Lattice thermal transport in La$_3$Cu$_3$X$_4$ compounds (X=P,As,Sb,Bi): Interplay of anharmonicity and scattering phase space

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Phys. Rev. B 95, 224306 — Published 30 June 2017

DOI: 10.1103/PhysRevB.95.224306
Lattice thermal transport in La$_3$Cu$_3$X$_4$ (X = P, As, Sb, Bi) compounds: Interplay of anharmonicity and scattering phase space

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(Dated: June 5, 2017)

Abstract

Thermal conductivity of La$_3$Cu$_3$X$_4$ (X=P, As, Sb, Bi) compounds are examined using first-principles density functional theory and Boltzmann transport methods. We observe a trend of increasing lattice thermal conductivity ($\kappa_l$) with increasing atomic mass, challenging our expectations as lighter mass systems typically have larger sound speeds and weaker intrinsic scattering. In particular, we find that La$_3$Cu$_3$P$_4$ has the lowest $\kappa_l$ despite having larger sound speed and the most restricted available phase space for phonon-phonon scattering, an important criterion for estimating and comparing $\kappa_l$ among like systems. The origin of this unusual behavior lies in the strength of the individual anharmonic phonon scattering matrix elements, which are much larger in La$_3$Cu$_3$P$_4$ than in the heavier La$_3$Cu$_3$Bi$_4$ system. Our finding provides insights into the interplay of harmonic and anharmonic properties of complex, low thermal conductivity compounds, of potential use for thermoelectric and thermal barrier coating applications.
I. INTRODUCTION

At the heart of efficient thermoelectric device design lies the identification and manipulation of a material with low lattice thermal conductivity ($\kappa_l$), large thermopower and high electrical conductivity [1-3]. Generally low $\kappa_l$ is observed in compounds composed of heavy elements with complicated crystal structures [4,5]. In this regard the rare earth based homologous compounds La$_3$Cu$_3$X$_4$ (X = P, As, Sb Bi) with large and complex unit cells (40 atoms) may be a promising class of materials for such applications. Among these La$_3$Cu$_3$Sb$_4$ and La$_3$Cu$_3$Bi$_4$ are experimentally known [6-9], and La$_3$Cu$_3$Sb$_4$ has been described as a degenerate $p$-type semiconductor with high electrical conductivity, moderate thermopower ($\sim 150 \ \mu V/K$), and $\kappa_l$ of 2.5 W/m-K at room temperature [6-9]. La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$As$_4$ have not been realized experimentally, however, our recent work [10] in crystal structure prediction and thermodynamic stability analysis demonstrates that these are likely to be formed in the space group $I-43d$, same as La$_3$Cu$_3$Sb$_4$ and La$_3$Cu$_3$Bi$_4$.

Even in isoelectronic, homologous compounds interesting variations in the landscape of $\kappa_l$ can be obtained simply from variance of the masses of the constituent elements, as these are a key feature in determining vibrational properties. Variation of constituent element masses alters the phonon dispersion and thereby the group velocities. Also it changes the phonon lifetimes via modulation of available scattering due to energy and momentum conservation conditions. Thus mass variance can be an effective tool to manipulate $\kappa_l$, and has been employed to engineer thermal transport in a variety of thermoelectric materials [1,11-14]. Here, we use a first principles phonon Boltzmann equation (PBE) method to examine and compare vibrational properties and $\kappa_l$ of La$_3$Cu$_3$P$_4$, La$_3$Cu$_3$As$_4$, La$_3$Cu$_3$Sb$_4$ and La$_3$Cu$_3$Bi$_4$.

