Theoretical studies of the thermoelectric properties of nanostructured materials

Submitted by Jawaher Mutlaq AL-Otaibi to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Physics.

In March 2016

This thesis is available for library use on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

I certify that all material in this thesis which is not my own work has been identified and that no material has previously submitted and approved for the award of a degree by this or any other university.

(Signature)
Dedication

This thesis is dedicated to all those who prayed, encouraged, and have been there for me all the way and still are.

To my parents, may Allah bless you with strength and long happy life.
To my siblings, Nouri, Faisal, Wafa, Abeer, Salman, Sultan, and Halah.
To my nephew Abdullah Khalid and my niece Deema.
To Abdul-Rahman Al-zuhair, who kept me connected to home.
Also, I would like to dedicate this work to the two people whom have a great influence on my career.
Dr. Salwa Al-Saleh and Prof. Mohammed Al-Salhi, may Allah grant your wishes.
A special dedication to Prof. G. P. Srivastava, my supervisor, who guided me patiently and kindly through this journey.
And finally, to the deceased King Abdul-Allah, may Allah rest his soul in peace.
Abstract

This project involves theoretical study of the thermoelectric properties of lead chalcogenide materials. Thermoelectric (TE) materials are used for the fabrication of devices that are designed to convert heat into electricity and vice versa. They can be described as a clean alternative for fossil fuel. These materials are characterized by their ability to operate at a broad range of temperatures ($2 - 800$) K. Lead chalcogenides, such as PbTe, PbSe, and PbS, represent a group of TE materials that have the appealing property of stability at high temperatures, hence they are considered attractive for thermoelectric applications. The simple rock-salt structure of lead chalcogenide combined with its narrow gap semiconductor’s nature has attracted great attention from experimental as well as theoretical researchers. These studies have focused on investigating electronic structures and elastic properties aiming for a better understanding that would lead to a significant improvement in their TE efficiency. In the first part of this thesis we evaluated the optimised parameters for the figure of merit for n-type PbTe: The electrical conductivity, the Seebeck coefficient, and the total thermal conductivity, \(\text{(i.e. the electronic and lattice thermal conductivity)}\), emphasising on the important role of optical phonons in heat conduction. In the second part, we extended the lattice thermal conductivity work to include PbSe, PbS, and SnTe, where we applied the Debye, Callaway, and Allen theories of thermal conductivity. In the third part we used the effective medium theory to evaluate the lattice thermal conductivity for PbTe-PbSe nanocomposites in three different configurations: nanospheres, nanowires, and superlattices.


Acknowledgement

I believe that actions always speak louder than words. That does not mean to forsake words altogether, for a kind word can be enchanting if it comes from the heart. For this it is my pleasure to acknowledge the roles of several individuals who were instrumental for completion of my Ph. D. project.

Foremost, I would like to express my sincere gratitude to Prof. Dr. G. P. Srivastava, my supervisor and mentor, who has been there for me every step of the way, guiding, motivating, and encouraging. I am truly grateful for his continuous support and advice. I will try employing whatever I have learned from him in my coming academic carrier. G. P. Srivastava, you should know that I will always be grateful to you.

Secondly, I am really thankful to King Saud University and the Saudi Arabia, Cultural Bureau, London - UK, for supporting me financially and giving me the opportunity to complete my Ph. D. project.

I also thank Exeter University for making this journey most enjoyable. A special thanks to my parents Mutlaq and Ghazwa. For your confidence, believes, and prayers that have got me through a lot. I will always be thankful that I’m blessed with such generous and kind hearted parents.

I also would like to address my gratitude to my brother Salman and my sister Abeer. Thank you for giving-up a lot to keep my company. I am sorry that there are no words that can convey how much I value your presence by my side.

Finally, I thank my siblings Faisal, Nouri, Wafa, Sultan, and Halah. Just being in my life have given me comfort and relief. I knew that whenever I needed you, you would be there for me emotionally and financially.
List of Abbreviations

TE .......... Thermoelectric
emf .......... Electromotive force
COP .......... Coefficient Of Performance
PGEC ........ Phonon Glass Electron Crystal
2D .......... Two Dimension
NW .......... Nano-Wire
QDSL ........ Qudatun Dot Superlattice
1D .......... One Dimension
0D .......... Zero Dimension
BTE ........ Boltzmann Transport Equation
smrt .......... single mode relation time
N .......... Normal process
U .......... Umklapp process
LA .......... Longitudinal acoustic
TA .......... Transverse acoustic
TO .......... Transverse optical
fcc .......... face-centered cubic
R .......... Resistive
EMA ........ Effective Medium Approximation
mEMA ........ modified Effective Medium Approximation

MFP ........ Mean Free Path

ND .......... nanosphere

SL .......... Superlattice
## List of Symbols and Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T$</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Temperature of the element cold end</td>
</tr>
<tr>
<td>$T_2$</td>
<td>Temperature of the element hot end</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>Potential difference</td>
</tr>
<tr>
<td>$S$</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>$I_e$</td>
<td>Electric current</td>
</tr>
<tr>
<td>$Q_P$</td>
<td>Peltier heat Current</td>
</tr>
<tr>
<td>II</td>
<td>Peltier coefficient</td>
</tr>
<tr>
<td>$R_L$</td>
<td>Load resistance</td>
</tr>
<tr>
<td>$R$</td>
<td>Thermoelements total internal resistance</td>
</tr>
<tr>
<td>$S_{p,n}$</td>
<td>Resultant Seebeck coefficient of thermoelements</td>
</tr>
<tr>
<td>$\eta_G$</td>
<td>Power generator efficiency</td>
</tr>
<tr>
<td>$W$</td>
<td>Electric power</td>
</tr>
<tr>
<td>$Q_a$</td>
<td>Heat absorbed from the source</td>
</tr>
<tr>
<td>$\kappa'$</td>
<td>Thermal conductance of thermoelements</td>
</tr>
<tr>
<td>$A_{p,n}$</td>
<td>the cross-section areas of the thermoelements</td>
</tr>
<tr>
<td>$l$</td>
<td>Length of the thermoelement branch</td>
</tr>
<tr>
<td>$m$</td>
<td>Ratio of load to thermoelements internal resistance</td>
</tr>
<tr>
<td>$Z$</td>
<td>Figure of merit</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>$ZT$</td>
<td>Dimensionless figure of merit</td>
</tr>
<tr>
<td>$\eta_{\text{max}}$</td>
<td>Maximum power generation efficiency</td>
</tr>
<tr>
<td>$\kappa_{\text{ph}}$</td>
<td>Phonon thermal conductivity</td>
</tr>
<tr>
<td>$\kappa_{\text{mp}}$</td>
<td>Electronic thermal conductivity</td>
</tr>
<tr>
<td>$d$</td>
<td>Characteristic length scale in a low dimensional structure</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>Carrier mean free path</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Carrier wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{el}}$</td>
<td>Electron wavelength</td>
</tr>
<tr>
<td>$\Lambda_{\text{ph}}$</td>
<td>Phonon mean free path</td>
</tr>
<tr>
<td>$\Lambda_{\text{el}}$</td>
<td>Electron mean free path</td>
</tr>
<tr>
<td>$\lambda_{\text{ph}}$</td>
<td>Phonon wavelength</td>
</tr>
<tr>
<td>$\kappa_{\text{ph}}$</td>
<td>Phonon thermal conductivity</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
</tr>
<tr>
<td>$\nabla T$</td>
<td>Temperature gradient</td>
</tr>
<tr>
<td>$J$</td>
<td>Electric current density</td>
</tr>
<tr>
<td>$U$</td>
<td>Heat current density</td>
</tr>
<tr>
<td>$L_{\text{EE}}, L_{\text{ET}}, L_{TE}$</td>
<td>Thermoelectric transport coefficients</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$L$</td>
<td>Lorenz number</td>
</tr>
<tr>
<td>$e$</td>
<td>Elementary electronic charge</td>
</tr>
<tr>
<td>$-e$</td>
<td>Electron charge</td>
</tr>
<tr>
<td>$+e$</td>
<td>Hole charge</td>
</tr>
<tr>
<td>$k$</td>
<td>Electron wave vector</td>
</tr>
<tr>
<td>$v_k$</td>
<td>Electron velocity in $k$ state</td>
</tr>
<tr>
<td>$f_k$</td>
<td>Electron distribution function</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$E_k$</td>
<td>Electron energy in $k$ state</td>
</tr>
<tr>
<td>$\bar{\mu}$</td>
<td>Electrochemical potential</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Electrostatic potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Force</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Reduced Planck’s constant</td>
</tr>
<tr>
<td>$r$</td>
<td>Position vector</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$f_0$</td>
<td>Fermi-Dirac equilibrium function of electron</td>
</tr>
<tr>
<td>$\dot{k}$</td>
<td>Time derivative of wave vector</td>
</tr>
<tr>
<td>$\nabla_k$</td>
<td>Momentum gradients</td>
</tr>
<tr>
<td>$\nabla_r$</td>
<td>Position gradient</td>
</tr>
<tr>
<td>$\tau_k$</td>
<td>Relaxation time</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$\nabla\bar{\mu}$</td>
<td>Electrochemical potential gradient</td>
</tr>
<tr>
<td>$\dot{E}$</td>
<td>Effective electric field</td>
</tr>
<tr>
<td>$I_s$</td>
<td>Common integral form for transport coefficients</td>
</tr>
<tr>
<td>$a$</td>
<td>Lattice constant</td>
</tr>
<tr>
<td>$a_i : i = 1, 2, 3$</td>
<td>Primitive translational vectors</td>
</tr>
<tr>
<td>$G$</td>
<td>Reciprocal lattice vector</td>
</tr>
<tr>
<td>$b_i : i = 1, 2, 3$</td>
<td>Basis vectors of the reciprocal lattice</td>
</tr>
<tr>
<td>$m_i : i = 1, 2, 3$</td>
<td>Integers</td>
</tr>
</tbody>
</table>
\( \Omega \) Volume of primitive unit cell in real space

\( E_c \) Conduction band minimum energy

\( m_e^* \) Electron effective mass

\( E_v \) Valence band maximum energy

\( m_h^* \) Hole effective mass

\( \epsilon_i \) Energy difference from the band edge

\( p \) Scattering parameter of the relaxation time dependence on energy

\( \tau_0 \) Relaxation time constant

\( K_s \) Transport coefficients integrals

\( g(\epsilon) \) Density of states.

\( A, B \) Transport coefficients integral limits

\( x \) Dimensionless variable

\( \zeta \) Reduced Fermi energy

\( N \) Number of atoms in crystal

\( \omega \) Phonon angular frequency

\( q \) Phonon wave vector

\( \bar{n}_q \) Phonon Bose-Einstein distribution function

\( b \) Position of the \( b \) atom

\( l \) Position of a \( l \) unit cell

\( \alpha; \beta = 1, 2, 3 \) Components of cartesian coordinates

\( u_\alpha(lb) \) Atomic displacement of the \( b \) atom in the \( l \) unit cell

\( C_{\alpha\beta}(lb; \dot{lb}) \) Interatomic force constant matrix element
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_\alpha(q; b)$</td>
<td>Amplitude of the vibration of $b$ atom in the $\alpha$ direction</td>
</tr>
<tr>
<td>$D_{\alpha\beta}(b</td>
<td>b</td>
</tr>
<tr>
<td>$x(l)$</td>
<td>Equilibrium position vector of the $l^{th}$ unit cell</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Number of unit cells</td>
</tr>
<tr>
<td>$s$</td>
<td>Phonon polarization; $s =$ TA, LA, TO, LO</td>
</tr>
<tr>
<td>$e$</td>
<td>Atomic vibrational vector</td>
</tr>
<tr>
<td>$c_s$</td>
<td>Phonon speed of polarization $s$</td>
</tr>
<tr>
<td>$q$</td>
<td>Phonon wave number</td>
</tr>
<tr>
<td>$q_D$</td>
<td>Debye radius</td>
</tr>
<tr>
<td>$c_g$</td>
<td>Phonon group speed</td>
</tr>
<tr>
<td>$\bar{c}$</td>
<td>Acoustic phonon average speed</td>
</tr>
<tr>
<td>$\psi_{qs}$</td>
<td>Deviation function of phonon from equilibrium</td>
</tr>
<tr>
<td>$C_v$</td>
<td>Volumetric specific heat</td>
</tr>
<tr>
<td>$\tau_{bs}$</td>
<td>Boundary scattering relaxation time</td>
</tr>
<tr>
<td>$L$</td>
<td>Effective boundary length</td>
</tr>
<tr>
<td>$\bar{M}$</td>
<td>Unit cell average mass</td>
</tr>
<tr>
<td>$f_i$</td>
<td>Fraction of the unit cells with mass $M_i$</td>
</tr>
<tr>
<td>$\bar{c}$</td>
<td>Average speed of acoustic phonon</td>
</tr>
<tr>
<td>$\Gamma_{pd}$</td>
<td>Isotropic mass parameter</td>
</tr>
<tr>
<td>$C_1$</td>
<td>Constant</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Atoms local dilation</td>
</tr>
<tr>
<td>$\alpha_{LA}$</td>
<td>Longitudinal speed of acoustic phonons</td>
</tr>
<tr>
<td>$\Xi$</td>
<td>Dilatational deformation potential</td>
</tr>
<tr>
<td>$z$</td>
<td>Reduced phonon energy</td>
</tr>
</tbody>
</table>
\( \xi \)  
Kinetic energy of phonon

\( \tau_{ep} \)  
Donor electron-phonon scattering relaxation time

\( \phi_3 \)  
Anharmonic potential of crystal

\( \gamma(T) \)  
Grüneisens constant

\( a_{qs}^+ \)  
Phonon creation operator

\( a_{-qs} \)  
Phonon annihilation operator

\( \rho \)  
Material density

\( \delta_{q+q'+q''} \)  
Kronecker delta function

\( \tau_{\text{anh}}^{-1} \)  
Phonon-phonon scattering rate

\( \tau_N^{-1} \)  
Normal processes scattering rate

\( \tau_U^{-1} \)  
Umklapp processes scattering rate

\( \kappa_{\text{smrt}} \)  
Single mode relaxation time (smrt)

\( \tau_R \)  
Resistive processes

\( \tau_C \)  
Callaway’s effective relaxation time

\( \beta_C \)  
Callaway’s correction coefficient

\( \kappa_C \)  
Callaway’s lattice thermal conductivity

\( \tau_A \)  
Allen’s effective relaxation time

\( \beta_A \)  
Allen’s correction coefficient

\( \kappa_A \)  
Allen’s lattice thermal conductivity

\( E_F(T) \)  
Fermi level

\( \zeta_g \)  
Reduced band gap

\( m_l^* \)  
Longitudinal effective mass

\( m_t^* \)  
Transverse effective mass

\( m_d^* \)  
density of states effective mass

\( N_{\text{val}} \)  
Number of band’s valleys
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_0$</td>
<td>Thermal electron concentration</td>
</tr>
<tr>
<td>$p_0$</td>
<td>Thermal hole concentration</td>
</tr>
<tr>
<td>$m_{de}^*$</td>
<td>Electron density of states effective mass</td>
</tr>
<tr>
<td>$m_{dh}^*$</td>
<td>Hole density of states effective masses</td>
</tr>
<tr>
<td>$\rho_{\text{int}}$</td>
<td>Intrinsic electrical conductivity</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Electrical mobility</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Electron mobility</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Intrinsic electron concentration</td>
</tr>
<tr>
<td>$p_i$</td>
<td>Intrinsic hole concentration</td>
</tr>
<tr>
<td>$\sigma_n$</td>
<td>Electron conductivity</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>Hole conductivity</td>
</tr>
<tr>
<td>$\kappa_{\text{bp}}$</td>
<td>Bipolar electronic thermal conductivity</td>
</tr>
<tr>
<td>$\omega_{\text{LA}}$</td>
<td>Frequency of longitudinal acoustic phonon</td>
</tr>
<tr>
<td>$\omega_{\text{TA}}$</td>
<td>Frequency of transverse acoustic phonon</td>
</tr>
<tr>
<td>$\omega_{\text{TO}}$</td>
<td>Frequency of transverse optical phonon</td>
</tr>
<tr>
<td>$\omega_{\text{LO}}$</td>
<td>Frequency of longitudinal optical phonon</td>
</tr>
<tr>
<td>$\omega_{\text{min}}_{\text{TO}}$</td>
<td>Minimum frequency at the zone centre</td>
</tr>
<tr>
<td>$\omega_{\text{max}}_{\text{LO}}$</td>
<td>Maximum frequency at the zone centre</td>
</tr>
<tr>
<td>$g_{\text{TA}}(\omega)$</td>
<td>density of states of TA phonon</td>
</tr>
</tbody>
</table>
$g_{\text{LA}}(\omega)$  density of states of LA phonon
$g_{\text{TO}}(\omega)$  density of states of TO phonon
$g_{\text{LO}}(\omega)$  density of states of LO phonon
$c_{\text{TA}}$  Speed of TA phonon
$c_{\text{TO}}$  Speed of TO phonon
$c_{\text{LO}}$  Speed of LO phonon
$B_{\text{pd}}$  Adjustable parameter
$N_d$  Concentration of donor’s atom
$R_{TBR}$  The thermal boundary resistance
$U_{1\to2}$  Current density from side 1 to 2 of the interface
$t_{12}$  Transmission probability from side 1 to 2
$t_{12}^a$  Acoustic mismatch model transmission probability
$t_{12}^d$  Diffusion mismatch model transmission probability
$\kappa^0$  Conductivity of homogeneous medium
$\kappa'(r)$  Conductivity of Perturbation term
$G$  Green function
$T$  Transition matrix
$I$  Unit tensor
$T_n$  Transition matrix of the n particle
$\kappa_{\text{eff},\perp}$  Effective thermal conductivity across the particle-host interface
$\kappa_h$  Host matrix thermal conductivity
$g$  
Structure-related dimensionless parameter

$d$  
Effective size of the inserted particle

$\kappa_p$  
Particle thermal conductivity

$V_f$  
Particle volume fraction

$\alpha$  
Dimensionless quantity

$\Phi$  
Interface density

$C_{v,h}$  
Host volumetric specific heat

$C_{v,p}$  
Particle volumetric specific heat

$\tau_{\text{eff,ND}}^{-1}(h)$  
Host effective phonon boundary scattering rate

$\tau_{\text{eff,ND}}^{-1}(p)$  
Particle effective phonon boundary scattering rate

$L_w$  
Length of the wire

$L_{\text{cell}}$  
Size of a unit cell for the nanocomposite system
Contents

List of Abbreviations iv

List of Symbols and Notations vi

1 Introduction to Thermoelectricity 1

1.1 Introduction ......................................................... 1

1.2 Thermoelectric Phenomenon ...................................... 2
  1.2.1 Seebeck Effect ................................................. 2
  1.2.2 Peltier Effect .................................................. 3
  1.2.3 Thomson Effect ................................................. 4

1.3 Efficiency of Thermoelectric Materials ......................... 4
  1.3.1 Efficiency of Power Generator and Figure of Merit .......... 5
  1.3.2 Choice of Materials ............................................ 7
  1.3.3 Figure of Merit Optimization ................................... 9

1.4 Thermoelectric Materials ......................................... 9
  1.4.1 Conventional Thermoelectric Materials ....................... 10
  1.4.2 Advanced Bulk Materials ...................................... 11
  1.4.3 Low Dimensional Materials .................................... 12
    1.4.3.1 Quantum Well Superlattices .............................. 14
    1.4.3.2 Quantum Wires ........................................... 15
    1.4.3.3 Quantum Dot Superlattices .............................. 16
CONTENTS

1.5 Nanocomposites ................................................. 17
1.6 Lead Chalcogenides ............................................. 18
1.7 Chapter Summary and Thesis structure ......................... 19

2 Theory of Electronic Thermal Coefficients .................... 29
  2.1 Introduction .................................................. 29
  2.2 Coupled Current Equations .................................. 30
      2.2.1 Boltzmann Transport Equation ............................. 32
  2.3 Electronic Thermal Transport Coefficients .................... 35
      2.3.1 Crystal Structure ......................................... 37
      2.3.2 Simple Band Structure of Common Semiconductors for Trans-
           port Calculations ........................................... 40
  2.4 Electronic Thermal Transport coefficients in Semiconductor structure 41
      2.4.1 Degenerate and non-degenerate Semiconductors ............. 45
  2.5 Chapter Summary ............................................... 47

3 Theory of Phonon Thermal Conductivity ....................... 50
  3.1 Introduction .................................................. 50
  3.2 Phonons ....................................................... 52
  3.3 Phonon Dispersion Relations .................................. 53
      3.3.1 Phonon Density of States within the Isotropic Continuum
           Approximation and the Debye Model ........................ 56
  3.4 Lattice Thermal Conductivity .................................. 57
      3.4.1 Relaxation Time Approximation ............................. 61
      3.4.2 Phonon Scattering Mechanisms ............................. 62
          3.4.2.1 Extrinsic Relaxation Times ........................... 62
      3.4.3 Intrinsic Relaxation Times ................................ 64
          3.4.3.1 Three-Phonon Processes ............................... 65
  3.5 Different Theories of Total Relaxation Times ................ 66
3.6 Isotropic Continuum model and Conductivity Expressions

3.7 Chapter Summary

4 Calculations of TE Properties of PbTe

4.1 Introduction

4.2 Electronic Transport Coefficients

4.2.1 Temperature Dependence of Fermi Level

4.2.2 Density of States Effective mass

4.3 Transport Coefficients for n-Type Semiconductors

4.3.1 Electrical Conductivity

4.3.2 Electronic Thermal Conductivity

4.3.3 Seebeck coefficient

4.4 Lattice thermal transport coefficient

4.4.1 Acoustic Phonon Lattice Thermal Conductivity

4.4.2 Phonon Scattering Rates

4.5 Results and Discussion

4.5.1 Electronic transport coefficients

4.5.2 Vibrational and Thermal Properties

4.5.2.1 Phonon Dispersion Curves and Density of States

4.5.2.2 Lattice Specific Heat

4.5.2.3 Lattice Thermal Conductivity

4.5.3 Total Thermal Conductivity

4.5.4 Thermoelectric Figure of Merit

4.6 Chapter Summary

5 Three-phonon Scattering Processes and Thermal Conductivity in IV-chalcogenides

5.1 Introduction

5.2 Pb-chalcogenides and SnTe Crystal Structure
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Dispersion Relations and Density of States</td>
<td>112</td>
</tr>
<tr>
<td>5.4</td>
<td>Lattice Thermal Conductivity</td>
<td>113</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Phonon Interactions</td>
<td>114</td>
</tr>
<tr>
<td>5.4.1.1</td>
<td>Extrinsic Phonon Interactions</td>
<td>114</td>
</tr>
<tr>
<td>5.4.1.2</td>
<td>Anharmonic Interaction</td>
<td>114</td>
</tr>
<tr>
<td>5.5</td>
<td>Results and Discussion</td>
<td>115</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Three-phonon Scatterings</td>
<td>118</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Lattice thermal Conductivity Results</td>
<td>122</td>
</tr>
<tr>
<td>5.6</td>
<td>Chapter Summary</td>
<td>134</td>
</tr>
<tr>
<td>6</td>
<td>Size and Dimensionality Dependent Phonon Conductivity in Nanocomposites</td>
<td>137</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>137</td>
</tr>
<tr>
<td>6.2</td>
<td>Thermal Boundary Resistance</td>
<td>140</td>
</tr>
<tr>
<td>6.2.1</td>
<td>The Acoustic Mismatch Model</td>
<td>142</td>
</tr>
<tr>
<td>6.2.2</td>
<td>The Diffuse Mismatch Model</td>
<td>143</td>
</tr>
<tr>
<td>6.3</td>
<td>Thermal Conductivity of Nanocomposites</td>
<td>144</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Host and Particle Bulk Thermal Conductivity</td>
<td>146</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Relaxation Rate in Nanocomposites</td>
<td>146</td>
</tr>
<tr>
<td>6.4</td>
<td>Results and Discussion</td>
<td>147</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Nanodots</td>
<td>150</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Comparative Conductivity Results for Nanodots and Nanowires</td>
<td>158</td>
</tr>
<tr>
<td>6.4.3</td>
<td>Comparative Conductivity Results for NDs, NWs and SLs</td>
<td>158</td>
</tr>
<tr>
<td>6.4.4</td>
<td>Role of Nanocompositing on Optimizing Thermoelectric Figure of Merit</td>
<td>161</td>
</tr>
<tr>
<td>6.5</td>
<td>Chapter Summary</td>
<td>163</td>
</tr>
<tr>
<td>7</td>
<td>Summary and Suggestions for future work</td>
<td>167</td>
</tr>
</tbody>
</table>
List of Figures

1.1 Schematic basic thermocouple. ........................................... 3
1.2 Schematic of thermoelectric (a) power generator and (b) refrigerator. 7
1.3 Classification of TE materials determined by the dependence of (a) 
$\sigma$ and $S$, (b) thermal conductivity on free carriers concentration. 
Taken from [13]. ................................................................. 8
1.4 Classification of TE materials for three operating temperature ranges. 
Taken from [16]. ................................................................. 10
2.1 The atomic structure for a rock salt crystal. The vectors $a_1$, $a_2$, and 
$a_3$ are the primitive translation vectors of the fcc lattice. .............. 39
2.2 The central or first Brillouin zone for the fcc lattice. From Srivas-
tava (unpublished). .............................................................. 39
2.3 Real electronic band structure, taken from [12] and for PbTe, PbSe, 
and PbS, and for SnTe the structure is taken from [13]. The rele-
vance of the red boxed area in PbTe is discussed in the text. ........... 42
2.4 Schematic electronic band structure in the nearly free electron ap-
proximation. ........................................................................ 43
2.5 Carrier density of states corresponding to the band structure in Fig. 
2.4. ....................................................................................... 44
3.1 Schematic dispersion curves for (a) mono-atomic and (b) diatomic 
linear chain in the first Brillouin zone. ...................................... 57
3.2 The phonon dispersion curves in PbTe, PbSe, and PbS. Symbols are experimental measurement using inelastic neutron technique and are taken from [16], [17], and [18] for PbTe, PbSe, and PbS, respectively. Solid and dashed lines are modeled data using shell model and force constant model, respectively [19].

3.3 The density of normal modes for: (a) mono-atomic chain and (b) diatomic chain.

3.4 The Debye model of the density of normal modes for mono-atomic unit cell for a three dimensional solid.

3.5 Schematic illustration of three-phonon processes class 1: (a) an N process \( q + q' = q'' \) and (b) an U process \( q + q' = q'' + G \).

4.1 Temperature variation of Fermi level in n-type PbTe with donor concentration \( 2.6 \times 10^{18} \text{ cm}^{-3} \). The conduction band and valence band edges are drawn as dashed and dashed-dot horizontal lines, respectively.

4.2 (a) Seebeck coefficient and (b) electrical resistivity for the n-type PbTe with donor concentration \( 2.6 \times 10^{18} \text{ cm}^{-3} \). The solid and dot curves for \( \rho \) represent the intrinsic (bipolar) and extrinsic (monopolar) contributions, respectively. The experimental data is taken from [14].

4.3 (a) Linearised phonon dispersion relations in PbTe, (b) the corresponding density of states, and (c) density of states obtained from a realistic phonon dispersion relations in [38].

4.4 Lattice specific heat at constant volume \( C_v \) for PbTe. The results from the present work are compared with the experimental measurements (Expt. (1954) [44]) and first-principles theoretical calculations (Theory (2009) [38] and Theory (2011) [43]).
4.5 Calculated lattice thermal conductivity $\kappa_{\text{ph}}$ results for sample 1. In panel (a) the black solid curve represents the results by considering the acoustic phonons as heat carriers but including their interaction with optical phonons, and the green dashed-dotted curve represents the results when both acoustic as well as optical phonons are considered as heat carriers and allowed anharmonic interactions among all branches are included. Panel (b) shows the percentage contribution from acoustic phonons. Panel (c) shows contributions from individual acoustic and optical branches. 96

4.6 Lattice thermal conductivity results ($\kappa_{\text{ph}}$) for three different n-PbTe samples taken from Refs. [14] (sample 1), [11] (sample 2) and [46] (sample 3). 97

4.7 The total anharmonic relaxation rate for LA, TA, and TO branches as a function of the reduced wave-vector at (a) $T = 300$ K, (b) $T = 900$ K for PbTe. 98

4.8 Anharmonic scattering rates at $T = 900$ K for (a) $ac + ac \rightarrow ac$ (N), (b) $ac + op \rightarrow op$ (N), (c) $op + ac \rightarrow op$ (N) and (d) $op + op \rightarrow op$ (N) processes. 99

4.9 Comparison between N and U scattering rates at $T = 900$ K for the relaxation of LA and TA phonons. 100

4.10 Relaxation rates of the total Normal processes and the total anharmonic processes for TO and TA phonons at $x = 0.342$ for (a) low temperatures and (b) high temperatures. Panel (c) presents the relaxation rate of the total Normal processes and the total anharmonic processes for TO and TA phonons at $x = 0.969$ as a function of temperature. 101

4.11 Total thermal conductivity ($\kappa_{\text{tot}} = \kappa_{\text{mp}} + \kappa_{\text{ph}}$) of sample 1 in Ref. [14]. 102
4.12 Figure of merit $ZT$ for the n-type sample of PbTe prepared and studied by Pei et al. [14] The experimental data is deduced from the measured values of $S$, $\rho$ and $\kappa_{\text{tot}}$ in Ref. [14]...

5.1 SnTe phonon dispersion relations at 100 K. The full lines are for calculations using the shell model [12] and the symbols are from inelastic neutron scattering techniques measurements[12]...

5.2 Phonon dispersion curves and density of states used in this work: (a) PbTe, (b) PbSe, (c) PbS, and (d) SnTe. The variable $x$ represents the reduced phonon wave-number: $x = q/q_D$...

5.3 Comparison of U and N relaxation rates in PbTe and SnTe. Here we have plotted the ratio of $\tau_{s,\text{process}1}/\tau_{s,\text{process}2}$. The curves are annotated as follows: $\text{LA}(U)/\text{LA}(N)$ represents $\tau_{\text{LA},U}/\tau_{\text{LA},N}$, $\text{TA}(U)/\text{TA}(N)$ represents $\tau_{\text{TA},U}/\tau_{\text{TA},N}$, and $\text{LO}(U)/\text{LO}(N)$ represents $\tau_{\text{LO},U}/\tau_{\text{LO},N}$...

5.4 Relative strengths of three-phonon scattering rates in PbTe and SnTe. Here we have plotted the ratio $\tau_{s}^{-1}/\tau_{\text{TA}}^{-1}$, where $s$ is a polarisation index...

5.5 Inverse relaxation time due to Class 1 three-phonon Normal processes for: (a) $\text{TO}$ phonons in PbTe at 300 K; (b) $\text{TO}$ phonons in SnTe at 300 K; (c) $\text{LO}$ phonons in PbTe at 300 K; (d) $\text{LO}$ phonons in SnTe at 300 K. Inverse relaxation time due to Class 2 three-phonon Normal processes for: (e) $\text{LO}$ phonons in PbTe at 300 K; (f) $\text{LO}$ phonons in SnTe at 300 K...

5.6 (a): The ratio $\tau_{\text{LO}}^{-1}/\tau_{\text{TO}}^{-1}$ in SnTe and PbTe. (b): comparison of $\tau_{\text{LO}}^{-1}$ in SnTe and PbTe...
5.7 The shadowed area represents the allowed phase space for \( \text{TO} + \text{TA} \rightarrow \text{LO}(\text{N}) \) and \( \text{TO} + \text{LA} \rightarrow \text{LO}(\text{N}) \) processes in in SnTe. The variables \( x = q/q_D \) and \( x' = q'/q_D \) represent the reduced wave-numbers for \( \text{TO} \) and \( \text{TA} \) modes in the left panel, and for \( \text{TO} \) and \( \text{LA} \) modes in the right panel.

5.8 Lattice thermal conductivity of (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS. Solid and dashed curves represent the theoretical results compared to different experimental measurements. Experimental results are represented with symbols: closed squares, circles, down triangle, up triangle, and diamonds are taken from Refs. \([1]\), \([14]\), \([2]\), \([15]\), and \([16]\), respectively.

5.9 Variation of conductivity with point defect parameter \( B_{pd} \) in SnTe at 100 K and 300 K. The numerical data (in symbols) are fitted to a curve using the variation \( \kappa \propto B_{pd}^3 s^3 \).

5.10 Percentage conductivity contributions from individual phonon polarizations in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.

5.11 The Normal-drift contribution to the lattice thermal conductivity using the original Callaway expression in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.

5.12 Comparison of the conductivity results using the (original) Callaway’s expression and the (modified) Allen’s expression in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.

6.1 Temperature variation of the thermal boundary \( R_{TBR} \) resistance at the PbTe/PbSe interface.

6.2 Lattice thermal conductivity results, computed using Callaway’s expression, for bulk PbTe and PbSe samples in [35].
6.3 Effective conductivity $\kappa_{\text{h,eff}}$ of PbTe host to which PbSe NDs of different diameters and different volume fractions have been inserted. 151

6.4 The parameter $\alpha$ for the PbSe ND insertion in the PbTe host. . . . . . . . . 153

6.5 The parameter $g$ for the ND insertion in the PbTe host. . . . . . . . . . . . 154

6.6 Thermal conductivity of the PbTe-PbSe ND nanocomposite. Low- and high-temperature results are presented in panels (a) and (c), and (b) and (d) respectively. 155

6.7 Variation of (a) $\alpha$, (b) $g$, (c) $\kappa_{\text{eff}}(\text{PbTe})$, and (d) $\kappa_{\text{mEMA}}$ for the ND composite at $T = 99$ K. The symbols represent the calculated results and the lines are guide to the eye. 157

6.8 Effective thermal conductivity across the PbSe infinite nanowires embedded in the PbTe matrix for different $\Phi$ with $V_f = 0.1$ at (a) low and (b) high temperatures. 159

6.9 Effective Thermal conductivity of the PbSe-PbTe nanocomposite as a function of (a) PbSe nanosphere diameter and (b) PbSe nanowire diameter embedded in the PbTe matrix. The symbols represent the calculated results and the lines are guide to the eye. 160

6.10 Effective Thermal conductivity for different PbTe-PbSe nanocomposite configurations. 162
List of Tables

4.1 The electronic parameters of PbTe. ........................................ 87
4.2 Parameters used for phonon transport calculations in PbTe. ........ 88
4.3 Effective boundary length $L$ and adjusted point defect parameter $B_{pd}$ used for fitting the experimental results of lattice thermal conductivity for three samples of PbTe. .............................. 95

5.1 The phonon speeds $c_{TA}$, $c_{LA}$, $c_{TO}$, and $c_{LO}$ for SnTe, PbSe, and PbS. 116
5.2 Material parameters for SnTe, PbTe, PbSe, and PbS. The dopant concentrations $n/p$ are taken from the experimental papers cited in the Table. The Debye radius $q_D$, the point defect constant $B_{pd}$, the deformation potential $\Xi$, and the Grüneisen constant $\gamma$ are treated as adjustable parameters. * These are the modified values when considering the contribution from four valleys. ......................... 116

6.1 Material parameters for PbTe and PbSe. The dopant concentrations $n$ are taken from the experimental paper cited in the Table. The Debye radius $q_D$, the point defect constant $B_{pd}$ .......................... 148
6.2 Expressions for the volume fraction $V_i$ and the corresponding interface density $\Phi$ for PbTe-PbSe nanocomposites, with PbSe insertion as nanosphere (ND), cylindrical nanowire (NW) and flat plate (SL). Here $r = d/2$ is the particle radius, $L_w$ is the length of the wire, $L_{PbSe}$ represents the thickness of PbSe plate layer, and $L_{cell}$ represents the effective size of the cubic host (PbTe) cell which is used to define $V_i$ and $\Phi$. The symbols $\parallel$ and $\perp$ represent the heat flow direction along and across the interface boundary. Note that the entry NW$\parallel$ is not required for the nanowire of infinite length. Similarly, we only require SL$\perp$ for the flat plate insertion resulting in PbSe-PbTe superlattice formation.
Chapter 1

Introduction to Thermoelectricity

1.1 Introduction

Heat conduction has been scientifically appreciated since the discovered correlation between the geographical regions inhabited by human and the ability to withhold heat loss from the body. Furs, skins, and wool have been used as means of protection against cold weather due to their ability to conserve heat, i.e. poor thermal conductivity. In many industrial applications material thermal properties are examined before being approved as a possible candidate for such applications. For applications that require a minimum heat conduction, materials making up the device should be characterized by a low thermal conductivity. On the other hand, other practical applications might need high thermal conductivity materials. However, for either application, such thermal properties will always be associated with other mechanical and electrical requirements, for example, the mechanical strength, the electrical conductivity, etc. [1].

