Electronic thermal conductivity as derived by density functional theory

M. X. Chen
Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, USA

R. Podloucky
Department of Physical Chemistry, University of Vienna, Sensengasse 8/7, 1090 Vienna, Austria

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Reliable evaluation of the lattice thermal conductivity is of importance for optimizing the figure-of-merit of thermoelectric materials. Traditionally, when deriving the phonon mediated thermal conductivity $\kappa_{ph} = \kappa - \kappa_{el}$ from the measured total thermal conductivity $\kappa$ the constant Lorenz number $L_0$ of the Wiedemann-Franz law $\kappa_{el} = TL_0\sigma$ is chosen. The present study demonstrates that this procedure is not reliable when the Seebeck coefficient $|S|$ becomes large which is exactly the case for a thermoelectric material of interest. Another approximation using $L_0 - S^2$, which seem to work better for medium values of $S^2$ also fails when $S^2$ becomes large, as is the case when the system becomes semiconducting/insulating. For a reliable estimation of $\kappa_{el}$ it is proposed, that a full first-principles calculations by combining density functional theory with Boltzmann’s transport theory has to be made. For the present study such an approach was chosen for investigating the clathrate type-I compound Ba$_8$Au$_{6-x}$Ge$_{40+x}$ for a series of dopings or compositions $x$. For a doping of 0.8 electrons corresponding to $x = 0.27$ the calculated temperature dependent Seebeck coefficient agrees well with recent experiments corroborating the validity of the density functional theory approach.

Thermal conductivity plays an important role for the thermoelectric performance of a material as expressed by the figure-of-merit $ZT = TS^2\sigma/(\kappa_{el} + \kappa_{ph})$ which includes the Seebeck coefficient $S$, the electrical conductivity $\sigma$, and the thermal conductivity $\kappa = \kappa_{el} + \kappa_{ph}$ summing up the contributions of electronic states and phonon mediated processes. Consequently, a low thermal conductivity in combination with large values of $S$ and $\sigma$ are desirable in order to achieve large values of $ZT$. Considerable efforts for lowering $\kappa$ by reducing $\kappa_{ph}$ were made by utilizing structural properties, such as building up superlattices and incorporating suitable filler atoms into structural cages. These concepts rely on the strong scattering of heat-transporting phonon modes. However, neither $\kappa_{el}$ nor $\kappa_{ph}$ are directly measured. Rather, $\kappa_{ph}$ is derived by subtracting $\kappa_{el}$ from the measured total thermal conductivity, i.e., $\kappa_{ph} \approx \kappa_{max} - \kappa_{el}$ in which the electronic thermal conductivity is estimated via the Wiedemann-Franz (WF) relation for simple metals, $\kappa_{el} \approx TL_0\sigma$. In this expression, $L_0$ is a universal constant and does not depend on temperature and materials properties. In the present work it is shown by a density functional theory (DFT) study for a typical thermoelectric material that the application of the WF law leads to unreliable estimates of $\kappa_{el}$ in particular when the Seebeck coefficient of the material is large, which is exactly the case of interest.

The present theoretical study is based on the same DFT concept as applied for first-principles calculations of Seebeck coefficients (for example, see Ref. 22). In the present work the WF law is generalized by introducing a material and temperature dependent Lorenz tensor $L$, for which Boltzmann’s transport theory in combination with electronic properties derived by DFT calculation is used. This procedure is applied for the clathrate type-I compound Ba$_8$Au$_{6-x}$Ge$_{40+x}$, which is a prototypical thermoelectric material and for which also very recent measurements of Seebeck coefficients are available enabling a test of the validity of the present theoretical approach.

For the present purpose, the WF law is generalized to

$$\kappa_{el} = TL_0\sigma,$$

in which the tensor $\kappa_{el}$ is linearly related to the conductivity tensor $\sigma$ (as defined in Eq. A.2 via the Lorenz tensor $L$. These quantities as well as the Seebeck tensor $S$ (Eq. A.3) are second rank tensors. In accordance with Boltzmann’s transport theory one derives

$$\kappa_{el} = \frac{1}{T} \left( K_2 - K_1^2 K_0^{-1} \right)$$

for which Eq. A.2 is utilized for the definition of the tensors $K$. The Lorenz tensor $L$ can now be formulated as

$$L = L_1 - S^2$$

whereby $L_1$ is expressed as

$$L_1 = \frac{1}{e^2T^2} K_2 K_0^{-1}.$$

For a free-electron like metal the second term at the right hand side of Eq. 3 is negligible, because $|S|$ is small. It is then obvious that the deviation from the free-electron like behavior is caused by the Seebeck coefficient in terms of $S^2$. At low temperatures the original WF law is a reasonable approximation, i.e. $L_1 \approx L_0$, whereby $L_0$ would be a tensor with constant coefficients.
\[ L_0 = \pi^2 \frac{k_B^2}{\hbar^2} = 2.44 \times 10^{-8} \text{W} \Omega/K^2, \] involving Boltzmann’s constant \( k_B \).