Despite having the smallest average mass La$_3$Cu$_3$P$_4$ exhibits the lowest $\kappa_l$ of this series of compounds. The origin of this atypical behavior is rooted in the complex interplay of vibrational features: atomic masses, phonon velocities, scattering phase space and anharmonicity, components that determine $\kappa_l$. Often these are examined individually to understand the dominant properties governing transport. However, considering each factor individually in the La$_3$Cu$_3$X$_4$ systems does not give a clear picture of the conductivity trends, in fact comparing individual trends leads to contradictory findings. In particular, we find an unusual interplay of individual scattering matrix elements and overall scattering phase space giving strongly opposite trends in determining $\kappa_l$ of these systems, the latter increasing $\kappa_l$ and the former decreasing $\kappa_l$ in going from La$_3$Cu$_3$P$_4$ to La$_3$Cu$_3$Bi$_4$. 
Here we provide quantitative, physical insights into the correlation of vibrational properties that determine $\kappa_l$ of the La$_3$Cu$_3$X$_4$ systems to provide a more fundamental understanding of lattice transport in these and other complex unit cell materials, elucidating avenues for engineering thermal transport in large unit cell systems. Section II briefly discusses the theoretical methods employed. Section III presents thermal conductivity results and discussion of these related to basic vibrational properties. Section IV provides a summary of this work.

**II. THEORETICAL METHODS**

The lattice thermal conductivities were calculated by solving the PBE using an iterative method [15] with interatomic forces from density functional theory (DFT). For the cubic systems considered here $\kappa_l$ is a scalar quantity given by:

$$\kappa_l = \kappa_l^{\alpha\alpha} = \frac{1}{NV} \sum_\lambda C_\lambda v_\lambda^{\alpha} v_\lambda^{\alpha} \tau_\lambda$$  \hspace{1cm} (1)

where $\lambda$ denotes a phonon mode in branch $p$ with wavevector $q$, $v_\lambda$ is the phonon group velocity, $C_\lambda$ is the specific heat, $\tau_\lambda$ is the lifetime with an applied temperature gradient in the $\alpha$th direction, $N$ is the number of $q$ points uniformly sampled in the Brillouin zone, and $V$ is the volume of the unit cell. $1/\tau_\lambda$ is given by the sum of all possible transition probabilities for mode $\lambda$ with modes $\lambda'$ and $\lambda''$ [16]:

$$\Gamma_{\lambda\lambda'}^{\pm} = \frac{\hbar}{8N_0} \left\{ n_\lambda^0 - n_{\lambda''}^0 \right\} |\Phi_{\lambda\lambda'}^{\pm}|^2 \frac{\delta(\omega_\lambda \pm \omega_{\lambda'} - \omega_{\lambda''})}{\omega_\lambda \omega_{\lambda'} \omega_{\lambda''}}$$  \hspace{1cm} (2)

that satisfy momentum and energy conversation [17]. $N_0$ is the number of unit cells in the crystal; $\omega_\lambda$ is the angular frequency corresponding to the $\lambda$th mode, the ± corresponds to phonon absorption and emission processes, and $|\Phi_{\lambda\lambda'}^{\pm}|^2$ are the scattering matrix elements given by:

$$\Phi_{\lambda\lambda'}^{\pm} = \sum_k \sum_{l'k'} \sum_{l''k''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0k, lk', l''k'') \frac{e^{i\mathbf{q}\cdot\mathbf{R}_l} e^{i\mathbf{q}'\cdot\mathbf{R}_{l'}} e^{i\mathbf{q''}\cdot\mathbf{R}_{l''}}}{\sqrt{M_k M_{k'} M_{k''}}}$$  \hspace{1cm} (3)

with $e^{i\mathbf{q}\cdot\mathbf{R}_l}$ the $\alpha$th component of an eigenvector, $M_k$ the atomic mass of the $k$th atom, and $\Phi_{\alpha\beta\gamma}(0k, lk', l''k'')$ the anharmonic IFCs. Diagonalization of the dynamical matrix gives the phonon frequencies $\omega_\lambda$ and eigenvectors.