Over the past decade, the quest for developing alternative energy resources, that do not depend on fossil fuels, has heightened the interest in the field of thermoelectrics. Thermoelectric materials (TE) are known by the ability to convert heat into electricity and vice versa. Such materials are used for power-generation
1.2 Thermoelectric Phenomenon

Three types of thermoelectric phenomenon are found in an electrically conductive material:

1.2.1 Seebeck Effect

The term ‘Seebeck effect’ is used in reference to the effect first discovered by Seebeck in the beginning of the 19th century [2]. Figure 1.1 demonstrates the Seebeck effect principle, where both ends of two dissimilar conductors A and B are joined. Seebeck showed that heating the junctions connecting the two different
1.2 Thermoelectric Phenomenon

Figure 1.1: Schematic basic thermocouple.

electrical conductors with different temperatures could induce an electromotive force (emf). If a temperature difference $\Delta T = T_1 - T_2$, with $T_1 > T_2$, is maintained at the junctions, a galvanometer inserted between the free ends of conductor B will indicate a flow of current, indicating the generation of an open circuit emf. The developed potential difference $\Delta V$ is written as

$$\Delta V = S\Delta T,$$

(1.1)

where $S$ is the Seebeck coefficient or the thermopower. The Seebeck effect represents a direct transformation of heat into electricity without the use of intermediate machines [3]. It has been widely applied for temperature measurement and is considered as the working principle of thermoelectric generators.

1.2.2 Peltier Effect

The reverse of the Seebeck effect is known as the Peltier effect. Peltier observed that a temperature difference is induced by the voltage difference at a junction of two dissimilar materials, i.e. a current $I_e$ flows through this junction. As the current flows, it carries a thermal energy causing a drop of temperature at one junction and increase at the other [4]. The rate of heating(cooling) $Q_p(-Q_p)$ is
related to the electric current $I_e$ as

$$Q_P = \Pi I_e,$$

(1.2)

where $\Pi$ is the Peltier coefficient. This effect should not be confused with the Joule heating effect. The Peltier effect is considered as the basis principle of thermoelectric refrigerators [5].

### 1.2.3 Thomson Effect

When a current is flowing in a homogeneous conductor with a certain temperature gradient, heat is absorbed or produced. This phenomenon is known as the Thomson effect [6]. When a unit electric current flows along a conductor that is subjected to a unit temperature gradient, the rate of heating generated or absorbed per unit length of the material is the Thomson coefficient.

### 1.3 Efficiency of Thermoelectric Materials

The principle of modern thermoelectric power generation devices is based on the Seebeck effect. For such devices, the usefulness is measured by the device efficiency $\eta_G$, which is defined as the ratio of the output power to the rate at which heat is absorbed from the source. On the other hand, thermoelectric refrigeration devices are known to utilise the Peltier effect. The performance of a refrigerator is generally expressed by its coefficient of performance (COP). This is given as the ratio of the produced cooling power to the rate at which electrical energy is supplied.

Figure 1.2 shows a typical configuration of thermoelectric power generator (a) and refrigerator (b). The thermoelectric module consists usually of several thermoelements, i.e. semiconducting materials, where one element is doped to produce an excess of electrons creating (n-type) while the other is doped to create
1.3 Efficiency of Thermoelectric Materials

an electron deficiency producing (p-type). These thermoelements are connected electrically in series and thermally in parallel. As shown in Figs. 1.2, the same module is used for both power generation and refrigeration. In the thermoelectric energy generator Fig. 1.2 (a), a current is driven through a load resistance when a temperature difference is imposed across the module. Conversely, when an electric current passes through the junction in Fig. 1.2 (b) heat is absorbed on one side of the junction, transferred through the thermoelements, and emitted at the other side providing a refrigeration capability [7].

1.3.1 Efficiency of Power Generator and Figure of Merit

For the single-couple thermoelectric generator shown in Fig. 1.2 (a), the thermoelements junction, at temperature $T_1$ (hot), is connected in series to the load resistance $R_L$, at temperature $T_2$ (cold). In the steady state, a temperature difference $T_2 - T_1$ is maintained across the element. Due to the Seebeck effect, an electrical current $I_e$ proportional to the temperature difference $\Delta T$ between the hot and cold junctions will be produced. If the total internal resistance of the two elements is $R$ and $S_{pn} \equiv S_p - S_n$ is the resultant Seebeck coefficient of the n-type and p-type thermoelements, the current can be defined as

$$I_e = \frac{S_{pn} \Delta T}{R + R_L}.$$  \hspace{1cm} (1.3)

The efficiency of the power generator is given as

$$\eta_G = \frac{W}{Q_a},$$  \hspace{1cm} (1.4)

where $W$ is the power delivered to the load and $Q_a$ is the rate at which heat is consumed from the heat source. Assuming that half of the total Joule heat, $I_e^2 R$, returns to the hot junction at $T_1$ while the other half is delivered to the cold junction and by assuming that for both elements $S$ is the same at both ends the
Thomson heat can be set to zero, then, $Q_a$ can be expressed as

$$Q_a = S_{pn}I_eT_1 + \kappa'\Delta T - I_e^2R/2.$$  \hspace{1cm} (1.5)

The first and second terms on the right-hand side of Eq. 1.5 are the Peltier heat and the transferred heat by thermal conduction, respectively. The third term is the returned electrical energy to the heat source. $\kappa'$ is known as the total thermal conductance and is defined as

$$\kappa' = \frac{\kappa_n A_n + \kappa_p A_p}{l},$$  \hspace{1cm} (1.6)

where $A_n(A_p)$, $\kappa_n(\kappa_p)$, and $l$ are the cross-section area of the n-type(p-type) thermoelement, the thermal conductivity of the n-type(p-type) thermoelement, and the length of the thermoelement, respectively. Putting $m = R_L/R$, the efficiency of the thermoelectronic generator in terms of thermoelectric material properties, $\eta_G$ can be expressed as [8]

$$\eta_G = \frac{T_1 - T_2}{T_1} - \frac{m/(m+1)}{1 + \frac{m+1}{ZT_1} - \frac{1}{2} \frac{\Delta T}{T_1} \frac{1}{m+1}},$$  \hspace{1cm} (1.7)

where the quantity $\frac{\kappa'R}{S_{pn}}$ is denoted by $1/Z$. For a single material this can be written as

$$Z = \frac{S^2\sigma}{\kappa},$$  \hspace{1cm} (1.8)

where $\sigma$ is the electrical conductivity. The above expression presents a standard measure of the thermoelectric performance and is usually referred to as the figure of merit, which is found to be directly proportional to the maximum efficiency of thermoelectric power generator [9]

$$\eta_{\text{max}} = \frac{T_1 - T_2}{T_1} \sqrt{1 + ZT - \frac{1}{T_1}}.$$  \hspace{1cm} (1.9)

This maximum could be achieved by choosing $R_L$ so that $W$ is a maximum. It is convenient to define the dimensionless figure of merit $ZT$ for a single material in the form

$$ZT = \frac{S^2\sigma}{\kappa}T.$$  \hspace{1cm} (1.10)
1.3 Efficiency of Thermoelectric Materials

Applications of TE materials have been bounded, for more than 30 years, by the upper limit $ZT \approx 1$. Equation 1.10 suggests that an increase in the figure of merit is possible by decreasing the thermal conductivity or increasing either $S$ or $\sigma$. Although there are no restrictions employed by thermodynamics on placing an upper limit on the dimensionless figure of merit, for many years, researchers have failed to achieve a value exceeding unity.

### 1.3.2 Choice of Materials

Materials are classified, according to their electronic structure, into metals, semiconductors, and insulators [10]. While metals are very good electrical conductors ($\sigma \approx 10^6 \Omega^{-1} \text{cm}^{-1}$), they exhibit a very low Seebeck coefficient $S \approx 5 \mu \text{VK}^{-1}$ at room temperature and a large thermal conductivity, giving rise to typical values for the figure of merit of $ZT \approx 3 \times 10^{-6}$ at 300 K. Hence, metals are marked as undesirable for power generation application. Insulators, on the other hand, have a large Seebeck coefficient $S \approx 1 \text{ mVK}^{-1}$ or higher. However, they exhibit
1.3 Efficiency of Thermoelectric Materials

![Diagram of TE material classification]

Figure 1.3: Classification of TE materials determined by the dependence of (a) $\sigma$ and $S$, (b) thermal conductivity on free carriers concentration. Taken from [13].

An extremely low electrical conductivity, it is found to be of the order $10^{-12}\Omega^{-1} \text{ cm}^{-1}$, and so insulators will have a lower power factor $S^2\sigma$ than what is generally desirable for power generator [11, 12].

Researchers have been engaged in several theoretical studies and experimental measurements to find materials that have the combined characterization of low thermal conductivity and high power factor. Materials with such features have the potential of being good thermoelectrics. Figure 1.3 shows that compared to other classes of materials, semiconductors have the largest power factor with a reasonably low thermal conductivity [5, 6, 14]. Therefore, recent researches have been focusing primarily on optimizing the performance of this class of materials.
1.3.3 Figure of Merit Optimization

A good TE material will have the ability to maintain the temperature gradient, which presents a crucial condition for a reliable TE device in addition to the desired intrinsic material parameters that appear in the figure of merit (see Eq. 1.10). This equation indicates that to optimise the performance of a thermoelectric device, a high Seebeck coefficient, a large electrical conductivity, \textit{i.e.} a large power factor, and a low thermal conductivity are required. However this task is far from being straightforward. Since the determination of these parameters, except for the lattice thermal conductivity, requires a full knowledge of the material electronic structure and carrier scattering mechanisms, it is not possible to manipulate them independently as can be seen from Fig. 1.3. In semiconductors the Seebeck coefficient and the electrical conductivity are interrelated, since they are both functions of the free charge carrier concentration [11]. This results in setting an upper limit on optimizing the figure of merit through maximizing the power factor. However, it is well known that heat is carried by charge carriers as well as by lattice vibrations. Therefore, the thermal conductivity $\kappa$ has two components, the lattice thermal conductivity $\kappa_{ph}$ and the electronic thermal conductivity, referred to as the charge carriers contribution $\kappa_{mp}$. Thus, the total thermal conductivity is the sum of these two components, $\kappa = \kappa_{ph} + \kappa_{mp}$, and since the lattice thermal conductivity is the only parameter that does not depend on the material electronic structure, it offers a promising opportunity to be controlled separately for enhancing the performance of TE power generator devices [15].

1.4 Thermoelectric Materials

Thermoelectric materials are classified into three classes corresponding to low, moderate, and high temperature ranges as shown in Fig. 1.4: for low temperature applications, up to 450 K, alloys based on bismuth combined with antimony,
1.4 Thermoelectric Materials

Figure 1.4: Classification of TE materials for three operating temperature ranges. Taken from [16].

tellurium and selenium are used; for the intermediate temperature applications, which range up to 850 K, the group of materials based on lead telluride (PbTe) is employed; and in the third class silicon germanium alloys are used for applications that require high temperatures up to 1300 K. In the following sections we will demonstrate some of the progress reported for different approaches employed to increase $ZT$.

1.4.1 Conventional Thermoelectric Materials

In 1950s, bulk thermoelectric materials with $ZT \approx 0.8$ and efficiency between 5 – 6%, were discovered [17]. Up until 1990s, there was little interest in the thermoelectric field because of the low efficiency. In mid-1990s, thermoelectric materials gained more interest and extensive works have been in progress to reveal new research directions that would lead to well performing thermoelectric materials. As a consequence, two research approaches were adopted for developing new thermoelectric materials: the first approach is based on the use of new advanced bulk thermoelectric materials, and the second is based on employing low-dimensional systems [18].
In the first approach alloying has provided a significant reduction of the lattice thermal conductivity without much degradation in the electrical conductivity. Alloying thermoelectric materials through the mass difference scattering with fine tuning of carrier concentration has succeeded in improving the figure of merit in some thermoelectric materials. Alloy TE materials of n-type have shown $ZT$ values in the range of 0.8 to 1.1. On the other hand, mid-temperature materials alloyed, particularly with AgSbTe$_2$, have led to $ZT$ values greater than unity, while p-type alloy (GeTe)$_{0.58}$(AgSbTe$_2$)$_{0.15}$ has exceeded 1.2 [16].

For many years, Bi-Sb and Bi$_2$Te$_3$ alloys, have been the best recognised materials with a decent $ZT$ value below room temperature. Kanatzidism’s group at Michigan State University, has grown new chalcogenides composed mostly of heavy elements. These materials are based on CsBi$_4$Te$_6$ with $ZT \approx 0.8$ at $T = 220$ K [19]. Another group of complex chalcogenides recognised by Sharp et al. [20] were Tl$_2$SnTe$_5$ and Tl$_2$GeTe$_5$. Those compounds are characterised by a very low thermal conductivity of $\approx 0.5$ Wm$^{-1}$K$^{-1}$ and a figure of merit of about 0.6 at 300 K.

The strong interrelation between the three parameters in the figure of merit has, for many years, set a limit upon improving $ZT$ for bulk materials. In such systems, the Wiedemann-Franz law shows the electronic thermal conductivity to be directly proportional to $\sigma$, and as seen in Fig.1.3 (a) materials with high Seebeck coefficient tend to have a low $\sigma$. Consequently, an increase in the electrical conductivity leads to a disadvantageous alteration in both $\kappa$ and $S$ [21].

### 1.4.2 Advanced Bulk Materials

In 1995, Slack (see Ref. 18 in Ch. 8 in [6]) described a good thermoelectric material as a narrow gap semiconductor with high carrier mobility and low thermal conductivity. According to Slack the ideal TE material is a semiconductor with
1.4 Thermoelectric Materials

one of the atoms or molecules weakly bound in an over-sized atomic cage, referred to as the Phonon Glass Electron Crystal (PGEC) approach. This situation produces large vibrational amplitudes (rattlers) at partially filled structural sites, thereby they act as traps for acoustic phonons (vibrations with low frequencies for small wave vectors) and prevent them from conducting heat, hence decreasing the thermal conductivity for the whole system. The most prominent of these bulk materials are the partially filled skutterudites based on alloy of CoSb$_3$ [22]. Another way to reduce the thermal conductivity is by increasing the lattice period, i.e. large unit cell. As this will result in shortening the phonon mean free path. This effect was observed in the complex structures of ternary and quaternary bismuth chalcogenides [23]. Chen et.al. [18] have shown a reduction of up to one order of magnitude in the lattice thermal conductivity at room temperature when going from binary compounds to more complex structure. Recently, the maximum $ZT$ value achieved was 1.4 at 875 K in Ce$_{f}$Fe$_{4-x}$Co$_{4-x}$Sb$_{12}$ ($f \leq 1$, $0 < x < 4$). Another class of PGEC materials are clathrates which have a figure of merit value of 0.34 above 700 K [18].

1.4.3 Low Dimensional Materials

A novel enhancement direction adopted recently promises to be beneficial in manipulating the properties of electrons and phonons in a given material. This approach is based on reducing the dimensionality of the whole structure [24], commonly known as low-dimensional materials, where materials could be fabricated as quantum wells, superlattices, quantum wires, and quantum dots. Such a regime is found to offer new means to manipulate the figure of merit coefficients separately [25]. Here, a new design parameter, known as the characteristic length scale $d$, is introduced to ease the correlation between the figure of merit parameters [26].
This approach was adopted on the basis of two main ideas, that can be summarised as follows: firstly, it is known that in semiconductors the electrical charge can be carried by electrons and holes while heat is dominantly carried by phonons. These carriers have two different length scales associated with their motion, the mean free path \( \Lambda \) and the wavelength \( \lambda \). In typical semiconductors operating near room temperature the dominant heat-carrying phonons have wavelengths of \((1 - 3)\) nm and mean free paths of \((10 - 100)\) nm [27]. The latter is reported to be similar to electron mean free paths (see Ch. 27 in [28]). Ioffe [29] argued that while atomic size defects are sufficient to scatter electrons in metals, only atomic aggregation can achieve that for electrons in semiconductors. Therefore, small size defects (e.g. at interfaces), do not scatter electrons effectively. However, phonons get scattered strongly with even point defects. So now controlling \( d \) in the nanometer scale structure such that \( d \gg \Lambda_{el} \) results in electronic transport properties similar to that of the bulk materials and if \( d \approx \Lambda_{ph} \) this will give rise to a reduction in the thermal conductivity [26, 30]. Secondly, the reduction in the system size would cause an increase in the power factor. The size quantization effects could cause an increase in the Seebeck coefficient even when the density of charge carriers is not changed [30, 31, 32, 33]. To achieve this result, a certain condition had to be set on the material characteristic length such that \( d \approx \Lambda_{ph} \geq \Lambda_{el} \) [26, 30]. When the characteristic length, which is often compared to the value of the dominant phonon mean free path, is reduced to be smaller than \( \Lambda_{ph} \), the lattice thermal conductivity will be reduced due to the increased boundary scattering [34]. For a sample size that is comparable to the phonon wavelength, \( \lambda_{ph} \), the reduction in \( \kappa \) is reported to be due to the elastic scattering by grain boundaries and defects [35, 36, 37]. Finally, for samples with a characteristic length smaller than \( \lambda_{ph} \), a decrease in \( \kappa \) is reported as phonon confinement leads to modification in phonon dispersion relations and group velocities [38]. The ratio of surface to volume in quantum wires and quantum dots is another pa-
parameter that can be used to enhance the TE material performance. It is believed that as the ratio of surface to volume increases, boundary effects will cause a decrease in the lattice thermal conductivity $\kappa_{\text{ph}}$ as phonons are being scattered diffusely or reflected specularly (see Ch. 14 in [6]). This will result in decreasing the mean free path of phonons without major changes in the carrier transport properties due to the difference in their wavelengths, i.e. $\lambda$ of the dominant phonon is shorter than $\lambda_{\text{el}}$, hence electrons are less likely to be scattered diffusely at the interface, leading to $ZT$ enhancement [18, 39]. The dispersion of nanoparticles, for example nanodot or nanowire, in a homogeneous matrix, known as nanocompositing, will give rise to a thermal boundary resistance at the particle matrix interface affecting the heat transport across the interface [23, 33, 40, 41] (also see Ch. 10 in [6]).

Some of the well known low dimensional systems are mentioned next.

### 1.4.3.1 Quantum Well Superlattices

Hicks and Dresselhaus [42] assumed that in the absence of electron scattering at the interface, the transport coefficient of superlattices can be explained through an alternating arrangement of quantum well and barrier materials, e.g. a narrow gap semiconductor sandwiched between two wide gap semiconductors. Since the carrier will be confined in the quantum well layer, the barrier potential will not contribute to the carrier transport, hence the carrier mobility in a direction parallel to the layers, will not change. The figure of merit of the superlattice ($Z_{sl}$) would depend on the lattice properties of the two materials.

In a single quantum well, phonon spatial confinement will change phonon dispersion relations induced by boundaries [43]. Spatial confinement is reported to increase the presence of a large number of branches for each polarizational type as compared to the bulk. This high number of branches will lead to flattening of the dispersion curves, hence producing smaller group velocities over the whole
range of wave vectors [44]. In multi quantum well superlattice of Pb/Pb$_{1-x}$Eu$_x$Te, Harman and co-workers [45] have succeeded in breaking through the unity barrier of $ZT$. This modulation doped sample showed an enhanced Seebeck coefficient and carrier mobility which resulted in a $ZT$ value of more than 1.2 compared to 0.45 in bulk material at room temperature. A theoretical modelling performed in 1998 by Sun (see Ref. 37 in [46]) on Si/ Si$_{1-x}$Ge$_x$ quantum wells showed that a quantum well of width 2 nm has an enhancement in $ZT$ by a factor of 2 over the bulk value at 300 K. In 2001 a value of $ZT$ equal to 2.4 was observed by Venkatasubramanian et al. [47] for a p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice. Although in those systems there were some changes in the electronic properties, the significant contribution was the decrease in the lattice thermal conductivity [48], which was found to be equal to 0.22 W m$^{-1}$ K$^{-1}$. For an n-type PbTe/ PbTe$_{0.75}$Se$_{0.25}$ with a period of 70 Å (n=1 ×10$^{19}$ cm$^{-3}$), the thermal conductivity was 0.5 W m$^{-1}$ K$^{-1}$ with $ZT$ value equal to 0.63 at room temperature in the stacking direction compared to 0.4 in the PbTe bulk material at the same temperature. This value of $ZT$ has increased significantly to 1.75 at higher temperature ($T = 450$ K) [33].

1.4.3.2 Quantum Wires

Theoretical predictions have suggested that thermoelectric materials could reach a higher figure of merit value in 1 Dimensional quantum wire systems (1D) compared to 2 Dimensional (2D) quantum wells. It has been claimed that the existence of hetero-interfaces would cause dramatic changes in the electronic band structure and in the properties of phonons in quantum wire systems [33]. The drastic increase in the density of states will increase the power factor compared to both the bulk and 2D system. The band diagram of Bi$_{1-x}$Sb$_x$ alloy nanowires was calculated to reveal a change in the position of the energy band edges with changing the wire thickness. For p-type wires of 35 – 45 nm in diameter and with $x \approx 0.13 – 0.14$, the figure of merit was found to be equal to 1.2 at 77 K. Moreover,
a strong reduction in the lattice thermal conductivity was observed with decreasing the wire diameter [49]. The single crystalline PbTe nanowires have shown a decreased thermal conductivity with decreasing the wire diameter, for a 182 nm nanowire at 300 K the lower thermal conductivity was 1.29 W m$^{-1}$ K$^{-1}$ which is claimed to be half the value of bulk PbTe [50]. A possible explanation was that reducing the wire diameter will decrease the phonon mean free path due to surface scattering, since the wire has a high surface to volume ratio. In addition, further calculation on PbSe/PbTe nanowire superlattices with similar diameters and segment length as PbSe/PbS have indicated larger value of $ZT$ because of the higher mobilities of the carriers in PbTe relative to PbS. Moreover, n-type PbSe/PbTe superlattice nanowires exhibit higher $ZT$ value than their p-type counterparts (see Ch. 39 in [6]).

Nanowires (NW) and nanotubes offer a pronounced modulation of the phonon energy dispersion. The group velocity in NW was supposed to be smaller, a reduction in the phonon mean free path and an enhancement in phonon-phonon, phonon-surface, phonon-carrier scattering rates will take part in decreasing $\kappa_{\text{ph}}$. Further reduction in the thermal conductivity is expected with reducing the NW diameter, probably as a result of reducing $\Lambda_{\text{ph}}$ and enhancing the boundary scattering. In a Si NW, the primary contributor in increasing the figure of merit was found to be the reduction in thermal conductivity by almost 100 fold [33].

1.4.3.3 Quantum Dot Superlattices

For further improvement in thermoelectric efficiency, researchers started to investigate the potential of quantum dot systems. The quantum dots will be distributed randomly in a superlattice system, so that the phonon scattering will be more efficient without significant changes of the carriers transport properties. Harman et al. (See Ref. 27 in [31]) have grown a quantum dot superlattice of PbTe/Pb$_{0.98}$Te$_{0.02}$ with Bi as n-type dopant values of $ZT \approx 1.6$ at room temper-
ature and 3.5 at 570 K were achieved. Quantum Dot Superlattice (QDSL) is expected to increase the power factor and decrease the lattice thermal conductivity significantly [31]. Harman et al. [51] have experimentally recorded an increase for PbSe$_{0.98}$Te$_{0.02}$/PbTe QDSL in $ZT$ equal to 0.9 at room temperature as a consequence of significant enhancements in Seebeck coefficients and power factors. An experimental work by Harman [51] has demonstrated a $ZT$ value of about 3 for PbTeSe QDSL embedded in PbTe and $ZT = 2$ for PbSnSeTe QDSL, at high and at room temperatures, respectively. An explanation for these impressive values of the figure of merit has been offered due to the creation of mini-bands in the quantum dot arrays (see Refs. 16-17 in Ch. 39 [6]).

### 1.5 Nanocomposites

The concept of modifying thermoelectrical material properties through using lower dimensional structures has produced theoretically significant increases in the material electronic properties compared to the bulk values [42]. Furthermore, we have discussed in previous sections that nanostructures, such as quantum wells (2D structures), nanowires (1D structures), and quantum dots (0D structures), fabricated to form thin-film superlattice could possibly cause a significant reduction in the lattice thermal conductivity [52].

The idea of enhancing $ZT$ through nanostructuring was ignited by the reported enhancement of $ZT$ in thin film structures and nanowires. However, fabricating materials using atomic layer deposition techniques to be used commercially, is found to be time and money consuming. The main contribution for superlattices $ZT$ enhancement has been considered to come from reduction in the phonon transport. This result which can be achieved by using materials that have high density interfaces, has led to the idea of nanocomposites [52, 53, 54]. A nanocomposite is a type of bulk nanostructured material which could be fabri-
The concept is to disperse nanoparticles of one material into a host matrix in different types of structures. The construction of such structures has the following constraints, $d < \Lambda_{ph}$ and $d > \Lambda_{el}$, so only phonons are strongly scattered by the interfaces. The fabrication of nanocomposites is faced with several challenges. Firstly, creating a bulk material consisting of nanoscale structures within is not an easy task. Overcoming this challenge, i.e. succeeding in fabricating such a bulk material, will be followed by the second challenge of applying proper fabrication conditions that result in a structure with improved figure of merit. Finally, the previous efforts will be fruitless unless a stable TE material which can maintain the nanoscale structures while operating as a commercial device can be produced [52].

One technique used to fabricate nanocomposites is known as matrix encapsulation. The idea of this technique is based on the fact that some materials are soluble in others in their liquid state but not in the solid state. Cooling the liquid mixture rapidly, the insoluble minority phase will precipitate, forming nanoparticles embedded in the host phase [55]. This technique has been applied with considerable success. A PbTe with two percent Sb that is matrix encapsulated has reported thermal conductivity of about 0.8 W m\(^{-1}\) K\(^{-1}\) compared to 2 W m\(^{-1}\) K\(^{-1}\) at 300 for the bulk PbTe [52].

### 1.6 Lead Chalcogenides

As mentioned earlier there are three classes of operating temperatures for thermoelectric materials, each with a certain group of semiconductors. Our interest is captured by lead chalcogenides. They belong to a semiconductor group that consists of lead and elements of group six (sulfur, selenium and tellurium in particular). Many physical and chemical properties are common in this family of
semiconductors. They have the same crystal structure, and their preparation and doping methods are also similar. Most lead chalcogenides are stable and exhibit relatively high melting points. For example, the melting temperature of PbTe is 923 °C compared to 585 °C for Bi₂Te₃. Therefore, lead chalcogenides, typically PbTe, are suitable for thermoelectric applications over a wide range of temperatures, particularly in the range 300 – 800 K. Furthermore, with a band gap of 0.32 eV PbTe meets the condition \( E_g = 10k_B T \). Considering a semiconductor with parabolic electronic band structure within the relaxation time approximation, Mahan [56] has found this optimum gap condition to be realistic in both degenerate and the classical regimes. A narrow gap would result in creation of electrons as well as holes in the system and result in decreasing the Seebeck coefficient of the material which in turn would prevent the optimization for power-generation applications [33] (and Ref. 8 in [33]).

Since 1951, IV-VI semiconductors, such as PbTe, PbSe, PbS, and SnTe, due to their practical applications in electronic devices, have received considerable attention. On the other hand, despite their simple cubic NaCl (rock-salt) structure, their lattice thermal conductivity is found to be as low as \( \kappa_{ph} = 1.9 \text{ W m}^{-1} \text{ K}^{-1} \) at room temperature. Therefore, lead chalcogenides promoted a novel research direction for new thermoelectric materials to enhance the figure of merit, especially in the form of (2D) quantum superlattices and QDSL’s.

### 1.7 Chapter Summary and Thesis structure

This Chapter presents an introduction to the principle of thermoelectricity and thermoelectric materials. A brief review of the efforts that have been spent to improve the efficiency are covered, showing the new approaches that were established for providing new enhanced thermoelectric materials.
This thesis is organized into seven chapters, as follows:

Chapter 1: Introduction to Thermoelectricity.

In this Chapter we present a brief background on thermoelectricity and a short review on the TE materials developments.

Chapter 2: Theory of Electronic Thermal Coefficients.

Here we are seeking explicit quantitative expressions for the Seebeck coefficient, electrical conductivity, and electronic thermal conductivity for semiconductor materials. This is done by solving the Boltzmann transport equation (BTE) within the relaxation time scheme to determine the electron distribution function. For the energy and wave vector calculation we adopted the nearly free electron model. Expressions for the electronic thermal transport coefficients are derived for degenerate and nondegenerate semiconductors.

Chapter 3: Theory of Phonon Thermal Conductivity.

The phonon density of states and dispersion relations are derived by applying the Debye model within the isotropic continuum approximation. Here, we present three models for phonon thermal conductivity: the Debye (smrt), Callaway, and Allen’s improvement over Callaway’s model. The basic derivation of the theory for the lattice thermal conductivity is done by following the procedures outlined in The Physics of Phonons by Srivastava [57]. Calculations of phonon scattering rates are derived, for phonon scattering from a boundary, mass defect, and donor electron, using the perturbation approach. The crystal anharmonicity is limited to three-phonon interaction, corresponding to the cubic term in the crystal potential. This we think will be sufficient to describe the effect of anharmonicity. Applying the conservative law of momentum and energy we consider the interaction of: acoustic-acoustic phonons, optical-optical phonons, and acoustic-optical phonon for Normal and Umklapp class 1 and class 2 events. Although this expression is analytical, it should be evaluated numerically. The calculations for the lattice thermal conductivity are performed over a wide range of tempera-
The following Chapters are based on three articles that have been published or accepted to be published in scientific journals.

Chapter 4: Calculations of TE Properties of PbTe.

In this Chapter, which is the core material and published in *Journal of Applied Physics*, 116, 043702 (2014), we present the results of the electronic transport coefficients for bulk n-PbTe. We used the theory developed in Chapter 2 for transport in a single band semiconductor. The electron scattering mechanism is considered for scattering from acoustic phonons only. The effect of the band non-parabolicity is also included. The electronic thermal conductivity is calculated including the monopolar $\kappa_{\text{mp}}$ and bipolar $\kappa_{\text{bp}}$ contributions at low and high temperatures, respectively. The theory of the lattice thermal conductivity introduced in Chapter 3 for the single mode relaxation time approximation, *i.e.* Debye model, is expanded to include the role of optical phonons in heat conduction as well as acoustic phonons. Results for the lattice conductivity with and without the contribution of optical phonons in heat conduction are presented. The crystal anharmonicity effects on the thermoelectric properties of n-type PbTe are studied by considering different three phonon processes and a comparison between three-phonon Normal (N) and Umklapp (U) relaxation rates are presented for longitudinal acoustic (LA) and (TA) transverse acoustic phonons. The important role of transverse optic (TO) phonons in conduction heat is emphasised. The figure of merit results are calculated when all phonon polarizations are regarded as heat conductors and when the role of the optical phonons is limited to the scattering off acoustic phonons.

Chapter 5: Three-phonon scattering processes and thermal conductivity in IV-chalcogenides.

In this Chapter, which is the core material and published in *Journal of Physics: Condensed Matter* 27, 33580 (2015), we present a systematic study of allowed three-phonon scattering processes, involving acoustic and optical branches, and their relative roles in explaining the low thermal conductivity of IV-chalcogenide ther-
moelectric materials PbTe, PbSe, PbS, and SnTe. Using numerical results for the lattice thermal conductivity, computed by employing the isotropic continuum scheme for the phonon dispersion relation, we studied the extent of the additional contribution the Callaway theory and the Allen theory provide over the Debye model, and taking into account the phonon scattering from crystal boundary, mass defect, donor electron, and for phonon-phonon N and U scatterings involving acoustic as well as optical branches are considered. Applying the Callaway model, a comparison of the acoustic ($TA$, $LA$) and ($TO$) phonons contribution to the lattice thermal conductivity is presented for PbTe, PbSe, PbS, and SnTe.

Chapter 6: Size and Dimensionality Dependent Phonon Conductivity in Nanocomposites.

In this Chapter, which is the core material and published in *Journal of Physics: Condensed Matter* 28, 145304 (2016), we have studied size and dimensionality dependent phonon conductivity of PbTe-PbSe nanocomposites by considering three configurations: superlattice, embedded nanowire and embedded nanodot. A brief description of the two models usually used for calculating the thermal boundary resistance, known as acoustic and mismatch model, are represented. In the framework of an effective medium theory, the calculations of the lattice thermal conductivity are performed. We make use of the bulk thermal conductivities of PbTe and PbSe calculated by using Callaway’s effective relaxation-time theory, and by accounting for relevant scattering mechanism including three-phonon N and U interactions involving acoustic as well as optical branches. The thermal interface resistance is computed using the diffuse mismatch theory. The effect of the size and volume fraction of PbSe on the effective thermal conductivity of the nanocomposite are investigated. A comparison of the reduction in the nanocomposite lattice thermal conductivity in the three configurations is offered showing the advantage of nanocompositing over alloying.
Chapter 7: Summary and Suggestion for Future Work.

We present a general discussion with regards to the results in Chapter 4, Chapter 5, and Chapter 6. We then make suggestions for future work on this research topic.
Bibliography


Chapter 2

Theory of Electronic Thermal Coefficients

2.1 Introduction

Transport phenomena, which govern the behaviour of bulk materials, represent the basis for many technologies. Hence, calculations of transport properties are in demand for theoretical and practical purposes. Transport processes can be promoted by the application of electric fields alone or in conjunction with magnetic fields, or by setting up temperature gradients either in the presence or in the absence of electric and magnetic fields. During their motion, the electric carriers will transport both electricity and heat. The terminology of electronic and thermal transports are used to refer to the electronic charge flow and heat flow in solids, respectively. In this chapter, our attention will be confined to the electronic and thermal electronic transport coefficients of the electric charge carrier, particularly, the electrical conductivity, the Seebeck coefficient, and the electronic thermal conductivity. Formulating general expressions for the electronic transport coefficients, under the application of small electric field and temperature gradient, requires the determination of the carrier perturbed distribution function.
This is carried out by using the linearised Boltzmann transport equation within
the relaxation time approximation. Employing the nearly free electron scheme
for the dispersion relations, the transport coefficients are expressed for general as
well as for two extreme cases of doping, i.e. degenerate and non-degenerate semi-
conductors. The expressions are given in terms of the transport integrals (Fermi
integrals).

