Guest host interaction and low energy host structure dynamics in tin clathrates

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The two binary clathrates with vacancies (\(\mathcal{C}\)) Rb\(_2\)Sn\(_{44}\)), and Cs\(_8\)Sn\(_{44}\), have been examined using powder inelastic neutron scattering (INS). Rattling energies of Rb and Cs are found to be similar by both experiment and calculations, \(\hbar \omega_{\text{Rb}}/\hbar \omega_{\text{Rb}}|_{\text{calc}} = 0.98(1)\) and \(\hbar \omega_{\text{Cs}}/\hbar \omega_{\text{Rb}}|_{\text{calc}} = 1.0\), despite the significant mass difference: \(m_{\text{Rb}}/m_{\text{Cs}} = 1.6\), which shows that guest-host interaction is non-negligible for the studied system. For Rb\(_2\)Sn\(_{44}\)), a low energy phonon mode is observed at \(\approx 3.5\) meV, below the phonon mode which in the literature is attributed to the guest atom. The 3.5 meV mode is interpreted to have significant spectral weight of Sn host atoms based on temperature dependence and comparison with published theoretical phonon calculations. The record of low thermal conductivity of the tin clathrates can be attributed to the host structure dynamics rather than the guest atom rattling. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4793081]

I. INTRODUCTION

A large part of all consumed energy is wasted as heat. Recovering a fraction of this energy would contribute significantly to the reduction of overall energy consumption. Thermoelectrics are ideal for this task, owing to their scalability, reliability, and wide temperature range of application.

Thermoelectric materials are evaluated on the figure of merit, \(zT = TS^2/\kappa\), where \(T\) is the absolute temperature, \(S\) is the Seebeck coefficient, \(\sigma\) and \(\kappa\) are the electrical and thermal conductivities, respectively. Larger \(zT\) corresponds to better energy efficiency, and one way to improve \(zT\) is by reducing \(\kappa\). Both electrons and phonons in the crystal lattice contribute to the conduction of heat and \(\kappa\) is commonly split into two components, \(\kappa = \kappa_e + \kappa_l\).

The use of nanograins to reduce lattice thermal conductivity has resulted in significant improvements in \(zT\), but the long-term stability of nanoparticles is still a largely unresolved problem. To circumvent this problem, thermoelectric materials with intrinsically low lattice thermal conductivity are of great interest. To a large extent, such materials depend on heavy elements such as Pb, Te, and Bi to achieve low \(\kappa_l\). The extended use of heavy elements poses both environmental and economic problems; hence mechanisms independent of atomic mass and grain boundaries are greatly desired.

Type I clathrates have experienced a surge in interest within recent years due to their promising thermoelectric properties especially caused by a very low thermal conductivity (\(\kappa < 2\) W/Km). The basic formula for type I clathrates is \(A_x Y_{x} M_{46-x}\), where \(M = Si, Ge, Sn; Y = Al, Ga, In, Ni, Cu, Zn, Au, vacancy (\(\square\)), etc; and \(A\) is an alkaline or alkaline earth metal. The \(M\) and \(Y\) atoms form the host structure consisting of nano cages confining the guest atoms, \(A\). The guest atoms have large atomic displacement parameters (ADP) and have, therefore, been termed “rattlers.” The guest atoms interact with the phonon dispersion of the host structure, causing decrease in phonon velocity over a range in the low energy regime, which is critical to the conduction of heat. Furthermore, the guest atom will increase the number of high momentum phonon states at low energy. Phonon states with momentum \(k_1\) and \(k_2\) that fulfil \(k_1 + k_2 > K/2\), where \(K\) is a reciprocal lattice vector, can scatter in umklapp processes. Thus by decreasing the energy of high momentum states, umklapp processes will become appreciable at lower temperature.

The large primitive unit cell of the clathrates will in itself reduce heat conductance as a result of phonon branches splitting at the zone boundary.

Clathrates of Si, Ge, and Sn have significantly lower thermal conductivity than their diamond phase counterparts. It is noteworthy that high temperature lattice thermal conductivity of the diamond phase is very dependent on atomic mass. The clathrate compounds, however, seem largely independent of host structure atomic mass and no clear trend emerges by comparing literature values: \(n\)-type Ba\(_9\)Ga\(_{16}\)Ge\(_{30}\): 1.3 W/mK at 300 K, \(1.4\) W/mK at 250 K, \(p\)-type Ba\(_9\)Ga\(_{16}\)Ge\(_{30}\): 1.1 W/mK at 250 K, Ba\(_8\)Ga\(_{16}\)Si\(_{30}\):
II. EXPERIMENTAL DETAILS

