Detailed calculation of the thermoelectric figure of merit in an $n$-doped SiGe alloy

Iorwerth O. Thomas and G. P. Srivastava

School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom

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In this study, we develop a detailed numerical approach towards the theoretical calculation of the phonon contribution to the dimensionless figure of merit $ZT$ that parameterizes the efficiency of the thermoelectric effect, and apply it to the case of an $n$-doped Si$_{0.75}$Ge$_{0.25}$ alloy sample. This is achieved by using accurate lattice dynamical eigensolutions from the application of the density functional perturbation theory, supplemented by a semiempirical approach for crystal anharmonicity. The success of the application of the theoretical method for lattice thermal conductivity, within the single-mode relaxation time scheme, in explaining available experimental data is highlighted. Using well-known phenomenological theories, based on the nearly-free electron model, for the behavior of the electronic components of $ZT$, we are then able to calculate the figure of merit over a temperature range of 300–1200 K.

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I. INTRODUCTION

The concept of conversion of electricity into heat and vice versa—the thermoelectric effect—has been considered very useful for several decades (see, e.g., Refs. 1–4). This has recently been the subject of intense theoretical and experimental interest.5,6 This interest has arisen largely since it has been shown experimentally that the efficiency of thermoelectric conversion (which is described by the figure of merit $ZT$) can be substantially increased with nanostructuring.5–7 In general, existing three-dimensional thermoelectric (TE) materials are found to exhibit high efficiency ($ZT > 0.5$) either at low temperatures (such as Bi$_2$Te$_3$, between 200–500 K) or in an intermediate temperature range (such as PbTe, between 600–900 K), or at high temperatures (such as SiGe alloys, between 800–1300 K). It has also been suggested that it may soon be possible to engineer thermoelectric structures that function optimally across a wide variety of temperatures,5 leading to obvious industrial applications.

However, in order to properly engineer nanostructured TE materials, we must understand not only how nanostructuring affects the various parameters governing thermoelectric efficiency but which parameters produce the greatest effect. At present, it seems that approaches that attempt to minimize the phonon contribution to the thermal conductivity show most promise.5,6 However, the theoretical behavior of this quantity is not currently well understood.

Over the past several decades, a large number of theoretical investigations have been undertaken in order to assess $ZT$ of semiconductor single crystals. While the electronic properties are reasonably well formulated within the nearly-free-electron model, numerical calculations that fully account for the temperature variation of that most basic of quantities, viz., the Fermi energy $E_F$, have not necessarily been made. The quantity that has remained the least well convincingly studied is the lattice contribution to thermal conductivity $\kappa_{\text{ph}}$. In this respect, four publications deserve to be mentioned. Meddins and Parrott9 do not elaborate on any specific method for evaluating the electrical conductivity $\sigma$, Seebeck coefficient $S$ and the bipolar contribution to thermal conductivity and resort to a high-temperature interpolative scheme for the calculation of $\kappa_{\text{ph}}$ for SiGe alloys. Vining’s10,11 improvements on Vining’s10 and Slack and Hussein’s12 similar treatment of the electronic parameters of the system, but performs the phonon conductivity calculations using an approach similar to that used by Vining. Slack and Hussein12 themselves use an empirical approach to the phonon conductivity. Hicks and Dresselhaus8 have attempted to explicitly include the Fermi energy $E_F$ in their formulation of $\sigma$ and $S$, but did not account for its temperature variation. Although they have discussed the effects of reducing dimensionality on the various TE coefficients, in their treatment, $\kappa_{\text{ph}}$ is considered to be no more than a temperature-independent adjustable parameter. Thus it seems reasonable to conclude that—to our knowledge—there is currently no publication that presents a systematic numerical calculation of the TE coefficients of semiconductors over a wide range of temperatures.13

In this paper, we aim to provide as complete and accurate a theoretical approach as possible to the calculation of the phonon contribution to the thermal conductivity (and hence to the calculation of $ZT$) in alloyed systems, which we hope will serve as a basis for future work performed on more complex, nanostructured systems.

In the next section of the paper, we shall outline the theoretical background of our calculation. Firstly, we discuss the behavior of the electronic components of $ZT$ using the well-known expressions based on the nearly-free-electron model for the electronic band structure. The behavior of these components is well understood in bulk materials—our
treatment of them will hence be phenomenological and a summary in nature, as it is the calculation of the contribution arising from phonons that is most challenging and which shall therefore command the majority of our attention. Next, we turn to our theoretical scheme for the computation of the lattice contribution to $ZT$, viz., the phonon conductivity. One important element in our approach that should be emphasized is that we make use of an expression for the anharmonic crystal potential that includes contributions from the optical as well as acoustic modes; this expression is defined in a semiempirical fashion, and we expect this approach to complement other, recently developed approaches such as those of Refs. 14–16. This will be discussed in more detail in the second section of the paper.

The third section details our approach for calculating the phonon eigenmodes, frequencies and velocities through the use of density functional perturbation theory (DFPT) (reviewed in Ref. 18). In the fourth section, we detail the results of our study, beginning with the results of our fitting of the electronic parameters to the experimental data, and then, turning to the focus of this paper, we initiate our discussion of the phonon-dependent aspects of the sample with an examination of the form of the dispersion relations of the model cell used in the DFPT calculations and how they are affected by bond relaxation, and a discussion of some theoretical issues surrounding the notion of a “mean-free path” and its definition within the context of the study of thermal conductivity. Lastly, we discuss the results of our calculation of the total thermal conductivity and the figure of merit $ZT$ and how they compare to the experimental results for $ZT$ of sample 7 in Meddins and Parrott, before summarizing our conclusions.

II. THEORETICAL BACKGROUND

As indicated above, a typical measure of the efficiency of thermoelectric conversion is given by the dimensionless figure of merit $ZT$, defined as follows:

$$ZT = \frac{S^2 \alpha T}{\kappa},$$

where $S$ is the Seebeck coefficient for the material, $\alpha$ is its electrical conductivity, $T$ its temperature, and $\kappa$ is its total thermal conductivity. We can treat the thermal conductivity as a sum:

$$\kappa = \kappa_{el} + \kappa_{ph},$$

where $\kappa_{el}$ is the electronic and $\kappa_{ph}$ is the phonon (lattice) contributions. Obviously, it is through the latter term that the phonon physics of the material affects the figure of merit. Following previous theoretical works, we will evaluate $\alpha, S,$ and $\kappa_{el}$ within the application of the nearly-free electron model. We present an extensive theoretical approach for calculation of the lattice thermal conductivity $\kappa_{ph}$. 

A. Electronic components of $ZT$

Firstly, we shall examine the behavior of the components of $ZT$, which are primarily electronic in nature ($S, \alpha, \kappa_{el}$), as a prelude to examining the more difficult phonon conductivity contribution $\kappa_{ph}$. Since we are more interested in the fine detail of the latter, our examination of the former is of necessity somewhat brief, being more concerned with suitable phenomenological modeling of the quantities in question as opposed to the minutiae of their physics. To this end, we shall discuss the application of our expressions to the relevant data in this section, so as not to detract from the main focus of our study.

1. Temperature variation of Fermi energy

Numerically accurate values of the Fermi energy are required at each temperature we wish to calculate the electronic transport coefficients. For the system under study, we use the following expression for the incompletely ionized, extrinsic semiconductors, but replacing the first term with one more suited to the case of strongly degenerate semiconductors:

$$E_F = \frac{(3\pi^2 N_{don})^{2/3}}{2n^2(2N_{val})^{3/2}}m_{don}^{*} + \frac{k_B T}{2} \ln \frac{N_{don}}{2A_e N_{val}} - k_B T \sinh^{-1} \left[ \frac{A_e N_{val}}{8N_{don}} e^{-(E_F-E_d)/2k_B T} \right].$$

Here, $m_{don}^{*}$ is the density-of-states effective mass and $N_{val}$ is the number of valleys in the conduction band. We define $A_e/h = 2(m_{don}^{*}/k_B T)^{3/2}$, and the quantity $N_{don}$ represents the number of donor impurities.

