ON THE INHERENT FIGURE OF MERIT OF THERMOELECTRIC COMPOSITES

A.A. Snarskii$^{1,2}$, G.V. Adzhigai$^3$, I.V. Bezusnov$^3$

$^{1,2}$ Institute of Thermoelectricity, Chernivtsi, Ukraine;  
$^2$ “KPI” National Technical University of Ukraine, Kyiv, Ukraine;  
$^3$ “Nauka-Service” Ltd, Moscow, Russia

The paper introduces and analyzes a new characteristic of thermoelectric composites – their intrinsic figure of merit characterizing the influence of thermoelectric phenomena on the effective properties of composites and governing thermal into electric energy conversion within a composite.

**Introduction**

The homogeneous semiconductor material is characterized by three material constants – electric conductivity $\sigma$, thermal conductivity $\kappa$ and differential thermopower $\alpha$. When describing energy processes (efficiency, cooling power, etc.) the above three constants make possible a natural (and unique) way of introducing a dimensionless temperature

$$\tilde{T} = \frac{\sigma \alpha^2}{\kappa} T.$$  \hspace{1cm} (1)

This dimensionless temperature and, respectively, the combination $\sigma \alpha^2/\kappa = Z$, first introduced by A. Ioffe (see, for example, [1]) and referred to as figure of merit, Ioffe’s number, is decisive for the efficiency. The higher $\tilde{T} = ZT$, the higher the thermocouple efficiency.

The material used is often a composite. Hereinafter we shall consider two-phase macroscopically inhomogeneous media. The properties of each of the phases in this case can be characterized by their local constants $\sigma_i$, $\kappa_i$, $\alpha_i$ ($i=1,2$), each of the phases being considered isotropic. Randomly inhomogeneous media are generally characterized by effective kinetic coefficients (EKC) $\sigma_e$, $\kappa_e$, $\alpha_e$, that by definition interrelate volume average thermoelectric forces and flows [2, 3]. For thermoelectric media it means that if the following holds true locally

$$\mathbf{j} = \sigma \mathbf{E} - \sigma \alpha \nabla T,$$

$$\mathbf{q}/T = -\kappa \left(1 + \frac{\sigma \alpha^2}{\kappa} T\right) \nabla T + \sigma \alpha \mathbf{E},$$

where $\mathbf{j}$ and $\mathbf{q}$ are the densities of electric current and heat flow, and $\nabla T$ is temperature gradient, then for volume average current $\langle \mathbf{j} \rangle$, field $\langle \mathbf{E} \rangle$, heat flow $\langle \mathbf{q} \rangle$ and temperature gradient $\langle \nabla T \rangle$

$$\langle \mathbf{j} \rangle = \sigma_e \langle \mathbf{E} \rangle - \sigma_e \alpha_e \langle \nabla T \rangle,$$

$$\langle \mathbf{q}/T \rangle = -\left(1 + \frac{\sigma \alpha^2}{\kappa_e} T\right) \kappa_e \langle \nabla T \rangle + \sigma_e \alpha_e \langle \mathbf{E} \rangle.$$  \hspace{1cm} (3)

The EKC $\sigma_e$, $\kappa_e$ и $\alpha_e$ are functionals of $\mathbf{E}(\mathbf{r})$ and $\nabla T(\mathbf{r})$ and intricately depend on the local values of $\sigma_i$, $\kappa_i$, $\alpha_i$ and phase concentrations. Their calculation methods are described in a brief review [3].

