Chapter 16 Theoretical Model of Thermoelectric Transport Properties

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A generic theoretical model for five bulk thermoelectric materials (PbTe, Bi$_2$Te$_3$, SnSe, Si$_{0.7}$Ge$_{0.3}$, and Mg$_2$Si) has been developed here based on the semiclassical model incorporating nonparabolicity, two-band Kane model, Hall factor, and the Debye-Callaway model for electrons and phonons. It is used to calculate thermoelectric transport properties: the Seebeck coefficient, electrical conductivity, electronic and lattice thermal conductivities at a temperature range from room temperature up to 1200 K. The present model differs from others: Firstly, thorough verification of modified electron scattering mechanisms by comparison with reported experimental data. Secondly, extensive verification of the model with concomitant agreement between calculations and reported measurements on effective masses, electron and hole concentrations, Seebeck coefficient, electrical conductivity, and electronic and lattice thermal conductivities. Thirdly, the present model provides the Fermi energy as a function of temperature and doping concentration. Fourthly, the velocities of sound are calculated using the Debye model rather than taken from literature. After verification of the present model, we were able to examine a recently attracted material of SnSe, indicating a significant improvement on the dimensionless figure of merit.

16.1 Introduction

Thermoelectric (TE) materials directly convert thermal energy to electricity or vice versa without moving parts, maintenance, and sounds. Hitherto, they have been used only in niche applications such as space exploration or electronic temperature control due to their low thermal efficiencies.[1, 2] It has long been thought that if their efficiencies are improved they could be used for waste heat recovery or large scale solar power conversion. Since the early 1910s, a great deal of effort on understanding the physics for TE transport properties recently brought a remarkable improvement, especially with nanostructures.[3-5] It is known that the modeling of nanostructures is based on the framework of bulk structures.[6] Many models and experiments are reported in the literature.[6-17] Semiclassical theories based on the linearized Boltzmann transport equation (BTE) with the relaxation time approximation (RTA) have successful agreement with the experiments even with their limitations (elastic scattering).[6, 18, 19] A specific model was typically developed for a specific material, which leaves it uncertain whether it could also work for other materials. The RTA incorporates the electron and phonon scattering mechanisms, which are of great importance for determining the TE transport properties.[20] Notably, a variety in the use of electron scattering mechanisms prevails in literature. Ab initio numerical calculations lead to understanding electron and phonon band structures, dispersion relations, density-of-states effective masses.[21, 22] However, they are intrinsically incapable of predicting experimental values due to its inability to handle temperature-dependent band gaps.
and density-of-states effective mass[3, 23]. Therefore, the theoretical model becomes important for correctly predicting the TE transport properties. It is interesting to note that, although there are a great number of research reports in literature, few complete theoretical models thorough from electrons to phonons have been reported.[6, 15, 18] Since electrons and phonons interrelated, it is important to include both in the model. In this work, an attempt is made to develop a generic transport model without the fitting parameters. This work discusses the two-band Kane model, bipolar effect, electron and phonon scattering mechanisms, anisotropy of effective mass (Hall factor), nonparabolicity, electrical and lattice thermal conductivities, and specific heat. Although some materials[6, 24] may have more than two bands, here we deliberately choose materials[10, 25-28] for which two bands suffice. The present model uses the BTE[29, 30] with the RTA[29] and the Debye-, Klemens-Callaway expressions[31, 32]. The binary compounds with the comprehensive experimental data are PbTe[26], Bi₂Te₃[25], SnSe[28], Si₀.₇Ge₀.₃[10], and Mg₂Si[27].

The organization of the chapter is as follows. First, in Section II, a theoretical model is provided with the equations: carrier transport properties, electron scattering mechanisms, lattice thermal conductivity, phonon relaxation times, and phonon density of states and specific heat. In Section III, the calculated results for five binary compounds are discussed and compared with recently reported experimental data. Finally, in Section IV, the conclusions are given. The formulation of anisotropy factor in Hall factor is given in Supplementary.

16.2 THEORETICAL EQUATIONS

16.2.1 Carrier Transport Properties

In this work the nonparabolic two-band Kane model including the Hall factor for the transport properties is derived. For many semiconductors, electrons respond to applied fields with an effective mass that depends on the crystallographic orientation of the field. Herring (1955 and 1956)[8, 33] and Ziman (1960)[30] observed that most actual band structures have ellipsoidal energy surfaces which require longitudinal and transverse effective masses in place of the three principal effective masses. In the Kane model that considers nonparabolicity, the energy dispersion is given by[12, 34]

$$E\left(1+\frac{E}{E_g}\right) = \frac{\hbar^2}{2m_i}\left(\frac{k_i^2}{m_i} + \frac{2k_i^2}{m'_i}\right)$$

(16.1)
where $E$ is the carrier’s kinetic energy, $\hbar$ the Planck constant ($\hbar/2\pi$), $E_g$ the band gap, $k_l$ and $k_t$ the longitudinal and transverse wavevectors, respectively, and $m^*_l$ and $m^*_t$ the longitudinal and transverse effective masses. The density of states (DOS) is given by[12]

$$g_i = \frac{\sqrt{2}N_{v,i}m^*_d,i^{3/2}}{\pi^2\hbar^3} \left( \frac{E^* + \frac{E^{*2}}{E_g^*}}{1 + \frac{2E^*_F}{E_g^*}} \right)^{1/2}$$

(16.2)

where subscript $i$ denotes 1 for the majority carrier and 2 for the minority carrier (for n-type semiconductors the majority carriers are electrons while the minority carriers are holes). $N_{v,i}$ is the degeneracy of the carrier valleys, $m^*_d,i$ the DOS effective mass of single valley (see Eq. (16.9a)), $k_B$ the Boltzmann constant, $T$ the absolute temperature, $E_g^*$ the reduced band gap ($E_g^* = E_g/k_B T$), and $E_F^*$ the reduced Fermi energy ($E_F^* = E_F/k_B T$). The Hall coefficient is defined by[12, 35]

$$R_{H,i} = \frac{1}{n_{H,i}e_i} = \frac{A_i}{n_i e_i}$$

(16.3)

where $n_{H,i}$ is the Hall carrier concentration, $n_i$ the carrier concentration, $e_i$ the carrier charge (negative for electrons and positive for holes), and $A_i$ the Hall factor[12]. Measurements of the Hall coefficient $R_{H,i}$ are the most widely used method for determination of the carrier concentration in semiconductors[35]. The Hall coefficient $R_{H,i}$ is taken negative when $e_i$ is negative. It is important to understand that when the Hall factor $A_i$ is assumed to be unity, the measured carrier concentration $n_i$ becomes the Hall carrier concentration $n_{H,i}$. For brevity, a general Fermi integral with three exponents ($l$, $n$, and $m$) and carrier index ($i$) is[6]

$$\int_{E_i}^{E_{F,i}} \left( -\frac{\partial f_{0,1}}{\partial E^*} \right) \tau_i^{-1} \left( \frac{E^*}{E_g^*} \right)^{3/2} \left( 1 + \frac{2E^*_F}{E_g^*} \right)^m dE^*$$

(16.4)

Where

$$\tau_i^{-1} = \sum_j \tau_{i,j}^{-1}$$

(16.5)
where $\tau_i$ is the combined carrier relaxation time in which the scattering rates (where $j$ indexes the scattering rates) are added according to Matthiessen’s rule as will be discussed in detail in Section II B. The Fermi-Dirac distributions $f_{0,j}$ are given by

$$f_{0,1} = \frac{1}{e^{E^*-E_j^*+1}} \quad \text{and} \quad f_{0,2} = \frac{1}{e^{E^*-E_j^*+E_j^*+1}}$$

(16.6)

Note that for the Fermi-Dirac distribution $f_{0,2}$ the reduced Fermi energy $E_F^*$ in the first part $f_{0,1}$ is substituted by $-E^*_e - E_F^*$[15], which fixes the coordinates of the band structures so that the majority carriers are in the positive direction. The Hall factor $A_i$ is given by[12]

$$A_i(E_F^*, T, n_d) = A\kappa A_i \left( \frac{3K(K+2)}{(2K+1)^2} \right) \frac{F_{0,j}^{K-1}F_{0,j}^{K-1}}{\left(0F_{0,1}^{-1}\right)^2}$$

(16.7)

where $A\kappa$ [33, 36, 37] and $A_i$ [12] are the anisotropy factor of the effective mass and the statistical factor, respectively, and $K = m_l^*/m_i^*$ is the ratio of the longitudinal to the transverse component of the effective mass. Most measurements[25, 28] of carrier concentration assume the Hall factor of unity. However, in this study, the effect of the Hall factor is considered. $A_i$ is derived from the energy transport in a low magnetic field (See Supplementary). The Hall carrier concentrations including the Hall factor are then given by[12, 26]

$$n_{H,j}(E_F^*, T, n_d) = A_i^{-1} \frac{N_{s,d}(2m_d^*,k_B T)^{3/2}}{3\pi^2 h^3} F_{0,j}^0$$