### 2.2 Coupled Current Equations

Under the application of a small static electric field $E$ and temperature gradient
$\nabla T$, phenomenological expressions can be written to describe the densities of the
electric current $J$ and the heat current $U$ in a solid [1]

$$\begin{align*}
J & = L_{EE} E + L_{ET} \nabla T \\
U & = L_{TE} E + L_{TT} \nabla T
\end{align*}$$

(2.1)

The first subscript of the coefficients $L_{EE}, L_{ET}, L_{TE},$ and $L_{TT}$ indicates which
current it contributes to and the second denotes which source it takes into account
between the electric field and the temperature gradients. The coefficients are gen-
erally tensors and used to describe the carrier transport in solids. In the absence of
a magnetic field, $L_{ET}$ and $L_{TE}$ are internally related through the Kelvin-Onsager
relation [1] $L_{ET} = -L_{TE}/T$. The coefficients are not observed directly, instead
the apparatus is arranged in two configurations which will enable the measur-
ing of the electronic and thermal properties. In the first arrangement an electric
field is applied with constant temperature along the apparatus and the electrical
conductivity $\sigma$ is determined as

$$\sigma = L_{EE}. $$

(2.2)

In the second set-up an open circuit prevents the flowing of electric current through
the apparatus and the temperature gradient is maintained. Setting $J = 0$, which
gives a relation between \(E\) and \(\nabla T\), the monopolar (mp) electronic thermal conductivity is expressed as \([1]\),

\[
\kappa_{mp} = -\left[ L_{TT} + T(L_{ET}^2/L_{EE}) \right]. \tag{2.3}
\]

The electric current derived by the heat flux is stopped by an electric field that builds up along the device and reduces the thermal current slightly \([1]\). It is conventional to express the electronic thermal conductivity in terms of the Lorenz number, \(L\), defined from the Wiedemann-Franz Law as \(\kappa_{mp}/\sigma T\). Then, from Eqs. 2.2 and 2.3,

\[
L = -\frac{1}{T} \left[ L_{TT}/L_{EE} + T(L_{ET}^2/L_{EE}) \right]. \tag{2.4}
\]

The induced electric field subjected by the thermal gradient is expressed simply as \(E = S\nabla T\), and the Seebeck coefficient is defined as

\[
S = -L_{ET}/L_{EE}. \tag{2.5}
\]

The coefficients are defined by combining the electric current density and the heat current density. For electric current density, the contribution from all carriers in a given band can be written as \([2]\)

\[
J = \frac{e}{4\pi^3} \int v_k f_k \, dk, \tag{2.6}
\]

where \(e\) is the carrier electronic unit charge, with \(e = -e\) for electron and \(e = +e\) for hole, \(k\) is the carrier wave-vector and \(dk\) is a volume element about \(k\). \(v_k\) and \(f_k\) are the carrier velocity and the carrier distribution function in \(k\) state, respectively. Similarly for the heat current density, we write \([3]\)

\[
U = \frac{1}{4\pi^3} \int v_k (E_k - \bar{\mu}) f_k \, dk, \tag{2.7}
\]

where \(E_k\) is the band dispersion relation and \(\bar{\mu}\) (free energy) is the electrochemical potential. For systems of charged particles \(\bar{\mu}\) represents the sum of two terms, the chemical potential \(\mu\) and the electrostatic part \(e\phi\), where \(\phi\) is the electrostatic
potential. Here, we have employed the thermodynamic definition of heat, which defines heat as the internal energy minus the free energy of the carrier. Hence, the use of the term \((E_k - \bar{\mu})\) in the heat current equation is to account for the total energy transferred by each carrier.

In principle, the carrier transport coefficients are known once the the carrier distribution function \(f_k\) in the presence of an electric field and temperature gradient has been determined. The way in which the distribution function develops with time is described by the carrier transport equation, known also as the Boltzmann transport equation.

### 2.2.1 Boltzmann Transport Equation

The presence of external fields will develop a driving force \(F\) that will cause the carrier to accelerate, i.e. will change the carrier wave-vector as

\[
\hbar \frac{d k}{d t} = F, \tag{2.8}
\]

where \(\hbar\) is the reduced Planck’s constant. The carrier distribution function \(f(k, r, t)\) (henceforward denoted as \(f\)), which measures the occupation probability of the carrier in the \(k\) state in space neighbouring \(r\) at time \(t\), will no longer be described by the equilibrium Fermi-Dirac function \(f_0\). Assuming there is no scattering, after a time interval \(dt\) the external force will cause the carrier to move to a new state with position \(r + v dt\) and wave-vector \(k + \dot{k} dt\). The rate of change of the distribution function can be written as

\[
\left(\frac{df}{dt}\right)_{\text{drift}} = \frac{1}{dt} \left[ f(k - \dot{k} dt, r - v dt, t - dt) - f(k, r, t) \right]. \tag{2.9}
\]

In the absence of the scattering, the above rate represents the continuous flow of carriers and hence is known as the drift term. Expanding the first term on the
right hand side of Eq. 2.9 and keeping up to the second term, one writes
\[ f(k - \dot{k} dt, r - v dt, t - dt) = f(k, r, t) - \left[ k \cdot \frac{\partial f}{\partial k} + v \cdot \frac{\partial f}{\partial r} + \frac{\partial f}{\partial t} \right] dt \]
\[ \equiv f(k, r, t) - \left[ \dot{k} \nabla_k f + v \cdot \nabla_r f + \frac{\partial f}{\partial t} \right] dt, \quad (2.10) \]

where
\[ \dot{k} \cdot \nabla_k f = k_x \frac{\partial f}{\partial k_x} + k_y \frac{\partial f}{\partial k_y} + k_z \frac{\partial f}{\partial k_z}, \quad (2.11) \]
\[ v \cdot \nabla_r f = v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z}. \quad (2.12) \]

Now the drift term in Eq. 2.9 can be written using Eq. 2.10 as
\[ \left( \frac{df}{dt} \right)_{\text{drift}} = - \left[ v \cdot \nabla_r f + \dot{k} \cdot \nabla_k f + \frac{\partial f}{\partial t} \right]. \quad (2.13) \]

The right hand side of the above equation can be interpreted as follows. The first term is the change due to the external fields and the second term represents the change due to the diffusion processes. On the other hand, the distribution function will be altered as a consequence of carrier scattering, and we define the rate of change due to collision (scattering) by \( (\partial f/\partial t)_{\text{coll}} \). The total shift of the distribution function from equilibrium is governed by the Boltzmann equation, which relates the changes of the carrier distribution function \( f(k, r, t) \) due to the applied fields and scattering of carriers. The general form of the transport equation is [6].
\[ \left[ \frac{df}{dt} \right]_{\text{tot}} = \left[ \frac{df}{dt} \right]_{\text{drift}} + \left[ \frac{df}{dt} \right]_{\text{coll}}. \quad (2.14) \]

In the steady state, Eq. 2.14 vanishes, since there will be no changes in \( f \). The effects of the diffusion and the external fields are balanced by the scattering processes
\[ \left[ \frac{df}{dt} \right]_{\text{drift}} + \left[ \frac{df}{dt} \right]_{\text{coll}} = 0. \quad (2.15) \]

Considering only the application of a static electric field, we put \( k = (e/\hbar)E \) and Eq. 2.15 may now be written as [7]
\[ \left[ v \cdot \nabla_r f + \frac{e}{\hbar} E \cdot \nabla_k f \right] = \left[ \frac{\partial f}{\partial t} \right]_{\text{coll}}. \quad (2.16) \]
This is called the carrier Boltzmann transport equation. To solve this transport equation we apply the most common approach known as the relaxation time approximation [8]. This approach is based on the assumption that the scattering processes can be described by a relaxation time $\tau_k$, which in general is a function of $k$, that specifies the rate at which the system returns to equilibrium, i.e. how the distribution function approaches its equilibrium value $f_0$. Therefore, the collision term in the relaxation time approximation is written as

$$\left[\frac{\partial f}{\partial t}\right]_{\text{coll}} = -\frac{f - f_0}{\tau_k},$$  \hspace{1cm} (2.17)

where $f - f_0$ is the deviation of the distribution function $f$ from its equilibrium value $f_0$, and $\tau_k$ is the relaxation time. If the fields are not too strong so that $f$ is not too far from equilibrium $f_0$, further simplification is achieved by replacing $f$ on the left hand side of Eq. 2.16 by $f_0$, hence

$$v \cdot \nabla f + \frac{e}{\hbar} E \cdot \nabla_k f_0 = -\frac{f - f_0}{\tau_k}.$$  \hspace{1cm} (2.18)

Under thermal equilibrium, the time average of the population of a quantum state having an energy $E_k$ is given by the Fermi Dirac distribution function $f_0$

$$f_0 = \left[1 + \exp\left(\frac{E_k - \bar{\mu}}{k_B T}\right)\right]^{-1},$$  \hspace{1cm} (2.19)

where $k_B$ is Boltzmann’s constant. The term $\nabla_r f_0$, for constant $k$, becomes [6]

$$\nabla_r f_0 = \frac{\partial f_0}{\partial E_k} \left[-\nabla \bar{\mu} - \frac{E_k - \bar{\mu}}{T} \nabla T\right],$$  \hspace{1cm} (2.20)

where $\nabla \bar{\mu}$ is the electrochemical potential gradient. Also,

$$\nabla_k f_0 = \frac{\partial f_0}{\partial E_k} \cdot \nabla_k E_k$$

$$= \hbar v_k \frac{\partial f_0}{\partial E_k},$$  \hspace{1cm} (2.21)

where we make use of the relation

$$\hbar v_k = \nabla_k E_k.$$  \hspace{1cm} (2.22)
2.3 Electronic Thermal Transport Coefficients

By substituting Eqs. 2.20 and 2.21 into Eq. 2.18 we get

\[ v \cdot \frac{\partial f_0}{\partial E_k} \left[ \left( \frac{E_k - \bar{\mu}}{T} \right) \nabla T + e \hat{E} \right] = -\frac{f - f_0}{\tau_k}, \]  

(2.23)

where \( \hat{E} \) is the effective electric field acting on the carrier and is defined as \[ \hat{E} = E - \frac{1}{e} \nabla \bar{\mu}. \]  

(2.24)

This is because in addition to the current driven by the electric field, there is a diffusion current which is derived from the electrochemical potential gradient. The distribution function \( f \) in the presence of a weak electric field and temperature gradient is written as a linear combination of the driving forces in the form

\[ f = f_0 - \tau_k v \cdot \left[ -\frac{E_k - \bar{\mu}}{T} \frac{\partial f_0}{\partial E_k} \nabla T + e \frac{\partial f_0}{\partial E_k} \hat{E} \right]. \]  

(2.25)

This equation will apply equally well for electrons and holes as long as \( E_k \) and \( \bar{\mu} \) are measured from the appropriate band edge and in the appropriate direction. This solution of the Boltzmann equation will be used to describe the electric and heat current densities, hence to obtain the transport coefficients.

### 2.3 Electronic Thermal Transport Coefficients

The electric current density in Eq. 2.6 and the heat current density in Eq. 2.7 can be expressed in term of the distribution function in Eq. 2.25. Since with an equilibrium distribution there are no currents flowing, substituting the perturbed distribution function in Eq. 2.25 causes the integral containing the equilibrium distribution to vanish. The remaining terms are

\[
\begin{align*}
J &= -\frac{e^2}{4\pi^3} \hat{E} \int vv\tau_k \frac{\partial f_0}{\partial E_k} \, dk + \frac{e}{4\pi^3} \nabla T \int \frac{1}{T} vv\tau_k (E_k - \bar{\mu}) \, dk \\
U &= -\frac{e}{4\pi^3} \hat{E} \int vv\tau_k (E_k - \bar{\mu}) \frac{\partial f_0}{\partial E_k} \, dk + \frac{1}{4\pi^3} \nabla T \int \frac{1}{T} vv\tau_k (E_k - \bar{\mu})^2 \, dk
\end{align*}
\]  

(2.26)
These equations can be directly compared with those of Eqs. 2.1 and the phenomenological coefficients can be identified for an isotropic medium [9]

\[ L_{EE} = -\frac{e^2}{3(4\pi^3)} \int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk, \]  
\[ (2.27) \]

\[ L_{ET} = \frac{e}{3(4\pi^3)T} \int v^2 \tau_k (E_k - \bar{\mu}) \frac{\partial f_0}{\partial E_k} \, dk, \]  
\[ (2.28) \]

\[ L_{TE} = -\frac{e}{3(4\pi^3)} \int v^2 \tau_k (E_k - \bar{\mu}) \frac{\partial f_0}{\partial E_k} \, dk = -TL_{ET}, \]  
\[ (2.29) \]

Inserting these expressions for the phenomenological coefficients into Eqs. 2.2, 2.3, 2.4, and 2.5, we can write the electric conductivity

\[ \sigma = -\frac{e^2}{3(4\pi^3)} \int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk, \]  
\[ (2.31) \]

and the electronic thermal conductivity,

\[ \kappa_{mp} = \frac{1}{T} \left( \frac{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} E_k \, dk}{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk} \right)^2 - \left( \frac{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk}{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk} \right)^2 \int v^2 \tau_k \frac{\partial f_0}{\partial E_k} E_k \, dk. \]  
\[ (2.32) \]

where we have expanded the factor \((E_k - \bar{\mu})^2\) that appears in Eq. 2.30, and the Lorenz number

\[ L = \frac{1}{e^2 T^2} \left( \frac{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} E_k \, dk}{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk} \right)^2 - \left( \frac{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk}{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk} \right)^2 \left( \int v^2 \tau_k \frac{\partial f_0}{\partial E_k} E_k \, dk \right)^2 \int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk. \]  
\[ (2.33) \]

The Seebeck coefficient can be expressed as

\[ S = -\frac{1}{eT} \left[ \bar{\mu} - \frac{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} E_k \, dk}{\int v^2 \tau_k \frac{\partial f_0}{\partial E_k} \, dk} \right]. \]  
\[ (2.34) \]

The integrals in Eqs. 2.31, 2.32, 2.33, and 2.34 have similar forms and can be expressed as

\[ K_s = -\frac{T}{4\pi^3} \int v^2 \tau_k E_k \frac{\partial f_0}{\partial E_k} \, dk. \]  
\[ (2.35) \]

In order to have explicit expressions for transport coefficients in semiconductors, the band structure, the density of states and the scattering mechanisms, should be identified. For that, in the next sections we will discuss the crystal structure and the electronic band structure with the corresponding density of states that is common for semiconductors and used in thermoelectric applications.
2.3.1 Crystal Structure

We are concerned with semiconductors that have a cubic sodium chloride structure, such as PbTe. The crystal structure of PbTe, shown in Fig. 2.1, is based upon the face-centered cubic (fcc) lattice. Each Pb (Te) atom is surrounded by six Te (Pb) atoms (this number is called the coordination number) and the Pb and Te atoms are located at \( a(1/2, 1/2, 1/2) \) and \((0, 0, 0)\), respectively, with \( a \) as the cubic lattice constant. This configuration of atoms is plotted in the direct or real space where the primitive translational vectors \( a_1 \), \( a_2 \), and \( a_3 \) are expressed as [10]

\[
\begin{align*}
    a_1 &= a(0, \frac{1}{2}, \frac{1}{2}) \\
    a_2 &= a(\frac{1}{2}, 0, \frac{1}{2}) \\
    a_3 &= a(\frac{1}{2}, \frac{1}{2}, 0).
\end{align*}
\]  

(2.36)

For transport calculations, in fact for all solid state physics, it is conventional to use the concept of reciprocal (momentum) space to describe the electronic band structure and the spectra of the lattice vibrations. In the reciprocal space the primitive unit cell is called the first Brillouin zone. The reciprocal lattice translational vector \( G \) is written as a linear combination of the basis vectors of the reciprocal lattice \( b_1, b_2, \) and \( b_3 \) as

\[
G = m_1 b_1 + m_2 b_2 + m_3 b_3,
\]  

(2.37)

where \( m_1, m_2, \) and \( m_3 \) are integers and the reciprocal lattice basis vectors are related to the primitive translational vectors in the direct lattice by the relations [10]

\[
\begin{align*}
    b_1 &= \frac{2\pi}{\Omega} (a_2 \times a_3) = \frac{2\pi}{a} (-1, 1, 1), \\
    b_2 &= \frac{2\pi}{\Omega} (a_3 \times a_1) = \frac{2\pi}{a} (1, -1, 1), \\
    b_3 &= \frac{2\pi}{\Omega} (a_1 \times a_2) = \frac{2\pi}{a} (1, 1, -1).
\end{align*}
\]  

(2.38)
where $\Omega = a_1.(a_2 \times a_3)$ is the volume of the primitive unit cell in real space. The Brillouin zone boundaries satisfy the condition [10]

$$k \cdot \hat{G} = \frac{1}{2}|G|. \quad (2.39)$$

for a general $k$ vector inside the zone

$$k = ub_1 + vb_2 + wb_3, \quad (2.40)$$

with $u, v,$ and $w$ restricted as

$$0 \leq u, v, w \leq 1, \quad (2.41)$$

$$u + v + w \leq 3/2. \quad (2.42)$$

The first Brillouin zone for the fcc lattice is shown in Fig. 2.2. The region of $k$ space in the first Brillouin zone according to the condition in Eqs. 2.40-2.42 [11], which is called the irreducible part of the Brillouin zone, is defined as

$$0 \leq k_x \leq k_y \leq k_z \leq +2\pi/a$$

$$k_x + k_y + k_z \leq \frac{3}{2}\frac{2\pi}{a}. \quad (2.43)$$

This region is shown in Fig. 2.2 by the pentahedra with the six vertices at $\Gamma, X, U, L, K, and W$. The vertices are located at

$$\Gamma = \frac{2\pi}{a}(0, 0, 0)$$

$$X = \frac{2\pi}{a}(1, 0, 0)$$

$$L = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$$

$$K = \frac{2\pi}{a}(\frac{3}{4}, \frac{3}{4}, 0)$$

$$U = \frac{2\pi}{a}(1, \frac{1}{4}, \frac{1}{4})$$

$$W = \frac{2\pi}{a}(1, \frac{1}{2}, 0). \quad (2.44)$$

One can define three principal symmetry directions: $\Delta$ along [100] or $\Gamma - X$, $\Sigma$ along [110] or $\Gamma - K$ and $\Lambda$ along [111] or $\Gamma - L$. These symmetry directions will be used latter when dealing with the lattice vibrations in chapter 3.
Figure 2.1: The atomic structure for a rock salt crystal. The vectors $a_1$, $a_2$, and $a_3$ are the primitive translation vectors of the fcc lattice.

Figure 2.2: The central or first Brillouin zone for the fcc lattice. From Srivastava (unpublished).
2.3.2 Simple Band Structure of Common Semiconductors for Transport Calculations

As discussed in Chapter 1, semiconductors have the required electronic structure for optimizing the figure of merit in TE applications. It is well known that semiconductors exhibit the most peculiar characteristic that it is possible to change their conductivity by several orders of magnitude with the introduction of appropriate dopants. The added impurities can be regarded as donors or acceptors and the system known as n-type and p-type semiconductors, respectively.

In Fig. 2.3 we show a realistic electronic band structure of PbTe, PbSe, PbS, and SnTe. In transport theory, the important carrier states are those shown in the red boxed area in Fig. 2.3, which are positioned either near the minimum of the conduction band or near the maximum of the valence band. Electrons in these bands can be considered to be only weakly perturbed by the periodic potential of the ion cores of the crystal. Therefore, the electronic band structure is usually described by the nearly free electron model [4, 14]. In this model the function \( E_k \) is approximated by quadratic forms in the neighborhood of the band extrema [15]. The relation between \( E_k \) and \( k \) for the states of interest in the conduction band has the form [2]

\[
E_k = E_c + \frac{\hbar^2 k^2}{2m_e^*} \text{ (electrons)},
\]

(2.45)

where \( E_c \) is the minimum energy of the conduction band, \( k \) is the modulus of electron wave-vector \( k \), and \( m_e^* \) is the effective mass of electrons. By analogy, the states near the maximum energy of the valence band can be expressed in a similar manner. If this occurs at \( k = 0 \), the corresponding expression to that in Eq. 2.45 is

\[
E_k = E_v - \frac{\hbar^2 k^2}{2m_h^*} \text{ (holes)},
\]

(2.46)

where \( E_v \) is the maximum energy of the band and \( m_h^* \) is the effective mass of the
2.4 Electronic Thermal Transport coefficients in Semiconductor structure

valence band. For convenience we define a new variable $\epsilon_i$ of the form

$$\epsilon_i = \frac{\hbar^2k^2}{2m_i^*}, \quad (2.47)$$

where $\epsilon_i = \epsilon_e = E - E_c$ and $m_i^* = m_e^*$ for electrons, and $\epsilon_i = \epsilon_h = E_v - E$ and $m_i^* = m_h^*$ for holes. Under this approximation the electronic band structure is schematically plotted in Fig. 2.4.

### 2.4 Electronic Thermal Transport coefficients in Semiconductor structure

Assuming spherical parabolic energy bands, i.e. an isotropic crystal, the carrier velocity can be written in terms of the semiconductor parameters $m_i^*$ and $\epsilon_i$ by combining Eqs.2.22 and 2.47

$$v_i^2 = \frac{2\epsilon_i}{m_i^*}. \quad (2.48)$$

To evaluate the integral in Eq. 2.35, we allow $\tau$ to be a function of the energy $\epsilon_i$ [16]

$$\tau_i = \tau_0 \epsilon_i^p, \quad (2.49)$$

where the power $p$ is different for different scattering mechanisms and $\tau_0$ is a constant which does not depend on energy or temperature. The integrals in Eqs. 2.35 are now of the form

$$\int \frac{dk}{4\pi^3} O(E(k)). \quad (2.50)$$

This integral depends on $k$ only through the electronic energy, and since we are dealing with spherical surfaces by applying the nearly free electron model, we define a volume element $dk$ in $k$ space using spherical polar coordinates

$$dk = k^2 \sin \theta \, d\theta \, d\phi \, dk. \quad (2.51)$$
Figure 2.3: Real electronic band structure, taken from [12] and for PbTe, PbSe, and PbS, and for SnTe the structure is taken from [13]. The relevance of the red boxed area in PbTe is discussed in the text.
and hence the integral becomes

$$\frac{1}{4\pi^3} \int_0^{\theta=\pi} \sin \theta \ d\theta \int_0^{\phi=2\pi} d\phi \ k^2 \ dk \ O(E(k)) = \frac{k^2 dk}{\pi^2} O(E(k)). \quad (2.52)$$

The integration over the modulus $k$ of $k$ in Eq. 2.35 can be changed using Eq. 2.52 into an integration over the variable $\epsilon_i$. The integrals in Eq.2.35 are then written as

$$K_s = -\frac{2T}{3m_i^*} \tau_i \int^B_A (E_0 \pm \epsilon_i)^p \epsilon_i^{p+1} \frac{\partial f_0}{\partial \epsilon_i} g(\epsilon_i) d\epsilon_i, \quad (2.53)$$

where the $v_i^2$ and $\tau_i$ are eliminated in terms of $m_i^*$, $p$, and $\tau_0$ using Eqs. 2.48 and 2.49. The plus (minus) sign is for electrons (holes) with $E_0 = E_c \ (E_0 = E_v)$, $A = 0 \ (\infty)$, and $B = \infty \ (0)$. Here the density of states $g(\epsilon_i)$, which is defined as the distribution function for the quantum states near the conduction band minimum or the valence band maximum, is given by [17]

$$g(\epsilon_i) = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} (\epsilon_i)^{1/2}. \quad (2.54)$$

Figure 2.5 illustrates the density of states corresponding to the dispersion relation given in Eq. 2.47. If we consider electrons and choose to start from the conduction band edge, the integrals in Eq. 2.53 are of the form [18]

$$K_s = -\frac{T}{3\pi^2 m_e^*} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} \tau_0 \int^\infty_0 \epsilon_e^{s+p+3/2} \frac{\partial f_0}{\partial \epsilon_e} d\epsilon_e. \quad (2.55)$$
On integrating by parts, one gets
\[
\int_{0}^{\infty} \epsilon_{e}^{s+p+3/2} \frac{\partial f_0}{\partial \epsilon_e} d\epsilon_e = -(s + p + \frac{3}{2}) \int_{0}^{\infty} \epsilon_{e}^{s+p+1/2} f_0 d\epsilon_e.
\] (2.56)

Changing the variable from \(\epsilon_e\) to the dimensionless variable \(x\)
\[
x = \frac{\epsilon_e}{k_B T},
\] (2.57)
and making use of the reduced energy \(\zeta\), given as
\[
\zeta = \frac{\mu}{k_B T},
\] (2.58)
we have
\[
f_0 = \frac{1}{\exp(x - \zeta) + 1}.
\] (2.59)
and the integral in Eq. 2.56 is now written in the form
\[
-(s + p + \frac{3}{2})(k_B T)^{(s+p+\frac{3}{2})} F_{s+p+1/2},
\] (2.60)
where
\[
F_n(\zeta) = \int_{0}^{\infty} \frac{x^n}{1 + \exp(x - \zeta)},
\] (2.61)
is called the Fermi-Dirac integral of order \(n\). Then we may write the integrals in Eq. 2.55 in terms of the Fermi-Dirac integral as
\[
K_s = \frac{T}{3\pi^2 m_e^*} \left(\frac{2m_u^*}{\hbar^2}\right)^{3/2} \tau_0 (s + p + \frac{3}{2})(k_B T)^{(s+p+\frac{3}{2})} F_{s+p+1/2}.
\] (2.62)
The electronic transport coefficients may be written in terms of the integrals $K_s$ as

$$\sigma = \frac{e^2}{T} K_0, \quad (2.63)$$
$$\kappa_{mp} = \frac{1}{T^2} \left[ K_2 - \frac{K_1^2}{K_0} \right], \quad (2.64)$$
$$S = \pm \frac{e}{eT} \left[ \bar{\mu} - \frac{K_1}{K_0} \right], \quad (2.65)$$

where henceforth the upper sign refers to electron and the lower sign to holes. The Lorenz number, which is conveniently used to describe the electronic thermal conductivity, can be written in terms of $K_s$ as

$$L = \frac{1}{e^2 T^2} \left[ \frac{K_2}{K_0} - \frac{K_1^2}{K_0^2} \right]. \quad (2.66)$$

Generally, the electronic thermal transport coefficients are obtained numerically from Eqs. 2.63-2.65. However, there are two limiting cases where it is possible to use a simple approximation to the Fermi Dirac distribution and obtain simplified forms for the transport integrals $K_s$. This occurs when $\bar{\mu}$ is either much greater than $k_B T$ or much less than $-k_B T$.

### 2.4.1 Degenerate and non-degenerate Semiconductors

First, we consider the case when $\zeta$ is large and negative, i.e. $\zeta = \bar{\mu}/k_B T \ll 0$, that is, $\bar{\mu}$ lies well away from the appropriate band edge. This approximation refers to the non-degenerate semiconductor. In this case the Fermi-Dirac integrals become

$$F_n(\zeta) = \exp(\zeta) \int_0^\infty x^n \exp(-x) dx = \exp(\zeta) \Gamma(n + 1), \quad (2.67)$$

where $\Gamma(n)$ is the Gamma function of $n$. This function has the property that

$$\Gamma(n + 1) = n \Gamma(n). \quad (2.68)$$
When \( n \) is an integer, \( \Gamma(n + 1) = n! \). Another useful value is \( \Gamma\left(\frac{1}{2}\right) = (\pi)^{\frac{1}{2}} \). In terms of the Gamma function, the transport integrals take the form

\[
K_s = \frac{T}{3\pi^2 m_e^*} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \tau_0 (k_B T)^{(s + p + \frac{3}{2})} \Gamma(s + p + \frac{5}{2}) \exp(\zeta). \tag{2.69}
\]

Hence, the electronic conductivity of a non-degenerate semiconductor is

\[
\sigma = \frac{1}{3\pi^2 m_e^*} e^2 \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \tau_0 (k_B T)^{(p + \frac{5}{2})} \exp(\zeta). \tag{2.70}
\]

For the electronic thermal conductivity we will write it using the Lorenz number in the non-degenerate approximation expressed as

\[
\frac{\kappa_{mp}}{\sigma T} = L = \left(\frac{k_B}{e}\right)^2 (p + \frac{5}{2}). \tag{2.71}
\]

Similarly, the Seebeck coefficient of a non-degenerate semiconductor is found from Eqs. 2.65 and 2.69 to be

\[
S = \pm \frac{k_B}{e} \left[ \zeta - (p + \frac{5}{2}) \right]. \tag{2.72}
\]

The second limiting case occurs when \( \zeta \gg 0 \). This means that \( \bar{\mu} \) lies well above the minimum energy of the conduction band for electrons or well below the valence band edge for holes. In other words, the degenerate semiconductor becomes metallic. \( F_n(\zeta) \) are expressed in a series of the form [19]

\[
F_n(\zeta) = \frac{\zeta^{n+1}}{n + 1} + n\zeta^{n-1} - \frac{\pi^2}{6} + n(n - 1)(n - 2)\zeta^{n-3} - \frac{7\pi^4}{360} + \ldots \tag{2.73}
\]

This series converges rapidly when \( \zeta \gg 0 \). Therefore, one uses as many terms of the series as are necessary to yield non-zero values for the transport coefficients.

In the degenerate approximation, the electronic conductivity is expressed by employing only the first term in the series. Then

\[
\sigma = e^2 \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \tau_0 \zeta^{p + \frac{3}{2}}. \tag{2.74}
\]

For the Seebeck coefficient, the first two terms are used

\[
S = \mp \frac{\pi^2 k_B}{3 e} (p + \frac{3}{2}) \zeta. \tag{2.75}
\]
For the Lorenz number, the first two terms of the series are also needed

\[ L = \frac{e^2}{3} \left( \frac{k_B}{e} \right)^2, \]  

(2.76)

which is a constant, and shows that the Lorenz number is the same for all metals and independent of both \( p \) and \( \zeta \).

### 2.5 Chapter Summary

The Chapter presents the basic theory for calculating the thermoelectric transport coefficients. Explicit expressions for the electrical conductivity, Seebeck coefficient, and the thermal component of the electronic conductivity have been provided for a semiconductor with parabolic band structure. The transport coefficients for the two extreme cases of non-degenerate and degenerate semiconductors are also considered.
Bibliography


Chapter 3

Theory of Phonon Thermal Conductivity

3.1 Introduction

In chapter 2 we described the electronic transport coefficients. It is well recognized that heat can be transported by lattice vibrations as well as by electric charges. In a non-metallic crystal, the vibrations are considered as the dominant source for heat transfer. Throughout history, measurement of the thermal conductivity was widely used to investigate imperfections or lattice defects in solids. Both the high and low thermal conductivity materials are important in technological applications. The evaluation of lattice thermal conductivity coefficient requires information about the behaviour of atomic vibrations in solids. For this, the topic of lattice dynamics is very important in solid state physics. Traditionally, this had been done at two levels: at the continuum level, where the concept of second order elastic constants is applied to a continuum crystal; the second level is based on using the inter-atomic harmonic force constants concept, which requires dealing with solids at the atomic level. There are two famous approaches which have been used to obtain the inter-atomic force constants: the
first-principles and phenomenological models [1]. In this chapter, for lattice dynamics we follow the first approach, since it is more affordable computationally. That is, we define forces acting on the atoms as the second derivative of the crystal potential with respect to small displacements. Hence, the lattice motion is regarded as a superposition of simple harmonic oscillators, and this approximation is referred to as the harmonic approximation. The phonon spectrum and density of normal modes are calculated adopting the Debye scheme [2], where the crystal is treated as an elastic continuum taking account of only \(3N\) modes, \(N\) being the number of atoms, which means the presence of an upper limit frequency or the Debye cut off frequency. Adopting the harmonic approximation, \(i.e.\) preventing the interactions among phonons will result in an infinite thermal conductivity. In (1929) Peierls [3] showed that the anharmonic nature of the interatomic forces should be considered to obtain finite conductivity. So for qualitative calculations of the lattice thermal conductivity we applied the relaxation time approximation in the Boltzmann equation and presumed that the three-phonon processes will sufficiently describe the anharmonicity effect. Such a scheme is valid for systems of size larger than the phonon mean free path. The scattering relaxation rates for different elastic scattering mechanisms, denoted as extrinsic, such as: boundary, isotropic mass defect, and donor electron scattering are calculated by perturbation techniques. The term intrinsic is used to describe the scattering rate due to three-phonon processes. Here, since we are representing the phonon wave vector in the reduced-zone scheme, we can make a distinction between three-phonon Normal (N) and Umklapp (U) processes. While N processes conserve the momentum leading to a redistribution of phonons and make an indirect contribution to the thermal conductivity, U processes, which conserve the momentum by means of a reciprocal lattice vector \(G\), will control the thermal conductivity directly. The expression for the lattice thermal conductivity within the Debye continuum approximation and relaxation time approximation is for-
mulated using three models: Debye model, Callaway model, and Allen’s theory which will be discussed later on.