When assuming a constant relaxation time \( \tau = \text{const} \) – as it is the standard approach for first-principles calculations of the Seebeck coefficients (for example, see Ref.\(^{[22]}\) – then \( \tau \) cancels out in the components of \( \mathbf{L} \) since it appears in the numerator as well as in the denominator in Eqs.\(^{[3]} \) and \([4]\). The same holds for the Seebeck coefficients because of Eq.\(^{[X,3]} \). For the following discussion it should be noted that the crystal structure of the material under study is of cubic symmetry. As a consequence of this high symmetry all second rank tensors are diagonal and the three diagonal coefficients are equal. Therefore, only one coefficient needs to be considered for each tensor. However, the derivations and calculations can be done for a general crystal symmetry and for tensors with less symmetry and more components. If the tensors are symmetry averaged (as needed for a polycrystalline material), again only one coefficient needs to be considered.

What remains to be done is the DFT calculation of the electronic structure of the actual material, \( \text{Ba}_8 \text{Au}_6 \text{Ge}_{40} \). For that purpose, the Vienna \( \text{Ab initio} \) Simulation Package (VASP\(^{[27,28]} \)) was used for which the pseudopotentials were constructed according to the projector augmented wave method\(^{[27,28]} \). The exchange-correlation functional was parametrized in terms of the local density approximation according to Ceperley and Alder\(^{[29]} \). The valence state configuration for the construction of the pseudopotentials included the \( 5s, 5p \) and \( 6s \) atomic states for Ba, the \( 6s \) and \( 5d \) states for Au, and the \( 3d, 4s \) and \( 4p \) states for Ge. For the Brillouin zone integration a \( 5 \times 5 \times 5 \) grid of \( \mathbf{k} \)-points was found to be sufficiently accurate concerning the relaxed structural parameters as mentioned in the caption of Fig.\(^{[1a]} \). Electronic transport properties were derived by utilizing the Boltzmann transport equations within the constant relaxation time approximation as implemented in the program package BoltzTraP\(^{[22,30,31]} \). For that purpose the Kohn-Sham eigenvalues \( \varepsilon_i(\mathbf{k}) \) were determined on a very dense \( 25 \times 25 \times 25 \) grid of \( \mathbf{k} \)-points. For the investigation of the thermoelectric properties of off-stoichiometric compounds \( \text{Ba}_x \text{Au}_{6-x} \text{Ge}_{40+x} \) with varying \( x \) or number of valence electrons (i.e., doping \( \Delta N \)) the rigid-band construction was used which consists in shifting the Fermi energy according to the doping without changing the underlying electronic structure.

Fig.\(^{[1a]} \) shows the density of states (DOS) around Fermi energy. A gap of about 0.3 eV occurs about 0.15 eV above the Fermi energy \( E_F \) for the undoped case. Electron dopings of up to \( \Delta N = 1.2 \) places \( E_F \) closer to the gap where the DOS diminishes rather strongly. For such a situation a large Seebeck coefficient is expected, as is indeed the case (see inset in Fig.\(^{[2]} \). Assuming two valence electrons for each Ba atom, one valence electron for each Au atom and for valence electrons for each Ge atom, the total number of valence electrons of \( \text{Ba}_8 \text{Au}_6 \text{Ge}_{40} \) amounts to 182. Finally, by adding \( \Delta N = 2 \) electrons the corresponding \( E_F \) falls into a gap because then the total number of valence electrons is 184, which is precisely the total number of valence electrons of Ge\(_{46} \) in its clathrate structure, which at Fermi energy has a rather large gap of about 1.6 eV. This is a remarkable feature since the electronic structure of Ge in its diamond ground state structure reveals no gap at all when a local approximation of the DFT exchange-correlation interactions is utilized, as it is the case here. Such an un-

\[ \Delta N = 0 \]

\[ \Delta N = 0.8 \]

\[ \Delta N = 2 \]

\[ \tau = 1 \times 10^{-14} \text{s} \]
recalculating of standard DFT calculations. Assuming that the gap is preserved when filler atoms such as Ba are placed in the voids of the clathrate structure and elements such as Au are substituting Ge according to the composition Ba$_8$Au$_{6-x}$Ge$_{40+x}$, then the relation $x = \Delta N/3$ can be established. The critical composition, i.e. the Fermi energy falls into the gap, would then be $x_{\text{crit}} = 2/3$.

