# **Carderock Division, Naval Surface Warfare Center**

West Bethesda, Maryland 20817-5700

NSWCCD-TR-64—97/06 June 1997

Survivability, Structures, and Materials Directorate Research and Development Report

# Seebeck Coefficient and the Thermoelectric Figure of Merit in Semiconductors and Conducting Polymers

by

Barbara F. Howell Joseph W. Dickey Herbert Überall





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#### ABSTRACT

Interest in the use of thermoelectric materials for cooling and refrigeration devices has recently intensified because of the potential of such devices for reducing the present use of chlorofluorocarbon-emitting compression cooling devices, as well as for creating a means to cool quickly to superconductor operating temperature (77°K). Both semiconductors and conducting polymers are being investigated in this connection. The thermopower of conducting polymers can be manipulated at room temperature, and preliminary experimental studies have shown much Optimization of the figure of merit for such promise here. materials now becomes imperative, e.g., via judicious doping. For such a purpose, the theoretical predictability of the necessary parameters (Seebeck coefficient, electric and thermal appears desirable as a guide for relevant conductivities) Such analytical predictions, in experimental investigations. terms of Fermi-Dirac functions, are presented here in a systematic fashion. They are validated by the example of recent comprehensive experimental results for certain semiconductors (skutterudites), and are further used here in applications to a number of conducting polymers for which some experimental data have become available.

#### ADMINISTRATIVE INFORMATION

This project was initially funded by the NSWC Carderock Division Independent Research Program with contributory sponsorship from the Machinery Systems Directorate. Dr. Barbara Howell (now retired) was joined by Prof. Herbert Uberall (Emeritus Professor, The Catholic University of America) under the ASEE program and Dr. Joseph Dickey (Johns Hopkins University) in the completion of the analyses presented in this report. The work is administered by the Nonmetallic Materials Department, Code 64, under the direction of Dr. E.C. Fischer. We are grateful to Dr. Dickey for his collegial assistance in this project.

#### INTRODUCTION

Practical use of thermoelectric materials for purposes of refrigeration via direct electric power or, conversely, of electric power production through heat absorption, has been made previously to a limited extent only, and was based on the following three known thermoelectric effects<sup>1</sup>:

(a) The Seebeck effect is observed when a voltage develops between two locations on a conductor held at different temperatures; if two different materials are joined at these locations to close the circuit ("thermocouple"), a current will flow.

(b) The Peltier effect, in which a current is sent through the junction of two different conductors, with the ensuing creation or absorption of heat.

(c) The Thomson effect, in which a current is made to flow between two different parts of a conductor held at different temperatures, again with an ensuing creation or absorption of heat.

Earlier applications of these effects for the purposes mentioned have been described in the two basic monographs on thermoelectric topics by  $Ioffe^2$  (1956) and by Goldsmid<sup>3</sup> (1964); see also Ref. 4. The thermoelectric effects were originally discovered in metals for which, e.g., the Seebeck coefficient ("thermoelectric power") was found too small for practical applications. The materials used later are ceramics, primarily bismuth telluride (Bi<sub>2</sub> Te<sub>3</sub>) alloys which do lend themselves to practical applications, but with a fairly low efficiency.

A customary parameter measuring thermoelectric efficiency for applications of a given material is the "thermoelectric figure of merit" Z, which when multiplied by the absolute temperature T becomes a dimensionless number,

$$ZT = S^2 \sigma T / \kappa, \qquad (1)$$

where S is the Seebeck coefficient (in customary units  $\mu VK^{-1}$ ,  $\mu$  denoting micro and K degrees Kelvin),  $\sigma$  the electrical conductivity (units Siemens cm<sup>-1</sup>, Siemens  $\equiv \Omega^{-1}$ ; we also may consider the resistivity  $\rho = \sigma^{-1}$  having units  $\Omega$  cm), and  $\kappa$  the thermal conductivity (units W cm<sup>-1</sup> K<sup>-1</sup>), the latter consisting of an electronic contribution  $\kappa_{e\ell}$  furnished by the charge carriers, and a phonon contribution  $\kappa_{ph}$  furnished by lattice vibrations, with

$$\kappa = \kappa_{\rm e\ell} + \kappa_{\rm ph}. \tag{2}$$

Note that if the charge carriers are holes rather than electrons,  $\kappa_{e\ell}$  will still refer to these. In bismuth telluride alloys, maximum values of ZT≤1 have been achieved<sup>5</sup> at room temperature (T = 300°), while efficient applications would require<sup>6</sup> ZT≥3, e.g., for rendering thermoelectric home refrigerators economically competitive with traditional compressor-based refrigerators. However, it has frequently been found that trying to improve Z by raising S in simple materials also decreases  $\sigma$  and raises  $\kappa_{e\ell}$ , so that Z changes little<sup>5</sup>.

It is interesting to note that both  $Ioffe^2$  and  $Goldsmid^7$  have proposed the use of semiconductors for practical applications of thermoelectric materials, the reason being that S can be rather large here and the electric conductivity  $\sigma$ , while not very large

intrinsically, can be increased by doping<sup>8</sup> which raises the concentration of charge carriers n. The schematic picture of Fig. 1 shows the dependence of S,  $\sigma$  and  $\kappa_{e\ell}$  on carrier concentration<sup>4</sup>, indicating an optimal carrier concentration of n ~ 10<sup>19</sup> cm<sup>-3</sup> that maximizes the numerator of Eq. (1).