3.2 Phonons

The atomic dynamics in solids is explained as the superposition of a number of simple harmonic vibrations with respective frequencies $\omega$. These travelling waves, which can always be analyzed into plane waves [4, 5], are known as the normal modes of the system and are characterized by a wave-vector $q$. The energies of the normal modes are quantized and equally spaced, and these quanta are called phonons, analogous to the quantum (photon) used in an electromagnetic field. Thus a phonon is the excitation quantum in a normal mode [6]. A phonon is treated as a quasiparticle, therefore, we might associate a momentum $\hbar q$ with it. The phonon momentum cannot increase indefinitely. When $\hbar q$ increases by an amount $\hbar G$, it is transferred to the lattice as a whole: due to the crystal periodicity it becomes $\hbar q' = \hbar q + \hbar G$, so the total momentum transferred to the lattice is zero [7]. Since the energy of phonons is quantized as $\hbar \omega$ [8], the average number of phonons in the $q$th mode at thermal equilibrium at temperature $T$ is given by the Bose-Einstein distribution function [6]

$$\tilde{n}_q = \frac{1}{\exp(\hbar \omega(q)/k_B T) - 1}. \quad (3.1)$$

As they propagate through a crystal, phonons will carry heat, thus they contribute to the total thermal conductivity of a system. Their contribution is referred to as the lattice (phonon) thermal conductivity. In order to calculate the lattice thermal conductivity component, one has to know the phonon dispersion relations and the corresponding density of states. To obtain the normal modes of a crystal, i.e. the phonon dispersion relations, we solve the equation of motion for atoms within the harmonic approximation, this means ignoring phonon-phonon
3.3 Phonon Dispersion Relations

In lattice dynamics problems the subject is to calculate the phonon frequencies at desired wave vectors inside the Brillouin zone of a crystalline structure. Adopting the atomic level approach we visualise a crystal lattice as an n-dimensional structure of atoms that are joined together by harmonic springs. The lattice dynamical problem of the $l^{th}$ atom of mass $m_b$ in the $l^{th}$ unit cell, that is displaced in the $\alpha$ direction, with $\alpha = 1, 2, 3$, by an amount $u_\alpha(lb)$, can be set up by applying Newton’s second law combined with Hook’s law [9]

$$m_b\ddot{u}_\alpha(lb) = -\sum_{l\beta} C_{\alpha\beta}(lb; \dot{lb})u_\beta(\dot{lb}), \quad (3.2)$$

where $C_{\alpha\beta}(lb; \dot{lb})$ is the inter-atomic force constant matrix element representing the negative of the $\alpha$ component of the net force acting on atom $(lb)$ due to a unit displacement of atom $(\dot{lb})$ along $\beta$ direction. $C_{\alpha\beta}(lb; \dot{lb})$ can also be written as the second derivative of the potential energy $\phi$ [9]

$$C_{\alpha\beta}(lb; \dot{lb}) = \frac{\partial^2 \phi}{\partial u_\alpha(lb) \partial u_\beta(\dot{lb})}. \quad (3.3)$$

A trial displacement solution can be written as a summation over the normal modes of the system, such that

$$u_\alpha(lb) = \frac{1}{\sqrt{m_b}} \sum_q U_\alpha(q; b)\exp[i(q \cdot x(l) - \omega t)], \quad (3.4)$$

where $x(l)$ is the equilibrium position vector of the $l^{th}$ unit cell and $U_\alpha(q; b)$ is the amplitude of the vibration and is independent of $l$. When this is substituted into Eq. 3.2 we get [9]

$$\omega^2 U_\alpha(q; b) = \sum_{b\beta} D_{\alpha\beta}(bb|q)U_\beta(q; \dot{b}), \quad (3.5)$$
3.3 Phonon Dispersion Relations

where $D_{\alpha\beta}(bb|q)$ is referred to as the dynamical matrix element. The expression of the dynamical matrix element in Fourier space is given as

$$D_{\alpha\beta}(bb|q) = \frac{1}{\sqrt{m_b m_b}} \sum_i C_{\alpha\beta}(0b; \dot{i}b) \exp(iq \cdot x(\dot{i})).$$  \hspace{1cm} (3.6)

To obtain non-trivial solutions for Eq. 3.5 we set the condition

$$|D_{\alpha\beta}(bb|q) - \omega^2 \delta_{\alpha\beta} \delta_{bb}| = 0.$$ \hspace{1cm} (3.7)

For a three-dimensional crystal with $N_0$ unit cells and if there are $p$ atoms per unit cell, there will be $3p$ phonon branches, each with $N_0$ distinct values of the wavevector $q$, i.e. Eq. 3.7 will have $3p$ different solutions of the form $\omega^2(q_s)$, with $s$ as the phonon branch polarization. The branches with the property of $\omega(q) \to 0$ are called acoustic branches, referred to as $ac$. The remaining $(3p - 3)$ branches where $\omega(q) \to$ constant as $q \to 0$ [10] are known as optical branches, referred to as $op$. The acoustic branches are characterized by a large group velocity and lower energy than that of optical branches [11]. Acoustic as well as optical phonons, depending on the phonon travelling direction relative to the atomic vibrations could be classified as longitudinal, i.e. $(e||q)$ or transverse i.e. $(e\perp q)$. The unit vector $e$ denotes the atom motion direction. In an isotropic crystal, as in lead chalcogenides and SnTe, a three dimensional unit cell will produce three acoustic and three optical branches. One longitudinal and the other two are transversely polarized. The transverse polarization could have a degenerate frequency [12]. The concept of a purely longitudinal or a purely transverse polarization in an anisotropic crystal can only be identified along directions of high symmetry of $q$, such as, the [100], [110] and [111] directions in cubic crystals [13].

A schematic description of the dispersion relations for a mono-atomic and a diatomic linear lattice are shown in Fig. 3.1 (a) and (b), respectively. This simple yet essential picture for the normal modes could be expanded to accommodate $3p$ normal modes for any number of atoms in three-dimensional solids. The mono-atomic linear chain in Fig. 3.1 (a) shows the presence of one acoustic branch,
and in Fig. 3.1 (b) the diatomic linear chain shows the presence of acoustic and optical branches. The acoustic curves in Figs. 3.1 (a) and (b) are linear in the long wavelength limit. In the long wavelength limit the phonon group velocity and their phase velocity are the same. At the zone edge the group velocity tends to zero, i.e. the lattice waves become standing waves \[9, 14\]. Brockhouse \[15\] and others have used the neutron-scattering technique to determine realistic phonon dispersion spectra for silicon and germanium. The same technique is used to determine a realistic dispersion relation for PbTe, and the results are presented in Fig. 3.2. The figure also shows calculated dispersion relations along three symmetry directions. In the transport processes, excitations with small energy and small wave-vectors \( q \) are important, since at low temperatures, the excited phonons are mostly confined to small \( q \) or long wavelength acoustic modes \[9\]. Hence, simplifying the dispersion relations, in isotropic crystals, by treating the crystal as a continuum is justified. In this approximation the velocities of the acoustic branches are assumed to be independent of \( q \), that is \( \omega = c_s q \), which is simply the dispersion relation for a continuum solid. This approximation is known as the continuum approximation and is shown by the dashed lines in Fig. 3.2.

Another approximation, known as the Debye model, will be used in the phonon transport theory. In this model the realistic Brillouin zone for a three dimensional cubic system is replaced by a sphere with radius \( q_D \) \[20\]. Debye has assumed that the volume of the Debye sphere, hence the correct number of total acoustic modes, that is \( 3N \) modes for a crystal with \( N \) atoms, is given by \[21\]

\[
q_D = \left( \frac{6\pi^2 N}{N_0 \Omega} \right)^{1/3},
\]

where \( N_0 \Omega \) is the volume of the crystal with \( q_D \) the Debye radius. However, in practice \( q_D \) is treated as an adjustable parameter to accommodate any increase in the number of modes. For example, optical phonon modes for unit cells with
comparable atom masses can be accommodated in a larger Debye sphere in the spirit of an extended zone representation [9].

### 3.3.1 Phonon Density of States within the Isotropic Continuum Approximation and the Debye Model

The density of states $g(\omega)$, is considered a very important function in lattice vibrational studies. This is defined as the possible number of normal modes in a particular frequency range $\omega, \omega + d\omega$ for a polarization $s$. A general expression for the density of normal modes is of the form [9]

$$g(\omega) \propto \frac{1}{|\nabla q\omega_s|}.$$  \hspace{1cm} (3.9)

Figures 3.3 (a) and (b) show the density of normal modes for mono-atomic and diatomic linear chains, respectively. For a mono-atomic linear chain Fig. 3.3 (a) shows that at $\omega = 0$ the density of states is finite and remains almost constant for a large range of frequencies, and at $\omega = \omega_{\text{max}}$ reaches an infinite value. For the diatomic chain, Fig. 3.3 (b) there are three critical points, indicated as $\omega_1$ and $\omega_2$, and $\omega_3$. In view of the isotropic continuum model, the density of states calculations for three-dimensional solids are simplified by equating the group velocity to the phase velocity, i.e. $c_g = c$, hence the density of states can be written in the isotropic continuum model or Debye approximation as [9]

$$g(\omega) = \frac{N_0 \Omega}{2\pi^2} \sum_s \frac{\omega^2}{c_s^3}.$$  \hspace{1cm} (3.10)

The Debye density of states is proportional to $\omega^2$. Figure 3.4 show a schematic illustration of the Debye density of states for a mono-atomic unit cell for a three dimensional solid. The Debye constraint for the correct number of acoustic modes in a crystal can be written as

$$3N = \frac{N_0 \Omega \omega_D^2}{2\pi^2 c_D^3},$$  \hspace{1cm} (3.11)
3.4 Lattice Thermal Conductivity

The phonon thermal conductivity for small temperature gradient $\nabla T$ and under zero electric current condition ($J = 0$) is defined from Eq. 2.1 in the form of Fourier’s law as [1]

$$U = -\kappa_{\text{ph}} \nabla T.$$  \hspace{1cm} (3.13)

The externally applied temperature gradient in Eq. 3.13 is maintained by the randomness of the phonon propagation from the hot to the cold end. This means the energy transfer in a non straight path from one end of a crystal to the other [22]. Considering that the zero point energy carries no heat current [8], i.e. the zero point energy can be taken as the origin [23], the heat current carried by a phonon of wave-vector $q$ in branch $s$ is $\hbar \omega(qs)c_s(q)$, where $c_s(q)$ is the phonon group velocity in the mode $qs$. For the heat flow per unit volume of the crystal,
Figure 3.2: The phonon dispersion curves in PbTe, PbSe, and PbS. Symbols are experimental measurement using inelastic neutron technique and are taken from [16], [17], and [18] for PbTe, PbSe, and PbS, respectively. Solid and dashed lines are modeled data using shell model and force constant model, respectively [19].
Figure 3.3: The density of normal modes for: (a) mono-atomic chain and (b) di-atomic chain.

Figure 3.4: The Debye model of the density of normal modes for mono-atomic unit cell for a three dimensional solid.
3.4 Lattice Thermal Conductivity

a multiplication by the average number of phonons in the $q_s$ mode, and a sum over all modes is performed to get [10]

$$U = \frac{1}{N_0 \Omega} \sum_{q_s} \hbar \omega(q_s) n_{q_s} c_s(q). \quad (3.14)$$

Since the phonon heat current arises as a consequence of the deviation of the phonon distribution from equilibrium, $n_{q_s} - \bar{n}_{q_s}$, Eq. 3.14 can be written as

$$U = \frac{1}{N_0 \Omega} \sum_{q_s} \hbar \omega(q_s) \psi_{q_s} \bar{n}_{q_s} (\bar{n}_{q_s} + 1) c_s(q), \quad (3.15)$$

where $\psi_{q_s}$ is a measure of the deviation from equilibrium distribution for phonons in the mode $q_s$: $n_{q_s} - \bar{n}_{q_s} = \psi_{q_s} \bar{n}_{q_s} (\bar{n}_{q_s} + 1)$. In a cubic crystal, the thermal conductivity from Eqs. 3.14 and 3.15 can be written as a scalar quantity in the form [9]

$$\kappa_{ph} = -\frac{1}{N_0 \Omega |\nabla T|^2} \sum_{q_s} \hbar \omega(q_s) \psi_{q_s} \bar{n}_{q_s} (\bar{n}_{q_s} + 1) c_s(q). \nabla T, \quad (3.16)$$

Based on the particle-like behaviour of phonons, and for phonon transport in structures larger than the phonon wavelength, the Boltzmann transport equation is valid for heat transfer analysis. Determining the phonon deviation function $\psi_{q_s}$ is possible by several methods that adopt the phonon Boltzmann equation [9]. Other theoretical approaches, such as the Green-Kubo method and molecular-dynamics simulations [24], have also been used to predict the phonon thermal conductivity. The second method is based on a statistical mechanical approach and is in contrast to the Boltzmann transport equation, since the calculation is performed in real space and the only requirement is the determination of the equilibrium atomic positions and an appropriate inter-atomic potential [25, 26]. In our attempt to calculate the phonon thermal conductivity, we solve the phonon Boltzmann transport equation within the relaxation time approximation [8].
3.4 Lattice Thermal Conductivity

3.4.1 Relaxation Time Approximation

The relaxation time approximation for the phonon scattering term, i.e., linearising the scattering term, can be written as [9].

\[
\left[ \frac{\partial n_{qs}}{\partial t} \right]_{\text{scatt}} = - \frac{n_{qs} - \bar{n}_{qs}}{\tau_{qs}}. \tag{3.17}
\]

The linearised phonon Boltzmann equation within the relaxation time approximation is written in the form [9]

\[-c_s(q) \nabla T \frac{\partial \bar{n}_{qs}}{\partial T} = \frac{\psi_{qs} \bar{n}_{qs} (\bar{n}_{qs} + 1)}{\tau_{qs}}. \tag{3.18}\]

The expression for the lattice thermal conductivity in Eq. 3.16 can be written within the relaxation time approximation as

\[
\kappa_{ph} = \frac{\hbar^2}{3 N_0 \Omega k_B T^2} \sum_{qs} \bar{c}_s^2(q) \omega_{qs}^2 \tau_{qs} \bar{n}_{qs} (\bar{n}_{qs} + 1), \tag{3.19}
\]

where \(\frac{1}{3} \bar{c}_s^2\) is the average of \(c_s^2 \cos \theta\), with \(\theta\) being the angle between \(\nabla T\) and \(c_s\), for a cubic crystal. Using the following shorthand notation

\[
\langle f \rangle = \sum_{qs} f_{qs} \bar{n}_{qs} (\bar{n}_{qs} + 1), \tag{3.20}
\]

Eq. 3.19 can be written as

\[
\kappa_{ph} = \frac{\hbar^2}{3 N_0 \Omega k_B T^2} \langle \tau \omega^2 c^2 \rangle. \tag{3.21}\]

For phonon speeds and relaxation times that are not dependent on \(q\), the phonon thermal conductivity in Eq. 3.21 can be expressed using elementary kinetic theory as [10]

\[
\kappa_{ph} = \frac{1}{3} C_v \bar{c}^2 \bar{\tau}, \tag{3.22}
\]

where \(\bar{c}\) is the average phonon speed, \(\bar{\tau}\) is the phonon average relaxation time, and \(C_v\) is the specific heat at a constant volume defined as [23]

\[
C_v = \frac{\hbar^2}{3 N_0 \Omega k_B T^2} \sum_{qs} \omega_{qs}^2 \bar{n}_{qs} (\bar{n}_{qs} + 1). \tag{3.23}
\]

In order to calculate the lattice thermal conductivity, appropriate phonon scattering mechanisms should be evaluated.
3.4 Lattice Thermal Conductivity

3.4.2 Phonon Scattering Mechanisms

Several scattering mechanisms will contribute to the phonon relaxation time $\tau$ in Eqs. 3.21 and 3.22. Therefore, to evaluate the lattice thermal conductivity it is essential to provide expressions of the phonon relaxation time for important phonon scattering mechanisms in the crystal. In the harmonic approximation, the lifetime of phonons is limited by phonon scattering from the finite sample size (boundary scattering), static imperfections (mass isotope), alloying, etc. But in real crystals phonons will interact with other phonons. This kind of scattering produces intrinsic relaxation times and arises from the anharmonicity term in the crystal potential [21].

3.4.2.1 Extrinsic Relaxation Times

(i) Boundary Scattering. At low temperatures, and for a crystal of a finite size the only significant scattering mechanism for lattice waves with long wavelengths are from boundaries [23]. For purely diffusive phonon scattering, the boundary scattering process is considered with a relaxation time that is independent of frequency and temperature [10]

$$\tau_{bs}^{-1} = \frac{c_s}{L},$$

where $L$ is the effective boundary length.

(ii) Isotopic Mass Defect Scattering. This is classified as a static point imperfection in solids. Density variations with different isotopes, which occur naturally in real crystals, cause the phonons to scatter. For phonons with wavelengths longer than the imperfection size, the scattering is of Rayleigh type [21]. For a crystal with an average mass $\bar{M}$ per unit cell, and $f_i$, the fraction of the unit cells with mass $M_i$, and $N_0$ unit cells in the crystal, the relaxation time of a phonon mode $q_s$, within the isotropic continuum approximation, due to isotopic mass defects is [9]

$$\tau_{pd}^{-1} = \frac{\Gamma_{pd} \Omega}{4\pi c_s^3} \omega^4(q_s),$$

(3.25)
where \( \bar{c} \) is the average acoustic phonon speed and \( \Gamma_{pd} \) is the isotropic mass parameter given by

\[
\Gamma_{pd} = \sum_i f_i \left( \frac{\Delta M_i}{\bar{M}} \right)^2.
\]

(3.26)

Here, \( \Delta M_i = M_i - \tilde{M} \), with \( \tilde{M} = f_i M_i \).

(iii) Scattering by Donor Electrons. Atomic vibrations which are described in terms of phonons might interact with free donor electrons, with effective mass \( m_e^* \), that are assumed to be moving in a partially full parabolic band. At low temperatures there are few carriers with low energy in semiconductors, hence the phonon-electron interaction will involve phonons with long wavelengths [23]. As the lattice vibrates it will cause a shift in the periodic potential, this shift or deformation is seen as a small perturbation by electrons and will cause them to be scattered into a new state. The dilation produced by the longitudinal vibrations will change the \( E-k \) curves due to the changed lattice spacing. Since electrons near the conduction band edge are of interest, we may approximate the change in the electron energy by the deformation potential term \( C_1 \Delta \), where \( C_1 \) is constant and \( \Delta \) is the local dilation of the atoms [27]. Considering the scattering processes by which an electron in the state of wave-vector \( k \) absorbs a phonon of wave-vector \( q \) and is scattered into the state of wave-vector \( k' \), the momentum conservation condition is [28, 29]

\[
k' = k + q.
\]

(3.27)

and the energy conservation, in the isotropic continuum model, may be written as

\[
E_{k'} = E_k + hqc_{LA},
\]

(3.28)

where \( c_{LA} \) is the speed of longitudinal acoustic phonons. Applying Fermi’s golden rule will result in the following expression for the relaxation rate of a phonon
mode $q_s$ [28]

$$
\tau^{-1}_{ep} = \frac{m^* \Xi^2 k_B T}{2\pi g_{\text{LA}} \hbar^4} [z - \ln \left( \frac{1 + \exp(\xi - \zeta + z^2/16\xi + z/2)}{1 + \exp(\xi - \zeta + z^2/16\xi - z/2)} \right)], \quad (3.29)
$$

where $\Xi$ is the dilatational deformation potential, $z = \hbar \omega / k_B T$, $\xi = m^* c_{\text{LA}}^2 / 2 k_B T$, and $\zeta = \Delta \bar{\mu} / k_B T$.

### 3.4.3 Intrinsic Relaxation Times

As the temperature increases, the harmonic approximation for the crystal potential is not valid. Generally, in real crystals the potential is anharmonic, and as the temperature increases, the phonon-phonon interaction becomes stronger and cannot be ignored. The anharmonicity may adequately be included by considering solely the cubic term in the crystal potential. This term, in the first order perturbation, governs the interactions as three-phonon processes. The three-phonon processes can be classified as either class 1 or class 2. In class 1 processes a $(q, \omega)$ phonon interacts with another phonon $(q', \omega')$, both get annihilated and a third phonon $(q'', \omega'')$ is created. In class 2, a phonon $(q, \omega)$ decays into two phonons $(q', \omega')$ and $(q'', \omega'')$. If the momentum sum of the two annihilated or created phonons is confined to the first Brillouin zone, the process is referred to as an N process. On the other hand, if a reciprocal lattice vector $G$ is required to satisfy the momentum conservation condition, the process is called an U process. The momentum and energy conservation conditions for the three-phonon processes are [21, 1]:

Class 1 : $q + q' = q'' + G$ ; $\omega + \omega' = \omega''$, \quad (3.30)

Class 2 : $q + G = q' + q''$ ; $\omega = \omega' + \omega''$, \quad (3.31)

where $G$, for U-processes within an isotropic continuum model, is the pseudo reciprocal lattice vector constructed by Parrott [30] as follows

$$
G = 2q_D \frac{q \pm q'}{|q \pm q'|}, \quad (3.32)
$$
3.4 Lattice Thermal Conductivity

Figure 3.5: Schematic illustration of three-phonon processes class 1: (a) an N process $q + q' = q''$ and (b) an U process $q + q' = q'' + G$.

where $+$ and $-$ signs refer to class 1 and class 2 processes, respectively. Figure 3.5 show a schematic illustration for a class 1 three-phonon processes.

3.4.3.1 Three-Phonon Processes

To express the cubic anharmonic crystal potential, the crystal is treated as an isotropic anharmonic elastic continuum, and the cubic anharmonic potential for acoustic phonons is written as [1, 9, 23]

$$\phi_3 = \frac{1}{3!} \sqrt{\frac{\hbar^3}{2\rho N_0 \Gamma}} \frac{\gamma(T)}{c} \sum_{q,s,s'} \sqrt{\omega(qs)\omega(q's')\omega(q''s'')} \times \left( a_{qs}^\dagger - a_{-qs} \right) \left( a_{q's'}^\dagger - a_{-q's'} \right) \left( a_{q''s''}^\dagger - a_{-q''s''} \right) \delta_{q+q'+q'',G};$$

where $\gamma(T)$ is a mode-average but temperature-dependent Grüneisen constant, $a_{qs}^\dagger, a_{-qs}$ etc. are phonon creation and annihilation operators, $\rho$ is the material density, and the Kronecker $\delta_{q+q'+q'',G}$ is defined as [9]

$$\delta_{q+q'+q'',G} = \frac{1}{N_0 \Omega} \int d^3r \exp[i(q + q' + q'').r].$$

Applying Fermi’s golden rule to evaluate the transition probability for both class 1 and class 2 processes and following the procedure given in [9], the single-mode relaxation time for a $q_s$ phonon mode due to three-phonon interactions is written as

$$\tau_{\text{anh}}^{-1}(q_s) = \frac{\pi \hbar \rho^2 \gamma^2}{N_0 \Omega c^2} \sum_{q'_s,q''_s,G} \omega(q_s)\omega(q'_s)\omega(q''_s)\bar{n}(q'_s)$$
\[ \times \left\{ \frac{(\tilde{n}(q''s'') + 1)}{\tilde{n}(qs)} + \frac{1}{2} \frac{\tilde{n}(q''s'')}{\tilde{n}(qs)} \delta(\omega(qs) - \omega(q's') - \omega(q''s'')) \delta_{q+q',q''} + \right\}, \quad (3.35) \]

The first and second terms in Eq. 3.35 describe the processes of Class 1 and Class 2, governed by the momentum and energy conservation conditions given in 3.31. For U processes \( G \) is considered as given in 3.32.

For a phonon of mode \( qs \) the inverse of the total single mode relaxation rate \( \tau^{-1}{qs} \) in Eq. 3.19 can be expressed as the sum of the relaxation times from different scattering mechanisms

\[ \tau^{-1}{qs} = \tau^{-1}\text{elastic} + \tau^{-1}\text{anh}, \quad (3.36) \]

where \( \tau^{-1}\text{elastic} \) is given as

\[ \tau^{-1}\text{elastic} = \tau^{-1}\text{(bs)} + \tau^{-1}\text{(pd)} + \tau^{-1}\text{(ep)} \quad (3.37) \]

and \( \tau^{-1}\text{anh} \) is expressed as

\[ \tau^{-1}\text{anh} = \tau^{-1}_N + \tau^{-1}_U, \quad (3.38) \]

where \( \tau^{-1}_N \) and \( \tau^{-1}_U \) refer to the scattering rates due to N and U processes, respectively.

### 3.5 Different Theories of Total Relaxation Times

Development of the relaxation time approximation methods given in Eq. 3.19, has led to several theories for the lattice thermal conductivity.

**(a) Single-mode relaxation-time model.**

The simplest picture involving three-phonon processes is the single mode relaxation time (smrt) also known as the Debye model. In this model, \( \tau_{qs} \) in Eq. 3.19 is calculated for phonons of mode \( qs \), assuming all other phonon modes are
3.5 Different Theories of Total Relaxation Times

in equilibrium. The lattice thermal conductivity in Eq. 3.19, hence, can be expressed as

\[ \kappa_{\text{smrt}} \equiv \kappa_D = \frac{\hbar^2}{3N_0\Omega k_B T^2} \sum_{qs} c_s^2(q)\omega_s^2(qs)\tau(qs)\tilde{n}(qs)(\tilde{n}(qs) + 1). \] (3.39)

(b) Callaway’s effective relaxation-time model.

Following the observation of Peierls [3] that N processes do not by themselves cause the relaxation of phonons towards the equilibrium Bose-Einstein distribution and that the U processes can decay the system to zero current state, several attempts have been made to modify the single-mode relaxation time [32]-[36]. Klemens [8] has argued that, even though the N processes do not contribute directly to the thermal resistance of the crystal, their role in the establishment of thermal equilibrium must be considered. Klemens noted that N processes tend to relax the phonon system to a displaced equilibrium distribution. Callaway [31] has succeeded in adding a term that accounts for the N processes. In Callaway’s model, there are two distinguishable relaxation times, the N processes relaxation time \( \tau_N \) and resistive (R) processes relaxation time processes \( \tau_R \). The total relaxation time \( \tau \) is written as

\[ \tau^{-1} = \tau_N^{-1} + \tau_R^{-1}, \] (3.40)

where \( \tau_R^{-1} = \tau_{\text{elastic}}^{-1} + \tau_{\text{U}}^{-1} \). The elastic relaxation time \( \tau_{\text{elastic}} \) is defined in Eq. 3.37.

The effective total relaxation time \( \tau_C \) developed by Callaway is expressed as

\[ \tau_C = \tau_{\text{smrt}} \left( 1 + \beta_C \frac{\tau_N^{-1}}{c_s^2} \right). \] (3.41)

where the coefficient \( \beta_C \) is defined using the notation in Eq. 3.20

\[ \beta_C = \frac{\langle \omega^2\tau_\text{N}^{-1} \rangle}{\langle q^2\tau_\text{N}^{-1}\tau_\text{R}^{-1} \rangle}. \] (3.42)

A derivation of Eq. 3.42 is given in appendix A. Callaway’s conductivity can be
written in the form

\[ \kappa_C = \frac{\hbar^2}{3N_0\Omega k_B T^2} \left[ \sum_{qs} c_s^2(q)\omega^2(qs)\tau_{qs}\bar{n}(qs)(\bar{n}(qs) + 1) \right. \]

\[ + \beta_C \sum_{qs} \omega^2(qs)\tau_{qs}\tau_{qs,N}^{-1}\bar{n}(qs)(\bar{n}(qs) + 1) \right] \]

(3.43)

\[ \kappa_C = \frac{\hbar^2}{3N_0\Omega k_B T^2} \sum_{qs} c_s^2(q)\omega^2(qs)\tau_{C,qs}\bar{n}(qs)(\bar{n}(qs) + 1). \]  

(3.44)

(c) Allen’s improvement of Callaway’s model.

Allen [37] has proposed an improvement over Callaway’s model for lattice thermal conductivity. In this scheme, the total relaxation time is defined as

\[ \tau_A = \tau_{\text{smrt}} \left( 1 + \beta_A \frac{\tau_{N}^{-1}}{C^2} \right). \]  

(3.45)

where \( \tau_A \) is Allen’s total relaxation time and \( \beta_A \) is given as

\[ \beta_A = \frac{<\omega^2\tau>}{<q^2\tau^{-1}_R>}. \]  

(3.46)

A derivation of Eq. 3.46 is given in appendix B. Allen’s expression for the lattice thermal conductivity is written as

\[ \kappa_A = \frac{\hbar^2}{3N_0\Omega k_B T^2} \left[ \sum_{qs} c_s^2(q)\omega^2(qs)\tau_{qs}\bar{n}(qs)(\bar{n}(qs) + 1) \right. \]

\[ + \beta_A \sum_{qs} \omega^2(qs)\tau_{qs}\tau_{qs,N}^{-1}\bar{n}(qs)(\bar{n}(qs) + 1) \right] \]

\[ \kappa_A = \frac{\hbar^2}{3N_0\Omega k_B T^2} \sum_{qs} c_s^2(q)\omega^2(qs)\tau_{A,qs}\bar{n}(qs)(\bar{n}(qs) + 1). \]  

(3.47)

(3.48)

### 3.6 Isotropic Continuum model and Conductivity Expressions

The lattice thermal conductivity can be expressed by a simple expression. This form is obtained by converting the summation over \( q \) in Eqs. 3.39, 3.44, and 3.48 to an integral form using the relation [9]

\[ \sum_{q} = \int g(\omega) d\omega. \]  

(3.49)
Within Debye’s isotropic continuum model the density of states, \( g(\omega) \), is expressed by applying Eq. 3.11, and changing the integration variable to \( x \), with \( x = q/q_D \). The simplified lattice thermal conductivity expressions for Debye, Callaway, and Allen’s models are written as

\[
\kappa_D = \frac{\hbar^2 q_D}{6\pi^2 k_B T^2} \sum_s c_s^4 \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1), \quad (3.50)
\]

\[
\kappa_C = \frac{\hbar^2 q_D}{6\pi^2 k_B T^2} \left[ \sum_s c_s^4 \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1) + \sum_s c_s^2 \int_0^1 dx x^4 \tau^{-1} \bar{n}(\bar{n} + 1) \right], \quad (3.51)
\]

\[
\kappa_A = \frac{\hbar^2 q_D}{6\pi^2 k_B T^2} \left[ \sum_s c_s^4 \int_0^1 dx x^4 \tau \bar{n}(\bar{n} + 1) + \sum_s c_s^2 \int_0^1 dx x^4 \tau^{-1} \bar{n}(\bar{n} + 1) \right], \quad (3.52)
\]

where \( \tau \) and \( \bar{n} \) are functions of \( x \) and the phonon polarisation \( s \). \( \beta_C \) and \( \beta_A \) given by Eqs. 3.42 and 3.46 are expressed in integral forms. It can be seen that, the N-drift term in both Callaway and Allen’s expressions is an additional summation over the phonon polarization to the (smrt) contribution \( \kappa_{\text{smrt}} \).

The three-phonon acoustic-acoustic process relaxation time can be evaluated numerically by adopting the the Debye elastic isotropic continuum model and applying the properties of the Dirac-delta function. Following the procedure in [9], the anharmonic phonon relaxation time for three acoustic-acoustic phonon interaction is expressed as

\[
\tau_{\text{an}}^{-1} = \frac{\hbar q_D^2 c^2(T)}{4\pi \rho c^2 q_D^3} \sum_{s' s'' s^\epsilon} c_s c'_{s^\epsilon} \times \left[ \int dx' x'^2 x'' \left[ 1 - \epsilon + \epsilon (C x + D x') \right] \frac{\bar{n}_{s' s''}(\bar{n}_{s^\epsilon} + 1)}{(\bar{n}_{s^\epsilon} + 1)} \right. \\
+ \left. \frac{1}{2} \int dx' x'^2 x'' \left[ 1 - \epsilon + \epsilon (C x - D x') \right] \frac{\bar{n}_{s' s''} \bar{n}_{s^\epsilon}}{\bar{n}_{q s}}, \right] \quad (3.53)
\]

where \( x = q/q_D, x' = q'/q_D, x'' = C x \pm D x', C = c_s/c_{s''}, \bar{n}_{s^\epsilon} = \bar{n}(x_{s^\epsilon}^\epsilon) \), and \( \epsilon = 1(-1) \) for N (U) processes.

So far, the contribution to thermal conductivity involves only the acoustic
phonons. In the next chapter the contribution from optical as well as acoustic branches will be considered.

3.7 Chapter Summary

Applying the Boltzmann equation within the relaxation time approximation the lattice thermal conductivity expressions are derived for the Debye model, Callaway model, and Allen’s improvement over the Callaway model. The acoustic phonon dispersion and density of states are expressed using the Debye model within the continuum approximation. The scattering of phonons from the boundary, mass defect, and donor electrons are considered. The scattering rates for these mechanisms are obtained by employing the first order perturbation techniques. For the phonon-phonon interaction the anharmonicity is considered to be adequately described by the three-phonon processes.
Bibliography


Chapter 4

Calculations of TE Properties of PbTe

4.1 Introduction

As we mentioned earlier, in a vast variety of applications, TE thermoelectric materials have been widely used as direct heat-to-electricity converters and electronic coolers [1]. The widespread adoption of thermoelectric technology was strongly motivated by the production of large-scale bulk materials with high $ZT$. Lead telluride (PbTe) and its alloys are considered as some of the best thermoelectric materials in the mid temperature range [2]. A significant contributing factor that renders the large $ZT$ value for PbTe is its low lattice thermal conductivity, which is $\kappa_{\text{ph}} \sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [3, 4, 5] despite its simple rock salt structure. Detailed understanding of factors resulting in this low $\kappa_{\text{ph}}$ value is lacking from the literature. Recent studies on p-type samples of optimised doping level reveal $ZT$ values of approximately 1.4 at 750 K [6, 7]. The thermal conductivity ($\kappa$) and the Seebeck coefficient ($S$) of several specimens of PbS, PbSe and PbTe have been measured by Greig [8] in the temperature range $4 - 100$ K.

A majority of theoretical studies of the electronic components of the TE transport coefficients of semiconductors are performed using the nearly free electron model and isotropic effective mass theory. It has been reported in Refs. [9, 10] that
the electronic band structure of PbTe is non-parabolic and this effect could appear as a strong temperature dependence of effective mass and Lorentz number at relatively elevated temperatures and carrier concentrations [9]. Furthermore, the non-parabolicity may influence a change in the energy dependence of carrier relaxation time due to the increase in the density of states [11, 12]. However, the calculation of the electron transport coefficient could still be made using the parabolic band approximation with some adjustable parameters. So far, there is no complete understanding of the factors causing the low $\kappa_{ph}$ value in PbTe. It has been suggested that the strong anharmonic coupling between the transverse optical (TO) and the longitudinal acoustic (LA) phonons, which was identified using a combination of inelastic neutron scattering measurements and first-principles computations of phonons [13], could be used in explaining the low thermal conductivity of PbTe. However, no theoretical formalism or numerical results are available to establish details of the role the TO phonons play in the lattice thermal conductivity and the thermoelectric figure of merit of PbTe.

In this Chapter we compute the electronic transport coefficients for bulk n-PbTe. These coefficients are evaluated within the isotropic-nearly-free-electron approximation and assuming the acoustic phonons to be the main scatterer for charge carriers. The band non-parabolicity, which will manifest itself directly through effective mass dependence on energy and indirectly through relaxation time, is also included in this study. The electronic thermal conductivity is calculated including the mono-polar $\kappa_{mp}$ and bipolar $\kappa_{bp}$ contributions. The lattice thermal conductivity is computed in detail within the single mode relaxation time scheme, employing the isotropic continuum model for the dispersion relation, and an isotropic continuum model for crystal anharmonicity as was discussed in Chapter 3. Here, the theory of the lattice conductivity is expanded to include the optical phonon branches as well as acoustic branches. The results for the lattice conductivity are evaluated with and without the optical phonons contribution to
heat conduction. The crystal anharmonic effects in the thermoelectric properties of n-type PbTe are studied by considering different three-phonon processes and a comparison between N and U relaxation rates is presented for LA and TA phonons. Our numerical work has been carried out with the material parameters relevant to the sample employed in the experimental study reported in Ref. [14]. Finally, we present the figure of merit results.

