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The relationship between the thermoelectric generator efficiency and the device engineering figure of merit $Z_{d,eng}$. The maximum efficiency η_{max}

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Thermoelectric materials are used today in thermoelectric devices for heat to electricity(thermoelectric generators-TEG) or electricity to heat(heat pumps) conversion in a large range of applications. In the case of TEGs the final measure of their performance is given by a quantity named the maximum efficiency which shows how much from the heat input is converted into electrical power. Therefore it is of great interest to know correctly how much is the efficiency of a device to can make commercial assessments. The concept of engineering figure of merit, Z_{eng}, and engineering power factor, P_{eng}, were already introduced in the field to quantify the efficiency of a single material under temperature dependent thermoelectric properties, with the mention that the formulas derivation was limited to one leg of the thermoelectric generator. In this paper we propose to extend the concept of engineering figure of merit to a thermoelectric generator by introducing a more general concept of device engineering thermoelectric figure of merit, $Z_{d,eng}$, which depends on the both TEG materials properties and which shall be the right quantity to be used when we are interested in the evaluation of the efficiency. Also, this work takes into account the electrical contact resistance between the electrodes and thermoelement legs in an attempt to quantify its influence upon the performance of a TEG. Finally, a new formula is proposed for the maximum efficiency of a TEG. [http://dx.doi.org/10.1063/1.4979328]

I. INTRODUCTION

The history of the thermoelectric generators starts back in 1821 with the discovery of the heat conversion into electricity by the German physicist Thomas Johann Seebeck into a closed loop formed by two different metals for which a temperature difference was applied between junctions.This is called Seebeck effect. Today, thermoelectric generators use the Seebeck effect to convert heat into electricity by means of thermocouple devices(TCDs) (Fig. 1), packed inside the TEG, at a certain efficiency.

Mathematically, the TEG efficiency is given by the ratio between the input heat rate, $\dot{Q}_{in}$, into the TEG(at hot junction) and the electrical power, $P_{e,out}$, dissipated in an external load:

$$\eta = \frac{P_{e,out}}{\dot{Q}_{in}} \tag{1}$$

An TEG contains at least one TCD (Fig. 1) which is the main element of energy conversion, a hot source, a heat sink and mechanical parts with the role of facilitating the heat transfer from the hot source to the TCD and from this one to the heat sink and also to pack and accommodate the TCD in the generator ensemble.

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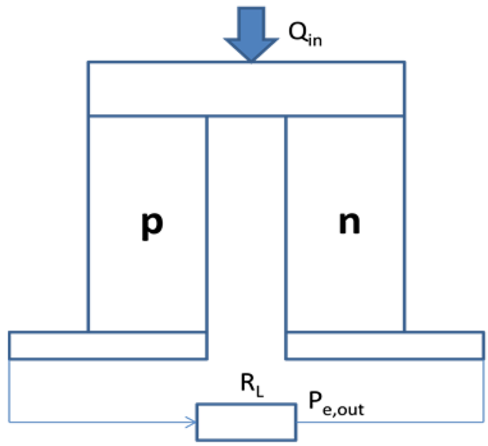

FIG. 1. The thermocouple device, TCD, and the connection to an external load.

The TEG efficiency as defined by (1) depends on the temperatures of the hot and cold side of a TCD and on a quantity named the device figure of merit, Z_d.

Almost one half of a century ago Ioffe derived the expression of the TCD figure of merit Z_d:[1]

$$Z_d = \frac{(S_p + |S_n|)^2}{(\sqrt{k_n \rho_n} + \sqrt{k_p \rho_p})^2} \tag{2}$$

where S_p, ρ_p, k_p, S_n, ρ_n, k_n are the Seebeck coefficient, electrical resistivity and thermal conductivity of the p-type and respectively n-type legs of the TCD. From equation (2) we see that the TCD figure of merit is a function of thermoelectric properties of both TCD legs. The last ones are in most cases temperature dependent so the Z_d is temperature dependent.

In Ref. 1 the maximum efficiency of a TCD it is also derived and it has the following mathematical expression:

$$\eta_{max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + Z_d T_m} - 1}{\sqrt{1 + Z_d T_m} + \frac{T_c}{T_H}} \tag{3}$$

where: $T_{H,}$ T_C, T_m=(T_H+ T_C)/2 are respectively the hot side temperature, cold side temperature and average temperature and Z_d is given by equation (2).

The first observation that we make in this paper is that many authors[2–5] report on the thermoelectric efficiency as a function of the Carnot efficiency and the "material" figure of merit ZT($ZT=S^2T/\rho k$). This way of defining efficiency is however incomplete because the efficiency is a quantity which characterizes a TCD, a device build up from two, n and p-type, materials so it cannot be characterized by one material figure of merit but an overall Z_dT shall be used instead. In the case discussed in this paper Z_d is given by the equation (2) and is therefore a function of both materials thermoelectric properties. When substituted in (3), this equation correctly describes the efficiency of a TCD.

The second observation is that the figure of merit as described by equation (2) is temperature dependent in the sense that at a given temperature the figure of merit has a certain value. This formula cannot be used directly in equation (3) due to the simple fact that it doesn't have a definition for a double temperature dependence as the efficiency is(on T_h and T_c). For this reason, in practice, two approximations are used to define the figure of merit when a temperature interval is employed.[6–8] One of them is to calculate the average Z_d using the integral way, i.e. $Z_{d,mean} = \frac{1}{\Delta T}\int_{T_c}^{T_h} Z_d\,(T)\,dT$ and the other one is to calculate Z_d in the T_m value, i.e. $Z_{d,m} = Z_d(T_m)$,with T_m=(T_h+T_c)/2.

When the above figures of merit values are substituted in equation (3) the resulted efficiencies, as we shall demonstrate in this paper, are overestimating the one calculated based on the *device* engineering figure of merit. The last one and the maximum efficiency together with the mathematical approach to obtain them is introduced in the next paragraph.

II. THEORY

In this section the derivation of the device engineering figure of merit in absence of Thompson effect will be done. We'll start from Fig. 2 in which the main heat transfer mechanisms which take place in a TCD when subjected to a temperature difference are presented.

Based on this figure and taking into account the efficiency definition, i.e. eq. (1), we shall calculate first the heat rate that enters into the device, $\dot{Q}_{in}$ (use the notation $Q_{in} = \dot{Q}_{in}$ for simplicity), which is given by:

$$Q_{in} = Q_{F,p} + Q_{F,n} + Q_{P,p} + Q_{P,n} - Q_{J,p} - Q_{J,n} + Q_{tot,c} \tag{4}$$

where: $Q_{F,p}$, $Q_{F,n}$ are, respectively, the Fourier heat rates entering the p and n materials, $Q_{P,p}$, $Q_{P,n}$ are the Peltier heat rates at the materials p and m and n and m interfaces, $Q_{J,p}$, $Q_{J,n}$ are the heat rates due to Joule heating in p and n materials and $Q_{tot,c}$ is the Joule heating due to the total contact resistances.

