Mapping Thermoelectric Transport in a Multicomponent Alloy Space

Ramya Gurunathan,* Suchismita Sarker, Christopher K. H. Borg, James Saal, Logan Ward, Apurva Mehta,* and G. Jeffrey Snyder*

1. Introduction

High entropy alloy systems with multiple principal elements are considered attractive for thermoelectric materials because the mass and strain fluctuations introduced into the lattice can effectively scatter phonons and suppress the lattice thermal conductivity. Additionally, the multicomponent alloy space comprises a largely uncharted compositional territory for thermoelectric materials. Several recent reviews discuss the potential benefits of these multinary alloys to thermoelectric performance given their potential for unique, entropy-enabled characteristics.[1–3] For example, in addition to the substantial lattice distortions mentioned previously, entropy-stabilization also favors high crystal symmetry, which can lead to high electronic band degeneracy, and regions of extended solubility, which can facilitate doping.

Some recent experimental investigations of multinary alloys have given way to highly alloyed phases which substantially out-perform end-member compounds. Androulakis et al.[4] demonstrated that the large lattice mismatch and strain effects in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te}-\text{PbS} \) alloys lead to the formation of phase boundaries with nanoscale separation that scatter phonons and produce an over 70% reduction in lattice thermal conductivity relative to \( \text{PbTe} \). In other instances, large electronic bandstructure changes in the multinary alloy space can produce peaks in thermoelectric performance, resulting, for example, from the convergence of electronic bands or opening of a band gap.[5,6]
However, both charge carriers and heat-carrying phonons are known to experience scattering due to alloying effects. Analytic alloy scattering models, which predict how transport properties will vary with alloy composition, have been established both for carrier mobility as well as lattice thermal conductivity (κL) on the basis of a virtual crystal approximation (VCA) perturbation theory.[8–10] If the end-member transport properties are well-established, these simple, physics-based expressions have been shown to capture the alloy effects on thermal and charge transport in numerous materials systems. However, these methods have thus far been applied only to binary alloy systems, often using the Makowski and Glicksman[9] expression for alloy scattering of charge carriers and the Klemens model for alloy scattering of phonons.[10,12] Here, we show a multi-component extension to these VCA-based approaches, allowing us to predict both the carrier mobility and lattice thermal conductivity across the full compositional range of high dimensional alloys, combining 3 or more end-member compounds. For thermoelectric systems, the electronic transport coefficient σE0 best captures the trade-offs between electrical conductivity, Seebeck coefficient, and the electronic thermal conductivity in thermoelectric performance. So, we additionally focus on how alloy mobility effects modify the σE0 coefficient.

The multicomponent alloy scattering strength for phonon and charge carrier transport parallels the functional form used to compute the excess Gibbs free energy (GΔ), which closely relates to the enthalpy of mixing, in solid solutions. Two common techniques, the Redlich–Kister polynomial and Muggianu geometric method, are used to calculate the GΔ for high-dimensional alloys in sub-regular solution model, where the interaction energies between components may vary with composition of the alloy.[13,14] In the context of scattering, these methods allow one to treat scattering potentials that vary along the compositional range of the alloy, which can occur when the lattice properties of the end-members differ considerably. By borrowing these thermodynamic expressions, one can extrapolate more complex scattering profiles to the high-dimensional alloy space.

From our multicomponent lattice thermal conductivity model, we find that the κL is lowest along the binary system with the largest mass contrast such that adding additional alloying elements is not necessarily beneficial from the standpoint of alloy scattering. Therefore, the only way to reduce the κL when entering a multinary alloy space is to rely on introducing a scattering mechanism that acts orthogonally or independently of mass defect scattering such as dislocation strain or boundary scattering.

Our analysis approach is applied here to predict the thermoelectric performance across the full compositional range of several pseudo-ternary half-Heusler alloys: (Ti, Zr, Hf) NiSn, (Ti, Zr, Hf)CoSb, (V, Nb, Ta)FeSb, and (V, Nb, Ta)CoSn. We additionally compare our predictions to the experimental datasets and studies is only suitable when the measured samples are confirmed to be optimally doped. In contrast, the material quality factor B is a doping-independent parameter that is correlated to the peak zT achievable in a material, if the carrier concentration is optimized. The quality factor B has the form

$$B = \left( \frac{\sigma_0}{\kappa_L} \right)^2 \frac{\sigma_{E0}}{\kappa_L} T \tag{1}$$

where σE0, the electronic transport coefficient, is closely related to the drift mobility weighted by the density-of-states effective mass, also referred to as the weighted mobility. In this study, we focus on B as a metric for thermoelectric performance. The following sections will discuss alloy scattering models for κL and σE0, emphasizing the generalization to multiple alloying elements.