(16.8)

where $A_i$ is the Hall factor as a function of the Fermi energy $E_F^*$, temperature $T$, and doping concentration $n_d$. The doping concentration $n_d$ is the absolute difference between the electron concentration and hole concentration. The Fermi energy $E_F^*$ is exclusively determined by solving Eq. (16.9)[6], where the Fermi energy is a function of both the temperature $T$ and doping concentration $n_d$. Understanding the variability of the Fermi energy is of great importance for the transport properties. The importance of the Fermi energy can be seen through Eqs. (16.4) and (16.6), where the derivative of the Fermi-Dirac distribution function is non-zero only for energy levels within about ± 0.2 eV at the Fermi energy. Since the doping concentration $n_d$ is obtained from the Hall coefficient $R_{H,j}$, we have
\[
n^* = n_{H,1} (E^*_F, T, n_d) - n_{H,2} (E^*_F, T, n_d)
\]  
(16.9)

The present nonparabolic two-band Kane model provides expressions for the transport properties as follows: the electrical conductivity is given by \[6, 23\]
\[
\sigma_i = \frac{N_{e,i} e^2 (2m^*_d k_B T)^{3/2}}{3 \pi^2 m^* c_i \hbar^3} 0_F^{-1}
\]  
(16.10)

where
\[
m^*_d = (m_i^* m_c^*)^{1/3}
\]  
(16.11)
\[
m^*_c = 3 \left( 1/m_i^* + 2/m_c^* \right)^{-1}
\]  
(16.12)

where \( m^*_d \) is the DOS effective mass and \( m^*_c \) is the conductivity (or inertial) effective mass which is usually in the crystallographic direction\[38\] (thermoelectric transport direction)\[26\].

For later use, the total DOS effective mass \( m^* \) is defined by \( m^* = N^2 m^*_d \). The electrical conductivity \( \sigma \) is the sum of the conductivities for the separate bands\[39\].
\[
\sigma = \sigma_1 + \sigma_2
\]  
(16.13)

Using the relationship of \( \mu_H = A \) \[33\], \( \sigma = ne \mu \) \[40\], and \( n = An_H \) \[26\], the Hall mobility \( \mu_{H,j} \) for electrons and holes is derived as\[12\]
\[
\mu_{H,j} = A \frac{e_i}{m_{e,i}^*} \frac{0 F^{-1}_{1,j}}{0 F^0_{0,j}}
\]  
(16.14)

which is also expressed in terms of the averaged relaxation time as\[12\]
$$\mu_{ij} = A_i \frac{e_i \langle \tau_i \rangle}{m^*_{e,i}}$$

(16.15)

where \( \langle \tau_i \rangle \) is the averaged relaxation time \( \frac{0 F_{1,i}^{-1}}{0 F_{0,i}^{-1}} \). Note that the Hall factor is included in Eq. (16.14). The Seebeck coefficients \( \alpha_{1,2} \) for the majority and minority carriers are obtained by\[12, 23\]

$$\alpha_1 = \frac{k_B}{e_i} \left( \frac{1}{F_{1,1}^{-1}} - E_F^* \right), \quad \alpha_2 = \frac{k_B}{e_2} \left( \frac{1}{F_{1,2}^{-1}} + E_g^* + E_F^* \right)$$

(16.16)

The total Seebeck coefficient is given by\[39\]

$$\alpha = \frac{\alpha_1 \sigma_1 + \alpha_2 \sigma_2}{\sigma}$$

(16.17)

If we assume a parabolic single band model, we could have a simple but conceptual Mott formula\[41\], or slightly different version of the formula\[42\], which is

$$\alpha = \frac{\pi^2}{3 e k_B} \left( \frac{g(E)}{n} + \frac{1}{\mu} \frac{\partial \mu}{\partial E} \right)$$

(16.18)

which is not used in this work but in interpretation of the formula, where the Seebeck coefficient \( \alpha \) is proportional to the carrier density of states \( g(E) \) but inversely proportional to the carrier concentration \( n \). The Lorenz number is derived by\[26\]

$$L = \left( \frac{k_B}{e_i} \right)^2 \left[ \frac{2}{F_{1,i}^{-1}} - \left( \frac{1}{F_{1,i}^{-1}} \right)^2 \right]$$

(16.19)

The electronic thermal conductivity is given by\[39\]

$$k_{\text{elect}} = L_1 \sigma_1 T + L_2 \sigma_2 T + \frac{\sigma_1 \sigma_2}{\sigma} T (\alpha_2 - \alpha_1)^2$$

(16.20)
16.2.2 Scattering Mechanisms for Electron Relaxation Times

The electron relaxation time is the average flight time of electrons between successive collisions or scattering events with the lattice or impurities. The relaxation time plays the most important role in determining the transport properties such as the electron mobility, the electrical conductivities, thermal conductivity and the Seebeck coefficient. Bardeen and Shockley (1950)\cite{43}, Brooks (1951)\cite{44}, Howarth and Sondheimer (1953)\cite{45}, Wilson (1953)\cite{29}, Ehrenreich (1957, 1961)\cite{46, 47}, Ravich (1971)\cite{48}, Nag (1980)\cite{49}, and Lundstrom (2000)\cite{16} studied the fundamental scattering mechanisms by acoustic phonons, polar optical phonons, and ionized impurities. Ravich (1971) used the three fundamental scattering mechanisms, derived formulae, and compared with experiments. His formulae were based on the frame work of those semiclassical theories shown above. Later, Zayachuk (1997)\cite{50} and Freik (2002)\cite{51} extended the work of Ravich (1971) by adding two scattering mechanisms (nonpolar optical phonons and short range deformation potential of vacancies) to the three fundamental scattering mechanisms. Thus, five mechanisms have been studied so far. There is a diversity in the use of the scattering mechanisms. For example, Bilc (2006)\cite{23}, Huang (2008)\cite{52}, and Ahmad (2010)\cite{53} used the five mechanisms for PbTe and Bi$_2$Te$_3$. Ravich (1971), Harris (1972)\cite{14}, Broido (1997)\cite{54}, Zhou (2010)\cite{6} and Bahk (2014)\cite{24} used the fundamental three mechanisms for PbTe, Bi$_2$Te$_3$ and Mg$_2$Si. Vineis (2008)\cite{20} used acoustic phonon, polar optical phonon, and nonpolar optical phonon mechanisms for PbTe. Kolodziejczak (1967)\cite{55} used acoustic phonon, polar optical phonon, and nonpolar optical phonon mechanisms. Amith (1965)\cite{56} used polar optical phonon and ionized impurities mechanisms for GaAs. Vining (1991)\cite{15} and Minnich (2009)\cite{18} used acoustic phonon and ionized impurity mechanisms for Si$_{0.7}$Ge$_{0.3}$. Pei (2012)\cite{26} used only acoustic phonon mechanism for PbTe. Bux (2011)\cite{57} showed that acoustic phonon mechanism was dominant for Mg$_2$Si. Chen (2014)\cite{58} used only acoustic phonon mechanism for SnSe.

There are also many reports that used only the acoustic phonon mechanism for their analyses\cite{43, 59-61}.

**Acoustic Phonon Scattering**

Longitudinal acoustic phonons may deform the electron band structure leading to electron scattering due to the deformation potential. The main body of the expression for acoustic phonon scattering was originally provided by Bardeen and Shockley (1950)\cite{43} and widely used. Ravich (1971)\cite{48} added the effect of nonparabolicity at the energy band edge as a function of the ratio of electron energy to band gap. The electron relaxation time for acoustic phonon scattering modified\cite{51} is given by
\[ \tau_{a,i} = \frac{\tau_{0a,i} \left( E^* + \frac{E^*}{E_g} \right)^{-1/2} \left( 1 + \frac{2E^*}{E_g} \right)^{-1}}{\left( (1 - A_g)^2 - B_a \right)} \]  

(16.21)

where

\[ \tau_{0a,i} = \frac{2\pi \hbar^4 v_s^2 d}{\Phi_{a,i}^2 \left( 2m_d^a T_k \right)^{3/2}}, \quad A_a = \frac{E^* (1-K_a)}{1+ \frac{2E^*}{E_g}}, \quad B_a = \frac{8E^* \left( 1 + \frac{E^*}{E_g} \right) K_a}{3 \left( 1 + \frac{2E^*}{E_g} \right)^2} \]  

(16.22)

where \( \Phi_a \) is the acoustic deformation potential, \( v_s \) the velocity of sound (see Eq. (16.23)), \( d \) the mass density (see Eq. (16.23c)), and \( K_a \) the ratio of the acoustic deformation potential for the valence and conduction bands \( K_a = \Phi_{av} / \Phi_{ac} \) [48], which is often assumed to be unity [51]. Note that the relaxation time for acoustic phonon scattering is a function of energy \( \tau \approx \tau_0 E^{-1/2} \) where the exponent \(-1/2\) is known the scattering parameter.

