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The best thermoelectric

G. D. MAHAN*[†] AND J. O. SOFO[‡]

*Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200; [†]Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6030; and [‡]Instituto Balseiro, Centro Atomico Bariloche, (8400) Bariloche, Argentina

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ABSTRACT What electronic structure provides the largest figure of merit for thermoelectric materials? To answer that question, we write the electrical conductivity, thermopower, and thermal conductivity as integrals of a single function, the transport distribution. Then we derive the mathematical function for the transport distribution, which gives the largest figure of merit. A delta-shaped transport distribution is found to maximize the thermoelectric properties. This result indicates that a narrow distribution of the energy of the electrons participating in the transport process is needed for maximum thermoelectric efficiency. Some possible realizations of this idea are discussed.

Thermoelectric materials can be used to make refrigerators or power generators (1, 2). These solid state devices have no moving parts and are extremely reliable. Their efficiency is low, so they are used in products where reliability is more important than efficiency. Thermoelectric refrigerators are used to spot cool electronic components such as infrared sensors or computer chips. Power generators are used in space stations and satellites.

There has been much effort to find the best thermoelectric materials (1–3). There has also been numerous discussion of the physical limits—i.e., what are the best possible thermoelectrics allowed by nature (4)? Here we provide a new and simple estimate of the maximum efficiency of thermoelectric materials.

The efficiency of thermoelectric energy converters depends on the transport coefficients of the constituent materials through the figure of merit (1):

$$Z = \frac{\sigma S^2}{\kappa_e + \kappa_l},\tag{1}$$

where σ is the electrical conductivity and S is the Seebeck coefficient. The quantity in the denominator is the thermal conductivity; it is given by the sum of contributions from the electronic carriers κ_e and the lattice κ_l . The efficiency is increased by making ZT as large as possible, where T is the mean operating temperature of the device.

At room temperature, the best thermoelectric material now known is Bi₂Te₃, which has $ZT \approx 1$ (1, 2). With this value, the coefficient of performance of thermoelectric coolers is about one-third the value for conventional compressor systems. At room temperature, with the current design, thermoelectric refrigerators will be competitive with conventional compressor systems if a material is found with $ZT \approx 4$. However, any small increment in this value ($ZT \ge 1$) will result in many new applications for these devices. This technology is environmentally cleaner and more reliable than traditional compressor systems. Therefore, it is worth exploring the possibility of increasing ZT to find a material with ZT > 1. No materials are found at lower temperatures: they are used in power generators.

From the definition of the figure of merit given in Eq. 1, it is clear that, to increase Z, we have to decrease the thermal conductivity of the material and/or increase the thermopower and electrical conductivity. Among the four quantities involved in Eq. 1, three of them are mainly related to the electronic structure of the material (σ , S, and κ_e) and one is mainly related to the lattice (κ_l) . One possible way to improve the figure of merit is to reduce the lattice thermal conductivity without significantly altering the electronic properties of the material. This approach has been explored extensively in the past (5, 6) through the enhancement of phonon scattering. However, a very comprehensive review done by Spitzer (7) shows that 2 mW/cm·K is the practical lower limit for the lattice thermal conductivity of semiconductors. Another traditional way to improve the thermoelectric properties of a material is to maximize σS^2 by varying the doping concentration, which varies the electron density.

The methods mentioned in the previous paragraph are reasonable approaches to the optimization of a given material. However, in this study, we want to formulate the problem from a different point of view. We will try to answer the following question. What is the best electronic structure a thermoelectric can have? In other words, for a given lattice thermal conductivity, if we are given the freedom to choose the distribution of energy levels and scattering of the carriers, what would be our choice?