4.2 Electronic Transport Coefficients

For evaluating the electronic transport coefficients in Chapter 2 we have considered the effective contribution of the transport processes to be from one band of semiconductor; this is reasonable for extrinsic semiconductors when the Fermi level is much closer to one band than to any other. In semiconductors, it is convenient to replace $\bar{\mu}$ which appears in Eq. 2.19 with the Fermi level $E_F(T)$. This level represents a normalizing parameter that can be, at thermodynamic equilibrium, used to describe the occupancy of all electron states at all energy [15]. The Fermi level does not have to coincide with any of electron states. At sufficiently high temperatures, electrons in the valence band could gain sufficient energy and cross the forbidden energy gap to the conduction band. In this case, the valence band starts to contribute effectively to the transport processes, i.e. the semiconductor becomes intrinsic. The electronic transport coefficients will be labeled with the subscripts (ext) and (int) to describe the coefficients for extrinsic and intrinsic regimes, respectively. We have already noted from Chapter 2 the significance of determining the Fermi level position, with respect to the band of interest, in calculating the electronic transport coefficients. Therefore to proceed in evaluating the extrinsic and intrinsic electronic transport coefficients we have to determine the Fermi level position at low and high temperatures.
### 4.2 Electronic Transport Coefficients

#### 4.2.1 Temperature Dependence of Fermi Level

In semiconductors the Fermi level position depends on temperature as well as impurity concentration [15]. At a temperature near absolute zero the Fermi level could be located within a continuous range of energies or else within a region of forbidden energy [15, 16]. As the temperature increases only states that are lying within a few $k_B T$ of the Fermi level will have a major change in their occupation [16]. Assuming a thermal equilibrium condition for all the various energy states we can use a common Fermi level [17]. For non-degenerate semiconductors, the Fermi level is found to be located in the forbidden gap, and the condition $|E - E_F|/k_B T \gg 1$ is satisfied for both electrons and holes in the conduction and valence bands, respectively. Considering the conduction band, the Fermi Dirac distribution function can be approximated by

$$f_0(E) \approx \exp\left[-\frac{(E - E_F)}{k_B T}\right],$$  \hspace{1cm} (4.1)

which is the Boltzmann approximation. We have established in chapter 2 that for transport calculations the band structure of the semiconductor can be adequately described by the nearly-free electron approximation. In the temperature range over which the Boltzmann approximation is valid and for the case of completely ionized impurities, the Fermi level for an n-type semiconductor is expressed as [18]

$$E_F(T) = \frac{1}{2} (E_v + E_c) + \frac{3}{4} k_B T \ln\left(\frac{m^*_h}{m^*_e}\right) + k_B T \sinh^{-1} \left(\frac{N_d}{2 \sqrt{U_c U_v} \exp(-\zeta_g)}\right).$$  \hspace{1cm} (4.2)

Here $E_v$ and $E_c$ are the energies of the valence and conduction band edges, $m^*_e$ and $m^*_h$ are the density-of-states effective masses for the conduction and valence bands, $N_d$ is the concentration of ionised donors. $U_{c(v)}$ is written as

$$U_{c(v)} = 2 (m^*_{c(\text{v})} k_B T / 2\pi \hbar^2)^{3/2}.$$  \hspace{1cm} (4.3)

and $\zeta_g$ is the the reduced band gap given by

$$\zeta_g = (E_c - E_v)/k_B T.$$  \hspace{1cm} (4.4)
As the temperature increases the number of thermally excited carriers will exceed the donors and the expression in Eq. 4.2 will be reduced to the following form for the intrinsic regime [18]

\[ E_F(T) = \frac{1}{2}(E_V + E_C) + \frac{3}{4}k_B T \ln \left( \frac{m^*_h}{m^*_e} \right). \]  

### 4.2.2 Density of States Effective mass

In Chapter 2 Fig. 2.4(a) showed the band edges of the conduction and valence bands for PbTe to be located at the L point. For this, the constant energy surfaces are considered to be ellipsoidal and a distinction should be made between the effective mass along the longitudinal and transverse axes of an ellipsoid, which will be denoted as \( m^*_l \) and \( m^*_t \), respectively. The density of states effective mass for a single band is described by a longitudinal effective mass and a degenerate transverse effective mass as

\[ m^*_d = \left( m^*_l m^*_t^2 \right)^{1/3}. \]  

(4.6)

If a band has \( N_{\text{val}} \) valleys, the density of states effective mass is given by [15]

\[ m^*_d = N_{\text{val}}^{2/3} \left( m^*_l m^*_t^2 \right)^{1/3}. \]  

(4.7)

For PbTe the conduction band reaches the lowest energy at the eight locations on the zone boundary \( L = [\pm 1/2 \ \pm 1/2 \ \pm 1/2] \), i.e. the energy surfaces can be represented by eight half ellipsoidal surfaces which are equivalent to four full ellipsoidal surfaces. In calculating the electrical conductivity the contribution from all these valleys should be added up to find the total electrical conductivity.

## 4.3 Transport Coefficients for n-Type Semiconductors

In n-type semiconductors and at low temperatures excess electrons can be thermally excited and become available for conduction purposes. The electron density determination can be found using the approximation in Eq. 4.1 since the
4.3 Transport Coefficients for n-Type Semiconductors

non-degenerate condition is satisfied for low carrier concentration. The densities per unit volume of the thermally excited electrons \( n_0 \) and holes \( p_0 \) can be written as [19]

\[
n_0 = \frac{N_{\text{val}}}{2\pi^2} \left( \frac{2m^*_e k_B T}{\hbar^2} \right)^{3/2} F_{1/2}^1(\zeta - \epsilon_e/k_B T), \quad (4.8)
\]

\[
p_0 = \frac{N_{\text{val}}}{2\pi^2} \left( \frac{2m^*_h k_B T}{\hbar^2} \right)^{3/2} F_{1/2}^1(\epsilon_h/k_B T - \zeta), \quad (4.9)
\]

where \( m^*_e \) and \( m^*_h \) are electron hole density of states effective masses, respectively, \( \zeta \) is the reduced Fermi energy and \( F_{1/2}^1(x) \) is the Fermi integral defined in Eq. 2.61 with \( n = 1/2 \). Our intention is to calculate the extrinsic electrical conductivity since the only effective contribution in this temperature range is from electrons in the conduction band.

### 4.3.1 Electrical Conductivity

**i. Extrinsic Electrical Conductivity.** To calculate the electrical conductivity numerically in the low temperature regime we apply Eq. 2.63. The expression shows the dependence of the electrical conductivity on the position of the reduced Fermi level \( \zeta \) and the relaxation time constant \( \tau_0 \). Electrons subjected to acceleration as a result of applied electric field will collide with phonons, impurity atoms, etc.. For moderately doped extrinsic (non-degenerate) semiconductors and insulators electrons are dominantly scattered by acoustic phonons, however in degenerate semiconductor at normal temperatures the dominant scattering of electron is from the ionized impurities [20]. For this reason we exclusively consider scattering of electrons with acoustic phonons [21, 22, 23, 24]. To calculate the electrical conductivity we need to have an expression for the relaxation time constant that appears in Eq. 2.63. There are several models to work out this expression. We have employed the deformation potential model to find the electron phonon matrix element and by following the procedure given in [25] we express the electron-
acoustic phonon relaxation rate as

\[
\frac{1}{\tau} = \frac{\sqrt{2} \Xi^2 m_{de}^{*3/2} k_B T}{\hbar^3 \rho c_i^2} E^{1/2},
\]

(4.10)

where \(e\) is the magnitude of the electronic charge, \(\Xi\) is the deformation potential, and \(\rho\) is the material density. Substituting the relaxation time constant \(\tau_0\) from Eq. 4.10 into Eq. 2.63 and setting \(s = 0\) with \(p = -1/2\) we get

\[
\rho_{\text{ext}}^{-1} = N_{\text{val}} \frac{2\hbar e^2 \rho c_i^2}{3\pi \Xi^2 m_{de}^*} F_0(\zeta).
\]

(4.11)

Here the contribution from the four valleys is considered \((N_{\text{val}} = 4)\).

**ii. Intrinsic Electrical Conductivity.** A doped semiconductor changes from extrinsic to intrinsic at high temperatures and the dopant carriers become totally ionized, hence thermally excited host electrons and holes begin to contribute to the transport properties. Therefore, the contribution from the valence band as well as from the conduction band should be considered for calculating the transport coefficients. For convenience we express the electrical conductivity given by Eq. 2.63 in the form

\[
\rho_{\text{int}}^{-1} = ne\mu,
\]

(4.12)

where \(\mu\) is the carrier mobility. The electrical conductivity from both types of carriers is

\[
\rho_{\text{int}}^{-1} = e(n\mu_e + p\mu_h).
\]

(4.13)

Under the non-degenerate condition, when the band edges become separated by an energy that is far from the thermal energy \(k_B T\), the Fermi integral in Eqs. 4.8 and 4.9 can be written as

\[
F_{1/2}(\zeta) = e^\zeta \Gamma(1/2 + 1).
\]

(4.14)

Thus, the electron and hole concentrations are written as [18]

\[
n_i = p_i = 2 \left( \frac{k_B T}{2\pi^2 \hbar^2} \right) \left( m_{de}^* m_{dh}^* \right)^{3/4} \exp(-\zeta_{\text{g}}/2),
\]

(4.15)
where \( n_i \) and \( p_i \) are the electron and hole intrinsic concentration. The intrinsic electrical conductivity can be expressed as

\[
\rho_{\text{int}}^{-1} = \sqrt{\pi e} \left( \frac{2k_B T}{\hbar^2} \right)^{3/2} \left( m_{de}^* m_{dh}^* \right)^{3/4} \times (\mu_e + \mu_h) \exp(-\zeta_g/2).
\] (4.16)

For electron scattering from acoustic phonons the mobility is expected to have the following dependence on temperature [20]

\[
\mu_e \propto T^{-2/3}.
\] (4.17)

Blakemore [15] has shown that in almost every semiconductor the mobility temperature dependence departs from that given in Eq. 4.17. This was attributed at low temperatures to the effects of band non-parabolicity and the effective mass dependence on the energy. At high temperatures the departure from \(-2/3\) was attributed to the large change in energies of electrons when they are scattered from the optical phonons. This result was confirmed in Refs.[26, 27], where the variation of the mobility with temperature at sufficiently high temperatures was observed in the range \(20 - 50\) K for low carrier densities and at higher temperatures for samples with larger carrier densities. The variation was reported [11] to follow the power law as

\[
\mu \propto T^{-r},
\] (4.18)

where the power exponent \( r \) is usually found to be between 2 and 3: for most cases it is found to be \( r = 5/2 \). This dependence, for non-degenerate semiconductors, is found to be \( 3/2, -3/2 \) and \( 1/2 \) for the acoustical scattering, ionized impurities scattering, and polar optical vibrations scattering, respectively. However, \( \text{PbTe} \) is highly ionic, with the ionicity fraction of \( 0.63 \) on the Phillips scale. Ioffe in Ref. [28] has reported that for ionic semiconductors the mobility temperature dependence is predicted to be proportional to \( T^{-1/2} \). Following this suggestion we may then express in the form Eq. 4.16

\[
\rho_{\text{int}}^{-1} = DT \exp(-\zeta_g/2),
\] (4.19)
where \( D \) is an appropriate constant.

### 4.3.2 Electronic Thermal Conductivity

#### i. Mono-polar Electronic Thermal Conductivity

The carrier contribution to the thermal conductivity can be expressed using Eq. 2.66 in terms of Lorentz number as

\[
\kappa_{mp} = L \rho^{-1} T, \tag{4.20}
\]

where \( L \) is given as

\[
L = \left( \frac{k_B}{e} \right) \left[ \frac{3F_2}{F_0} - \left( \frac{2F_1}{F_0} \right) \right]. \tag{4.21}
\]

Hence, the mono-polar electron thermal conductivity can be written as

\[
\kappa_{mp} = \left( \frac{k_B}{e} \right)^2 \left[ \frac{3F_2(\zeta)}{F_0(\zeta)} - \left( \frac{2F_1(\zeta)}{F_0(\zeta)} \right)^2 \right] \rho^{-1} T, \tag{4.22}
\]

where \( \rho \) is the extrinsic electrical resistivity: \( \rho = \rho_{ext} \).

#### ii. Bipolar Electronic Thermal Conductivity

When the temperature increases there will be more than one type of carrier. This effect is observed in an intrinsic or near intrinsic semiconductor and is known as the bi-polar thermal conductivity [29]. The contributions to the electrical conductivity and Seebeck coefficient from both carriers can be expressed as follows [30].

\[
\sigma = \sigma_n + \sigma_p, \tag{4.23}
\]
\[
S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p}, \tag{4.24}
\]

where \( \sigma_n \) and \( \sigma_p \) are the electron and hole conductivity, respectively. \( S_n \) and \( S_p \) are the Seebeck coefficients in the conduction and valence band, respectively. The overall electronic thermal conductivity \( \kappa_{bp} \) is found to be [31]

\[
\kappa_{bp} = \frac{b}{(b+1)^2} \left[ \zeta_0 + 4 \right]^2 \left( \frac{k_B}{e} \right)^2 \rho^{-1} T, \tag{4.25}
\]

where \( b \) is the carrier mobility ratio \( \mu_n/\mu_p \) and \( \rho \) is the intrinsic electrical resistivity: \( \rho = \rho_{int} \).
4.3.3 Seebeck coefficient

For n-type semiconductors the Seebeck coefficient can be written using Eq. 2.65 as

\[
S = -\frac{k_B}{e} \left[ \zeta - \frac{2F_1(\zeta)}{F_0(\zeta)} \right],
\]

(4.26)

For a non-degenerate semiconductor this expression can be simplified to the form in Eq. 2.72 with \( p = -1/2 \) for scattering from lattice vibrations.

4.4 Lattice thermal transport coefficient

The expressions for the lattice conductivity were derived in Chapter 3 under the assumption that acoustic phonons are the sole heat carriers. However, the PbTe dispersion relations in Fig. 3.2 showed the optical branches as low lying branches. This suggests that the role of the transverse optical phonons in heat transfer should be taken into account. Therefore, the lattice thermal conductivity \( \kappa_{ph} \) of PbTe is computed within the single mode relaxation time scheme using Debye’s model and adopting an extension of the isotropic acoustic continuum approximation presented in Ref. [32]. The Brillouin zone of the (fcc) lattice for the rock-salt structure is treated as a Debye sphere of radius \( q_D \) and the dispersion relations for the acoustic and optical phonons are approximated as

\[
\begin{align*}
\omega_{TA} &= c_{TA}q; \\
\omega_{TA} &= c_{LA}q \\
\omega_{TO} &= \omega_{TO}^{\min} + c_{TO}q; \\
\omega_{LO} &= \omega_{LO}^{\max} - c_{LO}q = \omega_{LO}^{\min} + c_{LO}(q_D - q),
\end{align*}
\]

(4.27)

(4.28)

where \( q \) is the magnitude of phonon wave-vector, \( c_s \) is the speed for phonons of polarisation \( s \), \( \omega_{TO}^{\min} \) is the minimum frequency (at the zone centre) of the TO phonon, and for the LO phonon \( \omega_{LO}^{\max} \) is the maximum frequency (at the zone centre) and \( \omega_{LO}^{\min} \) is the minimum frequency (at the Debye sphere radius). The corre-
4.4 Lattice thermal transport coefficient

The corresponding density of states expressions are

\[ g_{\text{TA}}(\omega) = \frac{V_{\text{crys}}}{2\pi^2} \frac{\omega^2}{c_{\text{TA}}^3}; \quad g_{\text{LA}}(\omega) = \frac{V_{\text{crys}}}{2\pi^2} \frac{\omega^2}{c_{\text{LA}}^3} \]  
\[ g_{\text{TO}}(\omega) = \frac{V_{\text{crys}}}{2\pi^2} \frac{(\omega - \omega_{\text{TO}}^\text{min})^2}{c_{\text{TO}}^3} \quad (\text{for } \omega \geq \omega_{\text{TO}}^\text{min}) \]  
\[ g_{\text{LO}}(\omega) = \frac{V_{\text{crys}}}{2\pi^2} \frac{(\omega_{\text{LO}}^\text{max} - \omega)^2}{c_{\text{LO}}^3} \quad (\text{for } \omega_{\text{LO}}^\text{min} \leq \omega \leq \omega_{\text{LO}}^\text{max}), \]

where \( V_{\text{crys}} \) is crystal volume. In the above equations, we have considered three acoustic (LA, doubly degenerate TA) and three optical (LO and doubly degenerate TO) phonon branches for the two atom unit cell of the rock-salt structure. In other words, the total frequency-integrated density of states \( \int g(\omega)d\omega = \sum_s \int g_s(\omega)d\omega \) represents a total of \( 3N \) phonon modes in a crystal containing \( N \) atoms. The single-mode relaxation time expression for the lattice thermal conductivity is then written as

\[ \kappa_{\text{ph}} \equiv \kappa_{\text{smrt}} = \frac{\hbar^2}{3k_B T^2V_{\text{crys}}} \sum_s \int_{\omega_{\text{min}}}^{\omega_{\text{max}}} d\omega g_s(\omega) \omega^2 c_s^2 \tau_s(\omega, T) \bar{n}(\bar{n} + 1), \]

where \( \tau_s(\omega, T) \) is the frequency and temperature dependent relaxation time for a phonon of polarisation with frequency \( \omega \), the average phonon speed \( \bar{c} \) is computed from \( 3/\bar{c}^3 = 2/c_{\text{TA}}^3 + 1/c_{\text{LA}}^3 \), and \( \bar{n} = 1/\exp(\hbar\omega/k_B T) - 1 \) is the Bose-Einstein distribution function. Using Eqs. (4.28) we express Eq. (4.32) as

\[ \kappa_D \equiv \kappa_{\text{smrt}} = \frac{\hbar^2 q_{\text{D}}^5}{6\pi^2 k_B T^2} \sum_s \int_0^1 dx x^2 (\eta_s + x)^2 \tau_s \bar{n}(\bar{n} + 1), \]

where \( x = q/q_{\text{D}}, k_B \) is the Boltzmann constant, \( \eta_s = \omega_{\text{LO}}^\text{min}/c_s q_{\text{D}} \) for branches with upward dispersion from the zone centre (for TA, LA and TO branches), \( \eta_s = 1 + \omega_{\text{LO}}^\text{min}/c_s q_{\text{D}} \) for the LO branch, and double counting of the transverse branches is implicit.

4.4.1 Acoustic Phonon Lattice Thermal Conductivity

By applying Eq. 4.32 for the lattice thermal conductivity, we treated the optical phonon as means to scatter the acoustic phonons ignoring their role as heat
carrier.

### 4.4 Lattice thermal transport coefficient

#### 4.4.2 Phonon Scattering Rates

For an n-type single crystal sample of PbTe, we considered the scattering mechanisms discussed in Chapter 2, which are

(i) Boundary scattering rate $\tau_{bs}^{-1}$. At low temperature phonon scattering is dominant by the sample boundary (bs) and the scattering rate can be calculated from Eq. 3.24.

(ii) Point defect scattering rate $\tau_{pd}^{-1}$. The point defect scattering rate which is due to phonons scattering from isotopic defects is calculated by expressing Eq. 3.25 as [33]

$$
\tau_{pd}^{-1} = A_{pd}g(\omega)\omega^2 = B_{pd}(\omega_0 - \omega)^2\omega^2 \quad \text{(for } \omega_{\text{min}} \leq \omega_0 \leq \omega_{\text{max}}),
$$

where $\omega_0$ is taken as $\omega_{\text{min}}$ for TA, LA, TO and as $\omega_{\text{max}}$ for LO phonons, and the constants $A_{pd}$ and $B_{pd}$ are directly related to the type and concentration of defects. As usually the nature and concentration of point defects are unknown, we treat $B_{pd}$ as an adjustable parameter.

(iii) Donor electron scattering rate $\tau_{ep}^{-1}$. The scattering rate for phonon-electron interaction is calculated using Eq. 3.29.

(iii) Phonon-phonon scattering rate $\tau_{anh}^{-1}$. As was established in Chapter 3, we expect three-phonon processes to adequately describe anharmonic interactions. Expressions for the relaxation rates for a phonon mode $qs$ undergoing N and U three-phonon processes of class 1 type ($qs + q's' \rightarrow q''s''$) and class 2 type ($qs \rightarrow q's' + q''s''$) have been derived in Chapter 3 when all phonons are from the acoustic branches. To include the TO branches (which are quite similar to the acoustic branches except only that for $q = 0$ the frequency of such a mode does not go to zero as it does for the acoustic branches) the formulation presented in Eq. 3.35 should be modified to deal with allowed three-phonon processes,
including acoustic as well as optical phonons. In this work we use Eqs. (4.28) and (4.31), and follow the procedure described in Ref. [34] to derive the following expression for the anharmonic scattering rate for a phonon mode \( q_s \) (with \( s = \text{TA, LA, TO, LO} \))

\[
\tau_{\text{anh}}^{-1}(x, s) = \frac{\hbar q_D^5 \gamma^2}{4 \pi \rho c^2} \sum_{s' s''} \gamma_{s s' s''} \int dx' (C \xi + D \xi' - \eta'') \left\{ 1 - \varepsilon + \varepsilon (C \xi + D \xi' - \eta'') \right\} \frac{\tilde{n}' (\tilde{n}'' + 1)}{\tilde{n} + 1} + \frac{1}{2} \int dx' (C \xi - D \xi' - \eta'') \left\{ 1 - \varepsilon + \varepsilon (C \xi - D \xi' - \eta'') \right\} \frac{\tilde{n}' \tilde{n}''}{\tilde{n}} \right]
\]

(4.35)

Here \( \gamma \) is the Grüneisen constant, \( x = q/q_D, x' = q'/q_D, \xi = \eta + x \) for \( s = \text{TA, LA, TO} \) and \( \xi = \eta + 1 - x \) when \( s = \text{LO} \), with similar notations for \( \xi' \) and \( \xi'' \). The first and second terms in Eq. (4.35) are contributed by class 1 and class 2 events, respectively. The argument for the Bose-Einstein factor \( \tilde{n}_+ \) is \( C \xi \pm D \xi' - \eta'' \). The variable \( x \) is limited to \( 0 \leq x \leq 1 \), and for a given \( x \), the limits for \( x' \) are determined by satisfying the energy and momentum conservation conditions in Eqs. 3.30 and 3.31 which can be re-written as

\[
\omega \pm \omega' = \omega''
\]

\[
q \pm q' = q'' + G,
\]

(4.36)

For the assumed isotropic continuum we expressed \( G \) by Eq. 3.32 and following previous suggestions [34, 35, 36] we take

\[
G = 2q_D (x \pm x') / [(x \pm x')].
\]

(4.37)

Following Matthiessen’s rule, we express \( \tau^{-1} \) in Eq. 4.33 as

\[
\tau^{-1} = \tau_{bs}^{-1} + \tau_{pd}^{-1} + \tau_{ep}^{-1} + \tau_{\text{anh}}^{-1}.
\]

(4.38)
4.5 Results and Discussion

Table 4.1 presents the electronic parameters for PbTe used in the electronic calculations. Our choice for the deformation potential is different than what we have published in Ref [32]. Here we include the contribution from the four valleys and this we find is equivalent to using a deformation potential $\Xi = 8.9 \text{ eV}$ rather than $\Xi = 4.5 \text{ eV}$. This choice for the deformation potential is quite close to the one reported in the Monte Carlo simulation by Palankovski et al. [37]. For phonon calculations we used the parameters listed in table 4.2. It was found that $|\gamma| = 0.8$ (resulting in the value $(\gamma/\bar{c})^2 = 4.9 \times 10^{-11} \text{s}^{-2} \text{cm}^{-2}$) was a good choice for explaining the high temperature conductivity results for all the three samples. The semi-adjustable choice for $\gamma$ is lower than the thermodynamically deduced estimate of approximately 1.4 reported in the work by Ravich et al. [11] and the theoretically calculated acoustic-phonon value of 2.18 [38].

<table>
<thead>
<tr>
<th>parameter</th>
<th>unit</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varrho \times 10^3$</td>
<td>(kg/m)</td>
<td>8.242</td>
</tr>
<tr>
<td>$n \times 10^{18}$</td>
<td>(cm$^{-3}$) [14]</td>
<td>2.6</td>
</tr>
<tr>
<td>$\Xi$</td>
<td>(eV)</td>
<td>8.9</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>(kg)</td>
<td>0.41 $m_0$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>(eV)</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 4.1: The electronic parameters of PbTe.

4.5.1 Electronic transport coefficients

Each of the electronic transport coefficients is expressed in terms of a Fermi integral of the type given in Eq. 2.61. These integrals have been evaluated using Simpson’s rule which is described in Appendix C. It was found that the upper
4.5 Results and Discussion

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_D \times 10^3$ (m$^{-1}$)</td>
<td>0.908</td>
</tr>
<tr>
<td>$c_{TA}$ (m/s)</td>
<td>1038</td>
</tr>
<tr>
<td>$c_{LA}$ (m/s)</td>
<td>1633</td>
</tr>
<tr>
<td>$c_{TO}$ (m/s)</td>
<td>1175</td>
</tr>
<tr>
<td>$c_{LO}$ (m/s)</td>
<td>1073</td>
</tr>
<tr>
<td>$</td>
<td>\gamma</td>
</tr>
</tbody>
</table>

Table 4.2: Parameters used for phonon transport calculations in PbTe.

The temperature variation of the Fermi level in the n-PbTe sample studied in this work is shown in Fig. 4.1. As the temperature increases more and more donors get ionised and the level decreases below the conduction band minimum. The intrinsic nature of the Fermi level is observed at approximately above 650 K where all donors are expected to be ionised. From these results we find that the reduced Fermi energies $\zeta$ for $T \geq 350K$ indicate that this n-PbTe sample is a non-degenerate one. Figure 4.2 (a) shows the Seebeck coefficient $S$ variation with the temperature. As the temperature increases, the magnitude $|S|$ increases showing a turning point at about 650 K. This is believed to be due to the additional bipolar contribution (from holes as well as electrons which can be excited through this narrow band semiconductor at high temperatures). Our computed results for the Seebeck coefficient show good agreement with the experimental data from Ref. [14]. The extracted Fermi level from the Seebeck coefficient measurements demonstrate that Eq. (4.2) offered a reliable simple analytical expression for the temperature variation of Fermi level in n-type PbTe.

The band non-parabolicity influence on acoustic phonon scattering is taken into
Figure 4.1: Temperature variation of Fermi level in n-type PbTe with donor concentration $2.6 \times 10^{18} \text{ cm}^{-3}$. The conduction band and valence band edges are drawn as dashed and dashed-dot horizontal lines, respectively.

account through the effective mass temperature dependence [11]. In Ref. [39], this dependence is reported to vary as $\propto T^{0.5}$ for electrons. Accordingly we used $m^*_{de}(0) = 0.02 m_0$ for the electrical conductivity calculation. The significant temperature dependence of the effective mass is considered to be a consequence of the large non-parabolicity for PbTe in its lowest conduction band, combined with its narrow gap characteristic and by the thermal distribution of electrons over the non-parabolic band [40]. Furthermore, considering the suggestion of Ravich and Moyzhes in Ref. [12], the energy dependence of the relaxation time for acoustic is expected to deviate from the $1/2$ power law as a consequence of the non-parabolicity. In Fig. 4.2 (b) we present the results for the electrical resistivity $\rho$. Accounting for scattering with acoustic phonons, the extrinsic contribution shows a reasonable agreement up to 600 K with the experimental data presented in Ref. [14]. As the temperature increases and the specimen is assumed to be intrinsic, the resistivity results in in Fig.4.2 (b) are obtained by treating the depen-
dence of the effective mass, mobility and the variation of energy gap that appear in Eq. (4.19) by fitting the constant $D = 0.794 \, \Omega \, \text{cm}$ [41]. There is very good agreement between the computed extrinsic contribution and the experimental data at temperatures above 700 K. On the whole, we regard the agreement between our theoretical results and the experimental data as reasonable. With the electrical resistivity $\rho$ computed, the electronic contribution to the thermal conductivity was computed by using the Wiedemann-Franz relationship. In particular, in the ex-

![Figure 4.2](image-url)

Figure 4.2: (a) Seebeck coefficient and (b) electrical resistivity for the n-type PbTe with donor concentration $2.6 \times 10^{18} \, \text{cm}^{-3}$. The solid and dot curves for $\rho$ represent the intrinsic (bipolar) and extrinsic (mono-polar) contributions, respectively. The experimental data is taken from [14].
4.5 Results and Discussion

Intrinsic regime $\kappa_{mp}$ was computed using Eq. (4.22) and in the intrinsic regime $\kappa_{bp}$ was computed using Eq. (4.25).

4.5.2 Vibrational and Thermal Properties

4.5.2.1 Phonon Dispersion Curves and Density of States

Figures 4.3 show our modelled phonon linear dispersion relations and the corresponding density of states. The choices for the Debye radius $q_D$ and the branch speeds $c_s$ listed in table 4.2 were made to obtain reasonable agreement with the neutron scattering data and a theoretical modelling for the dispersion curves and the density of states presented by Cochran et al. [42]. Our computed density of states curve also shows reasonably good agreement with first-principles results obtained in Refs. [38, 43]. For comparison the results obtained from [38] are presented in Fig. 4.3 (c). Our results (Fig. 4.3 (b)) show three peaks at almost similar frequencies to those in Ref. [38]. Also, our results show that these peaks have almost similar heights, in agreement with the results in Ref. [38]. It is interesting to note that the doubly-degenerate $\tau_0$ is a low-lying branch and its slope is comparable to that of the doubly-degenerate $\tau_A$ branch.

4.5.2.2 Lattice Specific Heat

The specific heat calculations at constant volume ($C_v$), shown in Fig. 4.4, in the low temperature range up to 50 K agree very well with experimental measurements [44] and first-principles calculations [38, 43] in the low temperature range up to 50 K. Some discrepancy between the experimental and theoretical results can be noticed above this temperature, the estimated theoretical values are lower than experimental data. There is no full understanding for this discrepancy [38]. Some difference is observed between theoretical results in both low and high temperature ranges. Generally, on the whole, our results agree better
Figure 4.3: (a) Linearised phonon dispersion relations in PbTe, (b) the corresponding density of states, and (c) density of states obtained from a realistic phonon dispersion relations in [38].

with the first-principles results obtained by Bencherif et al. [43]. Perusal of the experimental and theoretical results suggests that $C_v$ of PbTe assumes the classical value for temperatures above 200 K. In our estimation the LO branch is the reason for the low calculated $C_v$ values. The LO branch shows large dispersion along the [001] direction while for the other directions it tends to be flatter. We adopted simple isotropic elastic continuum model for the dispersion relation calculations, and for this reason we think that by calculating the average speed of LO along the [001], [110] and [111] directions we have underestimated the phonon velocity in the branch. The results could be improved by 5% when the LO speed is increased,
4.5 Results and Discussion

Figure 4.4: Lattice specific heat at constant volume $C_v$ for PbTe. The results from the present work are compared with the experimental measurements (Expt. (1954) [44]) and first-principles theoretical calculations (Theory (2009) [38] and Theory (2011) [43]).

but will remain lower than the experimental data.

4.5.2.3 Lattice Thermal Conductivity

The integrals in Eqs. 4.33 and 4.35 are evaluated by employing the 24-point Gauss-Legendre scheme; as described in Appendix D.

Figure 4.5 (a) shows two separate calculations of the conductivity for the sample from Ref. [14]: the black solid curve represents results by considering acoustic phonons as heat carriers but including their interaction with optical phonons, and the green dashed-dotted curve represents the results when both acoustic as well as optical phonons are considered as heat carriers and allowed anharmonic interactions among all branches are included. The lattice thermal conductivity at room temperature is found to be $\sim 1.1 \text{ W m}^{-1} \text{ K}^{-1}$ when optical phonons are not considered to transfer heat but are allowed to interact with acoustic phonons. The lattice thermal conductivity increases to $\sim 1.9 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature when all phonon modes participate in conducting heat with a full range of interaction between acoustic and optical phonons dictated by the momentum and
energy conservation conditions. It is clear that the optical phonon modes do indeed contribute significantly to the lattice thermal conductivity in PbTe. We note, however, that the difference between acoustic alone ($\kappa_{\text{ph}}(\text{ac})$) and acoustic+optical ($\kappa_{\text{ph}}(\text{ac+op})$) is not a simple constant. As seen from Fig. 4.5 (b), the percentage contribution from the acoustic phonons slightly decreases with increase in temperature: being 56% at 300 K and 53% at 800 K. In Fig. 4.5 (c) we have broken the lattice thermal conductivity into its components. We notice that the $\text{TA}$ and $\text{TO}$ branches contribute, respectively, up to 43% and 38% of the total thermal conductivity at room temperature. As the temperature increases the contribution of the $\text{TO}$ branch becomes a little larger than the contribution of the $\text{TA}$ branch.

Recently, Tian et al. [45] have made ab initio calculations of the lattice thermal conductivity of PbTe in the limited temperature range of 300 – 700 K. Our results in general agree with their results. Both works conclude that the optical phonons in this material play an important role in heat conduction. In agreement with our work, Tian et al. conclude, by accounting for all acoustic and optical branches, that the omission of ac-op scattering increases the conductivity by roughly a factor of five. Our work also agrees with Tian et al. in that the $\text{LO}$ phonons make the lowest contribution and the $\text{TA}$ phonons contribute the most. However, our work differs with Tian et al. with respect to the contributions from the $\text{LA}$ and $\text{TO}$ phonons. While Tian et al. find that $\text{LA}$ phonons contribute much more than $\text{TO}$ phonons, our work suggests that the $\text{TO}$ contribution is approximately 10% larger than the $\text{LA}$ contribution.

It would not be inappropriate to comment that Zhang et al. [38] reported two different results (1.66 and 2.01 W m$^{-1}$ K$^{-1}$) for the room-temperature lattice thermal conductivity of PbTe using two differently calculated (and much larger) values of the acoustic-phonon Grüneisen constant (2.18 and 1.96, respectively). Although their results are quite similar to the results presented in this work and the experimental results in Fig. 4.6, it should be emphasized that these authors used
4.5 Results and Discussion

<table>
<thead>
<tr>
<th>Sample Ref.</th>
<th>Effective boundary length $L$ ($\mu$m)</th>
<th>Point defect parameter $A_{pd}$ ($s^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 [14]</td>
<td>0.34</td>
<td>$1.039 \times 10^{-41}$</td>
</tr>
<tr>
<td>Sample 2 [11]</td>
<td>0.50</td>
<td>$2.078 \times 10^{-42}$</td>
</tr>
<tr>
<td>Sample 3 [46]</td>
<td>0.05</td>
<td>$1.039 \times 10^{-42}$</td>
</tr>
</tbody>
</table>

Table 4.3: Effective boundary length $L$ and adjusted point defect parameter $B_{pd}$ used for fitting the experimental results of lattice thermal conductivity for three samples of PbTe.

A grossly simplified expression for phonon anharmonic interaction and did not take into account any other form of phonon interaction (such as defect scattering). In Fig. 4.6 we present our computed results for the lattice thermal conductivity $\kappa_{ph}$ for three samples of PbTe, in the temperature range 100 – 900 K. Our results are validated against several experimental results taken from [14] (sample 1), [11] (sample 2) and [46] (sample 3), both for the magnitude and the temperature variation. Experimental measurements are available in the temperature ranges 300 – 750 K for sample 1, 100 – 800 K for sample 2, and 300 – 700 K for sample 3. The results for samples 2 are slightly lower than that for sample 3 in the common temperature range for which these have been presented. The results for sample 1 fall lower than those for samples 2 and 3 below 500 K, indicating that it is more defective. In order to reproduce the experimental data for these n-type samples we had to adjust the boundary length and the point defect concentration. The values of the effective boundary length and the adjusted point defect parameter are given in Table 4.3. As shown in the table, in order to fit the experimental data for samples 2 and 1 we had to use almost twice and ten times the point-defect scattering rate compared to that for sample 3. The agreement between theory and experiment was refined by choosing slightly different boundary lengths for the three samples, as presented in the table.
Figure 4.5: Calculated lattice thermal conductivity $\kappa_{ph}$ results for sample 1. In panel (a) the black solid curve represents the results by considering the acoustic phonons as heat carriers but including their interaction with optical phonons, and the green dashed-dotted curve represents the results when both acoustic as well as optical phonons are considered as heat carriers and allowed anharmonic interactions among all branches are included. Panel (b) shows the percentage contribution from acoustic phonons. Panel (c) shows contributions from individual acoustic and optical branches.
4.5 Results and Discussion

Figure 4.6: Lattice thermal conductivity results ($\kappa_{ph}$) for three different n-PbTe samples taken from Refs. [14] (sample 1), [11] (sample 2) and [46] (sample 3).