In this work the velocity of sound \( v_s \) is derived using the Debye model rather than taking it from the literature. Thus we can not only reduce one piece of input data but also we can see the effect of atomic mass on transport properties. There can be a marginal difference between the derived and measured velocities. The velocity of sound used in this work is given by [62]

\[ v_s = \frac{k_B}{\hbar} \left( \frac{6\pi^2}{\theta_D a} \right)^{1/3} \]  

(16.23)

where \( \theta_D \) is the Debye temperature and the atomic size \( a \) is obtained by [15]

\[ a = \left( a_A^3 y + a_B^3 (1-y) \right)^{1/3}, \quad a_A = \left( M_A / N_A d_A \right)^{1/3} \quad \text{and} \quad a_B = \left( M_B / N_A d_B \right)^{1/3} \]  

(16.24)

where \( M_{A,B} \) are the atomic masses of component A or B, and \( d_{A,B} \) are the mass densities of component A or B.
**Polar Optical Phonon Scattering**

In a polar solid when the two atoms in a unit cell are not alike, the longitudinal optical vibrations produce crystal polarization that scatters electrons[46], a mechanism that is difficult to be expressed in terms of the relaxation time[45]. However, at high temperatures ($T \gg \theta_D$), the energy change after collision is small compared to the electron energy, which allows the use of the relaxation time.[16, 45] Howarth and Sondheimer (1953)[45] and Ehrenreich (1961)[47] derived an expression for polar optical phonon scattering. Ravich (1971)[48] used that expression along with experimental data including nonparabolicity, the screening effect, and the concept of the ionic charge derived by Callen (1949)[63]. The screening effect usually reduces $\tau$.

There is a problem that this expression eventually dominates the other mechanisms. It was, briefly speaking, found that, when $8\pi$ is added to the magnitude of the formula given by Ravich, it unravels this problem giving good agreement with experimental data, even that of Ravich and others (further discussion is given in Section III). A similar expression with $8\pi$ was actually derived in the works of Nag (1980)[49] and Lundstrom (2000)[16]. The final relaxation time with $8\pi$ for the polar optical phonon scattering is especially of importance at low carrier concentrations.

The electron relaxation time for polar optical phonons is

$$\tau_{po,i} = \frac{8\pi \hbar^2 \left( E^* + \frac{E^*^2}{E_g} \right)^{1/2} \left( 1 + \frac{2E^*}{E_g} \right)^{-1}}{\varepsilon_i^2 \left( 2m^*_i, k_B T \right)^{1/2} \left( \varepsilon_\infty - \varepsilon_0 \right) G_{po}}$$

(16.25)

where $\varepsilon_0$ and $\varepsilon_\infty$ are the static and high frequency permittivities,

$$G_{po,i} = 1 - \delta_i \ln \left( 1 + \frac{1}{\delta_i} \right) - \frac{2E^*}{E_g} \left( 1 + \frac{E^*}{E_g} \right) \left( 1 - 2\delta_i + 2\delta_i^2 \ln \left( 1 + \frac{1}{\delta_i} \right) \right)$$

(16.26)

$$\delta_i = \left( 2k_i r_{0,i} \right)^2$$

(16.27)
where \( k_i \) is the carrier wavevector and \( r_{0,i} \) is the screening radius of the optical phonon.

**Ionized Impurity Scattering**

Ionized impurity scattering becomes most important at low temperatures, where phonon effects are small. Conwell and Weisskopf (1950)[64], Brooks (1951)[44], Blatt (1957)[65], and Amith (1965)[56] studied ionized impurity scattering suggesting the Brooks-Herring formula[65] to take account of the screening effect. Later, Ravich (1971)[48], Nag (1980)[49], Chattopadhyay (1981)[66], Zayachuk (1997)[50], Lundstrom (2000)[16], Freik (2002)[51], Bilc (2006), and Zhou (2010)[6] provided a modified Brooks-Herring formula in magnitude (a factor of either 1 or \( \pi^2 \)) and the screening radius (a factor of either 1 or \( 1/4\pi \)), whereas the main body of the formula except the magnitude and screening radius is the same as the Brooks-Herring formula. It is found in this work that the original Brooks-Herring formula with magnitude factor of 1 and screening radius factor of \( 1/4\pi \) fit the experimental data used here (Chattopadhyay)[66]. The ionized impurity scattering is finally given by

\[
\tau_{i,i} = \frac{\left(2m^*_{d,i}\right)^{3/2}E_0^2(k_B T)^{3/2}}{\pi N_1(Ze_i)^2} \left(E^* + \frac{E^{*2}}{E_g^*}\right)^{3/2} \left(1 + \frac{2E^*}{E_g^*}\right)^{-1} \left[\ln(1+b_i) - \frac{b_i}{1+b_i}\right] \tag{16.30}
\]

\[
b_i = \left(2k r_{i,i}\right)^2 \tag{16.31}
\]

\[
k_i = \left(\frac{2m^*_{d,i}k_B T}{\hbar}\right)^{1/2} \left(E^* + \frac{E^{*2}}{E_g^*}\right)^{1/2} \tag{16.32}
\]
where $r_{i,j}$ is the screening radius of the ionized impurities.

### 16.2.3 Lattice Thermal Conductivity

The thermal conductivity consists of two parts: the electronic and lattice thermal conductivities $(k = k_e + k_l)$. Since the equation of the electronic contribution to the thermal conductivity was given in Section II A, we focus here on the lattice thermal conductivity. Many efforts have been made to understand the lattice thermal conductivity. Debye (1912)[62], Herring (1954)[67], Klemens (1955)[68], Ziman (1956)[69], Callaway (1959)[31], Steigmeier and Abeles (1964)[70], and Vining (1991)[15] studied the fundamental theories and models. Callaway suggested an expression based on the work of Debye and Klemens, which is widely used.[31, 68]

The lattice thermal conductivity $k_l$ is given by

$$k_l = k_1 + k_2$$  \hspace{1cm} (16.34)

$$k_1 = \frac{k_B}{2\pi^2v_s}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_b/\tau_c} \tau_c \frac{x^4 e^{-x}}{(e^x - 1)^2} dx$$  \hspace{1cm} (16.35)

$$k_2 = \frac{k_B}{2\pi^2v_s}\left(\frac{k_B T}{\hbar}\right)^3 \left(\frac{\beta}{\beta_U} \int_0^{\theta_b/\tau_c} \frac{1}{\tau_U} \frac{\tau_c}{(e^x - 1)^2} \frac{x^4 e^x}{dx^2} \right)$$  \hspace{1cm} (16.36)

where $\beta$ is the ratio of the Umklapp processes to the N-processes, $\tau_c$ and $\tau_U$ are the combined and Umklapp relaxation times (see Eqs. (16.44) and (16.37) for $\tau_c$ and $\tau_U$), respectively, and $x = \hbar \omega/k_B T$. The N-processes cannot be usually presented as the scattering processes[71]. The second Callaway term $k_2$ is large for a pure crystal but decrease rapidly with addition of defects so that it is dominant over a wide temperature range for the pure crystal but becomes almost
negligible for an impure crystal.[71] Most doped crystal compounds that have intrinsic defects are impure in fact, so that \( k_i \approx k_i \).

### 16.2.4 Phonon Relaxation Times

Extensive studies[72-80] have been made into phonon relaxation times, including normal-mode processes (N-processes), Umklapp processes, point defects, electron-phonon, and boundary scattering. We use here the expressions suggested by Steigmeier and Abeles (1964).[70] Vining (1991)[15] and Minnich (2009)[18] also used those scattering expressions.

**Scattering by N-Processes and Umklapp Processes**

The Umklapp processes are 3-phonon scattering involving anharmonicity. As mentioned in Section II C, the N-processes do not directly cause the scattering but help the Umklapp processes contribute to the scattering. Therefore, they can be expressed in terms of the relaxation time in \( k_i \) even when \( k_2 \) is neglected in Eq. (16.20a). The Umklapp scattering rate is the inverse of the relaxation time, which is first studied by Leibfried and Schlömann (1954).[72] Later, a modified expression including the effect of the N-processes was given by[15, 70, 81]

\[
\tau_u^{-1} = \frac{20\pi}{3} N_A \hbar \left( \frac{6\pi^2}{4} \right)^{1/3} \left( 1 + \frac{5}{9} \beta \right) \frac{\gamma^2}{1 + \beta} \left( \frac{T}{\theta_D} \right)^3 x^2
\]

(16.37)

where \( N_A \) is Avogadro’s number, \( \gamma \) the Grüneisen anharmonicity parameter, \( M_{AB} \) the atomic mass of compounds A and B, \( a \) the mean atomic size (see Eq. (16.24)), and \( x = \hbar \omega/k_B T \).

The N-process scattering rate is given by

\[
\tau_N^{-1} = \beta \tau_u^{-1}
\]

(16.38)

where \( \beta = 2 \) is often used for a good approximation.