A. Inelastic neutron scattering

The preparation of the samples used in the presented paper has been described by Kaltzoglou et al.\textsuperscript{21} Samples were characterized with powder X-ray diffraction to confirm phase purity. The INS experiments on powder samples of Rb\textsubscript{8}Sn\textsubscript{44}\textsubscript{44} and Cs\textsubscript{8}Sn\textsubscript{44}\textsubscript{44} were performed on an empty sample holder and a vanadium standard to account for background and detector efficiency. The collected data were initially treated using the program IDA.\textsuperscript{24}

B. Theoretical calculations

The low energy rattler mode was modelled using density functional theory (DFT) as implemented in VASP.\textsuperscript{25,26} Calculations were performed using the PBE functional\textsuperscript{27} and PAW potentials\textsuperscript{28,29} with a plane wave energy cut off of 315 eV on a 3\times3\times3 k-mesh. The experimental structure was used for calculations (space group Ia\overline{3}d) without relaxing lattice parameters and atomic positions.\textsuperscript{21} Occupancy of the 24c site was reduced from 0.33 to 0 to form the hypothetical Rb\textsubscript{8}Sn\textsubscript{44}\textsubscript{44}, A = Cs, Rb phase which is disorder free.

III. RESULTS AND DISCUSSION

The neutron-weighted generalized phonon density of states (GDOS) has been calculated from the measured scattering function $S(h\omega,Q)$, Figure 2, within the one-phonon, incoherent approximation,

$$ G(h\omega) = \frac{C}{A} \int_{Q_{\text{min}}}^{Q_{\text{max}}} \frac{\partial}{\partial Q} S(h\omega,Q,T) \times n(h\omega,T)^{-1} dQ. $$

$n(h\omega,T)$ is the Bose-Einstein (BE) factor which accounts for thermal population of the phonon states at energy $h\omega$ and temperature $T$. $S(h\omega,Q,T)$ is integrated from the smallest measured momentum transfer $Q_{\text{min}}$ to the maximal $Q_{\text{max}}$.\textsuperscript{31}
and then normalized to the integration area $\Delta Q = Q_{\text{max}} - Q_{\text{min}}$. $C$ is a scale factor which has not been determined for the reported data.\cite{30,31} Although the measured $Q$-space samples more than 30 symmetry inequivalent Brillouin zones, the incoherent approximation is not well fulfilled as the main contribution to the dynamical scattering function comes from only a few Brillouin zones: (530), (321), (532), and (431), indexed according to high temperature structure. However, the strict fulfilment of the incoherent approximation is only important when comparing GDOS directly to calculations.

The GDOS for both compounds shows a low energy feature below 5 meV, Figures 3(a) and 3(c), which is typical for the clathrates described in literature.\cite{6,7,32} The literature assignment of modes is used, i.e., the peak at 4-5 meV is dominated by contributions from the rattling guest atoms and it is referred to as the “guest mode,” though also host structure atoms will be contributing. High energy peaks (>6 meV) are predominantly attributed to host structure vibrations.\cite{11,33,34} Peak positions are determined from the dynamic structure factor $S(h\omega, T = 298\text{ K})$ obtained by averaging $S(h\omega, Q, T)$ over the accessible momentum-space, Figures 3(b) and 3(d). The temperature dependence of dynamic structure factor of all experiments has been rescaled to $T = 298\text{ K}$ to ensure comparability between datasets obtained at different temperatures, $S(h\omega, T = 298\text{ K}) = S(h\omega, T) \cdot n(h\omega, 298\text{ K})/n(h\omega, T)$, where $n(h\omega, T) = (\exp\left(\frac{h\omega}{kT}\right) - 1)^{-1}$ is the BE-factor. We choose to fit the $S(h\omega)$ and not the GDOS because features at low energies are thereby enhanced. Each region has been fitted using 1-3 Gaussians with a linear contribution as indicated in Figures 3(b) and 3(d). The number of Gaussians was chosen to best reproduce the peak shape. Each peak is the projection of multiple 3D phonon branches into 1D, so no direct physical meaning can be extracted from the number of Gaussians; the aim is to get reliable peak profile to extract accurate peak positions. The extracted peak position is the global maximum of the fitted function. Results are presented in Figure 4.

The dynamic structure factor shows no visible change upon crossing the structural phase transition around 360 K. The guest mode, Figures 3(b) and 3(d), is significantly broader than the instrumental resolution and appears wider than observed for other clathrates.\cite{32,36} Instrument resolution of the elastic line is 0.24 meV (measured). The energy resolution ($\Delta E$) at different non-zero energy transfers has been calculated based on Unruh et al.,\cite{33} $\Delta E(4\text{ meV}) = 0.37\text{ meV}$ and $\Delta E(10\text{ meV}) = 0.63\text{ meV}$. The width of all fitted peaks exceeds the instrumental resolution. The broad experimental peak shape indicates contributions from several or highly dispersive modes in addition to the contribution from finite phonon lifetimes and instrumental effects.