Fig. 1(b) depicts the coefficients $L$ and $L_1$ of the cubic Lorenz tensor (see Eqs. 3 and 4) at 300 K as functions of doping. The inset shows the carrier-density-dependency of the resistivity $\rho$ which is the inverse of the conductivity $\sigma$ in Eq. 2. Significant deviations between the Lorenz coefficients occur in the range of $0 \leq \Delta N \leq 4$, which increase strongly when the doping is near to $\Delta N = 2$. At $\Delta N = 2$ the coefficients $L$ and $L_1$ are undefined because in the gap no electronic states are available for transport and therefore at lower temperatures the electrical conductivity $\sigma$ is zero (or the resistivity has a pole, see inset in Fig. 1(b)), and as a consequence the Lorenz coefficients reveal singularities. The comparison between $L_1$ and $L$ demonstrates the influence of the Seebeck coefficient in terms of $-S^2$, which increases dramatically as the Fermi level approaches the gap upon doping.

For thermoelectric applications, both $S$ as well as $\sigma$ should be large for obtaining a large power factor $S^2\sigma$. For such a purpose, a suitable carrier concentration is required. In the case of Ba$_8$Au$_{6-x}$Ge$_{40+x}$, a doping $\Delta N$ up to 1.2 yields a carrier concentration of about $n = -2 \times 10^{20}$ e/cm$^3$, which is within the desired range for thermoelectric materials. The negative sign of $n$ refers to hole carriers, i.e., Fermi energy is below the gap, a positive sign just refers to the opposite case, i.e., Fermi energy above the gap.

For dopings $\Delta N > 4$, $\Delta N < 0$ the coefficients $L$ and $L_1$ nearly coincide and their values become comparable to the constant Lorenz number but $L_0$ could still be off by 20%. The results suggest that the approximation by $L_1$ is not useful for thermoelectric materials with large Seebeck coefficients.

Fig. 2 reveals the temperature dependency of $L_1$ and $L$ for no doping and $\Delta N = 0.8$. The inset compares DFT-derived and experimental Seebeck coefficients revealing very good agreement between measurement and DFT calculation for a doping of $\Delta N = 0.8$. Such a doping refers to an off-stoichiometry of $x = 0.27$, which is within the experimental error measuring the composition. Both $L_1$ and $L$ approach the WF limit $L_0$ at low temperatures but deviate significantly at elevated temperatures. Overall, $L$ and $L_1$ exhibit a strong temperature dependency and the deviation of the constant value $L_0$ becomes large in particular around 700 K, which is in the temperature range of technological applications.

As demonstrated by the inset of Fig 2 the assumption of a constant relaxation time $\tau$ works well for the evaluation of the Seebeck coefficient. Nevertheless, we tested an energy dependent relaxation time $\tau(\varepsilon) = \text{const } \varepsilon^{-1/2}$ according to Ref. 33 recalculating of $L$ as well as $S$. This ansatz for $\tau(\varepsilon)$ is supposed to model the scattering of electrons by acoustic phonons. The energy $\varepsilon = |E_F - \varepsilon_k|$, was defined as the absolute value of the difference of Fermi energy and the respective band energy for band $\nu$ and vector $\vec{k}$.

By considering this specific $\tau(\varepsilon)$, based on the energy dispersions of the two-band Kane approximation Huang et al. demonstrated for Bi$_2$Te$_3$ that a constant relaxation time yields a slightly larger Lorenz number than the energy dependent ansatz. We performed similar calculations for Ba$_8$Au$_{6-x}$Ge$_{40}$ for the dopings $\Delta N = 0.8$, 1.2 by utilizing the DFT-derived electronic structure. In this context, it should be noted that for deriving the relation $\tau(\varepsilon) \propto \varepsilon^{-1/2}$ bands with parabolic dispersions near Fermi energy are assumed, which is not really the case for the material under study. Nevertheless, the results for $S(T)$ and $L(T)$ in Fig. 3 show that the influence of the assumed energy dependency of $\tau(\varepsilon)$ is rather small, although it becomes more pronounced at elevated temperatures and larger dopings with Fermi energy approaching the gap.

