion channel, packages can shuffle between trucks. The proximity of two trucks may represent the lifetime matrix, $\tau_{ss'}(\mathbf{q})$, and whether or not the cargo will fit into the receiving truck (i.e. shape of the box or the mode shape) represents the velocity matrix $v_{ss'}(\mathbf{q})$. Just as in random walk theory, if there is a gradient in cargo density (i.e. a temperature gradient) there will be a net diffusion of cargo. Both mechanisms are always present and contribute additively to cargo conduction. However, one may dominate over the other depending on the state of traffic.

The two channel nature of vibrational thermal transport stems back to Hardy’s early work (see Eq. 2.14 and Eqs. 3.29 to 3.31 of Ref.¹⁵), and recently large strides have been made applying it in a lattice dynamical context by Simoncelli *et al.*⁶ and Isaeva *et al.*⁴. Hardy’s heat current operator is commonly used along with the Green-Kubo method to extract κ_{vib} from molecular dynamics (MD) simulations. MD is an invaluable tool in pioneering heat conduction beyond the phonon-gas model^{3,5,25,26}. Since MD uses Hardy’s heat current operator directly, and does not explicitly assume the phonon-gas model for heat conduction, it naturally captures other mechanisms of vibrational heat conduction. However, the atomistic nature of MD approaches comes with limitations of interpretation. In an attempt to interpret MD-based computational experiments of amorphous materials, a ‘descriptive’ taxonomy has been established to classify vibrational modes as propagons, diffusions, or locons. Quantitative metrics have even been defined to characterize the nature of heat conduction³. However, an intuitive physical picture is critical for the ‘predictive’ design of defective and complex crystals, as well as amorphous materials²⁶. Standard lattice dynamics (LD) (as computed by common computational suites such as phono3py²⁷), by design, only captures the phonon-gas channel. However, as we outline in Figure 1 the two-channel LD approach^{4,6} captures vibrational heat conduction beyond the phonon-gas model. One benefit of the two-channel LD framework is that it can provide an intuitive physical picture which can help facilitate predictive materials design. MD approaches tend to behave as

computational experiments and thus provide a more descriptive understanding. Both approaches are important.

It might be helpful to consider early simulations on diffusons in amorphous Si^{2,16,28} as an extreme case of band folding illustrated in Figure 1b, where a 1000+ atom simulation cells are used with periodic boundary conditions. This results in extreme band folding and a very small maximum $\mathbf{q}$ -vector (measured from the Γ -point) meaning the $\mathbf{q}$ -vector, to some extent, loses its meaning. Therefore, theoretical treatments of amorphous materials tend to collapse down to spectral treatments where properties are expressed only as a function of energy, rather than as wavevector and energy. As we show here, Yb₁₄MSb₁₁ seems to be somewhere in between these extremes.

Results

Band structure and density of states

The phonon band structures of Yb₁₄MgSb₁₁ and Yb₁₄MnSb₁₁, obtained from density functional theory (DFT) based lattice dynamics are shown in Figure 3. The many crossing points and close proximity of bands suggests that there should indeed be a significant diffuson channel contribution to κ_{vib} . Here, we examine the computed vibration density of states and compare this to experimental inelastic neutron scattering data.

Dense polycrystalline pellets of Yb₁₄(Mg, Mn)Sb₁₁ were synthesized (see the Synthesis section and Figure S2) and the vibrational properties were measured using time-of-flight neutron spectroscopy (details in the Inelastic neutron scattering section). The neutron scattering intensity measured versus energy and momentum transfer are shown in the left panels of Figures 3a and c. The right panels show the neutron scattering strength simulated using the DFT-based harmonic lattice dynamics, displayed in Figures 3b and d. The harmonic band structure is plotted along the Γ -N and Γ -X directions (labeled in Figure 2b). The atom projected and total vibrational density of states (DOS) are shown next to the band structures. These have been convoluted with a 1.5 meV Gaussian which is consistent with the experimental instrument resolution.

Starting at the top of Figure 3b, Yb₁₄MgSb₁₁ is expected to have very flat high energy optical modes at around 30 meV, which are dominated by Mg character with a small amount of Sb character. Though relatively faint, this mode is clearly observed in the neutron scattering data and simulation in Figure 3a. This can be attributed to the Mg atoms oscillating at high frequency within their Sb₄ tetrahedron cage while interacting very little with the rest of the atoms (see Figure S4a). The same type of behavior is expected in Yb₁₄MnSb₁₁ (Figure S4d), except for a shift in energy to around 23 meV and the modes have been split in energy. Between approximately 3 and 17 meV many flat branches packed very closely in energy are expected. These modes exhibit both Yb and Sb character, where lower energy ones are more heavily weighted in Yb character (Figures S4c and f) and the modes near 17 meV are more heavily weighted in Sb character (Figures S4b and

d), as expected from atomic mass considerations. Finally, the acoustic modes (defined here as the three lowest energy modes at a given $\mathbf{q}$ -point) only extend up to 2.5 to 3 meV.

The number of optical branches can be expected from the concept of zone folding shown in Figure 1b. With N=104 atoms per primitive unit cell, Yb₁₄MSb₁₁ has $3N-3=309$ optical modes. What may not have been obvious without the DFT-based LD simulations is their close proximity in energy, which as we outline in Figure 1c and the related text, is important for diffuson channel conduction. The LD simulations also indicate that the mode overlap observed in Figures 3a and c is not expected to disappear if large enough single crystals are able to be grown and measured. Additionally, we conclude that mode overlap observed in Figures 3a and c is not a consequence of the 1.5 meV resolution as demonstrated by the data obtained in a more narrow energy range (25 meV) with better resolution, see Figure S1.

These results are now compared to inelastic neutron scattering obtained density of states. However, before a direct comparison can be made the atom projected density of states ($g_i(E)$) must be weighted by their neutron scattering strength, resulting in the neutron weighted density of states

$$g_{\text{n}0}(E) = \frac{\sum_i N_i (\sigma_i/M_i) g_i(E)}{\sum_i N_i (\sigma_i/M_i)}. \quad (5)$$

N_i is the number of atoms of species i in the formula unit, σ_i is its neutron scattering cross-section, and M_i is its atomic mass. The results of this comparison are shown in the right-most panels of Figure 3c and d. Note, the maximum energy is scaled by 96% for comparison of computational and experimental neutron-weighted density of states. The shift in energy is expected due to the use of the PBE functional which is known to slightly over-estimate lattice parameters and slightly under-estimate elastic moduli and vibrational mode energy. This level of agreement is consistent with current state of the art methods²⁹. We also note that temperature effects were not considered when computing inter-atomic force constants and that the experimental data shown is at 300 K. The standard error for the experimental data is shown by the error bars, which is equal to or smaller than the data point size. The data agree well with the simulations, especially below 20 meV. In particular we note the agreement in the relative magnitude and shape of the peaks at around 8 meV and modes higher in energy. Whereas, the Mg peak seems to be stronger than predicted, the relative position in energy seems to be well represented. This level of agreement lends confidence to the band structure results shown in Figure 3, which suggest that Yb₁₄MSb₁₁ will exhibit significant heat conduction through the diffuson conduction channel.