Harmonic IFCs, were obtained using the finite displacement method with the
Phonopy [18,19] package using $2 \times 2 \times 2$ supercells and $3 \times 3 \times 3$ k-point grids. The effect of supercell sizes on the phonon frequencies was investigated by using $2 \times 2 \times 2$ (160 atoms), and $3 \times 3 \times 3$ (540 atoms) supercells for La$_3$Cu$_3$Bi$_4$. The phonon dispersion was found to be nearly identical for both the cases, ensuring well converged phonon frequencies for $2 \times 2 \times 2$ supercell. Anharmonic IFCs were calculated using $2 \times 2 \times 2$ supercells and Γ-point only calculations. Interactions were considered out to third-nearest neighbors of the unit cell atoms for anharmonic IFCs. DFT calculations employed the projector augmented wave (PAW) method [20] as implemented in the Vienna ab initio simulation package (VASP) [20-22] with the generalized gradient approximation according to Perdew, Burke, and Ernzerhof [23]. Eleven valence electrons for La ($5s^25p^65d^16s^2$), 11 for Cu ($3d^{10}4s^1$), 5 for P ($3s^23p^3$), 5 for As ($4s^24p^3$), 5 for Sb ($5s^25p^3$), and 5 for Bi ($6s^26p^3$) were used in the PAW potentials. For accurate phonon frequencies, a high energy cutoff of 600 eV and strict energy convergence criterion of $10^{-8}$ eV were used. The ShengBTE [24-26] package was employed to iteratively solve the PBE. Within ShengBTE a Gaussian function is used to approximate the Dirac delta distribution which arises from the conservation of energy for each scattering process. The convergence of room temperature $\kappa_l$ as function of q-point integration grid at various Gaussian widths (marked as SB) is shown in Appendix Figure 10 for La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$Bi$_4$. The remaining two systems exhibit similar convergence behavior. For well converged $\kappa_l$ values, a q-grid of $25 \times 25 \times 25$ and a Gaussian smearing parameter of 0.5 was used. All calculations are performed using fully relaxed crystal structures with optimized lattice parameters. Relaxed crystal structures and calculated IFCs can be found in Supplementary Material [27].

III. RESULTS AND DISCUSSION

Figure 1(a) gives calculated $\kappa_l$ versus temperature for La$_3$Cu$_3$P$_4$ (pink diamonds), La$_3$Cu$_3$As$_4$ (green circles), La$_3$Cu$_3$Sb$_4$ (red squares) and La$_3$Cu$_3$Bi$_4$ (blue triangles). Each material demonstrates the typical $\kappa_l$~1/T behavior, characteristic of intrinsic three-phonon scattering resistance. We find that phonon-isotope scattering [28,29] is insignificant in all systems for the temperatures considered 100K<T<1000K, at most reducing $\kappa_l$ by 2% at 100K. For example $\kappa_l$ of isotopically pure (natural) La$_3$Cu$_3$Sb$_4$ is found to be 8.67 W/m-K (8.50 W/m-K) at 100 K and 2.6 W/m-K (2.58 W/m-K) at 300 K. Measured data for $\kappa_l$ is only available for polycrystalline La$_3$Cu$_3$Sb$_4$ [7] and is given by black x’s. Calculated and measured $\kappa_l$ values seem to approach each other at the highest measured temperatures. However, the measured $\kappa_l$ versus T behavior does not give the typical trend dictated by Umklapp resistance and the $\kappa_l$ values at the lowest temperatures are significantly suppressed. Likely extrinsic scattering
mechanisms such as grain boundaries present in polycrystalline samples are causing this discrepancy and the nearly flat temperature behavior of $\kappa_l$.

Figure 1. (a) Calculated $\kappa_l$ versus temperature for La$_3$Cu$_3$P$_4$ (pink diamonds), La$_3$Cu$_3$As$_4$ (green circles), La$_3$Cu$_3$Sb$_4$ (red squares) and La$_3$Cu$_3$Bi$_4$ (blue triangles). Measured $\kappa_l$ values (black ×’s) are given for La$_3$Cu$_3$Sb$_4$ [7]. (b) Cumulative thermal conductivity scaled by the total $\kappa_l$ for each system as a function of frequency at 300K. The inset in (a) represents the crystal structure of these compounds.