2. Seebeck coefficient

We adopt the nearly free electron model and use the following expression for the absolute value of the Seebeck coefficient:

$$|S| = \frac{k_B}{e} \left[ M(\alpha) - \eta_R \right],$$

$$M(\gamma) = \left( s + 2.5 \right) F_{s+3/2}(y) \left( s + 1.5 \right) F_{s+1/2}(y),$$

where $\alpha = \eta_R - (E_F/k_B T)$, $\eta_R = E_F/k_B T$ with $E_F$ being the Fermi energy, $s$ is determined by the dominant electron scattering mechanism, and we make use of the Fermi integrals

$$F_s(y) = \int \frac{x^s}{e^{x-y} + 1} dx.$$

3. Electrical conductivity

We adopt the nearly-free electron model and write the expression for the conductivity derived in Drabble and Goldsmid, generalized to the case of multiple valleys, as

$$\sigma = N_{val} e^2 \tau_0 \left( \frac{2m_{don}^{*} k_B T}{h^2} \right) \left( p + \frac{3}{2} \right) F_{p+1/2}(\alpha),$$

where $N_{val}$ is the number of energy valleys, $m_{don}^{*}$ is the conductivity effective mass, and $\tau_0$ represents the energy-independent portion of the relaxation time

$$\tau = \tau_0 (\alpha k_B T)^p.$$
with $p$ being a constant depending on the type of scattering. We have considered ionized impurity (imp) scattering, acoustic phonon (ac) scattering, and optical phonon (op) scattering as being relevant to our work. Expressions for these scattering rates from each valley are

$$
\tau_{\text{imp}}^{-1} = \frac{Z^2 e^4 N_i C}{16\pi \epsilon^2 (2m_{\text{doo}})^{1/2} k_B T} \alpha^{-3/2},
$$

$$
\tau_{\text{ac}}^{-1} = \frac{\sqrt{2} E_D^2 m_{\text{doo}}^{1/2} (k_B T)^{3/2}}{\pi h^2 \rho \omega_{\text{ph}}} \alpha^{1/2},
$$

$$
\tau_{\text{op}}^{-1} = \frac{(2m_{\text{doo}})^{1/2} L^2}{4\pi h^3 \rho \omega_{\text{op}}} [\tilde{n} + 1] \sqrt{(ak_B T - \hbar \omega_0)}
$$

(11)

In the above expressions, $m_{\text{doo}}$ is the conductivity effective mass, $\rho$ is the density of the sample, $c_L$ the speed of LA phonons, $E_D$ is an acoustic deformation potential, $\omega_{\text{ph}}$ is the frequency of the highest longitudinal optical mode, $D_{\text{ph}}$, is an optical deformation parameter, $\epsilon$ is the host dielectric constant, $Ze$ is the impurity charge, $N_i$ is the impurity concentration, and $C$ is a constant that is usually between 1.4 and 2.22 The first and second terms in the optical scattering expression are contributions from phonon emission and absorption events, respectively. From the above expressions, it is clear that the parameter $p$ takes values 3/2 for impurity scattering and -1/2 for acoustic and optical phonon scattering. The conductivity expressions, considering individual scattering mechanisms, then become

$$
\sigma_{\text{imp}} = \frac{64\sqrt{3} N_{\text{val}}^2 (m_{\text{doo}})^2}{\pi m_e^2 Z^2 e^2 N_i C} \left( \frac{k_B T}{\hbar} \right)^3 F_2(\alpha),
$$

$$
\sigma_{\text{ac}} = \frac{2N_{\text{val}}^2 \hbar \rho c_L^2}{3\pi E_D^2 m_e^*} F_0(\alpha),
$$

$$
\sigma_{\text{op}} = \begin{cases} 
\sigma_{\text{op}, \text{ab}} & E \leq \hbar \omega_0 \\
\sigma_{\text{op}, \text{ab}} + \sigma_{\text{op}, \text{em}} & E > \hbar \omega_0 
\end{cases}
$$

(14)

$$
\kappa_{\text{el}} = \frac{k_B^2}{e^2} \left[ L(\alpha) \sigma_\alpha T + L(\beta) \sigma_p T + \frac{\sigma_\alpha \sigma_p T}{\sigma} \left[ \frac{(E_c - E_v)}{k_B T} + M(\alpha) + M(\beta) \right]^2 \right],
$$

$$
L(y) = \frac{(s + 3.5)(s + 1.5) F_{s+5/2}(y) F_{s+5/2}(y)}{(s + 1.5)^2 F_{s+1/2}(y)^2},
$$

(18)

where we have defined $\beta = (E_c - k_B T) / \hbar \omega_0$.

The hole density can be written as $n_h \approx n_{\text{in}}^2 / N_{\text{dom}},$ where $n_{\text{in}} = \sqrt{A_e A_e} \exp[-(E_c - E_e)/2k_B T]$, allowing us to make use of the following simplified expression:

$$
\sigma_p = eG \exp[-(E_c - E_e)/k_B T],
$$

with $G$ treated as an adjustable parameter.

B. Phonon contribution to thermal conductivity

Here, we move the focus of our discussion to the theoretical heart of our work: the calculation of the lattice (phonon)

$$
\sigma_{\text{op}, \text{ab}} = \frac{4N_{\text{val}}^2 \rho \omega_{\text{ph}} k_B T}{3\pi D^2 \hbar m_e^*} F_0(\alpha),
$$

$$
\sigma_{\text{op}, \text{em}} = \frac{4N_{\text{val}}^2 \rho \omega_{\text{op}} k_B T}{3\pi D^2 (\tilde{n} + 1)m_e^*} F_0(\alpha).
$$

(15)

(16)

Using Matthiessen’s rule, we sum the resistivity contributions as follows:

$$
\sigma_n^{-1} = \sigma_{\text{ac}}^{-1} + \sigma_{\text{op}}^{-1} + \sigma_{\text{imp}}^{-1}.
$$

(17)

We denote the conductivity as $\sigma_n$ since it is the electronic contribution to the conductivity. For our system, and in the temperature range of interest (i.e., above 300 K), the impurity and optical phonon scattering rates are found, respectively, to be approximately four and two orders of magnitude smaller than the acoustic phonon scattering rate. We thus considered only the dominant acoustic contribution and neglected the others. We remark that there also exists a small contribution to the conductivity from holes, which we denote $\sigma_h$, and model in a simple fashion described later in this paper. This last does not significantly contribute to the overall conductivity, which is dominated by $\sigma_n$, however, it will prove important when considering the bipolar contribution to the thermal conductivity, which we discuss next.

4. Electronic and bipolar contributions to thermal conductivity

The electronic contribution to the thermal conductivity is typically taken to be $\kappa_{\text{el}} \propto \sigma_\alpha T$, with the Lorentz number $L$ being the constant of proportionality (see, for example, Refs. 19,21, and 23). However, a complication arises when we deal with the behavior of the system at high temperatures, which require an account of the effects of thermally excited holes. The thermal conductivity contributions arising from electrons and holes are not simply additive; in combination they give rise to an additional contribution known as the bipolar term, which may be quite large even if $\sigma_h/\sigma_n$ is small. Following the derivation given in Ref. 21, we may write the total electronic conductivity (including this term) as

$$
\kappa_{\text{el}} = \frac{k_B^2}{e^2} \left[ L(\alpha) \sigma_\alpha T + L(\beta) \sigma_p T + \frac{\sigma_\alpha \sigma_p T}{\sigma} \left[ \frac{(E_c - E_v)}{k_B T} + M(\alpha) + M(\beta) \right]^2 \right],
$$

where $\kappa_{\text{ph}}$ of the thermal conductivity $\kappa$. Working within the single-mode relaxation time approximation, we write the following expression for the thermal conductivity:

$$
\kappa_{\text{th}} = \frac{\hbar^2}{3V k_B T^2} \sum_{q s} c_i^2(q) \alpha^2(q) \tau(q) H_q(s) \tilde{n}_q(s \tilde{n}_q + 1)
$$

(20)

where the total volume of the system is $V = N_{\text{cell}} \Omega_0$ ($N_{\text{cell}}$ being the number of unit cells in the system and $\Omega_0$ being the volume of each unit cell), $q$ being the phonon wave vector, $s$...
is the label of the phonon branch, $c_i(q)$ is the magnitude of the velocity for a given mode $q$, $\omega(q,s)$ is the frequency, and $n_{BE}$ is the Bose-Einstein distribution at equilibrium. The total single-mode relaxation time $\tau(q,s)$ is given by

$$\tau^{-1}(q,s) = \tau^{-1}_B(q,s) + \tau^{-1}_{MD}(q,s) + \tau^{-1}_{EP}(q,s) + \tau^{-1}_{AH}(q,s), \quad (21)$$

where we have contributions from boundary scattering $\tau^{-1}_B(q,s)$, mass-defect effects $\tau^{-1}_{MD}(q,s)$, electron-phonon interactions $\tau^{-1}_{EP}$, and anharmonic phonon-phonon interactions $\tau^{-1}_{AH}$. We shall discuss the first three contributions separately from the latter.

### 1. Harmonic scattering processes

The boundary scattering of phonons is expressed as

$$\tau^{-1}_B(q,s) = \frac{c_s(q)}{L}, \quad (22)$$

where $L$ is a measure of the effective size of the crystallite microstructure in the sample studied in Ref. 9. Mass-defect scattering arises due to the perturbation in crystal potential from the difference between the average mass of the alloy and the actual mass at a given atomic site of a particular species or isotope. We use the form given in Ref. 27,

$$\tau^{-1}_{MD}(q,s) = \frac{\omega^2(q,s)\omega_s(\omega)P_{\text{Neff}}}{4\pi} \Gamma_{\text{MD}}, \quad (23)$$

where $\omega_s(\omega)$ is the phonon density of states and $P_{\text{Neff}}$ is the average mass of the species $S$, $\bar{m}$ is the average mass of the alloy, and $\Gamma_{\text{MD}}$ determines the average effect of species and isotope masses on the relaxation time. We use the formulation in Ref. 29, which incorporates both alloying and isotope effects in a relatively simple fashion, and express it for the alloy $\text{Si}_{x}\text{Ge}_{1-x}$ as

$$\Gamma_{\text{MD}} = x \left( \frac{m_S}{\bar{m}} \right)^2 \Gamma_{\text{IS}}(\text{Si}) + (1-x) \left( \frac{m_G}{\bar{m}} \right)^2 \Gamma_{\text{IS}}(\text{Ge}). \quad (24)$$

Here, $m_S$ is the average mass of the species $S$, $\bar{m}$ is the average mass of the alloy constituents, and $\Gamma_{\text{IS}}(S)$ incorporates the effects of the different isotope masses

$$\Gamma_{\text{IS}}(S) = \sum_i f_i \left( \frac{m_i - m_S}{m_S} \right)^2, \quad (25)$$

where $m_i$ is the mass of the $i$th isotope and $f_i$ its frequency. We use isotope data from Ref. 30 for Ge and from Ref. 31 for Si.