2. Methods and Theoretical Background

The efficiency of a thermoelectric device is related to the material properties through the figure-of-merit \(zT = S^2\sigma(\kappa_L + \kappa_s)\), where S is the Seebeck coefficient, \(\sigma\) is the electrical conductivity, and \(\kappa_L\) and \(\kappa_s\) are the electronic and lattice components of the thermal conductivity, respectively. Each constituent of the zT equation depends independently on doping level, such that the overall zT tends to be maximized at an optimal carrier concentration. Therefore, comparing zT values across different datasets and studies is only suitable when the measured samples are confirmed to be optimally doped. In contrast, the material quality factor B is a doping-independent parameter that is correlated to the peak zT achievable in a material, if the carrier concentration is optimized. The quality factor B has the form

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2.1. Klemens Alloy Thermal Conductivity Model

The alloy scattering model used here for thermal conductivity is the Klemens/Callaway model, which derives a point defect scattering strength \(\Gamma\) based on the atomic mass and atomic radius differences between defect and host atoms. The basis of this model is the virtual crystal approximation, in which the true, defective lattice is compared to a reference, periodic lattice with the configurationally averaged atomic mass \((\langle M \rangle_h)\) and radius \((\langle R \rangle)\) at each lattice site. The later work by Tamura[18] emphasized the importance of sublattice-specific models when working with a multivalent lattice (i.e., multiple atoms in the primitive unit cell). For each sublattice, the atomic mass and radius variance should be calculated when considering the population of atoms that can occupy that sublattice, including the host and any substitutional atoms. We will first focus on quantifying the mass variance scattering, as the radius variance can be treated analogously. First, the average mass variance on the nth sublattice is defined as

$$\langle \Delta M^2 \rangle = \sum_i \langle x_i (M_i - \langle M_i \rangle) \rangle^2 \tag{2}$$

where \(i\) indexes all species that can occupy the sublattice, \(M_i\) is the species mass, and \(\langle M_i \rangle\) is the average mass on the nth sublattice.

A final stoichiometric average over all sublattices (indicated by \(\langle \rangle\) in the formula unit must then be performed to get an aggregate value for the scattering strength due to mass contrast, or \(\Gamma_M\). Finally, this averaged mass variance parameter is normalized by the average atomic mass in the entire system \(\langle M \rangle_h\).

$$\Gamma_M = \left( \frac{\langle \Delta M^2 \rangle}{\langle \Delta M^2 \rangle_h} \right) = \sum_i d_i \frac{\langle \Delta M^2 \rangle}{\sum_i d_i \langle \Delta M^2 \rangle_h} \tag{3}$$
Here, \( d_B \) is the degeneracy or stoichiometric ratio of each sublattice in the formula unit. For the example compound \( \text{Ti}_2\text{FeSb} \), the sublattices are the Ti, Fe, and Sb sites with degeneracies of 2, 1, and 1, respectively.

The total phonon scattering strength \( \Gamma_{ph} \) value is simply the sum of the mass and radius (or strain) scattering parameters. This yields the following expression for \( \Gamma_{ph} \) for a generic multi-atom lattice, containing an arbitrary number of point defects on each sublattice.

\[
\Gamma_{ph} = \Gamma_M + \Gamma_R = \frac{\langle \Delta M^2 \rangle}{M^2} + \frac{\langle \Delta R^2 \rangle}{R^2} + \varepsilon
\]

(4)

The \( \varepsilon \) parameter is known as the strain scattering parameter, and its value depends on the anharmonic coefficient \( \gamma \) (i.e., the Grüneisen parameter) as well as elastic properties such as the Poisson ratio of the host lattice. In practice, it is difficult to quantitatively estimate the influence of point defect strain on interatomic force constants, and \( \varepsilon \) is instead fit to \( \kappa \) measurements along binary alloy systems.

Although the basis of this model is in point defect perturbations, in several materials systems, this model has shown to be predictive beyond the dilute defect limit as it has been used to describe the full compositional range of several binary alloy systems. Additionally, the expressions we show here naturally extend to higher order systems in which multiple alloying elements can substitute on various sublattices in the system, as the procedure for calculating the average mass variance remains the same.

