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ABSTRACT

The thermoelectric figure of merit $ZT$, which is defined using electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature $T$, has been widely used as a simple estimator of the conversion efficiency of a thermoelectric heat engine. When material properties are constant or slowly varying with $T$, a higher $ZT$ ensures a higher maximum conversion efficiency of thermoelectric materials. However, as material properties can vary strongly with $T$, efficiency predictions based on $ZT$ can be inaccurate, especially for wide-temperature applications. Moreover, although $ZT$ values continue to increase, there has been no investigation of the relationship between $ZT$ and the efficiency in the higher $ZT$ regime. In this paper, we report a counterintuitive situation by comparing two materials: although one material has a higher $ZT$ value over the whole operating temperature range, its maximum conversion efficiency is smaller than that of the other. This indicates that, for material comparisons, the evaluation of exact efficiencies as opposed to a simple comparison of $ZTs$ is necessary in certain cases.

Thermoelectric technology has attracted much attention because of the strong demand for eco-friendly energy harvesting. As a thermoelectric heat engine does not contain any moving parts and has a small volume, it can be highly applicable for energy harvesting if the conversion efficiency is sufficient. Over the past decades, the dimensionless thermoelectric figure of merit $ZT = (x^2/\rho k) T$ has been considered as a good estimator for maximum thermoelectric conversion efficiency, where $x$, $\rho$, $k$, and $T$ are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Consequently, the discovery of high-$ZT$ thermoelectric materials has been central to the achievement of high-performance thermoelectric devices.

The $ZT$-based efficiency theory follows from the constant property model (CPM), in which all thermoelectric properties (TEPs: $x$, $\rho$, and $k$) are considered to be $T$-independent. In this model, the temperature distribution inside a one-dimensional ideal thermoelectric engine is uniquely determined as a quadratic polynomial. As a result, the hot-side heat flux and the generated power are analytically determined. Finally, the thermoelectric efficiency ($\eta$) under the operating temperature between the hot-side temperature $T_h$ and the cold-side temperature $T_c$ is bounded above by $\eta_{\text{max}} = \Delta T \sqrt{1 - ZT_m^{-1}}$, where $\Delta T = T_h - T_c$ and $T_m = (T_h + T_c)/2$. Note that in CPM, there is a monotonically increasing relationship between $ZT$ and the maximum thermoelectric efficiency.

However, in reality, charge and heat transports are strongly temperature-dependent. Within the degenerate limit, the electrical resistivity and Seebeck coefficient of materials are roughly proportional to $T^{-1}$. In non-degenerate semiconductors, $\rho$ decreases as $T$ increases. The lattice thermal conductivity of crystalline materials is roughly proportional to $T^{-1}$ above room temperature owing to anharmonic three phonon processes. Therefore, for wide-temperature applications, single parameter $ZT$ estimation could give non-negligible errors in the prediction of the efficiency of thermoelectric heat engines.
Although nonlinearity in thermoelectric equations indicates that there is no analytical expression for thermoelectric efficiency,\textsuperscript{7,10,12} there have been several efforts to generalize the relations in non-CPM conditions. Several average $ZT$ schemes have been proposed and their proportionality on efficiency is tested in conditions when the peak or average $ZT$ is smaller than 2.6.\textsuperscript{3,23–30} However, it is unclear whether average $ZT$ schemes work as well in a higher $ZT$ regime as they do in the low $ZT$ regime.

In this Letter, we report a counterintuitive example of relations between $ZT$ and thermoelectric efficiency. We find two distinct sets of thermoelectric property (TEP) curves, where one set of TEPs has higher $ZT$ curves over the whole operating temperature range, but its maximum conversion efficiency is smaller than that of the other set. Our finding highlights the mathematical inexactness of $ZT$ in efficiency prediction, especially for high $ZT$ (>10). For a low $ZT$, we also find additional examples that the efficiency is lower although the average or peak $ZT$ is higher.

We consider an ideal thermoelectric heat engine containing a one-dimensional single thermoelectric leg sandwiched by hot and cold sides.\textsuperscript{31} The thermoelectric leg has a length of $L$ and cross-sectional area of $A$. The Dirichlet thermal boundary condition is adopted with hot-side temperature $T_h$ at $x = 0$ and cold-side temperature $T_c$ at $x = L$. In this heat engine, the thermal and electrical currents flow along the leg. In this ideal engine, only thermal diffusion and Peltier heat through solids are allowed; radiative and convective heat is neglected. For simplicity, we assume a time-independent steady-state condition and positive Seebeck coefficient in the operating temperature range. The heat engine forms a closed circuit with a load resistance $R_l$. Therefore, by applying a non-zero temperature difference, voltage ($V_{\text{gen}}$) is generated and current ($I$) flows from the hot to the cold side. With the internal resistance of thermoelectric material denoted by $R$, the induced current is written as:\textsuperscript{12} as follows:

$$I = \frac{V_{\text{gen}}}{R + R_l} = \frac{V_{\text{gen}}}{R(1 + \gamma)},$$

where $V_{\text{gen}} \equiv \int_0^L (\frac{-\alpha dx}{\partial x}) dx = \int_{T_h}^{T_c} \alpha(T) dT, \quad R = \int_0^L \rho(T) \frac{dx}{A}$, and

$$\gamma \equiv \frac{R_l}{R}.$$

The thermoelectric efficiency is defined as the ratio of the external power delivered ($P$) to the hot-side heat flux ($Q_h$). Thus, the efficiency ($\eta$), at a given relative $\gamma = \frac{R_l}{R}$, is computed using the exact temperature distribution $T(x)$ as follows:\textsuperscript{12}

$$\eta(\gamma) = \frac{P}{Q_h} = \frac{I(V_{\text{gen}} - IR)}{-\kappa A \frac{dT}{dx}/T_h + I \alpha(T_h) T_h} = \eta(\gamma) = \eta(I) = \frac{P}{Q_h} = \frac{I(V_{\text{gen}} - IR)}{-\kappa A \frac{dT}{dx}/T_h + I \alpha(T_h) T_h}.$$

Then, the maximum efficiency $\eta_{\text{max}}$, which satisfies the relation $\eta(\gamma) \leq \eta_{\text{max}}$ for all $\gamma \geq 0$, is searched using the Brent-Dekker optimization method. Note that a positive $\gamma$ indicates that the heat engine is in power generation mode. To determine $T(x)$, we solve the second order differential equation for a one-dimensional leg given as follows:\textsuperscript{5,10}

$$\frac{d}{dx} \left[ \kappa(T) \frac{dT}{dx} \right] + \rho(T) T - \frac{d^2(T)}{dT} dx = 0,$$

where $I = I/A$. Here, the temperature satisfies the boundary conditions of $T(x = 0) = T_h$ and $T(x = L) = T_c$.

The analysis considers a one-dimensional thermoelectric heat engine with a leg length of 1 mm and a leg cross-sectional area of 1 mm$^2$, operating at $T_h = 900$ K and $T_c = 300$ K. When the electrical circuit of the heat engine is open, only thermal current flows from the hot to the cold side. If the material has a non-zero Seebeck coefficient, it generates voltage. When the circuit is closed, the induced voltage generates an electrical current and the power is delivered to the outside load resistance.

Two imaginary thermoelectric materials, mat1 and mat2, are considered for the thermoelectric leg. We assume that the materials have linear TEP curves for the Seebeck coefficient, electrical resistivity, and thermal conductivity (see Table I and Fig. 1). The two materials have the same linear resistivity and constant thermal conductivity; the resistivity is $1 \times 10^{-5}$ $\Omega$ m at 300 K and $3 \times 10^{-5}$ $\Omega$ m at 900 K, and thermal conductivity is set to 1 W/m/K. However, the Seebeck coefficients are different for the two materials. In mat1, the Seebeck coefficient is constant and set to 816 $\mu$V/K. Thus, its $ZT$ is 20 at 300 K and 900 K. In mat2, the Seebeck coefficient is a linear function of $T$ with a coefficient $\alpha_{\text{coeff}}$ and a constant $\alpha_{\text{const}}$.

### Table I. Thermoelectric properties and engine performances of imaginary materials: mat1 and mat2 for absolute $ZT$ inversion and mat3 to mat5 for average $ZT$ inversion and peak $ZT$ inversion. The engine performances are computed within an operating temperature range from $T_h = 300$ K to $T_c = 900$ K.

