

Thermoelectric Efficiency and Compatibility

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The intensive reduced efficiency η_r is derived for thermoelectric power generation (in one dimension) from intensive fields and currents, giving $\eta_r = \frac{E \cdot J}{-\nabla T \cdot J_s}$. The overall efficiency is derivable from a thermodynamic state function, $\Phi = 1/u + \alpha T$, where we introduce $u = \frac{J}{\kappa \nabla T}$ as the *relative current density*. The method simplifies the computation and clarifies the physics behind thermoelectric devices by revealing a new materials property $s = (\sqrt{1+zT} - 1)/(\alpha T)$, which we call the compatibility factor. Materials with dissimilar compatibility factors cannot be combined by segmentation into an efficient thermoelectric generator because of constraints imposed on u . Thus, control of the compatibility factor s is, in addition to z , essential for efficient operation of a thermoelectric device, and thus will facilitate rational materials selection, device design, and the engineering of functionally graded materials.

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Introduction.—In a thermoelectric material, heat can be transported or used to generate electricity based on the Peltier and Seebeck effects. Since the advent of semiconductor physics, thermoelectric devices have found wide use in commercial and government applications. The efficiency of a thermoelectric device is traditionally described in terms of the extensive or system parameters such as hot and cold side temperature, length and area of thermoelectric element, and applied voltage or load resistance. In only the most simplified cases can the efficiency be computed analytically, where it can be shown that the thermoelectric figure of merit z is the intensive material property of prime importance. In general, however, the calculation of efficiency is complex and is usually done by finite element methods that include both volume and surface terms using averaged material parameters [1–5]. It is well known that certain functionally graded or segmented thermoelectric materials can enhance efficiency [6–8]. Numerical methods can be used to predict the performance of these complex designs but, until now, no accurate physical picture explaining the performance gains has been given.

In this Letter, we reformulate the general equation for the efficiency of a thermoelectric generator in terms of intensive properties and variables. Doing so reveals thermoelectric efficiency as an intensive thermodynamic quantity derivable from a thermodynamic state function. The derivation identifies an intensive constrained variable, which eliminates the need for explicit knowledge of the position variable. This formalism clarifies the materials physics of thermoelectrics by introducing the compatibility factor, s , which in addition to z must be controlled for efficient operation of a thermoelectric device and allows the rational engineering of functionally graded materials.

We begin with the extensive definition of efficiency for the one-dimensional, steady-state, power generation problem common to most books on the topic [9–11] and

use a notation similar to [10]. Consider a single thermoelectric element of length l , and cross-sectional area A , in the generator. The hot side of the element is at absolute temperature T_h and the cold side is at temperature T_c , with the difference being ΔT . An electrical current $I = JA$ and heat power Q (W) enters uniformly into the hot side of the element. The efficiency, η , for power generation is defined as the electrical power output divided by the thermal power supplied. The electrical power P is derived from the difference between the thermoelectric voltage and the Ohm's Law voltage drop. The heat power Q is the sum of the Peltier heat term and the solid conduction term:

$$\eta = \frac{P}{Q} = \frac{J \int_{T_c}^{T_h} \alpha dT - J^2 \int_0^l \rho dx}{J T_h \alpha_h + \kappa_h \nabla T_h}. \quad (1)$$

The relevant material properties are the Seebeck coefficient α , the thermal conductivity κ , and resistivity ρ , which all vary with temperature. $J > 0$ flows from T_h to T_c and ∇T is assumed to be positive [$T(x=0) = T_c$, $T(x=l) = T_h$]. The subscripts h and c denote the value of a function at a particular temperature [$\kappa_h = \kappa(T_h)$, $\nabla T_h = \nabla T(T_h)$]. The Peltier effect is often considered a surface effect between two materials but the heat transported is a property of a single material [12]. The Joule and Thomson source terms, often explicitly included in Q , are not necessary if using the solid conduction at T_h : $\kappa_h \nabla T_h$ [1]. This definition of efficiency for a single thermoelectric element is similar to that of a complete generator, η_{np} , with n -type and p -type elements [1], which can be derived from (1) using a weighted average for generators thermally in parallel:

$$\eta_{np} = \frac{\eta_p Q_p + \eta_n Q_n}{Q_p + Q_n}. \quad (2)$$

Equation (1) is also valid for segments of a thermoelectric element divided in series. For two such segments

thermally in series, the combined efficiency is given by

$$\eta_{1\&2} = \frac{P_1 + P_2}{Q_1} = 1 - (1 - \eta_1)(1 - \eta_2). \quad (3)$$