The Klemens model then relates the scattering parameter \( \Gamma \) to the ratio of the defective thermal conductivity to that of the reference pure thermal conductivity \( \kappa_0 \). Here, \( \kappa_0 \) the speed of sound \( v_s \), and the average volume per atom \( V_0 \) interpolate between endpoint values using Vegard’s law.

\[
\frac{\kappa}{\kappa_0} = \frac{\tan^{-1} u}{u} = \left( \frac{6\pi V_0 c}{2 k_B v_s} \right) \frac{v_s}{k_0} \Gamma
\]

(5)

While the focus here is on isoelectronic alloying elements, these methods have been applied to model the phonon scattering due to aliovalent dopant atoms as well. In this case, however, increased carrier concentration can globally perturb bonding and lead to lattice softening (\( v_s \) reduction), which should be accounted for in the thermal model.

### 2.2. Electronic Transport Function \( \sigma_{00} \) and its Extension to Alloys

The electronic transport function \( \sigma_{00} \) is correlated to the maximum achievable thermoelectric power factor (Scalp) for an optimally-doped sample. The electronic transport function \( \sigma_{00} \) can be fit directly to the Seebeck coefficient \( S \) versus conductivity \( \sigma \) relation (Jonker plot), using the following relationship:

\[
\sigma_{00} = \frac{1}{1 + \exp\left[ \frac{1}{k_{B} T} \left( E + \frac{1}{2} \nu \right) \right]} + \frac{3}{\pi^2} \frac{1}{\nu \sigma_{0}^2} \left[ 1 + \exp\left( \frac{1}{k_{B} T} \left( E + \frac{1}{2} \nu \right) \right) \right]
\]

(6)

It is advisable to fit a single \( \sigma_{00} \) coefficient to a series of \( S-\sigma \) pairs, measured at various carrier concentrations. Otherwise, computing the \( \sigma_{00} \) from a the \( S-\sigma \) pair of an optimally doped sample (maximized \( S^2/\sigma \)) is also suitable.

The Bardeen–Shockley equation predicts the carrier mobility by applying deformation potential theory, which considers the effect of phonon scattering on charge carriers. By treating phonons as a source of dilatational strain, and calculating the shift in conduction band or valence band energies in response to this strain (neglecting higher order effects like the change in effective mass), the deformation potential \( \Xi \) is calculated in units of eV. The expression for \( \sigma_{00} \) based on deformation potential theory is given as

\[
\sigma_{00} = \frac{2\pi \varepsilon N_{e} e^2}{3\pi m_{e}^* \Xi}
\]

where \( E_{L} \) is the longitudinal elastic constant (often the bulk modulus is used), \( N_{e} \) is the valley degeneracy, and \( m_{e}^* \) is the inertial effective mass. Depending on whether the n-type or p-type \( \sigma_{00} \) is desired, the band properties of either the conduction or valence band are applied.

In our implementation, we assume that the end-member compounds in the alloy systems are described by Equation (7). Alloy compositions will then have additional mobility effects due to alloy scattering of charge carriers. The alloying elements will be assumed to be isovalent substitutions and therefore uncharged. Significant aloivalent alloying to modify carrier concentration would imply a scattering cross-section that depends on charge state and the dielectric permittivity of the matrix. The scattering potential, in this case, will be determined solely from changes in the lattice potential at the defect site (i.e., pure potential scattering), meaning no significant spin disorder.

Here we will invoke the virtual crystal approximation (VCA) once more, by comparing the disordered lattice to a reference, periodic lattice with the averaged lattice properties of the alloy components. The coherent potential approximation (CPA) is also frequently applied to this problem, and involves self-consistently determining the self-energy of electronic states in an alloy to determine their scattering rates. In the limit of small perturbations (low defect concentration or low site energy change), the CPA also reduces down to the VCA. It is common to evaluate the CPA correction to virtual crystal band energies, and if it is determined to be small, the VCA is appropriate to use for determining alloy scattering rates.