To answer the question formulated in the previous paragraph, we will first note that the transport coefficients can be written as a functional of a single kernel function. The transport coefficients are given by solutions of the Boltzmann equation as (8):

$$\sigma = e^2 \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon), \qquad [2]$$

$$T\sigma S = e \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon)(\varepsilon - \mu), \qquad [3]$$

$$T\kappa_0 = \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon) (\varepsilon - \mu)^2$$
 [4]

where μ is the chemical potential, *e* the electron charge,

$$\left(-\frac{\partial f_0}{\partial \varepsilon}\right) = \frac{1}{k_B T} \frac{e^{\left(\frac{\varepsilon-\mu}{k_B T}\right)}}{\left(e^{\left(\frac{\varepsilon-\mu}{k_B T}\right)} + 1\right)^2},$$
[5]

and $\Sigma(\varepsilon)$, which we will call the transport distribution function, is given by:

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$$\Sigma(\varepsilon) = \sum_{\vec{k}} \nu_x(\vec{k})^2 \tau(\vec{k}) \delta(\varepsilon - \varepsilon(\vec{k})), \qquad [6]$$

where the summation is over the first Brillouin zone, $v_x(\vec{k})$ is the group velocity of the carriers with wave vector \vec{k} in the direction of the applied field (x), $\tau(\vec{k})$ is the carrier's lifetime, and $\varepsilon(\vec{k})$ is the dispersion relation for the carriers. In the case that many bands contribute to the transport process, the summation has to be extended to all the bands. In some particular cases, such as for parabolic bands, the transport distribution defined in Eq. 6 takes a much simpler form:

$$\Sigma(\varepsilon) = N(\varepsilon) \nu_x(\varepsilon)^2 \tau(\varepsilon), \qquad [7]$$

where $N(\varepsilon)$ is the density of states. However, we will not be limited to this particular case; we will analyze the transport distribution in its general form.

The electronic thermal conductivity κ_0 is when the electrochemical potential gradient inside the sample is zero and is related to the thermal conductivity for zero electric current κ_e by:

$$\kappa_e = \kappa_0 - T\sigma S^2.$$
 [8]

Our strategy for finding the maximum figure of merit is to start from the above definitions, and ask the following question: What functional form of $\Sigma(\varepsilon)$ gives the largest value of Z? Previous workers (1-4) have treated this as a physics problem and tried to find the form of the electron lifetime $\tau(\varepsilon)$ or density of state $N(\varepsilon)$ that gives the largest Z. Here we treat it as a problem in mathematics. Given this functional form, what mathematical function $\Sigma(\varepsilon)$ gives the largest Z? This is a simple question, to which we have found a simple answer.

After some rearrangement, the transport coefficients can be written as:

$$\sigma = \sigma_0 I_0,$$

$$\sigma S = \left(\frac{k_B}{e}\right) \sigma_0 I_1,$$

$$\kappa_0 = \left(\frac{k_B}{e}\right)^2 T \sigma_0 I_2,$$

[9]

where $\sigma_0 = e^2/(\hbar a_0) \approx 46,000 \ (\Omega \text{cm})^{-1}$, with \hbar being the reduced Plank's constant, and a_0 being the Bohr's radius. The dimensionless integrals I_n have been defined as:

$$I_n = \int_{-\infty}^{+\infty} dx \; \frac{e^x}{(e^x + 1)^2} \, s(x) x^n, \qquad [10]$$

where $s(x) = \hbar a_0 \Sigma(\mu + xk_BT)$ is the dimensionless transport distribution function, measured from the chemical potential and scaled by the inverse temperature.

In terms of these integrals, ZT can be written as:

$$ZT = \frac{T\sigma S^2 / \kappa_l}{\kappa_0 / \kappa_l - T\sigma S^2 / \kappa_l + 1} = \frac{\alpha I_1^2 / I_0}{\alpha I_2 - \alpha I_1^2 / I_0 + 1}$$
 [11]

$$=\frac{\xi}{1-\xi+A},$$
[12]

$$\xi = \frac{I_1^2}{I_0 I_2},$$
 [13]

$$A = \frac{1}{\alpha I_2},$$
 [14]

where $\alpha = (k_B/e)^2 T \sigma_0 / \kappa_l$ is related to the parameter β , defined by Chasmar and Stratton (9). In our definition of α , σ_0 is completely determined by physical constants, whereas in the definition of β by Chasmar and Stratton, σ_0 preserves some characteristics of the material. We prefer to keep all the properties characterizing the material inside the transport distribution function.