**Scattering by Point Defects**

The point defects may include vacancies, isotopes, dislocations, substitute atoms, etc. A defect with dimensions much smaller than the phonon wavelength can be considered as a point defect[71]. The scattering is then caused by the difference in mass and the difference in bonding
between the atoms.[71] The scattering rate for point defects is given by Klemens (1960)[75], which is

\[ \tau_{PD}^{-1} = V_0 \Gamma \left( \frac{k_B T}{\hbar} \right)^4 x^4 \]

where \( V_0 \) is the atomic volume \( (a^3) \) and the mass-fluctuation-scattering parameter \( \Gamma \) for a binary compound is given by[70]

\[ \Gamma = y(1-y) \left( \frac{\Delta M}{M_{AB}} \right)^2 + \epsilon_s \left( \frac{\Delta a}{a} \right)^2 \]

\[ \Delta M = M_A - M_B, \quad M_{AB} = M_A y + M_B (1 - y) \]

\[ d = M_{AB} / N_A a^3 \quad \text{and} \quad \Delta a = a_A - a_B \]

where \( y \) is the fraction of component A, \( d \) the density of compound and \( \epsilon_s \) the strain parameter.[70]

**Scattering by Electron-Phonon**

The scattering of phonons by electrons will be active when the band degeneracy temperature is comparable with the temperature of the lattice.[69] Ziman (1956) derived an expression for the electron-phonon scattering, which is

\[ \tau_{EP,i}^{-1} = \frac{\Phi_a^2 m_d^* v_i^2}{4\pi\hbar^4 dE_{rc}} \left( x - \ln \left( \frac{1 + e^{\left( E_{rc}, - E_{F,r} + \frac{x^2}{16E_{rc}} \right)}}{1 + e^{E_{rc}, - E_{F,r} + \frac{x^2}{16E_{rc}}}} \right) \right) \]

where \( \Phi_a \) is the acoustic deformation potential, \( E_{rc,i} = m_d^* v_i^2 / (2k_B T) \) and \( x = \hbar \omega / k_B T \).

**Boundary Scattering**

The phonon-boundary scattering rate is assumed independent of temperature and frequency. The boundary scattering rate with an assumption of purely diffuse scattering is given by[30]
\[ \tau_B^{-1} = \frac{v_x}{L} \]  

(16.43)

where \( L \) is the effective length of the sample. The total scattering time can be approximated by adding the scattering rates in accordance with Matthiessen’s rule,

\[ \frac{1}{\tau_c} = \frac{1}{\tau_N} + \frac{1}{\tau_U} + \frac{1}{\tau_{PD}} + \frac{1}{\tau_{EP}} + \frac{1}{\tau_B} \]  

(16.44)

### 16.2.5 Phonon Density of States and Specific Heat

This analysis is based on the Debye model, in which the lattice vibrates as if it were an elastic continuum, but the vibration frequencies cannot exceed a certain maximum value, chosen to make the total number of modes equal to the total number of classical degrees of freedom. The Debye model replaces all branches of the vibrational spectrum with three branches, each with the same linear dispersion relations. The velocity of sound is taken as constant for each branches, as it would be for a classical elastic continuum. In the Debye model the optical modes are unceremoniously lumped into the top end of the distribution of acoustic modes, as if they were merely elastic waves of very short wavelength. Despite its obvious crudity, the Debye approximation has the great advantage of supreme simplicity. If any one parameter is required to measure the energy scale of the vibrations of a solid, the Debye temperature is the most appropriate. If any one function is required to represent the distribution of the lattice frequency, the phonon density of states is the simplest.

The total number of modes \( N \) is found by dividing a sphere in wavevector-space by the volume of the primitive cell \( N = V \omega^3 / (6\pi^2 v_s^3) \), where \( V \) is the volume of the crystal. The phonon density of states for each branch is obtained by taking derivative of \( N \) with respect to \( \omega \) leading to \( g_{ph} = V \omega^2 / (2\pi^2 v_s^3) \). After all, the phonon density of states per each branch per mode is obtained by

\[ g_{ph} = \frac{3\omega^2}{\omega_D^3} \]  

(16.45)

where \( \omega \) is the phonon frequency and \( \omega_D \) the Debye frequency. Using \( \omega_D = \theta_D k_B / \hbar \) (cutoff frequency), \( x = \hbar \omega / k_B T \), and \( g_{ph} = (3h/k_B T)(T/\theta_D)^3 x^2 \), the Debye specific heat in terms of \( g_{ph} \) is then obtained by
\[
c_v = 3 \frac{N k_B T}{V} \int_{0}^{\theta_D / T} \frac{x^2 e^x}{(e^x - 1)^2} g_{\nu} dx
\]  
(16.46)

or equivalently,
\[
c_v = 9 \frac{N k_B}{V} \left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\theta_D / T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]  
(16.47)

where \( N \) is the number of modes, \( V \) is the volume of a crystal, and \( N/V \) is assumed to be the atomic volume \( 1/a^3 \) for a cubic structure[30, 75]. Eq. (16.47) is called the Debye formula[30].

16.2.6 Dimensionless Figure of Merit

The dimensionless figure of merit \( ZT \) is defined to represent the performance of the thermoelectric materials by

\[
ZT = \frac{a^2 \sigma}{k} T
\]  
(16.48)

where \( T \) is the absolute temperature, \( a \) the Seebeck coefficient, \( \sigma \) the electrical conductivity, and \( k \) the thermal conductivity, which were defined in the preceding section. The commercial value is \( ZT \approx 1 \). The higher the dimensionless figure of merit the better the performance.

16.3 RESULTS AND DISCUSSION

16.3.1 Electron or Hole Scattering Mechanisms

Mobility for PbTe

The three fundamental scattering mechanisms (acoustic phonons, polar optical phonons, and ionized impurities) presented in Section II B are examined here and compared to experiments. Since \( \mu_{H,i} = A_i \langle \tau_i \rangle / m_{i}^* \) (Eq. (16.15)), the Hall mobility was best known to represent the individual or combined scattering mechanisms. Scattering rates that are the reciprocals of the
relaxation times are assumed to be independent each other, so that Matthiessen’s rule can be applied. [29, 30] Ravich (1971) studied the three fundamental scattering rates, presenting three equations similar to Eqs. (16), (18), and (19). Zayachuk (1997) [50] and Freik (2002) [51] extended the work of Ravich (1971). [13]

Figure 16.1 (a) depicts the calculated mobility-versus-carrier concentration for n-type PbTe at room temperature, which is in agreement with the experiments by Ravich (1971) [13] and Pei (2012) [26], and also very close to the predictions (not shown in the figure) by Ravich and Pei. The acoustic phonons appear dominant at high concentrations while both the polar optical and acoustical phonons contribute proportionally to the total mobility at low concentrations. Ionized impurities have a negligible effect on the total mobility. According to some theoretical works [44, 56, 64, 66], ionized impurities are expected to be important at low temperatures. In Figure 16.1 (b), both the ionized impurities and the acoustic phonons contribute proportionally to the total mobility at 77 K, which leads to an anticipation that the ionized impurities will predominate the other mobilities if the calculations and experiments are conducted at near zero temperatures. Figure 16.1(c) depicts the Hall mobility versus temperature at the carrier concentration of about $3 \times 10^{19}$ cm$^{-3}$ showing that the acoustic phonons are dominant over the range of temperatures. In Figures 1 (a) and (c), two separate experiments by Ravich and Pei are in agreement with the present calculations. It is seen in general that the present scattering model fits both the experiments and predictions by the theories. And the assumption on the dominance of the acoustic phonon scattering for PbTe ensures the validity at room temperature, which is the reason why PbTe has been preferably selected for many analyses of transport properties such as the Pisarenko’s expression [83].

![Graph showing mobility versus carrier concentration](image_url)
For n-type PbTe, (a) the Hall mobility at room temperature versus carrier concentration, (b) the Hall mobility at 77 K versus carrier concentration, and (c) the Hall mobility versus temperature at a carrier concentration of about $3 \times 10^{19}$ cm$^{-3}$.

**Mobility for Bi$_2$Te$_3$**

A question arises to how the preceding predictions will work for other binary compounds. We are obviously interested in Bi$_2$Te$_3$ which is one of the most widely used TE materials, known to be predominated by the acoustic phonons[39, 84]. The predominance by the acoustic phonons is
clearly seen in Figure 16.2 (a) and (b) and its temperature dependence is in agreement with experiments by Jeon (1991).[25]

![Graph of Hall mobility versus carrier concentration](image1)

(a)

![Graph of Hall mobility versus temperature](image2)

(b)

Figure 16.2 For p-type Bi$_2$Te$_3$, (a) the Hall mobility versus carrier concentration at room temperature, (b) the Hall mobility versus temperature at a carrier concentration of $1.1 \times 10^{19}$ cm$^{-3}$.

**Mobility for Si$_{0.7}$Ge$_{0.3}$**

The next interesting compound is Si$_{0.7}$Ge$_{0.3}$. Scattering is dominated by acoustic phonon and ionized impurities because silicon germanium is not a polar material[18]. Figure 16.3 (a) and (b) indicate that ionized impurities are dominant at room temperature while acoustic phonons...
gradually increase their contribution becoming dominant at 1000 K. The effect of polar optical phonons is minimal over these ranges of carrier concentrations and temperatures except at very low concentrations.