The denominator of Eq. (1),  $\kappa_{e\ell} + \kappa_{ph}$ , should be minimized in addition, in order to lead to a maximal value of Z. From Eqs. (1) and (2) it is obvious that a large phonon contribution  $\kappa_{\rm ph}$  will not be helpful in this respect. In (hard) semiconducting ceramics  $\kappa_{\rm ph}$ may exceed  $\kappa_{el}$  by factors of 5 or more<sup>6</sup>, thus greatly reducing the figure of merit, while soft materials are expected to possess only small values of  $\kappa_{ph}$ . The recent investigations of conducting polymers (for which such is the case), with a view towards their use for thermoelectric applications, have therefore become of great interest.<sup>9-11</sup> In contrast to the material quantities relevant for thermoelectric properties, namely S,  $\sigma$ , and  $\kappa_{el}$ , all of which may be calculated from explicit analytic expressions based on band theory (see below), the phonon thermal conductivity  $\kappa_{ph}$  cannot be calculated in this way, and only approximate estimates are available for it<sup>12</sup>, such as those found from the Debye relation

$$\kappa_{\rm ph} = (1/3) \, C_{\rm y} C_{\rm s} \ell \,, \tag{3}$$

where  $C_v$  is the lattice specific heat at constant volume,  $c_s$  the velocity of sound, and  $\ell$  the phonon mean free path. Numerical order-of-magnitude estimates for conducting polymers are  $\kappa \sim 10^{-3}$  W cm<sup>-1</sup> K<sup>-1</sup>, while typical values for ceramic semiconductors at room temperature are<sup>6</sup>  $\kappa_{\rm ph} \sim 1 \times 10^{-2}$ W cm<sup>-1</sup>K<sup>-1</sup>,  $\kappa_{e\ell} \sim 4 \times 10^{-3}$ W cm<sup>-1</sup>K<sup>-1</sup>. This

points again toward the need for investigations of conducting polymers as candidates for thermoelectric applications. Note that if in Eq. (1) the thermoelectric values are known (or calculated) except that of  $\kappa_{\rm ph}$  of Eq. (2), an upper limit of Z can nevertheless be found by setting  $\kappa_{\rm ph} = 0$ . While for ceramics this upper limit may be a crude one, for conducting polymers it can be expected to be fairly close to the actual Z.

Before leaving this introductory chapter, let us briefly review potential applications and their usefulness for Navy as well as civilian purposes. Development of an inexpensive thermoelectric material which has a better cooling capacity and efficiency than any currently available would have many practical advantages. For example, it would allow production of quiet, low-maintenance, chlorofluorocarbon-free cooling systems for both military and commercial applications. On board ship or submarines it would allow a quiet, decentralized cooling architecture, it would eliminate usage of chlorofluorocarbons in, e.g., vapor compression (mechanical) air conditioners, and would provide less type expensive and lighter weight cooling systems. Thermoelectric units are easily miniaturized, and because they possess no moving parts, they are quiet and highly reliable. Small scale devices based upon this thermoelectric effect do exist, and are already used in specialized applications for which practicality and reliability are more important than economy.<sup>3,13</sup> This includes laboratory cooling plates, small refrigerated chests, or portable thermoelectric coolers that can be powered from a car battery for food storage; as

well as for devices providing localized cooling and temperature stabilization on circuit boards<sup>14</sup> or other electronic devices<sup>15</sup> (infrared detectors, low-noise amplifiers, computer chips). Finally, and most importantly, thermoelectric generators are used as power sources for many of NASA's deep space probes<sup>6</sup>, for example on the Voyager I and II satellites which employ a radioactive material as a heat source. Launched in 1977, these satellites are still sending back pictures today<sup>15</sup>.

In addition to such mainly room-temperature devices, there is also need for superconducting-temperature (T~100°K) thermoelectric cooling devices for use the field of cryoelectronics in (superconducting electronics). The skutterudite ceramics whose thermoelectric properties were studied recently<sup>6</sup>, show e.g., for La Fe<sub>3</sub>Co Sb<sub>12</sub> a Seebeck coefficient of S =  $100.9\mu VK^{-1}$  at T =  $300^{\circ}K$ , and of S = 28.7 $\mu$ VK<sup>-1</sup> at T = 100°K while the corresponding electric conductivities are  $\sigma = 638.6\Omega^{-1} \text{cm}^{-1}$  (300°) and  $\sigma = 896.8\Omega^{-1} \text{cm}^{-1}$  (100°), indicating their persistence of thermoelectric properties down to superconductivity temperatures. At room temperatures, studying conducting polymers, a Seebeck coefficient of  $1800 \mu VK^{-1}$  was found in polyoctylthiophene doped with ferric chloride<sup>11</sup>, but with a quite low electric conductivity ( $\sigma = 0.0074 \ \Omega^{-1} \text{cm}^{-1}$ ); in later studies<sup>10</sup> of poly(3-octylthiophene) samples, materials with S =  $9930 \mu VK^{-1}$  and  $\sigma$ = 0.0847  $\Omega^{-1}$  cm<sup>-1</sup> were found. An extremely high Seebeck coefficient, S = 11,600 $\mu$ VK<sup>-1</sup>, with a conductivity of around  $\sigma$  = 1  $\Omega^{-1}$  cm<sup>-1</sup> was found for cis-polyacetylene doped with iodine<sup>16</sup>. These values yield a figure of merit equal to 0.132, if the thermal conductivity is

assumed to be  $\kappa \sim 10^{-3}$ W cm<sup>-1</sup>K<sup>-1</sup>, a figure much higher than for bismuth telluride which has a figure of merit of about  $10^{-3}$ ; however, the instability of polyacetylene in air precludes its use in a practical cooling device. Stretching of polyacetylene samples doped with FeC $\ell_3$ , and thus aligning the polymeric chains, may lead to conductivities as high as  $\sigma \sim 30,000\Omega^{-1}$ cm<sup>-1</sup> (at 220°)<sup>17</sup>.

