Performance of Miniature Thermoelectric Energy Converters: Size and Nonlinear Phenomena

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Abstract

A theory of efficiency for microminiature thermoelectric generator is suggested. The theory takes into consideration boundary effects on the characteristic length and nonlinearity of kinetic coefficients. The system of equations for energy balance of electrons and phonons with electron-phonon interaction in limited samples was solved by perturbation theory method. The consideration of the nonlinearity of kinetic coefficients leads to insignificant reduction of the TEG's efficiency. On the contrary, a mismatch between electrons' and phonons' temperatures at the interface is resulted in increase of the efficiency.

Introduction

The microminiaturization of electronic and photoelectronic components is the objective tendency of modern technics. This trend automatically leads to the microminiaturisation of thermoelectric energy converters that have to supply power for such microelectronic components. On the other hand the essentially novel structures with submicron and nano-inhomogeneities were suggested recently as very effective thermoelectrics; the structures use different kinds of quantum superlattices. The sizes of such structures that are used as materials for thermoelectric generators are comparable with microscopic characteristic lengths of charge carriers and phonons. It is obvious that traditional methods of calculation of the efficiency of thermoelectric generators should be reconsidered in the In researched conditions [1,2].

The thermoelectric theory in microminiature thermoelectric coolers was proposed in [3]. The theory [3] based on the concept of the mismatch between electrons' and phonons' temperatures $\Theta = T_e - T_p$ [1, 2]. Two followed factors lead to the mismatch: (a) the nonlinearity of kinetic coefficients and (b) effects at interfaces between semiconductor legs and metal junctions.

An analytical solution of the equation of heat transport can not be reached even in traditional problem formulation (if the mismatch between electrons' and phonons' temperatures is not considered). Different methods are used for approximate solution of the equation of heat transport and for calculation of the TEG's efficiency (see [2, 4]): the approximation of average parameters, the infinite cascades approach, numerical calculations, and the assumption of relatively small current terms.

In the present paper we suggest a theory of efficiency for microminiature thermoelectric energy converter. The theory takes into consideration the mismatch between electrons' and phonons' temperatures, boundary effects on the characteristic length and temperature dependence of all kinetic coefficients. The principle of energy balance's equations is used.

A thermoelectric circuit consisting from homogeneous isotropic semiconductor plate (for definiteness of n-type) by the length $2a$ and the resistance R_s (index s) closed on the metal loading R_m (index m) is examined. The one-dimensional problem is investigated (Fig.1).

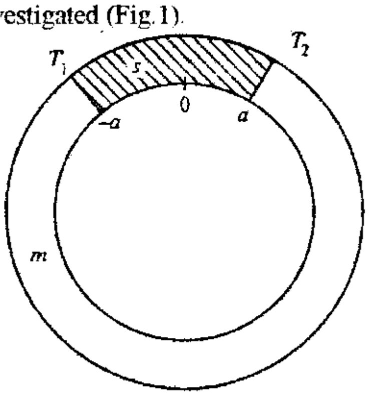

Fig.1. Electric circuit

Method of solution

Thermoelectrics as a rule have high carriers' concentration, therefore the approach of electrons' (or holes') and phonons' temperatures can be used in the theory [1]. Thus the following equations for electrons and phonons heat flow densities $\vec{q}_{e,p}$ and for the density of current $\vec{j}$ can be introduced [2]:

$$\vec{q}_e = -\kappa_e(T_e)\nabla T_e + \Pi(T_e)\vec{j}\,, \qquad (1)$$

$$\vec{q}_e = -\kappa_p(T_p)\nabla T_p\,, \qquad (2)$$

$$\vec{j} = \sigma(T_e)\vec{E}^* - \sigma(T_e)\alpha(T_e)\nabla T_e\,, \qquad (3)$$

where $\sigma(T_e)$, $\alpha(T_e)$, $\kappa(T_e)$, $\Pi(T_e) = T_e\alpha(T_e)$ are the coefficients of electric conductivity, thermo-emf, heat conductivity of electrons and Peltier coefficient, $\kappa(T_p)$ – coefficient of phonons heat conductivity, $\vec{E}^* = -\nabla\tilde{\varphi}$, $\tilde{\varphi}$ - electrochemical potential, $T_{e,p}$ – electrons' and phonons' temperatures.