(i) Total anharmonic relaxation rates: In order to emphasise the relative importance of different phonon branches in the thermal conductivity, we plot the inverse anharmonic relaxation times of phonons as a function of the reduced wave number in Fig. 4.7 (a) and (b). For all wave numbers, $\tau^{-1}_{(LA)}$ is much larger than $\tau^{-1}_{(TA)}$ and $\tau^{-1}_{(TO)}$. Also, for all wave numbers $\tau^{-1}_{(TO)} \sim \tau^{-1}_{(TA)}$ at both low and high temperatures. Figure 4.7 (a), (b) also demonstrates that in the low frequency range the relaxation rate for the LA branch follows the $\omega^2$ behaviour, as predicted by Klemens [47], while the TO and TA branches show a mixture of linear and quadratic behaviours. As the reduced wave number increases the behaviour of $\tau^{-1}_{LA}$ in general shows a polynomial type dependence on $\omega$. This analysis is in good agreement with the trend noted by Tian et al. [45].

(ii) Normal anharmonic relaxation rates involving different polarisations and branches: Normal anharmonic relaxation rates for several class 1 processes $s + s' \rightarrow s''$ in-
Figure 4.7: The total anharmonic relaxation rate for \( \text{LA} \), \( \text{TA} \), and \( \text{TO} \) branches as a function of the reduced wave-vector at (a) \( T = 300 \) K, (b) \( T = 900 \) K for PbTe.

Involving different phonon polarizations and branches are presented in Fig. 4.8. A few observations can be made. The scattering rates for the processes involving only acoustic phonons (i.e. \( \text{ac} + \text{ac} \rightarrow \text{ac} \)) or only optical phonons (i.e. \( \text{op} + \text{op} \rightarrow \text{op} \)) are the weakest, as seen form the results in panels (a) and (d). The results in panels (b) and (c) indicate that the strongest \( \text{ac} + \text{op} \rightarrow \text{op} \) interactions involve \( \text{TA} \) and \( \text{TO} \) phonons merging together to produce \( \text{LO} \) phonons. N processes are not allowed for certain ranges of \( x \) values, due to the demand of simultaneous momentum and energy conservation considerations. This is very clearly seen in panel (d), which suggests that the process \( \text{TO} + \text{TO} \rightarrow \text{LO} \) is not allowed for \( x < 0.1 \) and for \( x > 0.7 \). It is also found that the maximum strengths for the processes
4.5 Results and Discussion

Figure 4.8: Anharmonic scattering rates at $T = 900$ K for (a) $ac + ac \rightarrow ac$ (N), (b) $ac + op \rightarrow op$ (N), (c) $op + ac \rightarrow op$ (N) and (d) $op + op \rightarrow op$ (N) processes.

$TO + TA \rightarrow TO$ (N) and $TO + LA \rightarrow LO$ (N) are almost similar, except that the former (latter) is more effective for shorter (longer) wave numbers.

(iii) **Comparison between N and U relaxation rates:** The results presented in Fig. 4.9 compare the N and U relaxation rates for two (randomly chosen) processes. Both for $LA + TA \rightarrow LA$ and $TA + TA \rightarrow TO$ the N process is stronger than the U process for almost all wave numbers of the relaxing phonon (indicated as $s$ in the process $s + s' \rightarrow s''$). Only when the wave number gets closer to the Debye radius (typically when $x = 0.9$) does the U process become comparable to the N process. Such a comparison between N and U processes has been noted before [48]. We also mention that the results in Fig. 4.8(a) and Fig. 4.9(a) further suggest that the relaxation rate of $LA$ phonons via the process $LA + TA \rightarrow LA$ (N) is approximately three times stronger than that of $TA$ phonons via the process $TA + LA \rightarrow LA$ (N).

(iv) **Frequency and temperature dependence of anharmonic relaxation rate:** The total
4.5 Results and Discussion

three-phonon Normal scattering rate and the total relaxation rate for the $\text{TO}$ and $\text{TA}$ phonons, at a given reduced wave number, as a function of low temperatures, are shown in Fig. 4.10 (a). The dependences of $\tau_{\text{TO},\text{TA}}^{-1}$ are not linear in the low temperatures range, with $\tau_{\text{TO}}^{-1} > \tau_{\text{TA}}^{-1}$. The latter can be explained by noticing that for a given $q$, $\omega_{\text{TO}} > \omega_{\text{TA}}$ and that at low temperatures $\tau^{-1}(\omega, T) \propto \omega^n T^{5-n}$ [49].

As the temperature increases beyond 100 K the scattering rates change linearly with $T$. In fact, the linear behaviour starts earlier than 100 K for the $\text{TA}$ mode, which may be attributed to a low $\text{TA}$ Debye temperature. Panel (c) offers a comparison between the relaxation rates for the $\text{TO}$ and $\text{TA}$ modes at a high reduced wave number $x = 0.969$, where it is noted that at a given temperature the scattering rate of $\text{TO}$ is much weaker than that of $\text{TA}$. Our work provides support to the previous suggestion [13] that the $\text{TO}$ phonons are involved in strong anharmonic interactions. However, although the work in Ref. [13] has identified strong $\text{TO}-\text{LA}$ interaction, our work suggests that $\text{TO}-\text{TA}$ interaction is stronger.

4.5.3 Total Thermal Conductivity

The total thermal conductivity is expressed as

$$\kappa_{\text{tot}} = \kappa_{\text{mp}} + \kappa_{\text{ph}},$$

(4.39)
Figure 4.10: Relaxation rates of the total Normal processes and the total anharmonic processes for $\text{TO}$ and $\text{TA}$ phonons at $x = 0.342$ for (a) low temperatures and (b) high temperatures. Panel (c) presents the relaxation rate of the total Normal processes and the total anharmonic processes for $\text{TO}$ and $\text{TA}$ phonons at $x = 0.969$ as a function of temperature.
4.5 Results and Discussion

where $\kappa_{\text{mp}}$ is the contribution from the carriers (donor electrons (mono-polar) in the extrinsic regime and electron-hole pairs (bipolar) in the intrinsic regime, and $\kappa_{\text{ph}}$ is the phonon conductivity. Our computed results for sample 1 are compared with the experimental results reported by Pei et al. [14] in Fig. 4.11. There is very good agreement between theory and experiment. Considerable decrease in the conductivity is noted as the temperature increases: for example, from 1.7 W K$^{-1}$ m$^{-1}$ at room temperature to 1.1 W K$^{-1}$ m$^{-1}$ at 650 K. The upward change in the slope of the $\kappa - T$ curve above 500 K is due to the electronic contribution (largely due to the bipolar contribution).

4.5.4 Thermoelectric Figure of Merit

The dimensionless figure of merit $ZT$ temperature variation is shown in in Fig. 4.12. Here we considered two scenarios of the lattice thermal conductivity: (i) by considering only acoustic phonons as heat carriers (but incorporating the ac-op interactions), and by (ii) considering acoustic as well as optical phonons as heat carriers (and incorporating all allowed interactions among the acoustic and optical phonons). The larger figure of merit is achieved when optical phonons are not considered as heat carriers ($i.e.$ for scenario (i)). The room-temperature result
Figure 4.12: Figure of merit $ZT$ for the n-type sample of PbTe prepared and studied by Pei et al. [14] The experimental data is deduced from the measured values of $S$, $\rho$, and $\kappa_{\text{tot}}$ in Ref. [14]).

for the figure of merit $ZT$ increases from 0.1 for scenario (ii) to 0.17 for scenario (i). This clearly indicates the important role played by the existence of the low-lying $\text{TO}$ branch in PbTe.

While our theoretical work reproduces the experimentally obtained data for $S$, $\rho$, and $\kappa_{\text{tot}} = \kappa_{\text{mp}} + \kappa_{\text{ph}}$, we did not manage to match our calculated $ZT$ values with the results in Ref. [14]. However, our results for the figure of merit $ZT$, with the contribution to the lattice thermal conductivity by all branches considered, are consistent with the values extracted directly from the measurements of $S$, $\rho$, and $\kappa_{\text{tot}}$ reported in [14]. It appears, therefore, that there are numerical errors in the $ZT$ values presented in Ref. [14]. This has been confirmed [50] by one of the authors of Ref. [14].

### 4.6 Chapter Summary

The effect of the crystal anharmonicity on the thermoelectric properties of n-type PbTe is investigated. The lattice thermal transport coefficient is computed by
employing an isotropic continuum model for the dispersion relation for acoustic as well as optical phonon branches, an isotropic continuum model for crystal anharmonicity, and the single-mode relaxation time scheme. While employing the nearly-free-electron for electronic components of the transport coefficients we find that the effect of the band non-parabolicity should be considered. Our approach for electronic transport coefficients was satisfactory. We find that electrons interact strongly with the deformation potential of acoustic phonons. We also reveal the important role of the transverse optical branches in the phonon conductivity, hence in the thermoelectric figure of merit optimization.
Bibliography


[50] One of the authors of Ref. [14] was contacted regarding the difference between their presented experimental data for $S$ and $\sigma$ and their computed maximum of $ZT$. They have confirmed the inconsistency in their graphs, indicating that their corrected $ZT$ results are consistent with ours.
Chapter 5

Three-phonon Scattering Processes and Thermal Conductivity in IV-chalocogenides

5.1 Introduction

We have introduced Pb-chalcogenides in Chapter 1 as good thermoelectric materials due to their very low phonon conductivity ($\kappa_{\text{ph}}$) [1, 2, 3]. The low phonon conductivity in these materials is caused by strong anharmonicity, which in turn is contributed by several factors [4, 3]. SnTe and Pb-chalcogenides have shown significantly different vibrational characteristics from those of traditional group-IV, III-V and II-VI semiconductors [5]. In Chapter 3 it was shown in Pb-chalcogenides, \( \text{TO} \) branches are low-lying and disperse upwards with wave-vector away from the Brillouin zone centre. In Pb-chalcogenides the \( \text{LO} \) branch has the highest frequency at the zone centre and disperses downwards with wave-vector away from the Brillouin zone centre. In Sn-chalcogenides, at least in SnTe [5], both the \( \text{TO} \) and the \( \text{LO} \) phonon branches are low-lying and disperse upwards with wave-vector away from the Brillouin zone centre.
Over the past fifty years, many theoretical calculations of phonon conductivity in IV-chalcogenide materials have been reported. Agrawal and Verma [6], in one of the earliest works, employed the Callaway’s effective relaxation time expression [7] and used a single averaged linearly-dispersive acoustic phonon polarisation branch to compute phonon conductivity $\kappa_{\text{ph}}$. Shiga et al. [8] and Lee et al. [9], among their most recent works, computed $\kappa_{\text{ph}}$ for IV-chalcogenides using a first-principles approach for phonon dispersion relations and third-order force constants, and the single mode relaxation time (smrt) theory which we referred to as the Debye model for conductivity. In Chapter 3 we showed that the effective relaxation time theories (such as the original Callaway theory [7] or Allen’s improvement [10] of the Callaway theory) predict important changes to the conductivity value over and above the smrt estimate. With this in mind, the agreement that was claimed between experiment and the smrt numerical data by Shiga et al. [8] for PbTe and by Lee et al. [9] or several IV-chalcogenides has to be accepted with caution. Notwithstanding this point, in their detailed first-principles investigation, Shiga et al. have quantified mode-dependent phonon relaxation times, mode-dependent thermal conductivity and phonon-phonon scattering processes. These authors attributed the low thermal conductivity in PbTe equally to the strongly anharmonic $\text{LA-TO}$ scattering and the small group velocity of the $\text{TA}$ phonons. Lee et al. [9] have explained that rock-salt IV-VI compounds are characterised by long-range resonant bonding which causes optical phonon softening, leading to strong anharmonic scattering and thus low thermal conductivity. Delaire et al. [4], by a detailed experimental study, have determined strong $\text{LA-TO}$ scattering in PbTe. However, neither the theoretical works in Refs. [8, 9] nor the experimental work in Ref. [4] have been able to provide a detailed analysis of the $\text{LA-TO}$ interaction, in that it is unclear whether the $\text{LA}$ and $\text{TO}$ phonons coalesce to produce another phonon or whether the $\text{TO}$ phonon decays into the $\text{LA}$ and another phonon. Moreover, these works do not examine in any detail the in-
teraction of $\Gamma\Omega$ phonons with $\Lambda\Sigma$ phonons, which show dispersion and frequency span of the same order as $\Lambda\Lambda$ phonons. To the best of our knowledge, dominant phonon-phonon scattering processes in SnTe have not yet been established.

To identify the dominant three-phonon scattering processes and their role in explaining the low thermal conductivity of IV-chalcogenide thermoelectrics PbTe, PbSe, PbS, and SnTe, we adopted the same systematic approach described previously in Chapters 3 and 4. We find this approach provides a clear recognition of phonons of different polarisations, allowing for an unambiguous description of allowed class 1 (coalescence) and class 2 (decay) three-phonon processes of $N$ and $U$ types constrained by momentum and energy conservation requirements. Numerical results are obtained by using the Debye, the Callaway, and the Allen expressions of the relaxation-time theory and the isotropic continuum scheme for acoustic as well as optical phonon branches.

### 5.2 Pb-chalcogenides and SnTe Crystal Structure

Group IV-VI materials are known to crystallize in three closely related structures, cubic, orthorhombic and rhombohedral. They exhibit several properties that are significantly different from group-IV, III-V and II-VI semiconductors. In particular, Pb-chalcogenides and SnTe have the rock-salt structure. The crystal structure shown in Fig. 2.1 for PbTe can be used to illustrate the crystal structure for PbSe, PbS, and SnTe by replacing the tellurium atom, respectively, with selenium and sulfide to get PbSe and PbS and by replacing the lead atom by tin atom to have SnTe. The effects of anharmonicity on the dispersion curves can be performed on the tin telluride with its simple sodium chloride structure rather than using the complicated perovskite structure of strontium titanate [11]. Here, tin telluride as well as Pb-chalcogenides are used to study the the effects of anharmonicity on lattice thermal conductivity.
5.3 Dispersion Relations and Density of States

Figure 3.2 in Chapter 3 has shown the phonon frequency dependence on the wave-vector or simply the phonon dispersion relations to be similar in the three lead chalcogenides. This similarity is shown in the presence of six phonon branches; three acoustic and three optical (the transverse branches have degenerate frequencies) and the upward \( \text{TO} \) phonon branches. Figure 5.1 shows that the dispersion relations for SnTe have the same features as Pb-chalcogenides regarding the acoustic and the low lying \( \text{TO} \) branches, but in SnTe the \( \text{LO} \) branch is also present as an upward phonon branch. Following the procedures that are established in chapter 3 for calculating phonon dispersion relations we replaced the Brillouin zone of the fcc lattice by the Debye sphere of radius \( q_D \) for Pb-chalcogenides as well as for SnTe. The steps for calculating phonon dispersion relations in PbSe and PbS are similar to what was done for PbTe. For the acoustic and optical phonons in these materials, we apply the isotropic continuum approximation given in Eqs. 4.28. The same procedure is applied to the acoustic and transverse optical phonons in SnTe, but recalling that the \( \text{LO} \) phonon branch in SnTe is directed upward, the dispersion relations for this branch is obtained by the expression

\[
\omega_{\text{LO}} = \omega_{\text{LO}}^{\text{min}} + q_{\text{LO}}. \tag{5.1}
\]

For the density of states \( g(\omega) \) calculations, except for the \( \text{LO} \) branch in SnTe, we apply Eqs. 4.31. The density of states for the \( \text{LO} \) branch corresponding to the dispersion relation given in Eq. 5.1 is written as

\[
g_{\text{LO}}(\omega) = \frac{V_{\text{crys}}}{2\pi^2} \frac{(\omega_{\text{LO}}^{\text{max}} - \omega)^2}{c_{\text{LO}}^3}. \tag{5.2}
\]
Figure 5.1: SnTe phonon dispersion relations at 100 K. The full lines are for calculations using the shell model [12] and the symbols are from inelastic neutron scattering techniques measurements[12].

5.4 Lattice Thermal Conductivity

Using the smrt or the Debye model we computed the lattice thermal conductivity in PbTe in the previous Chapter. Here, applying the Debye model expression in Eq. 4.33, the lattice conductivity is determined for PbSe, PbS and in SnTe. In Eq. 4.33, \( \eta_s = \omega^\text{min}_s/c_s q D \) will also be applied for the \text{LO} branch in SnTe. Furthermore, the bulk lattice thermal conductivity is calculated by Callaway and Allen’s expressions. The expressions given in Eqs. 3.51 and 3.52 are modified to accommodate all phonon branches in these materials. Hence, we re-write these equations in the following forms

\[
\kappa_C = \frac{\hbar^2 q_D^5}{6\pi^2 k_B T^2} \sum_s c_s^4 \int_0^1 dx x^2 (\eta_s + x)^2 \tau_s \bar{n} (\bar{n} + 1) \\
\times \left[ 1 + \frac{\tau_{s,N}}{	au_s} \sum_p c_p^4 \int_0^1 dx x^2 (\eta_p + x)^2 \tau_p \tau_{p,N}^{-1} \bar{n} (\bar{n} + 1) \right], \quad (5.3)
\]

\[
\kappa_A = \frac{\hbar^2 q_D^5}{6\pi^2 k_B T^2} \sum_s c_s^4 \int_0^1 dx x^2 (\eta_s + x)^2 \tau_s \bar{n} (\bar{n} + 1)
\]
\[
\times \left[ 1 + \frac{\tau_{s,N}}{c_s^2} \sum_{p}^{TA,LA,TO,LO} \frac{c_p^4}{t_p^2} \int_{0}^{1} dx x^2 (\eta_p + x)^2 \tau_p \bar{n} (\bar{n} + 1) \right],
\]

(5.4)

where the double counting of the transverse branches is implicit.

### 5.4.1 Phonon Interactions

#### 5.4.1.1 Extrinsic Phonon Interactions

We considered for extrinsic phonon interactions, the same mechanisms discussed in Chapter 3. Applying Eqs. 3.24 and 4.34 we calculated the scattering rates from the sample boundary (bs) and point defects (pd). For moderately doped samples the electron concentration in the conduction band given by Eq. 4.8 can be reduced to the form

\[
n_0 = 2N_{\text{val}} \left( \frac{2m^*_d k_B T}{\pi \hbar^2} \right)^{\frac{3}{2}} \exp(\zeta)
\]

(5.5)

Thus, Parrott [13] used the expansion of \(\tau_{ep}^{-1}\) in a Taylor series about \(n_0 = 0\), to reduce the scattering rate of phonons by donor electrons to the form

\[
\tau_{ep}^{-1} = \frac{2m^*_d \sqrt{\pi} \zeta}{\varrho c_{LA}^2 \hbar} \exp \left[ - \left( \frac{\xi + z^2}{16 \xi} \right) \right] \sinh(z/2).
\]

(5.6)

For \(z \to 0\), Eq. 5.6 will take the form

\[
\tau_{ep}^{-1} = \frac{n_0 \sqrt{\pi} \omega}{\varrho c_{LA}^2 k_B T} \sqrt{ \frac{\pi m^*_d c_{LA}^2}{2 k_B T} } \exp \left( - \frac{-m^*_d c_{LA}^2}{2 k_B T} \right).
\]

(5.7)

#### 5.4.1.2 Anharmonic Interaction

Application of Debye’s elastic isotropic continuum model in PbSe, PbS, and SnTe results in the smrt anharmonic phonon relaxation rates for a phonon mode \(q_s\), with \(s = TA, LA, TO, LO\) given in Eq. 4.35 for Class 1 and Class 2 N and U processes. For all branches in SnTe and upward dispersion curves in PbSe and PbS, \(\xi = \eta + x\), and for the LO branches, the downward dispersion curves in PbSe and PbS, \(\xi = \)
The argument for the Bose-Einstein factor \( \bar{n}_\pm \) as well as the limits for \( x' \) are defined in Chapter 4.

### 5.5 Results and Discussion

The material parameters used in our work are presented in Tabs. 5.1 and 5.2. The phonon speeds in PbTe are given in Tab.4.2. The phonon dispersion curves and density of states employed in the phonon conductivity calculations are presented in Fig. 5.2. The results of PbTe phonon dispersion curves and density of states are re-presented here for purpose of comparison with that of other materials. Our modelled results show overall qualitative agreement, and good quantitative agreement in the low frequency regimes, with well documented realistic results [5]. Compared with II-VI, III-V and Group IV semiconductors, the phonon frequency spectrum in these IV-chalcogenides is much narrower. More importantly, for all these semiconductors, the \( \text{TO} \) phonon branch disperses upwards away from the Brillouin zone centre, and acquires quite low frequency at the zone centre (less than 1 THz for PbTe and SnTe, approximately 1.5 THz for PbSe, and approximately 2 THz for PbS). In Pb-chalogenides at the zone centre the \( \text{LO} \) mode is significantly split from the \( \text{TO} \) mode, and the \( \text{LO} \) branch disperses downwards away from the zone centre. However, in SnTe the \( \text{LO} \) branch is degenerate with the \( \text{TO} \) branch at the zone centre and disperses upwards away from the zone centre. The \( \text{LO} \) branch in SnTe, thus, is as peculiar as the \( \text{TO} \) branch is in all the four IV-VI materials considered in this work, and very different from that in traditional II-VI, III-V and Group IV semiconductors. As we will discuss in the next section, this will make the role of the \( \text{LO} \) branch for lattice thermal conduction in SnTe very different from that in other semiconductors.
Table 5.1: The phonon speeds $c_{TA}$, $c_{LA}$, $c_{TO}$, and $c_{LO}$ for SnTe, PbSe, and PbS.

<table>
<thead>
<tr>
<th>Material</th>
<th>$c_{TA}$ (m/s)</th>
<th>$c_{LA}$ (m/s)</th>
<th>$c_{TO}$ (m/s)</th>
<th>$c_{LO}$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnTe</td>
<td>1627</td>
<td>3118</td>
<td>1830</td>
<td>3525</td>
</tr>
<tr>
<td>PbSe</td>
<td>970</td>
<td>2370</td>
<td>750</td>
<td>264</td>
</tr>
<tr>
<td>PbS</td>
<td>1104</td>
<td>2176</td>
<td>1400</td>
<td>263</td>
</tr>
</tbody>
</table>

Table 5.2: Material parameters for SnTe, PbTe, PbSe, and PbS. The dopant concentrations $n/p$ are taken from the experimental papers cited in the Table. The Debye radius $q_D$, the point defect constant $B_{pd}$, the deformation potential $\Xi$, and the Grüneisen constant $\gamma$ are treated as adjustable parameters. $*$ These are the modified values when considering the contribution from four valleys.
Figure 5.2: Phonon dispersion curves and density of states used in this work: (a) PbTe, (b) PbSe, (c) PbS, and (d) SnTe. The variable $x$ represents the reduced phonon wave-number: $x = q/q_D$. 
5.5 Results and Discussion

5.5.1 Three-phonon Scatterings

Our approach to include both three-phonon N and U processes in the form of the integral expressions in Eqs. (3.35) and (4.35) is capable of providing accurate information regarding the role of different phonon polarizations and regarding the relative strengths of allowed three-phonon processes. One of the issues that has been debated for several decades (see, e.g., Parrott [17]), but still has not been satisfactorily resolved, is the relative importance of three-phonon N and U processes. Our work suggests that the ratio $\tau_{U}^{-1}/\tau_{N}^{-1}$ is typically smaller than 0.5 for low wave-number phonons ($x \equiv q/q_D < 0.5$), but increases and may reach unity or a somewhat larger value as the phonon wave-number $q = xq_D$ gets closer to the zone edge (Debye sphere). A similar conclusion was reached by Parrott [17] in his attempt to fit experimental results for the thermal conductivity of SiGe alloys by employing Callaway’s relaxation time theory. As seen from Fig. 5.3, the precise ratio depends on the material and also on temperature. In the previous Chapter, (the results have been published in our paper [18]), we discussed the relative strengths of the intrinsic lifetimes of $\text{TA}$, $\text{LA}$ and $\text{TO}$ phonons in PbTe in some detail. In that material $\text{LO}$ phonons do not contribute much to heat conduction, but reduce the heat conduction ability of the $\text{TA}$, $\text{LA}$ and $\text{TO}$ phonons by affecting their intrinsic lifetimes. The same behaviour is expected for PbSe and PbS. In Fig. 5.4 we compare the temperature and material variation of the ratio of the relaxation rate of phonons in branch $s$ and the $\text{TA}$ branch, $\tau_{s}^{-1}/\tau_{\text{TA}}^{-1}$, by considering PbTe and SnTe. The ratio $\tau_{\text{LA}}^{-1}/\tau_{\text{TA}}^{-1}$ is larger than unity throughout the zone for both materials. The ratio $\tau_{\text{LO}}^{-1}/\tau_{\text{TA}}^{-1}$ is larger than unity for wave-numbers throughout the zone in SnTe but only for wave-numbers closer to the zone edge in PbTe. In both these materials, the ratio $\tau_{\text{TO}}^{-1}/\tau_{\text{TA}}^{-1}$ decreases(increases) with increase in wave-number at high(low) temperatures. While the ratio $\tau_{\text{TO}}^{-1}/\tau_{\text{TA}}^{-1}$ is of similar value in SnTe to PbTe, the ratios $\tau_{\text{LA}}^{-1}/\tau_{\text{TA}}^{-1}$ and $\tau_{\text{LO}}^{-1}/\tau_{\text{TA}}^{-1}$ are larger in SnTe. As seen in Fig. 5.2, the
Figure 5.3: Comparison of U and N relaxation rates in PbTe and SnTe. Here we have plotted the ratio of $\tau_{\text{process1}}^{-1}/\tau_{\text{process2}}^{-1}$. The curves are annotated as follows: $\frac{LA(U)}{LA(N)}$ represents $\tau_{\text{LA,U}}^{-1}/\tau_{\text{LA,N}}^{-1}$, $\frac{TA(U)}{TA(N)}$ represents $\tau_{\text{TA,U}}^{-1}/\tau_{\text{TA,N}}^{-1}$, and $\frac{TO(U)}{TO(N)}$ represents $\tau_{\text{TO,U}}^{-1}/\tau_{\text{LA,N}}^{-1}$. 
5.5 Results and Discussion

Figure 5.4: Relative strengths of three-phonon scattering rates in PbTe and SnTe.
Here we have plotted the ratio $\tau_s^{-1}/\tau_{TA}^{-1}$, where $s$ is a polarisation index.
essential difference in the vibrational properties of Pb-chalogenides and SnTe lies in the dispersion relation of the LO phonons. We have therefore concentrated on examining the important three-phonon relaxation rates of the TO and LO phonons in PbTe and SnTe. In Fig. 5.5 we have displayed the relaxation rate results for: TO phonons undergoing Class 1 Normal events at 300 K for PbTe and SnTe in panels (a) and (b), respectively; LO phonons undergoing Class 1 Normal events at 300 K for PbTe and SnTe in panels (c) and (d), respectively; LO phonons undergoing Class 2 Normal events at 300 K for PbTe and SnTe in panels (e) and (f), respectively. Figure 5.6 provides information regarding the overall relaxation rates of the LO and TO phonons in the two materials. We make several observations, as follows:

(i) Due to simultaneous energy and momentum conservation requirements, the process TO + TA → LA is allowed in SnTe, but not allowed in PbTe. The largest contribution to the anharmonic relaxation rate of low and high frequency TO phonons comes from the processes TO + TA → TO and TO + TA → LO, respectively. In SnTe, the overall relaxation rate of TO phonons in the intermediate frequency range is largest for the process TO + TA → LA.

(ii) In both materials the process TO + TA → LO is stronger than the process TO + LA → LO, especially for intermediate and high frequency TO phonons. This can be explained by noting in Fig. 5.7 that intermediate and large wave-number TO phonons have access to bigger phase space area for the former interaction process. This result differs from previously held view [4] that the TO-LA interaction is dominant in PbTe.

(iii) While the process LO + TA → TO is allowed in PbTe, it is not allowed in SnTe. On the other hand the processes LO + LA → LO and LO + TO → LO are allowed in SnTe but not in PbTe. In other words, while only LO-TA interaction is allowed in PbTe, both LO-TA and LO-LA interactions are allowed in SnTe.

(iv) The decay (via Class 2 N processes) of LO phonons is significant only for a
small range of phonon wave-vectors in the zone in SnTe but for almost the whole range of vectors in PbTe.

(v) The ratio $\tau_{\text{LO}}^{-1}/\tau_{\text{TO}}^{-1}$ increases as the phonon wave-vector increases, and for all wave-vectors is much larger in SnTe than in PbTe. The overall anharmonic relaxation rate of the LO phonons is smaller(larger) than that of the TO phonons for short(long) wave-numbers. While this is in broad agreement with the results for PbTe presented by Shiga et al. [8], we find it much more evident in SnTe.

(vi) At a given temperature, $\tau_{qs}^{-1}(\omega)$ generally shows a polynomial-like dependence on $\omega$. At low frequencies, such a dependence is close to quadratic, as previously noted [18, 19].

### 5.5.2 Lattice thermal Conductivity Results

In Fig. 5.8 we present the conductivity results for SnTe, PbTe, PbSe, and PbS. For each material the theoretical results obtained from the Callaway model are compared with two sets of experimental data. For SnTe experimental results are available up to 500 K from Damon [1], and between 350 K - 800 K from Tan et al. [14]. For PbTe the experimental data with magenta (up triangle) symbols in the temperature range 100 K - 850 K are from Devyatakova et al. [15], and the data with turquoise (down triangle) symbols in the range 300 K - 750 K are from Pei et al. [2]. For PbSe, the turquoise and magenta symbols represent, respectively, the experimental data from Pei et al. [2] and Devyatakova et al. [15]. For PbS, the closed triangles and closed diamonds represent, respectively, the experimental data from Pei et al. [2] and Ravich [16]. The rise in the lattice thermal conductivity in the experimental data for PbSe from Devyatakova et al. and for PbS from Pei et al. is due to the additional bipolar contribution (from electron-hole pairs). For these samples, we only compare our lattice thermal conductivity results up to the temperature before the rise in the experimental data.
Figure 5.5: Inverse relaxation time due to Class 1 three-phonon Normal processes for: (a) TO phonons in PbTe at 300 K; (b) TO phonons in SnTe at 300 K; (c) LO phonons in PbTe at 300 K; (d) LO phonons in SnTe at 300 K. Inverse relaxation time due to Class 2 three-phonon Normal processes for: (e) LO phonons in PbTe at 300 K; (f) LO phonons in SnTe at 300 K.
5.5 Results and Discussion

Figure 5.6: (a): The ratio $\tau_{LO}^{-1}/\tau_{TO}^{-1}$ in SnTe and PbTe. (b): comparison of $\tau_{LO}^{-1}$ in SnTe and PbTe.

Figure 5.7: The shadowed area represents the allowed phase space for $TO + TA \rightarrow LO(N)$ and $TO + LA \rightarrow LO(N)$ processes in SnTe. The variables $x = q/q_D$ and $x' = q'/q_D$ represent the reduced wave-numbers for $TO$ and $TA$ modes in the left panel, and for $TO$ and $LA$ modes in the right panel.
We first discuss the thermal conductivity results for SnTe (using the Callaway expression). We reproduced available experimental measurements of the thermal conductivity for two samples, as reported in Refs. [1] and [14]. For both samples, we used $4 \mu m$ for boundary length, $\Xi = 5$ eV for the deformation potential, and $\gamma = 2.26$ for the Grüneisen constant. Both samples were p-type, with hole concentrations $p = 1.6 \times 10^{20} \text{cm}^{-3}$ and $p = 4.7 \times 10^{20} \text{cm}^{-3}$ as deduced from Refs. [1] and [14], respectively. Consistent with the relative hole concentrations, we had to use the point defect parameter $B_{pd} = 0.132 \times 10^{-41} \text{s}^3$ and $B_{pd} = 0.726 \times 10^{-41} \text{s}^3$ for the samples in Refs. [1] and [14], respectively.

The effect of phonon-hole scattering is to reduce the thermal conductivity at low temperatures, typically below 20 K. In contrast, the role of phonon-defect scattering is dominant in a large temperature range, typically at all temperatures above 10 K. The overall effect of the phonon scattering by point defects was to reduce the conductivity by 42 % at 12 K and 5 % at 300 K for the purer (Damon) sample, and by 74 % at 15 K and 21 % at 300 K for the more defective (Tan) sample. Above 400 K, the intrinsic conductivity (that of a defect-free and isotope-free sample within the smrt) varies as $\kappa_{3\text{ph}} = 1816/T$. Consideration of phonon-defect scattering leads to the high-temperature conductivity variation as $T^{-0.75}$ for the purer sample and as $T^{-0.54}$ for the more defective sample. A weaker than $T^{-1}$ variation of the conductivity was also reported in Ref. [1], though with a slightly different rate. Below the Debye temperature, the temperature dependence of the conductivity is more strongly controlled by the defect scattering. Our work confirms the results of experimental measurements in Ref. [1] that at 100 K the thermal conductivity varies approximately as the inverse square-root of point defect concentration: $\kappa \propto B_{pd}^{-0.45}$. At room temperature, however, the conductivity varies only as $B_{pd}^{-0.39}$. These results are shown in Fig. 5.9. A comparison of the values in Tab. 5.2 of the parameter $B_{pd}$ required to fit the experimental results suggests that the defect concentration in the sample by Tan et al. [14] is roughly 5
5.5 Results and Discussion

The conductivity results for the PbTe samples from Devyatakova et al. [15] and Pei et al. [2] are almost identical at temperatures above 500 K, as seen in Fig. 5.8(b), indicating that the anharmonic interactions control the high-temperature results. Below 400 K there is a clear difference between the results for the two samples, being higher for the sample from Devyatakova et al. Both samples have small donor concentration. The adjusted values of the parameter $B_{pd}$ suggest that the concentration of defects in the Pei sample is an order of magnitude higher than that in the sample by Devyatakova et al.

The experimental data for the thermal conductivity for the two PbSe samples, from Devyatakova et al. [15] and Pei et al. [2], include the bi-polar contribution, though with different estimates. The lattice thermal conductivity results of the two samples can only be compared in the range 300-500 K (due to the bipolar contribution included in the experimental results for the former sample). Both samples contain reasonably small levels of donors. A comparison of the fitted values of the parameter $B_{pd}$ suggests that the point defect concentration in the sample by Devyatakova et al. is approximately 1.5 times that in the sample by Pei et al.