Substituting in eq. 4 the definition of each heat rate and taking into account that the thermoelectric properties, S, ρ, k, are temperature dependent we obtain:

$$\begin{aligned} Q_{in} &= \frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT + \pi_{mn} I + \pi_{pm} I - \frac{1}{2}I^2 r_p - \frac{1}{2}I^2 r_n + I^2 R_c \\ &= \frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT + (S_m - S_n)T_h I + \left(S_p - S_m\right)T_h I - \frac{1}{2}I^2 r_p - \frac{1}{2}I^2 r_n + I^2 R_c \\ &= \frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT + \left(S_p + |S_n|\right)T_h I - \frac{1}{2}I^2 r_p - \frac{1}{2}I^2 r_n + I^2 R_c \end{aligned} \tag{5}$$

where: A_p and A_n are the cross section areas of the p and n legs, π_{mn} and π_{pm} are the Peltier coefficients of the interfaces mn and pm, r_p and r_n are the electrical resistances, L is the legs length, I is the close circuit electrical current through the TCD and R_c is the total contact resistance.

The electrical power dissipated in the load resistor is:

$$P_{e,out} = I^2 R_L \tag{6}$$

Thus, using eq. (1), the TCD efficiency has the following expression:

$$\eta = \frac{I^2 R_L}{\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT + \left(S_p + |S_n|\right)T_h I - \frac{1}{2}I^2 r_p - \frac{1}{2}I^2 r_n + I^2 R_c} \tag{7}$$

Introducing the notation $= \frac{R_L}{R_c+r_p+r_n}$, $r = \frac{R_c}{r_p+r_n}$ and taking into account that $I = \frac{V_{oc}}{R_L+R_c+r_p+r_n}$ $= \frac{V_{oc}}{(R_c+r_p+r_n)(m+1)}$, where V_{oc} is the Seebeck open circuit generated voltage we obtain the following

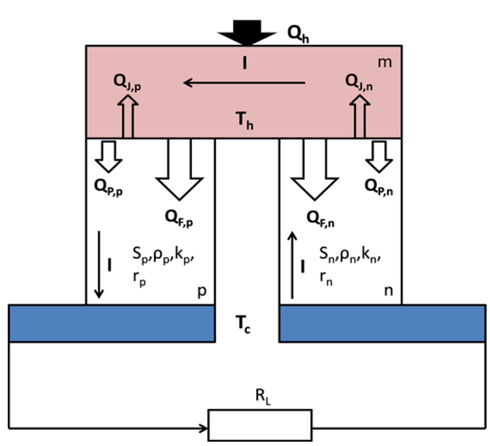

FIG. 2. The TCD and the main heat transfer mechanisms.

expression for (7):

$$\eta = \frac{\frac{{V_{oc}}^2 R_L}{(R_c+r_p+r_n)^2(m+1)^2}}{\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT + \frac{V_{oc}T_h(S_p+|S_n|)}{(R_c+r_p+r_n)(m+1)} - \frac{{V_{oc}}^2(r_p+r_n)}{2(R_c+r_p+r_n)^2(m+1)^2} + \frac{{V_{oc}}^2 R_c}{(R_c+r_p+r_n)^2(m+1)^2}}$$
$$= \frac{\frac{m}{(m+1)}}{\frac{(m+1)(r+1)(r_p+r_n)\left(\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT+\frac{A_n}{L}\int_{T_c}^{T_h} k_n dT\right)}{{V_{oc}}^2} + \frac{T_h(S_p+|S_n|)}{V_{oc}} - \frac{1}{2(m+1)(r+1))} + \frac{r}{(m+1)(r+1)}} \tag{8}$$

By writing:

$$r_{p,n} = \frac{1}{\Delta T}\frac{L}{A_{p,n}}\int_{T_c}^{T_h} \rho_{p,n} dT \tag{9}$$

and substituting this expressions in (8) we obtain:

$$\eta = \frac{\frac{m}{(m+1)}}{\frac{(m+1)(r+1)\left(\frac{L}{A_p}\int_{T_c}^{T_h} \rho_p dT+\frac{L}{A_n}\int_{T_c}^{T_h} \rho_n dT\right)\left(\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT+\frac{A_n}{L}\int_{T_c}^{T_h} k_n dT\right)}{\Delta T{V_{oc}}^2} + \frac{T_h(S_p+|S_n|)}{V_{oc}} - \frac{1}{2(m+1)\,(r+1))} + \frac{r}{(m+1)(r+1)}} \tag{10}$$

Following the idea of Ioffe[1] the TCD efficiency given by (10) is maximum when for certain values of S, ρ and k and an arbitrary value of the ration m and r the expression:

$$RK = \left(\frac{L}{A_p}\int_{T_c}^{T_h} \rho_p dT + \frac{L}{A_n}\int_{T_c}^{T_h} \rho_n dT\right)\left(\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT\right) \tag{11}$$

is minimum (see (10).

To find the minimum of (11) we must find the value of the cross section areas, A_p and A_n, ratio for which the derivative of RK in respect to $x = \frac{A_p}{A_n}$ is zero. Setting: $= \int_{T_c}^{T_h} \rho_p dT$, $B = \int_{T_c}^{T_h} \rho_n dT$, $C = \int_{T_c}^{T_h} k_p dT$, $D = \int_{T_c}^{T_h} k_n dT$ we obtain for the derivative:

$$\frac{d(RK)}{dx} = \frac{d}{dx}\left(AC + \frac{1}{x}AD + xBC + BD\right) = -\frac{1}{x^2}AD + BC = 0 \tag{12}$$

It follows that:

$$x = \sqrt{\frac{AD}{BC}} \tag{13}$$

And for this value of x, the minimum RK becomes:

$$RK_{min} = \left((AC)^{0.5} + (BD)^{0.5}\right)^2 = \left(\left(\int_{T_c}^{T_h} \rho_p dT\int_{T_c}^{T_h} k_p dT\right)^{0.5} + \left(\int_{T_c}^{T_h} \rho_n dT\int_{T_c}^{T_h} k_n dT\right)^{0.5}\right)^2 \tag{14}$$

so

$$\left[\left(\frac{L}{A_p}\int_{T_c}^{T_h} \rho_p dT + \frac{L}{A_n}\int_{T_c}^{T_h} \rho_n dT\right)\left(\frac{A_p}{L}\int_{T_c}^{T_h} k_p dT + \frac{A_n}{L}\int_{T_c}^{T_h} k_n dT\right)\right]_{min}$$
$$= \left(\left(\int_{T_c}^{T_h} \rho_p dT\int_{T_c}^{T_h} k_p dT\right)^{0.5} + \left(\int_{T_c}^{T_h} \rho_n dT\int_{T_c}^{T_h} k_n dT\right)^{0.5}\right)^2 \tag{15}$$

