Maximization of the Thermoelectric Cooling of a Graded Peltier Device by Analytical Heat-Equation Resolution

E. Thiébaut,[1,*] C. Goupil,[2] F. Pesty,[1] Y. D'Angelo,[3] G. Guegan,[4] and P. Lecoeur[1]
[1]*Centre de Nanosciences et de Nanotechnologies, CNRS, Université Paris-Sud,*
Université Paris-Saclay, C2N-Orsay, 91405 Orsay, France
[2]*Laboratoire Interdisciplinaire des Energies de Demain (LIED), UMR 8236, Université Paris Diderot,*
CNRS, 5 Rue Thomas Mann, 75013 Paris, France
[3]*Laboratoire de Mathématiques J.A. Dieudonné, Université de Nice Sophia Antipolis,*
CNRS UMR 7351, Parc Valrose, 06108 Nice Cedex, France
[4]*STMicroelectronics-Tours, 10 Rue Thales de Milet, CS97155, 37071 Tours Cedex 2, France*

(Received 1 August 2017; revised manuscript received 26 October 2017; published 4 December 2017)

Increasing the maximum cooling effect of a Peltier cooler can be achieved through material and device design. The use of inhomogeneous, functionally graded materials may be adopted in order to increase maximum cooling without improvement of the ZT (figure of merit); however, these systems are usually based on the assumption that the local optimization of the ZT is the suitable criterion to increase thermoelectric performance. We solve the heat equation in a graded material and perform both analytical and numerical analysis of a graded Peltier cooler. We find a local criterion that we use to assess the possible improvement of graded materials for thermoelectric cooling. A fair improvement of the cooling effect (up to 36%) is predicted for semiconductor materials, and the best graded system for cooling is described. The influence of the equation of state of the electronic gas of the material is discussed, and the difference in term of entropy production between the graded and the classical system is also described.

DOI: 10.1103/PhysRevApplied.8.064003

I. INTRODUCTION

Thermoelectric materials are used to promote energy harvesting and build cooling devices using direct thermoelectric conversion with no moving parts. Different parameters can be used to evaluate the performance of a thermoelectric system. For cooling applications, an important parameter is the maximum cooling temperature. A thermoelectric system made of homogeneous materials can impose a maximum cooling limited by its figure of merit (ZT) and equal to $\Delta T = ZT_c^2/2$. The figure of merit is defined as $ZT_c = \alpha^2 T_c/(\kappa\rho)$, where α is the Seebeck coefficient, κ the thermal conductivity, ρ the electrical resistivity, and T_c the temperature of the cold side.

In thermoelectric systems based on the constant properties model (CPM), the Peltier effect is localized at the interface and the Joule effect is homogeneously spread across the device. Inhomogeneity leads to the Peltier-Thomson or extrinsic Peltier effect within the material and gives rise to inhomogeneous Joule heating. In a real device, the temperature dependence of the thermoelectric material properties leads to such inhomogeneities. The CPM is, therefore, realistic only for small temperature differences. However, the simplicity of such a system allows it to be easily used as comparison with more realistic systems. Resolution of inhomogeneous thermoelectric systems is complex and numerical computations of segmented systems with temperature-dependence properties were performed in the 1960s [1]. At the same time, material conditions for a segmented device to improve thermoelectric performance were investigated [2]. In addition to the segmented device, the graded device was investigated with analytical resolution in the 1960s for linear variation of the Seebeck coefficient and a constant figure of merit [3]. Graded and segmented thermoelectric devices are sufficiently promising to be patented [4]. With improved computer capabilities, numerical research on optimal solution for segmented [5–7] and graded [8] systems were performed during the 1990s.

The performance of a thermoelectric system depends on the current density going through the material. In a segmented device, the current that optimizes each segment might be different. The compatibility approach ("$u = s$") is used to optimize a thermoelectric system through the concept of reduced current (u equals the electrical flux divided by the heat flux) [9]. The optimization is obtained when u is equal to s, which depends on the material properties. The efficiency of a thermoelectric generator (TEG) and the coefficient of performance of a thermoelectric cooler (TEC) has been investigated using this approach for segmented devices [9–12] and graded devices [13–17]. The reduced current is the local version of the Prandtl number [18].

On the experimental side, segmented thermoelectric generators based on Bi_2Te_3 materials have been designed and measured [19,20]. These works lead to a 15% improvement of the generator efficiency.

---

[*] etienne.thiebaut@u-psud.fr

However, unlike graded devices, segmented devices pose the disadvantage that their contact resistances can reduce the performance of the system [21]. The fabrication of graded material can be achieved, for example, by alloying silicon and germanium [22].