Unlike the previous section on phonon–point-defect scattering (Section 2.1), in which the variance in atomic mass and radius defined the scattering strength, the lattice quantity defining the scattering strength in this case is \( U \), the on-site potential in a tight-binding representation. The carrier lifetime associated with alloy scattering is related to the average variance in \( U \), the density of site defects \( n_{d} \), and the 3D electronic density of states \( g(e) \).

\[
\tau_{alloy}^{-1} = \frac{2\pi}{h} n_{d} V_{0} (\Delta U)^{2} g(e)
\]

(8)

The practical definition of \( U \) has been a source of discrepancy. The original work of Makowski and Glicksman on III–IV zinc-blende compounds used the bandgap to define \( U \), while subsequent work by Harrison and Hauser defined \( U \) as the electron
affinity, or the conduction band edge position relative to the vacuum level. However, neither definition has shown a very robust correspondence to binary alloy data, and so, in practice, the value of $\Delta U$ between two components is fit to binary alloy mobility data.

As in the mass difference case, when the factor of $(\Delta U)^2$ is generalized to multiple defects indexed by $i$ with site fraction $x_i$ and site potential $U_i$, it can be written as the average $U$ variance compared to the virtual crystal site potential $\langle U \rangle = \sum_i x_i U_i$. Note that here we will use angular brackets $\langle \rangle$ to signify configurational averages over the component site potentials. A rearrangement of the average $U$ variance puts it into a form particularly convenient for the charge carrier alloy scattering problem since $\Delta U_{ij} = U_i - U_j$ values between two components are nearly always fit to binary alloy data. The scattering parameter for the multicomponent alloy is written as a sum over “binary” terms, involving just two components in the alloy.

$$\langle \Delta U^2 \rangle = \langle (U - \langle U \rangle)^2 \rangle = \langle U^2 \rangle - 2 \langle U \rangle \langle U \rangle + \langle U \rangle^2 = \sum_{ij} x_i x_j \Delta U_{ij}^2$$

(9)

In Wang et al., the following expression for $\sigma_{\text{el}}$ is derived by including the effects of deformation potential phonon scattering and alloy scattering, combined using Matthiessen’s rule.\[19]\] The resulting expression is then a modification of the reference pure $\sigma_{\text{el}}$ value shown in Equation (7). Note that $\sigma_{\text{el}}$ represents the properties of the virtual crystal, and is defined as the Vegard’s law interpolation between end-member values (similar to $\kappa_0$ in Equation (5)).

$$\sigma_{\text{el}} = \sigma_{\text{el}}^0 + \left( 1 + A \sum_{i \neq j} x_i x_j (\Delta U_{ij})^2 \right)$$

(10)

where $A = \frac{3}{2} \pi^2 E^2 V_n}{\Xi^2 k_B T}$

In the coefficient $A$, quantities such as the longitudinal elastic constant $E_1$ and average volume per atom $V_n$ also varying according to Vegard’s law between end-member values. Finally, to relate this problem back to the previous case on point defect scattering of phonons, let us define the electronic alloy scattering strength $\Gamma_{el}$ as

$$\Gamma_{el} = \sum_{i \neq j} x_i x_j (\Delta U_{ij})^2$$

(11)

In contrast to previous expressions presented by Makowski and Glicksman,\[7\] Harrison and Hauser,\[8\] and Mehrotra,\[9\] Equation (10) is generalizable to multiple alloying elements. We additionally note that the final form of Equation (9) is similar to those used for excess Gibbs energy calculations in a multicomponent solution.

In the following section, we present an extrapolation scheme from binary alloy data to higher order systems based on the Muggianu model. A benefit of this extrapolation scheme is that it preserves the relationship between $\sigma_{\text{el}}$ and alloy composition shown in Equation (10) even if $\Delta U_{ij}$ itself, is allowed to vary with composition, which can occur if there are significant differences in bandstructure and host lattice properties between endmembers. The compositional variation in alloy scattering potential has only been rigorously investigated via first-principles for Si$_x$Ge$_{1-x}$ alloys, where changes in $\Delta U$ with respect to $x$, determined through DFT or tight-binding bandstructures, were fit to polynomial expressions. In this particular example, only a light dependence on composition was observed such that the assumption of a uniform alloy scattering potential resulted in a good fit of mobility data.\[8,15\] In Section 3.2, we discuss a quaternary reciprocal IV–VI semiconductor system in which the composition dependence is more pronounced.

