

P.V. Gorsky, S.V. Melnychuk



P.V. Gorsky

Institute of Thermoelectricity of the NAS and MES
Ukraine, 1, Nauky Str. Chernivtsi, 58029, Ukraine



S.V. Melnychuk

**FUNDAMENTAL CONSTANTS
AND SIMILARITY CRITERIA IN
THERMOELECTRICITY**

In the paper, for reasons of dimensionality it is shown that all characteristics of thermoelectric materials (TEM) that are important for thermoelectric applications can be expressed through fundamental constants and dimensionless groups depending on material parameters and their application conditions. Therefore, materials possessing identical sets of these dimensionless groups should have identical thermoelectric characteristics. It is demonstrated how this method can be used for the estimation of achievable values of thermoelectric figure of merit of materials based on single crystals.

Key words: fundamental Seebeck coefficient, fundamental electric conductivity, fundamental power factor, fundamental thermal conductivity, fundamental thermoelectric figure of merit, fundamental dimensionless thermoelectric figure of merit.

Introduction

Similarity methods and dimensionality theories are widely employed in the simulation of many “macroscopic” physical objects and phenomena in mechanics, hydro- and aerodynamics [1], thermal physics [2], scattering media optics [3], etc. They are equally widely used in thermoelectricity in the simulation of operating modes of various devices. In so doing, a broad spectrum of various similarity criteria is used. To such criteria one can refer, for instance, the Ioffe criterion or the so-called thermoelectric figure of merit of material which is important in the determination of generator efficiency or refrigerator coefficient of performance. In the description of conditions of heat exchange between any thermoelectric device and the environment of significant importance is the so-called Biot criterion describing convective heat exchange in boundary layer. The Reynolds criterion is one of similarity criteria describing, for instance, the work of generator modules with permeable legs whose channels carry liquid or gas. Dimensionless current in the theory of thermoelectric cooling can serve one of similarity criteria for operating modes of various refrigerators. This list goes on, but it is used exceptionally for solving design and development, rather than material science problems, aside from the fact that the Ioffe factor or the related dimensionless thermoelectric figure of merit are mainly responsible for the choice of thermoelectric material. Moreover, it is assumed that in the microscopic “ab initio” description of the properties of condensed media, such as TEM, the similarity and dimensionality methods are of rather limited application, or not used at all, with the exception of renormalization group method which is well known to experts in theory of phase transitions and critical phenomena [4]. Therefore, the purpose of this paper is to illustrate the way of using these methods to get the estimates of the upper limits of thermoelectric figure of merit of TEM.

Fundamental thermoelectric characteristics and corollaries

We shall call fundamental thermoelectric characteristics the values that have proper dimensions and are expressed only through fundamental constants. In this respect, the simplest way is to introduce the fundamental Seebeck coefficient α_0 as follows:

$$\alpha_0 = k/e. \quad (1)$$

In this formula, k is the Boltzmann constant, e is electron charge modulus. The numerical value of this quantity is $86.25 \mu\text{V/K}$.

The fundamental electric conductivity can be introduced equally easily. Its introduction, though, is not so unambiguous, but for reasons of dimensionality it is easy to check that as such one can take, for instance, the value:

$$\sigma_0 = e^2/(ha_B), \quad (2)$$

where h is the Planck constant, a_B is the radius of the first Bohr orbit in hydrogen atom. The numerical value of this quantity is $7.32 \cdot 10^5 \text{ S/m}$. This value is about an order higher than the conductivity of bismuth telluride. This choice raises the question as to why as the fundamental length the radius of the first Bohr orbit in hydrogen atom was taken, rather than, say, a similar radius of hydrogen-like exciton in some semiconductor thermoelectric material, or some of lattice parameters of this material, which, at first sight, would be more natural. However, the radius of the first Bohr orbit in hydrogen atom is widely known and is really a fundamental value expressed in turn through other fundamental constants. However, the radius of exciton in thermoelectric material, just as its lattice parameter, is purely individual value determined by specific composition and structure of material, as well as by its manufacturing technique. Therefore, establishment of such peculiar “thermoelectric standard of length” requires, in the first place, some agreement on “standard” thermoelectric material “reproducing” this length and, in the second place, some strictly specified and reliably reproduced requirements to its composition, structure and manufacturing technique.