Figure 16.3 For n-type Si$_{0.7}$Ge$_{0.3}$ the Hall mobility at room temperature versus carrier concentration, and (b) the Hall mobility versus temperature at a carrier concentration of 6.7 x 10$^{19}$ cm$^{-3}$.
Mobility for Mg$_2$Si
Bahk (2014)[24] demonstrated that the calculated transport properties for Mg$_2$Si are in good agreement with the measurements of Tani (2005)[27] using the three fundamental scattering mechanisms which are the acoustic phonons, polar optical phonons, and ionized impurities. On the other hand, Satyala (2012)[85] also showed that their predictions for Mg$_2$Si are in a good agreement with the measurements of Tani (2008)[86] using only two mechanisms which are the acoustic phonons and ionized impurities. Our calculated results using the three fundamental mechanisms are presented in Figure 16.4 (a) and (b), where the combination of the three mobilities more or less proportionally determines the total mobility over the wide range of carrier concentration (Figure 16.4 (a)). At a high concentration of 4 x 10$^{19}$ cm$^{-3}$ in Figure 16.4 (b), only two mechanisms (acoustic phonons and ionized impurities) contribute to the total mobility. It is also seen that our calculation is in a good agreement with the measurements of Bux (2011).[57] The present work successfully supports the individual work of Bahk and Satyala. It may be interesting to note that in Figure 16.4 (b) the exact slope of the experimental data cannot be achieved without combining the two individual slopes of the acoustic phonons and ionized impurities.
Figure 16.4  For n-type Mg$_2$Si, (a) the mobility versus carrier concentration at room temperature, (b) the mobility versus temperature at a carrier concentration of $4 \times 10^{19}$ cm$^{-3}$.

**Mobility for SnSe**

Tin selenide has recently drawn much attention for possible high performance due to the unusually high anisotropy reported by Zhao (2014)[28]. There has been little theoretical modeling of the electron scattering mechanisms. Chen (2014)[58] calculated the transport properties for SnSe using only acoustical phonons. However, we calculated the Hall mobility using the three fundamental mechanisms, shown in Figure 16.5 (a) and (b). At low carrier concentrations, on the order of $10^{17}$ cm$^{-3}$, acoustic phonons and polar optical phonons equally contribute to the total mobility. In Figure 16.5 (b), it is seen that the calculated mobility reasonably agrees with the measurements of Zhao.
Figure 16.5  For p-type SnSe, (a) The mobility versus carrier concentration at room temperature, (b) mobility versus temperature at a carrier concentration of $3.3 \times 10^{17} \text{ cm}^{-3}$. We have seen that the present calculations for Hall mobility are basically in agreement with the theoretical predictions and with experimental data for five binary compounds which supports the present model with the semiclassical theories for the scattering mechanisms or equivalently the carrier relaxation times.

Table 16.1 Input data for five binary compounds used.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>n-type PbTe (AB)</th>
<th>p-type BiTe3 (AB)</th>
<th>p-type SnSe (AB)</th>
<th>n-type Si$<em>{0.7}$Ge$</em>{0.3}$ (AB)</th>
<th>n-type MgSi (AB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_A$ (g)</td>
<td>Atomic mass A</td>
<td>207.2$^a$</td>
<td>208.98$^a$</td>
<td>118.71$^a$</td>
<td>28.086$^a$</td>
<td>24.3$^a$</td>
</tr>
<tr>
<td>$M_B$ (g)</td>
<td>Atomic mass B</td>
<td>127.6$^a$</td>
<td>127.6$^a$</td>
<td>78.96$^a$</td>
<td>72.61$^a$</td>
<td>28.08$^a$</td>
</tr>
<tr>
<td>$d_A$ (g/cm$^3$)</td>
<td>Mass density A</td>
<td>11.34$^a$</td>
<td>9.8$^a$</td>
<td>5.76$^a$</td>
<td>2.33$^a$</td>
<td>1.74$^a$</td>
</tr>
<tr>
<td>$d_B$ (g/cm$^3$)</td>
<td>Mass density B</td>
<td>6.25$^a$</td>
<td>6.25$^a$</td>
<td>4.81$^a$</td>
<td>5.32$^a$</td>
<td>2.33$^a$</td>
</tr>
</tbody>
</table>
able to calculate thermoelectric (TE) transport properties using the equations shown in Section II

With the carrier relaxation times computed in the preceding section, the present model is now able to calculate thermoelectric (TE) transport properties using the equations shown in Section II.
A and the input data listed in Table 16.1. There are always small disagreements between models and measurements. The disagreements may be here managed by varying the deformation potential for electrons and the Grüneisen parameter for phonons.

**Transport Properties for n-type PbTe**
The single crystals of lead telluride have been well known since the early 1950s for thermoelectric generators at a mid-temperature range from 500 K – 800 K [13, 59, 96-100]. The effective mass for n-type PbTe was measured by Ravich (1971) [13] as 0.22 $m_0$ (where $m_0$ is the free electron mass) and also predicted with the *ab initio* numerical calculations by Vineis (2008) [20] to be 0.23 $m_0$. The temperature-dependent total DOS effective mass and the degeneracy of band valleys used are $0.22 \times (T/300K)^{1/2}$ and 4 from Table 16.1, respectively, which are in good agreement with measurement and *ab initio* calculations [48, 90].

The first calculation is to determine the Fermi energy using Eq. (16.8), which is a function of doping concentration and temperature. The Fermi energy versus temperature curves at two doping concentrations of $1.8 \times 10^{19}$ cm$^{-3}$ and $2.9 \times 10^{19}$ cm$^{-3}$ are plotted along with the conduction and valence band edges in Figure 16.6 (a), where the valence band edge first decreases with increasing temperature, then being constant from 450 K [101]. The band gap is about 0.35 eV here. The Fermi energy along with the doping concentration is shown in Figure 16.6 (b), where the Fermi energy rises above the conduction band edge from the doping concentration of about $10^{19}$ cm$^{-3}$. The electron concentration in Figure 16.6 (c) is the same as the doping concentration over three temperatures and the doping concentration is not affected at all by the bipolar carriers (holes).

Note that the carrier concentration could differ from the doping concentration if there is a sufficient bipolar effect. Figures 6 (a), (b), and (c) are rarely reported in literature, but it is important to understand the variability of the Fermi energy for studying the transport properties. Figure 16.6 (d) shows the Seebeck coefficient versus carrier (actually doping) concentration at room temperature along with the measurements by Pei (2012)(n-type) [26] and Crocker and Rogers (1967)(p-type) [102]. This also shows good agreement with Pisarenko relation (not shown here) [83]. The Seebeck coefficient for the lowest and highest carrier concentrations are related to the Fermi energy in Figure 16.6 (b) [102].
(a) 

Temperature (K)

- $n = 1.8 \times 10^{19} \text{ cm}^{-3}$
- $n = 2.9 \times 10^{19} \text{ cm}^{-3}$

- Conduction band minimum
- Valence band maximum

(b) 

Doping Concentration (cm$^{-3}$)
Figure 16.6 For n-type PbTe, (a) Fermi energy versus temperature, (b) Fermi energy versus doping concentration, (c) Carrier concentration versus temperature, and (d) Seebeck coefficient versus doping concentration at room temperature along with measurements by Pei (2012) (n-type)[26] and Crocker and Rogers (1967) (p-type)[102].

The TE transport properties are now calculated for two slightly different doping concentrations, which are shown in Figure 16.7 (a), (b), and (c). The calculations for the Seebeck coefficient, electrical conductivity, and thermal conductivity are in excellent agreement with the measurements by Pei (2012), precisely agreeing even with the slight difference of the carrier concentrations. Figure 16.7 (d) shows the electronic and lattice components of the thermal conductivity. The measurements of thermal conductivity can knowingly be only conducted for
the total thermal conductivity so the lattice component is obtained by subtracting the calculated electronic component from the measurements. It is noted that the lattice component is one approach for improvement of the figure of merit. The other approach is to look at electronic properties. The superb agreement between the calculations and measurements tells us that the present transport model complies well with the subtle physics of electrons and phonons including the scattering, particularly with the BTE under the RTA and the Debye model. Then, if the present model is so precise, two questions immediately arise: 1) How well the simply calculated electron density of states (DOS) compares to sophisticated \textit{ab initio} numerical calculations, and 2) how the simple Debye model enables to precisely predict the complex lattice thermal conductivity. It has been challenging to obtain the electron DOS even with \textit{ab initio} numerical calculations\cite{103,104} or to obtain phonon DOS that involves acoustical and optical branches where each has one longitudinal and two transverse directions\cite{105-108}.
Figure 16.7 For n-type PbTe, (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity and (d) electrical and lattice contributions to total thermal conductivity.