| Example Material | Absolute $ZT$ inversion | Average $ZT$ inversion and peak $ZT$ inversion |
|------------------|-------------------------|-----------------------------------------------|
|                  | mat1                    | mat2                                          | mat3 | mat4 | mat5 |
| $\rho$ (\(\Omega\) m) | 300 K | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ | Linear on T |
|                  | 900 K | $3 \times 10^{-5}$ | $3 \times 10^{-5}$ | $3 \times 10^{-5}$ | $3 \times 10^{-5}$ | Constant or linear on T |
| $\alpha$ (V/K)   | 300 K | $816 \times 10^{-6}$ | $816 \times 10^{-6}$ | $327 \times 10^{-6}$ | $173 \times 10^{-6}$ | 0 |
|                  | 900 K | $1155 \times 10^{-6}$ | 0 | 365 $\times 10^{-6}$ | |
| $\kappa$ (W/m/K) | 300 K | 1 | 1 | 1 | 1 | Constant |
|                  | 900 K | 1 | 1 | 1 | 1 | Constant |
| $ZT$             | 300 K | 20 | 20 | 3.2 (peak) | 0.9 | 0 |
|                  | 900 K | 40 (peak) | 29.1421 | 0.8 | 0.9 | 1 |
| $[ZT]_{\text{avg}}$ | 20.0000 | 29.1421 | 0.8 | 0.9 | 1 |
| $[ZT]_{\text{avg}}$ | 0 | 0.1716 | -1 | 0 | 1 | 1 |
| $\alpha_{\text{opt}}$ | 4.59 | 6.79 | 1.25 | 1.58 | 1.97 | 241 |
| $\eta_{\text{max}}$ (%) | 48.585 | 47.422 | 15.089 | 14.675 | 13.448 |
We compute the maximum thermoelectric efficiency by solving the thermoelectric differential equation for temperature distribution as previously described. Table II and Fig. 2 show the computed ideal thermoelectric efficiency as a function of $\gamma = R_L/R$. Each TEP curve set has a single maximum value. The maximum efficiencies of mat1 and mat2 are computed as 48.585% and 47.422%, respectively.

Therefore, mat1 and mat2 have counterintuitive outcomes: the maximum efficiency of mat1 is definitely larger than the maximum efficiency of mat2 ($\eta_{\text{max}}^{\text{mat1}} = 48.585% > \eta_{\text{max}}^{\text{mat2}} = 47.422%$), whereas the ZT of mat1 is definitely smaller than the ZT of mat2 ($ZT_{\text{mat1}} = 20 < ZT_{\text{mat2}}$). This is the first type of the ZT paradox, the absolute ZT inversion, that the higher efficiency appears with smaller ZT values over the whole operating temperature range.

We investigate a TEP condition where the absolute ZT inversion occurs by performing a parametric study for $\eta_{\text{max}}$ and ZT. Figures 3(a) and 3(b) show the relation between $\eta_{\text{max}}$ and ZT for a wide ZT range from 0.2 to 4.4. In each figure, we consider a 31 x 31 uniform ZT mesh for the cold side ZT ($ZT_c$) and hot side ZT ($ZT_h$). At this moment, for the TEP parameter space, we consider the linear Seebeck coefficient on $T$ ($dS/dT = \text{const.}$), linear electrical resistivity ($\rho/T = \text{const.}$), and constant thermal conductivity. Note that the highly asymmetric behavior of $\eta_{\text{max}}$ can be observed in the higher ZT regime. The value of $\eta_{\text{max}}$ increases when $ZT_c$ increases. However, for given $ZT_c \sim 10$, the change of $ZT_h$ does not lead to the change of $\eta_{\text{max}}$. Moreover, for $ZT_c > \sim 10$ and $ZT_h > \sim 15$, an absolute ZT inversion can occur such that a higher ZT gives a lower $\eta_{\text{max}}$. This inversion is even observed in an average ZT scheme. We use the engineering ZT ($ZT_{\text{eng}}$) an average scheme for ZT, which is given as follows:

$$ZT_{\text{eng}} = \frac{Z_{\text{eng}} \Delta T}{T} = \left(\int_a^b \frac{\rho(T)dT}{\int_a^b \kappa(T)dT} \right)^2 (T_h - T_c).$$

### Table II. Calculated thermoelectric conversion efficiencies for single-leg thermoelectric heat engines with mat1 and mat2. The maximum efficiency and the corresponding optimum $\gamma_{\text{opt}}$ values are indicated by bold letters, and * and **.

| | mat1 | | mat2 |
|---|---|---|---|
| $\gamma$ | Current | Efficiency | Current | Efficiency |
| I (A) | $\eta$ (%) | I (A) | $\eta$ (%) |
| 4.10 204 | 4.52 480 | 48.518% | 4.74 071 | 46.055% |
| 4.22 449 | 4.43 005 | 48.549% | 4.65 217 | 46.210% |
| 4.34 694 | 4.33 899 | 48.870% | 4.56 684 | 46.352% |
| 4.46 939 | 4.25 140 | 48.851% | 4.48 456 | 46.481% |
| 4.59 184 | 4.16 711 | 48.858% | 4.40 517 | 46.599% |
| 4.71 429 | 4.08 595 | 48.850% | 4.32 850 | 46.707% |
| 4.83 673 | 4.00 774 | 48.659% | 4.25 442 | 46.804% |
| 4.95 918 | 3.93 235 | 48.551% | 4.18 281 | 46.893% |
| 5.08 163 | 3.85 962 | 48.527% | 4.11 353 | 46.972% |
| 6.30 612 | 3.25 349 | 48.035% | 3.52 774 | 47.394% |
| 6.42 857 | 3.20 289 | 47.967% | 3.47 809 | 47.407% |
| 6.55 102 | 3.15 379 | 47.897% | 3.42 979 | 47.416% |
| 6.67 347 | 3.10 614 | 47.824% | 3.38 279 | 47.421% |
| 6.79 592 | 3.05 987 | 47.749% | 3.33 704 | 47.422% |
| 6.91 837 | 3.01 492 | 47.672% | 3.29 250 | 47.420% |
| 7.04 082 | 2.97 125 | 47.593% | 3.24 912 | 47.414% |
| 7.16 322 | 2.92 879 | 47.512% | 3.20 684 | 47.406% |
| 7.28 571 | 2.88 749 | 47.429% | 3.16 564 | 47.394% |