#### ANALYSIS

majority of experimental studies done so far on The semiconductors and conducting polymers have proceeded by measuring S,  $\sigma$  and, if possible,  $\kappa$  for many samples of a given material with empirically impurity concentrations, thus and different "optimizing" the material for the largest possible figure of merit. A different approach, described by Wolfe<sup>18</sup>, "is to determine the fundamental properties (such as  $\mu$ , the carrier mobility; m, the effective mass of the carriers in a given band;  $\kappa_{\rm ph}$ , the phonon thermal conductivity, etc.) of any specimen of the semiconductor, and then to predict what the maximum figure of merit would be in material with optimum doping. This second method is indirect, but it can be carried out on a single sample (in principle) and it provides more basic information about the material". Wolfe then goes on to describe e.g. the determination of mobility  $\mu$  via the relation<sup>19</sup>

$$\sigma = n e \mu, \tag{4}$$

measuring  $\sigma$  and obtaining n from Hall effect measurements.

It appears to us that a useful complement to this approach

should be the <u>analytic</u> determination (or prediction) of the basic thermoelectric and other material properties of a given specimen. Not only will this approach avoid the lengthy, purely experimental "trial and error method" of having to prepare and measure many samples with different dopant concentrations, it will even shorten Wolfe's second method by only having to measure <u>some</u> of the fundamental material properties (essentially for calibration purposes) while analytically predicting the others by swift computerized calculations.

Such analytical formulas, based on the band theory of the carriers and of their scattering mechanism, has been available since 1955 without any indications of their having been extensively used. They are quoted in Ioffe's book<sup>2</sup> (and, in later literature, are generally attributed to this source), but Ioffe seems to credit them to an earlier source<sup>20</sup>. The formulas have later on been reproduced by Rittner<sup>8</sup> (with one change to the power of  $k_B$ , the Boltzmann constant, in the expression for  $\kappa_{el}$  which leads to the correct dimensionality), and have subsequently been generalized to the case of a non-isotropic medium by Hicks and Dresselhaus<sup>5</sup> (with the exception of the carrier relaxation time  $\tau$  which has been retained as isotropic). In the following, we shall make use of the Hicks-Dresselhaus formulas in their form when specialized back to isotropy (the case to be considered by us), because this form is more convenient to use than the listed by Rittner.

To establish the identity between the Rittner<sup>8</sup> and the Hicks-Dresselhaus<sup>5</sup> expressions, we shall first list the former:

$$S = \pm (k_{\rm p}/e) \left( \left[ (r+2)/(r+1) \right] F_{r+1}/F_{r-1} - \zeta^{*} \right), \tag{5}$$

$$\sigma = (16\pi/3h^3) \text{ me}^2 \ell_o (k_B T)^{r+1} (r+1) F_r, \qquad (6)$$

$$n = (4\pi/h^3) (2mk_BT)^{3/2} F_{1/2},$$
(7)

$$\kappa_{e\ell} = (16\pi/3h^3) \ m\ell_o \ k_B^{r+3} \ T^{r+2} \ ((r+3)F_{r+2} - [(r+2)^2/(r+1)] \\ \times (F_{r+1}^2/F_r))$$
(8)

(the expression for n only appearing in Ioffe<sup>2</sup>). These expressions depend on the following parameters:

- $k_{B}$  = the Boltzmann constant = 86.17 x 10<sup>-6</sup> eVK<sup>-1</sup>
- e = the elementary charge
- $\zeta \star = \zeta / k_{\rm B} T$  where  $\zeta =$  the chemical potential
- T = absolute temperature
- h = Planck's constant =  $6.626 \times 10^{-27}$ erg s
- m = effective mass of charge carriers
- n = density of charge carriers.

The  $\pm$  sign on S must be chosen - for electron carriers (for which  $\zeta$  is the Fermi level measured with respect to the conduction band edge), or + for hole carriers (for which  $\zeta$  is the Fermi level measured with respect to the valence band edge). The value of r is determined by the carrier scattering mechanism<sup>2,8</sup>. The carrier free path length  $\ell$  is written as

$$\ell = \ell_0 E^r, \tag{9}$$

E being the energy of the charge carrier. For lattice scattering in a nonpolar material, n = 0; for ionic lattice scattering r = 1/2below the Debye temperature, and r = 1 above the Debye temperature. For scattering by impurity ions, r = 2.

The dimensionless Fermi-Dirac integrals are given by

$$F_{4} = F_{4}(\zeta^{*}) = \int_{0}^{1} x^{j} dx / (e^{x-\zeta^{*}} + 1); \qquad (10)$$

they depend on  $\zeta$ \* and, through this quantity, on  $\zeta$  and on the temperature. Previously, they have only been available in tabulated form (see, e.g., Refs. 21-23); with present-day computers their evaluation is straightforward.

The above formulas can be used for metals, semimetals, and semiconductors. They are valid for a parabolic one-band material: Hicks and Dresselhaus<sup>5</sup> have shown that the figure of merit is maximum for one-band materials (such as heavily doped semiconductors), Z being reduced for a material with several bands, especially conduction plus valence (overlapping) bands, but even for several bands of one kind. They therefore did not find it worthwhile to consider the case of several-band materials.