The maximum efficiency for all heat engines is given by the Carnot efficiency, $\eta_c = (\Delta T)/T_H$, where $\Delta T = T_h - T_c$. The reduced efficiency, η_r , is the efficiency relative to Carnot, defined by $\eta = \eta_c \eta_r$. In the limit $\Delta T \rightarrow 0$, the reduced efficiency of Eq. (1) is finite for $\nabla T > 0$:

$$\eta_r = \frac{u \frac{\alpha}{z} (1 - u \frac{\alpha}{z})}{u \frac{\alpha}{z} + \frac{1}{zT}}, \quad (4)$$

where z is the thermoelectric figure of merit $z = \alpha^2/(\kappa\rho)$, and what we call the relative current density u is the ratio of the electric current density to the heat flux by thermal conduction defined by

$$u = \frac{J}{\kappa \nabla T}. \quad (5)$$

Within a thermoelectric element, u is a constrained quantity due to the heat equation

$$\frac{d(\kappa \nabla T)}{dx} = -T \frac{d\alpha}{dT} J \nabla T - J^2 \rho, \quad (6)$$

where $T \frac{d\alpha}{dT}$ is the Thomson coefficient. For n -type thermoelectric material ($\alpha < 0$) operating efficiently, $J < 0$ and $u < 0$. The spatial variable x can be eliminated to show that u can be described as varying only with T :

$$\frac{d(1/u)}{dT} = -\frac{1}{u^2} \frac{du}{dT} = -T \frac{d\alpha}{dT} - u \rho \kappa. \quad (7)$$

In a thermoelectric element, only an initial condition, u_h for example, is required to compute $u(T)$ for the remainder of the element using Eq. (7).

The overall efficiency of a finite segment can be derived using the series efficiency Eq. (3) [9]:

$$\eta = 1 - \exp \left[- \int_{T_c}^{T_h} \frac{\eta_r(u, T)}{T} dT \right]. \quad (8)$$

Using Eqs. (4), (7), and (8), the efficiency of a finite segment can be calculated from properties of the end points

$$\eta = 1 - \frac{\alpha_c T_c + \frac{1}{u_c}}{\alpha_h T_h + \frac{1}{u_h}}. \quad (9)$$

The maximum efficiency of a thermoelectric element is computed by finding the initial u (for example u_h) that maximizes Eq. (9). Once u is optimized, the optimal current density, J , can be computed by integrating Eq. (5) giving:

$$\int_{T_c}^{T_h} \kappa u dT = J l. \quad (10)$$

Sherman [1] gives the analogous expression for the efficiency, η_{np} , of a combined n -type and p -type thermoelectric couple. Despite the generality of Sherman's method, it is not commonly used. This is certainly due to the need for nonanalytic optimization (of initial u values) and the abstract appearance (e.g., no explicit reference to Carnot efficiency or the thermoelectric figure of merit, z). However, it is exact and more importantly leads to a greater understanding of the thermoelectric phenomena.

Reduced efficiency.—The above method reveals thermoelectric efficiency to be an intensive, thermodynamic quantity. The reduced efficiency [Eq. (4)] has been reduced to a function of two variables: $u(T)$ and T . Explicit reference to the geometric factors A and l and the spatial variable x has been eliminated (compare to [3,7]). The relative current density, u , is an intensive variable because it is the ratio of intensive variables. Reduced efficiency is, by a similar argument, also an intensive quantity.

The existence of an intensive efficiency suggests that there should be a derivation starting from intensive fields not requiring action at a distance: The electric power produced in a volume dV is the dot product of the net electric field E and current density J times the volume dV . The heat flux, q , transported in the direction of the temperature gradient is $q \cdot \nabla T \frac{dV}{dT}$. Noting that q is related to the entropy flux J_S by $q = T J_S$ gives

$$\eta_r = \frac{E \cdot J}{-\nabla T \cdot J_S}. \quad (11)$$

The relationship is simply the ratio of the products of conjugate forces and fluxes using the framework of Onsager [13]: E is the conjugate electric force for charge flux J ; $-\frac{\nabla T}{T}$ is the conjugate thermal force for heat flux q . This formulation enables a more direct comparison to other energy conversion processes, most notably heat engines, as shown in [14]. The existence of analogous expressions, related through the framework of Onsager, suggests that similar intensive quantities and/or state function representations may exist for other systems and can be generalized.