The $ZT_{\text{eng}}$ value of mat1 (20) is smaller than that of mat2 (~29.1). See Table I. This kind of strong counterintuitive phenomenon seems not to occur for the low ZT regime [see Fig. 3(b)].

Also we find that weak counterintuitive situations can occur for the low ZT regime. Figure 4(a) shows the relation between $\eta_{\text{max}}$ and engineering $ZT_{\text{eng}}$. For the TEP parameter space, we consider the same space as that given in the previous paragraph. In the TEP space, we consider three cases for the Seebeck coefficient curves: the first one is the linear decreasing Seebeck coefficient with $0$ at $T_h$, the second one...
is constant, and the third one is the linear increasing Seebeck coefficient with 0 at $T_c$. We find that a large $|ZT|_{eng}$ can provide a small $\eta_{max}$ for a certain case. For efficiency comparison, three realistic materials (mat3, mat4, and mat5) are considered, as shown in Table I. They have $|ZT|_{eng}$ values of 0.8, 0.9, and 1.0, respectively. Although mat3 has the least value of $|ZT|_{eng} = 0.8$, the value of $\eta_{max}$ of mat3 is higher than those of mat4 and mat5, and mat5 has the least value of $\eta_{max}$. Thus, we find the second type of the $ZT$ paradox, the average $ZT$ inversion. Note that this can occur even in the realistic material cases of $|ZT|_{eng} \leq 1$.

Figure 4(a) shows the $ZT$ curves of mat3, mat4, and mat5. Here, we find the second type of $ZT$ paradox, the peak $ZT$ inversion. mat5 has the highest peak $ZT$ of 4.0 at 900 K and the $ZT$ values of mat5 are greater than those of mat4 if $T > 585$ K. However, $\eta_{max}$ of mat5 is less than that of mat4, having a constant $ZT$ of 0.9.

Our finding indicates that efficiency evaluation is important when evaluating a material’s thermoelectric performance. As materials of high figure of merit $ZT$ continue to be developed, highly accurate efficiency calculation methods, or exact efficiency evaluation, will be required to properly assess their thermoelectric application, especially over wide temperature ranges. Even in the low $ZT$ regime, the efficiency can be changed when the shape of the TEP curves varies while the average $ZT$ is kept constant.

The failure of traditional $ZT$ formula in efficiency prediction can be understood by the asymmetric distribution of Joule heat and non-zero Thomson effect inside the leg. Since the thermoelectric properties are temperature-dependent, the heat source in Eq. (3) is not uniformly distributed and the temperature solution of the one-dimensional leg can be largely deviated from the quadratic polynomial of the CPM, limiting the applicability of the CPM-based traditional $ZT$ model for efficiency prediction. As shown in Fig. 4, the different slopes in the Seebeck coefficients can significantly affect the efficiency. It implies that, together with $ZT$, hidden parameters describing the asymmetric Joule heat distribution and Thomson heat generation could be important factors for the determination of efficiency.

In conclusion, we have found a counterintuitive example in the relation between $ZT$ and thermoelectric efficiency in the higher $ZT$ regime. Whereas $ZT$ is widely accepted as a good estimator for thermoelectric material efficiency in the low $ZT$ regime, a higher maximum efficiency can appear with smaller $ZT$ values, if $ZT$ is large enough. Thus, as material $ZT$ values rise, greater care should be taken in the evaluation of materials; efficiency itself, rather than $ZT$, should be determined and compared.

AUTHORS’ CONTRIBUTIONS

B.R. and J.C. found the counterintuitive example. J.C. and B.R. developed a computational code, called pykeri2019, for efficiency calculation of one-dimensional thermoelectric heat engines. B.R., J.C., E.A.C., P.Z., and S.D.P. all discussed the results. B.R. wrote the manuscript. S.D.P. advised the project. All authors revised the manuscript.

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