We parameterize the electron-phonon scattering through a generalization of the expression for medium-high doping used in Ref. 9:

$$\tau^{-1}_{EP}(q,s) = n_s \beta_1 |E_{\text{def}}^i|^2 \frac{\sqrt{\pi} \alpha_1 e^{-\alpha_1}}{\hbar \omega_c(q)^2}. \quad (26)$$

Here, $\rho$ is the density of the system, $\alpha_1 = m^* c_s(q,s)^2/2k_B T$ and $\beta_1 = h\omega_c(q,s)/k_B T$, and we approximate $n_s$ with $N_{\text{def}}$. $E_{\text{def}}^i$ is the deformation potential, expressed as

$$E_{\text{def}}^i = A \sum_i \hat{q} \cdot \hat{e}_{qi}. \quad (27)$$

In this expression, $\hat{e}_{qi}$ is a member of the set of $N_{\text{def}}$ eigenvectors of an acoustic phonon mode $q$, $N_{\text{def}}$ is the number of atoms in the unit cell, and $A$ is an empirically adjustable parameter that controls the strength of the deformation potential and thus determines the magnitude of the electron-phonon scattering. Since this expression is only valid for acoustic phonons, in our numerical calculations, we set it equal to zero when the frequency corresponding to a mode $(q,s)$ is greater than some cutoff value corresponding to the largest value of an acoustic frequency at the Brillouin zone boundary (in our case, this is 170 cm$^{-1}$, which is the largest value at the X point in the $z$ direction).

### 2. Anharmonic scattering processes

The calculation of the anharmonic contribution to the phonon relaxation time is far from simple. The behavior of this aspect of the system is determined by the values of the third-order force constants, whose effects can be summarized through a number of parameters such as the mode-dependent Grüneisen constants $\gamma_{\text{MD}}$, which determine the strength of the scattering for different three-phonon processes. One might think that the $ab\text{ initio}$ calculation of the third-order constants using DFPT methods such as those described in Refs. 18 and 32 or the force-displacement approach of Ref. 33 would be sufficient unto themselves, but there are a number of caveats that suggest that these approaches may be complemented by others such as the one employed in this paper.

Firstly, Lopuszyński and Majewski have shown that in the elastic limit, $ab\text{ initio}$ calculations carried out via the theory of nonlinear elasticity show that while values of $\gamma_{\text{MD}}$ for longitudinal acoustic (LA) modes are in reasonable agreement with experiment with discrepancies of around 0.9 to 10%, the difference between experimental and theoretical values of the transverse acoustic (TA) modes can be between roughly 84% to 98%. They suggest that this could be an indication that the final value of $\gamma_{\text{MD}}$ is very sensitive to numerical errors in the third-order elastic constants on which it depends. Something similar could be true in the case of $ab\text{ initio}$ calculations performed outside of elastic limit, for in their recent, state-of-the-art calculation Esfarjani, Chen, and Stokes employ the method of Ref. 33 in order to calculate force-constants $ab\text{ initio}$ and find that the values of the TA modes are again rather different from experiment due to a truncation in the number of third-order force constants used (they note that a large number are needed in order to calculate these modes correctly). While we are not presently aware of any calculations of the various $\gamma_{\text{MD}}$ for the method of Ref. 32, on the strength of the foregoing one should perhaps avoid assuming unreservedly that an $ab\text{ initio}$ DFPT calculation will exactly reproduce the values of quantities that may be very sensitive to numerical error.

A further interesting issue is the temperature dependence of the $\gamma_{\text{MD}}$ and their constituent force constants; if we examine the experimental behavior of the mode-averaged Grüneisen constant $\gamma$ in Si and Ge in Figs. 61 and 51 on p. 373 and p. 413, respectively, of Ref. 35, we can see a rather strong temperature dependence as $T$ is increased from 0 K to around 300 K, with $\gamma$ decreasing from a positive value to a negative minimum before increasing once more and finally tending towards a positive value that is not necessarily identical to the
value close to \( T = 0 \) K. This implies that the behavior of the \( \gamma_{\text{MD}} \) is also temperature dependent, something that can also be inferred from measurements of the temperature dependence of the linear expansion constants\(^3\) from which \( \gamma_{\text{MD}} \) may be derived. However, DFT and DFPT calculations are carried out at \( T = 0 \) K and do not give the behavior of the force constants as temperature is varied. Studies of the lattice heat transport in Si, Ge, and SiGe alloys\(^4\) do give experimentally compatible values for various temperature ranges (see Ref. 14 for the entirety of the \( T = 0–300 \) K range, Ref. 16 for \( T = 100–500 \) K, and Ref. 15 for \( T = 300–600 \) K), and that deviations from experiment outside of those ranges may be accounted for by additional scattering effects as discussed in Ref. 16 for their results; but these studies contain no discussion of the effects of temperature on the force constants. One exception to this is Ward and Broido’s \emph{ab initio} examination of phonon relaxation times in Si and Ge,\(^5\) where the effects of temperature on lattice properties via thermal expansion have been tested by varying the lattice constant by an amount appropriate for the temperature. They find that this gives results for the overall thermal conductivity that are within 1–2\% of the appropriate for the temperature. They make use of the third approximation (that of the elastic Debye-type approximations and accounts for the effects of anharmonic phonon-phonon scattering through the use of similar terms with \( \mathbf{q} \) interchanged) but we believe that it can provide good qualitative results nonetheless. This complexity of the anharmonic contribution to the properties of the potential problems we have raised is perhaps due to the anharmonic phonon-phonon scattering through the use of \( N \) similar terms with \( \mathbf{q} \) interchanged.

That the aforementioned calculations work so well in spite of the potential problems we have raised is perhaps due to the complexity of the anharmonic contribution to the properties of the systems of interest. Simply put, it is difficult to tell how the individual mode contributions to each allowed three-phonon scattering event sum or cancel, since there are so many, and it is possible that much of the detailed variation due to error or temperature may be counteracted by their weighting as they enter into the calculation of the relaxation time. It is hard to tell at this point; perhaps more work is needed. This complexity also renders the calculations somewhat opaque to theoretical analysis despite their accuracy, and hence there is still much need for an approach to anharmonic and similar effects that is intermediate between that of a full \emph{ab initio} approach and traditional long-wavelength limit calculations.

In future work, we intend to examine how lattice scattering is modified due to the properties of various nanostructures and, consequently, how the thermal conductivity (and therefore \( ZT \)) are affected by this modification. A full calculation would probably work against our aim of understanding the mechanisms involved since the complexity of the anharmonic contributions to systems in question might obscure the major details of the underlying mechanisms, and so we choose a semiempirical approach that employs \emph{ab initio} DFPT elements, which we hope will capture as many of these factors as possible. The price we pay is the loss of a certain amount of predictive power regarding a given system; however, the prize we gain is that it becomes relatively simple to predict the effects of changes in structure between systems and account for the mechanisms underlying them, while in addition (hopefully) attaining good qualitative estimates of the magnitude of these effects. However, to begin with, we here test our approach using as detailed a calculation of the lattice contribution to the thermal conductivity as possible for a known system where experimental results are available, not only for reasons of simple validation, but because it gives an idea of plausible semiempirical parameter ranges suitable for cases of nanostructured systems of similar composition where appropriate experimental results may not yet be available.