The temperature dependence of phonon modes gives information about the anharmonicity of the atomic potentials. As a result of thermal expansion phonon energies are generally expected to decrease (soften) in response to heating.\cite{7} Such behaviour is observed for the host structure peak at $\approx 6.4\text{ meV}$ and $9\text{ meV}$ Figures 4(b) and 4(c). In contrast, the phonon energy of the guest mode peak at $\approx 4.5\text{ meV}$ increases in response to heating (hardens), Figure 4(a). Hardening is a characteristic property of phonon modes which have large guest atom contributions and is observed in several guest-host systems.\cite{7,35,36} The unusual temperature dependence is indicative of a U-shaped potential of an atom confined inside an oversized nano cage\cite{80} which is an intermediate between a harmonic potential with no T dependence and an infinite well potential. In the present study, we intend to use the temperature dependence of phonon modes as an experimental indicator to whether guest or host atoms are the dominant contributor to phonon modes in a guest-host system. The degree of anharmonicity of the guest atom potentials is estimated from the slope of linear fits (Figure 4(a): Rb$_8$Sn$_{4\text{d4}2\text{c}}$: $16(6) \cdot 10^{-3}\text{meV/K}$, Cs$_8$Sn$_{4\text{d4}2\text{c}}$: $12(1) \cdot 10^{-4}\text{meV/K}$). Both slopes are larger than obtained for n/p-Ba$_{16}$Ga$_{16}$Ge$_{30}$, but half the value obtained for Sr$_8$Ga$_{16}$Ge$_{30}$.\cite{35} For the host structure peaks, see Figure 4(b), the anharmonic effect is smaller and the slopes are Rb$_8$Sn$_{4\text{d4}2\text{c}}$: $-10(2) \cdot 10^{-4}\text{meV/K}$, Cs$_8$Sn$_{4\text{d4}2\text{c}}$: $-4(1) \cdot 10^{-4}\text{meV/K}$. The anharmonic terms in the atomic potentials are important for the thermal conductivity as they facilitate phonon-phonon scattering;\cite{12} however, no clear connection has been made between anharmonicity of the guest mode and thermal conductivity of the metal clathrates.\cite{7}

![Graph](image-url)

**FIG. 3.** Generalized phonon densities of states (GDOS) for Rb$_8$Sn$_{4\text{d4}2\text{c}}$ (a) and Cs$_8$Sn$_{4\text{d4}2\text{c}}$ (c) at 298 K plotted together with Raman data corrected for Bose-Einstein statistics. Raman data from Shimizu et al.\cite{35} Dynamic structure factor $S(h\omega)$ of Rb$_8$Sn$_{4\text{d4}2\text{c}}$ (b) and Cs$_8$Sn$_{4\text{d4}2\text{c}}$ (d) rescaled to 298 K for comparison. Full black lines are fits to data. Individual Gaussians are shown as dashed red lines. Dashed black lines indicate the extracted peak maxima.
Assuming identical spring constants, and were obtained. A spring constant ratio of \( \frac{K_{\text{Cs}}}{K_{\text{Rb}}} = 1.57 \) was found, giving a ratio between the vibrational energies of \( \frac{\hbar \omega_{\text{Cs}}}{\hbar \omega_{\text{Rb}}} \rangle_{\text{Calc.}} = 1.00 \), close to the observed value. The actual calculated vibrational energies were found to be around 4.9 meV. The higher values compared to the experimental findings can be attributed to the simplicity of the model.

Making the assumption that \( K \propto \langle V_{\text{guest}} / V_{\text{cage}} \rangle \) gives an expected spring constant ratio of \( \frac{K_{\text{Cs}}}{K_{\text{Rb}}} = 1.47 \). The guest atom volume \( V_{\text{guest}} \) was calculated from the Pauling ionic radii of Cs\(^+\) (169 pm) and Rb\(^+\) (148 pm). This spring constant ratio is comparable to the value obtained using DFT calculations.

Substituting Cs for Rb has a larger effect on the energy of host structure vibrations compared to the guest atom vibrations. The host mode energy for Cs\(_8\)Sn\(_{44}\) is on average increased by 0.22(3) meV compared to Rb\(_8\)Sn\(_{44}\). The larger size of Cs acts to stiffen the host structure, causing an overall energy increase of host structure vibrational energies.