Hicks and Dresselhaus further went on to (a) generalize Eqs. (5), (6) and (8) to the case of anisotropic materials (with the exception of  $\tau$  as mentioned), thereby introducing different parabolic-band curvatures in the x, y and z directions, i.e. different effective masses  $m_x$ ,  $m_y$  and  $m_z$  as well as the mobility  $\mu_x$  in the direction of conduction; and (b) to cast the equations in a more practical form (eliminating  $\ell_o$ ). Since we shall consider the isotropic case only, we shall use the Hicks-Dresselhaus equations (which were given by them for the case x = 1/2 only) in their isotropic form as follows:

$$S = \pm (k_{B}/e) [(5F_{3/2}/3F_{1/2}) - \zeta^{*}]$$
(11)

(this expression having the same form in both the isotropic and the

anisotropic case);

$$\sigma = (1/2\pi^2) (2k_B T/\hbar^2)^{3/2} F_{1/2} m^{3/2} e\mu, \qquad (12)$$

 $\hbar = h/2\pi$ ; note this equation has the form of Eq. (4) since

$$n = (1/2\pi^2) (2k_{\rm B}T/\hbar^2)^{3/2} m^{3/2} F_{1/2}; \qquad (13)$$

and

$$\kappa_{e\ell} T = (1/3\pi^2) (2k_B T/\hbar^2)^{3/2} F_{\kappa} m^{3/2} (k_B T/e)^2 e\mu, \qquad (14)$$

where we have denoted

$$F_{r} = (7/2)F_{5/2} - (25/6)F_{3/2}^{2}/F_{1/2}.$$
 (15)

This form of the Hicks-Dresselhaus equations was slightly reformulated by us, in order to eliminate the carrier relaxation time appearing in their form for  $\kappa_{e\ell}$ , in favor of  $\mu$  by<sup>19</sup>

$$\mu = e\tau/m. \tag{16}$$

Equations (12) and (14) then show a remarkable analogy, which taken one step further, directly leads to an explicit, compact expression for the Wiedemann-Franz law,

$$\kappa_{ot}/\sigma T = \mathcal{L}, \tag{17a}$$

where

$$\mathcal{L} = (2/3) (k_{\rm B}/e)^2 F_{\rm g}/F_{1/2}$$
(17b)

is the Lorentz number.

The identity of Eqs. (5)-(8) (case r = 1/2 only) with Eqs. (11)-(15) can be shown by using the following approach: first, the coefficient  $\ell_o$  in the mean free path, Eq. (9), should be expressed by more familiar quantities such as the mobility  $\mu$ . Reference 19,

2nd edition, p. 239 defines the mean free path as  $\ell = \tau u$  where u is the average electron velocity. Taking for the latter the Fermi velocity  $u_F = \hbar k_F/m$ , and the energy in Eq. (9) as  $E = m u_F^2/2$ , and further using Eq. (16) leads, for r = 1/2, to

$$\ell_{o} = 2^{1/2} \, \mathrm{m}^{1/2} \mu / \mathrm{e} \,, \tag{18}$$

which inserted in Eqs. (6) and (8) leads to the corresponding Eqs. (12) and (14), respectively.

Using their equations, Hicks and Dresselhaus have been able to derive a compact expression for the dimensionless figure of merit ZT,

$$ZT = (3/2) ((5/3) F_{3/2} / F_{1/2} - \zeta^*)^2 F_{1/2} / (B^{-1} + F_{\kappa}), \qquad (19)$$

depending on the single open parameter B which for the isotropic case is

$$B = (1/3\pi^2) (2k_BT/\hbar^2)^{3/2}m^{3/2} (k_BT/e)^2 e\mu/(\kappa_{ph}T), \qquad (20)$$

and contains the often unknown phonon conductivity  $\kappa_{ph}$ . As we mentioned above, if  $\kappa_{ph}$  can be neglected e.g., for polymers, one has  $B \rightarrow \infty$  and the corresponding expression for ZT will present an upper limit on the figure of merit.

The expression of Eq. (19) can form the basis of an <u>analytic</u> optimization procedure, which is very much what we advocated following Eq. (4) as a computational equivalent (and simplification) of Wolfe's second method. Reference 5 proposes to vary  $\zeta$ \*, for a given value of B as calculated for the sample material, until ZT as given by Eq. (19) reaches a maximum, the corresponding value of  $\zeta$ \* being denoted  $\zeta$ \*<sub>opt</sub>. Experimentally, this variation of  $\zeta$ \* corresponds to varying dopant types and

concentrations, and the dopant concentration that renders  $\zeta^*$  equal to  $\zeta^*_{opt}$ , while evidently not directly affecting the value of B, Eq. (20), will optimize the figure of merit. These optimal dopant concentrations can, via the corresponding calculated values of  $\zeta^*_{opt}$ , be determined for varying values of B, which latter depend essentially only on the intrinsic properties of the sample material, and it was shown<sup>5</sup> that ZT increases rapidly (beyond values of 10 or more) with B increasing up to values of 10 or more.

### NUMERICAL PROCEDURES

In this Section, we use the above equations to relate intrinsic, properties of thermoelectric materials to other, measured ones, in the spirit of Wolfe's<sup>18</sup> approach. Incidentally, the Introduction has listed the units in which the quantities S,  $\sigma$ and  $\kappa$  and others are usually expressed. It thus appears useful to rewrite the corresponding equations in a form such that numerical coefficients, which lead to all the physical quantities that enter these equations being given in their customary units, are explicitly expressed by their corresponding numerical values. Starting with Eq. (11), we the write

$$S|_{\mu V/K} = \pm 86.17 (\mu V/K) (5F_{3/2}/3F_{1/2} - \zeta^*),$$
 (21)

which illustrates our intentions. If now S is measured, the corresponding value of  $\zeta$ \* can be determined by calculating the right-hand side of Eq. (21) as a function of  $\zeta$ \* (at the given

temperature T of measurement) and equating to the measured value of S; we shall call this ensuing value  $\zeta_{\circ}^*$ .