The approach we have chosen is developed from the concepts presented in Refs. 26, 39, and 40. In brief, we describe the anharmonic phonon-phonon scattering through the use of a continuum model to treat acoustic as well as optical phonon modes, and express the three-phonon scattering strength using the \emph{mode-averaged} Grüneisen’s constant \( \gamma \), which we treat as a semiempirical adjustable parameter that can also be made temperature dependent if desired. The relevant expression for phonon anharmonic relaxation time in this approach is

\[
\tau_{\text{AH}}^{-1}(\mathbf{q} s) = \frac{\pi \hbar \bar{\gamma}^2}{\rho V} \sum_{q', q''} \frac{\left( B_{q', q''} \right)^2}{q' + G} \delta(\omega(q) + \omega(q') + \omega(q'')) \times \left[ \frac{\bar{n}_{q'} \bar{n}_{q''} (\bar{n}_{q'} + 1)}{(\bar{n}_{q'} + 1)} \delta(\omega(q) + \omega(q')) - \omega(q'') \delta_{q + q', q + q''} + \frac{\bar{n}_{q'} \bar{n}_{q''} \bar{n}_{q'} \bar{n}_{q''}}{\bar{n}_{q'}} \delta(\omega(q)) - \omega(q'' - \omega(q'')) \bar{n}_{q + q', q + q''} \right],
\]

where

\[
B_{i, j, k} = \{ (\omega(i) + \omega(j)) | \omega(i) + \omega(j) | | \omega(k) - \omega(k)| / c(k) + \text{similar terms with } i, j, \text{and } k \text{ interchanged]}/3!,
\]

with \( \omega_{c}(k) \) being the frequency at the \( \Gamma \) point (zone center) for mode \( k \), and \( c(k) \) is the phonon speed for the branch and momentum labeled by \( k \). A zero (nonzero) reciprocal lattice vector \( G \) accounts for a Normal (an Umklapp) process and \( \bar{\gamma} \) is a mode-averaged \emph{rescaled} Grüneisen constant.

The reasoning behind this generalization is discussed in the Appendix to this paper. We observe that this approach does not make use of two of the three approximations examined in Ref. 37 as it uses complete phonon dispersions rather than Debye-type approximations and accounts for the effects of optical modes in addition to acoustic modes. It does, however, make use of the third approximation (that of the elastic continuum) but we believe that it can provide good qualitative results nonetheless.

### III. Numerical and Computational Details

#### A. Electronic parameters for sample under study

Before discussing the electronic transport coefficients \( \sigma \), \( \kappa_{\text{el}} \), and \( \kappa_{\text{ph}} \), we first note that the system of the present study, sample 7 of Meddins and Parrott’s study,\(^7\) is a sintered Si\(_0\)Ge\(_{0.246}\) \( n \)-type doped alloy with P impurities acting as donors. In their study, Meddins and Parrott determined the carrier concentration of the sample at room temperature to be \( 9.4 \times 10^{25} \text{ m}^{-3} \) (we take this value to be a reasonable approximation of \( N_{\text{don}} \) and its density to be around...
TABLE I. Parameters for the electronic contributions to $ZT$ derived from comparison with experimental data. We list the name of the parameter, its value, the measured quantity with which it is associated, the corresponding equation for that quantity, and the figures in which the theoretical behavior of that quantity is plotted alongside experimental measurements. A dagger indicates that this quantity was selected rather than directly fitted.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Quantity</th>
<th>Equation</th>
<th>Figure</th>
</tr>
</thead>
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<td>$</td>
<td>S</td>
<td>$</td>
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<td>$\sigma_n$</td>
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<td>4</td>
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<td>(32)</td>
<td>4</td>
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<td>10.5 eV</td>
<td>$\sigma_n$</td>
<td>(13)</td>
<td>4</td>
</tr>
<tr>
<td>$m_*$</td>
<td>0.45$m_e$</td>
<td>$\sigma_n$</td>
<td>(32)</td>
<td>4</td>
</tr>
<tr>
<td>$v$</td>
<td>4.0</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$m_0^*$</td>
<td>1.10$m_e$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$m_0^-$</td>
<td>0.35$m_e$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$G$</td>
<td>$3.2 \times 10^{21}$ $(\frac{E}{2})^{1/2}$ m$^{-1}$ V$^{-1}$ s$^{-1}$</td>
<td>$\kappa$</td>
<td>(2) via (18) and (19)</td>
<td>4, 10</td>
</tr>
</tbody>
</table>

2860 kg m$^{-3}$ (this is lower than might be expected through a weighted averaging of the masses of the component elements and could indicate that the sample is somewhat porous). For our calculations, we will also require the relative locations of the conduction band edge $E_c$, the donor energy level $E_d$, and the valence band edge $E_v$. Since Meddin and Parrott did not measure these values in their study, we must estimate them. We set $E_c = 0$ so that it functions as a reference energy, and take our values for the valence band edges from Fig. 8 of Ref. 41 and the donor levels from Table 9.1 on page 269 of Ref. 19. Accordingly, for Si, we take $E_d = 0.045$ eV and $E_v = E_c - 1.170 + [4.73 \times 10^{-4}/(636 + T)]^2$ eV; and for Ge, we take $E_d = 0.012$ eV and $E_v = E_c - 0.7437 + [4774 \times 10^{-4}/(235 + T)]^2$ eV. We then estimate the corresponding values for the alloy as a weighted average of the values for Si and Ge. This gives us values of $E_d = -0.037$ eV and a set of temperature dependent values for $E_v$. We take $N_{\text{Si}} = 6$, as the composition of our sample places us within the Si-like region. The value of $c_L$ is taken to be 7504 m s$^{-1}$, which is the speed of the LA mode at the $q$ point closest to $\Gamma$ in the Monkhorst-Pack grid used in our phonon calculations. Table I lists the electronic parameters used in this work.

B. Technical aspects for calculations of phonon-related quantities

Firstly, we replace Brillouin zone integration of required functions with summation over a set of momenta and associated weighting factors generated through a Monkhorst-Pack (MP) scheme. In order to avoid complication in the numerical calculation of velocities of phonons, we chose to use a shifted set of MP points (i.e., a set that does not include symmetry points in the zone). Secondly, we note that Eq. (28) includes a number of $\delta$-function terms that are difficult to evaluate numerically and must be approximated. We follow the approximations used in Refs. 39 and 40 and replace the exact momentum conservation condition with an approximation as follows:

$q + q' \pm q'' - G = 0 \rightarrow |q_{\mu} + q'_{\mu} \pm q''_{\mu} - G_{\mu}| \leq \Delta_{\mu},$

(30)

with $\Delta_{\mu}$ being the absolute value of the smallest momentum division of the MP grid in the $\mu$ direction. This replacement is required as the use of the MP grid entails that the exact condition can never be fulfilled; an approximation is needed in order to obtain nonzero values of the inverse anharmonic relaxation time. Previous calculations have shown that this procedure yields reasonable results. We use a set of 26 $G$ vectors, which produces a stable result in this case. Thirdly, we use the definition of the Dirac $\delta$ function in terms of a Gaussian function:

$\delta(y) = \lim_{\sigma \rightarrow 0} \frac{1}{\sigma \sqrt{\pi}} e^{-y^2/\sigma^2},$

(31)

where $0 \leq y \leq 0$, the energy conservation condition has been rescaled by $\omega_{\text{MAX}}$ (the largest zone-center frequency), and we choose a broadening factor $\sigma$ that is numerically appropriate (for this study, we use $\sigma = 0.5$). If $\delta(y) < 0.01$ for a given set of modes, we instead set it to zero, in order to avoid spurious contributions arising from large quantities far from the center of the Gaussian. Table II lists the parameters used in the calculations of phonon-related quantities.

C. Calculations of phonon eigensolutions and velocities

As discussed in the previous section, for numerical evaluation of $\omega_{\text{ph}}$, we require to calculate phonon frequencies [$\omega(q\vec{s})$], eigenvectors ($\vec{e}(q\vec{s})$), and velocities ($\vec{v}(q\vec{s})$). We obtained these quantities through the application of density functional theory and linear response theory [the combination known as density functional perturbation theory (DFPT)] as implemented in the routines incorporated into the QUANTUM ESPRESSO package. Norm-conserving pseudopotentials utilizing a local density approximation (LDA) to the DFT were employed in our calculations.