Thermal conductivity

Here, we apply the two-channel lattice dynamics approach given in Eq. 1 to more quantitatively estimate the contributions of the phonon-gas and diffuson channels in Yb₁₄(Mn, Mg)Sb₁₁. Additionally, we demonstrate how modifying the energy of phonon modes by varying atomic mass can

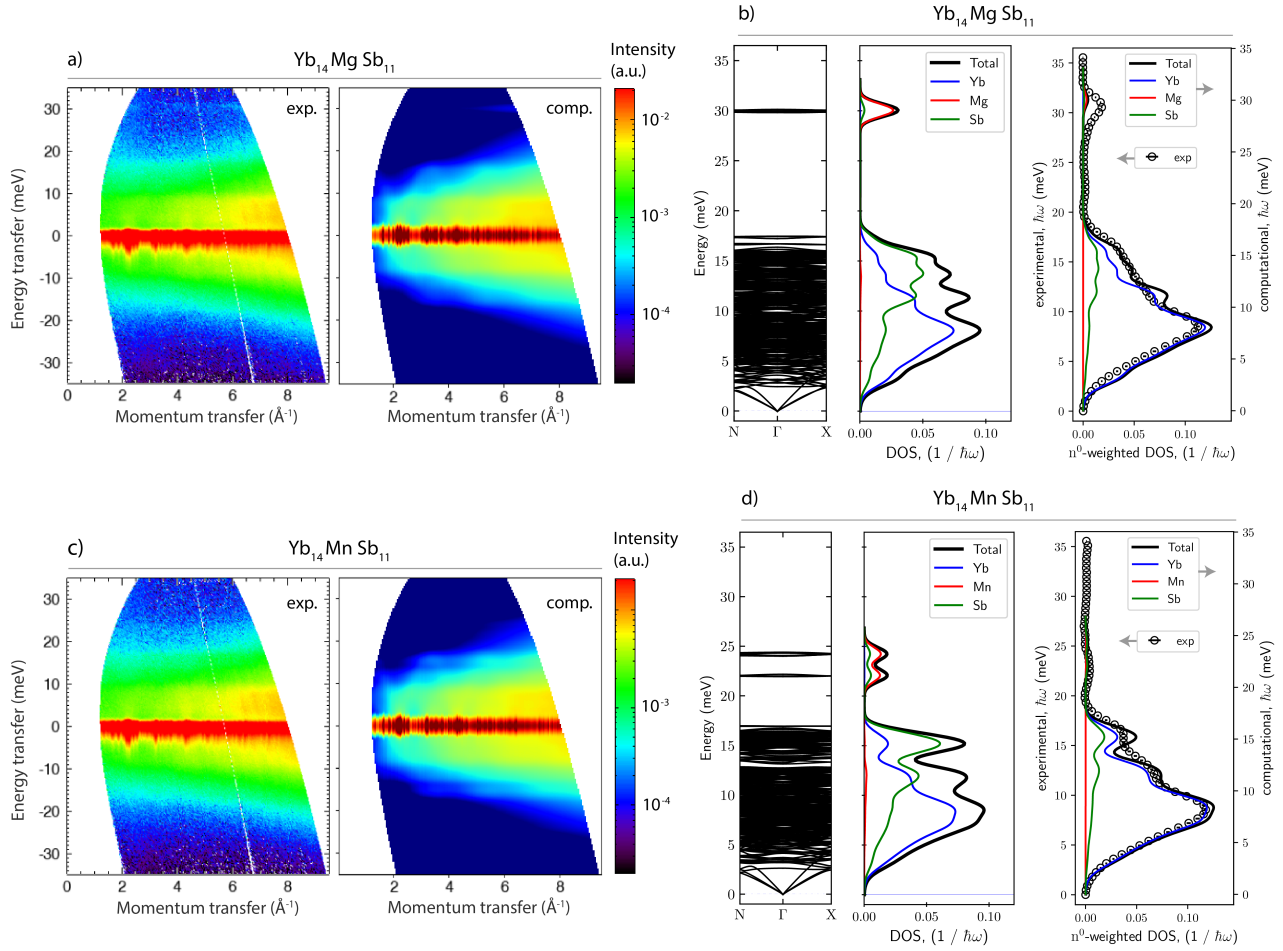


Figure 3. The phonon band structure and vibrational density of states (DOS) computed from DFT-based lattice dynamics and measured with inelastic neutron scattering. Panels a) and c) show the neutron scattering strength versus energy and momentum transfer measured on the ARCS spectrometer, next to the spectrum which is simulated using harmonic lattice dynamics. Panels b) and d) show the band structure, atom weighted and neutron weighted density of states of $\text{Yb}_{14}\text{MgSb}_{11}$ and $\text{Yb}_{14}\text{MnSb}_{11}$. All DOS calculations (atom and neutron weighted) shown are convoluted with a 1.5 meV full width half max Gaussian function which is consistent with the instrument resolution seen in the inelastic neutron experiments. Note, the maximum energy scales for the computational and experimental neutron-weighted density of state data are scale slightly (by 96%) for comparison.

systematically control κ_{diff} . Our thermal conductivity measurements and simulations for $\text{Yb}_{14}(\text{Mn}, \text{Mg})\text{Sb}_{11}$, displayed in Figure 4, indicate that the diffusion channel dominates above approximately 300 K. $\text{Yb}_{14}\text{MnSb}_{11}$ exhibits exceptional thermoelectric properties above 800 K^{10,11,13}. Details regarding the measurement of thermal conductivity, calculation of the vibrational thermal conductivity (κ_{vib}), and a discussion regarding experimental error are given in the ‘Transport measurements’ section.

The mathematical and computational details for our implementation of two-channel lattice dynamics are described in the Computational methods section (Eqs. 13 to 15). To summarize, we first compute harmonic inter-atomic force constants (IFCs) using density functional theory. Next, we take these IFCs and compute the dynamical matrix ($D(\mathbf{q})$) and its

gradient ($\nabla_{\mathbf{q}}^i D(\mathbf{q})$) on a uniform $\mathbf{q}$ -mesh to sample phonon properties throughout the Brillouin zone. The eigenvalues and eigenvectors obtained by diagonalizing $D(\mathbf{q})$, along with $\nabla_{\mathbf{q}}^i D(\mathbf{q})$ are then used to compute the required matrices: the heat capacity matrix $C_{ss'}(\mathbf{q})$ (Eq. 13), the velocity matrix $v_{ss'}(\mathbf{q})$ (Eq. 9), and the lifetime matrix $\tau_{ss'}(\mathbf{q})$ (Eq. 14). Finally these matrices are combined to compute the thermal conductivity matrix at each $\mathbf{q}$ -point

$$\kappa_{ss'}(\mathbf{q}) = C_{ss'}(\mathbf{q})v_{ss'}(\mathbf{q})v_{s's}(\mathbf{q})\tau_{ss'}(\mathbf{q}). \quad (6)$$

In order to examine the results obtained via two-channel lattice dynamics, it can be helpful to sum over $\mathbf{q}$ revealing which phonon branches mix and how much they contribute to κ_{vib} ,