The PbS sample from Pei et al. [2] has a very low level of donor concentration, and the sample from Ravich [16] has almost no free carriers. The conductivity experimental data for the Pei sample contains a bipolar contribution. Our attempt to fit the experimental data for the lattice thermal conductivity from the two samples suggests that the point defect concentration in the Ravich sample is approximately 5 times that in the Pei sample. From Fig. 5.8 it is evident that for PbS as well as all other chalcogenide materials studied here, a high defect concentration leads to $\kappa$ varying less strongly that $T^{-1}$. Figure 5.10 shows the percentage contributions to the conductivity from different phonon polarisation branches in SnTe, PbTe, PbSe, and PbS. For all these materials, at low tempera-
Figure 5.8: Lattice thermal conductivity of (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS. Solid and dashed curves represent the theoretical results compared to different experimental measurements. Experimental results are represented with symbols: closed squares, circles, down triangle, up triangle, and diamonds are taken from Refs. [1], [14], [2], [15], and [16], respectively.
Figure 5.9: Variation of conductivity with point defect parameter $B_{pd}$ in SnTe at 100 K and 300 K. The numerical data (in symbols) are fitted to a curve using the variation $\kappa \propto B_{pd}^{0.45}$. 
tures, typically below 100 K, the largest contribution (between 18 – 50%) comes from each of the $TA$ branches, each of the $TO$ branches contributes in the range 0 – 20%, and the $LA$ branch contributes between 0 – 15%. The present finding that transverse acoustic phonons are the major heat carriers at low temperatures is consistent with a previous theoretical work [20]. Above 100 K the contributions in each of these materials from the branches $TA$, $LA$ and $TO$ lie in the range 13 – 25%.

Throughout the temperature range of the present study, the $LO$ branch contributes negligibly small percentage in PbSe and PbS, less than 5% in PbTe, and less than 21.5% in SnTe. At room temperature, the contributions in SnTe from each of the $LA$, $TA$, $TO$ and $LO$ branches are 13.05%, 15.40%, 17.91% and 20.35%, respectively. Clearly, in SnTe both the $LO$ and $TO$ phonons are the largest heat carriers at high temperatures.

The results and discussions presented above have been based on the average values of the Grüneisen constant $\gamma$ as listed in Table 5.2. Our fitted values $\gamma = 2.26$ for SnTe and 1.4 for Pb-chalcogenides are close to the estimates reported previously [21]. These values indicate that SnTe is more anharmonic than are Pb-chalcogenides. Although it would be preferable to include polarization-dependent average values for $\gamma$, the procedure would become less transparent as there would be too many adjustable parameters to describe the temperature-dependent conductivity results. It is comforting to note that, at least for PbTe [8], the variation in the average values for $\gamma$ for $TA$, $LA$ and $LO$ polarizations is not significant. However, there is a huge dispersion of $\gamma$ values across the Brillouin zone for the $TO$ modes, and the average $\gamma_{TO}$ is expected to be much larger than those for the other polarizations. This would have the possibility of reducing the lifetime of $TO$ phonons to a much smaller value than we have estimated. However, we did not attempt to include a separate average value of $\gamma$ for $TO$ phonons. Relaxation-time lattice thermal conductivity results are usually obtained and presented using the Debye expression in Eq. (4.33). It is well documented that the Callaway ex-
Figure 5.10: Percentage conductivity contributions from individual phonon polarizations in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.
pression in Eq. (5.3) provides a physically more accurate representation of the conductivity. Recently, however, Allen [10] has argued in favour of a modified form of the Callaway expression, denoted in this work as the Allen expression in Eq. (5.4). Although we have based our theoretical modelling of the experimental results using the Callaway expression, in Figure 5.8 we provide a comparison of the conductivity results obtained from the three expressions. Figure 5.11 shows the extra contribution to the conductivity, over the smrt result from the Debye expression, when the Callaway expression is used. The results presented for a total of eight samples, two for each of the four materials, indicate that the extra contribution ranges between 0 (at very low temperatures) and 284% of the smrt result, depending on temperature, quality and composition of the material. In general, the purer the material, the larger is this correction. This is evident from the results presented in each panel of the figure for samples characterized with two different impurity concentrations. While in general the extra contribution increases with increase in temperature, there is no clear trend for the temperature region, or the range, where it becomes maximum. Figure 5.12 compares the results obtained from the usage of the Callaway expression and the Allen expression. In agreement with both Allen [10] and Ma et al. [22], we find that the numerical results obtained from the Allen expression are larger than those obtained from the Callaway expression for all temperatures beyond the boundary regime. In general, the ratio $\kappa_A/\kappa_C$ saturates at high temperatures. However, this ratio depends both on temperature as well as material and its purity. For the Pei sample of PbS, $\kappa_A$ is $1.9\kappa_C$ at 900 K. We notice that the temperature variation of this ratio shows similar behaviour for Pb- chalcogenides and the more defective sample of SnTe. For the purer, single crystal, SnTe sample the behaviour is quite different. It is clear from these observations that if either $\kappa_D$ or $\kappa_A$ were to be matched with experimental measurements, then a different set of impurity concentration $B_{pd}$ and anharmonic parameter $\gamma$ would need to be used.
Figure 5.11: The Normal-drift contribution to the lattice thermal conductivity using the original Callaway expression in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.
Figure 5.12: Comparison of the conductivity results using the (original) Callaway’s expression and the (modified) Allen’s expression in (a) SnTe, (b) PbTe, (c) PbSe, and (d) PbS.
5.6 Chapter Summary

The Chapter presents a systematic study of allowed three-phonon scattering processes, involving acoustic and optical branches, and their relative roles in explaining the low thermal conductivity $\kappa_{\text{ph}}$ of IV-chalcogenide thermoelectric materials PbTe, PbSe, PbS, and SnTe. The extent of the additional contribution which the Callaway theory and the Allen theory provide over the single-mode relaxation time theory has been examined using numerical results for $\kappa_{\text{ph}}$, computed by employing the isotropic continuum scheme. For all these materials the acoustic ($\text{TA}$, $\text{LA}$) and transverse optical ($\text{TO}$) phonons, within the Callaway model, are found to contribute between $10 - 25\%$ towards $\kappa_{\text{ph}}$ at and room temperature, with $\kappa_{\text{TO}} > \kappa_{\text{TA}} > \kappa_{\text{LA}}$. In SnTe, the longitudinal optical ($\text{LO}$) phonons contribution (22\%) is larger than that of $\text{TO}$ phonons (18\%), but in Pb-chalcogenides their contribution is negligible (< 5\%). As a consequence of high defect concentration in these materials, the high temperature conductivity varies less strongly than $T^{-1}$. In confirmation with experimental measurements, our study finds that below the Debye temperature the the conductivity of SnTe varies as the inverse square-root of the point defect concentration.
Bibliography


Chapter 6

Size and Dimensionality Dependent Phonon Conductivity in Nanocomposites

6.1 Introduction

Over the past decade, extraordinary physical and chemical properties of nanomaterials have attracted a great deal of research interest. Hicks and Dresselhaus [1], in the early 1990s, proposed the potential of enhancing the figure of merit $ZT$ of thermoelectric materials with nanostructuring. A number of recent studies on nanostructured materials have shown significant improvement in $ZT$ over their bulk values [2, 3, 4, 5]. In these studies, increased phonon scattering was considered to result in low thermal conductivity, leading to an enhancement in $ZT$ [6, 7].

Nanocomposites, which can be nano-spheres or nanowires embedded in a host matrix material, or mixtures of two different kinds of nanoparticles [6, 8], have shown an improvement in the electronic performance and a reduction in the phonon thermal conductivity [9]. The nanocomposite approach, thus, has
the potential to further advances in the development of high efficiency thermoelectric materials [6]. Although a dramatic effect of the interfacial thermal resistance on the thermal conductivity of the composites was evident in many experiments, theoretical efforts to quantify this effect were lacking. Thermal transport of composite materials was classically studied by Rayleigh [10] and Maxwell [11] by treating the interfaces between two heteromedia as nonresistive to heat flow. Theoretical models conducted by Hasselman and Johnson [12] and by Benveniste [13] have included the effect of the interface thermal resistance ($R_{TBR}$) on the effective thermal conductivity of composite structures. In their work, Hasselman and Johnson [12] modified the expressions of Rayleigh and Maxwell for the effective thermal conductivity by incorporating the thermal boundary (or, interface thermal) resistance at the interface of composites consisting of spherical, cylindrical and flat plate inclusions in a continuous matrix. Benveniste’s work derived a similar expression for the effective thermal conductivity of spherical inclusions by using a micromechanical model.

Nan et al. [14] have introduced a general form of the Effective Medium Approximation (EMA) for the effective thermal conductivity of a two-phase composite including the thermal boundary resistance. Their thermal conductivity expressions can be applied to a wide range of geometries. However, it was pointed out by Yang et al. [8] that to obtain physically meaningful results both the thermal boundary resistance and the size effects must be incorporated in the EMA theory. Yang et al. [8] attempted to incorporate these two effects by solving the relevant phonon Boltzmann equation. Prasher has also developed an analytical model for the nanocomposite thermal conductivity by solving the phonon Boltzmann equation [15]. In a more recent study, Minnich and Chen [16] have introduced a modified version of the EMA (mEMA) for a nanocomposite of spherical inclusions in a homogeneous matrix. Ordonez-Miranda et al. [17] have extended the Minnich-Chen mEMA model for the thermal conductivity of
nanocomposites with spheroidal inclusions. In the mEMA formulation, a modified bulk Mean Free Path (MFP) is introduced by accounting for the size effects in each phase of the nanocomposite and the modified thermal conductivities are calculated using the EMA expressions derived by Nan et al. However, the calculations by Minnich and Chen [16] were performed only for room temperature and using frequency-averaged phonon mean free paths. Much more recently, Behrang et al. [18, 19] extended the Minnich-Chen formalism by partially including a frequency-dependent mean free path and incorporating specularity of the phonon-interface interactions. However, Behrang et al. ignored the role of optical phonons in their calculations.

Several practical methods of producing nanostructured thermoelectric materials have been presented (see, e.g. [20, 21, 22]), with promise of enhancements in the figure of merit [23]. Sootsman et al. [20] employed a general liquid matrix encapsulation technique to prepare nanometre sized inclusions of Sb, Bi, and InSb in bulk PbTe. They reported significant reduction of $\approx 45\%$ and $\approx 27\%$ in the thermal conductivity of the nanocomposites relative to that of pristine PbTe as a result of the inclusions of InSb and 4% Sb in PbTe, respectively. Sootsman et al. concluded that the reduction in the thermal conductivity of the nanocomposites results from the enhancement of the acoustic phonon scattering in the PbTe matrix due to nanostructuring. Ikeda et al. [21] produced nanoscale multilayers of PbTe and Sb$_2$Te$_3$ by utilizing the decomposition of metastable Pb$_2$Sb$_6$Te$_{11}$ into PbTe and Sb$_2$Te$_3$. Androulakis et al. [22] employed the solid-state transformation phenomena of spinodal decomposition and nucleation and growth to create nanostructured Pb$_{1-x}$Sn$_x$Te-PbS thermoelectric materials with very low thermal conductivity.

In this Chapter we utilize the combined theoretical considerations of the modified Effective Medium Theory (mEMA) developed by Minnich et al. [16] and Behrang et al. [19] for PbSe spherical particles and nanowires dispersed in a PbTe
6.2 Thermal Boundary Resistance

matrix. For flat plate PbSe dispersed in a PbTe matrix (i.e. for PbSe/PbTe superlattices), we use the general expression for the effective thermal conductivity derived by Nan et al. [14]. The calculations are performed for the conductivity components both along and across the PbSe/PbTe interfaces. The thermal boundary resistance $R_{TBR}$ required for the conductivity across interfaces is evaluated using the diffuse mismatch theory [24]. The bulk thermal conductivity calculations are performed using the Callaway model [25], the continuum isotropic approximation for phonon dispersions, three-phonon N and U processes considering acoustic as well as optical phonons, and interactions of phonons with the boundary, imperfections and carriers. The host (PbTe) bulk thermal conductivity is computed as a function of the interface density $\Phi$ (surface area of the nanoparticles per unit volume of composite) and the particle (PbSe) diameter $d$, while the particle conductivity is computed as a function of the particle diameter.

6.2 Thermal Boundary Resistance

The thermal boundary resistance, also known as Kapitza resistance in reference to measurements at interfaces between copper and superfluid helium [26], is observed at the interface between two homogeneous materials. When a heat flux flows across the boundary between two materials, the phonon reflection due to the different acoustic properties of the two materials will give rise to a temperature discontinuity at the interface, i.e. the incident phonon on the boundary will have a transmitted probability of less than unity, hence the heat current out of the hotter material will be limited. The interface in this case acts as a thermal barrier, that is commonly known as thermal boundary resistance, through which the difference in temperature could be sustained [27, 28]. The thermal boundary resistance $R_{TBR}$ is defined as the ratio of the temperature discontinuity developed at the interface $\Delta T$ to the heat flux at the interface ($U$) flowing across the interface.
The thermal boundary resistance is determined by the number of incident phonons on the interface, the energy carried by each phonon, and by the transmission probability across the interface. Here, the transmission probability must be found in order to be able to calculate the thermal boundary resistance. Generally, this probability depends on the side from which the phonon is incident on the interface, the phonon incidence angle, the phonon frequency, the phonon polarization, and the interface temperature of both sides. Assuming both sides of the interface to be isotropic allows the transmission probability to be dependent on the phonon mode $s$, frequency of the phonon, and the angle between the incident phonon and the normal to the interface. For further simplification, we assume the transmission probability to be independent of temperature, which allows us to ignore any anharmonic interactions. With the second assumption it is adequate to calculate the transmission probability from only one side of the interface at two different temperatures [30].

The phonon energy flux can be defined as [27]

$$ E = \frac{1}{4\pi} \sum_s \int d\omega g_s(\omega)\hbar\omega_s(q)\bar{n}(q). $$

where $g_s(\omega)$, $\omega_s(q)$, and $\bar{n}$ are, respectively, the phonon density of states, the phonon frequency, and the phonon Bose-Einstein distribution function with polarization $s$ and wave-vector $q$. The current density from side 1 to 2, $U_{1\to2}$, can be written as

$$ U_{1\to2} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \sum_s \int_0^{\pi/2} d\omega \int_0^{\pi/2} d\theta \sin \theta \ c_s \cos \theta \ \hbar\omega_s(q) \ g_s(\omega) \ t_{12}, \quad (6.3) $$

$$ = \frac{1}{2} \sum_s \int_0^{\pi/2} d\omega \ \frac{c_s \hbar\omega_s}{g_s(\omega)\bar{n}(q)} \int_0^1 \cos \theta \ \text{d}(\cos \theta) \ t_{12}, \quad (6.4) $$

where $c$ is the phonon speed, $\phi$ is the angle of incidence, $\theta$ is the angle between the wave-vector of the incident phonon and the normal to the interface, and $t_{12}$ is
the transmission probability from side 1 to side 2. Equation 6.4 can be rearranged as [31]

\[ U_{1\rightarrow 2} = \Delta T \frac{1}{4\pi} \sum_{s} \int_{0}^{\omega_{D}} t_{12} c_{1s} \hbar \omega \frac{d\tilde{n}}{d\omega} g_{1s}(\omega) d\omega. \] (6.5)

Using the definition of the volumetric specific heat \( C_v = dE/dT \), assuming \( t_{12} \) and \( c \) are frequency independent the thermal boundary resistance can be written as

\[ R_{TBR} = \frac{4}{c_1 C_{1v} t_{12}}. \] (6.6)

To determine the transmission probability the interface properties should be known, \textit{i.e.} diffuse or specular. There are two well known limiting models to calculate the thermal boundary resistance: the acoustic mismatch model, and the diffuse mismatch model.

### 6.2.1 The Acoustic Mismatch Model

In this scheme phonons are assumed to be plane waves, the two materials are treated as continua, and the interface is treated as a plane. Application of the boundary conditions, that follow from classical acoustics, leads to the zero possibility of scattering at the interface, and the transmission probability is determined by ascribing an acoustic impedance for each medium. For phonons that are incident normal to the interface, the transmittance can be written in terms of the phonon speed as [31, 30]

\[ t_{12}^a = \frac{4c_1 c_2}{(c_1 + c_2)^2}, \] (6.7)

where the superscript \( a \) represents the acoustic mismatch model. \( c_1 \) and \( c_2 \) are the speeds in sides 1 and 2, respectively. The acoustic mismatch model predictions are found to be relatively successful when heat is transferred by small wave vector phonons, \textit{i.e.} at very low temperature. For high temperatures, where heat is carried by the short wavelength phonons the diffuse mismatch model is more appropriate [32].
6.2 Thermal Boundary Resistance

6.2.2 The Diffuse Mismatch Model

In the diffuse mismatch scheme, the complete specularity assumption in the acoustic mismatch model is replaced by the assumption that at the interface all incident phonons will be diffusely scattered [33]. This assumption leads to destroying the acoustic correlations at the interface. This means the transmission probability is determined by the phonon density of states and the detailed balance principle, i.e. the number of phonons of a certain state leaving one side equals the number of phonons returning from the other side into that state [30]. In the diffuse mismatch model no distinction can be made between a reflected phonon on the same side and a transmitted phonon from the other side; thus [32]

\[ t^d_{12} = 1 - t^d_{21}. \] (6.8)

If both sides of the interface are assumed to be at the same temperature, from the principle of detailed balance, i.e. the number of phonons leaving one side with energy \( h\omega \), is equal to the total number of phonons returning from the other side into that state, the heat flux from side 1 must be equal to that from side 2

\[ t^d_{12} \sum_s \int \omega \text{D}_0 \frac{h\omega}{c_1s} g_1s(\omega) \bar{n} d\omega = (1 - t^d_{21}) \sum_s \int \omega \text{D}_0 \frac{h\omega}{c_2s} g_2s(\omega) \bar{n} d\omega. \] (6.9)

Solving for the transmission probability

\[ t^d_{12} = \frac{\sum_s \int \omega \text{D}_0 h\omega c_1s g_1s(\omega) \bar{n} d\omega}{\sum_s \int \omega \text{D}_0 h\omega c_1s g_1s(\omega) \bar{n} d\omega + \sum_s \int \omega \text{D}_0 h\omega c_2s g_2s(\omega) \bar{n} d\omega}. \] (6.10)

A general expression can be derived for the transmission probability by applying the following relation between the phonon heat flux \( U \) and the specific heat \( C_v \) [24]

\[ \frac{dU}{dT} = \frac{1}{2} \sum_s \int \omega \text{D}_0 h\omega c_s g(\omega) \frac{d\bar{n}}{dT} d\omega = \frac{C_v}{2}. \] (6.11)

For inelastic phonon scattering, where all phonon frequencies can take part in the transmission process across the interface, the following expression can be derived
using Eqs. 6.10 and 6.11

\[ t_{12}^{d} = \frac{c_2 C_{v,2}}{c_1 C_{v,1} + c_2 C_{v,2}}. \]  

(6.12)

For a completely diffuse phonon scattering, the thermal boundary resistance in Eq. 6.6 is written as

\[ R_{TBR} = \frac{4(c_1 C_{v,1} + c_2 C_{v,2})}{C_{v,1} c_1 c_2 C_{v,2}}. \]  

(6.13)

### 6.3 Thermal Conductivity of Nanocomposites

A self-consistent effective-medium theory, based on multiple scattering theory, was developed by Nan and Jin [34]. Using this theory, in a composite medium the thermal conductivity variation from point to point is expressed by a homogeneous constant medium conductivity term \( \kappa^0 \), and a perturbed term \( \kappa'(r) \) [14]

\[ \kappa(r) = \kappa^0 + \kappa'(r). \]  

(6.14)

Using multiple-scattering theory, the perturbed part \( \kappa' \) is expressed in terms of the Green function \( G \) for the homogeneous medium and the transition matrix \( T \) for the entire composite medium, and the effective conductivity of the composite is expressed as

\[ \kappa_{\text{eff}} = \kappa^0 + \langle T \rangle (I + \langle GT \rangle)^{-1}, \]  

(6.15)

where \( I \) is the unit tensor, and \( \langle \rangle \) denotes spatial averaging. For a composite structure comprised of \( n \) particles dispersed in a host matrix, interparticle multiple scattering can be neglected and \( T \) can be approximated as

\[ T = \sum_n T_n + \sum_{n,m \neq n} T_n G T_m + \ldots, \]

\[ \approx \sum_n T_n = \sum_n \kappa'_n (I - G \kappa'_n)^{-1}. \]  

(6.16)

Using this approach Nan et al. [14] obtained explicit expressions for the thermal conductivity of composites with different particle sizes, shapes, volume fractions,
and topologies. For a two-component composite, the effective thermal conductivity across the particle-host interface can be expressed generally as

\[ \kappa_{\text{eff}} = g \kappa_h, \quad (6.17) \]

where \( \kappa_h = \kappa^0 \) is the thermal conductivity of the host matrix and \( g \) is a structure-related dimensionless parameter which is defined in terms of an effective size \( d \) of the inserted particle and the Kapitza thermal boundary resistance \( R_{\text{TBR}} \) between the particle and the host. For particle insertion in spherical, cylindrical and flat plate geometries (corresponding, respectively, to nanodots, nanowires, and superlattices) the explicit expressions for \( g \) are:

- Nanodots: \[ g_{\text{ND}} = \frac{\kappa_p(1 + 2\alpha) + 2\kappa_h + 2V_t[\kappa_p(1 - \alpha) - \kappa_h]}{\kappa_p(1 + 2\alpha) + 2\kappa_h - V_t[\kappa_p(1 - \alpha) - \kappa_h]}, \quad (6.18) \]
- Nanowires: \[ g_{\text{NW}} = \frac{\kappa_p(1 + \alpha) + \kappa_h + V_t[\kappa_p(1 - \alpha) - \kappa_h]}{\kappa_p(1 + \alpha) + \kappa_h - V_t[\kappa_p(1 - \alpha) - \kappa_h]}, \quad (6.19) \]
- Superlattices: \[ g_{\text{SL}} = \frac{\kappa_p}{\kappa_p - V_t[\kappa_p(1 - \alpha) - \kappa_h]}, \quad (6.20) \]

where \( \kappa_p \) is the thermal conductivity of the inserted particle, \( V_t \) represents the particle insertion volume fraction, and \( \alpha \) is a dimensionless quantity defined as \( \alpha = \kappa_h R_{\text{TBR}}/(d/2) \). For heat flowing parallel to the interface boundary the effective thermal conductivity is expressed simply as the volumetric weighted average of the two bulk components:

- Nanowires and superlattices: \[ \kappa_{\text{eff}||} = V_t \kappa_p + (1 - V_t) \kappa_h. \quad (6.21) \]

Minnich and Chen [16] pointed out that the thermal conductivity \( \kappa_p \) should be modified by taking into account the characteristic particle size \( d \), and similarly the thermal conductivity of the host \( \kappa_h \) should be modified by taking into account the particle interface density \( \Phi \). We will thus use Eqs. (6.17-6.21), with the recognition when dealing with \( \kappa_{\text{eff}} \), that within the mEMA \( \kappa_p = \kappa_p(d) \) and \( \kappa_h = \kappa_h(\Phi) \). We also, then, recognise that the scale factor \( g \) is controlled by the particle size \( d \), interface density \( \Phi \) and the interface boundary resistance \( R_{\text{TBR}} \). For the sake of
clarity we, thus, rewrite

\[ \kappa_p = \kappa_p(d), \]
\[ \kappa_h = \kappa_h(\Phi) = \kappa_h(d, V_f), \]
\[ g = g(d, \Phi, R_{TBR}) = g(\kappa_p(d), \kappa_h(\Phi), R_{TBR}). \] (6.22)

The mEMA is expected to provide physically more appealing results for the effective thermal conductivity of nanocomposite structures with particle characteristic sizes typically smaller than bulk mean free path. Assuming diffuse scattering, the thermal boundary resistance \( R_{TBR} \) can be calculated using Eq. 6.13, which can be written as [24]

\[ R_{TBR} \approx \frac{C_{v,h}c_h + C_{v,p}c_p}{C_{v,h}c_h C_{v,p}c_p}, \] (6.23)

where \( C_{v,h}(C_{v,p}) \) and \( c_h(c_p) \) are the host (particle) volumetric specific heat and the phonon velocity, respectively.

### 6.3.1 Host and Particle Bulk Thermal Conductivity

For calculating the bulk thermal conductivities \( \kappa_p^{\text{bulk}} = \kappa(\text{PbSe}) \) and \( \kappa_h^{\text{bulk}} = \kappa(\text{PbTe}) \) we used the Callaway’s relaxation time expression as described in Eq. 5.3. The total phonon relaxation time contribution from boundary (bs), point defect (pd), anharmonic (anh) and free carriers (ep) are calculated using the expressions given by Eqs. 3.24, 4.34, and 5.7.

### 6.3.2 Relaxation Rate in Nanocomposites

In evaluating the phonon relaxation rates for nanocomposites, we deal with the host as well as the particle phases. For the host phase, we account for the increased scattering due to the interface density by modifying the boundary scattering to include the size effect. Accordingly
(i) For spherical (or nanodot, ND) inclusions we use the modified relaxation rate expressions introduced by Minnich et al [16] and write the effective phonon boundary scattering rate for the host (h) and the particle (p) phases as

$$\tau_{\text{eff},ND}^{-1}(h) = \tau_{\text{ND}}^{-1}(h, \Phi) = \tau_{\text{bs}}^{-1}(\text{bulk}) + \frac{3V_f}{2d}, \quad (6.24)$$

$$\tau_{\text{eff},ND}^{-1}(p) = \tau_{\text{ND}}^{-1}(p, d) = \tau_{\text{bs}}^{-1}(\text{bulk}) + \frac{c_s}{d}, \quad (6.25)$$

with $d$ representing the particle diameter.

(ii) For nanowire (NW) inclusions we write the expression for the modified phonon boundary scattering rate following Behrang et al [19]. Here, we consider two directions for the heat flux relative to the wire axis: perpendicular ($\perp$) to the axis of the wire, and parallel ($\parallel$) to the axis of a finite length wire. The effective phonon relaxation rate expressions for the two cases are:

$$\tau_{\text{eff},NW}^{-1}(h) \mid_\perp = \tau_{\text{NW}}^{-1}(h, \Phi) \mid_\perp = \tau_{\text{bs}}^{-1}(\text{bulk}) + \frac{4V_f}{\pi d}, \quad (6.26)$$

$$\tau_{\text{eff},NW}^{-1}(p) \mid_\perp = \tau_{\text{NW}}^{-1}(p, d) \mid_\perp = \tau_{\text{bs}}^{-1}(\text{bulk}) + \frac{c_s}{d}, \quad (6.27)$$

$$\tau_{\text{eff},NW}^{-1}(h) \mid_\parallel = \tau_{\text{NW}}^{-1}(h, \Phi) \mid_\parallel = \tau_{\text{bs}}^{-1}(\text{bulk}) + c_s \left( \frac{V_f}{L_w} + \frac{4V_f\sqrt{V_f}}{\pi d(\sqrt{V_f} + 1)} \right), \quad (6.28)$$

$$\tau_{\text{eff},NW}^{-1}(p) \mid_\parallel = \tau_{\text{NW}}^{-1}(p, d) \mid_\parallel = \tau^{-1}(\text{bulk}) + \frac{c_s}{2L_w}, \quad (6.29)$$

where $d$ represents the diameter of (cylindrical) wire and $L_w$ is the (finite) length of the wire.

### 6.4 Results and Discussion

We present results for spherical, cylindrical and flat plate PbSe dispersed in the PbTe matrix. The parameters we used for the bulk PbTe and PbSe materials are listed in Tab. 5.1 and 6.4. Table 6.2 presents explicit expressions for the volume fraction $V_f$ and the interface density $\Phi$ of the PbSe insertion. For the nanocomposite structures, the total sample size of $L = 0.5 \, \mu m$ is divided into unit cells of
<table>
<thead>
<tr>
<th>Material[35]</th>
<th>$\Xi$ (eV)</th>
<th>$L$ ($\mu$m)</th>
<th>$q_D$ ($10^{10} \text{ m}$)</th>
<th>$\gamma$</th>
<th>$n/p$ ($10^{18} \text{ cm}^{-3}$)</th>
<th>$B_{pd}$ ($10^{-41} \text{ s}^{3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe</td>
<td>8.90</td>
<td>0.5</td>
<td>0.908</td>
<td>1.4</td>
<td>$n = 2.6$</td>
<td>0.779</td>
</tr>
<tr>
<td>PbSe</td>
<td>5.12</td>
<td>0.5</td>
<td>1.0</td>
<td>1.4</td>
<td>$n = 3.5$</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 6.1: Material parameters for PbTe and PbSe. The dopant concentrations $n$ are taken from the experimental paper cited in the Table. The Debye radius $q_D$, the point defect constant $B_{pd}$, the deformation potential $\Xi$, and the Grüneisen constant $\gamma$ are treated as adjustable parameters.

We first examine the temperature variation of the thermal boundary resistance $R_{TBR}$ between the host material PbTe and the inserted material PbSe. The results from Eq. (6.23) are shown in Fig. 6.1. Following the usual temperature variation of specific heat, $R_{TBR}$ decreases exponentially as the temperature rises, and becomes constant of temperature at high temperatures. Our computed value is $R_{TBR} = 2.785 \times 10^{-9} \text{ W}^{-1}\text{ m}^2\text{K}$ at and above 300 K. Here, we consider the PbTe and PbSe bulk samples from [35]. The conductivity results, evaluated using Eq. (5.3) are presented in Fig. 6.2. The PbTe sample is of an effective boundary length $L = 0.5 \mu \text{m}$ and is n-type doped with concentration $2.6 \times 10^{18} \text{ cm}^{-3}$. The effective sample size of the PbSe sample is $L = 0.5 \mu \text{m}$ with donor concentration $3.5 \times 10^{18} \text{ cm}^{-3}$. The conductivity in PbSe is higher than in PbTe at all temperatures. At room temperature $\kappa(\text{PbSe})$ is approximately 14% higher than $\kappa(\text{PbTe})$. For investigating the effective conductivity of PbTe-PbSe nanocomposites it would be helpful to individually examine the effective conductivity $\kappa_h(d, V_f)$ in the host PbTe matrix and the scale factor $g(\kappa_p(d), \kappa_h(\Phi), R_{TBR})$. 
Table 6.2: Expressions for the volume fraction $V_f$ and the corresponding interface density $\Phi$ for PbTe-PbSe nanocomposites, with PbSe insertion as nanosphere (ND), cylindrical nanowire (NW) and flat plate (SL). Here $r = d/2$ is the particle radius, $L_w$ is the length of the wire, $L_{\text{PbSe}}$ represents the thickness of PbSe plate layer, and $L_{\text{cell}}$ represents the effective size of the cubic host (PbTe) cell which is used to define $V_f$ and $\Phi$. The symbols $\parallel$ and $\perp$ represent the heat flow direction along and across the interface boundary. Note that the entry NW$\parallel$ is not required for the nanowire of infinite length. Similarly, we only require SL$\perp$ for the flat plate insertion resulting in PbSe-PbTe superlattice formation.

<table>
<thead>
<tr>
<th>System</th>
<th>$V_f$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND</td>
<td>$\frac{4\pi}{3} (\frac{r}{L_{\text{cell}}})^3$</td>
<td>$\frac{3}{r} V_f$</td>
</tr>
<tr>
<td>NW$\parallel$</td>
<td>$\pi (\frac{r}{L_{\text{cell}}})^2 \frac{L_w}{L_{\text{cell}}}$</td>
<td>$\frac{2}{L_w} V_f$</td>
</tr>
<tr>
<td>NW$\perp$</td>
<td>$\pi (\frac{r}{L_{\text{cell}}})^2$</td>
<td>$\frac{2}{r} V_f$</td>
</tr>
<tr>
<td>SL$\perp$</td>
<td>$\frac{L_{\text{PbSe}}}{L_{\text{cell}}}$</td>
<td>$\frac{V_f}{L_{\text{PbSe}}}$</td>
</tr>
</tbody>
</table>

Figure 6.1: Temperature variation of the thermal boundary $R_{TBR}$ resistance at the PbTe/PbSe interface.
6.4 Results and Discussion

Figure 6.2: Lattice thermal conductivity results, computed using Callaway’s expression, for bulk PbTe and PbSe samples in [35].

6.4.1 Nanodots

Figure 6.3 shows the effective conductivity $\kappa_{h}(d,V_{f})$ of the PbTe host with PbSe nanodots inserted. Results are presented for two PbSe dot diameters $d$ and two interface densities $\Phi$. For comparison, the PbTe bulk conductivity is also presented. The effective host conductivity in the nanocomposite structure is clearly much lower than the host bulk conductivity. The nanocomposite-induced lowering of the host conductivity is more significant at low temperatures, typically below room temperature. For a given volume fraction of insertion $V_{f}$ the effective conductivity of the host decreases as the diameter of the PbSe nanodot decreases. This is due to the $1/d$ term in the inverse effective relaxation time in Eq. (6.24). Similarly, following Eq. (6.24), for a given ND diameter $d$ the conductivity decreases when the insertion volume $V_{f}$ increases. Consistent with the interface density expression $\Phi = 6V_{f}/d$, the effective conductivity is lowest for the highest interface density $\Phi = 0.12$ with $d = 10$ nm and $V_{f} = 0.2$, and highest for the lowest interface density $\Phi = 0.003$ with $d = 200$ nm and $V_{f} = 0.1$.

The bulk host conductivity $\kappa_{h,\text{bulk}}$ and the effective host conductivity $\kappa_{h,\text{eff}} =$
Figure 6.3: Effective conductivity $\kappa_{\text{eff}}$ of PbTe host to which PbSe NDs of different diameters and different volume fractions have been inserted.
\( \kappa_h(d, V_f) \) can be used to express the parameter \( \alpha \) within the EMA and mEMA schemes as \( \alpha_{EMA} = \kappa_{h, bulk} R_{TBR} / (d/2) \) and \( \alpha_{mEMA} = \kappa_{h, eff} R_{TBR} / (d/2) \). We note that the parameter \( \alpha_{mEMA} = \alpha(d, \Phi, R_{TBR}) \) is a function of the size \( d \) of the inserted particle, the interface density \( \Phi \), the Kapitza resistance \( R_{TBR} \) and temperature \( T \). Figure 6.4(a) shows the results for \( \alpha \) over a large temperature range for the ND insertion parameters \( d = 10 \) nm and \( 20 \) nm, and \( V_f = 0.1 \) and \( 0.2 \). The difference between \( \alpha_{mEMA} \) and \( \alpha_{EMA} \) is more noticeable at low temperatures. As the ratio \( \alpha_{mEMA} / \alpha_{EMA} \) is rather similar for \( d = 10 \) nm and \( d = 200 \) nm, the difference between \( \alpha_{mEMA} \) and \( \alpha_{EMA} \) is that due to the particle interface density \( \Phi \). For a given \( V_f \) smaller \( d \) produces larger \( \alpha_{mEMA} \). Also, from Fig. 6.4(b) results we find that for a given \( d \) larger \( V_f \) produces smaller \( \alpha_{mEMA} \). Figures 6.5 show results for the scale factor \( g \) with ND insertion. We discuss the results for \( g_{EMA} = g(\kappa_{p, bulk}, \kappa_{h, bulk}, V_f, \alpha_{EMA}) \) and \( g_{mEMA} = g(\kappa_{p, eff}, \kappa_{h, eff}, V_f, \alpha_{mEMA}) \). While the main difference between \( \alpha_{mEMA} \) and \( \alpha_{EMA} \) is governed by the particle interface density \( \Phi \), the difference between \( g_{mEMA} \) and \( g_{EMA} \) is governed not only by \( \kappa_{h}(\Phi) \) but also by size-dependent particle conductivity \( \kappa_{p}(d) \). For the whole temperature range, increase in \( V_f \) decreases both \( g_{mEMA} \) and \( g_{EMA} \). For given \( V_f \) and \( d \), while the ratio \( g_{mEMA} / g_{EMA} \) is only a few percent smaller than unity at high temperatures, it is up to 60% lower at low temperatures. For given \( V_f \) and \( d \), both \( g_{mEMA} \) and \( g_{EMA} \) increase and quickly saturate with rising temperature. At low temperatures, the increase is much sharper for thicker particle size \( d \).