For a thermoelectric, the electric field is the difference between the fields due to the Seebeck and Ohmic effects: $E = \alpha \nabla T - \rho J$. The heat flux is the combination of the Fourier and Peltier terms: $q = T J_S = \kappa \nabla T - \alpha T J$. With the definition of u from (5), Eq. (4) (for the one-dimensional problem) is readily derived.

Thermoelectric potential.—The efficiency of a finite thermoelectric element [Eq. (9)] is a simple function of the initial and the final state of the material, regardless of external configuration. Let Φ be a function (with units of volts) of the state of the material given by

$$\Phi = 1/u + \alpha T. \quad (12)$$

Then efficiency [Eq. (9)] is simply the relative change of this thermoelectric potential,

$$\eta = \frac{\Delta\Phi}{\Phi_h} = \frac{\Phi_h - \Phi_c}{\Phi_h}, \quad (13)$$

where $\Delta\Phi$ is also the voltage, V , produced by the generator

$$V = \Delta\Phi = 1/u_h + \alpha_h T_h - 1/u_c - \alpha_c T_c, \quad (14)$$

and $I\Phi$ is the heat flow.

Relative current density.—This analysis reveals the relative current density, u , as the key constrained variable in the thermoelectric problem. The variation of reduced efficiency with u (Fig. 1) is analogous to the variation of overall efficiency (or power output) to the electrical current.

Whether in power generation or Peltier cooling mode, the reversible, useful thermoelectric effects compete with the irreversible Joule heating. Because the Peltier effect is linear compared to the Joule heating which is proportional to the square of the current, there is necessarily an optimum operating current to achieve the optimum efficiency. In terms of u , the efficiency increases from zero ($u = 0$, $I = 0$, $P = 0$) to a maximum value and then decreases through zero at $u = \frac{z}{\alpha}$. For (p -type) $u > \frac{z}{\alpha}$, the Ohmic voltage drop is greater than the Seebeck voltage produced, and thus the power output and efficiency are negative.

The variation of u within a thermoelectric leg is conveniently small. Since all segments in a thermoelectric element are electrically and thermally in series, the same current I and similar conduction heat $A\kappa\nabla T$ flow through each segment. When $I = 0$, the conduction heat is exactly uniform. When $I \neq 0$, the conduction heat is only slightly modified by the change in temperature gradient due to the

Thomson and Joule sources of heat [Eq. (6)]. Thermoelectric generators operating at peak efficiency typically have u that varies less than 20% throughout the entire element. To a reasonable approximation, u , once established, remains constant throughout the thermoelectric element [15].

If, however, the optimum u current of one segment is significantly different from another, there will be no suitable current where both parts are operating efficiently. This is the physical basis for thermoelectric compatibility.

Thermoelectric compatibility.—The value of u which maximizes the reduced efficiency [Eq. (4)] is defined as s , which we call the thermoelectric (power generation) compatibility factor:

$$s = \frac{\sqrt{1 + zT} - 1}{\alpha T}. \quad (15)$$

From Eq. (15), it is clear that the compatibility factor s is, like z , a temperature dependent materials property derived from the temperature dependent materials properties α , κ , and ρ . Thus, s cannot be changed with device geometry or the alteration of electrical or thermal currents.

If u is significantly different from s , then the material is not efficiently converting heat into electricity. However, once u is selected at one point, it cannot be adjusted in a segmented thermoelectric element to follow the variation of s . The change in u across a segmented interface [derived from Eq. (7), neglecting contact resistance], $\Delta u \cong u^2 T \Delta \alpha$, is typically only a few percent for efficient thermoelectric materials. Thus, the closer the compatibility factors are for two materials, the higher the combined efficiency will be when they are segmented.

Therefore, the compatibility factor is, again like z , a thermoelectric property essential for designing an efficient segmented thermoelectric device. If the compatibility factors differ by a factor of 2 or more, the maximum efficiency can in fact decrease by segmentation [3,15]. Such is the case for SiGe which, despite the high figure of merit, cannot be efficiently segmented with the other thermoelectric materials shown in Fig. 1.