$$\kappa_{ss'} = \sum_{\mathbf{q}} \kappa_{ss'}(\mathbf{q}). \quad (7)$$

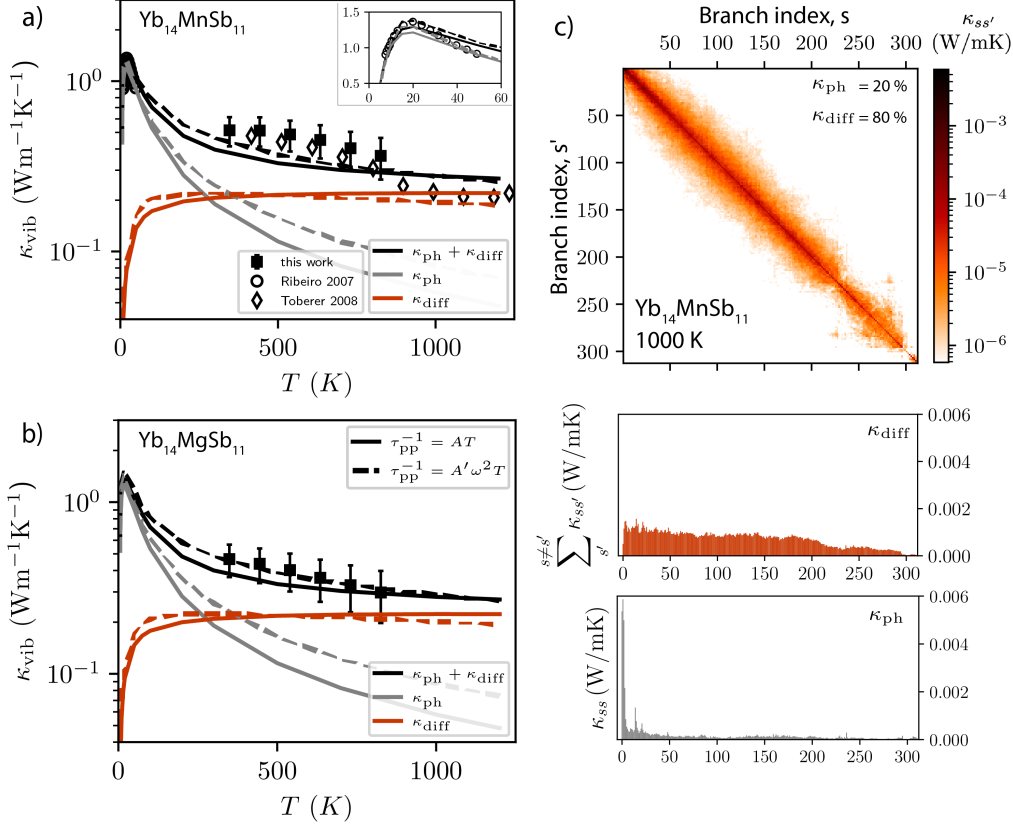


Figure 4. Measured vibrational (lattice) thermal conductivity of Yb₁₄(Mn,Mg)Sb₁₁ compared to two-channel lattice dynamics simulations (Eq. 1). a) The temperature dependence of the phonon-gas channel κ_{ph} , diffuson channel κ_{diff} and the vibrational (lattice) thermal conductivity $\kappa_{\text{vib}} = \kappa_{\text{ph}} + \kappa_{\text{diff}}$ for Yb₁₄MnSb₁₁. The analytical scattering rate coefficients are fixed using data below 50 K from Ribeiro *et al.*³⁰, and the simulation is then compared to data above room temperature measured in this work and provided by Toberer *et al.*¹¹. b) Vibrational thermal conductivity of Yb₁₄MgSb₁₁. In both (a) and (b), solid lines indicate $\tau_{\text{pp}}^{-1} = AT$ and dashed lines indicate $\tau_{\text{pp}}^{-1} = A'\omega^2 T$. c) The thermal conductivity matrix $\kappa_{ss'}$ (Eq. 7) for Yb₁₄MnSb₁₁ at 1000 K (the same for Yb₁₄MgSb₁₁ is given in Figure S10). Histograms of the for the diffuson and phonon-gas channels are shown below. The significant population of the off-diagonal ($s \neq s'$) elements throughout the density of states results in a κ_{diff} -dominated κ_{vib} . κ_{ph} contributions are isolated to the low index branches, which are acoustic in character.

Finally, the vibrational thermal conductivity is obtained by summing over s and s' , $\kappa_{\text{vib}} = \sum_{ss'} \kappa_{ss'}$. This is visually represented by summing each element of the matrix shown in Figure 4c.

We provide results for Si in Figure S5, where the lifetime for every mode $\mathbf{q}s$ is computed using third order IFCs and phono3py²⁷. Our results agree with those of Simoncelli *et al.*⁶ and we too conclude that thermal conductivity in Si is dominated by the phonon-gas channel, as expected. Additionally, we show that this dominance extends to high temperatures.

Due to its large unit cell size, third order IFCs for Yb₁₄MnSb₁₁ could not be reasonably obtained. Therefore, two analytical forms were applied for the phonon-phonon scattering rate (inverse of phonon lifetime) $\Gamma_{\text{pp}} = \tau_{\text{pp}}^{-1} = AT$ and $\Gamma_{\text{pp}} = \tau_{\text{pp}}^{-1} = A'\omega^2 T$. The coefficients A and A' are fixed using thermal conductivity below 50K provided by Ribeiro *et al.*³⁰ (inset of Figure 4a). The ω -independent form ap-

proximates phase space and anharmonicity contributions to the scattering rate as a constant (A) while maintaining the $\tau \propto 1/T$ relationship which is expected for phonon-phonon scattering. The ω^2 form is more commonly used, since this is the frequency dependence that is commonly expected for low frequency acoustic phonons³¹. However, the many optical branches may invalidate the ω^2 dependence over most of the frequency range from phase space considerations. Regardless, the conclusions presented here were insensitive to the ω -dependence of τ_{pp} , likely due to the close proximity of mode.

The treatment of higher order IFCs (3rd and 4th order) can influence the energy of phonon modes through renormalization and determines their linewidth, both of which may influence the conclusions regarding the magnitude of κ_{ph} and κ_{diff} ⁹. The moderate Grüneisen parameter obtained here for Yb₁₄MnSb₁₁ using the harmonic finite displacement method

(Figure S8), and the insensitivity to the ω -dependence of τ_{pp} suggest that these effect may be small in this case.

The thermal conductivity of $\text{Yb}_{14}\text{MnSb}_{11}$ below 50 K³⁰ was used to fix the analytical form of the phonon scattering rate which is defined as the Matthiessen's rule combination of the phonon-phonon (Γ_{pp}) and crystal boundary scattering ($\Gamma_{b,s}(\mathbf{q}) = |v_s(\mathbf{q})|/d$): $\Gamma = \Gamma_{pp} + \Gamma_b$. The simulation results shown in Figure 4a used $A = 4 \times 10^8 (\text{sK})^{-1}$ and $d = 0.8 \mu\text{m}$ when Γ_{pp} , and $A' = 1.5 \times 10^{-17} \text{s/K}$ and $d = 0.8 \mu\text{m}$ when $\Gamma_{pp} = A'\omega^2 T$. An $8 \times 8 \times 8$ $\mathbf{q}$ -mesh for Brillouin zone integration. We note that $\text{Yb}_{14}\text{MnSb}_{11}$ is intrinsically p-type with a carrier concentrations in the range of 10^{20} to 10^{21}cm^{-3} (our sample was measured to have $2.9 \pm 0.5 \times 10^{20} \text{cm}^{-3}$). While we do not explicitly consider electron-phonon scattering effects³², since we calibrate Γ to experimental data, they may influence the extracted coefficients, A and d . If the real line-widths are larger than we approximate, due to electron-phonon scattering effects, this is expected to suppress κ_{ph} and increase κ_{diff} .

After the analytical form of the phonon scattering rate was set, our two-channel lattice dynamics simulation captures the thermal conductivity above 300 K without any additional adjustable parameters, and indicates that κ_{diff} is the dominant channel above room temperature. Since Isaeva *et al.* demonstrated that the thermal conductivity computed via two-channel lattice dynamics (i.e. quasi-harmonic Green-Kubo, QHGK) is influenced by the magnitude of the line width⁴, it was important to set phonon line widths using low temperature experimental data. The diffusion channel is expected to become important in systems with many atoms per cell, making methods for approximating the line width without the use of 3rd order IFCs increasingly important.

Histograms visualizing κ_{diff} and κ_{ph} are shown for 1000 K in Figure 4c. For the κ_{ph} histogram, the large contribution from the three acoustic branches can be easily observed. The κ_{diff} histogram reveals significant contribution across all branches, with the most heat carried by branches with $s < 200$ which correspond to the densely packed branches below 17.5 meV (see Figure 3d).

We highlight that the importance of κ_{diff} in $\text{Yb}_{14}(\text{Mn}, \text{Mg})\text{Sb}_{11}$ comes mostly from crystal structure complexity and the resulting close energetic proximity of bands, rather than strong anharmonicity and large phonon line widths as is the case in CsPbBr_3 (Simoncelli *et al.*⁶). This conclusion is supported by Grüneisen parameter computations (Eq. 8 in Computational Methods), where we obtained $\gamma = 1.46$ for $\text{Yb}_{14}\text{MnSb}_{11}$ compared to $\gamma = 2.6$ for CsPbBr_3 . This indicates that while $\text{Yb}_{14}\text{MnSb}_{11}$ is less anharmonic it is still predicted to have a large κ_{diff} contribution.