Continuing, we purpose to determine the carrier mobility  $\mu$  from known values of  $\kappa_{et}$ , via Eq. (14), always quoting the units explicitly:

$$\mu \Big|_{\rm cm \, V}^{2^{-1} - 1} = 0.4948 \, \times \, 10^{3} \, {\rm F}_{\kappa}^{-1} \, (\kappa_{\rm e\ell} {\rm T}) \Big|_{\rm Wcm}^{-1} \, {\rm m}'^{-3/2} \, {\rm T}'^{-7/2} \, ({\rm cm}^{2} {\rm V}^{-1} {\rm s}^{-1}) \, ; \qquad (22)$$

here, the explicit temperature and effective-mass dependence is introduced by the factors  $m' = (m/0.511 \text{ MeV/c}^2)$ , the free electron mass being  $m_e = 0.511 \text{ MeV/c}^2$ , and  $T' = (T/300^\circ\text{K})$  while the numerical factor in Eq. (22) was calculated for  $T = 300^\circ\text{K}$ . The values of  $\kappa_{e\ell}$ and  $\kappa_{ph}$  can be obtained separately from measuring  $\kappa$  and  $\sigma$  and using the Wiedemann-Franz law as shown in Ref. 6. The presence of m' in Eq. (22) still represents an open question; it may often suffice to set m' = 1.

Similarly, the carrier density is given by Eq. (13) as

$$n|_{cm}^{-3} = 2.8317 \times 10^{19} F_{1/2} T'^{3/2} m'^{3/2} (cm^{-3});$$
 (23)

it can evidently be calculated here without measurements (and it also depends on m' again).

The electric conductivity is, as is  $\mu$  of Eq. (22), obtained from the measured  $\kappa_{el}$  by

$$\sigma |_{\Omega^{-1} \text{cm}^{-1}} = 2.2448 \times 10^3 (F_{1/2}/F_{\kappa}) (\kappa_{e\ell}T) |_{\text{Wcm}^{-1}} (T')^{-2} (\Omega^{-1} \text{cm}^{-1})$$
(24)

where the Wiedemann-Franz law has been implied. Measuring  $\sigma$ , Eq. (24) then determines  $\kappa_{el}$ . The Wiedemann-Franz law can also be expressed in its usual form:

$$(\kappa_{e\ell}|_{WCm}^{-1}K^{-1}) / (\sigma|_{\Omega}^{-1}Cm}^{-1}T) = 0.4951 \times 10^{-8} (F_{\kappa}/F_{1/2}) (W\Omega K^{-2}) \equiv \mathcal{L}(W\Omega K^{-2}). (25)$$

It may be used, together with Eq. (22), to express the mobility  $\mu$  in terms of  $\sigma$  rather than  $\kappa_{e\ell}$  as in Eq. (22):

$$\mu \Big|_{\mathfrak{m}_{V}^{2} \mathfrak{s}^{-1}} = 0.22042 \ \sigma \Big|_{\mathfrak{n}_{cm}^{-1} \mathfrak{m}^{-1}} / (F_{1/2} T'^{3/2} \mathfrak{m}'^{3/2}) (\mathfrak{cm}^{2} V^{-1} \mathfrak{s}^{-1}).$$
(26)

The measured (or otherwise known) quantities S,  $\sigma$  and  $\kappa_{el}$  may thus be used in order to express, using the above equations, intrinsic material properties such as  $\mu$  and n. As to  $\kappa_{ph}$ , this is related by

$$B = (\kappa_{e}T/F_{r})/(\kappa_{ph}T)$$
(27)

to the quantity B whose dependence on  $\zeta^*_{opt}$  was determined by Hicks and Dresselhaus as described above. In Eq. (27) the entering factor  $\kappa_{e\ell}$  can be expressed by  $\sigma$  or  $\mu$ , whichever is more convenient, by using the preceding equations.

These equations will now be used, or validated, by analyzing with them the experimental values of the thermoelectric quantities of certain ceramic semiconductors that have recently been obtained experimentally<sup>6</sup> at various temperatures to a high degree of completeness.

Sales et al.<sup>6</sup> have carried out measurements on a class of thermoelectric ceramics known as skutterudites over a range of temperatures up to T = 700°. For one of their samples, LaFe<sub>3</sub>CoSb<sub>12</sub>, we show in Table I some of their experimental results for S,  $\sigma$ ,  $\kappa_{e\ell}$  and  $\kappa_{ph}$ , as well as results for the Lorentz number  $\mathcal{L}_{exp}$  and the figure of merit (ZT)<sub>exp</sub>, derived from their experimental values via Eq. (17a) and (1) respectively, at temperatures between 300° and 700°. It is seen, incidentally, that  $\mathcal{L}_{exp}$  is largely constant, indicating that the Wiedemann-Franz law is closely satisfied. The figure of merit ZT rises from 0.14 at room temperature to 0.83 at T = 700°K. Note that the positive values of S indicate the carriers to be holes in this case.

We shall now apply our theoretical model to these data. The first step consists in plotting the theoretical expression for S, given by Eq. (11), versus  $\zeta *$  in order to find the value  $\zeta_o *$  of this variable that equates  $S_i$  to the experimental value  $S_{exp}$ . The resulting values of  $\zeta_o *$  are shown in column 3 of Table II. The subsequent columns list the values of the Fermi-Dirac functions  $F_i$ and  $F_k$  at these arguments  $\zeta_o *$ .