For finally deriving the electronic thermal conductivity $\kappa_{el}$ from Eq. 1 the full Lorenz coefficient $L$ together with its approximations $L_1$ and $L_0$ are used. The results in Fig. 4 reflect the behavior of the Lorenz coefficients in Fig. 2 showing again very significant deviations up to 40% between the full calculation and the result involving the approximations $L_1$ and $L_0$. Clearly, just using the simple WF law (i.e. $L_0$) may lead to rather unreliable values for the electronic thermal conductivity, and consequently for the lattice thermal conductivity when it is derived from the measured total thermal conductivity by $\kappa_{ph} = \kappa^{\text{meas.}} - \kappa_{el}$. The rather similar behavior of thermal conductivities $\kappa_{el}$ in Fig. 4 as calculated with $L$
FIG. 3. DFT results for Ba$_8$Au$_6$Ge$_{40}$: Seebeck coefficient $S(T)$ and the component $L(T)$ of the full Lorenz tensor for no doping and dopings of $\Delta N = 0.8$, 1.2. Results with constant relaxation time $\tau_0$ (full lines) and with the energy-dependent ansatz $\tau(\varepsilon) = \text{const} \ \varepsilon^{-1/2}$ (dotted lines).

FIG. 4. DFT derived electronic thermal conductivities $\kappa_{el}$ for Ba$_8$Au$_6$Ge$_{40}$+x. Results for a doping of $\Delta N = 0.8$ using $L_0$, $L_0 - S^2$, and $L$ as Lorenz coefficients. The corresponding carrier concentrations are also indicated.

and the approximation $L_{\text{app.}} = L_0 - S^2$ would suggest to use $\kappa_{el} \approx TL_{\text{app.}}\sigma$ for a reasonable estimation of $\kappa_{el}$. This would have the big advantage, that $\kappa_{ph}$ could be estimated from measurable quantities, namely the Seebeck coefficient $S(T)$ and the electrical conductivity $\sigma$. This observation, however, is only useful as long as $S^2$ is not too large and temperatures are sufficiently.

As Fig. 4, however reveals, for dopings $\Delta N \geq 0.8$ the use of the approximation $L_0 - S^2$ grossly underestimates the results obtained with $L$, the Lorenz coefficient calculated without any approximation (apart from the assumption of a constant relaxation time). The errors become larger the nearer $E_F$ approaches the gap. This is attribute to the fact that $L_1$ deviates $L_0$ significantly when the system becomes semiconducting/insulating as shown in the inset of Fig. 1(b). Likewise, only using the constant $L_0$ of the Wiedemann-Franz results in significant overestimations. Therefore the conclusion has to be made, that it is mandatory to derive the electronic thermal conductivity from DFT calculations in combination with Boltzmann’s transport theory in terms of the full Lorenz-tensor $L$. Otherwise the estimated $\kappa_{el}$ and, subsequently, $\kappa_{ph}$ might be rather wrong, which is undesirable for optimizing thermoelectric properties of a material.

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Appendix

The tensor needed in Boltzmann’s transport theory is

$$
K_n = \frac{1}{4\pi^2} \sum_{i,k} \tau_i(k) \nu_i(k) \otimes \nu_i(k)(\varepsilon_i(k) - \mu)\alpha \quad (A.1)
$$

$$
\left( - \frac{\partial f(\mu, T, \varepsilon_i)}{\partial \varepsilon_i} \right)
$$
in which $\tau_i(k)$ is the relaxation time of the electronic states with band index $i$, energy eigenvalue $\varepsilon_i$ and band velocities $v_i$ for wave vector $k$, whereas $f(\mu, T)$ denotes the Fermi-Dirac distribution function for the chemical potential $\mu$ at temperature $T$.

The electrical conductivity tensor $\sigma$ is given by

$$\sigma = e^2 K_0$$

(A.2)

and the Seebeck tensor $S$ is defined by

$$S = -\frac{1}{eT} K_1 K_0^{-1}.$$ 

(A.3)