Figures 6.6(a) and 6.6(b) show the thermal conductivity \( \kappa_{ND} = g \kappa_h \) for the ND nanocomposite with nanodot volume ratio \( V_f = 0.1 \). As expected from the discussion of the results for \( g \) and \( \kappa_h \), the conductivity of the nanocomposite, \( \kappa_{ND} \), is much lower for \( d = 10 \) nm than for \( d = 200 \) nm. For a given \( d \), the conductivity from the mEMA scheme is much lower than that from the EMA scheme. We find that for \( d = 200 \) nm, \( \kappa_{EMA} \) is very close to the bulk conductivity of the host material (PbTe). We also find that \( \kappa_{mEMA}(d = 200 \) nm) is practically the same
Figure 6.4: The parameter $\alpha$ for the PbSe ND insertion in the PbTe host.
Figure 6.5: The parameter $g$ for the ND insertion in the PbTe host.
Figure 6.6: Thermal conductivity of the PbTe-PbSe ND nanocomposite. Low- and high-temperature results are presented in panels (a) and (c), and (b) and (d) respectively.

as $\kappa_{EMA}(d = 10 \text{ nm})$ above 50 K. The EMA and mEMA high-temperature conductivity results can be more clearly differentiated in panel (b). For $d = 10 \text{ nm}$, and at room temperature, $\kappa_{mEMA}$ is approximately 14% lower than the bulk conductivity of PbTe. Results for $V_i = 0.2$ are shown in Figs. 6.6(c) and 6.6(d). In general, for a given $d$, comparison between $\kappa_{EMA}$ and $\kappa_{mEMA}$ does not alter much with the change in $V_i$. However, we observe a couple of interesting differences arising from the consideration of larger $V_i$. Firstly, for $d = 200 \text{ nm}$, $\kappa_{EMA}(V_i = 0.2)$ is lower(higher) than $\kappa_{EMA}(V_i = 0.1)$ at low(high) temperatures. Particularly,
\( \kappa_{\text{EMA}}(V_f = 0.2, \ d = 200 \ \text{nm}) \) has become noticeably higher than the bulk conductivity of the host material (PbTe). No such changes in \( \kappa_{\text{EMA}} \) are noticeable for \( d = 10 \ \text{nm} \). Secondly, for \( d = 200 \ \text{nm} \), the effect of increased \( V_f \) on \( \kappa_{\text{mEMA}} \) is only noticeable below 500 K. Significant reduction in \( \kappa_{\text{mEMA}} \) is noticed at all temperatures for \( d = 10 \ \text{nm} \) when \( V_f \) is increased from 0.1 to 0.2. Consistent with the difference between \( g^{\text{mEMA}} \) and \( g^{\text{EMA}} \), we find that \( \kappa_{\text{mEMA}} \) is significantly smaller than \( \kappa_{\text{EMA}} \), due to the role of size-dependent particle conductivity \( \kappa_p(d) \). The smaller the particle size, the bigger is the difference between \( \kappa_{\text{mEMA}} \) and \( \kappa_{\text{EMA}} \). We can examine the variation of the effective conductivity as a function of the particle interface density \( \Phi \). For this we have plotted in Fig. 6.7 \( \kappa_{\text{eff}} \) against \( \Phi \) for the particle size \( d = 10 \ \text{nm} \). Our results suggest that \( \kappa_{\text{eff}} \) decreases with \( \Phi \) in a non-linear manner.

In order to gain insight into the variation of the effective conductivity \( \kappa_{\text{mEMA}} \) of the nanocomposite with the interface density \( \Phi \), we need to examine the variation of the scale factor \( g \) and the effective conductivity \( \kappa_{\text{h,eff}} \) of the PbTe matrix. We also remind ourselves from Eqs. (6.18) and (6.22) that \( g \) depends on \( \alpha \), which itself depends on the parameters \( d \) and \( \Phi \). In Fig. 6.7 we show the variation of \( \alpha, \ g, \ \kappa_{\text{h,eff}} \) and \( \kappa_{\text{mEMA}} \). Each of these quantities varies non-linearly with \( \Phi \). The numerical results suggest that the non-linear variation of \( \kappa_{\text{h,eff}} \) is more significant than that of \( g \). Being the product of \( g \) and \( \kappa_{\text{h,eff}} \), the nanocomposite conductivity \( \kappa_{\text{mEMA}} \) shows stronger non-linear behaviour with \( \Phi \) than either \( g \) or \( \kappa_{\text{h,eff}} \) does.

The results here clearly suggest that the effect of the modified effective medium theory over the original effective medium theory is more significant for smaller nanodot insertions; i.e. at any temperature there is a significantly bigger difference between \( \kappa_{\text{mEMA}} \) and \( \kappa_{\text{EMA}} \) for \( d = 10 \ \text{nm} \) than for \( d = 200 \ \text{nm} \). Considering the joint effects of \( d \) and \( V_f \), the results verify the previously advocated view [16] that the interface density \( \Phi \) governs the thermal conductivity of a nanocomposite structure.
Figure 6.7: Variation of (a) $\alpha$, (b) $g$, (c) $\kappa_{\text{eff}}(\text{PbTe})$, and (d) $\kappa_{\text{mEMA}}$ for the ND composite at $T = 99$ K. The symbols represent the calculated results and the lines are guide to the eye.
Comparative Conductivity Results for Nanodots and Nanowires

Figures 6.8(a) and (b) show the results for $\kappa_{\text{mEMA}}$ at low and high temperatures, respectively, across PbSe NWs of infinite length embedded in the PbTe host. The NW volume fraction $V_f$ is set to 0.1 and different values of the interface density $\Phi$ are simulated by choosing nanowire diameter $d$ values 10 nm, 15 nm and 20 nm. With decrease in diameter $d$, the interface density $\Phi$ increases and the conductivity decreases. The decrease is more pronounced in the low temperature regime (see the range $10 - 400$ K) where interface scattering is expected to play a dominant role. This is in general similar to what is also found for the ND insertion. Figure 6.9 shows the variation of $\kappa_{\text{mEMA}}$ at $T = 201$ K for the ND and NW composites with $d$ when $V_f = 0.1$. Clearly, $\kappa_{\text{mEMA}}$ increases with $d$ in a non-linear manner, approximately as the square root of $d$. Noting the inverse relationship between $d$ and $\Phi$ for a given $V_f$ from Tab. 6.2, we suggest the approximate result $\kappa_{\text{mEMA}} \propto 1/\sqrt{\Phi}$.

Comparative Conductivity Results for NDs, NWs and SLs

From the results presented in Fig. 6.10 we can make a comparative study of the conductivity for the ND, NW and SL configurations of the PbSe-PbTe nanocomposite set at $V_f = 0.1$ and $d = 10$ nm. For this consideration of $V_f$ and $d$, the interface density $\Phi$ is 0.01 1/nm for SL, 0.02 1/nm along the finite length NW, 0.04 1/nm across the NW, and 0.06 1/nm for ND. As expected from Eq. (6.21), both the SL in-plane conductivity and the conductivity along the axis of the nanowire of infinite length are the weighted average of the conductivities of bulk PbSe and PbTe. At all temperatures, the conductivity results for the other systems or configurations are significantly lower than the bulk weighted average. It is also found that in the entire temperature range above 10 K, $\kappa_{\text{mEMA}}(\text{NW}_\perp)$ and $\kappa_{\text{mEMA}}(\text{ND})$ are lower than $\kappa_{\text{mEMA}}(\text{SL}_\perp)$. In the interface dominated low-temperature range 10 -
6.4 Results and Discussion

Figure 6.8: Effective thermal conductivity across the PbSe infinite nanowires embedded in the PbTe matrix for different $\Phi$ with $V_f = 0.1$ at (a) low and (b) high temperatures.
Figure 6.9: Effective Thermal conductivity of the PbSe-PbTe nanocomposite as a function of (a) PbSe nanosphere diameter and (b) PbSe nanowire diameter embedded in the PbTe matrix. The symbols represent the calculated results and the lines are guide to the eye.
50 K, $\kappa_{\text{mEMA}}(NW_\perp)$ is slightly higher than $\kappa_{\text{mEMA}}(ND)$. This is consistent with the NW interface density $\Phi(NW)$ being lower than the ND interface density $\Phi(ND)$ for the same $V_f$ and $d$. The difference between the SL$_\perp$, NW$_\perp$ and ND results is less significant at high temperatures. In fact, we find that $\kappa_{\text{mEMA}}(NW_\perp)$ is slightly lower than $\kappa_{\text{mEMA}}(ND)$ above 100 K. This can be explained by noticing that $\kappa_{\text{mEMA}}$ is the product of $\kappa_{\text{eff},h}$ and the scale factor $g$. Our numerical results (not presented here) show that while $\kappa_{\text{eff},h}(ND) < \kappa_{\text{eff},h}(NW)$, the scale factor $g_{ND}$ is slightly larger than $g_{NW}(\perp)$, making $\kappa_{\text{mEMA}}(ND)$ slightly lower than $\kappa_{\text{mEMA}}(NW_\perp)$. The conductivity along the superlattice growth direction (with PbSe and PbTe layers of thicknesses 10 nm and 90 nm, respectively, making $\Phi = 0.01 \, 1/\text{nm}$) is almost the same (except in temperature range 20 – 50 K) as that for the finite length nanowire (or PbSe pellet embedded in PbTe host) with $\Phi = 0.02 \, 1/\text{nm}$. The difference in the interface density $\Phi$ can be offered as the reason for explaining the slightly lower conductivity along the PbSe pellet direction compared to the conductivity along the SL growth direction.

### 6.4.4 Role of Nanocompositing on Optimizing Thermoelectric Figure of Merit

One of the important contributions in optimizing the thermoelectric figure of merit ($ZT$) of a material is by reducing its lattice thermal conductivity [36]. Prior to the development of the nanocompositing concept, the usual approach for optimizing $ZT$ of (doped) semiconductors, such as lead chalogenides, was to employ bulk alloys or materials with complex crystal structures [37, 38]. In this respect, it is interesting as well as important to compare the $\kappa_{\text{mEMA}}(\parallel)$ and $\kappa_{\text{mEMA}}(\perp)$ results for the PbTe-PbSe nanocomposites with the conductivity of bulk PbTeSe alloy. As mentioned in the previous sub-sections, $\kappa_{\text{mEMA}}(\parallel)$ is hugely larger than $\kappa_{\text{mEMA}}(\perp)$ at low temperatures (typically below 100 K). This difference is less
Figure 6.10: Effective Thermal conductivity for different PbTe-PbSe nanocomposite configurations.
pronounced at high temperatures (typically above 500 K). The work by Tian et al. [39] shows that the simple alloying approach is capable of generating thermal conductivity significantly lower than the weighted average of bulk PbTe and PbSe. The present work shows that the thermal conductivity of the PbTe-PbSe nanocomposites is appreciably lower than the conductivity of PbTeSe alloy: \( \kappa_{\text{EMA}}(\text{nanocomposite}) < \kappa(\text{PbTeSe alloy}) \). Thus, it can be concluded that nanstructuring is a promising avenue for optimizing \( ZT \) beyond what can be achieved via alloying.

### 6.5 Chapter Summary

The results of the phonon conductivity dependent on size and dimensionality for PbTe-PbSe nanocomposites by considering three configurations: superlattice, embedded nanowire and embedded nanodot, have shown that the size (thickness) and volume fraction of PbSe are the two main factors that control the effective thermal conductivity in these nanocomposites. In particular, for PbSe size \( d = 10 \) nm and volume fraction \( V_f = 0.1 \), our results predict significant reductions over the weighted average of room-temperature bulk results of 9%, 17% and 15% in the conductivity across the interfaces for the superlattice, embedded nanowire, and nanosphere structures, respectively. For a given \( V_f \), an increase in \( d \) reduces the interface density \( \Phi \) and the effective conductivity varies approximately as \( 1/\sqrt{\Phi} \). It is shown that nanocompositing in any of the three configurations can beat the alloy limit for lattice thermal conductivity.
Bibliography


Chapter 7

Summary and Suggestions for future work

In this dissertation we find that employing the nearly-free-electron approximation and a single non-parabolic electronic band, developed in Chapter 2, was successful for evaluating and reproducing the experimental electronic transport coefficients for an n-type sample of PbTe as presented in Chapter 4. The results also showed that the band non-parabolicity influences the electronic transport coefficients via a temperature-dependent effective mass temperature. The continuum theory of harmonic and anharmonic phonons, including the different acoustic and optical branches, has also been successful in reproducing the lattice thermal conductivity using the single relaxation time approximation or the Debye model, although we had to use a rather smaller Grüneisen constant than that published in the literature. The results of the individual branch contribution to the lattice thermal conductivity, have shown that the $\text{TO}$ phonons make a significant contribution to the lattice thermal conductivity, and are found to play an important role in determining the figure of merit $ZT$. The strongest anharmonic interaction is predicted to arise from the $(\text{N}) \text{TO} + \text{TA} \rightarrow \text{LO}$ process. The total anharmonic relaxation rate of the $\text{TO}$ phonons is quite similar to that of the $\text{TA}$ phonons but much
smaller than that of the LA phonons. It can be assumed that the suppression, or reduction, of the contribution of the TO branch, by an appropriate addition of scattering processes would enhance the thermoelectric properties of PbTe and increase the figure of merit considerably.

In Chapter 5 the theoretical studies of three-phonon scattering processes and the lattice thermal conductivity in the chalcogenide materials SnTe, PbTe, PbSe, and PbS by using three different versions of the relaxation time theory: the single-mode (or, Debye) expression, the Callaway expression, and the Allen expression have shown that the low-lying TO and LO phonon modes play an important role in three-phonon scattering events and thus in heat conduction in these materials.

The results also show that the three-phonon Umklapp processes are weaker (comparable or stronger) than Normal processes for phonons with low(high) wave-numbers. This supports a study by Parrott in 1963, who employed phenomenologically simple relaxation rate expressions for U and N processes to fit the thermal conductivity results of SiGe alloys.

The anharmonic lifetime of LO phonons is much shorter than that of TO phonons in these materials. In contrast to a previous study by Delaire et al. Ref. [4]), we find that, both in SnTe and PbTe, the TO-TA interaction is much stronger than the TO-LA interaction. While only LO-TA is allowed in PbTe, both LO-TA and LO-LA interactions are allowed in SnTe.

Callaway’s original treatment of the momentum-conserving Normal processes is found to generate a substantial addition to the conductivity obtained from the use of the single-mode expression. For the purer sample by Damon of SnTe, this additional contribution has been estimated to be 284% at high temperatures. The Allen expression ( a modified version of the Callaway expression) provides up to 90% addition to the high temperature conductivity results for the Pei sample of PbS from the original Callaway expression.
The presence of large point defect concentrations (such as vacancies) makes the high temperature variation of the conductivity weaker than $T^{-1}$. For SnTe this variation is found to be $T^{-0.75}$ for the Damon sample Ref. ([1]) and $T^{-0.54}$ for the sample from Tan et al. Ref. ([14]). Below the Debye temperature, the resistivity of SnTe varies as the square-root of the point defect concentration.

The largest contribution, at and above room temperature, to $\kappa$ is from TO phonons in Pb-chalcogenides and from both LO and TO phonons in SnTe.

In Chapter 6 we studied the lattice thermal conductivity of PbTe-PbSe nanocomposites within the framework of a modified effective medium approach based on the multiple scattering theory, accounting for interface resistance, and inputting results for bulk conductivities within Callaway’s relaxation time approach involving acoustic as well as optical phonons. With a view to study size and dimensionality effects we considered three structural forms of the nanocomposite: superlattice (SL) with thin PbSe layers embedded in PbTe host, PbSe thin (infinite- and finite-length) nanowires (NW) embedded in PbTe host, and thin PbSe nanodots (ND) embedded in PbTe host. The PbSe inclusion size $d$ was considered in the range 10-200 nm with volume fraction $V_f$ of 0.1 and 0.2. For a given ND or NW size $d$, the conductivity $\kappa_{\text{mEMA}}$ from the modified effective medium theory Ref. ([16]) is much lower than the conductivity $\kappa_{\text{EMA}}$ using the simple (or unmodified) effective medium theory Ref. ([14]). Our work also shows that the process of nanocompositing can produce appreciably lower thermal conductivity than what can be achieved via the alloying process.

*Dimensionality-related results:* we found that the in-plane SL conductivity as well as the conductivity along infinite-length NW is the weighted average of the bulk conductivities of PbSe and PbTe. At all temperatures above 10 K, the cross-plane SL conductivity is larger than the conductivity across the NW or ND. In the interface-dominated low-temperature range $10 – 50$ K, the conductivity across the NW is slightly larger than the conductivity across the ND. At high temperatures,
the conductivities along the SL growth direction, across the NW and across the
ND are very similar, with the NW result being slightly lower than the ND result
above 100 K. We also find that the conductivity along the SL growth direction
(with PbSe and PbTe layers of thicknesses 10 nm and 90 nm, making Φ = 0.01
1/nm) is almost the same (except in the temperature range 20-50 K) as that of
the finite length nanowire (or PbSe pellet of diameter 10 nm and height 10 nm
embedded in PbTe host) with Φ = 0.02 1/nm.

Size-related results: Size-related changes in the conductivity were studied for
the ND structure. For a given dot size d, the conductivity from the modified
effective medium theory κ_{mEMA} is much lower than that using the simple (or un-
modified) effective medium theory κ_{EMA}. For the PbSe NDs of thick size (d = 200
nm considered here) and volume fraction 0.1 the conductivity of the nanocom-
posite is very close to the bulk conductivity of PbTe host. For the same large
size (d = 200 nm) but larger volume fraction (say, Vf = 0.2) the conductivity of
the nanocomposite is noticeably higher than the bulk conductivity of PbTe host.
However, the effect of increased Vf is only noticeable below 500 K. For the NDs of
smaller sizes (say d = 10 nm), the conductivity of the nanocomposite is strongly
influenced by the interface density Φ, which increases with increase in Vf and
decrease in d.

Conductivity variation with interface density: Nanostructuring considered in this
work can be quantified by using two parameters: the insertion size d and the
insertion volume fraction Vf. These two parameters help define the interface den-
sity Φ. Our work shows that for a given Vf, the conductivity increases approx-
imately as κ ∝ √d. From this we interpret the important role of the interface
density in controlling the conductivity approximately as κ ∝ 1/√Φ.

Limits of the applicability of the effective medium theory: It is worth noting that a
nanocomposite structure is usually defined with inserted particle size d satisfying
d/Λ << 1, where Λ is the phonon mean free path in the host material. This means
that the simple formulation of the modified effective medium theory used in this work is expected to work for small $V_f$ (so that interparticle multiple scattering can be neglected and Eq. (6.16) can be used) and the particle insertion size $d$ is larger than 10 nm or so (so that the relaxation time approach to the Boltzmann equation can be expected to be meaningfully applied to both the insertion and host phases). The general features of the results obtained in this work for PbSe-PbTe nanocomposites can be expected to be true for any A-B nanocomposite, with a small volumetric inclusion of appropriately small size of a material A in a homogeneous medium of material B.

**Novelty of this work:**

Most of the studies performed on the lattice thermal conductivity have assumed an average phonon relaxation rate or several adjustable parameters for phonon-phonon interaction. For example the phonon scattering by U processes is taken to be proportional to $\omega^2$ and that by normal processes is proportional to $\omega^2$ with different adjustable constants. In this work we derived an analytical expression for evaluating the phonon-phonon relaxation rate and only adjusted the Grüneisen constant. To the best of our knowledge, there are no available studies on the scattering rates for N and U three-phonon processes. In addition, we performed the lattice conductivity treating the optical phonons with the same degree of importance that has been given to the acoustic phonons.

**Suggestions for future work:**

1- With the available different samples of n-PbTe, one can try to verify if electrons are dominantly scattered by acoustic phonons.

2- A detailed study on the n-PbTe electronic transport coefficients could be performed by applying the non-parabolic electronic structure scheme.

3- A detailed study on which phonon branch is most affected by the size effect
and interface density in the PbTe-PbSe nano-composite.

(iv) For a complete picture of PbTe-PbSe nano-composites, electronic transport coefficients need to be calculated and inserted in the figure of merit formula to indicate how much enhancement these configurations offer to the thermoelectric performance of nano-composites.
APPENDIX A

Klemens (Ref. 8 in Ch. 3) noted that the non-equilibrium distribution \( n(qs) \) for the \( N \) processes settles into a ‘drifted equilibrium’ given by

\[
n_{qs}(u) = \exp \left( \frac{\hbar \omega(qs)}{k_B T} - q \cdot u \right) - 1, \quad (A-1)
\]

where \( u \) is a constant vector parallel to \( \nabla T \). Callaway used this to express the rate of change in \( n(qs) \) due to the \( N \) processes as

\[
\frac{\partial n_{qs}}{\partial t} \bigg|_{N} = \frac{q \cdot u - \psi_{qs}}{\tau_{N,qs}} \bar{n}_{qs}(\bar{n}_{qs} + 1). \quad (A-2)
\]

The vector \( u \) is determined using the momentum conservation condition

\[
\sum_{q} q \frac{\partial n_{qs}}{\partial t} \bigg|_{N} = 0, \quad (A-3)
\]

\[
\sum_{q}(q \cdot u) \frac{\partial n_{qs}}{\partial t} \bigg|_{N} = 0. \quad (A-4)
\]

If \( \theta \) is the angle between \( q \) and the \( \nabla T \), we can express \( u \) using Eqs. A-2 and A-4 as

\[
u = \sum_{qs} \psi_{qs} q \cos \theta \tau_{qs}^{-1} \bar{n}_{qs}(\bar{n}_{qs} + 1)
\]

\[
\sum_{qs} q^2 \cos^2 \theta \tau_{qs}^{-1} \bar{n}_{qs}(\bar{n}_{qs} + 1), \quad (A-5)
\]

Using this, the phonon BTE reads as

\[
-\frac{\hbar \omega(qs)}{k_B T^2} c_s |\nabla T| q_s \bar{n}_{qs}(\bar{n}_{qs} + 1) = \frac{\partial n_{qs}}{\partial t} \bigg|_{\text{coll}} = - \left( \frac{\partial n_{qs}}{\partial t} \bigg|_{N} + \frac{\partial n_{qs}}{\partial t} \bigg|_{R} \right)
\]

\[
= \left( \frac{\psi_{qs} - q \cdot u}{\tau_{qs,N}} + \frac{\psi_{qs}}{\tau_{qs,R}} \right) \bar{n}_{qs}(\bar{n}_{qs} + 1), \quad (A-6)
\]

With this equation we obtain the following relation between \( \psi_{qs} \) and \( u \)

\[
\psi_{qs} = \tau_{qs} \cos \theta (q u \tau_{qs}^{-1} - \frac{\hbar \omega(qs)}{k_B T^2} c_s |\nabla T|). \quad (A-7)
\]

Inserting \( \psi_{qs} \) from Eq. A-7 into A-5, we determine \( u \) as

\[
u = \frac{\hbar |\nabla T|}{k_B T^2} A, \quad (A-8)
\]
where $\mathcal{A}$ is defined as

$$\mathcal{A} = \frac{\sum_{q_s} q \tau_{q_s} \tau_{N,q_s}^{-1} \bar{n}(q_s)(\bar{n}(q_s) + 1)}{\sum_{q_s} q^2 \tau_{N,q_s}^{-1}(1 - \tau_{q_s} \tau_{q_s,N})\bar{n}(q_s)(\bar{n}(q_s) + 1)} \tag{A-9}$$

Eqs. (A-8 - A-9) and A-2, produce Eqs. 3.41 and 3.42.
APPENDIX B

Rather than start with Klemens’ assumption and Callaway’s implementation of it, Allen [Ref. [37] in Ch. 3] starts with a fundamentally different standpoint. He starts with the Boltzmann ‘H-theorem’ [1] and follows the explanation offered in [2]. Allen states that the entropy $S$ of the phonon system should be maximised subject to two constraints. This means that the relevant quantity to maximise is

$$\frac{S}{k_B} - \beta \mathcal{E} - \mathbf{u} \cdot \mathbf{q} \, \mathbb{n}(\mathbf{r}),$$  

(B-1)

where $\beta$ and $\mathbf{u}$ are Lagrange multipliers. Maintaining the concept of local temperature $T(\mathbf{r})$ the multiplier $\beta$ is identified as $\frac{1}{k_B T}$. Allen defines a phonon displaced equilibrium distribution function as $\bar{n}_{qs}(\mathbf{u})$

$$\bar{n}_{qs}(\mathbf{u}) = \frac{1}{\exp \left[ \frac{\omega_{qs}}{k_B T} - \mathbf{u} \cdot \mathbf{q} \right] - 1}.$$  

(B-2)

The Bose-Einstein distribution is $\bar{n}_{qs} \equiv \bar{n}_{qs}(\mathbf{u} = 0)$, defined as

$$\bar{n}_{qs} = \frac{1}{\exp \left[ \frac{\omega_{qs}}{k_B T} \right] - 1}.$$  

(B-3)

In the steady state, the linearised phonon Boltzmann equation within the relaxation time approximation, for a small deviation, reads

$$-\mathbf{c}_s \cdot \nabla T \frac{\partial \bar{n}_{qs}}{\partial T} = \frac{n_{qs} - \bar{n}_{qs}}{\tau_{qs,R}} - \frac{n_{qs} - \bar{n}_{qs}(\mathbf{u})}{\tau_{qs,N}},$$  

(B-4)

with the effective relaxation time $\tau_{qs}$ as

$$\frac{1}{\tau_{qs}} = \frac{1}{\tau_{qs,R}} + \frac{1}{\tau_{qs,N}}.$$  

(B-5)

For $\mathbf{u} = 0$, the deviation from a local equilibrium can be expressed as

$$n_{qs} - \bar{n}_{qs} = \psi_{qs} \bar{n}_{qs}(\bar{n}_{qs} + 1).$$  

(B-6)

But when $\mathbf{u} \neq 0$, $\bar{n} \rightarrow \bar{n}(\mathbf{u})$ and for any $\mathbf{u}$, using Taylor expansion the deviation from the displaced equilibrium is written as

$$n_{qs} - \bar{n}_{qs}(\mathbf{u}) = \psi_{qs} \bar{n}_{qs}(\bar{n}_{qs} + 1) - \mathbf{u} \cdot \mathbf{q} \, \bar{n}_{qs}(\bar{n}_{qs} + 1).$$  

(B-7)
Hence

\[ n_{qs} = \bar{n}_{qs}(u) + \psi_{qs} \bar{n}_{qs}(\bar{n}_{qs} + 1) - u.q \bar{n}_{qs}(\bar{n}_{qs} + 1) \]

\[ n_{qs} - n_{qs}(u) = -u.q \bar{n}_{qs}(\bar{n}_{qs} + 1). \]  

(B-8)

From Eqs. B-4, B-6, and B-7, it is found that \( \psi \) and \( u \) are related as

\[ \psi_{qs} = -r_{qs} c_s \cdot \nabla T \frac{\hbar \omega}{k_B T} - \frac{\tau_{qs}}{\tau_{qs,N}} u.q. \]  

(B-9)

In contrast to Callaway, Allen assumes that the momentum for the actual distribution \( n_{qs} \) and the displaced equilibrium distribution should be the same. This gives

\[ 0 = \sum_{qs} q \left[ n_{qs} - \bar{n}_{qs}(u) \right] \]

\[ = \sum_{qs} q \left[ \psi_{qs} - u.q \right] \bar{n}_{qs}(\bar{n}_{qs} + 1). \]  

(B-10)

Inserting Eqs. B-9 into Eq. B-10 we get

\[ \sum_{qs} q \left[ r_{qs} c_s \cdot \nabla T \frac{\hbar \omega}{k_B T^2} + \frac{\tau_{qs}}{\tau_{qs,N}} u.q \right] \bar{n}_{qs}(\bar{n}_{qs} + 1) = \sum_{qs} \left[ q(u.q) \right] \bar{n}_{qs}(\bar{n}_{qs} + 1). \]  

(B-11)

\[ \sum_{qs} q r_{qs} c_s \cdot \nabla T \frac{\partial \bar{n}_{qs}}{\partial T} = \sum_{qs} q \left[ k_B T^2 \frac{\partial \bar{n}_{qs}}{\hbar \omega} - \frac{\tau_{qs}}{\tau_{qs,N}} \frac{k_B T^2}{\hbar \omega} \right] u.q \]

= \sum_{qs} q \left[ k_B T^2 \frac{\partial \bar{n}_{qs}}{\hbar \omega} - \frac{\tau_{qs}}{\tau_{qs,R}} \right] u.q. \]  

(B-12)

If we take \( \bar{u}.\bar{q} = \cos \theta \) then

\[ |u| = \frac{\hbar}{k_B T^2} \sum_{qs} q_i r_{qs} c_s \cdot \nabla T \omega \bar{n}_{qs}(\bar{n}_{qs} + 1) \]

\[ \sum_{qs} q_i q \cos \theta \frac{\tau_{qs}}{\tau_{qs,R}} \bar{n}_{qs}(\bar{n}_{qs} + 1). \]  

(B-13)

where \( q_i \) is a component of \( q \). Eq. B-13 can be written in the form

\[ |u| = \frac{\hbar |\nabla T|}{k_B T^2} c, \]  

(B-14)
where $\mathcal{L}$ is defined as

$$\mathcal{L} = -\sum_{qs} q_i \tau_{qs} c_s \nabla T \omega \bar{n}_{qs} (\bar{n}_{qs} + 1) \left/ \sum_{qs} q_i q \cos \theta \tau_{qs} \bar{n}_{qs} (\bar{n}_{qs} + 1) \right.$$

(B-15)

Substituting Eq. B-9 we obtain the form of the deviation function $\psi_{qs}$ in Allen’s improvement over the Callaway theory as

$$\psi = -\frac{\hbar |\nabla T|}{k_B T^2} \cos \theta \left[ \tau_{qs} c_s \omega + \tau_{qs} \tau_{qs,s,N}^{-1} q \mathcal{L} \right].$$

(B-16)

The lattice thermal conductivity expressed according to the argument given by Allen, can be formalised as

$$\kappa_{\text{Allen}} = \frac{\hbar |\nabla T|}{k_B T^2} \sum_{qs} \hbar \omega c_s \cos^2 \theta \bar{n}_{qs} (\bar{n}_{qs} + 1) \left[ \tau_{qs} c_s \omega + \tau_{qs} \tau_{qs,s,N}^{-1} q \mathcal{L} \right].$$

(B-17)

$$\kappa_{\text{Allen}} = \frac{\langle \cos \theta \rangle}{V k_B T^2} \sum_{qs} c_s^2 \omega^2 \bar{n}_{qs} (\bar{n}_{qs} + 1) \left[ 1 + \tau_{qs} \tau_{qs,s,N}^{-1} \right] \left/ \tau_{qs,s,N} \right. \mathcal{L}.$$ (B-18)

where $\tau_{\text{Allen}}$ is defined as

$$\tau_{\text{Allen}} = \tau + \frac{q}{\omega c_s} \tau_{qs,s,N}^{-1} \mathcal{L}. $$ (B-19)

If we put $q_i = q \cos \theta$, and apply the continuum approximation for the phonon dispersion relation then we can express Allen’s effective relaxation time as

$$\tau_{\text{Allen}} = \tau_{\text{smrt}} \left[ 1 + \frac{\langle \omega^2 \tau \rangle}{\langle q^2 \tau_{\text{smrt}}^{-1} \rangle} \left/ \tau_{\text{smrt}} \right. \mathcal{L} \right].$$ (B-20)

Allen’s expression for the lattice conductivity can be written in the form

$$\kappa_{\text{Allen}} = \kappa_{\text{smrt}} + \Delta \kappa,$$ (B-21)

where $\Delta \kappa$

$$\Delta \kappa = \frac{1}{3} \frac{\hbar^2}{V k_B T^2} \sum_{qs} c_s^2 \omega q \tau_{qs} \tau_{qs,s,N}^{-1} \bar{n}_{qs} (\bar{n}_{qs} + 1) \left/ \sum_{qs} q \tau_{qs} c_s \omega \bar{n}_{qs} (\bar{n}_{qs} + 1) \right. \mathcal{L}.$$ (B-22)
In the spirit of using a reasonable value of the Grüneisen constant for the materials used in this study, we preferred employing Callaway’s thermal conductivity theory over both Debye and Allen’s improvement over Callaway’s model. While the Debye model requires using a smaller Grüneisen constant than what is given in the literature, a larger one is required for Allen’s improvement of the thermal conductivity expression.
The Fermi integral is involved in the electronic transport coefficients description due to the application of Boltzmann transport equation approach. The Fermi integral takes the form

\[ F_n(\zeta) = \int_{0}^{\infty} \frac{x^n}{1 + \exp(x - \zeta)}, \quad (C-1) \]

where \( x = \epsilon_e / k_B T \) and \( \zeta \) is defined as

\[ \zeta = \frac{\mu}{k_B T}, \quad (C-2) \]

To evaluate this integral numerically we apply Simpson’s rule. This rule expresses a definite integral by a quadratic polynomials approximation. The interval \([a, b]\) of the integral will break up to \( N \) subintervals of width \( h \)

\[ h = \frac{b - a}{N}, \quad (C-3) \]

Simpson’s third rule is written in the form

\[ \int_{a}^{b} F_n(\zeta) d\zeta \approx \frac{h}{3} \left[ F_n(a) + 4 \sum_{j}^{N} F_n(\zeta_j) + 2 \sum_{k}^{N-1} F_n(\zeta_k) + F_n(b) \right], \quad (C-4) \]

where the subscripts \( j \) and \( k \) represent the even and odd terms of the polynomials.
APPENDIX D

The numerical evaluation of the lattice thermal conductivity integral is done by employing the n-point Gauss-Legendre quadrature scheme. A definite integral \( \int_{a}^{b} f(x)dx \) can be evaluated by Gauss-Legendre quadrature. We first make the change of variable from \([a, b]\) to \([-1, 1]\)

\[
\int_{a}^{b} f(x)dx = \frac{b - a}{2} \int_{-1}^{1} g(y)dy,
\]

where \( g(y) = f\left[ \frac{1}{2}(b - a)y + \frac{1}{2}(a + b) \right] \). Then Gauss-Legendre quadrature can be applied

\[
\int_{a}^{b} f(x)dx = \frac{b - a}{2} \int_{-1}^{1} g(y)dy = \frac{b - a}{2} \sum_{i=1}^{n} w_i g(y_i),
\]

where \( w_i \) and \( y_i \) are the weights and the abscissas of the Gauss-Legendre quadrature, respectively, and their values are tabulated in [3].
Bibliography