Thus, having decided upon fundamental electric conductivity in the form of (2), it can be easily understood that the fundamental power factor P_0 is determined as

$$P_0 = \alpha_0^2 \sigma_0 = k^2/(ha_B). \quad (3)$$

Its numerical value is $5.44 \cdot 10^{-3} \text{ W/(m}\cdot\text{K}^2)$

However, for a complete description of TEM these characteristics are insufficient. One must also introduce the fundamental thermal conductivity κ_0 . For this purpose only the Wiedemann-Franz relation is suitable. Using it, we get the expression for κ_0 :

$$\kappa_0 = k^2 T_0 / (ha_B). \quad (4)$$

In this case, as the fundamental temperature T_0 , one can take “standard” temperature of normal conditions, i.e. 273.16 K . By virtue of such selection, the numerical value of fundamental thermal conductivity is $1.48 \text{ W/(m}\cdot\text{K)}$, which is close to thermal conductivity of bismuth telluride parallel to cleavage planes at 300 K .

Now it is an easy matter to introduce a fundamental thermoelectric figure of merit Z_0 . Taking into account (3) and (4), it is not difficult to obtain that:

$$Z_0 = 1/T_0. \quad (5)$$

The numerical value of this value is $3.66 \cdot 10^{-3} \text{ K}^{-1}$. Therefore, the fundamental dimensionless thermoelectric figure of merit $Z_0 T_0$ is simply equal to unity.

Thus, thermoelectric characteristics of any TEM under any application conditions can be expressed through fundamental thermoelectric characteristics as follows:

$$\alpha = \alpha_0 f_\alpha(\{a_\alpha\}), \quad (6)$$

$$\sigma = \sigma_0 f_\sigma(\{a_\sigma\}), \quad (7)$$

$$\kappa = \kappa_0 f_\kappa(\{a_\kappa\}), \quad (8)$$

$$P = P_0 f_\alpha^2(\{a_\alpha\}) f_\sigma(\{a_\sigma\}), \quad (9)$$

$$Z = \frac{f_\alpha^2(\{a_\alpha\}) f_\sigma(\{a_\sigma\})}{T_0 f_\kappa(\{a_\kappa\})}, \quad (10)$$

$$ZT = \frac{T f_\alpha^2(\{a_\alpha\}) f_\sigma(\{a_\sigma\})}{T_0 f_\kappa(\{a_\kappa\})}. \quad (11)$$

In formulae (6) – (11), $f_\alpha, f_\sigma, f_\kappa$ are certain dimensionless functions depending on the sets of dimensionless groups $\{a_\alpha\}, \{a_\sigma\}, \{a_\kappa\}$, or similarity criteria, comprising both material parameters and characteristics of its application conditions. From this standpoint, the basic task of thermoelectric materials science (in its theoretical part) is to develop a detailed theory for said dimensionless functions.

As regards Eq. (11), at first sight it may seem an absurd tautology adding nothing to understanding the heart of the matter, as there are relationships (6 – 10). Nevertheless, imagine certain, though hypothetical, TEM for which the dimensionless functions $f_\alpha, f_\sigma, f_\kappa$ are such that in a certain temperature range the relationship $\frac{f_\alpha^2(\{a_\alpha\}) f_\sigma(\{a_\sigma\})}{f_\kappa(\{a_\kappa\})}$ is a weakly varying function of temperature

close to unity. Then for the dimensionless thermoelectric figure of merit of such hypothetical TEM in the mentioned temperature range the following simple formula is valid:

$$ZT = T/T_0. \quad (12)$$

In the authors' opinion, it is already something more than “mere nothing”. Let our hypothetical TEM fulfill the above specified conditions, say, in the temperature range from 523 to 773 K (it is a typical “generator” range). Then its dimensionless thermoelectric figure of merit in the above temperature range should linearly increase from 1.92 to 2.83. In case it could be created, it would be a fairly good TEM. It is interesting to compare its characteristics to the experimental data for some real generator TEM. This data [5] shows that the dimensionless thermoelectric figure of merit of even fairly good nanostructured and composite TEM at a temperature of 523 K, is at least a factor of 1.23 – 1.92 lower compared to our hypothetical TEM. Moreover, in practice there is either a decrease in dimensionless thermoelectric figure of merit with temperature, or the existence of maximum, rather than its monotonous increase. Exactly the latter fact, on the one hand, necessitates creation and use of functionally-graded TEM, and, on the other hand, causes the very possibility of this [6]. Hence, our requirement to dimensionless functions $f_\alpha, f_\sigma, f_\kappa$, simple at first sight, in fact, is a rather strict requirement to TEM which is far from being satisfied so far. At this point, however, we finish discussion of only small fraction of general considerations related to the use of methods of similarity and dimensions in theory of thermoelectricity and pass on to some specific examples.

