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The impact of commonly used approximations on the computation of the Seebeck coefficient and mobility of polar semiconductors

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Seebeck coefficient modeling and measurement has important applications in direct thermal to electrical energy conversion and solid-state physics. The computations of the Seebeck coefficient and mobility of polar semiconductors in the literature often employ certain approximations, notably the relaxation time approximation (RTA) and the truncation of the Boltzmann transport equation. We study the accuracy of these approximations as a function of the effective mass, temperature, and carrier concentration using a recently developed technique for rigorous solution of the Boltzmann transport equation. We find that the approximations give rise to considerable error in the computed Seebeck coefficients of heavily doped semiconductors with a low effective mass, and that the RTA is entirely inapplicable for the accurate computation of the mobility of several important materials. © 2012 American Institute of Physics.

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The importance of a material for high-efficiency thermal-to-electrical energy conversion, through the Seebeck effect, is guided by the metric $Z = S^2\sigma/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity. Computation of the Seebeck coefficient using a transport model like the Boltzmann transport equation (BTE), in combination with a first-principles electronic structure calculation, is an *ab initio* technique that has predictive value for the metric Z .¹ Measurement of the Seebeck coefficient, and fitting to a transport model, forms an important method for determining the effective mass of a semiconductor, especially one with poor mobility (e.g., see Refs. 2 and 3). High-temperature Seebeck coefficient measurements of thermoelectric materials are impacted by repeatability and accuracy issues⁴ due to the degradation of thermal epoxy, thermocouple inaccuracy, noise, etc., as evidenced by the number of different measurement techniques (e.g., Refs. 5–8) proposed in the literature. A recently proposed technique for high-temperature Seebeck coefficient measurements of thin-films addresses these challenges by using an epitaxially regrown thermometric reference material.⁹ Accurate computation of the Seebeck coefficient of the reference material is critical to the accuracy of this measurement.

In this letter, we examine the effect of commonly used approximations on the calculation of the Seebeck coefficient, as a function of material parameters and temperature, by comparison with the numerical solution of the Boltzmann transport equation computed using the method of Ref. 10. We will examine the impact of these approximations on mobility calculations in passing, since the high-temperature conductivity can be measured accurately by the van der Pauw technique.¹¹

In this paper, bold font is used to represent vectors, and normal font to represent their magnitudes and other scalars. The BTE is given by

$$\mathbf{v}(\mathbf{k}) \cdot \nabla_{\mathbf{r}} f + \frac{q\mathbf{F}}{\hbar} \cdot \nabla_{\mathbf{k}} f = \sum_{\mathbf{k}'} S(\mathbf{k}', \mathbf{k}) f(\mathbf{k}', \mathbf{r}) (1 - f(\mathbf{k}, \mathbf{r})) - \sum_{\mathbf{k}'} S(\mathbf{k}, \mathbf{k}') f(\mathbf{k}, \mathbf{r}) (1 - f(\mathbf{k}', \mathbf{r})). \quad (1)$$

Here, $f(\mathbf{k}, \mathbf{r})$ is the non-equilibrium distribution function that we wish to extract, $q\mathbf{F}$ is the electric force on the carrier of charge-magnitude q , $\mathbf{v}(\mathbf{k})$ is the group velocity, and $S(\mathbf{k}, \mathbf{k}')$ is the sum of probability rates for all scattering mechanisms for transition from a Bloch state $\mathbf{k}$ to a state $\mathbf{k}'$.

Assuming all spatial variations are along one dimension, the z -direction, the BTE can be formulated as an integral equation, as follows:

$$\frac{g(k, z)}{\tau_{eff}(k, z)} = - \left(v(k) \frac{\partial f_0}{\partial z} + \frac{qF(z)}{\hbar} \frac{\partial f_0}{\partial k} \right) + \int_{k'=0}^{\infty} g(k', z) \left(\frac{1}{\Gamma^{inelas}(k', k, z)} \right) dk'. \quad (2)$$

Here, $g(k, z)$ is the antisymmetric part of the distribution function, i.e., the part that contributes to carrier transport, and is present on both sides of the equation. Also, f_0 is the equilibrium distribution function, whose form is assumed unchanged by the applied electro-thermal field. It is thus given by the familiar expression of quasi-Fermi statistics as $f_0(k, z) = 1/[\exp(E(k) + E_C(z) - E_F(z))/k_B T(z) + 1]$, where $E_C(z)$ and $E_F(z)$ are the conduction band-edge and chemical potential profiles, respectively, $T(z)$ is the temperature profile, assumed 1D, and $E(k)$ is the dispersion relation for the carriers. The quantity $1/\tau_{eff}(k, z)$ roughly corresponds to the sum of the momentum relaxation rates for elastic scattering mechanisms plus out-scattering rates for inelastic mechanisms. The kernel $1/\Gamma^{inelas}(k', k, z)$ roughly corresponds to inelastic in-scattering. Expressions for $\tau_{eff}(k, z)$ and $1/\Gamma^{inelas}(k', k, z)$ in terms of transition probability rates are given in Ref. 10,