Over the entire temperature range, $\kappa_l$ is minimum for the lightest material, La$_3$Cu$_3$P$_4$, followed by La$_3$Cu$_3$As$_4$, La$_3$Cu$_3$Bi$_4$ and La$_3$Cu$_3$Sb$_4$ in increasing order of conductivity. In particular, we find $\kappa_l$ of La$_3$Cu$_3$P$_4$ is 1.31 W/m-K at 300 K, similar to that of the prototypical thermoelectric material Bi$_2$Te$_3$ [30,31] and nearly 2.5 times lower than that of heavier La$_3$Cu$_3$Bi$_4$. This is surprising as it is expected that lower mass materials should have larger $\kappa_l$. Based partly on the work of Leibfried and Schlömann [32], and in the context of high $\kappa_l$ materials, Slack outlined four crystal properties that govern $\kappa_l$ [4,33]: (i) average atomic mass, (ii) interatomic bonding (iii) crystal structure and (iv) anharmonicity. More specifically, large mass materials with weak bonding have lower frequency phonons, thus lower velocity heat carriers. This is often characterized by the Debye temperature $\Theta_D$ (defined in the Appendix) which gives a measure of properties (i) and (ii) and is correlated with $C_\lambda$ and $v_\lambda$ in Eq. 1. $M_{avg}$ and $\Theta_D$ for the La$_3$Cu$_3$X$_4$ are given in Table I along with the Debye velocity $v_{D-3} = \frac{2}{3} v_{TA}^{-3} + \frac{1}{3} v_{LA}^{-3}$, which gives a measure of the sound speed of these systems. $v_{LA}$ and $v_{TA}$...
are the longitudinal (LA) and transverse (TA) acoustic velocities near the zone center along the \( \Gamma \rightarrow N \) direction. Also given in Table I are the average specific heats \( C \) (defined in the Appendix) of the four compounds which show negligible variation, \( \sim1.4\% \). None of these harmonic parameters, alone or combined, predict the first principles \( \kappa_l \) ordering of these systems: 
\[
\kappa_{\text{La}_3\text{Cu}_3\text{P}_4} < \kappa_{\text{La}_3\text{Cu}_3\text{As}_4} < \kappa_{\text{La}_3\text{Cu}_3\text{Bi}_4} < \kappa_{\text{La}_3\text{Cu}_3\text{Sb}_4}\ 
\]
Thus, the anharmonic scattering of phonons in these systems must play a significant role in determining the \( \kappa_l \) behavior, whether by amount of scattering (phase space determined by conservation conditions) or by strength of each scattering process (anharmonic matrix elements - often measured by Grüneisen parameters).

### Table I. Average atomic mass \( (M_{\text{avg}}) \), average Grüneisen parameter \( (\gamma) \), Debye temperature \( (\Theta_D) \), room temperature specific heat \( (C) \) and calculated room temperature \( \kappa_l \) for each system. Definitions for \( \gamma, \Theta_D \) and \( C \) can be found in the Appendix.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( M_{\text{avg}} ) (amu)</th>
<th>( \gamma )</th>
<th>( v_D ) (m/s)</th>
<th>( \Theta_D ) (K)</th>
<th>( C ) (J/K.mol)</th>
<th>( \kappa_l ) (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_3\text{Cu}_3\text{P}_4 )</td>
<td>73.1</td>
<td>2.25</td>
<td>2700</td>
<td>298</td>
<td>488.2</td>
<td>1.31</td>
</tr>
<tr>
<td>( \text{La}_3\text{Cu}_3\text{As}_4 )</td>
<td>90.7</td>
<td>1.81</td>
<td>2709</td>
<td>292</td>
<td>492.5</td>
<td>1.69</td>
</tr>
<tr>
<td>( \text{La}_3\text{Cu}_3\text{Sb}_4 )</td>
<td>109.4</td>
<td>1.03</td>
<td>2791</td>
<td>287</td>
<td>493.7</td>
<td>3.35</td>
</tr>
<tr>
<td>( \text{La}_3\text{Cu}_3\text{Bi}_4 )</td>
<td>144.3</td>
<td>1.15</td>
<td>2291</td>
<td>234</td>
<td>495.0</td>
<td>2.60</td>
</tr>
</tbody>
</table>