Using the results of Table II, we are now in a position to validate the theoretical model against the data, and to make further predictions of physical properties of the sample material. Table III, in its column 2 and 3, shows the values of  $\mathcal{L}$  and ZT theoretically predicted from Eq. (25) and Eqs. (19), (27) respectively using the (calculated) entries of Table II. Comparing

these columns to the corresponding experimental values given in the last two columns of Table I indicates that the theoretical model, within rather narrow margins, may be considered highly reliable, and be made the basis for further predictions of physical properties of the sample. Such predictions are listed in the subsequent columns of Table III, presenting the carrier density n (units  $10^{19}$  cm<sup>-3</sup>) and the carrier mobility  $\mu$  (units cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) calculated from Eqs. (23) and (26), respectively. Note that while these results are uniquely determined as far as temperature is concerned, they still depend on the value of the effective mass which was here assumed to be equal to the free-electron mass (i.e., m' = 1). If m' is to be left open, then the column for n must be multiplied by  $m'^{3/2}$ , and that for  $\mu$  by  $m'^{-3/2}$ . Note that effective masses may be as low  $as^{24} m' = 0.1$ . It is well known, however, that n and  $\mu$  can be determined independently from Hall effect measurements<sup>4,18</sup>, and if obtained in this way, Eqs. (23) and/or (26) may then be used for a determination of the effective mass. It is interesting to observe that the carrier densities of Table III lie in the range of 10<sup>18</sup>-10<sup>19</sup> cm<sup>-3</sup> which is considered favorable for thermoelectric applications4,11,25.

After this validation of the theoretical model used, we shall now apply this model for prediction of physical parameters of a series of thermoelectric conducting-polymer materials, compiled in Refs. 10 and 11, for which measurements of S and  $\sigma$  have been made. Lacking measurements of  $\kappa$  for these samples, the figure of merit ZT may nevertheless be estimated from Eq. (1) in an order-of-magnitude

fashion by setting  $\kappa \sim 10^{-3} \text{ Wcm}^{-1}\text{K}^{-1}$ , see above. Note that Eq. (1) applies numerically if S is measured in units VK<sup>-1</sup>,  $\sigma$  in units  $\Omega^{-1}$  cm<sup>-1</sup> and  $\kappa$  in Wcm<sup>-1</sup>K<sup>-1</sup>.

Table IV lists these conducting polymers together with the data (all measured at room temperature), and the references hereto. The values of  $(ZT)_{est}$  listed here were estimated in the mentioned fashion. After numbering the samples, Column 1 lists the samples, Column 2 the references for the measurements, Columns 3 and 4 the measured values of S and  $\sigma$  and Column 5 our estimates for ZT. In the subsequent columns, Table IV (continued), we list the calculated values for  $\zeta_o$ \* and for the Fermi-Dirac functions, obtained as in the case of Table II.

The data of sample #1 are taken from the work of Ref. 11; they refer to the polymer poly(3-octylthiophene), abbreviated P3OT, or POT, with doping as indicated (see also sample #3). Samples #2-6 are taken from the work and the additional compilation of Ref. 11, with references as quoted. The last sample listed is bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>), given here for the sake of comparison with this previously employed standard thermoelectric material. The figure of merit of the latter, with the values of S and  $\sigma$  quoted, is as high as 12, but this estimate using  $\kappa \sim 10^{-3}$ Wcm<sup>-1</sup>K<sup>-1</sup> is unlikely to be realistic. It is remarkable to encounter values of ZT as high as 64.9, but this sample (polyacetylene) is not stable, and is unsuited for a thermoelectric material.

In the concluding part of Table IV we list our theoretical predictions based on Table IV (continued), in this sequence: first

the Lorentz number as obtained from Eqs. (17b) or (25). The following column lists predictions for  $(ZT)_{th}$  from Eq. (19), assuming that for the conducting polymers  $\kappa_{ph} << \kappa_{el}$  (i.e.,  $B^{-1} \rightarrow 0$ ). In the subsequent column, a theoretical value  $\kappa_{el}^{th}$  is given as obtained from the measured values of  $\sigma$  via the Wiedemann-Franz law in the form of Eq. (25).

The last two columns of Table IV list theoretical predictions at room termperature of n [from Eq. (23), assuming m' = 1], and of  $\mu$ , respectively [from Eq. (26), using the measured values of  $\sigma$  and again setting m' = 1].

#### CONCLUSIONS

At present, thermoelectric measurements are being conducted on semiconductors (including ceramics) and conducting polymers for the purpose of finding and optimizing such materials so that they may form the basis for commercially viable thermoelectric cooling or power-generating systems, or for devices useful for military applications. It is being advocated here, and by others<sup>18</sup>, that systematic measurements on many (differently doped, or different kinds of) samples could usefully be complemented, or speeded up, by obtaining the fundamental material parameters (n,  $\mu$ ) by separate specific measurements<sup>18</sup>, or by theoretical calculations which can also directly predict the thermoelectric parameters themselves. Such an approach can conceivably shorten greatly the optimization procedures for thermoelectric materials, provided the theory is based on reliable models.

We have here adopted the band-theoretical Fermi-Dirac model for the thermoelectric quantities as described, and further developed, in Refs. 2, 5, and 8, and have carried out some additional developments of our own. It has been gratifying to find that the validity of the model could be satisfactorily established on a very complete set of thermoelectric measurements for certain semiconducting ceramics (skutterudites) performed recently<sup>6</sup>. We subsequently used this model to predict thermoelectric and other material parameters for conducting polymers<sup>10,11</sup>, for which quite incomplete thermoelectric measurements (of S and  $\sigma$  only) have become available. Our application of the Fermi-Dirac model has been found useful for predicting further thermoelectric and other material parameters, including the figure of merit which is an indicator of the practical applicability of these materials for thermoelectric devices. The use of such a theoretical model can be expected to greatly accelerate attempts at optimization of the materials for thermoelectric applications, since calculations can proceed much more rapidly than an extended series of sample measurements.