While for the homogeneous material the figure of merit $Z = \sigma \alpha^2/\kappa$ is determined unambiguously, the two-phase composites lack this unambiguity and there are many different variants for making “dimensionless” temperature and, accordingly, “figures of merit”: $\sigma_e \alpha_e^2/\kappa_e$, $\sigma_i \alpha_i^2/\kappa_i$, $\sigma_2 \alpha_2^2/\kappa_2$, ...
\((\sigma_1 + \sigma_2)(\alpha_1 + \alpha_2)/(\kappa_1 + \kappa_2), \ldots\) As will be shown below, in addition to phase figure of merit \(Z_i = \sigma_i \alpha_i^2 / \kappa_i\) and effective figure of merit \(Z_e\)

\[
Z_e = \sigma_e \alpha_e^2 / \kappa_e, \tag{4}
\]

there is at least one more important combination with figure of merit dimensions that has a clear physical meaning. If \(Z_e\) assigns the thermocouple efficiency, i.e. \textbf{determines} conversion of heat from the external source to electricity, also transferred to the external circuit, there is a value that \textbf{determines} conversion of thermal into electric energy dissipating within a composite. It would appear natural that such “figure of merit” should be called the inherent figure of merit.

Note that even in the homogeneous case \(ZT\) acts in two capacities. On the one hand, \(ZT\) \textbf{determines} the efficiency, on the other hand, it \textbf{renormalizes} thermal conductivity. While a coefficient appearing in the expression for heat flow density (2) with temperature gradient and \textbf{determining} heat flow generated by temperature gradient at \(ZT \ll 1\) is a “conventional” thermal conductivity \(\kappa\), at \(ZT > 1\) this coefficient is already by a factor of \(ZT\) greater.

**Inherent figure of merit of thermoelectric materials**

As long as in this paper we are not aiming at calculation of specific devices, our objective is to show principal existence and physical meaning of the new introduced value – latent figure of merit \(\tilde{Z}\), let us refer to the case of simpler two-dimensional randomly inhomogeneous medium. In a number of cases it has a precise solution for EKC \(\sigma_e, \kappa_e, \alpha_e\) [4, 5, 6]. This solution takes place for the so-called self-dual media [4] (see also [7]), including two-dimensional randomly inhomogeneous media at flow threshold \(p_e\), which in a two-dimensional case is equal to \(p_e = 1/2\). In the case of self-dual media [5, 6] the EKC are of the form

\[
\sigma_e = \sigma_1 \sigma_2 \sqrt{\sigma_1 \kappa_2 + \sigma_2 \kappa_1} / \sqrt{(\sigma_1 \kappa_2 + \sigma_2 \kappa_1)^2 + T \sigma_1 \sigma_2 (\alpha_1 - \alpha_2)},
\]

\[
\kappa_e = \kappa_1 \kappa_2 \sigma_2 / \sigma_e,
\]

\[
\alpha_e = \sigma_1 \sqrt{\sigma_1 \kappa_2 + \sigma_2 \kappa_1} / \sqrt{\sigma_1 \kappa_2 + \sigma_2 \kappa_1}.
\]

Precise (valid for arbitrarily large inhomogeneity) expressions for \(\sigma_e, \kappa_e, \alpha_e\) in the entire concentration range are unknown (and hardly possible). One of the most successful approximations is that of a self-consistent field [8] (see also the books [9, 10]). In the case when corrections \(\kappa, \sigma_e\) and \(\kappa_e\) due to thermoelectric phenomena are small, according to [11] (see also [6])

\[
\alpha_e = \left(\frac{\alpha \sigma / \Delta}{\sigma / \Delta}\right) , \Delta = \left(\sigma_{\text{lin}} + \sigma\right)\left(\kappa_{\text{lin}} + \kappa\right),
\]

\[
\left\langle \frac{\sigma_{\text{lin}} - \sigma}{\sigma_{\text{lin}} + \sigma} \right\rangle = 0 , \left\langle \frac{\kappa_{\text{lin}} - \kappa}{\kappa_{\text{lin}} + \kappa} \right\rangle = 0,
\]

where the subscript denotes that the EKC are taken as a linear approximation, ignoring the influence of thermoelectric phenomena on the effective electric conductivity and thermal conductivity.