To gain further insights into the complicated combination of competing parameters that determine \( \kappa_l \) we first examine which modes provide the dominant conductivity. Figure 1(b) gives the accumulative lattice thermal conductivity (\( \kappa_{\text{accum}} \)) as a function of phonon frequency and scaled by the total \( \kappa_l \) for each system at 300 K. \( \kappa_{\text{accum}} \) gives the summed contribution from all modes below the specified frequency. For \( \text{La}_3\text{Cu}_3\text{P}_4, \text{La}_3\text{Cu}_3\text{As}_4 \) and \( \text{La}_3\text{Cu}_3\text{Bi}_4 \) phonons with frequency below \( \sim3\)THz transport more than 80\% of the heat, while for \( \text{La}_3\text{Cu}_3\text{Sb}_4 \) this is a bit less as some higher frequency modes within the optic spectrum are also contributing. Regardless, since the majority of the phonon transport is due to lower frequency acoustic phonons we restrict our subsequent discussions to the 0-3THz frequency window. Also, to further simplify discussions we compare only the lightest (\( \text{La}_3\text{Cu}_3\text{P}_4 \)) and heaviest (\( \text{La}_3\text{Cu}_3\text{Bi}_4 \)) systems in subsequent figures. Similar figures for \( \text{La}_3\text{Cu}_3\text{As}_4 \) and \( \text{La}_3\text{Cu}_3\text{Sb}_4 \) can be found in the Appendix.

Figures 2 (a) and (b) give the calculated low frequency phonon dispersions for \( \text{La}_3\text{Cu}_3\text{P}_4 \) and \( \text{La}_3\text{Cu}_3\text{Bi}_4 \), respectively. Phonon dispersions of \( \text{La}_3\text{Cu}_3\text{As}_4 \) and
La$_3$Cu$_3$Sb$_4$ compounds can be found in Figure 6 of the Appendix. A general feature in both systems is significant mixing of the longitudinal acoustic (LA) branch with low-frequency optic branches. We note that optic phonons provide scattering channels for heat-carrying acoustic modes. Despite having very similar crystal structure there are striking differences in the phonon dispersions of these materials. Most noticeable are the “avoided crossings” of the LA branch of La$_3$Cu$_3$P$_4$ with the low-lying optic branches, behavior not seen in La$_3$Cu$_3$Bi$_4$. This is particularly noticeable along the Γ-N direction (see insets). As discussed in previous studies, avoided crossings are a manifestation of strong acoustic-optic coupling and have been argued to give lower $\kappa_l$ in other systems [34-39]. Enhanced matrix elements have been correlated with these avoided crossing features in clathrates [39] and Fe$_2$Ge$_3$ [37]. Again, this anharmonicity can be characterized by mode Grüneisen parameters ($\gamma_\alpha$) [13,36,40]. As shown in Figure 8(b) of the Appendix La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$As$_4$ have larger $\gamma_\alpha$ over the entire frequency range, and their values peak in the frequency range of the avoided crossings in these systems.

![Figure 2](image)

Figure 2. Calculated phonon dispersions for (a) La$_3$Cu$_3$P$_4$ and (b) La$_3$Cu$_3$Bi$_4$. The insets represent the enlargements of the red squares.

To elucidate the dispersion differences further, Figures 3 (a) and (b) give the partial phonon density of states (PDOS) of each atom type in La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$Bi$_4$, respectively. Figure 7 in the Appendix compares the PDOS of La$_3$Cu$_3$As$_4$ and La$_3$Cu$_3$Sb$_4$. Typically, low frequency acoustic phonons are governed by the heaviest atoms; while the highest frequency optical phonons are governed by the lighter atoms. Indeed, we see that the heaviest atoms in La$_3$Cu$_3$P$_4$...
(La atoms) and La\textsubscript{3}Cu\textsubscript{3}Bi\textsubscript{4} (Bi atoms) provide the dominant character to the acoustic modes in each system. From the point of view of the acoustic phonons La\textsubscript{3}Cu\textsubscript{3}P\textsubscript{4} and La\textsubscript{3}Cu\textsubscript{3}Bi\textsubscript{4} are very different systems as the La and Bi atoms sit at different lattice sites in the crystal structure. This may be a contributing factor in the varying LA optic crossing behaviors, and ultimately varying thermal conductivities.

**Figure 3.** Calculated partial density of states (PDOS) for (a) La\textsubscript{3}Cu\textsubscript{3}P\textsubscript{4} and (b) La\textsubscript{3}Cu\textsubscript{3}Bi\textsubscript{4}. Despite having similar crystal structure the PDOS of each system displays significantly different features.