The open circuit total Seebeck voltage(generated by both n and p legs) is:

$$V_{oc} = \int_{T_c}^{T_h} \left(S_p + |S_n|\right) dT \tag{16}$$

By substituting (15) and (16) in (10) we obtain:

$$\eta_{max} = \frac{\frac{m}{m+1}}{\frac{(m+1)\left(\left(\int_{T_c}^{T_h}\rho_p dT\int_{T_c}^{T_h}k_p dT\right)^{0.5}+\left(\int_{T_c}^{T_h}\rho_n dT\int_{T_c}^{T_h}k_n dT\right)^{0.5}\right)^2}{\Delta T\left(\int_{T_c}^{T_h}(S_p+|S_n|)dT\right)^2}+\frac{T_h(S_p+|S_n|)}{\left(\int_{T_c}^{T_h}(S_p+|S_n|)dT\right)}+\frac{2r-1}{2(m+1)(r+1)}} \tag{17}$$

Equation (17) permits us to define, in a similar manner as authors did in Ref. 5 two quantities which will help the new definition of the new TCD efficiency. In Ref. 5 the authors defined an engineering figure of merit, Z_{eng}, an engineering power factor, $(PF)_{eng}$, and the intensity factor, $\hat{\alpha}$, as it follows:

$$Z_{eng} = \frac{\left(\int_{T_c}^{T_h}SdT\right)^2}{\int_{T_c}^{T_h}\rho dT\int_{T_c}^{T_h}kdT} \tag{18}$$

$$(PF)_{eng} = \frac{\left(\int_{T_c}^{T_h}SdT\right)^2}{\int_{T_c}^{T_h}\rho dT} \tag{19}$$

$$\hat{\alpha} = \frac{\Delta TS(T_h)}{\int_{T_c}^{T_h}SdT} \tag{20}$$

Consequently, using our mathematical derivation result represented by equation (17), we define the *device* engineering figure of merit $Z_{d,\,eng}$ by the following equation:

$$Z_{d,eng} = \frac{\left(\int_{T_c}^{T_h}\left(S_p+|S_n|\right)dT\right)^2}{\left(\left(\int_{T_c}^{T_h}\rho_p dT\int_{T_c}^{T_h}k_p dT\right)^{0.5}+\left(\int_{T_c}^{T_h}\rho_n dT\int_{T_c}^{T_h}k_n dT\right)^{0.5}\right)^2} \tag{21}$$

and the *device* intensity factor $\hat{\alpha}_d$:

$$\hat{\alpha}_d = \frac{\Delta T\left(S_p+|S_n|\right)}{\int_{T_c}^{T_h}\left(S_p+|S_n|\right)dT} \tag{22}$$

More precisely, taking into account that the Seebeck coefficients are the ones corresponding to the hot side temperature T_h, (22) can be rewritten as follows:

$$\hat{\alpha}_d = \frac{\Delta T\left(S_p(T_h)+|S_n(T_h)|\right)}{\int_{T_c}^{T_h}\left(S_p+|S_n|\right)dT} \tag{22$'$}$$

It can be observed that an device engineering power factor similar with the one presented in Ref. 5 cannot be defined due to the coupling between the electrical resistivity and thermal conductivity in the denominator of (21) but this doesn't mitigate the importance of the results of (21) and (22′).

By substituting (21) and (22′) in (17) and introducing the Carnot efficiency, $\eta_c = \frac{T_h-T_c}{T_h}$, the efficiency rewrites as:

$$\eta_{max} = \frac{\frac{m}{m+1}}{\frac{(m+1)(r+1)}{\Delta TZ_{d,eng}}+\frac{\hat{\alpha}_d}{\eta_c}+\frac{2r-1}{2(r+1)(m+1)}} = \frac{m}{\frac{(m+1)^2(r+1)}{\Delta TZ_{d,eng}}+\frac{\hat{\alpha}_d(m+1)}{\eta_c}+\frac{2r-1}{2(r+1)}} \tag{23}$$

For a given set of the thermoelectric properties of the p and n TCD legs we are looking for the maximum efficiency than can be obtained when quantity m is regarded as a variable. To find the maximum efficiency we shall take first the derivative in respect to m to find an optimum m_{opt} that cancels the first derivative. Taking the LHS and RHS of (23) we set the derivative of the efficiency in respect to m as:

$$\frac{d\eta_{max}}{dm} = \frac{d}{dm}\left[\frac{m}{\frac{(m+1)^2(r+1)}{\Delta TZ_{d,eng}}+\frac{\hat{\alpha}_d(m+1)}{\eta_c}-\frac{2r-1}{2(r+1)}}\right] = \frac{\left[\frac{(m+1)^2(r+1)}{\Delta TZ_{d,eng}}+\frac{\hat{\alpha}_d(m+1)}{\eta_c}+\frac{2r-1}{2(r+1)}\right]-m\left[\frac{2(m+1)(r+1)}{\Delta TZ_{d,eng}}+\frac{\hat{\alpha}_d}{\eta_c}\right]}{denominator^2} \tag{24}$$

Considering separately only the nominator of (24) we proceed to the further derivation by opening the brackets and reducing the similar terms:

$$nominator = \left[\frac{(m+1)^2(r+1)}{\Delta T Z_{d,eng}} + \frac{\hat{\alpha}_d(m+1)}{\eta_c} + \frac{2r-1}{2(r+1)}\right] - m\left[\frac{2(m+1)(r+1)}{\Delta T Z_{d,eng}} + \frac{\hat{\alpha}_d}{\eta_c}\right]$$
$$= -\frac{m^2(r+1)}{Z_{d,eng}\Delta T} + \frac{r+1}{Z_{d,eng}\Delta T} + \frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)} \tag{25}$$

Setting (25) equal to 0 we obtain the expression for the optimum m for which η is maximum:

$$m_{opt} = \sqrt{1 + \frac{Z_{d,eng}\Delta T}{r+1}\left(\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}\right)} \tag{26}$$

which is similar with S7 from Ref. 5, but now it contains the contact resistance ratio r, the engineering figure of merit, Z_{eng}, is given now by (21) and the so called intensity factor, $\hat{\alpha}$, is given by (22′).We shall observe that in (26) the last two quantities depends on the thermoelectric properties of both, n and p, materials(TCD legs) as it shall be correct.