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where Eq. (2) is derived from the BTE, Eq. (1). In this letter, we concern ourselves with single conduction bands that are spherical but possibly non-parabolic. Furthermore, throughout this work, n will stand for the electron concentration, and m^* for the effective mass at the conduction band-edge.

Three methods have been proposed in the literature for the exact calculation of the Seebeck coefficient starting from Eq. (2). Howarth and Sondheimer¹² reformulated the integral equation as a functional minimization problem, which was then solved by using a parametrized trial distribution function and minimizing the appropriate functional with respect to the parameters. This method is not widely used because of its mathematical complexity. Rode¹³ utilized numerical iteration combined with the phenomenological current equations.¹⁸ Despite the simplicity of the method, it has not gained popularity, although exceptions exist.¹⁴ A third, recently proposed technique¹⁰ employs Rode iterations coupled to a root-finding algorithm to determine the chemical potential profile in the material. Its advantages are that it is not restricted to infinitesimal temperature differences or to open-circuit conditions, and does not assume *a priori* the phenomenological current equations. Besides, the algorithm can easily be extended to systems with coupled bands, like p-GaAs.¹⁵ We will use this technique for the exact calculations in this work; for purposes of Seebeck coefficient calculations for a single band, the three methods are equivalent. The MATLAB® source code for implementation of the third technique is available from the authors upon request.

For mobility calculation, z and the derivatives with respect to z are dropped in Eq. (2). Two main methods exist for exact mobility calculation: variational¹² and iterative.^{13,16} We will use Rode's iterative method¹³ for mobility calculation. We mention in passing that Monte Carlo techniques are not well suited to low-field transport calculations because the statistical noise becomes significant due to the low average electron velocity. More sophisticated approaches like the Kubo formalism are not indicated for the problem under study, since Boltzmann transport theory, when properly applied, reproduces the mobility of polar semiconductors to within experimental error.^{10,17} Finally, carrier concentrations in excess of $5 \times 10^{18} \text{ cm}^{-3}$ are not well handled by the full BTE solution, due to the onset of impurity band transport, electron-electron interaction, and other effects that cannot be handled under the framework of the Boltzmann transport theory.

The relaxation time approximation (RTA)¹⁸ is the most widely used to compute transport coefficients.^{1,19–22} It consists of entirely neglecting the term $1/\Gamma^{\text{inelas}}(k', k, z)$ in Eq. (2), and is strictly valid only if all scattering mechanisms are elastic, or if any inelastic mechanisms that may be present are isotropic. In InGaAs and other polar semiconductors, scattering by polar optical-mode phonons is an important, often dominant mechanism, and it is inelastic and strongly anisotropic. The sole advantage of the RTA is the simplicity of the expressions that result from its application, which give insight into how various parameters affect the transport coefficients.

Sometimes in the literature,²² the starting point for transport calculations is not the full BTE, Eq. (1), but instead the truncated (or linearized) form derived by ignoring $f^2(k, r)$ terms therein. This approximation, together with the RTA, results in textbook expressions for transport coefficients.^{18,23,24}

However, this is potentially a severe approximation for degenerate semiconductors. In InGaAs doped to about $1 \times 10^{18} \text{ cm}^{-3}$, which is the regime for high thermoelectric efficiency, the average occupation of a state at the bottom of the conduction band is about 0.9 at 300 K, and this approximation seems to amount to ignoring 0.81 relative to 0.9. This approximation, however, remains valid for elastic scattering mechanisms because the non-linear terms in the first and second terms on the RHS of Eq. (1) cancel, but it causes gross errors in the scattering rates for inelastic mechanisms. Appropriate expressions for inelastic scattering rates for polar optical-mode phonon scattering without BTE truncation are given in Refs. 10 and 13.

Conduction band non-parabolicity is not ignored very often since it takes only a simple modification of the density of states to incorporate it, and hence we will not discuss its impact. The impact of overlap integrals²⁵ is discussed in Ref. 10.