The key missing feature not yet fully addressed is the anharmonicity, property (iv) discussed above. This governs the strength of phonon-phonon interactions through Eqns. 2 and 3, and ultimately determines the overall intrinsic thermal resistance - larger anharmonicity gives smaller phonon lifetimes. **Figure 4** shows the calculated intrinsic three-phonon scattering rates, $1/\tau_\lambda$, at 300 K for the heat-carrying acoustic modes of La\textsubscript{3}Cu\textsubscript{3}P\textsubscript{4} (pink diamonds) and La\textsubscript{3}Cu\textsubscript{3}Bi\textsubscript{4} (blue triangles). **Figure 8 (a)** of the Appendix gives the scattering rates for all systems. La\textsubscript{3}Cu\textsubscript{3}P\textsubscript{4} has the largest scattering rates for nearly all of the modes, especially at higher frequencies. The thermal resistance from these larger rates more than compensate the larger group velocities in La\textsubscript{3}Cu\textsubscript{3}P\textsubscript{4} thus giving lower overall $\kappa_l$ than the other systems.

Often anharmonicity is measured by average ($\gamma$) or mode ($\gamma_\lambda$) Grüneisen
parameters (defined in the Appendix). Table I gives the calculated $\gamma$ for each system, and follows the $\kappa_l$ trend from first principles calculations. This is surprising as $\gamma$ does not incorporate the complicated interplay of details in Eqn. 2: (i) anharmonic coupling strength, (ii) delta functions and (iii) phonon frequencies (directly and indirectly through the T-dependent Bose factors). In particular, a key missing feature is the microscopic structure of the “phase space” available for phonon-phonon scattering as limited by fundamental momentum and energy conservation conditions. Recently this scattering availability has emerged as a useful tool for understanding thermal transport in different classes of materials [41-46]. We note that phonon lifetimes and $\kappa_l$ typically vary inversely with the available phase space [47].

![Image](https://example.com/image.png)

**Figure 4.** Calculated anharmonic scattering rates as a function of frequency for La$_3$Cu$_3$P$_4$ (pink diamonds) and (b) La$_3$Cu$_3$Bi$_4$ (blue triangles).

**Figure 5(a)** gives the weighted scattering phase space (number of processes allowed by conservation conditions) for La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$Bi$_4$. This is defined as the sum of possible three-phonon scatterings given conservation of energy and momentum weighted by the frequency factors in Eq. 2:

$$W_{\lambda}^{\pm} = \frac{1}{2N} \sum_{q,q'} \left\{ \frac{n_{\lambda'}^{0} - n_{\lambda''}^{0}}{n_{\lambda'}^{0} + n_{\lambda''}^{0} + 1} \right\} \frac{\delta(\omega_{\lambda} \pm \omega_{\lambda'} - \omega_{\lambda''})}{\omega_{\lambda} \omega_{\lambda'} \omega_{\lambda''}}$$  \hspace{1cm} (4)
As the overall frequency scales of the La$_3$Cu$_3$X$_4$ systems are similar, particularly in the important lower frequency region, these frequency terms are likely not a significant factor driving phonon lifetime differences. Significantly more scattering is available for La$_3$Cu$_3$Bi$_4$, however, it has much smaller scattering rates (Figure 4) and larger $\kappa_l$. This is surprising as previous work has shown that the phase space is a robust indicator of $\kappa_l$ trends among similar simple systems [24,35,39,41,44,47-50]. Thus, we find that all of the harmonic properties and tools for understanding $\kappa_l$ (velocities, $M_{avg}$, $\Theta_D$ and scattering phase space) fail to describe the $\kappa_l$ trend in the La$_3$Cu$_3$X$_4$ systems.

Figure 5: (a) Weighted phase space as a function of frequency for La$_3$Cu$_3$P$_4$ (pink diamonds) and La$_3$Cu$_3$Bi$_4$ (blue triangles). (b) Calculated average matrix elements $|\Phi_{\alpha\alpha'}|$, from Eq. 3 as a function of frequency for La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$Bi$_4$, same symbols. Note that the $|\Phi_{\alpha\alpha'}|^2$ for La$_3$Cu$_3$P$_4$ are much larger, thus overpowering the effects of it having a lower scattering phase space.