Thus the equations of energy balance of electrons' and phonons' are the main equations of the problem. The temperatures and the electrochemical potential are changing only along the x- axis (Fig.1). In this case the energy balance determines by the equations [2]:

$$\kappa_e(T_e)\frac{d^2T_e}{dx^2} + \frac{d\kappa_e(T_e)}{dT_e}\left(\frac{dT_e}{dx}\right)^2 + \frac{j^2}{\sigma(T_e)} - \tau_T(T_e)\frac{dT_e}{dx}j = P(T_e,T_p)(T_e - T_p) \qquad (4)$$

$$\kappa_p(T_p)\frac{d^2T_p}{dx^2} + \frac{d\kappa_p(T_p)}{dT_p}\left(\frac{dT_p}{dx}\right)^2 = -P(T_e,T_p)(T_e - T_p)\,, \qquad (5)$$

where the function $P = P(T_e, T_p)$ is responsible on electrons-phonons interaction. $\tau_T(T_e)=\alpha(T_e)\dfrac{d\alpha(T_e)}{dT_e}$ - the Thomson coefficient.

The equations (4) and (5) should be added by the equation of continuity for electric current

$$\sigma(T_e)\frac{dE^*}{dx}+\frac{d\tau(T_e)}{dT_e}E^*-\sigma(T_e)\alpha(T_e)\frac{d^2T_e}{dx^2}= \\ =\frac{d(\sigma(T_e)\alpha(T_e))}{dT_e}\left(\frac{dT_e}{dx}\right)^2 \quad (6)$$

The typical for thermoelectric generator heat boundary conditions have the form (Fig.1)

$$T_{e,p}\big|_{x=-a}=T_1;\quad T_{e,p}\big|_{x=a}=T_2 \quad (7)$$

The Kirchhoff equation realizes the electrical boundary condition:

$$J(R_S(T_e)+R_m)+\int_{-a}^{a}\alpha(T_e)\frac{dT_e}{dx}dx=0 \quad (8)$$

where $R_s(T_e)$, and R_m – electric conductivity of a semiconductor's thermoelectric and a metal, J – the electric current.

Let us use the perturbation method [1, 2] for solution of the system of equations (4)-(6) at the boundary conditions (7), (8) with the small parameter γ:

$$\gamma\equiv\frac{T_2-T_1}{T^*}<<1,\quad T^*=\frac{T_2+T_1}{2} \quad (9)$$

We can decompose the temperatures, and each kinetic coefficient K in (4)-(6) by the parameter γ:

$$T_{e,p}=T^*+T_{e,p}^{(1)}+T_{e,p}^{(2)}+T_{e,p}^{(3)}+\ldots \quad (10)$$

$$K(T_{e,p})=K(T^*)+\frac{dK}{dT_{e,p}}\bigg|_{T_{e,p}=T^*}(T_{e,p}^{(1)}+T_{e,p}^{(2)}+\ldots)+ \\ +\frac{1}{2}\frac{d^2K}{dT_{e,p}^2}\bigg|_{T_{e,p}=T^*}(T_{e,p}^{(1)}+T_{e,p}^{(2)}+\ldots)^2+\ldots \quad , \quad (11)$$

the indexes in bracket numbers the order on the parameter γ.

As a result the densities of heat flow (1)-(2) and the density of electric current (3) can be written in the form

$$j=j^{(1)}+j^{(2)}+j^{(3)}+\ldots,\quad q_{e,p}=q_{e,p}^{(1)}+q_{e,p}^{(2)}+q_{e,p}^{(3)}+\ldots \quad (12)$$

Then the equations (4)-(6) are break up into unlimited set of linear differential equations of different orders on the parameter γ. A method of solution of the system of equation can be found in [2].