In this way, given α and a nonnegative function s(x), we can obtain a unique value for the figure of merit. The largest value of ZT is found by making ξ large and A small. It is known that $\xi \leq 1$; i.e., its largest value is 1. We have made a twodimensional map of ZT as a function of (ξ, A) and found that the largest value of ZT is when $\xi \rightarrow 1$ and $A \rightarrow 0$. The case that $\xi = 1$ gives that ZT = 1/A. It is easy to start from Eq. 12 to prove that

$$ZT = \frac{\xi}{1 - \xi + A} \le \frac{1}{A} = \frac{\kappa_0}{\kappa_l}.$$
 [15]

The proof of the inequality demands that $0 \le (1 - \xi)(1 + A)$, which is always obeyed. So ZT is always bounded by κ_0/κ_l .

What is the transport distribution function that fulfills the condition $\xi = 1$? In this case, we know that we will obtain the largest possible value of the figure of merit. We have found that the Dirac delta function is the only transport distribution function that fulfills this condition. To show this we first notice that the dimensionless integrals I_n are the moments of the function:

$$P(x) = D(x)s(x)$$
[16]

$$D(x) = \frac{e^x}{(e^x + 1)^2}.$$
 [17]

The variable x is the energy of the carriers measured in units of $k_{\rm B}T$. This function, P(x), quantifies the contribution of carriers of a given energy to the transport process. In this language, the thermal conductivity κ_e is proportional to the variance of the distribution P(x)—i.e.,

$$\kappa_e \propto \langle x^2 \rangle - \langle x \rangle^2.$$
 [18]

The condition $\kappa_0 = T\sigma S^2$, equivalent to $\kappa_e = 0$, is fulfilled by a distribution P(x) with zero variance, no spread around the mean value. This is the Dirac delta distribution.

In the case of a transport distribution given by a delta function, all the integrals in Eq. 9 can be easily calculated. Let's assume that the transport distribution has the form:

$$s(x) = f(x)\delta(x - b),$$
[19]

where f(x) is any arbitrary function and b indicates the position of the peak with respect to the Fermi level. The transport coefficients for this case are given by:

$$\sigma = \sigma_0 D(b) f(b),$$

$$S = \left(\frac{k_B}{e}\right) b,$$

$$\kappa_0 = \left(\frac{k_B}{e}\right)^2 T \sigma_0 D(b) f(b) b^2.$$
[20]

This gives for the optimal figure of merit, $ZT = \kappa_0/\kappa_l$.

Next we find the smallest value of A, which is the largest value of κ_0/κ_l . We assume that κ_l is fixed, and find the maximum of κ_0 . First consider the case f(x) = C, a constant independent of x. We maximize the function $b^2D(b)$, which is 0.439 at $b = \pm 2.4$. This is equivalent to having the resonance be $2.4k_BT$ above or below the Fermi level. It is clear that if f(x) is not a constant, the position of the maximum will be different.

However, since only variations of f(x) in an interval of width k_BT around the Fermi level are important, a constant is in general a good approximation.

As follows from Eq. 20, using b = 2.4, the value that optimizes the figure of merit, we obtain $S = 207 \ \mu V/K$, in reasonable agreement with typical experimental values for good thermoelectrics. The optimal value of ZT is:

$$(ZT)_{\max} = 0.439 \left(\frac{k_B}{e}\right)^2 \frac{\sigma_0 TC}{\kappa_l}.$$
 [21]

The transport distribution that maximizes the figure of merit is the Dirac delta function. An ideal delta function is not achievable in real materials. However, electronic *f*-levels are tightly bound in atoms, and bind little in solids (10–11). They give a contribution to the density of states in solids, which is a Lorentzian of very narrow width. This is nature's closest approximation to a delta function. YbAl₃ is a metallic conductor that has the highest value ever reported (12) for the "power factor" σS^2 . Photoemission data (13–15) shows that the *f*-level of the Yb is quite close to the chemical potential, although experimental groups argue (16) about its exact location. We offer this as experimental support for the idea that the best thermoelectric is found in materials which have a sharp singularity in the density of states very near to the chemical potential.