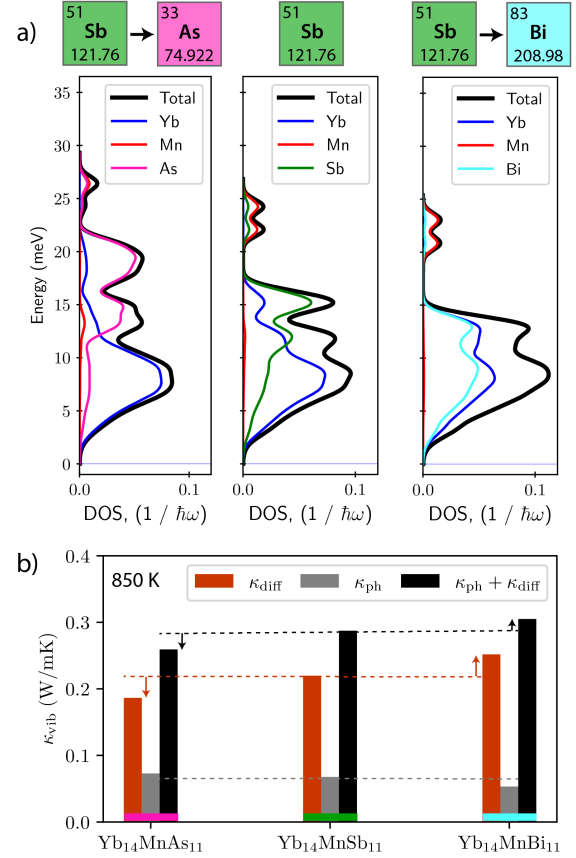


Figure 5. a) The influence of the Sb-site mass on the density of states. b) The decrease in overlap between Yb dominated modes and Sb-site dominated modes when the Sb mass is changed to that of As results in a 15 % decrease in κ_{diff} at 850 K. The increase in overlap when increasing Sb-site mass to that of Bi results in a 15 % increase in κ_{diff} . The trend in κ_{vib} is predicted to follow that of κ_{diff} .

Rational design of diffuson channel transport

The experimental and computational results presented above reveal that the energetic proximity of modes is an important metric governing the diffuson channel. Therefore, isolating a vibrational mode from others energetically seems to be a valid avenue for decreasing κ_{diff} . To test this hypothesis we changed the mass of Sb to that of As, keeping the structure and IFCs unchanged. The results shown in Figure 5 indicate that the Sb-site dominated modes were shifted up in energy away from the Yb dominated modes (band structures shown in Figure S6) and a 15% drop in κ_{diff} was indeed observed. Conversely, when the mass on the Sb-site was increased to that of Bi, the Sb-site dominated modes shifted down in energy increasing their overlap with Yb dominated modes and a corresponding 15% increase in κ_{diff} was seen. Overall, when increasing the mass on the Sb-site from As to Bi the simula-

tions showed a 35% increase of κ_{diff} and a 27% reduction in κ_{ph} . Nonetheless, an 18% increase in $\kappa = \kappa_{\text{diff}} + \kappa_{\text{ph}}$ was observed, which is consistent with our hypothesis that modifying the energetic proximity of vibrational modes is a valid design strategy for amorphous-like thermal conductivity. The lattice thermal conductivity of $\text{Yb}_{14}\text{MnBi}_{11}$ ³³ has been measured to be indeed larger than that of $\text{Yb}_{14}\text{MnSb}_{11}$ ¹¹, i.e. 0.35 W/mK versus 0.27 W/mK at 850 K, respectively.

We highlight that these findings are opposite of what is expected when only the phonon-gas channel is considered, where increasing atomic mass results in a lower frequencies, group velocities and lower thermal conductivity. Additionally, this trend is exactly opposite of what is expected for analytical (spectral) models of amorphous thermal conductivity, since these models have a direct correlation between κ_{vib} and average vibrational frequency and/or speed of sound^{21–23}. However, it is quite intuitive when the diffuson channel is considered in the mode-specific, two-channel lattice dynamical context (Figure 1).

It is often desired to minimizing the total vibrational thermal conductivity κ_{vib} . The approach to decreasing κ_{vib} depends on whether κ_{ph} or κ_{diff} dominates. If the κ_{ph} dominates, traditional defect scattering approaches can be used. If κ_{diff} dominates one could focus on increasing the energetic spacing between the phonon modes. Unfortunately, mechanisms that decrease κ_{ph} tend to increase κ_{diff} . However, the two-channel lattice dynamics framework indicates that if the average energetic spacing between optical modes and their lifetime can be increased, while the group velocity and lifetime of acoustic modes are decreased, it may be possible to decrease both simultaneously.

Discussion

By examining the vibrational properties of the $\text{Yb}_{14}\text{MSb}_{11}$ system in detail via computational and experimental methods, we show that for complex crystals one should not consider the phonon-gas model as incorrect, but rather as incomplete. The physical picture that emerges suggests that this general conclusion extends to defective and anharmonic crystals, as well as amorphous materials. To fully explain the vibrational thermal conductivity within a lattice dynamical framework, two conduction channels must be considered. The first is the standard phonon-gas channel (κ_{ph}), and the second we call the diffuson channel (κ_{diff}). By applying the two-channel lattice dynamical approach to $\text{Yb}_{14}(\text{Mn}, \text{Mg})\text{Sb}_{11}$ we find that the κ_{diff} dominates above 300 K. Therefore, this material can be thought of as a crystal which conducts heat like an amorphous material above room temperature. Using $\text{Yb}_{14}(\text{Mn}, \text{Mg})\text{Sb}_{11}$ as a model system, two-channel lattice dynamics is used to demonstrated materials design strategies for controlling κ_{diff} . We demonstrate how the κ_{diff} can be decreased by up to 35 % by increasing the energetic spacing between vibrational modes which was achieved computationally by reducing the atomic mass on the Sb-site from Bi, to Sb, to As.

Methods

Synthesis

Cylindrical pellets of polycrystalline $\text{Yb}_{14}\text{MgSb}_{11}$ and $\text{Yb}_{14}\text{MnSb}_{11}$ with final dimensions of approximately 12 mm in diameter and 15 mm in height were synthesized as follows. Raw elements were weighed in stoichiometric amounts in an Ar filled glove box and sealed in a ball mill vial. High purity Mn (99.99 at.% plates Alfa Aesar) Granules Alfa Aesar), Mg (at. 99.99% filings Alfa Aesar), and Sb (at. 99.999% shot 5N plus) were used as received from suppliers. Yb(99.9 at.% ingot Alfa Aesar) was arc melted five times to further purify it of oxide prior to synthesis. These raw elements were ball milled together for 5 hours, re-mixing the constituents in the glove box every hour. The resulting powder was pressed at 900 C for 20 minutes under 45 MPa of pressure in a uniaxial hot press.

The neutron diffraction histogram was refined to examine the phase purity of the samples. The diffraction signal (data points in Figure S2) was extracted from the elastic line (energy transfer between -1 and 1 meV) of time-of-flight neutron scattering intensity, with an incident neutron energy of 25 meV (Figure S1). This diffraction signal contained contributions from the Al sample can, while in the inelastic neutron scattering intensities shown in Figures 3 and S1, the Al sample can contribution has been removed. The diffraction signal was refined in GSAS-II³⁴ using $\text{Yb}_{14}\text{MSb}_{11}$ ($I4_1/acd$ no. 142 with $c/a > 1$) and Al ($Fm\bar{3}m$ no. 225) phases. The diffraction from the empty Al can was used to set initial values for the instrument line broadening parameters, which were then refined along with the lattice parameters, atomic displacement parameters, and phase fractions of both phases. Therefore, these refinements are only used for phase analysis and no physical interpretation is given to the peak broadening. These refinements and phase analysis indicate phase purity of the samples in the sense that the vibrational density of states obtained is dominated by the $\text{Yb}_{14}\text{MSb}_{11}$ phase.