Let us separate two kinds of effects that influence on the magnitude of TEG's efficiency. The effects connect with the volume's and the interface's mismatches between electrons' and phonons' temperatures.

Efficiency, volume temperatures' mismatch

The efficiency of a TEG can by determined by the formula

$$\eta=\frac{q(a)-q(-a)}{q(a)} \quad (13)$$

Taking into consideration the equation (12) and the conditions $q^{(2n)}(a)=-q^{(2n)}(-a)$, $q^{(2n+1)}(a)=q^{(2n+1)}(-a)$ (because $q^{(n)}\sim\gamma^n$) we can transform (13) into

$$\eta=2\frac{q^{(2)}(a)+q^{(4)}(a)+\ldots}{q^{(1)}(a)+q^{(2)}(a)+q^{(3)}(a)+q^{(4)}(a)+\ldots} \quad . \quad (14)$$

If we leave only the terms $q^{(1)}(a)$ and $q^{(2)}(a)$ in (14) the efficiency will have the form

$$\eta_1=2\frac{q^{(2)}(a)}{q^{(1)}(a)+q^{(2)}(a)} \quad . \quad (15)$$

This one is the well-known Ioffe formula [4].

Let us leave the terms including $q^{(4)}(a)$ in (14). With the exactitude of the second order on parameter γ (γ^3 << 1) we can obtain for the efficiency

$$\eta=\eta_0\left[1-\frac{q^{(2)}(a)}{q^{(1)}(a)}+\left(\frac{q^{(2)}(a)}{q^{(1)}(a)}\right)^2+\frac{q^{(4)}(a)}{q^{(2)}(a)}-\frac{q^{(3)}(a)}{q^{(1)}(a)}\right], \quad (16)$$

where

$$\eta_0=2\frac{q^{(2)}(a)}{q^{(1)}(a)}=\frac{\gamma(1-\nu)\nu\bar{Z}T^*}{1+\nu\bar{Z}T^*} \quad . \quad (17)$$

Here $\nu=\dfrac{R_s}{R_s+R_m}$, $\bar{Z}=\dfrac{\bar{\alpha}^2}{\bar{\rho}\bar{\kappa}}$, $\bar{\rho}=\dfrac{1}{\bar{\sigma}}$; hereinafter the feature mean the averaging of a kinetic coefficient K, the prime mean the derivative:

$$\bar{K}=K(T_{e,p})\Big|_{T_{e,p}=T^*},\quad \bar{K}'=\frac{dK(T_{e,p})}{dT_{e,p}}\Big|_{T_{e,p}=T^*},$$

$$\bar{K}''=\frac{d^2K(T_{e,p})}{dT_{e,p}^2}\Big|_{T_{e,p}=T^*}.$$

The expression (17) for the efficiency includes only the terms with the first order on parameter γ when (16) includes the terms of the first and the second orders.

The correct formula for the efficiency (16) can be present as

$$\eta=\eta_0\left(1-\frac{1}{2}\eta_0+g_\eta\right) \quad (18)$$

where

$$g_\eta=\frac{\gamma^2}{12}\left\{3\frac{(1-\nu)^2(\nu\bar{Z}T^*)^2}{(1+\nu\bar{Z}T^*)^2}+\frac{\bar{\tau}_T'T^*}{\bar{\alpha}}-\frac{\bar{\tau}_T}{\bar{\alpha}}-\frac{\nu\bar{\rho}''}{\bar{\rho}}T^{*2}-\right. \\ -\frac{2\nu\bar{\rho}'T^*}{\bar{\rho}}S-\frac{1}{1+\nu\bar{Z}T^*}\left[\frac{\bar{\kappa}_e''+\bar{\kappa}_p''}{2\bar{\kappa}}T^{*2}+\frac{\nu\bar{\tau}_T'\bar{Z}}{\bar{\alpha}}T^{*2}-\right. \\ \left.\left.-\frac{\nu^2\bar{\rho}''\bar{Z}}{2\bar{\rho}}T^{*3}+\nu\bar{Z}T^*\left(\frac{\bar{\tau}_T}{\bar{\alpha}}-\frac{\nu\bar{\rho}'}{\bar{\rho}}T^*\right)(1+S)\right]\right\},$$