The last derivation will be done to obtain the expression of maximum efficiency of a TCD. In order to obtain this we'll rewrite (26) in the following form:

$$Z_{d,eng}\Delta T = \frac{(m^2-1)(r+1)}{\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}} \tag{27}$$

Substituting (27) LHS in (20) RHS we obtain:

$$\eta_{max} = \frac{m}{\frac{(m+1)^2(r+1)}{(m^2-1)(r+1)}\left(\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}\right) + \frac{\hat{\alpha}_d(m+1)}{\eta_c} + \frac{2r-1}{2(r+1)}} = \frac{m(m-1)}{(m+1)\left(\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}\right) + \frac{\hat{\alpha}_d(m^2-1)}{\eta_c} + \frac{(2r-1)(m-1)}{2(r+1)}}$$
$$= \frac{m(m-1)}{m(m+1)\frac{\hat{\alpha}_d}{\eta_c} + 2m\frac{2r-1}{2(r+1)}} = \frac{\eta_c(m-1)}{\hat{\alpha}_d(m+1) - 2\eta_c\frac{2r-1}{2(r+1)}}$$

so

$$\eta_{max} = \frac{\eta_c(m-1)}{\hat{\alpha}_d(m+1) - 2\eta_c\frac{2r-1}{2(r+1)}} \tag{28}$$

and, finally, substituting for m from (26) in (28) we obtain the expression of the TCD maximum efficiency:

$$\eta_{max} = \eta_c\frac{\sqrt{1 + \frac{Z_{d,eng}\Delta T}{r+1}\left(\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}\right)} - 1}{\hat{\alpha}_d\left(\sqrt{1 + \frac{Z_{d,eng}\Delta T}{r+1}\left(\frac{\hat{\alpha}_d}{\eta_c} + \frac{2r-1}{2(r+1)}\right)} + 1\right) - 2\eta_c\frac{2r-1}{2(r+1)}} \tag{29}$$

This efficiency expression is similar with equation (S9) derived in Ref. 5 with the observation that it now contains the properties of both TCD legs, through the quantity $Z_{d,eng}$ and the contact resistance ratio r which is taking into account the magnitude of the contact resistance in respect to the TCD legs resistance.

Basically, the main result of the whole calculation represented by the equations (4)–(29)is to prove that the thermocouple device maximum efficiency can be put in a form similar to the one for a single material and therefore to offer to the user a mathematical formula for calculating this efficiency for a TCD. The main difference is the fact that equation (29) employs the contact resistance ratio r, the *device* engineering figure of merit, $Z_{d,eng}$ and and the *device* intensity factor, $\hat{\alpha}_d$, derived also here, which are in our case functions of thermoelectric properties of both TCD legs so the maximum efficiency is a function now of the both legs thermoelectric properties.

III. NUMERICAL AND DISCUSSION

In order to check our results given by (29) we did numerical calculations on η_{max} based on the data from literature employing the temperature dependent thermoelectric properties of several pairs(n and p) of materials.

We then calculated the temperature dependence of $\eta(\eta = f(Z_d, T_h - T_c), T_c = 25^oC)$ in three cases:

i) Based on equation (29)

ii) Based on the equation (3) using the following formula for

$$Z_d = Z_{d,mean} = \frac{1}{\Delta T}\int_{T_c}^{T_h} Z_d(T)\,dT \tag{30}$$

iii) Based on equation (3) using the following formula for

$$Z_d = Z_{d,m} = Z_d(T_m) \tag{31}$$

Both Visual Basic 6 and OriginLab 8 were used for building the numerical code used in the numerical evaluation of (29) and (3), for curve fitting and for data representation in graphical mode.

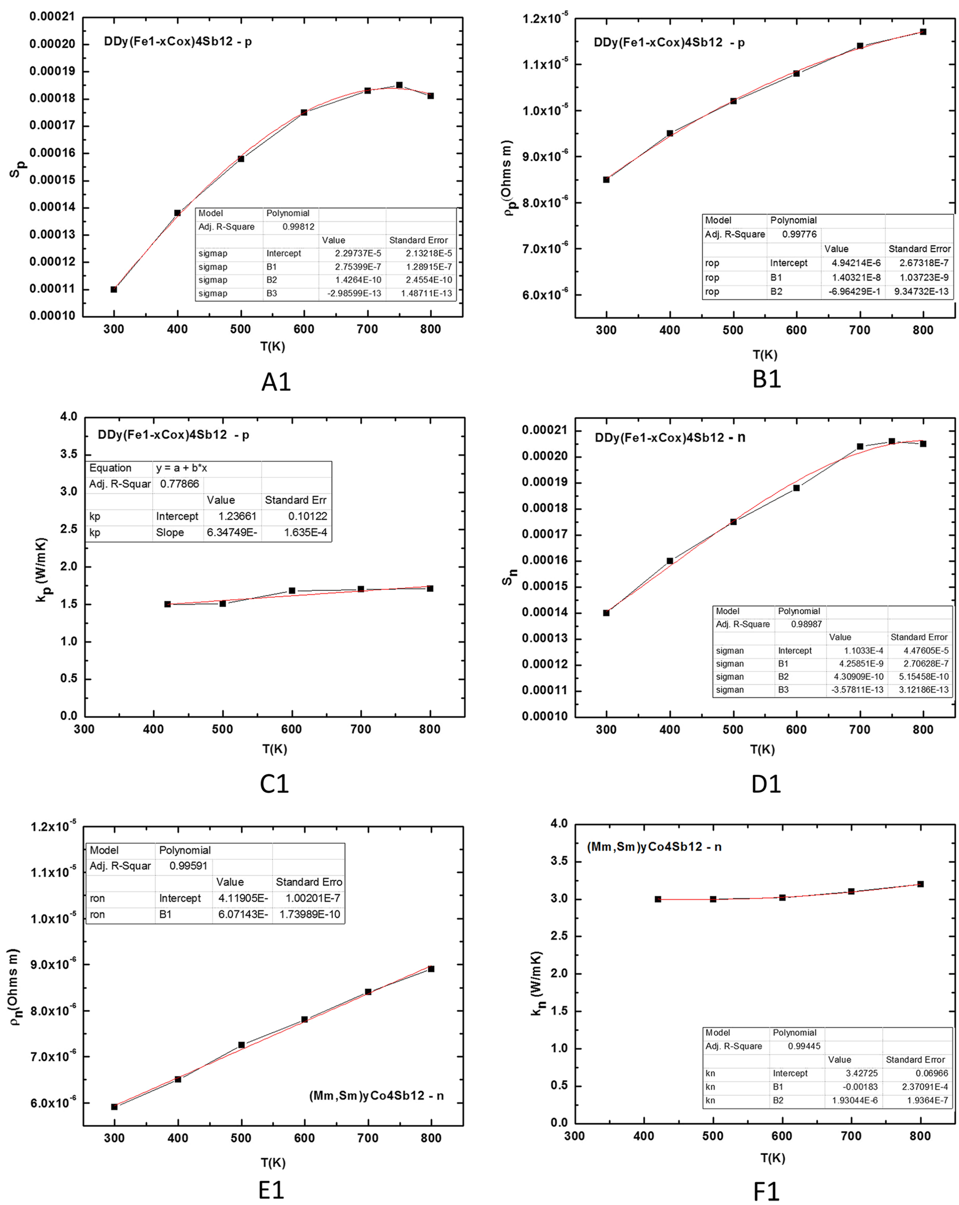

FIG. 3. The temperature dependence and curve fitting for the thermoelectric properties of p-type $DD_y(Fe_{1-x}Co_x)_4Sb_{12}$(A1,B1,C1) and n-type $(Mm,Sm)_yCo_4Sb_{12}$(D1,E1,F1).