The scattering function, \( S(\hbar \omega, Q) \) of Rb\(_8\)Sn\(_{44}\), Figure 2, exhibits a faint flat mode around \( \approx 3.5 \text{ meV} \) which is below the energy assigned to the rattling guest atom, >4 meV. To verify the presence of a low energy phonon mode below the guest rattling mode, the scattering function was integrated in steps of 0.3 \( \text{Å}^{-1} \) for both compounds, Figure 6. For Rb\(_8\)Sn\(_{44}\) at 373 K a low energy peak is clearly separated from the “guest” peak over a large range \( (Q = 2.2–3.4 \text{ Å}^{-1}) \), but at 298 K the two peaks appear to merge. For Cs\(_8\)Sn\(_{44}\) a peak at 3.5 meV can only be separated at \( Q = 3.1 \text{ Å}^{-1} \). Counting statistics is significantly lower for Cs\(_8\)Sn\(_{44}\) due to smaller sample amount compared to Rb\(_8\)Sn\(_{44}\). The inferior data quality makes fewer details visible. The background signal from the empty sample holder and cryostat has been integrated and plotted in Figures 6(e) and 6(f). There are no strong features in the background below 10 meV, therefore the peak at \( \approx 3.5 \text{ meV} \) originates from sample.

Integrating the scattering function over the interval: \( Q = 2.3–2.55 \text{ Å}^{-1} \) corresponding to the Brillouin zone boundary between the strongest reflections gave the maximal
contrast between neighbouring phonon modes. For Rb$_{8}$Sn$_{44}$w$_{2}$, the low energy mode at $\approx 3.5$ meV is resolved both below (298 K) and above (373 K) the structural phase transition, Figure 7. In Cs$_{8}$Sn$_{44}$w$_{2}$ no low energy phonon mode can be separated from the guest mode. Fitted peak positions for Rb$_{8}$Sn$_{44}$w$_{2}$ data are given in Figure 8. It is striking that the peak at $\approx 3.5$ meV softens upon heating like the host structure-peak (6.5 meV), while in contrast to the hardening guest peak (4 meV). The similar temperature dependence of the peaks at 3.5 meV and 6.5 meV is interpreted as a testament to their common origin, i.e., the peak at 3.5 meV has dominant spectral weight of host structure atoms. Similar low-energy host modes are usually not observed theoretically nor experimentally for germanium or silicon type I clathrates.$^{6,7,11,32-34,42}$ In a single study of Ba$_{8}$Zn$_{8}$Ge$_{38}$, a weak shoulder to the guest mode has been observed toward lower energy; however, the authors do not comment on its origin.$^{36}$

The possible effect of a structural transition must be addressed as data are compared above and below a structural phase transition. The primitive unit cell of the low temperature phase (Ia$\overline{3}$d) is expanded 4-fold compared to the high temperature phase (Pm$\overline{3}$n). Consequently the (primitive) Brillouin zone volume is reduced, causing a back-folding and possibly splitting of phonon branches. The phonon dispersion of the A$_8$Sn$_{44}$w$_{2}$ low temperature phase is expected
The calculations do not comment on it, the energies of host modes obtained by fitting transverse acoustic branches flattening at the zone boundary at 3.5 meV and adopts a sinusoidal dispersion we estimate a maximal transverse phonon speed of $3.2 \times 10^3$ m/s in the [100]-direction.

The phonon dispersion of the skutterudite CeOs$_8$Sb$_{12}$ has been studied using triple axis neutron scattering. The measured phonon dispersion shows no signs of a rattling mode interacting with the acoustical branches. This can be interpreted as the acoustic branches not to reaching the guest mode energy owing to heavy framework atoms.

Phonon-dispersions of the type II clathrates $A_3Ga_8Si_{128}$, $A = Cs, Rb$ have been calculated by ab initio methods. The type I and II clathrates are closely related in the sense that both contain loosely bonded guest atoms in similarly sized cages. Despite the higher mass of Cs, these calculations show Cs to have the highest rattler energy. The authors explain this by increased interaction between Cs and the host structure caused by the larger guest atom size. These calculations corroborate the trends of our experimental and theoretical calculations; however, any direct comparison is not possible due to the structural differences. Though Myles et al. do not comment on it, the energies of host modes in $Cs_8Ga_8Si_{128}$ are slightly increased, compared to $Rb_8Ga_8Si_{128}$. Although this effect is small and only visible at high energy, it is in good agreement with our findings, Figure 4(b).