The parameter S has the form

$$S=w_1T^*+\frac{3\bar{\kappa}_pw_2T^*}{\bar{\kappa}(ka)^2}\left(1-\frac{thka}{ka}\right), \quad (19)$$

where

$$w_1=\frac{\bar{\kappa}_e'+\bar{\kappa}_p'}{\bar{\kappa}}+\nu^2\bar{Z}+\nu^2\bar{Z}\frac{\bar{\tau}_T}{\bar{\alpha}},$$

$$w_2=\frac{\bar{\kappa}_e'}{\bar{\kappa}_e}-\frac{\bar{\kappa}_p'}{\bar{\kappa}_p}+\nu^2\bar{Z}\frac{\bar{\kappa}}{\bar{\kappa}_e}+\nu\bar{Z}\frac{\bar{\tau}_T\bar{\kappa}}{\bar{\alpha}\bar{\kappa}_e} \quad ,$$

$$\bar{\kappa}=\bar{\kappa}_e+\bar{\kappa}_p .$$

The parameter k corresponds to the inverse of cooling length [2]: $k^2 = \frac{\bar{P}}{\bar{\chi}}$, $(\bar{\chi}^{-1} = \bar{\kappa}_e^{-1} + \bar{\kappa}_p^{-1})$. For estimation we can obtain $k^2 \sim \frac{\bar{\kappa}}{\bar{\kappa}_p} \frac{\bar{\nu}_p \bar{\nu}_\varepsilon}{\bar{V}_T^2}$, where $\bar{\nu}_{\varepsilon,p}$ - the average electrons' scattering frequency of energy and of momentum, $\bar{V}_T$ - the heat velocity of electrons.

The efficiency (17) takes into account temperature dependences of all kinetic coefficients. Moreover it includes information about the mismatch between electrons' and phonons' temperatures; a value of the parameter S depends on the mismatch.

Let us study two different cases:

1. TEG with bulk legs: $k^2a^2 >> \max(1, 3\bar{\kappa}_p / 3\bar{\kappa}_e)$.

In this situation we have

$$S = \frac{\bar{\kappa}_e' + \bar{\kappa}_p'}{\bar{\kappa}} T^* + \nu \frac{\bar{\tau}_T}{\bar{\alpha}} \bar{Z} T^* + \nu^2 \bar{Z} T^*. \qquad (20)$$

It is possible to show that such value (20) is the same as value that gives the one-temperature theory (the theory that does not take into consideration mismatch between electrons' and phonons' temperatures). Let us underline that formula (20) gives the possibility of correct account of the nonlinearity (temperature dependences of all kinetic coefficients). Fig.2 presents efficiency as function of parameter γ for a typical thermoelectric based on Bi_2Te_3. The curves correspond to Ioffe formula (15) and to formula (19) with the parameter S (20). The relative changing of the efficiency $\frac{\eta_I - \eta}{\eta_I}$ also presented at Fig.2. We see that in any case correct account of the nonlinearity leads to reduction of the efficiency. We can show that this conclusion valid for any thermoelectric with real kinetic coefficients.

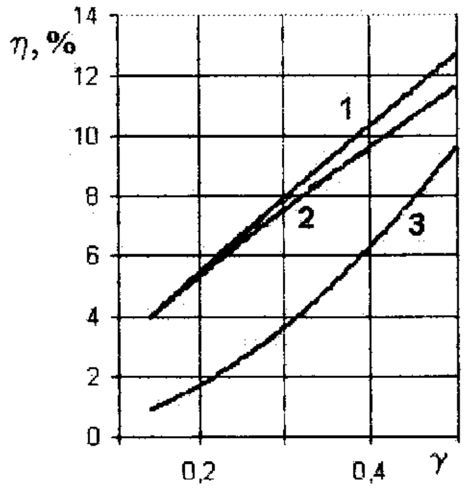

Fig.2. Calculated efficiency (curve 2), Ioffe efficiency (curve 1) and the relative changing of the efficiency $\frac{\eta_I - \eta}{\eta_I}$ (curve 3) as functions of γ