The compatibility approach has proven to be a powerful tool to optimize the efficiency of a TEG and the coefficient of performance of a TEC; however, it has been shown that optimizing the maximum temperature difference requires another approach, one that is discussed in Ref. [14]. The temperature difference and the efficiency are different optimization targets.

The maximum temperature difference that a thermoelectric cooler can impose is a key parameter of the thermoelectric performance of a device. This parameter has been investigated through different approaches.

A hypothetical material where ZT stays constant as the Seebeck coefficient varies due to doping has been investigated by numerical [23] and analytical means [24]. Numerical calculations of the maximum temperature difference based on experimental material properties [25,26] yield theoretical improvements of 27% for Bi_2Te_3 materials and 35% for silicon.

In this paper, we provide an analytical solution for a graded thermoelectric system, maximizing the temperature difference in the case of a general expression of the Seebeck coefficient as well as the electric conductivity as functions of the doping level. The analytical solution is studied by analytical and numerical means in the case of a simple semiconductor model.

In Sec. II, we present an analytical analysis of a graded material in a thermoelectric cooler. The optimization of the temperature maximum is based on the work initiated by Bian and Shakouri [24]. We show a local criterion that can be established to deduce the best graded material.

In Sec. III, the relation between the Seebeck coefficient and the electric conductivity is discussed as a consequence of the equation of state of the material in use. A graded system can be manufactured through different methods (doped semiconductors, alloy) and materials (silicon, oxides, classic thermoelectric materials, polymers). Each method or material leads to a different equation of state relating the Seebeck coefficient to the electrical conductivity.

As most good thermoelectrics are semiconductors, a good way to obtain a graded material should be to use a graded doped semiconductor. In Sec. IV, we apply the local criterion for a simple thermoelectric model of a semiconductor in order to evaluate the doping level as a function of the position and to calculate the improvement of the cooling effect.

From our optimization, the doping level maximizing the cooling is a linear profile. We analyze the influence of a linear doping level in a semiconductor. Under these conditions, the cooling as a function of the Seebeck coefficient at the cold side and the Seebeck coefficient at the hot side is plotted and discussed.

In Sec. V, to evaluate the validity of the analytical solution, the system is numerically computed and differences between numerical and analytical results are presented. However, the results validate the trend arising from the analytical solution. An evaluation of the entropy sources is performed based on the numerical results.

II. ANALYTICAL OPTIMIZATION OF A GRADED THERMOELECTRIC MATERIAL

The heat equation in a one-dimensional graded thermoelectric system in static regime includes three terms—heat conduction, the Thomson effect, and the Joule effect, respectively:

$$0 = \frac{\partial}{\partial x}\left[\kappa(x, T(x))\frac{\partial T}{\partial x}(x)\right] - JT(x)\frac{\partial \alpha}{\partial x}[x, T(x)] + \rho[x, T(x)]J^2. \tag{1}$$

Equation (1) in the general situation cannot be solved analytically. If we assume that the thermal conductivity is constant, the material properties are independent from temperature variations, and the temperature stays close to T_0 $[JT(x)[(\partial\alpha)/\partial x](x) = JT_0[(\partial\alpha)/\partial x](x)]$, we obtain

$$0 = \kappa\frac{\partial^2 T}{\partial x^2}(x) - JT_0\frac{\partial \alpha}{\partial x}(x) + \rho(x)J^2. \tag{2}$$

The system that is considered is composed of one n thermoelectric material from $x = -L$ to $x = 0$ and one p thermoelectric material from $x = 0$ to $x = L$. At the position $x = -L$ and $x = L$, the system is in contact with a thermostat. This is a symmetric system for the thermal conductivity (κ) and the electrical resistivity (ρ), and it is antisymmetric for the Seebeck coefficient (α). This system models a Peltier cooler where the cold side ($x = 0$) is at the interface between the n and the p thermoelectric element.

By integrating Eq. (2) twice, the maximal temperature can be computed and the current density can be optimized as shown in Ref. [24] to obtain the maximum temperature difference:

$$\Delta T = \frac{T_0^2}{4\kappa}\frac{[\int_0^L \alpha(v)dv]^2}{\int_0^L \int_0^v \rho(u)dudv} = \frac{A}{B}\frac{T_0^2}{4\kappa}. \tag{3}$$

Equation (3) was obtained and analyzed in Ref. [24], in which it was shown that a graded system can improve the maximum cooling a Peltier cooler can reach:

$$B = \int_0^L \int_0^v \rho(u)dudv, \tag{4}$$

$$A = \left(\int_0^L \alpha(v)dv\right)^2. \tag{5}$$

The temperature difference depends on the function of the Seebeck coefficient $[\alpha(x)]$ as a function of the position