In an explicit form, for a two-phase case of (7-8)
\[ \alpha_{\text{lin}}' = \frac{p\sigma_1\alpha_1\left(\sigma_{\text{lin}}' + \sigma_2'\right)(\kappa_{\text{lin}}' + \kappa_2') + (1-p)\sigma_2\alpha_2\left(\sigma_{\text{lin}}' + \sigma_1'\right)(\kappa_{\text{lin}}' + \kappa_1')}{p\sigma_1\left(\sigma_{\text{lin}}' + \sigma_2'\right)(\kappa_{\text{lin}}' + \kappa_2') + (1-p)\sigma_2\left(\sigma_{\text{lin}}' + \sigma_1'\right)(\kappa_{\text{lin}}' + \kappa_1')}, \quad (9) \]

\[ \sigma_{\text{lin}}' = \left(p - \frac{1}{2}\right)(\sigma_1 - \sigma_2) + \left(\frac{1}{2}\right)(\sigma_1 - \sigma_2)^2 + \sigma_1\sigma_2, \quad (10) \]

\[ \kappa_{\text{lin}}' = \left(p - \frac{1}{2}\right)(\kappa_1 - \kappa_2) + \left(\frac{1}{2}\right)(\kappa_1 - \kappa_2)^2 + \kappa_1\kappa_2. \quad (11) \]

For \( p = p_c = 1/2 \) from (10) and (11) it follows

\[ \sigma_{\text{lin}}'' = \sqrt{\sigma_1\sigma_2}, \quad \kappa_{\text{lin}}'' = \sqrt{\kappa_1\kappa_2}. \quad (12) \]

Equations to determine the EKC within the approximation of a self-consistent field in the general case with regard to the influence of thermoelectric phenomena on electric and thermal conductivity can be solved only numerically. According to [6] these equations are of the form

\[ pA_i + (1-p)A_2 = 1, \quad pB_i + (1-p)B_2 = 0, \quad pC_i + (1-p)C_2 = 0, \quad pD_i + (1-p)D_2 = 1, \quad (13) \]

where

\[ A_i = \frac{2}{\Delta_i}\left[\sigma_i(\chi_\alpha + \chi_\kappa) - \gamma_i(\chi_\alpha + \chi_\kappa)\right], \quad B_i = \frac{2}{\Delta_i}(\gamma_i\chi_\alpha - \chi_\alpha\gamma_i), \]

\[ C_i = \frac{2}{\Delta_i}(\gamma_i\sigma_i - \sigma_i\gamma_i), \quad D_i = \frac{2}{\Delta_i}\left[\chi_\alpha(\sigma_i + \sigma_i) - \gamma_i(\chi_\alpha + \chi_\kappa)\right], \]

\[ \Delta_i = (\sigma_i + \sigma_i)(\chi_\alpha + \chi_\kappa) - (\gamma_i + \gamma_i)^2, \quad \gamma = \sigma\alpha, \quad \chi = T^{-1}\kappa + \sigma\alpha^2. \]

As an illustration, with numerical calculations we shall consider the first composite phase to be metal and the second - semiconductor: \( \sigma_1 > \sigma_2 \), \( \kappa_1 > \kappa_2 \), \( \alpha > \alpha_1 \). For certainty, let us assume \( V_1 = 2.4 \times 10^{-6} \text{ V/K}, \quad V_2 = 2.6 \times 10^{-10} \text{ W/(m·K)}, \quad 1 = 2.6 \times 10^{-2} \text{ (Ohm·m)}^{-1}, \quad 2 = 2.6 \text{ (Ohm·m)}^{-1}, \quad T = 300 \text{ K}. \) ThermoEMF of the second phase \( \alpha_2 \) will be changed in the range \( (2.2 \times 10^{-4} - 900 \times 2.2 \times 10^{-4}) \text{ V/K} \). Generally speaking, the right boundary of \( \alpha_2 \) is strongly overrated as compared to currently available materials. With such value of \( V = 900 \times 2.2 \times 10^{-4} \text{ V/K} \) and with chosen \( \sigma_2 \) and \( \kappa_2 \), \( ZT = 12 \), which is much in excess of known values. However, in the first place, \( ZT \) of new materials is constantly growing, in the second place, large values of \( \alpha_2 \) and \( ZT \) allow a better perception of qualitative differences between the linear and nonlinear cases.