Transport measurements

Thermal conductivity was calculated from the relation $\kappa = DdC_p$, where D is the thermal diffusivity measured with a Netzsch LFA 457 laser flash apparatus, d is the geometrical density of the material, and C_p is the heat capacity at constant pressure. $d = 8.23\text{g/cm}^3$ for $\text{Yb}_{14}\text{MnSb}_{11}$ and $d = 8.13\text{g/cm}^3$ for $\text{Yb}_{14}\text{MnSb}_{11}$, which is 98% of the theoretical density for both, based on diffraction data. C_p of the compounds were calculated via the Dulong Petit law, where $C_p = 3RN/M$, where N is the number of atoms in a formula unit and M is the molar mass of the formula unit, and R is the molar gas constant. The measured κ_{tot} can be obtained by adding $\kappa_e = L\sigma T$ to the data in Figures 4a and b, where the polynomial expression for the measured σ is given in Figure S9.

The electrical conductivity (σ) and Hall coefficient measurements were determined using the 4-point probe Van der Pauw technique with a 0.8 T magnetic field under high vacuum.³⁵ The electrical conductivity measurements are shown

in Figure S9, along with polynomial fits which are used to compute the electronic contribution to the thermal conductivity, $\kappa_e = L\sigma T$, with $L = 2.44 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$. This use of L is consistent with Toberer *et al.*¹¹, but may be an over estimation in the $\text{Yb}_{14}(\text{Mn}, \text{Mg})\text{Sb}_{11}$. The error bars on our data in Figure 4a and b embody laser flash measurement error, along with an estimation of the potential errors in subtracting κ_e .

Inelastic neutron scattering

Inelastic neutron scattering experiments were conducted on the ARCS spectrometer at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory, with incident neutron energies of 25 meV and 45 meV, and a sample temperature of 300 K. The samples were dense polycrystalline cylindrical pellets approximately 12 mm in diameter and 15 mm in height. All data are first represented as a function of neutron energy transfer, E , and momentum transfer, $|\mathbf{Q}| = 4\pi \sin(\theta)/\lambda$, where θ is the scattering angle and λ is the neutron wavelength. The energy resolution is approximately 1.5 meV. An example of the scattering function (dynamic structure factor) $S(|\mathbf{Q}|, E)$ data obtained via the program Mslice in the Data Analysis and Visualization Environment (DAVE)³⁶ is shown in Figure 3. Due primarily to the large neutron absorption cross-section of Yb, neutron absorption corrections were included in the analysis as implemented by Mslice. This data was used to compute the vibrational density of state by first integrating $S(|\mathbf{Q}|, E)$ from $|\mathbf{Q}| = 4$ to $8 \text{\AA}^{-1}$, obtaining $S(E)$. Data at the highest scattering angles, from 120 to 136° were masked and data above 36 meV were removed to avoid any instrument related artifacts in $S(|\mathbf{Q}|, E)$. The background was subtracted from $S(E)$ and the data was converted from arbitrary units to counts by recognizing that the intensity and error bars obtained from Mslice are An and $A\sqrt{n}$, where n is counts and A is an arbitrary scaling factor. After these corrections, $S(E)$ was converted to the vibrational density of state $g(E)$ by removing the elastic scattering peak and multi-phonon contributions in the program isdos10³⁷, similar to the approach used in Ref.¹².

Computational methods

Interatomic force constants. The computation of harmonic interatomic force constants was performed using density functional theory (DFT) in the Vienna Ab initio Simulation Package (VASP)³⁸⁻⁴¹ and Phonopy⁴². First, the optimization of the electronic and ionic structures of $\text{Yb}_{14}\text{MgSb}_{11}$, $\text{Yb}_{14}\text{MnSb}_{11}$, Si, and CsPbBr_3 were performed with periodic DFT in VASP³⁸⁻⁴¹ with strict convergence criteria. For electronic and structural optimization, a criterion of $\Delta E < 10^{-7}$ and $\Delta E < 10^{-5}$ eV per cell was used, respectively. The projector augmented-wave method^{43,44} with a plane-wave cutoff of 520 eV and the Perdew–Burke–Ernzerhof (PBE) functional were used during these calculations⁴⁵. For Yb, we used Yb^{2+} pseudo-potentials where the f electrons are considered to be in

the core. Furthermore, the optimizations of the primitive unit cells were performed with a $4 \times 4 \times 4$ $\mathbf{k}$ -space mesh (where $\mathbf{k}$ is the electron wave-vector) for $\text{Yb}_{14}\text{MgSb}_{11}$ and $\text{Yb}_{14}\text{MnSb}_{11}$, a $17 \times 17 \times 17$ $\mathbf{k}$ -space mesh for Si, and a $7 \times 7 \times 5$ $\mathbf{k}$ -space mesh for CsPbBr_3 . Since Mn in this structure is expected to exhibit magnetic properties⁴⁶, we utilized a ferromagnetic model for $\text{Yb}_{14}\text{MnSb}_{11}$ during the optimization with magnetic moments on all Mn atoms in the primitive unit cell. We compare the results to an anti-ferromagnetic model in the Supporting Information (Figure S7). The phonon frequencies are only influenced slightly by the magnetic model (root mean square deviation between the phonon frequencies is smaller than 0.12 meV on a $8 \times 8 \times 8$ $\mathbf{q}$ -point grid).

Once the optimized ionic and electronic structures were obtained, the harmonic interatomic force constants (IFCs) were computed using the finite displacement method as implemented in Phonopy^{42,47}, with a displacement of 0.01 $\text{\AA}$ and with the help of the conventional cell of $\text{Yb}_{14}\text{MgSb}_{11}$ and $\text{Yb}_{14}\text{MnSb}_{11}$, a $3 \times 3 \times 2$ supercell of the conventional cell of CsPbBr_3 , and a $4 \times 4 \times 4$ supercell of the conventional cell of Si as the supercell. The forces for this evaluation were calculated at the Γ -point for $\text{Yb}_{14}\text{MgSb}_{11}$, $\text{Yb}_{14}\text{MnSb}_{11}$, and CsPbBr_3 , and with a $2 \times 2 \times 2$ $\mathbf{k}$ -space mesh for Si. Again, a ferromagnetic model was used for $\text{Yb}_{14}\text{MnSb}_{11}$. Furthermore, a higher plane-wave cutoff of 900 eV was used to calculate the second-order force constants for Si.

To obtain third-order force constants for Si, Phono3py²⁷ in combination with VASP was used. This was done with the default displacement of 0.03 $\text{\AA}$ and a $2 \times 2 \times 2$ supercell of the conventional cell. The forces were evaluated with the help of a $5 \times 5 \times 5$ $\mathbf{k}$ -space mesh and a plane-wave cutoff of 520 eV.