The only microscopic feature left to explore is the collection of individual transition matrix elements ($|\Phi_{\alpha\alpha'}|^2$) appearing in Eq. 2 and defined in Eq. 3. Figure 5(b) gives the average matrix elements calculated for each mode as a function of frequency for La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$Bi$_4$. These are averaged over thousands of transitions and can vary over many orders of magnitude dependent on the details of the interactions. As clearly shown in Figure 5(b), the matrix elements of La$_3$Cu$_3$P$_4$ are more than an order of magnitude stronger than those of La$_3$Cu$_3$Bi$_4$ over the entire frequency range. In fact, this difference is so large that the scattering rates in La$_3$Cu$_3$P$_4$ are significantly larger than in the other systems despite having the smallest available phase space: a smaller number of scattering
channels are providing more thermal resistance. Thus, La₃Cu₃P₄ has the smallest calculated \( \kappa_l \) despite harmonic features that would indicate that it should have the largest, corroborating the trend given by \( \gamma \) in Table I. We note that artificially adjusting the P atom mass to match that of Bi in the La₃Cu₃P₄ matrix elements accounts for only a small fraction of the differences of these terms with those of La₃Cu₃Bi₄. As seen in Eq. 3, \( |\Phi_{\lambda\lambda'\lambda''}|^2 \) terms are a complicated combination of masses, anharmonic IFCs, phase factors and eigenvectors. On comparing anharmonic IFCs we find that some La₃Cu₃P₄ terms are significantly larger than those in La₃Cu₃Bi₄, while others are significantly smaller. On average the La₃Cu₃P₄ anharmonic IFCs are ~16% larger, not enough to account for the matrix element differences shown in Figure 5(b). To test this further we recalculated \( \kappa_l \) of La₃Cu₃P₄ but with the anharmonic IFCs of La₃Cu₃Bi₄. This results in only ~5% increase in \( \kappa_l \), indicating that the magnitudes of the anharmonic IFCs are not driving the \( \kappa_l \) differences. However, the combination of La₃Cu₃P₄ harmonic IFCs with either anharmonic IFC set gives large scattering matrix elements. We again note that the heavy atoms that govern the heat-carrying acoustic vibrations sit at different symmetry sites on the crystal lattice. It is possible that this too plays a role in the varying magnitudes of the \( |\Phi_{\lambda\lambda'\lambda''}|^2 \) terms of these materials.

As shown in our recent work, these compounds are semiconducting with the bandgap in the range of 0.23 eV (for La₃Cu₃Bi₄) to 0.87 eV (La₃Cu₃P₄), which makes them interesting for potential thermoelectric applications [10]. All the compounds studied here exhibit large thermopower in the range of 180-250 \( \mu \text{V/K} \), even at room temperature. The high thermopower together with calculated low thermal conductivity gives rise to a large figure of merit. In particular a Figure of merit of 1.5 was calculated theoretically for La₃Cu₃P₄ and La₃Cu₃As₄ under \( p \)-type doping. The detailed analysis of thermoelectric properties can be found in reference [10].

IV. SUMMARY AND CONCLUSIONS

To summarize, we have employed first principles phonon Boltzmann transport simulations to calculate vibrational and transport properties of complex unit cell La₃Cu₃X₄ systems (X=P, As, Sb, Bi). All systems have low \( \kappa_l \) (1.31W/m-K for La₃Cu₃P₄ and <4W/m-K for the other systems at room temperature) due to structural complexity and strong anharmonicity. These values are comparable to prominent thermoelectric materials such as PbTe and Bi₂Te₃. Despite having the lightest average atomic mass, La₃Cu₃P₄ has the lowest \( \kappa_l \) of the series. All harmonic properties, including average mass, specific heat, Debye temperature and phonon velocities, suggest that La₃Cu₃P₄ should have the highest \( \kappa_l \). Even the
phase space for three-phonon scattering (an important tool for understanding phonon lifetimes) does not explain the thermal transport trends in these systems. We find that the anharmonic coupling elements from individual transition probabilities tend to be much stronger in La$_3$Cu$_3$P$_4$, giving strong thermal resistance despite having fewer scattering channels. This anharmonicity is also characterized by Grüneisen parameters and is correlated with observed avoided crossings of acoustic and optic branches in La$_3$Cu$_3$P$_4$ and La$_3$Cu$_3$As$_4$. The anharmonic coupling elements in combination with competing harmonic effects determine the overall $\kappa_t$ trends in the La$_3$Cu$_3$X$_4$ systems. This work highlights the important role of anharmonicity and the complex interplay with harmonic vibrational features in determining thermal transport properties in complex systems important for thermoelectric and thermal barrier coating applications.