The following cases were considered for study:

a) The p-type $DD_y(Fe_{1-x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$[3] thermoelectric properties are used in this case. In order to evaluate (21) five integrals need to be calculated while for the point ii), one integral needs to be calculated. For all integrals evaluation we need analytical expressions for the thermoelectric properties as a function of temperature. All integrals are numerical evaluated using code written in Visual Basic 6. The temperature dependent thermoelectric properties together with the curve fitting for this pair of materials are represented in Fig. 3. The curves were fitted with first, second and third order polynomials, as it was the case, to obtain analytical expressions for the thermoelectric properties in order to be further used in (21), (30), (31), (3), and (29) for the Z_d and η_{max} calculation.

From Fig. 3 we can see that the thermoelectric properties can be well fitted so in consequence this method of obtaining analytical expressions is reliable.

In Fig. 4 the figures of merit $Z_{d,eng}$, $Z_{d,mean}$ and $Z_d(T_m)$ are plotted against the hot and cold side temperature difference.

We can observe that for higher temperature differences between the hot and cold sides (the Skutterudites present higher figure of merit[9–12]) the $Z_{d,eng}$ and $Z_d(T_m)$ encounter different values having a maximum difference at ΔT=400K of 3.2% while $Z_{d,eng}$ and $Z_{d,mean}$ have almost the same temperature dependence. This relatively low value of the difference in the figures of merit calculated in three different ways resides in the fact that the thermoelectric properties of the two n and p Skutterudites considered doesn't vary much in temperature range 300-700K. These variations(the difference between the maximum and minimum attained values) have the following percentages: S_p-66%, ρ_p-37%, k_p-16% for $DD_y(Fe_{1-x}Co_x)_4Sb_{12}$ and S_n-46%, ρ_n-50%, k_n-7% for $(Mm,Sm)_yCo_4Sb_{12}$. These values show a weak dependence of the thermoelectric properties on temperature especially the thermal conductivities which are almost constant on the whole temperature interval. In the extreme case when all the thermoelectric properties are constant over the considered temperature interval the three quantities, $Z_{d,eng}$, $Z_{d,mean}$ and $Z_d(T_m)$ are all equal.

Regarding the variation with the temperature difference, T_h-T_c, of the TCD maximum efficiency, this one, calculated using equation (29) and equation (3)(with Z_d expressed by the equations (30) and (31)) are plotted in Fig. 5 for r=0.

From Fig. 5 we can observe that the efficiencies calculated in three different ways start do diverge for temperature differences greater than 200K. Thus at these higher temperatures the real efficiency of a TCD predicted by equation (29) is lower than the ones given by equation (3). The maximum(at ΔT=400K) difference in the calculated values reaches 7% between

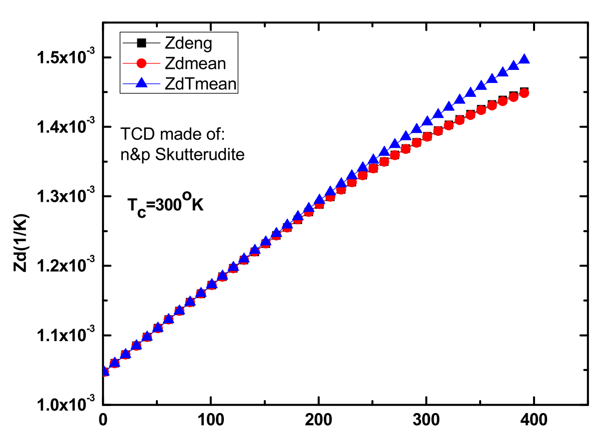

FIG. 4. The $Z_{d,eng}$, $Z_{d,mean}$ and $Z_d(T_m)$ plot as a function of temperature difference between hot and cold side for a TCD built with p-type $DD_y(Fe_{1-x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$.

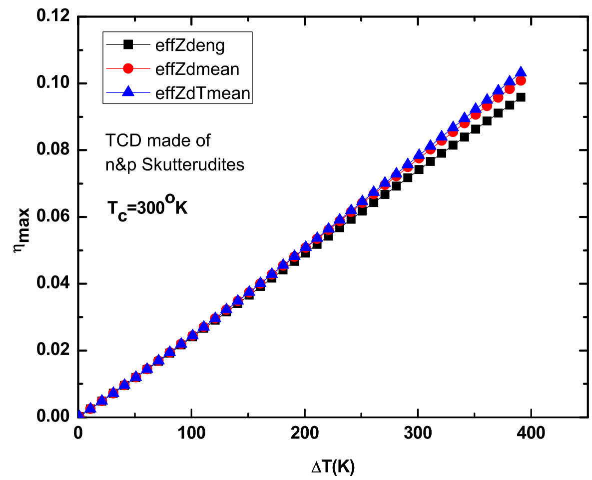

FIG. 5. The temperature dependence of the TCD efficiency based on equations (29), (3)($Z_d = Z_{d,mean}$) and (3)($Z_d = Z_d(T_m)$) for a TCD built with with p-type $DD_y(Fe_{1\text{-}x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$.

the efficiencies $\eta(Z_{d,eng})$-equation(26) and $\eta(Z_d(T_m))$-equation(3) and 4.8% between the efficiencies $\eta(Z_{d,eng})$ and $\eta(Z_{d,mean})$. These differences are quite small in the case of p-type $DD_y(Fe_{1\text{-}x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$ and the reason is the one described above in the figures of merit calculation. However this example shows clearly that the TCD efficiency calculated in these three different ways lead to different values especially at high temperature differences.

In Fig. 6 it is represented the temperature dependence of the maximum efficiency calculated with equation (29) for three different values of contact resistance ratio r in the case of p-type $DD_y(Fe_{1\text{-}x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$. It is observed that for very small contact resistance, r=0.01(1%), the influence of this quantity on the maximum efficiency is negligible. It starts to increase at r=0.1(10%), the relative change in the efficiency at maximum temperature difference being 7.3% and further increase shows a significantly larger relative difference, about 43%, for r=1(100%)(the contact resistance is equal to the TCD legs resistance).

b) The p-type $Na_{0.95}Pb_{20}SbTe_{22}$[13] and n-type PbS+x%$PbCl_2$(x=0.04)[14] thermoelectric properties are used in this case. Following the reasoning from point a) the temperature dependent thermoelectric properties together with the curve fitting for this pair of materials are represented in Fig. 6.