Both $Rb_8Sn_{44\square2}$ and $Cs_8Sn_{44\square2}$ have been investigated using Raman scattering. Low energy modes are observed in the energy range 3-5 meV. Raman scattering observes only phonon modes at the Brillouin zone centre which fulfill specific selection rules. Comparison with Raman data would be ideal to establish whether the low energy modes in the present case are originating from the zone centre or zone boundary. Observation at the zone centre would point to optic modes with guest atom character, whereas no Raman signal would be observed if the signal was originating from the acoustic phonons going flat at the zone boundary. However, the data quality of the Raman data is insufficient at low energy to resolve the modes clearly and make decisive conclusions. The most distinct peaks in the Raman spectrum are observed at 6.6, 9, and 20 meV, which is in agreement with our data, Figures 3(a) and 3(c).

The type I clathrate $Cs_8Ga_8Sn_{38}$ has been investigated by Raman scattering and theoretical phonon calculations. Authors conclude that the low energy Raman active modes below 5 meV are caused by Cs rattling. However, their calculations for guest free Sn$_{46}$ show transverse acoustic phonon branches to reach the zone boundary in the range 2.5–3.75 meV which is below the guest rattling modes.

Based on multi-temperature INS measurements and comparison to theoretical calculations of Tse et al., we interpret the peak at 3.5 meV to be the transverse acoustic branch reaching the Brillouin zone border below the guest mode energy. According to the “avoided crossing” model lowering of the room temperature thermal conductivity of clathrates happens through hybridization of the guest

![Diagram](Image)
 rattling modes with the host structure acoustic phonon branches. In the case of Sn clathrates, the transverse acoustic branch is merely indirectly affected by the presence of guest atoms, owing to its intrinsically low energy. Only the longitudinal branch has sufficiently high energy to possibly hybridize with the guest mode. Due to the lack of interaction, the guest atoms will have less effect in the reduction of the phonon velocity. The guest atom will create high momentum phonon states (with low group velocity) at low energy as needed for low temperature umklapp processes; however, our results suggest that such states are intrinsically present in the hypothetical guest-free tin clathrates, like calculated by Myles et al.. Therefore, the relative effect of guest atoms will be small compared to silicon and germanium clathrates where such low energy states are not present in the empty clathrate. The similar thermal conductivities for Rb$_2$Sn$_{44}$(C$_3$) and Cs$_8$Sn$_{44}$(C$_3$) are attributed to these intrinsic low energy phonon states, which reduce the effect of guest atom substitution. To achieve interaction between rattling modes and all acoustic branches, the guest atom must, as demonstrated, not only be heavier, but also have smaller volume. Alternatively the cages confining the guest atoms must be even bigger. These consideration are contained within the expression: $h \omega_{\text{Guest}} \propto \sqrt{V_{\text{Guest}}} / (m_{\text{Guest}} \cdot V_{\text{Cage}})$, which was used to approximate the ratio of rattling energies. In the case of A$_x$Ga$_{1-x}$Ge$_3$, A = Eu, Ba, Sr compared by Bentien et al., the thermal conductivity of Eu$_6$Ga$_{16}$Ge$_9$ is the lowest of the three compounds. This is in accordance with the Eu guest atom being both smaller and heavier than Ba and Sr.

### IV. CONCLUSION

A low energy phonon mode at $\approx 3.5$ meV is observed for Rb$_2$Sn$_{44}$(C$_3$) and the temperature dependence indicates that it has significant spectral weight Sn host atoms in agreement with theoretical calculations. The lowest energy mode in the tin clathrates is, therefore, not related to the rattling of the guest atoms, but due to the intrinsically low energies of the host structure phonon branches. The guest mode does not hybridize with transverse acoustic modes, thus the guest atom effect is reduced with regard to lowering the thermal conductivity.

The guest rattling energies of Rb$_2$Sn$_{44}$(C$_3$) and Cs$_8$Sn$_{44}$(C$_3$) are by both experiment and theory found to be almost identical despite the large mass difference: $h \omega_{\text{C}1} / h \omega_{\text{R}90} |_{\text{Exp.}} = 0.98(1) \text{ and } h \omega_{\text{C}1} / h \omega_{\text{R}90} |_{\text{Calc.}} = 1.0$. To achieve maximal effect on thermal conductivity, heavy guest atoms must be combined with large cages. The similar room temperature thermal conductivity of Rb$_2$Sn$_{44}$(C$_3$) and Cs$_8$Sn$_{44}$(C$_3$) is explained by the similar rattler energies and lack of interaction with transverse acoustic phonons.

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10. In literature the term, “rattler” has been loosely defined and some ambiguity surrounds its use (Refs. 4, 11, and 40). In the present paper we use the term “rattler” for guest atoms exhibiting excessive thermal motion vibrating at low energy.