To calculate the mode specific Grüneisen parameters ($\gamma_s(\mathbf{q}) = -d \ln \omega_s(\mathbf{q}) / d \ln V$) for $\text{Yb}_{14}\text{MnSb}_{11}$ and CsPbBr_3 , two additional structural optimizations were performed at a constant volume of $0.997^3 \times V_0$ and $1.003^3 \times V_0$ with V_0 as the DFT ground-state volume, allowing the lattice parameters to relax. The computational details were the same as for the structural optimization of the DFT ground-state structures. Furthermore, harmonic phonon calculations were performed with the same computational details as for the DFT ground-state structure of $\text{Yb}_{14}\text{MnSb}_{11}$ and CsPbBr_3 , respectively. Based on this set of phonon calculations of the DFT ground-state structure and the compressed and expanded structures, mode Grüneisen parameters were calculated as implemented in Phonopy. The mode specific Grüneisen parameters were used to compute the thermodynamic average Grüneisen parameter, which is defined as a heat capacity weighted average of $\gamma_s(\mathbf{q})$,

$$\gamma = \frac{\sum_{\mathbf{q}s} C_s(\mathbf{q}) \gamma_s(\mathbf{q})}{\sum_{\mathbf{q}s} C_s(\mathbf{q})}. \quad (8)$$

We obtained $\gamma = 1.46$ for $\text{Yb}_{14}\text{MnSb}_{11}$ and $\gamma = 2.6$ for CsPbBr_3 at 300 K. A plot of the mode specific Grüneisen parameters is shown in the Supporting Information Figure S8. The mode specific Grüneisen parameters of CsPbBr_3 are significantly larger than those of $\text{Yb}_{14}\text{MnSb}_{11}$. Raw

data for the phonon calculations can be accessed on <https://doi.org/10.5281/zenodo.3951927>.

Band structure, DOS, and INS. These harmonic IFCs were implemented in a lattice dynamical approach to obtain the phonon band structure. For the computation of the vibrational density of states (DOS), an 8x8x8 uniform $\mathbf{q}$ -mesh and the tetrahedron method was used to approximate the integration over the Brillouin zone. Additionally, the DOS was convoluted with a 1.5 meV full width half max Gaussian function which is consistent with the instrument resolution of the inelastic neutron scattering experiments.

Inelastic neutron scattering (INS) spectra for $\text{Yb}_{14}\text{MSb}_{11}$ were simulated using OCLIMAX²⁴. DFT phonon frequencies and polarization vectors sampled on a 5x5x5 gamma-centered $\mathbf{q}$ -point mesh were used as input. Full scattering (coherent, incoherent, elastic, inelastic) for powder samples was simulated, using the ARCS experiment parameters such as incident energy, detector coverage (scattering angles), resolution, and temperature. Multi-phonon scattering contributions up to 10-phonon events were also calculated based on incoherent approximation and included in the total spectra.

Thermal conductivity. Here we define the matrices required to compute κ_{vib} as defined in Eq. 1.

The velocity matrix is written as

$$v_{ss'}^i(\mathbf{q}) = \frac{1}{\omega_s(\mathbf{q}) + \omega_{s'}(\mathbf{q})} \langle \mathbf{q}s | \nabla_{\mathbf{q}}^i D(\mathbf{q}) | \mathbf{q}s' \rangle. \quad (9)$$

where $n_s^0(\mathbf{q})$ is the Bose-Einstein distribution function of mode s at temperature T , $\omega_s(\mathbf{q})$ is the phonon angular frequency of a phonon at wave vector $\mathbf{q}$ in branch s , V is the volume of the unit cell, N is the number of $\mathbf{q}$ -points considered on a discrete, uniform $\mathbf{q}$ -mesh.

The lifetime matrix is given by

$$\tau_{ss'}(\mathbf{q}) = \frac{2(\Gamma_s(\mathbf{q}) + \Gamma_{s'}(\mathbf{q}))}{4(\omega_s(\mathbf{q}) - \omega_{s'}(\mathbf{q}))^2 + (\Gamma_s(\mathbf{q}) + \Gamma_{s'}(\mathbf{q}))^2} \quad (14)$$

where $\Gamma_s(\mathbf{q})$ is the scattering rate or the inverse of phonon lifetime for a phonon at $\mathbf{q}$ in branch s . For off-diagonal elements, this equation resembles a Lorentzian function. For the diagonal components it reduces to simply the phonon relaxation time

$$\tau_{ss}(\mathbf{q}) = \Gamma_s(\mathbf{q})^{-1} = \tau_s(\mathbf{q}). \quad (15)$$

When third order IFCs are available Γ_s can be computed from first principles. However, due to its large unit cell size, third order IFCs for $\text{Yb}_{14}\text{MnSb}_{11}$ could not be reasonably obtained. Therefore, the simple analytical form $\Gamma_{\text{pp}} = \tau_{\text{pp}}^{-1} = AT$ was used for the phonon-phonon scattering rate (inverse of

This is a complex matrix which obeys the relationship, $v_{ss'}^i(\mathbf{q}) = v_{s's}^i(\mathbf{q})^*$. Its diagonal components ($s = s'$) have negligible imaginary contributions. Eq. 9 is equivalent to Eq. 8 in Simoncelli et al.⁶, by using Eq. 30 and Eq. 4 of Auerbach and Allen⁴⁸. The gradient of the dynamical matrix was computed at each $\mathbf{q}$ -point, where the gradient is taken analytically as implemented by phonopy. The diagonal elements of $v_{ss'}^i(\mathbf{q})$ are simply the group velocity

$$v_{ss}^i(\mathbf{q}) = v_s^i(\mathbf{q}) = \frac{\partial \omega_s(\mathbf{q})}{\partial k_i}. \quad (10)$$

The matrix element can be written explicitly as

$$\langle \mathbf{q}s | \nabla_{\mathbf{q}}^i D(\mathbf{q}) | \mathbf{q}s' \rangle = \epsilon_s^*(\mathbf{q}) \frac{\partial D(\mathbf{q})}{\partial k_i} \epsilon_{s'}(\mathbf{q}) \quad (11)$$

where $\epsilon_s(\mathbf{q})$ is the eigenvector of normal mode at $\mathbf{q}$ in branch s . The star indicates a complex conjugate. $D(\mathbf{q})$ is the dynamical matrix at $\mathbf{q}$ defined as the following

$$\epsilon_s^*(\mathbf{q}) D(\mathbf{q}) \epsilon_s(\mathbf{q}) = \omega_s(\mathbf{q})^2 \delta_{s,s'} \quad (12)$$

where $\omega_s(\mathbf{q})^2$ are the eigenvalues.

The heat capacity matrix, in units of $\text{J m}^{-3} \text{K}^{-1}$ is given as

$$C_{ss'}(\mathbf{q}) = \frac{\hbar^2 (\omega_s(\mathbf{q}) + \omega_{s'}(\mathbf{q}))}{4VNk_B T^2} [\omega_s(\mathbf{q}) n_s^0(\mathbf{q}) (n_s^0(\mathbf{q}) + 1) + \omega_{s'}(\mathbf{q}) n_{s'}^0(\mathbf{q}) (n_{s'}^0(\mathbf{q}) + 1)] \quad (13)$$

phonon lifetime). The coefficient A , which is meant to approximate anharmonicity and phase space effects, we set using low temperature thermal conductivity data. A Mattheissen's rule combination of the phonon-phonon (Γ_{pp}) and crystal boundary scattering was used ($\Gamma_{\text{b},s}(\mathbf{q}) = |v_s(\mathbf{q})|/d$): $\Gamma = \Gamma_{\text{pp}} + \Gamma_{\text{b}}$, and the coefficients $A = 4 \times 10^8 (\text{sK})^{-1}$, $d = 0.8 \mu\text{m}$ were obtained

Eqs. 13, 9, and 14 combine to give the thermal conductivity tensor (using index notation)

$$\kappa^{ij} = \sum_{\mathbf{q}ss'} C_{ss'}(\mathbf{q}) v_{ss'}^i(\mathbf{q}) v_{s's}^j(\mathbf{q}) \tau_{ss'}(\mathbf{q}). \quad (16)$$

In matrix notation κ^{ij} is represented as κ . By omitting the tensor superscripts in Eq. 1, we imply $\kappa = \kappa^{\text{xx}}$.

To test our numerical implementation, the phonon-gas channel of Si computed via our code was compared to the thermal conductivity computed directly from phono3py and the results converged to the same value.