Fig. 1 shows a concentration dependence of \( ZT \) obtained within the linear and nonlinear approximations. It is evident that account of nonlinearity leads to reduction of figure of merit, and the higher \( \alpha_2 \), i.e. the higher \( ZT \), the greater this reduction. It should be noted that the difference between figures of merit in the nonlinear and linear approximations \( Z_{\text{lin}}'' - Z_{\text{lin}}' \) with \( p \to 0,1 \) tends to zero, and for a homogeneous material it is not to be observed at all. The respective ratio between the effective electric conductivity and thermal conductivity has a similar behaviour – Fig. 2.
Fig. 1. Concentration dependence of $Z_eT$ in a linear (solid line) and a nonlinear (dashed line) case: 
a) $\varepsilon=0.066\ V/K$; b) $\varepsilon=0.198\ V/K$.

Fig. 2. The influence of inhomogeneity on the effective electric and thermal conductivity. Parameter values have been taken as follows: $i=2.4\cdot10^{-6}\ V/K$, $z=19.8\cdot10^{-2}\ V/K$, $i=2.6\ W/(m\cdot K)$, $z=2.6\ W/(m\cdot K)$, $i=2.6\cdot10^7\ (Ohm\cdot m)^{-1}$, $z=2.6\ (Ohm\cdot m)^{-1}$, $T=300\ K$.

With $p=p_c=1/2$, when analytical expressions for EKC are known not only in a linear, but also in a nonlinear case [6] (5-6), the influence of nonlinearity can be distinguished explicitly. Indeed, one can readily see that (5) can be rewritten as (see.(12))

$$
\sigma_{enlin} = \sigma_{enln} \sqrt{1 + \tilde{Z}T}, \quad \kappa_{enlin} = \kappa_{enln} \sqrt{1 + \tilde{Z}T},
$$

(14)

where

$$
\tilde{Z}T = \frac{\sqrt{\sigma_1 \sigma_2}}{\sqrt{\kappa_1 \kappa_2}} \left( \frac{\alpha_1 - \alpha_2}{\sigma_{enlin}} \right)^2 \left( \frac{1}{\sigma_1} + \frac{1}{\sigma_2} \right) \frac{1}{\sqrt{\kappa_1 \kappa_2}}\sqrt{T}.
$$

(15)

Here $\tilde{Z}T$ is a dimensionless parameter hereinafter referred to as the inherent figure of merit of composite for a two-phase case at the flow threshold.

For a material that is homogeneous, at least in thermoelectric properties ($\alpha_1 = \alpha_2$), the inherent figure of merit $\tilde{Z}T = 0$. At $\tilde{Z}T \ll 1$, $\sigma_{enlin} \rightarrow \sigma_{enln}^e$, $\kappa_{enlin} \rightarrow \kappa_{enln}^e$. The increase in the inherent figure of merit $\tilde{Z}T$ results in the reduction of effective electric conductivity and the increase in effective thermal conductivity (Fig. 2), leading to a decrease in effective figure of merit $\tilde{Z}_{nlin}^e \sim \sigma_{enlin}^e / \kappa_{enlin}^e$. 