2. TEG with limited legs. Let us examine two following cases:

2.1. $ka << 1$

We have from (19) in this case $S = \frac{\bar{\kappa}_e'}{\bar{\kappa}_e} T^* + \nu \frac{\bar{\alpha}^2}{L}\left(\nu + \frac{\bar{\tau}_T}{\bar{\alpha}}\right)$, where L is Lorentz number.

2.2. $1 << k^2a^2 << \frac{3\bar{\kappa}_p}{\bar{\kappa}_e}$

It can be received in these conditions:

$$S = \frac{3\bar{\kappa}_p}{\bar{\kappa}_e k^2 a^2}\left(-\frac{\bar{\kappa}_p'}{\bar{\kappa}_p} T^* + \nu \frac{\bar{\tau}_T}{\bar{\alpha}} \bar{Z} T^* + \nu^2 \bar{Z} T^*\right).$$

We can see that in both cases the main terms in the expression for efficiency (18) contain the parameter S. It can be proved that the efficiency will increase in TEGs with limited legs due to boundary effects if the inequality $\frac{\bar{\kappa}_e'}{\bar{\kappa}_e} T^* > 1$ takes place. Thus, in the case of limited legs the additive to efficiency will has the sign "plus" if electronic heat conductivity quickly enough increase with the temperature. But increasing of the relative changing of the efficiency $\frac{\eta - \eta_\infty}{\eta_\infty}$ for typical cases does not exceed few percents (η_∞ - the efficiency of a TEG with bulk legs).

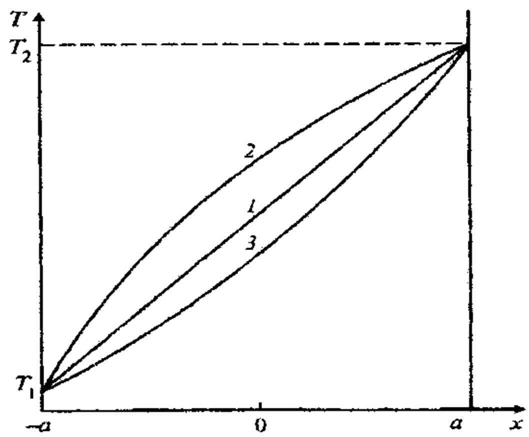

Fig.3. Mismatch between electrons' and phonons' temperatures in the body of a sample

The character of the mismatch between electrons' and phonons' temperatures in the body of a sample illustrates Fig.3. Let us underline that the volume mismatch $\Theta = T_e - T_p$ is proportional to γ^2.

Efficiency, boundary temperatures' mismatch

The boundary conditions (7) do not take into consideration the mismatch between electrons' and phonons' temperatures at contacts between legs and metal junctions; we can not neglect such mismatch in limited samples (if $ka \leq 1$) [2]. The conditions (7) can be used confidently only if $ka << 1$.

Let us consider one of legs of semiconductor TEG (index s) that is limited by metal junctions (index m). One can neglect temperature dependences of kinetic coefficients in conditions $ka \le 1$, so let us be limited only to the first order on γ. The boundary condition at the interface Σ now can be written as

$$-\kappa_p \frac{dT_p}{dx}\bigg|_\Sigma^m = -\kappa_p \frac{dT_p}{dx}\bigg|_\Sigma^S,$$

$$\left(-\kappa_e \frac{dT_e}{dx} + \alpha T_e j\right)\bigg|_\Sigma^m = \left(-\kappa_e \frac{dT_e}{dx} + \alpha T_e j\right)\bigg|_\Sigma^S.$$

On external borders of the leg the temperatures of hot T_1 and cold T_2 metal contacts usually are considered: $T|_{x=-a-b} = T_1$, $T|_{x=a+b} = T_2$.