Some specific examples of constructing model dimensionless functions and their corollaries

We begin with the simplest widely known case of calculating Seebeck coefficient of a semiconductor with isotropic square law of dispersion and power law of energy dependence of relaxation

time in impurity region. The above characteristic is a function of only two dimensionless parameters, namely $\eta = \zeta/kT$, where ζ is chemical potential of carrier gas, and power exponent r in the law of energy dependence of relaxation time, i.e. in this case $\{a_\alpha\} = \{\eta, r\}$. The respective model function is given by [7]:

$$f_\alpha(\{\eta, r\}) = \frac{(2r+5)F_{r+3/2}(\eta)}{(2r+3)F_{r+1/2}(\eta)} - \eta. \quad (13)$$

In this formula, $F_n(\eta)$ are the Fermi integrals. Note that braces, along with round brackets on the left side of formula (13), just as in subsequent similar formulae, will be used by the authors not in the least in order to artificially complicate or “cloud” material presentation, but in order to emphasize that in each specific case the respective dimensionless parameters are by no means casual, but make a certain unified closed set, clearly and unambiguously caused by selected model approach.

Consider some corollaries from relationship (13). For this purpose we will take into account the fact that according to general principles of quantum mechanics, power exponent r can vary from -0.5 to 3.5 . Let us analyze from this standpoint possible limits of change in the value of Seebeck coefficient of thermoelectric material $Bi_{0.5}Sb_{1.5}Te_3$. Using equation determining chemical potential, i.e. parameter η , in the form [7]

$$n_0 = \frac{8\sqrt{2}\pi(m^*kT)^{3/2}}{h^3} F_{1/2}(\eta), \quad (14)$$

we will get that, for instance, at hole concentration $n_0 = 3.2 \cdot 10^{19} \text{ cm}^{-3}$, density-of-state effective mass $m^* = 0.94 m_0$, temperature $T = 300 \text{ K}$ and $r = -0.5$, which corresponds to dominating at this temperature charge carrier scattering on the deformation potential of acoustic phonons $\alpha = 172 \mu\text{V/K}$. This theoretical value with an error less than 10 % is in agreement with the experimental data [8] for $Bi_{0.5}Sb_{1.5}Te_3$. However, if it were $r = 3.5$ (this case corresponds to a hypothetical TEM where there is ultimately strong energy filtration of charge carriers), the value of Seebeck coefficient would be $480 \mu\text{V/K}$. And this, with unvaried electric conductivity, would mean increase in the figure of merit of TEM by a factor of 7.79. However, such strong filtration is hardly realizable in any TEM. Therefore, it seems more correct to consider a case of charge carrier scattering on random potential of chaotically distributed charged impurities whose concentration will be considered to be equal to charge carrier concentration which corresponds to single ionization of impurity centres. To determine the mean free path of charge carriers in this case, it is necessary to know transport cross-section. From among relatively simple formulae that determine it and have correct asymptotics at low and high energies, the Conwell-Weiskopf formula in the authors' opinion is the most correct. It is based on the angular dependence (defined by Rutherford formula) of differential cross-section of charged particle scattering on unscreened Coulomb potential, which is identical both in classical and quantum case. The energy dependence of relaxation time in this case is given by:

$$\tau(\varepsilon) = \frac{16\pi\sqrt{2m^*}(\chi\varepsilon_0)^2\varepsilon^{3/2}}{e^4 N_i \ln \left[1 + \left(4\pi\chi\varepsilon_0 / e^2 N_i^{1/3} \right)^2 \varepsilon^2 \right]}, \quad (15)$$

In this formula, N_i is impurity concentration which in case of single ionization is taken to be equal to major-carrier concentration, m^* is charge carrier effective mass, χ is relative dielectric constant of TEM, and ε_0 is absolute dielectric constant of vacuum.

In the calculation of relaxation time based on this formula, quite a reasonable physical assumption is made that in a crystal there is no sense to consider impact parameters exceeding half the