TABLE II. The various parameters determining the behavior of $\omega_{\text{ph}}$, their values, and the quantities and equations associated with them.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Quantity</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>0.2 $\mu$m</td>
<td>$\tau_{BD}(q\vec{s})$</td>
<td>(22)</td>
</tr>
<tr>
<td>$P$</td>
<td>400.0</td>
<td>$\tau_{MD}(q\vec{s})$</td>
<td>(23)</td>
</tr>
<tr>
<td>$A$</td>
<td>0.8 eV</td>
<td>$\tau_{EP}(q\vec{s})$</td>
<td>(26) via (27)</td>
</tr>
<tr>
<td>$\bar{\rho}$</td>
<td>0.63</td>
<td>$\tau_{AH}(q\vec{s})$</td>
<td>(28)</td>
</tr>
</tbody>
</table>
We simulated the Si$_{0.75}$Ge$_{0.25}$ crystal structure by considering the eight-atom cubic unit cell depicted in Fig. 1. We do not expect there to be any significant error arising from the slight discrepancy in alloy composition, nor from the (inevitably) ordered nature of this alloy model when comparing our results with measurements on the Si$_{0.75}$Ge$_{0.25}$ disordered alloy studied in Ref. 9. Using a cell dimension of $a = 5.48\,\text{Å}$ consistent with Vegard’s law of the weighted average (i.e. $a = 0.75a_{\text{Si}} + 0.25a_{\text{Ge}}$), we adopted shifted $4 \times 4 \times 4$, $6 \times 6 \times 6$, $8 \times 8 \times 8$, and $10 \times 10 \times 10$ Monkhorst-Pack grids with kinetic energy and density cutoffs of 15.0 and 60.0 Ry, respectively, and performed an electronic calculation while allowing the atomic coordinates in the cell to relax. DFT calculations were carried out using the equivalent unshifted grids, and from the resulting force constants we calculated the phonon eigensolutions for the original shifted grids. From these results, the thermal conductivity matrix was calculated, and $\kappa_{ph}$ was taken to be the average value of the diagonal components, neglecting the off-diagonal values as artifacts of our model. Comparisons of the thermally averaged mean-free path due to anharmonic scattering for a system with $\gamma = 0.5$ at $T = 100$, 600, and 1200 K were made in order to check convergence (see Table III). As can be seen, these results are not very promising, however, if we compare values of $\kappa_{ph}$ for various grids calculated using the parameters (see Table II) obtained through the fitting procedure used on $10 \times 10 \times 10$ results and listed in Table IV, we see a very different picture. Here, the convergence is monotonic, and is of the order of less than 30% in the worst case ($T = 1200$ K) for the finest grid, which is at the limit of our computational capacity. We suspect that this difference in behavior may be due to divergences in the value of the anharmonic mean-free path that are present at low values of $q$; these may become troublesome as finer grids (containing ever smaller $q$ values) are employed. As Ziman notes in his discussion of the divergence problem in Ref. 38, the cure is the inclusion of additional forms of scattering (usually boundary scattering); since we have (as far as we are aware) accounted for all major sources of scattering in our final calculation of $\kappa_{ph}$, this may be the reason for the improvement in convergence. The decrease in convergence as $T$ is increased is likely due to the increasingly important role that the anharmonic scattering plays at higher temperatures; however, we should note that in the region of interest its lack of convergence is still somewhat tamed by the presence of other scattering mechanisms. This also indicates that the mean-free path for anharmonic scattering should not be used alone in order to estimate convergence; the effects of other scattering processes must be taken into account.

There remains only the choice of an appropriate MP grid for our calculation. As implied above, we used the eigensolutions corresponding to the $10 \times 10 \times 10$ grid in our calculation of $\kappa_{ph}$; it was felt that this grid presented the best trade-off between convergence and computational effort available.

IV. RESULTS

A. Electronic properties

Figure 2 shows the temperature variation of the Fermi energy $E_F$ for the n-doped sample number 7 in Ref. 9 with temperature. There is clear evidence that the system shows extrinsic-type behavior in the region of interest. We assumed that acoustic scattering was dominant and so fixed the value of the scattering parameter at $s = -0.5$. We then numerically fitted our expression for $|S|$ to the experimental data of Ref. 9 using the algorithms described in (for example) Ref. 45 in order to find an optimal value of $m^\text{ph}_e$ (displayed in Table I). Since this also required the calculation of $E_F$, we are able to display the behavior of that (see Fig. 2) and of $|S|$ (see Fig. 3) with temperature.

### TABLE III. Convergence of the mean-free path due to anharmonic scattering calculated on successively more fine shifted MP grids for $T = 100$ K and $\gamma = 0.5$. Here, $\Delta\lambda_{\text{AH}}^{\text{TE}}$ is the relative difference between the value of $\lambda_{\text{AH}}^{\text{TE}}$ computed for the present grid and the value of $\lambda_{\text{AH}}^{\text{TE}}$ computed for its successor, expressed as the nearest whole percentage of the smallest value.

<table>
<thead>
<tr>
<th>MP Grid</th>
<th>Number of grid points</th>
<th>$T = 100$ K</th>
<th>$T = 600$ K</th>
<th>$T = 1200$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{AH}}^{\text{TE}}$ (m)</td>
<td>$\Delta\lambda_{\text{AH}}^{\text{TE}}$</td>
<td>$\lambda_{\text{AH}}^{\text{TE}}$ (m)</td>
</tr>
<tr>
<td>$4 \times 4 \times 4$</td>
<td>12</td>
<td>0.3445 $\times 10^{-7}$</td>
<td>$\cdots$</td>
<td>0.3567 $\times 10^{-8}$</td>
</tr>
<tr>
<td>$6 \times 6 \times 6$</td>
<td>36</td>
<td>0.6586 $\times 10^{-6}$</td>
<td>18%</td>
<td>0.5530 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$8 \times 8 \times 8$</td>
<td>80</td>
<td>0.3251 $\times 10^{-6}$</td>
<td>100%</td>
<td>0.3041 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$10 \times 10 \times 10$</td>
<td>150</td>
<td>0.8427 $\times 10^{-6}$</td>
<td>159%</td>
<td>0.7355 $\times 10^{-7}$</td>
</tr>
</tbody>
</table>
TABLE IV. Convergence of $\kappa_{ph}$ at $T = 100$ K due to anharmonic scattering as MP grids are made successively more fine, using the parameters of Table II. Here, $\Delta\kappa_{ph}$ is the relative difference between the value of $\kappa_{ph}$ computed for the present grid and the value of $\kappa_{ph}$ computed for its successor, expressed as the nearest whole percentage of the smallest value.

<table>
<thead>
<tr>
<th>MP grid</th>
<th>$T = 100$ K</th>
<th></th>
<th></th>
<th>$T = 600$ K</th>
<th></th>
<th></th>
<th>$T = 1200$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\kappa_{ph}$ (W m$^{-1}$ K$^{-1}$)</td>
<td>$\Delta\kappa_{ph}$</td>
<td></td>
<td>$\kappa_{ph}$ (W m$^{-1}$ K$^{-1}$)</td>
<td>$\Delta\kappa_{ph}$</td>
<td></td>
<td>$\kappa_{ph}$ (W m$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>4 $\times$ 4</td>
<td>3.4321</td>
<td>$\cdots$</td>
<td></td>
<td>1.3251</td>
<td>$\cdots$</td>
<td></td>
<td>0.79718</td>
</tr>
<tr>
<td>6 $\times$ 6</td>
<td>4.8023</td>
<td>40%</td>
<td>4.2119</td>
<td>218%</td>
<td>3.8353</td>
<td>381%</td>
<td>2.3016</td>
</tr>
<tr>
<td>8 $\times$ 8</td>
<td>3.3913</td>
<td>42%</td>
<td>2.8882</td>
<td>45%</td>
<td>2.9478</td>
<td>28%</td>
<td>2.3016</td>
</tr>
<tr>
<td>10 $\times$ 10</td>
<td>3.3795</td>
<td>0.35%</td>
<td>3.3841</td>
<td>17%</td>
<td>2.9478</td>
<td>28%</td>
<td>2.3016</td>
</tr>
</tbody>
</table>

Figure 4 shows the temperature variation of $\sigma$. As with the Seebeck data, it can be seen from Meddins and Parrott’s experimental data that there is no obvious transition to a region of intrinsic-type conductivity for the temperature range of interest. However, in order to properly account for the region of intrinsic-type conductivity for the temperature range for which we possess experimental data. We modelled the hole conductivity using Eq. (19) and obtained the parametrization displayed in Table I through consideration of the total value of the thermal conductivity, as described below. We should note that although Fig. 4 displays the sum of the two conductivities, $\sigma_h/\sigma_n$ is small enough within the temperature range of the experimental data that the effect of the inclusion of the hole contribution on the curve is negligible (at $T = 1100$ K, $\sigma_h$ is about 2% of $\sigma_n$, and for lower temperatures it is smaller), supporting our decision to ignore it when fitting to the experimental conductivity data. These assumptions do not hold for extremely high temperatures, however, at $T = 1200$ K, $\sigma_h$ is about 8% of $\sigma_n$, and will likely increase; our value for $\sigma$ here is less trustworthy than for lower temperatures. However, this regime is outside the temperature range for which we possess experimental data.

B. Phonon dispersion curves and density of states

Figures 5 and 6 display the phonon dispersion curves along the Cartesian axes of the system and the density of states for the ordered Si$_{0.75}$Ge$_{0.25}$ alloy with eight-atom unit cell utilizing a 10 $\times$ 10 $\times$ 10 MP grid. Results are presented for both the relaxed and unrelaxed cases. We will note a number of general features of interest in the relaxed case. Firstly, the dispersions of phonon branches in the [001] direction differ from those in the [100] and [010] directions, which

![Figure 2](image2.png)  
**FIG. 2.** (Color online) Calculated behavior of $E_F$ with temperature for the system of our study.

![Figure 3](image3.png)  
**FIG. 3.** (Color online) Calculated behavior of $|S|$ compared with experimental data from Fig. 4 of Ref. 9. (Data used with the permission of IOP Publishing Ltd.)
FIG. 4. (Color online) Theoretical behavior of $\sigma$ compared with experimental data taken from Fig. 3 in Ref. 9. (Data used with the permission of IOP Publishing Ltd.)

are identical (see Fig. 5). This should not be surprising, as if we refer to Fig. 1, we can see that the positioning of the Ge atoms in the cell distinguishes that direction from the others. From the dispersion relations, we can also see that a pair of “gaps” appear in all three directions between frequencies of about 300–350 cm$^{-1}$ and about 400–425 cm$^{-1}$. By comparison with Fig. 6, we can see that the locations of these gaps roughly correspond to frequencies between approximately 310–345 cm$^{-1}$ and approximately 400–428 cm$^{-1}$ where the phonon density of states has fallen to zero. It is thus clear that two phononic gaps exist for the structure modelled in our work. The presence of such gaps in thin SiGe systems has been noted and discussed previously.48,49 This is a consequence of our use of an ordered model that resembles a superlattice of unequal period upon repetition of the unit cell in our DFPT calculations; strictly speaking, we should use a larger, cubically symmetric cell in our calculations, but we are limited by our computational resources. In order to overcome this, we assume as a first approximation that any macroscopic system will consist of randomly oriented cells of this kind, and hence that the isotropic lattice thermal conductivity can be considered to be the average of the diagonal components of the thermal conductivity matrix for a single cell. We do not feel that this approximation will lead to significantly different results from calculations carried out using a different choice of cell.