We now discuss the impact of the RTA and the truncation of the BTE on the computed transport coefficients. To do so, we first experimentally validate the full BTE solution. We use silicon-doped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (hereafter called Si:InGaAs) for validation because it is itself a reasonable thermoelectric material. Moreover, by co-depositing erbium during MBE growth of InGaAs, the figure of merit Z can be greatly improved²⁶ due to the precipitation of ErAs nanoparticles; thus, Si:InGaAs is an appropriate control for assessing the performance of ErAs:InGaAs and other rare-earth doped InGaAs.²⁷ Fig. 1 shows the experimental room-temperature (RT) Seebeck coefficient as a function of the carrier concentration (n) of Si:InGaAs. Fig. 1 also shows the values for Si:InGaAs computed from the full BTE solution of Ref. 10, from the RTA, from the truncated linearized BTE, and from combining the RTA and the truncated BTE. Acoustic phonon deformational potential, polar optical-mode phonon, screened ionized impurity, and alloy disorder scattering are taken into account. The Kane band-structure model²⁸ is used to account for the non-parabolicity of the conduction band and to correct for wave-function overlap. Pursuant to the recommendations of Vurgaftman *et al.*,²⁹ the electron effective mass m^* is taken to be $0.043m_0$ where m_0 is the free electron mass. The rest of the material parameters required

FIG. 1. Comparison to experiment shows that the full BTE solution underestimates the Seebeck coefficient of Si:InGaAs by 8%, compared to a 16% underestimation by the combined RTA and BTE truncation approximations.

for InGaAs simulation are taken from Refs. 29 and 31. For a fixed m^* , the percentage error due to the RTA increases with n , because the absolute value of the error remains fairly constant whilst the magnitude of the Seebeck coefficient reduces. It is seen from Fig. 1 that the errors in simulations due to the two considered approximations tend to work on the Seebeck coefficient in opposite directions.

The full BTE solution underestimates by $\sim 8\%$ the RT Seebeck coefficient of Si:InGaAs. While this is worse than the precision of typical room-temperature Seebeck coefficient measurements ($\pm 2\%$), it is comparable to the precision of high-temperature measurements, $\pm 5\%$.⁹ In contrast, the combined RTA-BTE truncation underestimates the RT Seebeck coefficient by $\sim 16\%$. It is to be noted that the Z figure of merit varies as the square of the Seebeck coefficient. Thus, the full BTE solution underestimates the room-temperature Z by 16%, compared to 30% by the combined RTA-BTE truncation approximations, assuming that the electrical and thermal conductivities are known accurately.

Fig. 2 shows that the experimental mobilities of Si:InGaAs, and hence the scattering rates, are quite accurately reproduced by the full BTE solution, while the RTA is profoundly unsatisfactory. No fitting parameters were used to enhance the agreement of the full BTE solution. The alloy scattering potential was set to the Phillips electronegativity difference, 0.53 eV, as recommended by Ref. 30, and furthermore, comparisons to experiment on a simple binary, n-type GaAs, gave similarly accurate results.¹⁷ No scattering by compensating acceptors was assumed since that would necessitate the introduction of a fitting parameter, the compensation ratio. The Hall scattering factor is approximately 1 in all data reported here, because InGaAs becomes degenerate (the Fermi level is above the conduction band-edge) at $n \geq 2 \times 10^{17} \text{ cm}^{-3}$.

Fig. 3 shows the percentage error in the computed Seebeck coefficient (relative to the full BTE solution) engendered by the approximations, as a function of the electron effective mass. Two different carrier concentrations are explored. If the order of the effective mass is known, this study will help decide if the approximations are good enough

FIG. 2. The full BTE solution accurately reproduces the mobility of Si:InGaAs. The RTA is highly unsatisfactory. Truncation of the BTE by itself does not have as large an impact, since it affects only inelastic scattering mechanisms.

for a specific material, and therefore has applications to effective mass determination by means of thermoelectric measurements. The rest of the parameters are the same as for InGaAs, except that alloy disorder scattering and conduction band non-parabolicity have been ignored. The simulations are conducted at 300 K. As m^* increases, polar optical-mode phonon scattering becomes less dominant. This is because the change in the magnitude of the wave-vector required for a fixed change in energy (namely, the optical phonon energy) becomes larger as m^* increases. However, polar optical-mode phonon scattering strongly disfavors large changes in wave-vector, with the transition probability rate proportional to the inverse cube of the magnitude of this change.²⁴ Thus, the RTA (which partly ignores polar optical-mode phonon scattering) becomes more accurate for materials with larger effective mass.