### 2.3. Redlich–Kister Polynomial and Muggianu Model for Excess Quantities

The Redlich–Kister polynomial is a simple change of variables that allows for the analytic calculation of excess Gibbs free energy ($G^E$) in a ternary, or higher order, alloy system. The method is especially useful in a subregular solution model, in which the interaction parameter ($A_{ij}$) between two components $i$ and $j$ is allowed to vary with composition. Here, we will adapt the notation and convention of Hillert.\[13,14\] The standard regular solution model for $G^E$ is shown below for constant binary interaction parameters

$$G^E = \sum_{i<j} x_i x_j A_{ij}$$

(12)

As shown, higher order systems can continue to be written in as a sum of binary terms of the form $x_i x_j A_{ij}$ within the regular solution model. However, once $A_{ij}$ is permitted to vary with composition, this relationship no longer holds true, largely because the symmetry of the problem is not maintained $1-x_1 \neq x_2$. To address this, in an example ternary composition ($x_1$, $x_2$, $x_3 = 1 - x_1 - x_3$), we define a new set of parameters using a simple change of variables: $v_{12} = (1 + x_1 - x_3)/2$ and $v_{23} = (1 + x_2 - x_3)/2$. In a binary system (where $x_1 + x_2 = 1$) these parameters reduce to simply $x_1$ and $x_2$, but they retain the relationship $v_1 + v_2 = 1$ even for higher order systems. The interaction term $A_{ij}$ can then be written as the following power series up to any arbitrary power $n$

$$A_{ij} = \sum_{i<j} {\sum_{k} C_{ijkl} v_i^{n_i} v_j^{n_j}}$$

(13)

To simplify the model, while retaining the more generic form of the interaction parameter $A_{ij}$ we can apply the Muggianu method, referred to as a geometric model because it relies on the geometric construction illustrated in Figure 1.\[13,14\] Here, ternary excess quantities are computed as a weighted sum of corresponding excess quantities along the binaries. Binary alloy systems are often well-studied experimentally and so it is possible to fit descriptive alloy scattering models described by Equation (10). The Muggianu method then provides the most straightforward extrapolation into the higher order space. The Muggianu method defines high-dimensional (h.d.) excess alloy properties as

$$G^E_{\text{h.d.}} = \sum_{i<j} x_i x_j C_{ij} (v_i, v_j)$$

(14)

In thermodynamic models for $G^E$, ternary interaction terms of the form $x_i x_j A_{ijk}$, which involve three different components of the alloy, may also be used. In scattering problems, these terms would represent multiple scattering events present at clusters of defects. In our applications of the Redlich–Kister
polynomial, these ternary interaction terms are negligible. Therefore, all terms in the scattering potential contain the site fractions and lattice properties of just two components in the alloy.

Relating this expression back to the problem at hand, the working formula for the higher order extension of the electronic alloy scattering strength (Equation (11)) is

\[
\Gamma_n(x_1, x_2, \ldots, x_n) = \sum_i \sum_j \Gamma_{ij} \left( \frac{1 + x_i - x_j}{2}, \frac{1 + x_j - x_i}{2} \right)
\]

(15)

Since the point defect scattering strength for phonons \( \Gamma_{ph} \) has the same form, we can apply the Muggianu method in the same fashion. If, perhaps, the strain scattering parameter \( \varepsilon \) (see Equation (4)) describing the sensitivity of the force constants to strain varies over the alloy compositional range, the Muggianu method can be applied to perform the extrapolation to multi-component alloys. In Section 3.2, we will discuss a quaternary reciprocal IV–VI semiconductor system in which the Redlich–Kister polynomials and Muggianu extrapolation are required to adequately describe the experimental data.

**3. Results and Discussion**

**3.1. Pseudoternary Half-Heusler Alloys**

Half-Heusler compounds represent a large class of semiconducting, thermoelectric materials, which tend to be limited in their performance by relatively high \( \kappa_L \) values. As a result, alloying strategies to impede phonon transport are heavily sought after. We have investigated several pseudoternary half-Heusler systems by alloying on a single sublattice, including: (Ti, Zr, Hf)NiSn, (Ti, Zr, Hf)CoSb, (V, Nb, Ta)CoSn, and (V, Nb, Ta)FeSb (typically doped with 20% Ti). For simplicity, we will also label the alloying site as \( X \). The methods described in Section 2 were applied to map out the transport function \( \sigma_{E0} \), lattice thermal conductivity \( \kappa_L \), and thermoelectric quality factor \( B \) over the full pseudoternary compositional space. These models require that the transport coefficients, elastic properties, and electronic bandstructure properties are well-defined for the end-member compounds, and literature values are used (see Section S4, Supporting Information).