Returning to our discussion of the DFPT results, we may support the notion that the ordering of the alloy is the chief factor in the existence of the phononic gaps by considering the phonon dispersion curves for the modelled SiGe alloy along each of the three Cartesian directions. A comparison between the relaxed and unrelaxed results shown in Fig. 5 indicates that the dispersions of low frequency branches (comprising the acoustic modes and optical modes below around 300 cm$^{-1}$) are relatively unaffected by bond relaxation (there is some small modification as 300 cm$^{-1}$ is approached, but nothing significant). However, the same cannot be said of the higher-frequency optical branches, whose behavior is considerably modified. Examination of the phonon density of states in Fig. 6 would seem to support this—the unrelaxed and

FIG. 5. (Color online) Comparison of phonon dispersion relations along the [100] (top left), [010] (top right), and [001] (bottom center) directions for the ordered Si$_{0.75}$Ge$_{0.25}$ system discussed in the text.
the relaxed cases are qualitatively similar (though not identical) below around 350 cm\(^{-1}\), which includes the lower of the two frequency gaps. Above this frequency, we can see that there are considerable differences in the locations of the peaks in either case, and the size of the higher frequency gap is slightly increased by bond relaxation from around 410–422 cm\(^{-1}\) to around 400–428 cm\(^{-1}\). We can therefore conclude that bond relaxation affects the size of one gap in the system, but that it does not give rise to the gaps themselves.

C. Phonon mean-free path

We now turn to an interesting question that has perhaps not received the consideration that it deserves: the notion of the mode-average phonon mean-free path (MFP) \(\lambda\). The issue in question is the precise form of the mode averaging that one can employ, and it is this which we examine in what follows.

One prescription that has been used in calculations of conductivity. For the ordered Si\(_{0.75}\)Ge\(_{0.25}\) alloy discussed in the text, note the pair of frequency “gaps” in the vicinity of 325 and 420 cm\(^{-1}\).

In Fig. 7, we plot the mean-free paths (MFPs) calculated using various methods, compared with that of the relaxation length of the mode whose weighted contribution to \(\kappa_{\text{ph}}\) is the greatest (\(\lambda_{\text{MAX}}\)).

Furthermore, we may also wish to calculate the MFPs arising from different contributions to scattering; in this case, we replace the total \(\tau(q,s)\) in a given equation with the \(\tau(q,s)\) corresponding to the contribution of interest. We will denote the contributions of interest with subscripts as follows: total anharmonic (AH), Normal (N), Umklapp (U), and also compare with the values of the following definition of the MFP:

\[
\frac{1}{\lambda_{\text{IN}}} = \frac{\sum_{q,s} \tau_{q,s}^{-1} c_s^{-1}(q) \bar{\kappa}_{q,s}}{\sum_{q,s} \bar{\kappa}_{q,s}},
\]

and with values of the variationally derived lower bound of the MFP: \(\lambda_{\text{LB}}\)

\[
\frac{1}{\lambda_{\text{LB}}} = \frac{\tilde{c}}{C} \sum_{q,s} C_{q,s} \tau_{q,s}^{-1}(q) \frac{\bar{\kappa}_{q,s}}{c_s^2(q)}.
\]

In Fig. 7, we plot the mean-free paths (MFPs) calculated using all these methods and utilising all available phonon modes. We also display \(\lambda_{\text{MAX}}\), which is the MFP associated with the mode whose weighted contribution to \(\kappa_{\text{ph}}\) is the greatest. We can see that there is a large and obvious difference between the results of the various methods, with \(\lambda_{\text{TE}}\) and \(\lambda_{\text{SH}}\) being the most similar, \(\lambda_{\text{IN}}\) being an order of magnitude smaller than the latter. \(\lambda_{\text{LB}}\) is smaller still; this is unsurprising since it is the lower bound of the MFP, \(\lambda_{\text{MAX}}\) is larger than all of these, consistent with the analysis of Ref. 52, which notes that mode-averaged MFPs are likely to greatly underestimate the degree to which modes with long MFPs contribute to \(\kappa_{\text{ph}}\) in systems where the effects of defect scattering are strong (as is in fact the case in this alloy—see the next section for more details). Because of this, one can immediately rule out \(\lambda_{\text{LB}}\) and \(\lambda_{\text{IN}}\) as good definitions of the MFP; they are far too small. With regards to \(\lambda_{\text{SH}}\), as we see here and in Richardson et al., \(\lambda_{\text{TE}}\) it also underestimates the contribution from long MFP modes. We find that \(\lambda_{\text{TE}}\) also offends in this regard (though not quite as badly as \(\lambda_{\text{SH}}\)). This entails that one must exercise caution when interpreting MFP data—not only can it be misleading in certain systems, but its value is strongly dependent on the method by which it is calculated; in the case of the present system, even...
if $\lambda^{\text{SH}}$ and $\lambda^{\text{LB}}$ did not likely underestimate the value of the MFP, they do not give the same answer as to its value. We do not know of any strong theoretical reason for preferring one definition over the other; however, in a practical sense (as far as thermal conductivity measurements are concerned) we are inclined to prefer $\lambda^{\text{SH}}$, for its calculation utilizes experimental quantities that are readily measured, as in Ref. 51. What is most important, however, is that whichever method one uses is clearly stated.

Figures 8 and 9 display the MFP due to total anharmonic, Normal, and Umklapp scattering for the above mode-averaging schemes. For all cases, we see that the MFP due to Normal processes is typically larger than that of the MFP due to Umklapp processes, suggesting that the latter are generally more important to the overall scattering. We should caution against taking these results as final and definitive, due to the badly convergent nature of the anharmonic MFP discussed in the previous section. However, we think they are likely to be qualitatively reliable.

D. Thermal conductivity

Due to the complexity involved in the implementation of the calculation of $\kappa$, numerical fitting proved unfeasible, and it was necessary to manually tune the semiadjustable parameters so as to attain results that displayed reasonable agreement with Meddin and Parrott’s9 measurements of the total thermal conductivity $\kappa$. The parameters listed in Table II (and used in Fig. 10) and those concerning $\sigma_p$ in Table I were obtained by choosing a given parameter set, calculating $\kappa_{\text{ph}}$ from the eigensolutions generated for a $10 \times 10 \times 10$ MP grid, adding the results to the $\kappa_{\text{el}}$ values to obtain $\kappa$, and then comparing this with the experimental results, and repeating the process with adjusted values of the parameters until good agreement was reached.

Figure 10 displays the resulting values of $\kappa$ alongside the experimental results of and a theoretical calculation from Ref. 9. Qualitatively speaking, it can be seen that our calculation is a better match to the data than theirs for the region in which they give theoretical values aside from the data point at the lowest temperature, which is somewhat undershot, and that our calculation has a wider range of validity. For temperatures greater than 900 K, where the bipolar contribution is dominant (and thus the behavior is determined by our parametrization of $\sigma_p$), the curve matches the data less well; in fact, the form of the data is such that it made selecting appropriate values for the behaviour of $G$ difficult, which should be kept in mind when considering the accuracy of our calculation in this region. It should be kept in mind that the value of the material density $\rho$ used for the calculation of $\kappa_{\text{ph}}$ is the weighted average value of 3077.5 kg m$^{-3}$ rather than the measured value of 2860 kg m$^{-3}$ found in Ref. 9; but any errors resulting from this difference will be absorbed into the values of $A$ and $\gamma$, which control the strength of the scattering processes that exhibit density dependence.

Examining the results displayed in Table II, we note that our fit was obtained using a value of $L$, which is the lower limit of that expected by Ref. 9, suggesting a fairly small crystallite size. $P$ is fairly large, indicating that we are accounting for scattering from a large number of defects consistent with our discussion of the mean-free path results; it would not be
These differences may both be a function of methodology and of the differing compositions of our materials.

However, one must be careful when drawing conclusions from these data as to the relative contributions of various frequencies to $\kappa_{ph}$. This is because in our actual calculations, we make use of the MP momentum summation scheme, and therefore each frequency displayed in Fig. 11 in fact makes a contribution to $\kappa_{ph}$ that is weighted according to the $q$ point with which it coincides. We display the percentage contribution to $\kappa_{ph}$ of each frequency following such weighting in Fig. 12. It is apparent that the general behavior with temperature is consistent with that of Fig. 11. However, we can also see that the weighting of the contributions has drastically altered our conception of how low frequencies contribute to $\kappa_{ph}$, for while the overall trend in the degree of contribution is still downwards for frequencies greater than 40 cm$^{-1}$, the contributions of a small number are strongly enhanced. For example, the contributions of two frequencies in the region of 45 cm$^{-1}$ are far greater than would be expected from Fig. 12, in fact contributing more than the subdominant frequency of that figure.