To examine the first question, the calculated electron DOS using Eq. (16.2) are compared (Figure 16.8 (a)) to the ab initio calculations of Martinez (1975) [103] and Bilc (2004) [109]. Considering that the effective range of the derivative of the Fermi-Dirac distribution function of Eq. (16.4) on the transport properties is within about ± 0.2 eV at the Fermi energy (here the conduction band edge at 0.31 eV), Figure 16.8 (a) is expanded as shown in Figure 16.8 (b), where the nonparabolic Kane model and parabolic model are shown along with the ab initio calculations. We can see that the Kane model closely agrees with ab initio calculations while the parabolic model is clearly deficient in that range. This is the reason why the calculated nonparabolic DOS predicts well in comparison with the sophisticated ab initio calculations.
Figure 16.8 For n-type PbTe, (a) Calculated electron DOS versus energy of electrons, and (b) close-up of Figure 16.8 (a) at the conduction band edge. The solid line is the calculated DOS and dashed line is the ab initio numerical computations by Martinez (1975)[110] and Bilec (2004)[109].

To examine the second question of how the simple Debye model so precisely predicts the lattice thermal conductivity, the calculated phonon DOS using Eq. (16.45) is compared to the \textit{ab initio} calculations by Zhang (2009)[105] (Figure 16.9 (a)). The \textit{ab initio} calculations involve many detailed frequency-dependent features with the six branches mentioned earlier.[105, 111] The integral of the phonon DOS curve directly contributes to the thermal conductivity by knowing that $k_l = 1/3Cvl$, where $C$ is the heat capacity proportional to the integral of the phonon DOS, $v$ the mean phonon velocity, and $l$ the phonon mean free path ($l = v\tau$).[29] The present Debye model[62] simply lumps the phonon DOS onto the top of the distribution of acoustic modes.
assuming elastic waves. However, the cutoff frequency (which is attained from the Debye temperature) is best determined from experiment (specific heat), which is shown in Figure 16.9 (a). This gives rise to the lumped amount of the integral of the present phonon DOS curve, being almost the same as the integral in the \textit{ab initio} calculations by Zhang. This is the reason why for the second question. The contributions of the individual phonon relaxation times to the total relaxation time are illustrated in Figure 16.9 (b), where the Umklapp processes are dominant up to about 1 THz and then the point defects become dominant at higher frequencies than 1 THz. The electron-phonon scattering is negligible except at the very low frequencies. It is interesting to note that the cutoff frequency limit in Figure 16.9 (a) is approximately in agreement with the frequency of the relaxation time in Figure 16.9 (b). The weighted phonon relaxation time is calculated by $\tau \cdot x^4 e^x / (e^x - 1)^2$.
Figure 16.9 For n-type PbTe, (a) calculated phonon DOS versus frequency [105], and (b) weighted phonon relaxation time versus frequency.

Finally, the temperature dependent specific heat using Eq. (16.46) is plotted in Figure 16.10, where the Debye temperature is a key parameter to fit the measurements. The Dulong-Petit limit \( \left( c_{r,DP} = 3k_B/a^3 \right) \) (see Eq. (16.24) for \( a \)) is calculated to be 11.8 cal/mol·K, which is in agreement with the experiments by Parkinson (1954)[96] as shown. The Debye temperature is the primary parameter in the velocity of sound, acoustic phonon scattering, relaxation time, electrical conductivity and consequently specific heat. Usually the Debye temperature is determined from measurement of specific heat at lower temperatures[96, 112]. The superb agreement so far between this model and the measurements indicates that not only the model is correct but also the Debye temperature shown in Table 16.1 is correct. This procedure was actually used to newly determine the Debye temperature for SnSe later.[62]

Figure 16.10 For n-type PbTe, specific heat versus temperature compared with the measurements by Parkinson and Quarrington (1954).[96] The calculated Dulong-Petit limit is 11.8 cal/mol·K which is in agreement with the measurements.

**Transport Properties for p-type Bi$_2$Te$_3$**

Single crystals of bismuth telluride have been widely used since the 1950s for both thermoelectric generators and coolers at room temperature.[39, 100, 113-116] The calculated Fermi energy for p-type Bi$_2$Te$_3$ is plotted in Figure 16.11 (a) along with the valence and conduction band edges, indicating that the Fermi energy appears nondegenerate (located within the band gap beyond ± 3 \( k_B T \) of the conduction and valence band edges). The reason for the
leveling off of the Fermi energy in the figure is due to the bipolar effect, which is shown in Figure 16.11 (c). For Figure 16.11 (b), increasing the Fermi energy above the valence band edge by increasing the doping concentration typically decreases the Seebeck coefficient and increases both the electrical conductivity and thermal conductivity (we will demonstrate this in Figure 16.16 (a)). It is not clear whether it improves or not until $ZT$ is plotted as a function of carrier concentration since an optimum usually exists at a doping concentration near $10^{19}$ cm$^{-3}$. The electron and hole concentrations were measured by Jeon (1991)[25] and compared with the calculated values using Eq. (16.8) as shown in Figure 16.11 (c). We could fit the measurements by varying either the electron or hole DOS effective mass. The most challenging work was that the total DOS effective mass of $0.6m_e$ in Table 16.1 entered to make fit to the experimental carrier concentration gives no further adjustment later on the transport properties such as the Seebeck coefficient, electrical conductivity, etc. It is interesting to note that using both the nonparabolic Kane model and the Hall factor always give better results than without either of them. In the same line of discussion, for n-type Bi$_2$Te$_3$ we could not achieve concomitantly the good comparison shown in Figure 16.11(c) and Figure 16.12 (a), (b), and(c) without the nonparabolicity and anisotropy (Hall factor).
For p-type Bi$_2$Te$_3$ at doping concentration of $1.1 \times 10^{19}$ cm$^{-3}$, (a) Fermi energy versus temperature, (b) Fermi energy versus doping concentration, (c) Carrier concentration versus temperature compared to experiment by Jeon (1991).

For electronic transport properties, Huang (2008)[52] and Zhou (2010)[6] reported computations using the nonparabolic Kane model. For lattice thermal conductivity, Huang used \textit{ab initio} calculations while Zhou used the effective medium approximation (EMA)[17]. Park (2010)[117] attempted to predict the Seebeck coefficient using \textit{ab initio} calculations. Considering the wide spread use of bismuth telluride (bulk), it is surprising to find that not many theoretical models have been reported in literature. As shown in Figure 16.12 (a), (b), and (c), we calculated the transport properties using the present model, and obtained agreement with the measurements by Jeon (1991)[25] and Goldsmid (1958)[74]. Since we used the total DOS effective mass of 0.6 $m_e$. 

![Figure 16.11](image-url)
the DOS effective mass of a single valley using the degeneracy (multivalley) of 12 valleys is 0.11 $m_o$ by using $m^* = N_v^{2/3}m_d^*$, whereby 0.11 $m_o$ used in this work is close to 0.106 $m_o$ measured by Kohler (1976)[116] and also 0.11 $m_o$ calculated by ab initio method by Kim (2005)[22]. Most works[39, 91, 118-120] used the degeneracy of 6 valleys except a few ab initio calculations used the degeneracy of 12 valleys[21, 22, 52]. Decreasing lattice thermal conductivity is important for seeking a high figure of merit.[121] Here we present the lattice thermal conductivity in Figure 16.12 (c), where the lattice thermal conductivity is dominant up to 300 K while the electronic thermal conductivity proportionally becomes significant and dominant at higher temperatures, obviously, due to the bipolar effect in Figure 16.11 (c). For this material, the bipolar effect negatively acts on the ZT, which leads to room for improvement if the bipolar effect is delayed or eliminated by a doping technique. The lattice thermal conductivity is mainly determined by the Umklapp processes where the Grüneisen parameter $\gamma$ is the important factor as shown in Eq. (16.37). Therefore, we make a fine adjustment of the lattice thermal conductivity curve only in magnitude by adjusting the Grüneisen parameter to be 1.79. This is also in agreement with the experimental value given by Madelung (1983)[88].
For p-type Bi₂Te₃ at a doping concentration of 1.1×10¹⁹ cm⁻³, (a) Seebeck coefficient, (b) electrical conductivity, and (c) electronic, lattice, and total thermal conductivities.

Figure 16.12

The electron and phonon DOS along with the energy and frequency, respectively, are presented in Figure 16.13 (a) and (b), where the nonparabolicity and the integrals between this model and other work are seen similar to those in case of lead telluride. In Figure 16.13 (b), the calculated phonon DOS is here compared to the real data measured by Rauh (1981)[122] not \textit{ab initio} calculations as before, which verifies the Debye model and accordingly the lattice thermal conductivity. The specific heat was calculated using Eq. (16.46) and is shown in Figure 16.13 (c) where the model show a good agreement with measurements by Bessas (2012).[123] The Dulong-Petit limit calculated is 124.7 J/mol·K which is in agreement with the measurements. It
is seen that the specific heat at low temperatures seems to follow $T^3$ law\cite{30, 87}. These features support the present model.