4
Unfortunately, at \( p \neq 1/2 \) the complexity of nonlinear equations (13) does not allow obtaining \( \sigma_{\text{nl}}^e \) and \( \kappa_{\text{nl}}^e \) in the explicit form and thus distinguishing \( \tilde{Z}(p) \). Numerical solutions of system (13) in the absence of analytical form of dependence of \( \sigma_{\text{nl}}^e \) and \( \kappa_{\text{nl}}^e \) on \( \tilde{Z}T \) do not allow obtaining concentration dependence \( \tilde{Z} = \tilde{Z}(p) \) even numerically. However, in a partial case, namely for composites having electric and thermal phase conductivities that meet the law of Wiedemann-Franz

\[
\frac{\sigma_1}{\kappa_1} = \frac{\sigma_2}{\kappa_2},
\]

one can numerically obtain \( \tilde{Z} = \tilde{Z}(p) \), or in more conservative terms, a function that is monotonously dependent on \( \tilde{Z}(p) \).

To distinguish from \( \sigma_{\text{nl}}^e \) and \( \kappa_{\text{nl}}^e \) the inherent figure of merit \( \tilde{Z} \) means to distinguish that part which appears with account of nonlinearity, and this part should be identical for \( \sigma_{\text{nl}}^e \) and \( \kappa_{\text{nl}}^e \). Exactly to this part the inherent figure of merit \( \tilde{Z} \) is proportional. Let us introduce the notations

\[
S(p) = \frac{\sigma_{\text{lin}}^e(p)}{\sigma_{\text{nl}}^e(p)}, \quad K(p) = \frac{\kappa_{\text{lin}}^e(p)}{\kappa_{\text{nl}}^e(p)}.
\]

In the case of \( p = 1/2 \)

\[
S(1/2) = K(1/2) = \sqrt{1 + \tilde{Z}T},
\]

the following holds true

\[
S(1/2) / K(1/2) = 1.
\]

Suppose that at \( p \neq 1/2 \) there is a certain function identical for \( \sigma_{\text{nl}}^e \) and \( \kappa_{\text{nl}}^e \) and determining the influence of nonlinearity. Then using \( S(p) \) and \( K(p) \) one can construct a certain combination similar to (19), that at any \( p \) will be identical to unity and at \( p = 1/2 \) will coincide with (19). As is shown by numerical calculation to an accuracy of \( 2 \cdot 10^{-6} \), such combination is \( S(p)/K(1-p) \). With fulfillment of (16) the following equation holds true

\[
S(p)/K(1-p) = 1.
\]

Then the value directly related to the inherent figure of merit \( \tilde{Z}(p) \), can be determined as (see. (18)) a certain function of \( a(p) = S(p)K(1-p) \) and \( b(p) = S(1-p)K(p) \)

\[
\tilde{Z}(p)T = M(a(p), b(p))^{-1}.
\]

This function \( M(a,b) \) should satisfy the following natural conditions: be 1) continuous, 2) symmetric \( M(a,b) = M(b,a) \), 3) the average of identical functions \( a(p) = b(p) \) should be equal to their total value \( M(a,a) = a \). These requirements are nothing but the so-called axioms of the average first formulated by A.I.Kholmogorov [12]. In his work it was shown that if function \( M(a,b) \) satisfies these axioms (for more than two variables one more axiom must be met), then \( M(a,b) \) is called the average value of \( a, b \) and can be written in the most general form as

\[
M(a,b) = \psi \left( \frac{\varphi(a) + \varphi(b)}{2} \right).
\]

where \( \varphi \) is a continuous, strictly monotonous function, and \( \psi \) is the inverse to it.
All known types of averages, such as arithmetic mean, quadratic mean, geometric mean, harmonic mean, etc are a partial case (22).