average distance between scattering centres. Using this formula, from the condition of coincidence of the observed and calculated values of electric conductivity for $Bi_{0.5}Sb_{1.5}Te_3$ we get that the effective relative dielectric constant of this TEM is of the order of 44. Such estimation based on the data of [7, 8] also seems to be reasonable. In this case the calculated value of Seebeck coefficient is $272 \mu\text{V/K}$. And it means thermoelectric figure of merit increase as low as 2.5 times. Taking into account that the figure of merit of our TEM at 300 K is $2.6 \cdot 10^{-3} \text{ K}^{-1}$, the predicted value of dimensionless thermoelectric figure of merit of TEM at 300 K provided that it is increased by a factor of 2.5, will be 1.95. It is shown that such or somewhat higher values of dimensionless thermoelectric figure of merit are attainable in good bulk nanostructured TEM obtained of nanopowders by hot pressing or electric spark plasma sintering techniques [9, 10]. It is considered that such values of thermoelectric figure of merit are attainable in good bulk nanostructured TEM obtained from nanopowders by hot pressing or electric spark plasma sintering. But this case also corresponds to sufficiently strong energy filtration of charge carriers. At first sight it may seem that the necessary energy filtration can be achieved by increasing the number of scattering centres in material, hence, by suppressing “harmful” in terms of Seebeck coefficient value charge carrier scattering on deformation potential of acoustic phonons. But the Conwell-Weiskopf formula implies that with increase in the number of impurities, the mean free path of charge carriers ceases to depend on energy. Moreover, conductivity increase does not compensate the drop in squared Seebeck coefficient, even though the contribution of lattice thermal conductivity is considered to be small, and thermoelectric figure of merit of material can be considered as the integral characteristic of a subsystem of free charge carriers in it. In this case, for the dimensionless thermoelectric figure of merit the following formula is valid:

$$ZT = \alpha^2 / L, \tag{16}$$

where L is the Lorentz number. In the case of simple isotropic parabolic zone this formula with regard to known relationships [7] yields the following expression:

$$ZT = \left[\frac{(2r+5)F_{r+3/2}(\eta)}{(2r+3)F_{r+1/2}(\eta)} - \eta \right]^2 \left[\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \frac{(r+5/2)^2 F_{r+3/2}^2(\eta)}{(r+3/2)^2 F_{r+1/2}^2(\eta)} \right]^{-1}. \tag{17}$$

Therefore, it is exactly “harmful” effect that we get. It is illustrated in Fig. 1.

From Fig. 1 it is seen that with increase in the degeneracy degree of free carrier gas, i.e. doping impurity concentration, the dimensionless thermoelectric figure of merit of material drops, and with increase in power exponent r , it increases. However, high values of r correspond to strong energy filtration of charge carriers in material.

Thus, to achieve even the value of 1.95 at 300 K for single crystal is problematic. This result differs radically from that in [11] according to which the thermoelectric figure of merit of TEM at $r = 1.5$ can reach 3. The difference is due to the fact that [11] does not take into account the difference of r from 1.5 at low charge carrier energies. Therefore, to achieve so high figure of merit, it is necessary to use

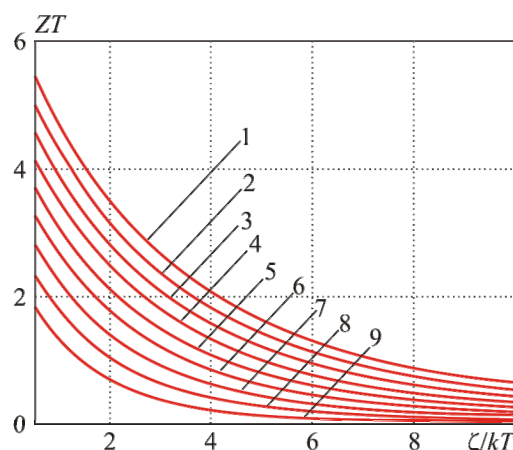


Fig. 1. Dependence of dimensionless thermoelectric figure of merit of material on the degeneracy degree of free carrier gas with different energy dependences of relaxation time. Curves 1 – 9 are constructed for r from -0.5 to 3.5 with increment 0.5 .

special additional measures for creation in TEM of a kind of quantum-mechanical “filtration barriers“, which is by no means always realizable in practice. Therefore, fundamental physical restrictions on power exponent r caused, in particular, by its drop at low energies, embound the achievable thermoelectric figure of merit of TEM based on a single crystal. Thus, it turns out that whereas the lower limit of dimensionless thermoelectric figure of merit of TEM determined by formula (12) might be attainable in a single crystal, the achievement of upper limit, at least at this stage, seems to be doubtful.

Conclusions

1. All thermoelectric characteristics of materials can be expressed through fundamental values of these characteristics and dimensionless groups comprising material parameters and characteristics of their application conditions.
2. The increase in thermoelectric material figure of merit is restricted by Seebeck coefficient drop with increase in charge carrier concentration and the energy dependence of charge carrier scattering factor.
3. For essential increase in the figure of merit of TEM based on single crystals it is necessary to create conditions whereby there is strong charge energy filtration of charge carriers.

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