If we assume that the delta function comes from the density of states $N(\varepsilon) = n_i \delta(\varepsilon - bk_B T)$, where n_i is the concentration of rare-earth energy levels, then we find:

$$(ZT)_{\max} = 0.146 \frac{\nu \ell n_i k_B}{\kappa_l},$$
 [22]

where the mean-free-path is $\ell = \nu \tau$. It is interesting that this quantity is independent of temperature. We have tried to estimate these parameters. A simple estimate to choose $\nu = 1$ Mm/s and $\kappa_l = 1$ W/m·K. The latter is typical of good thermoelectrics. We give each rare earth a volume of $n_i = 1/a^3$ and set $\ell = a = 0.3$ nm. These values give ZT = 14, which is ten times larger than any known material at any temperature. We think these values are achievable in rare-earth compounds.

Most theories of electron transport in rare-earth compounds note that the electron lifetime τ varies inversely as the density of states, so that the dependence on these parameters is quite complicated. (We shall take up these issues in a longer paper.)

In practice, the density of states has other terms besides a single delta function. We tried two delta functions, but they had lower ZT than a single one. A more realistic example has the addition of a constant background to the delta-shaped transport distribution. The function we are going to use has the form:

$$N(\varepsilon) = n_i \left[\delta(\varepsilon - bk_B T) + \frac{1}{W} \right]$$
 [23]

$$=\frac{n_i}{k_BT} \left[\delta(x-b)+a\right],$$
 [24]

$$a = \frac{k_B T}{W},$$
 [25]

$$s(x) = C[a + \delta(x - b)],$$
 [26]

$$ZT = \frac{b^2 D(b)}{(a+D) \left(\frac{1}{\alpha C} + a\frac{\pi^2}{3}\right) + ab^2 D}.$$
 [27]

Here we added a constant given by the inverse bandwidth W. In most metals this ranges in value form 1–10 eV. This



FIG. 1. Thermoelectric figure of merit ZT calculated for a transport distribution given by a delta plus *a* background versus the intensity of the background *a*. The values of αC in Eq. 27 are 1 (lower line), 3 (middle line), and 5 (upper line).

represents a crude model for the density of states of mixedvalence alloys. However, again we expect that only energy states near to the chemical potential are important, and in that narrow energy region, the background is nearly a constant. Note that the dimensionless constant a is quite small, since it is a thermal energy divided by an electron band width.

In Fig. 1, we show ZT as a function of the background contribution a. For each value of a, we have found the optimal value of b. We have used $\alpha C = 1$ (lower curve), $\alpha C = 3$ (middle curve), and $\alpha C = 5$ (top curve). As can be appreciated in the figure, the effect of the background contribution is dramatic. A 10% contribution of the background, corresponding to a = 0.1, reduces the figure of merit to 25% of its original value for a = 0. However, in mixed-valence alloys, the f-level contribution to the density of states is typically larger than 100 times the background value (10, 11). In this case, the negative effect on ZT of the background contribution is small.

In summary, we have written the thermoelectric figure of merit as a functional of the transport distribution. This function must be a Dirac delta function to maximize the figure of merit. Of course, this exact situation is not found in nature. However, our results indicate that we have to search for materials where the distribution of energy carriers is as narrow as possible, but with high carrier velocity in the direction of the applied electric field.

The addition of a constant background to delta-shaped transport distribution decreases dramatically the figure of merit. The physical meaning of this results is that a peak on top of a background density of states will not be our optimal choice to increase the figure of merit, unless the background is <1% of the integrated contribution of the peak.

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