The phonon-gas and diffuson channel thermal conductiv-

ity tensors computed for Yb₁₄MnSb₁₁ at 300 K are

$$\kappa_{\text{ph}} = \begin{bmatrix} 0.19 & 0.00 & 0.00 \\ 0.00 & 0.19 & 0.00 \\ 0.00 & 0.00 & 0.20 \end{bmatrix} \text{ W/mK}, \quad (17)$$

and

$$\kappa_{\text{diff}} = \begin{bmatrix} 0.21 & 0.00 & 0.00 \\ 0.00 & 0.21 & 0.00 \\ 0.00 & 0.00 & 0.19 \end{bmatrix} \text{ W/mK}. \quad (18)$$

The *xx* components are reported in the Results section.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division (neutron scattering and diffusion-channel calculations). RH acknowledges the DOE Science Graduate Research Award program (2018 Solicitation 2). Inelastic neutron scattering work at the BL-18 ARCS beamline used resources at the Spallation Neutron Source, a U.S. DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. JG acknowledges funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 837910. JG and GH furthermore thank the Consortium des Équipements de Calcul Intensif en Fédération Wallonie Bruxelles (CÉCI) for computational resources. GJS and MW acknowledge the support of award 70NANB19H005 from the U.S. Department of Commerce, National Institute of Standards and Technology as part of the Center for Hierarchical Materials Design (CHiMaD)

RH thanks Phillip B. Allen for helpful discussions surrounding the physical interpretation of simulated results and terminology. RH thanks Michele Simoncelli for correspondence regarding the computational details of the unified two-channel lattice dynamical approach.

Contributions

RH, RPH, GH and GJS initiated the work. RH, RPH, MM and DA conducted the inelastic neutron scattering. YC simulated the inelastic neutron scattering intensity, using lattice dynamics results provided by JG and RH. MW synthesized the samples and made the transport measurements. RH led the development of post DFT codes and two-channel thermal conductivity simulation. JG, AB and GH executed the DFT simulations for interatomic force constants, and JG and GH contributed to the development of post DFT codes. RH led authorship of the manuscript. All authors helped revise manuscript.

References

- McGaughey, A. J. H., Jain, A. & Kim, H.-y. Phonon properties and thermal conductivity from first principles, lattice dynamics, and the Boltzmann transport equation. *J. Appl. Phys.* **125**, 011101, DOI: [10.1063/1.5064602](https://doi.org/10.1063/1.5064602) (2019).
- Allen, P. B., Feldman, J. L., Fabian, J. & Wooten, F. Diffusions, locons and propagons: Character of atomic vibrations in amorphous Si. *Philos. Mag. B* **79**, 1715–1731, DOI: [10.1080/014186399255836](https://doi.org/10.1080/014186399255836) (1999). [9907132](https://doi.org/10.1080/014186399255836).
- Seyf, H. R. & Henry, A. A method for distinguishing between propagons, diffusions, and locons. *J. Appl. Phys.* **120**, DOI: [10.1063/1.4955420](https://doi.org/10.1063/1.4955420) (2016).
- Isaeva, L., Barbalinardo, G., Donadio, D. & Baroni, S. Modeling heat transport in crystals and glasses from a unified lattice-dynamical approach. *Nat. Commun.* 1–6, DOI: [10.1038/s41467-019-11572-4](https://doi.org/10.1038/s41467-019-11572-4) (2019). [1904.02255](https://doi.org/10.1038/s41467-019-11572-4).
- Seyf, H. R. *et al.* Rethinking phonons: The issue of disorder. *npj Comput. Mater.* **3**, DOI: [10.1038/s41524-017-0052-9](https://doi.org/10.1038/s41524-017-0052-9) (2017). [1504.03567](https://doi.org/10.1038/s41524-017-0052-9).
- Simoncelli, M., Marzari, N. & Mauri, F. Unified theory of thermal transport in crystals and disordered solids. *Nat. Phys.* DOI: [10.1038/s41567-019-0520-x](https://doi.org/10.1038/s41567-019-0520-x) (2019). [1901.01964](https://doi.org/10.1038/s41567-019-0520-x).
- Zhu, T. & Ertekin, E. Mixed phononic and non-phononic transport in hybrid lead halide perovskites: Glass-crystal duality, dynamical disorder, and anharmonicity. *Energy Environ. Sci.* **12**, 216–229, DOI: [10.1039/c8ee02820f](https://doi.org/10.1039/c8ee02820f) (2019).
- Luo, Y., Yang, X., Feng, T., Wang, J. & Ruan, X. Vibrational hierarchy leads to dual-phonon transport in low thermal conductivity crystals. *Nat. Commun.* 1–10, DOI: [10.1038/s41467-020-16371-w](https://doi.org/10.1038/s41467-020-16371-w).
- Xia, Y., Pal, K., He, J., Ozoliņš, V. & Wolverton, C. Particlelike phonon propagation dominates ultralow lattice thermal conductivity in crystalline t₃vse₄. *Phys. Rev. Lett.* **124**, 1–7, DOI: [10.1103/PhysRevLett.124.065901](https://doi.org/10.1103/PhysRevLett.124.065901) (2020).
- Brown, S. R., Kauzlarich, S. M., Gascoin, F. & Snyder, G. J. Yb₁₄ MnSb₁₁ : New High Efficiency Thermoelectric Material for Power Generation. *Chem. Mater.* **18**, 1873–1877, DOI: [10.1021/cm060261t](https://doi.org/10.1021/cm060261t) (2006).
- Toberer, E. S., Brown, S. R., Ikeda, T., Kauzlarich, S. M. & Jeffrey Snyder, G. High thermoelectric efficiency in lanthanum doped Yb₁₄MnSb₁₁. *Appl. Phys. Lett.* **93**, 062110, DOI: [10.1063/1.2970089](https://doi.org/10.1063/1.2970089) (2008).
- Möchel, A. *et al.* Lattice dynamics in the thermoelectric Zintl compound Yb₁₄MnSb₁₁. *Phys. Rev. B - Condens. Matter Mater. Phys.* **84**, 1–10, DOI: [10.1103/PhysRevB.84.184303](https://doi.org/10.1103/PhysRevB.84.184303) (2011).
- Grebenkemper, J. H. *et al.* High Temperature Thermoelectric Properties of Yb₁₄MnSb₁₁ Prepared from Reaction of MnSb with the Elements. *Chem. Mater.* **27**, 5791–5798, DOI: [10.1021/acs.chemmater.5b02446](https://doi.org/10.1021/acs.chemmater.5b02446) (2015).