Figure 2 shows an example property mapping for the \( X\)NiSn system, and the remaining half-Heusler alloys are depicted in Figure S1, Supporting Information. Experimental \( \kappa_L \) and \( \sigma_{E0} \) scatter points obtained from the literature are overlaid for comparison and summarized in tabular format in Section S2, Supporting Information. The half-Heusler data often show large variation in \( \kappa_L \) and \( \sigma_{E0} \) measurements, which may in part be due to variation in microstructure between samples. Of note, the alloy scattering model treats solid solution mixing, while some measured pseudoternary alloys in the \( X\)NiSn and \( X\)CoSb systems have been shown to phase separate, a microstructure modification that introduces new scattering mechanisms and may lead to deviation between the model and experiment.\(^{29,30}\) Still, in Figure 2, we plot the median value for compositions measured and reported multiple times in the literature, and the scatter points follow the general trend predicted by the model.

Inspection of the \( \kappa_L \) maps for the four half-Heusler compound families shows that the lattice thermal conductivity is not, in fact, minimized in the central region of the ternary, where greater compositional disorder would be expected.
Instead, $\kappa_L$ is minimized along the pseudobinary with the greatest mass difference between components located along the right edge of each pseudoternary diagram shown. In fact, additional alloying with the intermediate mass component tends to reduce the point defect scattering effect.

These $\kappa_L$ mappings suggest that multicomponent alloying does not by necessity lead to suppressed thermal conductivity, a result corroborated by recent first-principles thermal conductivity calculations.[31–33] The (Ti, Zr, Hf)NiSn $\kappa_L$ heatmap (Figure 2b) has been presented twice before from the standpoint of ab initio density functional theory (DFT).[31,33] Notably, these DFT studies continue to make the virtual crystal approximation when evaluating the alloy phonon bandstructures, using the compositional average of the atomic masses, harmonic, and anharmonic force constants. However, in contrast to the analytic expression here, the DFT-derived density-of-states, group velocities, anharmonic coefficients, and polarization vectors enter into the $\kappa_L$ calculation. We observe excellent correspondence between our model prediction and the DFT studies, which also show the minimum thermal conductivity along the (Ti, Hf) binary. Additionally, the computational work of Caro et al. used nonequilibrium molecular dynamics and the Green–Kubo method to evaluate the thermal conductivity of Lennard–Jones alloys between fictitious elements $A$, $B$, $C$, and $D$, which are assigned distinct atomic mass, radius, and cohesive energy.[34] A benefit of this model is that it does not require any assumptions about the phonon bandstructure or the scattering mechanisms. The thermal conductivity mapping of the quaternary alloy still, however, shows the lowest $\kappa_L$ along the binary with highest mass contrast.

In each of the half-Heusler alloy systems investigated, mass difference scattering alone appeared to adequately fit the experimental data, and the fitted value for the strain parameter $\varepsilon$ was very close to 0. This low strain scattering effect is compatible with conventional understanding of formation rules for multicomponent alloys. Large atomic size differences lead to insufficiently negative enthalpy of formation values and poor miscibility.[35] Additionally, as previously observed in the work of Liu et al.,[36] the atomic radii of the period-5 and period-6 alloy elements are very similar owing to the lanthanide contraction along the periodic table. As a result, there is very low atomic radius mismatch in the (Zr, Hf) and (Nb, Ta) binary systems of the compound families treated here. Choosing alloy elements with large mass mismatch but small radius mismatch is a strategy to decouple alloy effects on $\kappa_L$ and carrier mobility $\mu$. Systems with low radius contrast show less disruption to the periodic potential and lower alloy electronic scattering strength $\Gamma_{el}$.[36] The $\sigma_{E0}$ maps of the four compound families corroborate this point, showing little evidence of alloy scattering along the bottom binary system, containing the period-5 and period-6 X-site element (see Figure S1, Supporting Information).