In Fig. 3, the relative error in the Seebeck coefficient due to truncation of the BTE increases as the carrier concentration n increases, due to $f^2(\mathbf{k}, \mathbf{r})$ terms in the BTE becoming more significant. For a fixed value of n , relative errors due to BTE truncation reduce with increasing effective mass because the material becomes less degenerate. As a consequence of these remarks, the combined RTA and BTE truncation approximation is accurate to within 5% (compared to the full BTE solution) for materials with $m^* \geq 0.125m_0$ provided $n < 1 \times 10^{17} \text{ cm}^{-3}$. For $n = 1 \times 10^{18} \text{ cm}^{-3}$, m^* must be at least $0.25m_0$ for the relative error to be less than 5%. Also, for $n = 1 \times 10^{18} \text{ cm}^{-3}$, it is interesting to note the fortuitous cancellation that is seen in the error due to the two approximations combined, for m^* less than $\sim 0.1m_0$. This may in part explain the apparent agreement with experiment obtained by Ref. 22 despite using the RTA combined with the truncated BTE for computing the Seebeck coefficient of a polar semiconductor with a low effective mass ($0.048m_0$).

For the RTA mobility to agree with the full BTE solution within 25%, m^* must be $0.5\text{--}0.6m_0$ or higher, depending

FIG. 3. The RTA and BTE truncations result in large errors in the Seebeck coefficient, relative to the exact BTE solution, for heavily doped materials of low effective masses. The two approximations tend to work in opposite directions, giving rise to a spurious agreement with the full BTE solution at $n = 1 \times 10^{18} \text{ cm}^{-3}$ for m^* below $\sim 0.1m_0$. The effective masses of some common polar semiconductors (see Ref. 31) are shown along the x-axis, for reference.

on the carrier concentration. Truncation of the BTE affects the mobility less significantly. At $n = 1 \times 10^{18} \text{ cm}^{-3}$, it causes an error of less than 10% relative to the exact solution for effective masses of $0.075m_0$ or larger.

With the effective mass fixed at $0.05m_0$, Fig. 4 illustrates the errors in the Seebeck coefficient (relative to the full BTE solution) caused by the two approximations as a function of the temperature, from 300 to 1000 K. The remaining parameters are the same as for InGaAs, but with alloy disorder scattering and band non-parabolicity ignored. For a fixed value of n , the material becomes less degenerate at higher temperatures, which reduces the relative error due to BTE truncation. At $n = 1 \times 10^{17} \text{ cm}^{-3}$, BTE truncation alone causes virtually no error above 300 K, and hence is omitted in Fig. 4. Our results indicate that the relative error due to the RTA decreases slightly as the temperature increases, despite the increased occupation of optical phonon modes. This is due to the increasing magnitude of the Seebeck coefficient. The mobility is underestimated by the RTA by 50% or more for this value of effective mass ($0.05m_0$), with the accuracy deteriorating with temperature. Truncation of the BTE reduces the mobility by 15% at 300 K for $n = 1 \times 10^{18} \text{ cm}^{-3}$, but this error rapidly goes to nearly zero with increasing temperature due to the material becoming progressively less degenerate.

In conclusion, neither the relaxation time approximation nor the truncation (or linearization) of the BTE has any place in the accurate modeling of the mobility of polar semiconductors. The two approximations give large errors in the Seebeck coefficients of heavily doped polar semiconductors as the effective mass reduces: the RTA because of the increasing influence of polar optical-mode phonon scattering, and the truncation of the BTE because of increased degeneracy for a given electron concentration. The error in the room-temperature Seebeck coefficient caused by using the combined RTA-truncated BTE approximations becomes

FIG. 4. The relative error in the Seebeck coefficient due to the RTA decreases somewhat with temperature, while that due to BTE truncation decreases more rapidly due to the material becoming less degenerate. The effective mass is fixed at $0.05m_0$. The relative error due to truncation is close to zero for $n = 10^{17} \text{ cm}^{-3}$ and the relative error due to the RTA alone closely follows that due to the two approximations combined. Thus, only the latter is displayed for $n = 10^{17} \text{ cm}^{-3}$.

<5% compared to the full BTE solution only for materials with effective masses $0.25m_0$ or larger, provided the carrier concentration is less than or equal to $1 \times 10^{18} \text{ cm}^{-3}$. The errors in the Seebeck coefficient are significant in the context of accurate effective mass determination of semiconductors, as well as in providing good controls and references for high-temperature measurements on promising thermoelectric materials.

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