(a)

![Graph showing electron density of states versus energy](image1)

(b)

![Graph showing phonon density of states versus frequency](image2)
For p-type Bi₂Te₃ at a doping concentration of $1.1 \times 10^{19}$ cm⁻³, (a) electron density of states versus energy compared to *ab initio* calculations by Youn and Freeman (2001)[21], (b) phonon DOS versus frequency compared to experiment by Rauh (1981) [122] and (c) specific heat versus temperature compared to experiment by Bessas (2012)[123], where Dulong-Petit limit calculated is 124.7 J/mol·K.

**Transport Properties for p-type SnSe**

Single crystals of tin selenide have been used since the 1950s in applications such as solar cells, lasers, detectors, phase-change memory alloys, etc. Not much attention has been paid to thermoelectric applications until the recent times. Therefore, theoretical modeling is rarely found in literature, Wasscher (1963)[124] analytically studied the maximum dimensionless figure of merit $ZT \approx 0.15$. Chen (2014)[58] discussed a naive theoretical model assuming the parabolic one-band model with spherical Fermi surface and acoustic phonon scattering for the Seebeck coefficient and Hall mobility. Adouby (1998)[125] conducted experiments on crystal structures. Nariya (2009)[126], Banik (2014)[127], Sassi (2014)[128] Zhao (2014)[28] and Han (2015)[129] conducted measurements for the TE transport properties. To the author’s knowledge, Chen (2014) is the only work on theoretical modeling although there are many studies on the band structures and the lattice thermal conductivity using the *ab initio* calculations[3, 28, 130-135].

An attempt is made here to predict the TE transport properties for p-type SnSe using the present model. The input data are shown in Table 16.1, where the values given from the literature have the references but the values without references are estimations in this work. The majority carrier of p-type SnSe is holes. Since we could not find measured total DOS effective masses from literature, we had to estimate them by fitting the measurements of concentration by Zhao (2014)[28] as shown in Figure 16.14 (a). We obtained 0.65 $m_0$ for holes and 9.5 $m_0$ for electrons.
for the best fit indicating the unusually high anisotropy (for which the Hall factor 0.893 appears the smallest among other materials shown in Table 16.1), even showing the calculations slightly off from the measurements at the higher temperatures starting at 700 K. Since the present model uses the total DOS effective masses as shown above, the single valley DOS effective masses using the degeneracy of 2 valleys give 0.4 $m_o$ for holes and 5.9 $m_o$ for electrons, which are comparable to 0.34 $m_o$ and 3.0 $m_o$, respectively, calculated by ab initio method by Shi and Kioupakis (2015)\[3\]. However, we were then able to calculate the Fermi energy as a function of temperature and doping concentration. The Fermi energy was plotted in Figure 16.14 (b) along with the valence and conduction band edges, where similar ab initio calculations by Shi and Kioupakis (2015)\[3\] are superimposed for comparison. It should be noted that the temperature-dependent band gap (0.86 - $4 \times 10^{-4}T$) eV in Table 16.1 is in agreement with the 0.86 eV measured by Zhao (2014). The temperature-dependent band gap is however forced to fit the experimental transport properties. A strong bipolar effect at around 600 K is seen in the Fermi energy for both the present and ab initio calculations. Note that the measurements by Zhao (2014) were performed at a low doping concentration of $3.3 \times 10^{17}$ cm$^{-3}$ probably for a crystallographic reason. Unusual dynamics of the Fermi energy with respect to the doping concentration is shown in Figure 16.14 (c) corresponding to the bipolar effect. The calculated Seebeck coefficient in Figure 16.14 (d) was then compared to the similar measurements conducted by Chen (2014)\[58\] for the applicability of the present model as a function of doping concentration at two different temperatures of 300 K and 750 K, showing good agreement between the model and the measurements.

![Graph showing carrier concentration vs temperature](image-url)
Figure 16.14 For p-type SnSe at a doping concentration of $3.3 \times 10^{17}$ cm$^{-3}$, (a) carrier concentration versus temperature compared to experiments by Zhao (2014)[28], (b) Fermi energy versus temperature compared to the *ab initio* calculations by Shi and Kioupakis (2015)[3], (c) Fermi energy versus doping concentration, (d) Seebeck coefficient versus doping concentration compared to experiments by Chen (2014)[58].

Since the DOS effective masses for holes and electrons are forced to fit the measured temperature-dependent carrier concentrations in Figure 16.14 (a), there is no way to adjust the calculated Seebeck coefficient if it is in disagreement with the experiments (because the effect of carrier scattering on the Seebeck coefficient is very small). However, the calculated Seebeck coefficient in Figure 16.15 (a) is in agreement with experiments by Zhao, which supports the present model. The electrical conductivity is a strong function of the carrier scattering, depending on a combination of the scattering mechanisms or the relaxation times. As the detailed discussion showed in the earlier section, the three fundamental scattering mechanisms properly act on resulting in a good agreement with the measurements as shown in Figure 16.15 (b). As for expected in Figure 16.14 (a), the strong bipolar effect produce many holes adding to the majority holes, rapidly increasing the hole concentration as well as the electron concentration, correspondingly increasing the electrical conductivity as shown in Figure 16.15 (b). According to Zhao (2014), a phase transition from low-temperature *Pnma* to high-temperature *Cmcm* occurs at 750 K, where the present model cannot take into account the phase transition which causes the calculations apart from the measurements at the higher temperatures, which is shown in Figure 16.15 (b). The most spectacular feature is the ultralow thermal conductivity. The electronic and lattice contributions to the thermal conductivity are presented as shown in Figure 16.15 (c), where the lattice thermal conductivity is at glace dominant over the range of temperatures except
at the very high temperatures, in which the dominance of the lattice thermal conductivity is in good agreement with Zhao (2014) attributing to the low carrier concentration used. It is interesting to note that the Grüneisen parameter obtained here is 2.2 that is the highest among others in this work and in agreement with an average value 2.1 of *ab initio* calculations by Zhao (2014). The Grüneisen parameter characterizes crystal volume change due to phonon frequency, which affects, in turn, the band structure, the carrier scattering, and finally the phonon scattering. The $ZT$ at the doping concentration of $3.3 \times 10^{17}$ cm$^{-3}$ as a function of temperature are presented in Figure 16.15 (d) which is generally in agreement with the measurements, where $ZT$ is a very low value of about 0.12 at room temperature while $ZT$ is an unprecedented high value of about 2.6 at 923 K by measurement (about 2.1 in this work).
Figure 16.15 For p-type SnSe at a doping concentration of $3.3 \times 10^{17}$ cm$^{-3}$, (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and (d) figure of merit versus temperature. The model was compared to the experiments by Zhao (2014).[28]

The dynamics of transport properties as a function of carrier (actually doping) concentration are presented in Figure 16.16 (a). It is seen that, with increasing the carrier concentration, the Seebeck coefficient decreases while both the electrical and thermal conductivities increase. The summary result is conveniently presented by the dimensionless figure of merit [121] as shown in Figure 16.16 (b). It is quite interesting to see that the calculated $ZT$ values along with three different temperatures dramatically increases as the concentration increases from the measured
concentration of $3.3 \times 10^{17}$ cm$^{-3}$ to the calculated optimum concentration of about $3 \times 10^{19}$ cm$^{-3}$, where the $ZT$ values at 900 K, 600 K and 300K reveal about 13%, 660%, and 620% increases, respectively, compared to the values at the low carrier concentration. The predicted $ZT$ value at the mid-temperature ranges of about 600 K is about 1.5 which would be also very useful in some applications. It is hoped that the calculated maximum $ZTs$ at the optimum concentrations be experimentally examined in the future.

Figure 16.16 For p-type SnSe, (a) electronic properties versus carrier concentration, and (b) the dimensionless figure of merit versus doping concentration.
The electron DOS for p-type SnSe is presented in Figure 16.17 (a), showing that the nonparabolic Kane model fits well the *ab initio* calculations by He (2013) for the effective range of energy ($\pm 0.2 \text{ eV}$) at the Fermi energy. The specific heat is calculated and compared with the measurements by Zhao (2014), where the Debye temperature $\theta_D$ used is 155 K that agrees with neither a calculated value of 65 K by Zhao (2014)[28] nor a calculated value of 215 K by He (2013)[92]. The value of 155 K was determined by fitting the experimental data for both the transport properties and the specific heat.

Figure 16.17 For p-type SnSe at doping concentration of $1.1 \times 10^{19} \text{ cm}^{-3}$, (a) electron DOS versus energy compared to *ab initio* calculations by He (2013)[92], and (b) specific heat versus temperature compared to experiments by Zhao (2014)[28].
Transport Properties for n-type Si$_{0.7}$Ge$_{0.3}$

The single silicon-germanium crystals as a possible material for thermoelectric generators were taken as early as 1957 by Ioffe[83]. The crystals or alloys were considered to be a good candidate at high temperatures around 1000 K for energy conversion to electricity in space with radioisotope thermoelectric generators (RTG). Dismukes (1964)[10], Abeles (1962)[77] and Rosi (1968)[11] studied experimentally while Abeles (1963)[89], Parrott (1963)[136], Steigmeier (1964)[70], Amith (1965)[137], and Gaur (1966)[138] studied theoretically. Recently, Slack (1991)[93], Vining (1991)[15] and Minnich (2009)[18] studied the theoretical modeling. Since the discussions here are similar to those in the earlier sections, we here just present the calculated results for information. Figure 16.18 (a), (b), and (c) present the carrier concentration, the doping concentration, and Fermi energy, respectively. And the transport properties versus temperature along with the experiments as shown in Figure 16.19 (a), (b) and (c), where the two scattering mechanisms (the acoustic phonons and ionized impurities) dominantly determine the total scattering rate, or the relaxation time. The specific heat versus temperature is plotted in Figure 16.19 (d), where the Dulong-Petit limit is calculated to be 24.92 J/mol·K.