There is a caveat with regards to these data, however. We have naively plotted the frequency data without regard for degeneracy or the manner in which numerical error separates out what should be degenerate modes, entailing that we may be undercounting the contribution of some frequencies (for example, those corresponding to transverse acoustic modes). But it would seem likely that this would not overly affect our general conclusion, which is that when accounting for the contributions of various modes to $\kappa_{ph}$ one should take into account the degree to which each mode is weighted by the MP summation scheme, as it is entirely possible that not doing so might mislead as to which modes are in fact dominant, and to what degree.

### E. Figure of merit

Having calculated the relevant electronic and vibrational contributions, we are now in a position to calculate the figure of merit $ZT$ for Sample 7 in Ref. 9. In Fig. 13, we compare our
results with the calculation performed by Meddins and Parrott, which is based on their theoretical model detailed in Ref. 9. However, in quantitative terms, there is a discrepancy of around 16% at 1000 K, and at lower temperatures, our results are slightly larger than theirs. One factor that may account for much of this difference is that Meddins and Parrott do not appear to include the bipolar contribution to \( \kappa_{el} \) in their analysis, and since it is at high temperatures that that contribution is dominant, it is unsurprising that their values of \( ZT \) are greater than ours in this region. From our numerical results, we suggest that for the modelled Si\(_{0.75}\)Ge\(_{0.25}\) alloy values of \( ZT > 0.5 \) can be expected throughout the high-temperature range of around 750–1200 K, with a maximum of approximately 0.68 at around 1000 K.

A comparison with, and comment on, the work carried out by Minnich et al.,\(^{11} \) is also appropriate. These authors applied a detailed model, similar to that adopted by Vining,\(^{10} \) of the electronic behavior and of the phonon contribution to \( \kappa_{el} \) to experimental results for n-doped Si\(_{0.8}\)Ge\(_{0.2}\) (where \( N_{don} \) was obtained by fitting to experimental results) and for n- and p-doped Si\(_{0.7}\)Ge\(_{0.3}\) where a number of samples with different \( N_{don} \) were available. The results for the n-doped Si\(_{0.7}\)Ge\(_{0.3}\) sample with \( N_{don} = 7.3 \times 10^{23} \text{ m}^{-3} \) are the most relevant here, since the composition and \( N_{don} \) of this sample are reasonably close to that of the sample treated in this study. In the fourth panel of Fig. 1 in Ref. 11, they display \( ZT \) for their n-type Si\(_{0.7}\)Ge\(_{0.3}\) samples, and for the sample of interest, it can be seen that the results are qualitatively similar up to around \( T = 1000 \text{ K} \), with a peak at a slightly larger value of \( ZT \) (closer to the 0.8 of Meddins and Parrott’s results\(^{9} \) than the 0.7 of ours) and a far sharper decrease than we observe at higher temperatures. Some of this difference is likely to arise from our different approaches, and some of it from the differences in composition between our samples. However, the qualitative similarities are a good sign.

Our calculation of \( ZT \) in an SiGe alloy includes as complete as possible an account of the phonon scattering rates and the effects of the bipolar contribution to thermal conductivity. It is hoped that it will provided a benchmark for future theoretical explorations of the thermoelectric efficiency of more complex systems such as nanowires or superlattices.

## V. SUMMARY AND CONCLUSION

In this study, we have examined the theoretical behavior of the thermoelectric figure of merit \( ZT \) and its constituent quantities for the case of a sintered Si\(_{0.75}\)Ge\(_{0.246}\) doped with P impurities examined by Meddins and Parrott.\(^{9} \) We have established phenomenological models to account for the behavior of the electronic quantities, and have focused in detail on the mechanisms underlying the phonon contribution to the thermal conductivity \( \kappa \). In this respect, we have developed a full-scale theory of the lattice thermal conductivity considering the role of acoustic as well as optical phonons in Normal and Umklapp three-phonon interactions and included the bipolar contribution to thermal conductivity.

We have made use of density functional methods in order to obtain the required phonon eigensolutions and a detailed calculation of the anharmonic contribution to phonon scattering based on a semiempirical model for anharmonic crystal potential. The subsequent calculation of \( \kappa_{ph} + \kappa_{el} \) shows good agreement with measurements in the entire temperature range 300–1100 K. We have also examined the frequency dependence of \( \kappa_{ph} \), finding that it is consistent with the previously reported results of Ref. 15 apart from some differences in temperature dependence and have discussed some issues concerning the notion of a mean-free path.

From this information, we have calculated the dimensionless figure of merit \( ZT \) and compared it with the (incomplete) calculation in Ref. 9. While, in general, the qualitative behavior of the \( ZT \) versus \( T \) curve in our work is quite similar to that in Ref. 9, with the more complete theoretical treatment we have predicted values of greater than 0.5 in the temperature range of around 750 to at least 1200 K with a maximum of approximately 0.68 at around 1000 K.

In addition to the study of the thermoelectric properties, we have also examined a more conceptual issue: that of the calculation of the phonon mean-free path. We have shown that in the literature, there exist different prescriptions for evaluation of phonon mean free path, yielding different results. We suggest that care must be exercised in comparing results obtained from different methods of mode averaging procedures.

## ACKNOWLEDGMENTS

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## APPENDIX: THE ANHARMONIC INTERACTION TERM

While the anharmonic crystal potential involving acoustic phonons has been widely discussed, the contributions due to optical modes have not been fully considered, although Klemens\(^{53} \) and Ridley and Gupta\(^{54} \) have given simple presentations of the effects of scattering to and from optical modes.
In this work, we have expressed the anharmonic phonon relaxation time due to three-phonon Normal and Umklapp processes involving acoustic and optical phonon modes, using Eqs. (28) and (29). This form of the anharmonic phonon-phonon interaction was proposed by S. P. Hepplestone and was indeed employed in previously published works, but has not yet appeared in print. In this appendix, we shall attempt to justify and present the relevant expression for the cubic anharmonicity in crystal potential.

We shall begin with following expression for the third-order perturbative term in the elastic continuum potential, taken from Ref. 26:

\[ V_3 = \sqrt{\frac{\hbar^3}{8\rho^3\omega_0}} \sum_{q',q''} T^{s's''s'}_{q',q''} (a_q^\dagger - a_{q'}) (a_{q''}^\dagger - a_{q'''}) \times (a_{q'''}^\dagger - a_{q'''}) \delta_{q + q'' + q'''} \delta_{q'''} \]

(A1)

where

\[ T^{s's''s'}_{q',q''} = \frac{1}{3!} \sqrt{\frac{q q' q''}{c_s c_s' c_s''}} A^{s's''s'}_{q',q''} \]

(A2)

with \( a_q^\dagger \) (\( a_q \)) being the phonon creation (annihilation) operator for a given mode \( q \), \( c_s \) the magnitude of the momentum, and \( c_s' \), \( c_s'' \) being the speed of a phonon belonging to branch \( s \). Note that \( c_s \) is not dependent on \( q \) at this point; this expression is derived on the assumption that we are treating acoustic phonons in the continuum, \( q \to 0 \), limit, and so we can relate frequency and momentum through the dispersion relation \( \omega(q,s) \approx \omega(q) \). Our aim is to reverse-engineer from (A1) a starting point similar to that used by Klemens, from which we may derive an expression for the anharmonic term that includes aspects of the behavior of optical phonons while remaining true to the spirit of the original continuum, acoustical approach.

Taking the expression for the angularly averaged modulus of \( A^{s's''s'}_{q',q''} \) as a guide:\textsuperscript{26}

\[ \frac{|A^{s's''s'}_{q',q''}|^2}{\omega(q,s) \omega(q',s') \omega(q'',s'')} = \frac{4 \rho^2}{c_s^2} \gamma^2 c_s c_s' c_s'' , \]

(A3)

we put \( A^{s's''s'}_{q',q''} = (2\rho/c_s)\gamma c_s' c_s'' \), with \( \gamma \) being an average phonon speed and \( \gamma \) being the modulus of the Gr"uneisen constant, and so arrive (following a little algebra, and assuming acoustic dispersions at \( q \to 0 \)) at the expression

\[ T^{s's''s'}_{q',q''} = \frac{2 \rho \gamma}{\sqrt{\omega(q,s) \omega(q',s') \omega(q'',s'')}} B^{s's''s'}_{q',q''} , \]

(A4)

\[ B^{s's''s'}_{q',q''} = \frac{1}{3!} \sqrt{\frac{\omega(q,s) \omega(q',s') \omega(q'',s'')}} \omega(q,s) \omega(q',s') \omega(q'',s'') , \]

(A5)

Equation (A5) has the same general form as the approximation used by Klemens.\textsuperscript{56} Indeed, if we replace \( \gamma \) with the speed \( c_s' \), then in the limit of small \( q \) and assuming an acoustic dispersion, we obtain

\[ B^{s's''s'}_{q',q''} = \frac{1}{3!} \omega(q,s) \omega(q',s') \omega(q'',s'') , \]

(A6)

which is very similar to the expression Klemens has derived in order to motivate his approximation. We shall use this as the basis for our derivation of the general anharmonic term with which to treat three-phonon interaction involving both acoustic and optical modes.