Despite the similarity in motif for the $\kappa_L$ heatmaps, the quality factor plots for the four pseudoternary families (Figure 2 and Figure S1, Supporting Information) show different regions of high performance materials, arising from the trade-off between thermal and electronic transport coefficients. The magnitude of the quality factor predictions are similar between the four families. The XFeSb is typically doped with large quantities of Ti and so a 20% Ti content is used in the model. This family exhibits quality factor $B$ values about a factor of 3× higher than the other systems stemming from both high $\sigma_{E0}$ and low thermal conductivity (partially due to the addition of Ti). Quality factor values are particularly high along the (Nb,Ta) FeSb pseudobinary (Figure S1a–c, Supporting Information).
3.2. Quaternary Chalcogenide System: Pb(Sn)Te(Se)

We additionally apply this alloy model to the experimental mapping of thermoelectric transport properties performed by Ortiz et al.\cite{6} of the quaternary p-type PbTe-PbSe-SnTe-SnSe system. Although several previous works have investigated the six pseudobinary systems involving all pairs of these IV–VI compounds, this study is unique in that it reports on the multicomponent alloy space. In our analysis, we exclude values in the vicinity of SnSe, which were shown in the original work to be the Pnma rather than the Fm\(_{3}\)m phase.\cite{6}

To perform the \(\kappa_L\) analysis, we first fit the Klemens alloy scattering model (Equation (5)) to each of the pseudobinaries. The fit strain scattering parameters \(\varepsilon\) vary greatly, ranging from \(\varepsilon = 1\) for the SnTe-SnSe system to \(\varepsilon = 84\) for the PbTe-SnTe system. This implies that the anharmonic and elastic properties of the lattice vary too greatly over the compositional range for a single value of \(\varepsilon\) to be suitable. Therefore, we allow \(\varepsilon\) to vary with composition according to the Redlich–Kister polynomial up to the quadratic term \(k = 2\) (see Equation (13)). In order to adequately fit the experimental data, it was important to use the Muggianu model to extrapolate the \(\Gamma_R\) from the pseudobinary to the pseudoquaternary space.

In doing so, we predict that the minimized \(\kappa_L\) occurs near the equiatomic Pb\(_{0.5}\)Sn\(_{0.5}\)Te\(_{0.5}\)Se\(_{0.5}\) composition, correlating as expected with the region of maximal compositional disorder (see Figure 3). In contrast to the previous half-Heusler examples, this \(\kappa_L\) reduction is achieved by alloying on different sublattices, in this case the cation and anion sites. The form of the Klemens model suggests that point defect substitutions on different sublattices should scatter independently such that an improvement from combining these orthogonal effects could be expected. This orthogonality emerges because each sublattice contributes very differently to the overall phonon structure, for example more massive sublattices will dominate the low-frequency range. As a result, defects on each sublattice influence a different frequency window in the overall phonon spectrum. In Section S6, Supporting Information, we illustrate the separation in scattering frequency window for the Na and Cl sublattices comprising NaCl based on the Tamura model for phonon-impurity scattering.\cite{18}

We additionally applied an alloy scattering model to the Hall mobility (\(\mu\)) data for this p-type material. Visual inspection of the experimental data, alone, suggests that bandstructure changes independent of alloy scattering are likely at play. Rather than following the expected U-shaped curve behavior predicted by Nordheim’s rule, there is a horizontal band of relatively high mobility at about 20–30% Sn content that corresponds in location to a documented band inversion along both the PbTe-SnTe \cite{37–39} and PbSe-SnSe \cite{40} binary alloy systems. In the vicinity of the band inversion, the band gap shrinks and the valence and conduction bands linearize according to a Kane dispersion model, leading to a near zero effective mass that produces the peak in hole mobility (see Figure 4d). Such bandstructure changes are not captured by the perturbation theory alloy scattering model, and by plotting the deviation between experimental and model \(\mu\), we see the effective mass change highlighted around 30% Sn content in Figure 4c.

There is also a reduction in \(\mu\) at about 50% Sn content, which is likely due to an increase in doping level near the SnTe-SnSe side of the quaternary alloy that leads to a sampling of the second, heavier-mass \(\Sigma\)-pocket valence band. The alloy scattering potential is, therefore, expected to change in the vicinity of different end-member compounds. In the alloy mobility model fit to the data along the pseudobinaries, we allow the alloy scattering potential \(\Delta U\) to vary with alloy composition as

![Figure 3. Lattice thermal conductivity heatmap in the quaternary IV–VI semiconductor system. Both the a) experimental measurements (reproduced from\cite{6}) and b) alloy model show the thermal conductivity minimized near the equiatomic Pb\(_{0.5}\)Sn\(_{0.5}\)Te\(_{0.5}\)Se\(_{0.5}\) composition. In this system, c,d) substitution on both the cation and anion site yields a peak mass and strain contrast near the center of the compositional space.](image-url)
a Redlich–Kister polynomial up to the degree \( n = 2 \) in order to adequately describe the experimental data. The Muggianu method is then applied to extrapolate from the pseudobinary to pseudoquaternary space.