![Graph](image-url)
Figure 16.18 For n-type Si$_{0.7}$Ge$_{0.3}$, (a) carrier concentration versus temperature, (b) Fermi energy versus doping concentration, and (c) Fermi energy versus temperature.
Figure 16.19 For n-type Si$_{0.7}$Ge$_{0.3}$ at two carrier concentrations of $6.7 \times 10^{19}$ cm$^{-3}$ and $1.5 \times 10^{20}$ cm$^{-3}$, (a) Seebeck coefficient versus temperature compared to experiments by Dismukes (1964)[10], (b) electrical conductivity versus temperature compared to the experiments, (c) thermal conductivity versus temperature compared to the experiments, and (d) specific heat versus temperature compared to experiments by Rosi (1968).[11]

*Transport Properties for n-type Mg$_2$Si*

Mg$_2$Si single crystals have been well known since the 1950s as thermoelectric material which offers nontoxicity (not like Pb), cost effectiveness (not like Te), and abundance (not like Te, rare earths, etc.) at a mid-temperature range 500 K to 900 K. Many efforts have been drawn to
electronic structures[139-142], thermal conductivity[143], experiments[27, 144], \textit{ab initio} calculations[104, 145, 146], nanostructures[147, 148], and modeling of transport properties[6, 24, 85]. The carrier band structures appear somewhat complex, involving indirect band gaps and multiband. The conduction band edge consists of two nondegenerate bands separated by a distance of 0.4 eV. The valence band edge also consists of two degenerate bands, light-hole and heavy-hole, with no separation.[24, 104, 149] Furthermore, each band has two valleys (or pockets). In the present model, the two conduction band edges are lumped into one conduction band but increasing the valleys to match the total number. The two valence band edges are lumped into one valence band but increasing the number of valleys to match the total number. Thus, the present model assumes only two bands, one conduction band and one valence band each with four valleys, as shown in Table 16.1. In fact this model allows a fit to experimental data of transport properties simply by varying the total DOS effective masses. We obtained 1.0 \( m_o \) for electrons and 2.0 \( m_o \) for holes and recalculated the single valley DOS effective masses using the degeneracy of 4 valleys, leading to 0.4 \( m_o \) and 0.8 \( m_o \), which are unexpectedly in excellent agreement with the 0.46 \( m_o \) and 0.87 \( m_o \) measured by Morris (1958)[150]. The discussion of the results are similarly explained in the earlier sections, so here we just present the results for information. The carrier concentration and Fermi energy are plotted in Figure 16.20 (a), (b), and (c). The transport properties for Mg\(_2\)Si are presented in Figure 16.21 (a), (b), and (c). The specific heat is shown in Figure 16.21 (d). All the calculations are in good agreement with the measurements.
Figure 16.20 For n-type Mg$_2$Si, (a) carrier concentration versus temperature, (b) Fermi energy versus doping concentration, and (c) Fermi energy versus temperature.
Figure 16.21 For n-type Mg_{2}Si at two carrier concentrations of 4.3 \times 10^{17} \text{ cm}^{-3} and 1.1 \times 10^{20} \text{ cm}^{-3}, (a) Seebeck coefficient versus temperature compared to experiments by Tani (2005)[27], (b) electrical conductivity versus temperature compared to experiments by Tani (2005)[27], (c) thermal conductivity versus temperature compared to experiments by Tani (2005)[27], and (d) specific heat versus temperature compared to experiments by Gerstein (1967)[151].

The calculations of the transport properties for all the five binary compounds were found to be in agreement with the corresponding experimental data used here. It is somewhat surprising to find that the primary parameters in Table 16.1 (whether they are input data or calculated) are close to the widely accepted values (either measurements or \textit{ab initio} calculations), including the total DOS effective masses, degeneracy of valleys, band gap, Debye temperature (that is proportional
to the velocity of speed), and Grüneisen parameter. It is quite meaningful that the model is able to precisely predict the experimental values with the realistic input data. However, we had to vary the deformation potential to make it fit the measured electrical conductivity only in magnitude, not in slope (the slope is associated with the electron scattering), which is a common practice in modeling due to the usually unknown deformation potential. The most important parameter is the DOS effective mass that affects almost all electronic parts of the model such as the Fermi energy, carrier concentration, carrier density of states, electron scattering, transport properties, etc. Firstly, the calculations of transport properties are in agreement with the experiments. Then, the model can be said robust if the input values of the effective masses with the degeneracy of valleys are in agreement with the measured effective masses because they cannot simultaneously fit the various corresponding experimental values without the combination of both the realistic input values and the right model. The second important parameter is the Debye temperature which affects both the electronic and phonon parts of the model: the velocity of sound, acoustic phonon scattering, electrical conductivity, electronic and lattice thermal conductivity, point defects scattering, cutoff frequency, phonon DOS, and specific heat. The present model differs from other typical models in that the velocity of sound is taken from the literature and hence the Debye temperature affects only the lattice thermal conductivity (the specific heat is not usually included). The Debye temperature is typically experimentally determined from the specific heat measured at low temperatures. Hence only the Grüneisen parameter of the Umklapp processes allows to adjust the magnitude of the lattice thermal conductivity. Lastly, if the two parameters (DOS effective mass and Debye temperature) are close to the realistic values, the model can be said to be robust.

16.4 Summary

A theoretical model based on the linearized Boltzmann transport equation with the relaxation time approximation and the Debye model has been developed incorporating nonparabolicity, two-band (conduction and valence bands) Kane model, and Hall factor without the fitting parameters. It calculates the thermoelectric transport properties (Seebeck coefficient, electrical conductivity, and thermal conductivity) along with the Hall mobility, Fermi energy (as a function of temperature and doping concentration), carrier concentration, electron and phonon density of states, and specific heat. In particular, it provides electron relaxation times and electronic and lattice contributions to the thermal conductivity including the bipolar effect. We found that the present model is generally in good agreement with reported experiments for five thermoelectric bulk materials (PbTe, Bi₂Te₃, SnSe, Si₀.₇Ge₀.₃, and Mg₂Si). This theoretical model is important for nanostructured materials in which the modelling is based on that of the bulk materials and ab
*initio* numerical calculations are intrinsically incapable of precisely predicting the experimental values due to their inability to handle temperature-dependent band gap and effective masses. The present model differs from others as follows: Firstly, the three modified electron scattering mechanisms (acoustic phonons, polar optical phonons, and ionized impurities) are demonstrated to be responsible for the electron relaxation times. Secondly, concomitant agreement between input data, calculations, and experiments for the DOS effective masses, electron and hole concentrations, velocity of sound (calculated rather than taken from literature), Seebeck coefficient, electrical conductivity, electronic and lattice thermal conductivities, and Grüneisen parameter. Since the present model uses no fitting of parameters, it is able to examine a recently attracted material of SnSe, not only predicting the measured transport properties (the unprecedented $ZT$ value of 2.6 at 923 K), but also suggesting a significant improvement in $ZT$ value of about a 600 % increase (a $ZT$ value of 1.5) at 600 K and an increased doping concentration compared to the reported $ZT$ value of 0.13 at that temperature.

**REFERENCES**


123. Bessas, D., et al., *Lattice dynamics in Bi_{2}Te_{3} and Sb_{2}Te_{3}: Te and Sb density of phonon states*. Physical Review B, 2012. 86(22).


Problems

16.1. Derive Equation (16.2) (see Chapter 11).
16.2. Explain the difference between the Hall carrier concentration and the carrier concentration.
16.3. Briefly explain the three fundamental electron scattering mechanisms.
16.4. Derive the Hall mobility of Equation (16.11a).
16.5. Derive the following equation shown in Equation (16.9) as
\[
\sigma_i = \frac{N_{v,i} e^2}{3 \pi^2 m^*_v \hbar^3} \left[ \frac{2 m^*_v k_BT}{m^*_e \hbar^3} \right]^{3/2} F_{1,i}^{-1}.\]
16.6. Show the total electronic thermal conductivity in Equation (16.15).
16.7. Derive the Callaway-Klemens formula of Equation (16.20b).
16.8. Derive Debye formula shown in Equation (16.28a) as
\[
c_v = 9 \frac{N}{V} k_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\rho_0 T} \frac{x^4 e^x}{(e^x - 1)^2} dx.
\]