1. Treatment when \( q''s'' \) is an optical mode

We shall begin with the situation when \( q''s'' \) is an optical mode and consider three-phonon processes of the types \( ac + ac \leftrightarrow op \) and \( ac + op \leftrightarrow op \). For small values of \( q'' \), we express \( \omega(q,q'',s'') = \omega_1(s''')^2 - c_s' \omega(q)^2 \). Rearranging this, we may write

\[ q'' = \frac{\omega_1(s''')^2 - \omega_0(s''')^2}{c_s'} \approx \frac{1}{c_s'} \end{equation}

(A7)

Next, we observe that \( B^{s's''s'}_{q',q''} \) is identical under exchange of the modes \( qs \) and \( q's' \); we account for this in Eq. (A1) by simply multiplying \( B^{s's''s'}_{q',q''} \) by a factor of 2 and ignoring subsequent terms where those modes are exchanged. Replacing \( q'' \) in \( B^{s's''s'}_{q',q''} \) with this expression, we obtain

\[ B^{s's''s'}_{q',q''} = \frac{\omega(q,s) \omega(q',s') \sqrt{2 \omega_0(q''s'')} \omega_1(s''')^2}{c_s'} \omega(q,s) \omega(q',s') \omega(q'',s'') \]

(A8)

Instead of following Klemens or Ridley and Gupta and assuming that the dominant decay is of the form \( \omega(q'',s'') \approx \omega(q,s)/2 \approx \omega(q')/2 \), we shall be more general; examining the energy conservation condition

\[ \omega_0(q''s'') \approx \omega(q,s) + \omega(q',s') , \]

(A9)

we may see that

\[ \omega(q,s) = B \omega_0(q'',s'') = (1 - B) \omega_0(q'',s'') , \]

(A10)

\[ \omega(q',s') = (1 - B) \omega_0(q'',s'') , \]

(A11)

where we consider values of \( B \) between zero and unity. From Eq. (A9), we may write

\[ \sqrt{2 \omega_0(q''s'')} = \sqrt{2 \omega(q,s) + \omega(q',s')} \]

and so \( \omega(q,s) = \sqrt{B \omega(q,s) + \omega(q',s')} \), and hence

\[ B^{s's''s'}_{q',q''} = \frac{1}{3!} \omega(q,s) \omega(q',s') \omega(q'',s'') \omega_0(q,s) \omega(q',s') \omega(q'',s'') \]

(A12)

We may also write

\[ \frac{\omega(q',s') \omega(q'',s'')}{(1 - B)} \approx \frac{\omega(q',s') \omega(q'',s'')}{\omega(q,s) \omega(q',s') \omega(q'',s'')} = A^2 \frac{\omega(q,s) - \omega(q',s')}{\omega(q,s) - \omega(q'',s'')} , \]

(A13)
where $A$ is defined above, and so acquire

$$B_{qqq'}^{s's'} = \frac{A}{3} \sqrt{B(1 - B) \omega(qs) \omega(q's')} \frac{\omega(qs) + \omega(q's') + \omega(qs'')}{\omega(qs) \omega(q's') \omega(qs'')} c_{s'o}.$$  \hspace{1cm} (A14)

from which we may obtain

$$T_{qqq'}^{s's'} = \frac{2\rho \Gamma_o}{\sqrt{\omega(qs) \omega(q's') \omega(qs'')}} \frac{1}{3!} \frac{\sqrt{\omega(qs) \omega(q's') \omega(qs'')}}{\omega(qs) \omega(q's') \omega(qs'')} \frac{\omega(qs) + \omega(q's') + \omega(qs'')}{\omega(qs) \omega(q's') \omega(qs'')} c_{s'o}.$$  \hspace{1cm} (A15)

where $\Gamma_o = 2A \gamma \sqrt{B(1 - B)}$. It should be noted that in order for $\Gamma_o$ to have a meaningful value at $q = 0$, we require that $\gamma \sqrt{B(1 - B)} \propto |\omega_{\alpha}(s) - \omega_{\alpha}(q's')|^\alpha$ as $q \rightarrow 0$, where $\alpha \geq 1/2$, in order to cancel the zero-tending term in the denominator of $A$. This is a strict constraint on the behavior of $\gamma$; however, it is an artifact of the form of the term that we must adopt for numerical simplicity. One could consider using other forms, but then one would have to make use of a frequency window in order to distinguish optical and acoustic terms, a process that is cumbersome and which could introduce its own inaccuracies. In this case, we much prefer to choose the form given above, which is easy to implement numerically.

2. Treatment when $q''s''$ is an acoustic mode

To deal with three-phonon processes of the type $ac + ac \Rightarrow ac$, with $q''$ corresponding to an acoustic mode, we first observe that from the acoustic dispersion relation in the limit of small $q$, we may derive $q = |\omega_{\alpha}(s) - \omega_{\alpha}(q's')|/c_{sa}$, since $\omega_{\alpha}(s) = 0$. From Eqs. (A10) and (A11) and energy conservation, we may obtain $\sqrt{\omega(qs) \omega(q's')} = \sqrt{B(1 - B) |\omega(qs) + \omega(q's')|}$. These may be used to derive

$$T_{qqq'}^{s's'} = \frac{2\rho \Gamma_o}{\sqrt{\omega(qs) \omega(q's') \omega(qs'')}} \frac{1}{3!} \frac{\sqrt{\omega(qs) \omega(q's') \omega(qs'')}}{\omega(qs) \omega(q's') \omega(qs'')} \frac{\omega(qs) + \omega(q's') + \omega(qs'')}{\omega(qs) \omega(q's') \omega(qs'')} c_{s'o}.$$  \hspace{1cm} (A16)

where $\Gamma_o = 2A \gamma \sqrt{B(1 - B)}$. This expression for $T$ is essentially the same as in Ref. 26. (Note that the value of $B$ here is not necessarily identical to that of $B$ in the previous section when $q''$ was an optical mode, nor is it necessarily identical with values of $B$ considered for scattering between a different triad of phonon modes.)

3. Form for numerical calculations

For ease of calculation, we take $\Gamma_o = \Gamma_o = \bar{\gamma}$, by analogy with the use of the mode-averaged Gr"uneisen constant in typical computations of this form. Since contributions from both acoustic and optical $q''$ now share an identical form, we may suppress the indices which distinguish them and write an overall term:

$$\mathcal{V}_3 = \bar{\gamma} \frac{\hbar^3}{2\rho V} \sum_{q',q''} B_{q,q',q''} \delta_{q+q'+q''} \times (a_{q'}^d - a_{-q'}) (a_{q''}^d - a_{-q''}) (a_{q'}^d - a_{-q'}) (A17)$$

with

$$B_{i,j,k} = \sqrt{\omega(i) \omega(j)} |\omega(i) + \omega(j)| |\omega(k) - \omega(k)|/c(k)$$

+ similar terms with $i$, $j$, and $k$ interchanged $/3!$, \hspace{1cm} (A18)

where $i$, $j$, $k$ label phonon modes, and $c(k)$ is now the momentum dependent, i.e., phase speed for the mode $k$; here, we make a generalization to the case where $q$ no longer tends to zero. From this, we may obtain the expression for the anharmonic single-mode relaxation time used in our calculations—that is, Eq. (28).

We should remark that the assumptions made in deriving the above expression are perhaps somewhat crude: unlike Klemens or Ridley and Gupta, we have not properly considered distinctions in behavior arising from the different ways in which the displacement of optical and acoustic vibrations deform the crystal. However, given that Klemens’s expression is equivalent to that of Ridley and Gupta (as the latter have observed), and that the former’s derivation shows that the differences amount to a rescaling of the optical Gr"uneisen constant away from the value it would have were it derived assuming acoustic behavior, we should not be too worried; such a distinction would be ignored by our use of a mode-averaged form of the rescaled Gr"uneisen constant regardless of the final form of our expression. Indeed, given that all such expressions are strictly valid only in the continuum limit, and that our calculation by necessity extrapolates beyond that limit, we should not expect our expression to be any worse an approximation than the others, and in terms of simplicity of numerical implementation and avoidance of problems arising from ambiguities in the labeling of the phonon eigensolutions in the output of ab initio codes, we feel that it has much to recommend itself.
A very preliminary version of our findings was presented at the Fall 2011 Meeting of the Materials Research Society and published in I. O. Thomas and G. P. Srivastava, MRS Proceedings [http://www.mrs.org] (2012). However, we should note that many of the results presented therein have been considerably refined and corrected in the present work.


Unpublished. In fact, this appendix is our reconstruction of his probable reasoning, which is currently unavailable to us.