The crucial difference between cascaded and segmented [9,10] thermoelectric devices is now evident. In a segmented element all segments are thermally and electrically in series so that a single u_h defines $u(T)$ throughout the element. However, a cascaded device contains an independent electrical circuit for each stage, allowing an independent J and therefore u in each stage. Although cascading will always produce higher efficiencies, it is much more difficult to implement than segmentation.

The importance of compatibility has been made apparent for a segmented thermoelectric generator, but compatibility is also a consideration for all thermoelectric

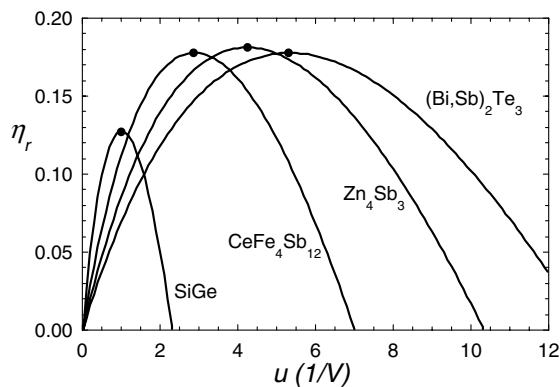


FIG. 1. Plot of reduced efficiency [Eq. (4)] as relative current density, u , varies at a constant temperature. p -type materials are compared at temperatures where they would contribute to an efficient segmented system: $(\text{Bi, Sb})_2\text{Te}_3$ (100°C), Zn_4Sb_3 (300°C), $\text{CeFe}_4\text{Sb}_{12}$ (550°C), SiGe (800°C). Maximum efficiency at the compatibility factor, $u = s$, is indicated with filled circles.

devices. Since the compatibility factor of a material is temperature dependent, the change in s from one end of the leg to the other will, in general, adversely affect device performance. We call the consideration of compatibility within the same material the issue of self-compatibility. Because of the explicit temperature dependence of s [Eq. (15)] in conjunction with the typical temperature dependence of z and α , the problems with self-compatibility are generally more apparent at low temperatures [15].

Example of constant coefficients.—When α , κ , ρ , and therefore z , are constant with respect to temperature, the maximum efficiency of a finite thermoelectric element can be calculated analytically. Using Eq. (7), the change in u from T_h to T_c is given by $1/u_c^2 - 1/u_h^2 = 2\Delta T\kappa\rho$. With this relation, Eq. (9) can be maximized to find the optimal u_h (and u_c): $1/u_h = 1/[s(\bar{T})] - [(\Delta T)/2]\kappa\rho s(\bar{T})$, $1/u_c = 1/[s(\bar{T})] + [(\Delta T)/2]\kappa\rho s(\bar{T})$, where $\bar{T} = (T_h + T_c)/2$. The resulting efficiency is given by

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + z\bar{T}} - 1}{\sqrt{1 + z\bar{T}} + T_c/T_h}. \quad (16)$$

This equation is normally derived starting with the extensive expression for efficiency [10] and the consistency of both methods confirms the accuracy of the method described in this Letter.

Equation (16) demonstrates the importance of z when s is nearly temperature independent. For real materials where α , κ , and ρ vary with temperature, an averaged z is commonly used [1–5]. It is the effect of the compatibility factor that explains why averaging works well in some cases (when s does not vary significantly) and not in others (when s varies by a factor of 2 or more).

Conclusions.—The intensive reduced efficiency is derived for thermoelectric power generation. The simple expression shows efficiency is derivable from a nonequilibrium thermodynamic state function of two variables, u and T . The use of u , an intensive variable, eliminates the need for explicit knowledge of the position variable, which greatly simplifies the problem. The equivalent result derived from intensive thermodynamic quantities suggests that a general thermodynamic description of efficiency is possible for other energy conversion processes. Although initially surprising [7], a local efficiency exists that depends only on local fields.

The derivation identifies the intrinsic constraint, as well as a new materials property, which we call the compatibility factor s , that in addition to z is essential for establishing the efficient operation of a thermoelectric

device. The method not only allows the straightforward computation and optimization of efficiency but also clarifies much of the fundamental physics behind thermoelectric devices. For example, the difference between segmented and cascaded devices is illustrated and the compatibility of thermoelectric materials is explained. The fundamental understanding of efficiency and compatibility will enable rational materials selection and device engineering.

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