Table I. Experimental thermoelectric data<sup>6</sup>

Т	S <sub>exp</sub>	$\sigma_{exp}$	K <sub>el</sub> exp	$\kappa_{\rm ph}^{\rm exp}$	$\mathfrak{L}_{exp}$	$(ZT)_{exp}$
(°K)	(µVK <sup>-1</sup> )	(Ω <sup>-1</sup> cm <sup>-1</sup> )	(Wcm <sup>1</sup> K <sup>1</sup> )	(Wcm <sup>1</sup> K <sup>1</sup> )	(10 <sup>8</sup> WΩK <sup>2</sup>	
300	100.9	638.6	0.0036	0.0126	1.88	0.14
400	134.5	565.6	0.0042	0.0118	1.85	0.28
500	164.6	516.9	0.0048	0.0111	1.86	0.48
600	185.0	480.5	0.0053	0.0105	1.84	0.67
700	197.3	456.1	0.0059	0.0099	1.85	0.83

for  $LaFe_3CoSb_{12}$ , and quantities derived therefrom.

Table II. Values of  $\zeta_{o}^{*}$  leading to  $S_{exp}$  of Table I, and corresponding values of the Fermi-Dirac functions.

Т	S <sub>exp</sub>	<u>ځ</u> *	F <sub>1/2</sub>	F <sub>3/2</sub>	F <sub>5/2</sub>	F,
(°K)	(µVK <sup>-1</sup> )					
300	100.9	3.58	4.98	14.18	54.0	20.77
400	134.5	2.31	2.92	6.78	22.1	11.76
500	164.6	1.50	1.90	3.88	11.6	6.99
600	185.0	1.04	1.43	2.74	7.84	5.56
700	197.3	0.80	1.22	2.27	6.35	4.62

Т (°К)	\$\mathcal{L}_{th}\$\$ (10 <sup>-8</sup> WΩK <sup>-2</sup> )	(ZT) <sub>th</sub>	n (10 <sup>19</sup> cm <sup>-3</sup> )	μ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
300	2.06	0.109	14.1	28.3
400	1.99	0.251	12.7	28.2
500	1.82	0.446	11.6	27.9
600	1.93	0.600	11.45	26.2
700	1.87	0.783	12.3	23.1

Table III. Theoretical predictions of the thermoelectric model used, for the sample material of Table I.

Sample No.	Thermoelectric Sample	Ref.	S (μV/K)	σ (Ω <sup>-1</sup> cm <sup>-1</sup> )	ZT (est.)
1	P3OT (I doped)	11	79 0	0.0199	4x 10 <sup>-5</sup>
2	Schiffbase	11	22.5	0.0401	6x 10 <sup>-6</sup>
3	POT-PVA (FeCl <sub>3</sub>	26	23	0.32	5x 10 <sup>-5</sup>
4	-doped) Polyacetylene (1%	17	84.9	30 000	64.9
5	Polypyrrhole	27	40	9	0.004
6	Polyparaphenylene	28	12	10-3	4x 10 **
7	Bismuth telluride (Bi2Te3)	10	205	952	12.0

Table IV. Thermoelectric data for various conducting polymers: S and  $\sigma$ , measured; (ZT)<sub>est</sub>, estimated value; other entries: theoretical model predictions.

Table IV (continued)

Sample No.	ζ,*	F <sub>1/2</sub>	F <sub>3/2</sub>	F <sub>5/2</sub>	Γĸ
1	4,974	7.779	27.5	125.7	34.88
2	18.91	55	632.7	8740	263.5
3	18.49	53.19	598.6	8094	259.7
4	4.557	6.89	22.91	99.5	30.84
5	10.48	22.86	150.1	1204	107.5
6	35.64	142	3049	78118	631.5
7	0.665	1.112	2.032	5.669	4.37

# Table IV (concluded)

Sample No	$\mathcal{L}_{th}$ (10 <sup>-8</sup> WΩ K <sup>-2</sup> )	(ZT) th	$\kappa_{e1}^{\text{th}}$ (Wcm <sup>-1</sup> K <sup>-1</sup> )	$(10^{19} \text{cm}^{-3})$	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
1	2.22	0.2892	0.0013x10 <sup>-4</sup>	22	5.64x10 <sup>-4</sup>
2	2 37	0.0284	0.0029x10 <sup>-4</sup>	155.7	1.61x10 <sup>-4</sup>
2	2.42	0.0284	0.0232x10 <sup>-4</sup>	150.6	13.3x 10 <sup>-4</sup>
4	2.22	0.3324	0.1998	19.5	960
5	2.33	0.0751	0.6291x10 <sup>-4</sup>	64.7	0.0868
6	2.2	0.016	10 <sup>-10</sup>	402.1	10-7
7	1.95	2.174	0.0056	3.15	189



Figure 1. Schematic dependence of electrical conductivity  $\sigma$ , Seebeck coefficient S, and thermal conductivity  $\kappa$ on the concentration n of free carriers (see Ref. 4).