The system of equations for energy balance of electrons and phonons in semiconductor leg and metal junctions at above boundary conditions was solved in one-dimension case. The solution has a complicated form, and it is not presented here.

From the analysis of the solution it is possible to be convinced that the thermoelectric current always reduces the mismatch of quasi-particles temperatures. The order of the mismatch is

$$\Theta_{ms} \approx \frac{T_1 - T_2}{2k_m a}.$$

The relative changing of the efficiency in comparison with the efficiency that was calculated in one-temperature approximation η_1 (if the effect of temperatures mismatch is not take into account) is

$$\frac{\eta}{\eta_1} \approx \left(1 + \frac{\kappa_{mp}}{\kappa_m}\frac{\Theta_{ms} - \Theta_{sm}}{T_1 - T_2}\right)^2.$$

It can be proved that in any case $\Theta_{ms} - \Theta_{sm} > 0$. Therefore the mismatch in all cases results in increase of the efficiency. Let's emphasize, that relative increase of efficiency will be more appreciable at enough low temperatures as downturn of temperature usually causes reduction of k.

Fig.5 illustrates the character of the mismatch between electrons' and phonons' temperatures in the interface. Very important that the interface mismatch is proportional to γ. According to our assumption (9) the interface's mismatch is more majorly than the volume's mismatch. Therefore in limited samples ($ka \le 1$) the interface's mismatch suppress the volume's mismatch; then in limited samples the mismatch in all cases leads to increase of the efficiency.

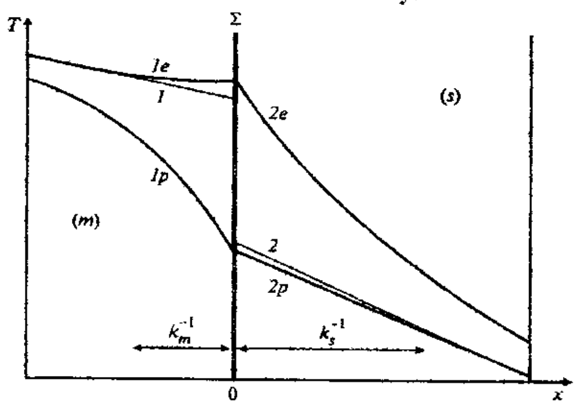

Fig.4. Mismatch between electrons' and phonons' temperatures at the interface Σ

Conclusions

Two kinds of effects influence on the magnitude of a TEG's efficiency:

A. Volume effects

This type of effects results in additive to the traditional TEG's efficiency proportional to the square of parameter γ (γ^2).

1. Temperature dependence of kinetic coefficients of a thermoelectric leads to the mismatch between electrons' and phonons' temperatures in the body of legs. In real thermoelectrics the electrons' temperature exceeds the phonons' temperature: $\Theta = T_e - T_p > 0$.

2. The correct account of the nonlinearity of kinetic coefficients leads to reduction of the TEG's efficiency in any real case. The relative changing of the efficiency $\frac{\eta_1 - \eta}{\eta_1}$ due to temperature dependence of kinetic coefficients can exceed 10 percents.

3. In the limited legs $ka \le 1$ the efficiency will increase if the inequality $\frac{\bar{\kappa}_e'}{\bar{\kappa}_e}T^* > 1$ takes place (electronic heat conductivity quickly enough increase with the temperature). Increasing of the relative changing of the efficiency $\frac{\eta - \eta_\infty}{\eta_\infty}$ for typical cases does not exceed a little percents (η_∞ - the efficiency of a TEG with bulk legs).

B. Interface effects

This type of effects results in additive to the efficiency proportional to the parameter γ.

1. The order of the interface's mismatch is $\Theta_{ms} \approx \frac{T_1 - T_2}{2k_m a}$.

2. The interface's mismatch in all cases leads to increase of the TEG's efficiency. The increasing strongly depends on a thickness of a sample, and starts to be noticeable if the thickness becomes commensurable with the cooling length of the material.

3. The relative increase of efficiency will be more appreciable at enough low temperatures.

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