### 3.3. Multicomponent Alloy Design Rules

In this section, we mainly focus on multicomponent alloy strategies to reduce \( \kappa_L \). As alluded to in Section 3.1, however, strategies to decouple the \( \kappa_L \) reduction from adverse electronic effects exist in the literature. In the context for the half-Heusler alloy systems, the large mass contrast and small radius contrast between period-5 and period-6 elements produces a sufficiently large thermal perturbation \( (\Gamma_{ph}) \) and small electronic perturbation \( (\Gamma_{el}) \). Additionally, the work of Wang et al.\[42\] demonstrated in PbSe that high carrier mobility can be maintained by alloying on sites with low contribution to the conduction (for n-type) or valence (for p-type) band edges.

For the reduction of alloy thermal conductivity, point defect perturbation theory points to scenarios in which multicomponent alloying can be beneficial over a simple binary alloy. As demonstrated in several of the pseudoternary half-Heusler alloy systems, increasing configurational entropy by forming multicomponent alloys is not always an effective strategy to reduce the thermal conductivity. In fact, introducing an alloy element of intermediate atomic mass and radius can reduce the overall mass and strain contrast scattering.

Instead, the additional alloy element being used for thermal conductivity engineering should introduce an orthogonal phonon scattering effect, that is, a scattering effect that, to first order, acts independently of the ones already at play in the lower dimensional alloy system. Within the realm of phonon–point-defect scattering, the following strategies exist (depicted in Figure 5):

1. Alloy on different sublattices of the compound (e.g., \( \text{Pb}_{1-x}\text{Sn}_x\text{Te}_{1-y}\text{Se}_y \))
2. Use separate alloy elements to introduce mass and strain contrast into the system

The first strategy is demonstrated in the quaternary chalcogenide system discussed earlier, where the cation and anion site are both alloyed. The minimum thermal conductivity occurs away from the binary alloy compositions and in the vicinity of the equiatomic \( \text{Pb}_{0.5}\text{Sn}_{0.5}\text{Te}_{0.5}\text{Se}_{0.5} \) composition. The same multi-site alloying strategy may explain the origin of the \( \kappa_L \) reduction in the recently reported high-performance PbSe-based multicomponent thermoelectric alloy.\[43\]

The latter strategy is likely more exotic, since atomic mass and size are often correlated within the same coordination environment. However, if mass and strain contrast are each maximized along different \( n \)-nary alloy systems, it is likely that entering an \( n + 1 \)-nary system will lead to a region of further...
Multicomponent alloy design strategies for reduced thermal conductivity due to point defect scattering should take advantage of orthogonal scattering effects. a) Schematic of lattice with 2-atom primitive unit cell basis (encircled by dotted line). b) Alloy elements, labeled 1 and 2, substitute on different sublattices. c) Alloy element 1 contributes significant mass contrast while alloy element 2 contributes significant strain contrast.

4. Conclusion

Multicomponent alloys formed between three or more thermoelectric compounds are an uncharted territory of high interest, primarily because of the large degrees of compositional disorder which should be effective in scattering heat-carrying phonons. Here, we show an extension of virtual crystal approximation alloy scattering models to higher order alloy systems. We show for both electronic and thermal transport that the scattering parameter $\Gamma$ can be written as a sum over “binary terms,” those which depend only on two components in the system. Their functional form mimics that of excess Gibbs free energy, allowing for an analogy to be made to computational thermodynamics literature. We are therefore able to apply the Redlich–Kister polynomial and Muggianu method to better extrapolate alloy scattering models to higher dimensions. Our modeling indicates that additional alloying and increased configurational entropy does not, by necessity, reduce the thermal conductivity. To produce a thermal conductivity reduction through multicomponent alloying, the additional alloying element should introduce an orthogonal form of scattering. Within the realm of point defect scattering, this may include combining alloy elements that occupy different sublattices or using separate alloy elements to introduce mass and strain contrast into the system. Additionally, seeking microstructure changes via alloying, through modifications of dislocation density for example, is also a viable strategy to achieve a lattice thermal conductivity reduction. Given that multicomponent alloys are currently being investigated for a wide class of energy materials, we hope that these analytic alloy models can be applied to a wide range of transport-related phenomena beyond thermoelectric research.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

alloys, charge transport, high entropy, heat transport, thermoelectric materials

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