Thus, \( M(a(p), b(p)) \) (21) can be written in the form of various averages and is not determined unambiguously

\[
M_1(p) = \frac{S(p)K(1-p) + S(1-p)K(p)}{2}, \quad (23)
\]

\[
M_2(p) = 2\frac{S(p)K(1-p)S(1-p)K(p)}{S(p)K(1-p) + S(1-p)K(p)}, \quad (24)
\]

\[
M_3(p) = \sqrt{S(p)K(1-p)S(1-p)K(p)}, \ldots \quad (25)
\]

In all these cases \( \tilde{Z}(p=1/2) \) from (21) coincides with its value \( \tilde{Z} \) from (15). Fig. 3 shows a concentration dependence of \( \tilde{Z}(p)T \) from (21) for three types of function \( M \) (23), (24) and (25). As can be seen from Fig.3, the difference between the concentration dependences \( \tilde{Z}(p)T \) for selected numerical values of local coefficients is slight.

![Fig. 3. Concentration dependence of the inherent figure of merit, related to average \( M \), (top-down in order) (23), (24), (25).](image)

Note that among the axioms of average the axiom of symmetry \( M(a,b) \) is, in our view, natural for the determination of the inherent figure of merit. When this axiom is abandoned, the class of functions for \( \tilde{Z}(p)T \) from (21) is expanded considerably.

It is of interest to study the inherent figure of merit \( \tilde{Z} \) in a three-dimensional case. It is also interesting to consider \( \tilde{Z} \) beyond the approximation limits of a self-consistent field (even in a two-dimensional case). Apparently, it is possible only with numerical simulation of thermoelectric processes in the inhomogeneous media, with the use of special application packages, and will be the subject of a separate publication.

The authors express their gratitude to M.I. Zhenirovsky for the discussion of problems covered and help in numerical solution of a system of nonlinear equations.
Conclusions

1. In addition to figure of merit (Ioffe’s number) of composite material $Z = \sigma \alpha^2 / \kappa$, characterizing «external» thermal into electric energy conversion (for example, thermocouple efficiency) there is yet another characteristic, i.e. the inherent figure of merit $\tilde{Z}$, governing energy conversion within a composite.

2. The inherent figure of merit $\tilde{Z}$ determines renormalization of composite effective thermal and electric conductivity due to thermoelectric phenomena and is a limiting factor for the effective figure of merit of composite material.

References

1. Ioffe A.F. Energy fundamentals of semiconductor thermopiles. Selected works. V. 2. – Leningrad: Nauka Publ., 1975. – P. 271-295.

2. Snarskii A.A., Tomchuk P.M. Kinetic phenomena in macroscopically inhomogeneous media (Review) // Ukrainsky Fizychny Zhurnal. – 1987. – V.32. – P.66-92.

3. Snarskii A.A., Bezsudnov I.V. Thermoelectric properties of macroscopically inhomogeneous composites // J. of Thermoelectricity. – 2005. – N3. – P. 31-47.

4. Dykhne A.M. Conductivity of a two-dimensional two-phase system // – Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki. – 1970. – V.59. – P. 110-115.

5. Balagurov B.Ya. Reciprocity ratios in a two-dimensional flow theory // Zhurnal Eksperimentalnoi. i Teoreticheskoi Fiziki. – 1981. – V.81. – P.665-671.

6. Balagurov B.Ya. On thermoelectric properties of inhomogeneous thin films // Fizika i Tekhika Poluprovodnikov. – 1982. –16. – N2. – P. 259-265.

7. Dykhne A.M., Snarskii A.A., Zhenirovsky M.I. Stability and chaos in two-dimensional randomly inhomogeneous media and LC-arrays // Uspekhi Fizicheskikh Nauk. –2004. – 174. – N8. – P. 887-894.

8. Bruggeman D.A.G. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen, II // Ann. Physik. – 1936. – V.25. – P.645-672.

9. Shvidler M.I. Statistic hydrodynamics of porous media. – M.: Nedra Publ

10. Vinogradov A.P. Electrodynamics of composite materials. – M.: Editorial URSS, 2001. – 208 p.

11. Webman I., Jortner J., Cohen M.H. // Phys.Rev.B. – 1977. – V.16. – P.2950.

12. Kholmogorov A.N. On the determination of average. Selected works. – M.: Nauka Publ., 1985. – P. 136-138.