14. Wang, Y. *et al.* First-principles calculations of lattice dynamics and thermodynamic properties for Yb₁₄MnSb₁₁. *J. Appl. Phys.* **123**, 045102, DOI: [10.1063/1.5013601](https://doi.org/10.1063/1.5013601) (2018).
15. Hardy, R. J. Energy-Flux Operator for a Lattice. *Phys. Rev.* **132**, 168–177 (1963).
16. Allen, P. B. & Feldman, J. L. Thermal conductivity of disordered harmonic solids. *Phys. Rev. B* **48**, 12581–12588, DOI: [10.1103/PhysRevB.48.12581](https://doi.org/10.1103/PhysRevB.48.12581) (1993).
17. Allen, P. B. & Feldman, J. L. Thermal Conductivity of Glasses: Theory and Application to Amorphous Si. *Phys. Rev. Lett.* **62**, 645–648, DOI: [10.1103/PhysRevLett.62.645](https://doi.org/10.1103/PhysRevLett.62.645) (1989).
18. Toberer, E. S., Zevkink, A. & Snyder, G. J. Phonon engineering through crystal chemistry. *J. Mater. Chem.* **21**, 15843, DOI: [10.1039/c1jm11754h](https://doi.org/10.1039/c1jm11754h) (2011).
19. Mukhopadhyay, S. *et al.* Two-channel model for ultralow thermal conductivity of crystalline Ti₃VSe₄. *Science* **360**, 1455–1458, DOI: [10.1126/science.aar8072](https://doi.org/10.1126/science.aar8072) (2018).
20. Snyder, G. J., Agne, M. T. & Gurunathan, R. Thermal conductivity of complex materials. *Natl. Sci. Rev.* **6**, 380–381, DOI: [10.1093/nsr/nwz040](https://doi.org/10.1093/nsr/nwz040) (2019).
21. Cahill, D. G. & Pohl, R. Heat flow and lattice vibrations in glasses. *Solid State Commun.* **70**, 927–930, DOI: [10.1016/0038-1098\(89\)90630-3](https://doi.org/10.1016/0038-1098(89)90630-3) (1989).
22. Clarke, D. R. Materials selection guidelines for low thermal conductivity thermal barrier coatings. *Surf. Coatings Technol.* **163-164**, 67–74, DOI: [10.1016/S0257-8972\(02\)00593-5](https://doi.org/10.1016/S0257-8972(02)00593-5) (2003).
23. Agne, M. T., Hanus, R. & Snyder, G. J. Minimum thermal conductivity in the context of diffuson-mediated thermal transport. *Energy Environ. Sci.* **11**, 609–616, DOI: [10.1039/C7EE03256K](https://doi.org/10.1039/C7EE03256K) (2018).
24. Cheng, Z. *et al.* Diffuson-driven ultralow thermal conductivity in amorphous Nb₂O₅ thin films. *Phys. Rev. Mater.* **3**, 025002, DOI: [10.1103/PhysRevMaterials.3.025002](https://doi.org/10.1103/PhysRevMaterials.3.025002) (2019).
25. Giri, A., Donovan, B. F. & Hopkins, P. E. Localization of vibrational modes leads to reduced thermal conductivity of amorphous heterostructures. *Phys. Rev. Mater.* **2**, 1–12, DOI: [10.1103/PhysRevMaterials.2.056002](https://doi.org/10.1103/PhysRevMaterials.2.056002) (2018).
26. DeAngelis, F. *et al.* Thermal Transport in Disordered Materials. *Nanoscale Microscale Thermophys. Eng.* **0**, 1–36, DOI: [10.1080/15567265.2018.1519004](https://doi.org/10.1080/15567265.2018.1519004) (2018).
27. Togo, A., Chaput, L. & Tanaka, I. Distributions of phonon lifetimes in brillouin zones. *Phys. Rev. B* **91**, 094306, DOI: [10.1103/PhysRevB.91.094306](https://doi.org/10.1103/PhysRevB.91.094306) (2015).
28. Feldman, J. L., Kluge, M. D., Allen, P. B. & Wooten, F. Thermal conductivity and localization in glasses: Numerical study of a model of amorphous silicon. *Phys. Rev. B* **48**, 12589–12602, DOI: [10.1103/PhysRevB.48.12589](https://doi.org/10.1103/PhysRevB.48.12589) (1993).
29. Petretto, G. *et al.* High-throughput density-functional perturbation theory phonons for inorganic materials. *Sci. Data* **5**, 1–12, DOI: [10.1038/sdata.2018.65](https://doi.org/10.1038/sdata.2018.65) (2018).
30. Ribeiro, R. A. *et al.* Low-temperature thermoelectric properties of Yb₁₄MSb₁₁ (M = Mn, Zn). *J. Physics: Condens. Matter* **19**, 376211, DOI: [10.1088/0953-8984/19/37/376211](https://doi.org/10.1088/0953-8984/19/37/376211) (2007). Thermal conductivity measured via the steady heat flow method above 50 K may be influenced by radiation losses³⁵.
31. Herring, C. Role of Low-Energy Phonons in Thermal Conduction. *Phys. Rev.* **95**, 954–965, DOI: [10.1103/PhysRev.95.954](https://doi.org/10.1103/PhysRev.95.954) (1954).
32. Liao, B. *et al.* Significant reduction of lattice thermal conductivity by the electron-phonon interaction in silicon with high carrier concentrations: A first-principles study. *Phys. Rev. Lett.* **114**, 1–6, DOI: [10.1103/PhysRevLett.114.115901](https://doi.org/10.1103/PhysRevLett.114.115901) (2015). [1409.1268](https://doi.org/10.1103/PhysRevLett.114.115901).
33. Hu, Y. & Kauzlarich, S. M. Yb₁₄MgBi₁₁: structure, thermoelectric properties and the effect of the structure on low lattice thermal conductivity. *Dalton Transactions* **46**, 3996–4003, DOI: [10.1039/c7dt00183e](https://doi.org/10.1039/c7dt00183e) (2017).
34. Toby, B. H. & Von Dreele, R. B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *J. Appl. Crystallogr.* **46**, 544–549, DOI: [10.1107/S0021889813003531](https://doi.org/10.1107/S0021889813003531) (2013).
35. Borup, K. a. *et al.* Measuring thermoelectric transport properties of materials. *Energy Environ. Sci.* **8**, 423–435, DOI: [10.1039/C4EE01320D](https://doi.org/10.1039/C4EE01320D) (2015).
36. Azuah, R. T. *et al.* DAVE: A Comprehensive Software Suite for the Reduction, Visualization, and Analysis of Low Energy Neutron Spectroscopic Data. *J. Res. Natl. Inst. Standards Technol.* **114**, 341, DOI: [10.6028/jres.114.025](https://doi.org/10.6028/jres.114.025) (2009).
37. Sergeev, I. *Priv. Comm.* (2019).
38. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **47**, 558–561, DOI: [10.1103/physrevb.47.558](https://doi.org/10.1103/physrevb.47.558) (1993).
39. Kresse, G. & Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal – amorphous-semiconductor transition in germanium. *Phys. Rev. B* **49**, 14251–14269, DOI: [10.1103/physrevb.49.14251](https://doi.org/10.1103/physrevb.49.14251) (1994).
40. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186, DOI: [10.1103/physrevb.54.11169](https://doi.org/10.1103/physrevb.54.11169) (1996).
41. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **6**, 15–50, DOI: [10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0) (1996).
42. Togo, A. & Tanaka, I. First principles phonon calculations in materials science. *Scripta Materialia* **108**, 1–5, DOI: [10.1016/j.scriptamat.2015.07.021](https://doi.org/10.1016/j.scriptamat.2015.07.021) (2015).

43. Blochl, P. E. Projector-Augmented Plane-Wave Method. *Phys. Rev. B* **50**, 17953, DOI: [10.1142/9789814365031_0023](https://doi.org/10.1142/9789814365031_0023) (1994).
44. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775, DOI: [10.1103/PhysRevB.59.1758](https://doi.org/10.1103/PhysRevB.59.1758) (1999).
45. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868, DOI: [10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865) (1996). [0927-0256\(96\)00008](https://arxiv.org/abs/0927-0256(96)00008).
46. Chan, J. Y., Olmstead, M. M., Kauzlarich, S. M. & Webb, D. J. Structure and Ferromagnetism of the Rare-Earth Zintl Compounds: $\text{Yb}_{14}\text{MnSb}_{11}$ and $\text{Yb}_{14}\text{MnBi}_{11}$. *Chem. Mater.* **10**, 3583–3588, DOI: [10.1021/cm980358i](https://doi.org/10.1021/cm980358i) (1998).
47. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl_2 -type SiO_2 at high pressures. *Phys. Rev. B - Condens. Matter Mater. Phys.* **78**, 1–9, DOI: [10.1103/PhysRevB.78.134106](https://doi.org/10.1103/PhysRevB.78.134106) (2008).
48. Auerbach, A. & Allen, P. B. Universal high-temperature saturation in phonon and electron transport. *Phys. Rev. B* **29**, 2884–2890, DOI: [10.1103/PhysRevB.29.2884](https://doi.org/10.1103/PhysRevB.29.2884) (1984).