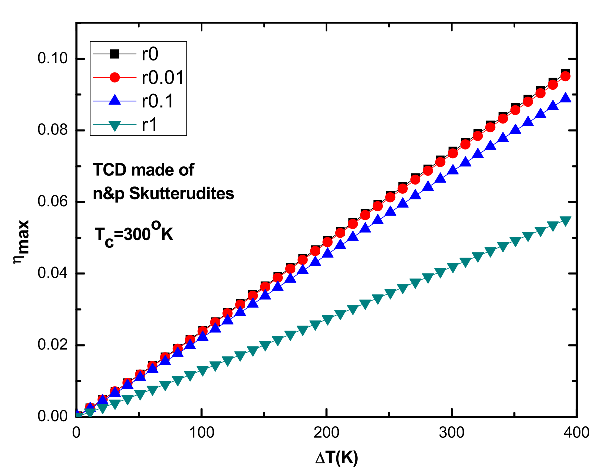

FIG. 6. The temperature variation of the maximum efficiency calculated with equation (29) for r=0.01, 0.1 and 1 in the case of p-type $DD_y(Fe_{1\text{-}x}Co_x)_4Sb_{12}$ and n-type $(Mm,Sm)_yCo_4Sb_{12}$.

From Fig. 7 we can see, as in the case of Fig. 3, that the temperature dependence of these n and p type materials is well fitted by polynomials of second and third order.

In Fig. 8 the figures of merit $Z_{d,eng}$, $Z_{d,mean}$ and $Z_d(T_m)$ are plotted against the hot and cold side temperature difference.

We can observe, in this case, that for temperature differences greater than 200K the three figures of merit significantly diverge reaching at maximum temperature difference of 400K a 28% variation between $Z_{d,eng}$ and $Z_d(T_m)$ and a 16% variation between $Z_{d,eng}$ and $Z_{d,mean}$ values which are about 9 times greater than the ones obtained in the case of Skutterudites materials. This is due to the much greater change in the thermoelectric properties over the temperature range of interest for these materials compared to the Skutterudites. These changes are as it follows: : S_p-287%, ρ_p-820%, k_p-112% for

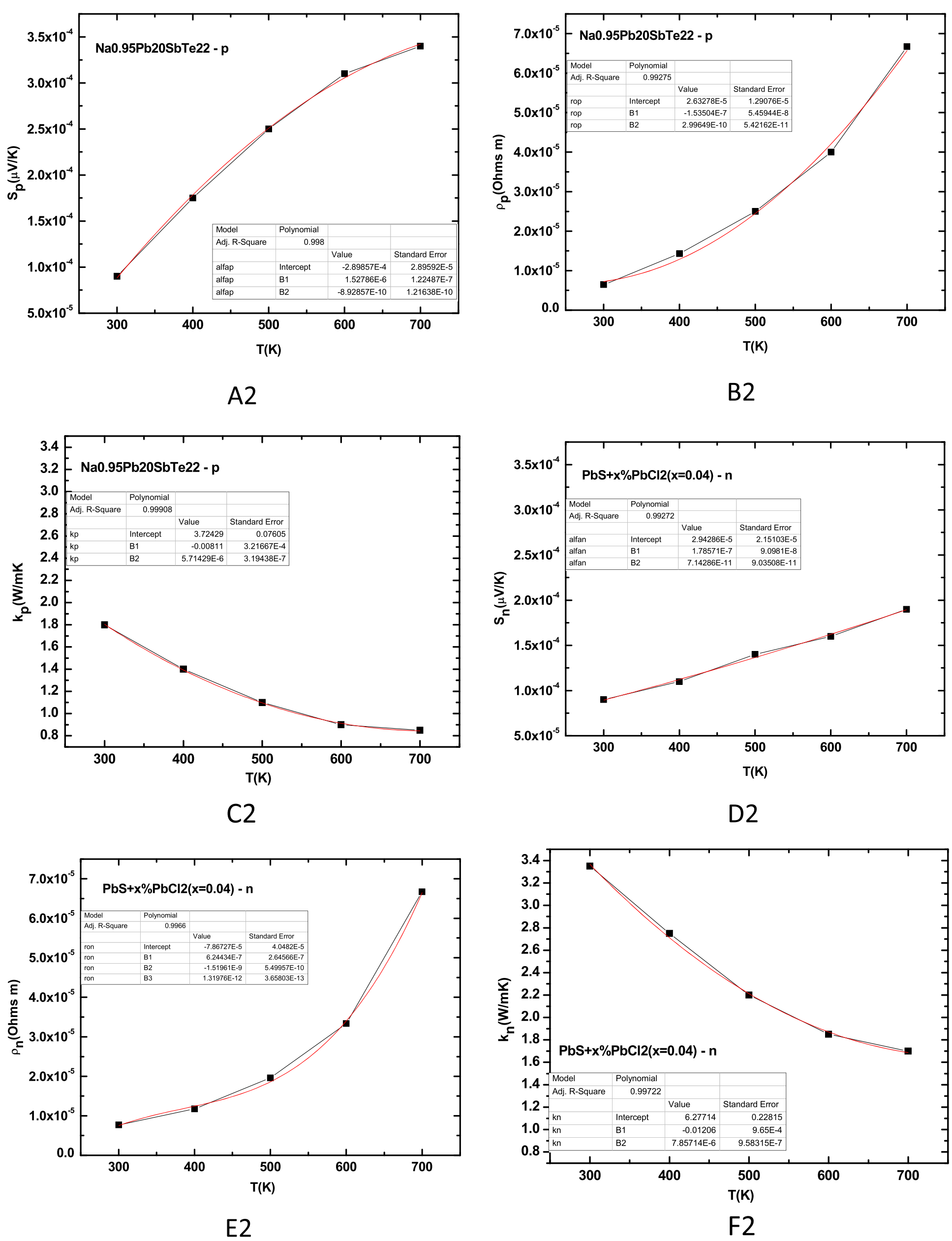

FIG. 7. The temperature dependence and curve fitting for the thermoelectric properties of p-type $Na_{0.95}Pb_{20}SbTe_{22}$(A2,B2,C2) and n-type $PbS+x\%PbCl_2$(x=0.04)(D2,E2,F2).