#### REFERENCES

- 1. <u>Thermoelectricity</u>, P. H. Egli, ed., John Wiley and Sons, New York (1960).
- 2. Ioffe, A. F. <u>Polyprovodnikovye Termoelementy</u>; Ioffe, A. F., L. S. Stil'bans, E. K. Iordanishvili, and T. S. Stravitskaya, <u>Termoelekticheskoe Okhlazhdenie</u>, Publishing House of the USSR Academy of Sciences, Moscow-Leningrad (1956). English translation: Ioffe, A. F., <u>Semiconductor Thermoelements and Thermoelectric Cooling</u>, Infosearch Ltd., London (1957).
- 3. Goldsmid, H. J., <u>Thermoelectric Refrigeration</u>, Plenum, New York (1964). See also Goldsmid, H. J., <u>Applications of</u> <u>Thermoelectricity</u>, John Wiley and Sons, New York (1960).
- 4. Rowe, D. M., and C. M. Bhandari, <u>Modern Thermoelectrics</u>, Reston Publ. Co., Reston, VA (1983).
- 5. Hicks L. D., and M. S. Dresselhaus, "Effect of quantum-well structures on the thermoelectric figure of merit," <u>Phys. Rev.</u> Vol. B47, pp. 12727-12731 (1993).
- 6. Sales, B. C., D. Mandrus, and R. K. Williams, "Filled skutterudite antimonides: A new class of thermoelectric materials," <u>Science</u>, vol. 272, pp. 1325-1328 (1996).
- 7. Goldsmid H. J., and R. W. Douglas, "The use of semiconductors in thermoelectric refrigeration," <u>Brit J. Appl. Phys.</u>, vol. 5, pp. 386-390 (1954); Goldsmid, H. J., "Thermoelectric applications of semiconductors," <u>J. Electronics</u>, vol. 1, pp. 218-222 (1955).
- 8. Rittner, E. S. "On the theory of the Peltier heat pump," J.

<u>Appl. Phys</u>., vol. 30, pp. 702-707 (1959).

- 9. Howell, B., "Thermoelectric properties of conducting polymers," NSWC, Carderock Div., Bethesda, MD Report CARDIVNSWC-SSM-64-94/12 (July 1994).
- 10. Gratt, J., "Progress on thermoelectric conducting polymers," NSWC, Carderock Div., Bethesda, MD Report CARDIVNSWC-TM-64-96/01 (February 1996).
- 11. Howell, B. F., Th. Gracik, and H. Zinnen, "Thermoelectric properties of polyoctylthiophene and other conducting polymers," in <u>Electromagnetic Interactions</u>, A. Guran, R. Mittra, and P. Moser, eds., Series on Stability, Vibration and Control of Structures, A. Guran et al., eds., World Scientific, Singapore and New York (1996).
- 12. Piraux, L., E. Ducarme, J. P. Issi, D. Begin and D. Billiard, "Thermal conductivity of oriented polyacetylene films," <u>Synthetic Metals</u>, vol. 41-43, pp. 129-132 (1991).
- 13. Goldsmid, H. J., <u>Electronic Refrigeration</u>, Pion, London (1986).
- 14. Pollock, D. D., <u>Thermoelectricity: Theory, Thermometry, Tool</u>, ASTM, Ann Arbor, MI (1985).
- 15. Tritt, T. M., "Thermoelectrics run hot and cold," <u>Science</u>, vol. 272, pp. 1276-1227 (1996).
- 16. Chien, J. C. W., J. M. Warakomski, F. E. Karasz and M. A. Schen, "Effect of polyacetylene molecular weight and dopant concentration on the temperature dependence of transport properties," <u>Macromolecules</u>, vol. 18, pp. 2380-2389 (1985).

- 17. Park, Y. W., C. O. Yoon, C. H. Lee, H. Shirakawa, Y. Suezaki, and K. Akagi, "Conductivity and thermoelectric power of the newly processed polyacetylene," <u>Synthetic Metals</u>, vol. 28, pp. D27-D34 (1989).
- 18. Wolfe, R., "Determination of the fundamental properties of thermoelectric semiconductors," Chapter 7 of Ref. 1.
- 19. See, e.g., Kittel, C. <u>Introduction to Solid State Physics</u>, seventh edition, John Wiley and Sons, New York, NY (1996), p. 220.
- 20. Samilovich, A. G., and L. L. Korenblit, <u>Usp. Fiz. Nauk</u>, vol. 57, pp. 578-586 (1955).
- 21. Rhodes, P., "Fermi-Dirac functions of integral order," Proc. <u>Roy. Soc</u>., vol. A204, pp. 396-405 (1950).
- 22. Beer, A. C., M. N. Chase, and P. F. Choquard, "Extension of McDougall-Stoner tables of the Fermi-Dirac functions," <u>Helv.</u> <u>Phys. Acta</u>, vol. 28, pp. 529-542 (1955).
- 23. Dingle, R. B., "The Fermi-Dirac integrals," <u>Appl. Sci. Res.</u>, vol. B6, pp. 225-239 (1956).
- 24. Slack G. A., and V. G. Tsoukala, "Some properties of semiconducting IrSb<sub>3</sub>," <u>J. Appl. Phys</u>., vol. 76, pp. 1665-1671 (1994).
- 25. Fuller-Mora, W. W., K. L. Stokes, T. M. Tritt, A. C. Ehrlich, J. Z. Liu, and R. N. Shelton, "Electronic transport properties of PrBa<sub>2</sub>Cu<sub>3-x</sub>Ga<sub>x</sub>O<sub>7-δ</sub>," Proceedings of the International Conference on Thermoelectrics, March 26-29, 1996, Pasadena, CA, pp. 180-182 (IEEE Catalog No. 96TH8169).

- 26. Isotalo, H., <u>Comment. Phys. Math. (Finland)</u>, vol. 108, pp. 10-27 (1990).
- 27. Maddison, D. S., R. B. Roberts, and J. Unsworth, <u>Synthetic</u> <u>Metals</u>, vol. 33, pp. 281-287 (1989).
- 28. Ueno H., and K. Yoshino, <u>J. Phys. Soc. Japan</u>, vol. 55, pp. 4382-4387 (1986).

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