ACKNOWLEDGMENTS

This work is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division.
The Debye temperature ($\Theta_D$) can be determined by [51]:

$$\Theta_D = \frac{\hbar}{k_B} v_D^3 \sqrt{\frac{6\pi^2 N_0}{V}} \quad (5)$$

where $N_0$ is the number of atoms, $V$ is the crystal volume and $v_D$ is the Debye velocity given by $v_D^{-3} = \frac{2}{3} v_{TA}^{-3} + \frac{1}{3} v_{LA}^{-3}$. $v_{LA}$ and $v_{TA}$ are the longitudinal and transverse sound velocities near the zone center along the $\Gamma - N$ direction.

The average Grüneisen parameter is defined as [52]:

$$\gamma = \frac{\sum_\lambda \gamma_\lambda \left| \gamma_\lambda \right|}{\sum_\lambda C_\lambda} \quad (6)$$

where $\gamma_\lambda$ are mode Grüneisen parameters given by [53,54]:

$$\gamma_\lambda = -\frac{1}{6\omega_\lambda^2} \sum_{k,l,k',l',l''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0k,l'k',l''k'') \left( \frac{e_{\alpha l}^* e_{\beta l}^*}{\sqrt{m_k m_{l'}}} e_{l''l'} R_l r_{l''l'} k'' \gamma \right) \quad (7)$$

where $lk$ denotes the $k^{th}$ atom in the $l^{th}$ unit cell, $e_{\alpha l}^*$ is the $\alpha^{th}$ component of the phonon eigenvector, $R_l$ is the lattice vector of $l^{th}$ unit cell, $r_{l''l'}$ is the $\alpha^{th}$ component of the vector locating the $k^{th}$ atom in the $l^{th}$ unit cell, and $\Phi_{\alpha\beta\gamma}(0k,l'k',l''k'')$ are the third order IFCs.

The volume normalized mode specific heat is computed as:

$$C_\lambda = \frac{\hbar \omega_\lambda (\partial n_\lambda^0/\partial T)}{V} \quad (8)$$

where $n_\lambda^0$ is the equilibrium Bose distribution, $\omega_\lambda$ is the phonon frequency in mode $\lambda$ and $V$ is the crystal volume.
Figure 6: Calculated low frequency phonon dispersions for (a) La$_3$Cu$_3$As$_4$, and (b) La$_3$Cu$_3$Sb$_4$. The insets represent the enlargements of the red circles.

Figure 7: Calculated phonon density of states (PDOS) per formula unit for (a) La$_3$Cu$_3$As$_4$, and (b) La$_3$Cu$_3$Sb$_4$. Despite similar crystal structures, the PDOS have significantly different features.
Figure 8: Calculated (a) anharmonic scattering rates and (b) mode Grüneisen parameters ($\gamma_\lambda$) as a function of frequency for $\text{La}_3\text{Cu}_3\text{P}_4$ (pink diamonds), $\text{La}_3\text{Cu}_3\text{As}_4$ (green circles), $\text{La}_3\text{Cu}_3\text{Sb}_4$ (red squares) and $\text{La}_3\text{Cu}_3\text{Bi}_4$ (blue triangles).
Figure 9: Calculated weighted phase space as a function of frequency for La$_3$Cu$_3$P$_4$ (pink diamonds), La$_3$Cu$_3$As$_4$ (green circles), La$_3$Cu$_3$Sb$_4$ (red squares), and La$_3$Cu$_3$Bi$_4$ (blue triangles).

Figure 10: Convergence of room temperature $\kappa_l$ for La$_3$Cu$_3$Bi$_4$ (solid lines) and La$_3$Cu$_3$P$_4$ (dotted lines) as a function of q-point grid at various Gaussian widths (shown by SB). $\kappa_l$ is well converged for q-point integration grid of 25×25×25 and Gaussian width (SB) of 0.5.