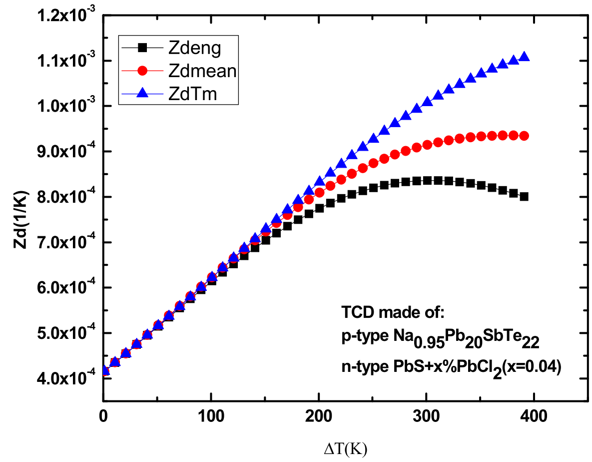

FIG. 8. The $Z_{d,eng}$, $Z_{d,mean}$ and $Z_d(T_m)$ plot as a function of temperature difference between hot and cold side for a TCD built with p-type $Na_{0.95}Pb_{20}SbTe_{22}$ and n-type PbS+x%$PbCl_2$(x=0.04).

p-type $Na_{0.95}Pb_{20}SbTe_{22}$ and S_n-110%, ρ_n-752%, k_n-98% for n-type PbS+x%$PbCl_2$(x=0.04) which are in average 10 times greater than the ones for Skutterudite materials. This is a direct proof that the greater are the changes in the thermoelectric properties the bigger is the difference in the values of the three figures of merit and the bigger will be the discrepancy in the corresponding efficiencies. These differences are evidenced at temperature differences greater than 200K.

As we mentioned above the three TCD efficiencies calculated by means of formula (29) and (3)(with Z_d= $Z_{d,mean}$ and Z_d= $Z_d(T_m)$) show the same strong divergence trend for temperature differences greater than 200K and are plotted in Fig. 9 for r=0.

From this figure we can observe that at 400K the values for the three maximum efficiencies are:5.87% for $\eta(Z_{d,eng})$-equation(29), 7.22% for $\eta(Z_{d,mean})$-equation(3) and 8.24% for $\eta(Z_d\ (T_m))$-equation(3).The biggest difference is between $\eta(Z_{d,eng})$ and $\eta(Z_d\ (T_m))$ which at 400K reaches 40% followed by the difference between $\eta(Z_{d,eng})$ and $\eta(Z_{d,mean})$ that at the same temperature is 23%. These values are about six times greater than the same differences for the Skutterudites from point a). In the case of currently discussed materials we can see obviously that equation (3) overestimates the results for the TCD efficiency with 23% and 40% and equation (29) needs to be employed to get more realistic results.

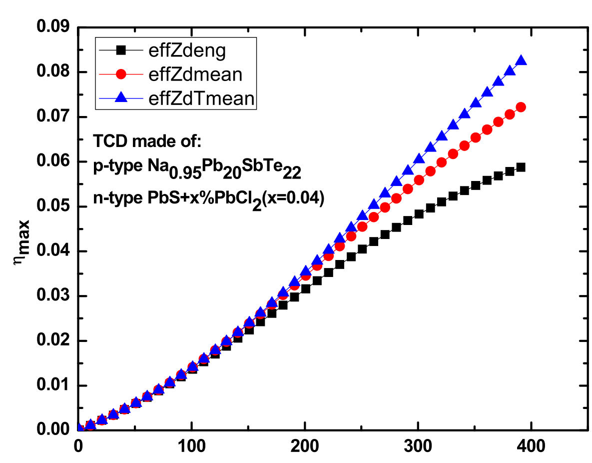

FIG. 9. The temperature dependence of the TCD efficiency based on equations (29), (3)(Z_d= $Z_{d,mean}$) and (3)(Z_d= $Z_d(T_m)$) for a TCD built with p-type $Na_{0.95}Pb_{20}SbTe_{22}$ and n-type PbS+x%$PbCl_2$(x=0.04).

In Fig. 10 it is represented the temperature dependence of the maximum efficiency calculated with equation (29) for three different values of contact resistance ratio r for p-type $Na_{0.95}Pb_{20}SbTe_{22}$ and n-type PbS+x%$PbCl_2$(x=0.04). It is observed that for very small contact resistance, r=0.01(1%), the influence of this quantity on the maximum efficiency is also negligible. It starts again to increase at r=0.1(10%), the relative change in the efficiency at maximum temperature difference being 7.6%(similar with the previous case) and further increase in r shows a large relative difference, about 44%, for r=1(100%)(the contact resistance is equal to the TCD legs resistance)

c) For the demonstration purpose arbitrary values are assigned at this point to the thermoelectric properties of two imaginary n and p thermoelectric materials for which even more variation of thermoelectric properties is assumed i.e. the values corresponding to 700K are 10 times different compared to the values from 300K. The variation assumed is linear for simplicity. For this purpose the thermoelectric properties of the two n and p materials are chosen as follows:

1.) For p type

$$S_p \in [100, 1000]\,\frac{\mu V}{K}$$

$$\rho_p \in [500, 5000]\,E-8\,Ohms\,m$$

$$k_p \in [2, 20]\frac{W}{mK}$$

2.) For n-type

$$S_n \in [200, 2000]\,\frac{\mu V}{K}$$

$$\rho_n \in [200, 2000]\,E-8\,Ohms\,m$$

$$k_n \in [1, 10]\frac{W}{mK}$$

Using these two sets of properties the resulting efficiencies calculated with equations (26) and (3) are plotted in Fig. 9.

From Fig. 11 it can be seen that the discrepancy between the three efficiencies calculated at the maximum temperature difference, 400K, is even higher than in the case of point b), as expected, because of the larger variation in the thermoelectric properties. At 400K the values for $\eta(Z_{d,eng})$, $\eta(Z_{d,mean})$ and $\eta(Z_d\,(T_m))$ are 13.6% and 24.7%, 19.2% respectively. The biggest difference in the

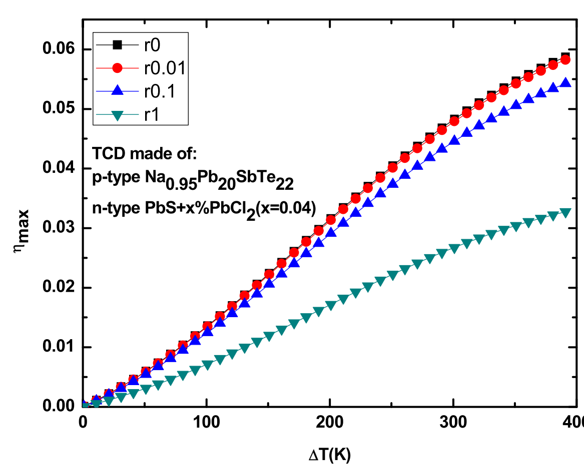

FIG. 10. The temperature variation of the maximum efficiency calculated with equation (29) for r=0.01, 0.1 and 1 in the case of p-type $Na_{0.95}Pb_{20}SbTe_{22}$ and n-type PbS+x%$PbCl_2$(x=0.04).

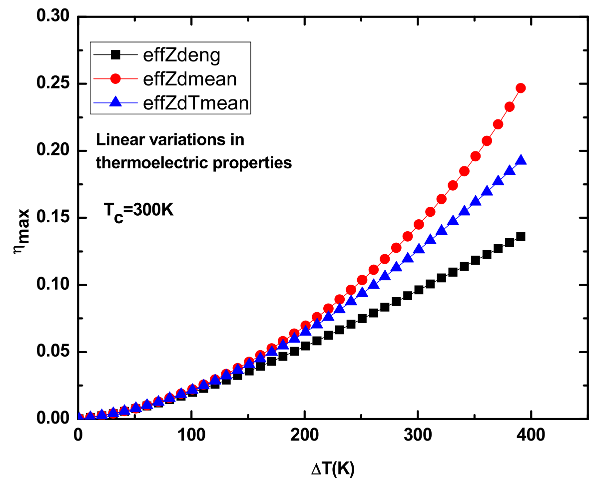

FIG. 11. The calculated TCD efficiencies based on equations (26) and (3) in the case of an imaginary pair of n and p materials with 10 times variation in the thermoelectric properties in the temperature range [300, 700]K.

efficiencies is between $\eta(Z_{d,eng})$ and $\eta(Z_{d,mean})$ of 82% followed by the one between $\eta(Z_{d,eng})$ and $\eta(Z_d\ (T_m))$ of 41%. These values are about 2 times greater than the ones obtained at point b).

In Fig. 12 it is represented the temperature dependence of the maximum efficiency calculated with equation (29) for three different values of contact resistance ratio r for the imaginary pair of thermoelectric materials considered in study. It is observed again that for very small contact resistance, r=0.01(1%), the influence of this quantity on the maximum efficiency is negligible. It starts also to increase at r=0.1(10%), the relative change in the efficiency at maximum temperature difference being 4.6% and further increase in r shows a large relative difference, about 30%, for r=1(100%)(the contact resistance is equal to the TCD legs resistance). The lower values of the relative change of the maximum efficiencies obtained in this case compared with cases a) and b) we suppose that are due to the higher variation of the thermoelectric properties considered in study in case c).

The calculations performed at this point demonstrates that, theoretically, higher discrepancies appear in the calculated values of efficiency based on equations (29) and (3) if bigger variations are present in the thermoelectric properties. This is a clear proof of the fact that equations (29) and (3) predict different values for efficiency, the last one overestimating the real efficiency for which the first one is more proper to be used.

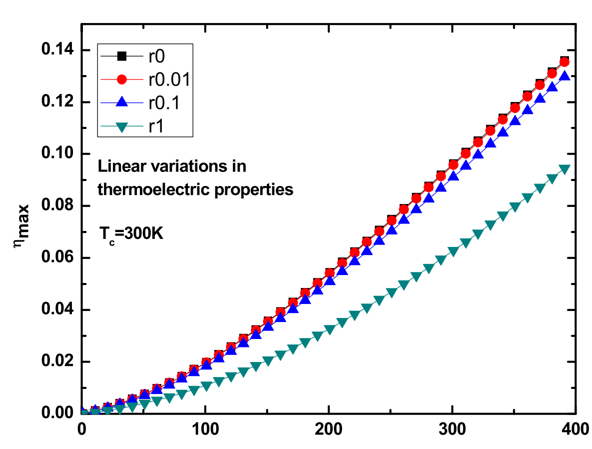

FIG. 12. The temperature variation of the maximum efficiency calculated with equation (29) for r=0.01, 0.1 and 1 in the case of an imaginary pair of thermoelectric materials having a 10 times variation thermoelectric properties.

To study the contact effects, we defined the relative contribution of the contact resistance as the ratio between the contact resistance and the intrinsic resistance of the thermoelectric leg. Applying this relationship for both the electrical and thermal contact resistances, it can be shown that the electrical contact resistance effects equal to ${}^{2\sigma}\!/_{\Sigma_c l}$ are the dominant ones vs the thermal contact resistance effects equal to ${}^{2\kappa}\!/_{\Gamma_c l}$. For instance, given the typical values, $\sigma \sim 10^5\ \Omega^{-1}\mathrm{m}^{-1}$, the contact electrical conductance $\Sigma_c \sim 10^8\ \Omega^{-1}\mathrm{m}^{-2}$, thermal conductivity $\kappa \sim$ 1-2W/mK and the thermal contact conductance Γ_c is $\sim 10^5 \mathrm{m}^2$K/W, then $\kappa/\Gamma_c\ l$ is only ~1% of $\sigma/\Sigma_c\ l$. Therefore the interface thermal resistance effects can be neglected in typical applications. The fundamental reason is that good thermoelectrics have high electrical conductivity and low thermal conductivities, therefore electrical contact resistances play the key role vs thermal contact resistances.

IV. CONCLUSIONS

In this paper the quantity named the *device engineering figure of merit,* $Z_{d,eng}$, was introduced and is taking into account the thermoelectric properties of both TCD legs materials being the recommended quantity to be used when a thermoelectric device is employed. We showed that for a relatively small variation with the temperature of the thermoelectric properties of the n and p materials, 7 to 66%, a maximum 7% variation in the efficiency calculation appears when one use equation (29) and (3). For a higher variation in the thermoelectric properties of 98 to 820% a maximum of 40% variation in the TCD efficiency was obtained at point b) which pointed out that the thermoelectric properties variation with the temperature plays an important role in the maximum efficiency calculation. Even higher variation in the TCD efficiency was obtained for the extreme case c) which employed a 10 times variation of the thermoelectric properties in the temperature domain of interest the maximum variation obtained being 82%. Also, a study on the dependence of the maximum efficiency upon the contact resistance ratio r for r=0.01,0.1 and 1 was performed showing that a relative change in the efficiency of about 4.6-7.6% appears for r=0 and r=0.1 while a higher variation, 30-44%, was obtained in the case of r=0, r=1. These results show that the contact resistance plays an important role in the calculation of the maximum efficiency of a TCD reducing its performance for r>0.1. Finally, these results showed the importance of gaining of a good understanding of the processes that takes place in a TCD in order to develop a mathematical approach which will give insight onto the mathematical quantities that characterize the performance of a TCD and consequently a thermoelectric generator namely the *device engineering figure of merit,* $Z_{d,\ eng}$ and the maximum device efficiency. This paper shows that a good characterization of a thermoelectric generator implies the handling of the right mathematical expression for the device efficiency in order to get realistic results and have realistic expectations from a thermoelectric device from the performance point of view.

ACKNOWLEDGMENTS

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