(x) and on the function of the electrical resistivity $[\rho(x)]$ as a function of the position. The maximization of ΔT leads to finding a local criterion by solving Eq. (6), where the functional derivative of ΔT by $\alpha(x)$ has to be considered. The local criterion obtained takes the form of a condition on $[(\partial\rho)/\partial\alpha](x)$ where $\rho(\alpha)$ is material dependent:

$$\frac{\partial \Delta T}{\partial \alpha(x)} = 0, \tag{6}$$

$$A\frac{\partial B}{\partial \alpha(x)} = B\frac{\partial A}{\partial \alpha(x)}, \tag{7}$$

$$\frac{\partial B}{\partial \alpha(x)} = \int_0^L \int_0^v \frac{\partial \rho(u)}{\partial \alpha(x)} du dv, \tag{8}$$

$$\frac{\partial A}{\partial \alpha(x)} = 2\left(\int_0^L \frac{\partial \alpha(v)}{\partial \alpha(x)} dv\right)\left(\int_0^L \alpha(v) dv\right). \tag{9}$$

So if $x > v$, x is not in the $[0, v]$ interval:

$$\int_0^v \frac{\partial \rho(u)}{\partial \alpha(x)} du = 0. \tag{10}$$

If $x < v$, x is in the $[0, v]$ interval:

$$\int_0^v \frac{\partial \rho(u)}{\partial \alpha(x)} du = \frac{\partial \rho(x)}{\partial \alpha(x)} \int_0^L \delta_x(u) du, \tag{11}$$

$$\frac{\partial B}{\partial \alpha(x)} = (L - x)\frac{\partial \rho}{\partial \alpha}(x) \int_0^L \delta_x(u) du, \tag{12}$$

$$\frac{\partial A}{\partial \alpha(x)} = 2\left(\int_0^L \delta_x(u) du\right)\left(\int_0^L \alpha(v) dv\right), \tag{13}$$

with δ_x being the Dirac δ function centered on x. Using Eqs. (7), (12) and (13), we get

$$\frac{\partial \rho}{\partial \alpha}(x) = \frac{1}{1 - \frac{x}{L}} \frac{\partial \rho}{\partial \alpha}(0). \tag{14}$$

Equation (14) gives a local criterion of an optimized graded thermoelectric cooler.

III. THE EQUATION OF STATE

From Eq. (14), we deduce that the optimization strongly relies on the relation between the Seebeck coefficient and the electronic conductivity. This relation depends on the equation of state of the electron gas that is considered. As an example, we use a nondegenerated Lorentz-gas equation of state to evaluate the maximum cooling in a semiconductor; however, other equations of state (Price relation for a semiconductor [27], exciton [28], oxides [29], nanomaterial [30], polymers [31]) might be used, yielding different improvements of the maximum cooling.

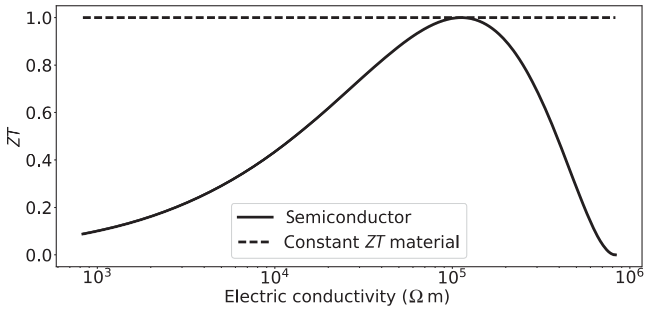

FIG. 1. The figure of merit as a function of the electric conductivity for a semiconductor (the solid line) and for a hypothetical constant ZT material (the dashed line). The maximum ZT of the semiconductor is equal to the ZT of the constant ZT material, which means that the maximum temperature difference will be the same for a homogeneous material.

In Ref. [24] the considered materials have a ZT independent of the carrier concentration (and of the electrical conductivity). For any material, the ZT parameter depends on the carrier concentration; this will impact the maximum cooling temperature.

A numerical investigation with experimental properties of Bi_2Te_3 yields a 27% increase [26], and a 35% increase is predicted with silicon [25]. For a comparison between the semiconductor model we investigate and the constant ZT material that Bian and Shakouri used [25], we plot the figure of merit (in Fig. 1) and the Seebeck coefficient (in Fig. 2) as functions of the electric conductivity. One consequence drawn from this work is that an upper limit is established for the possible cooling temperature.

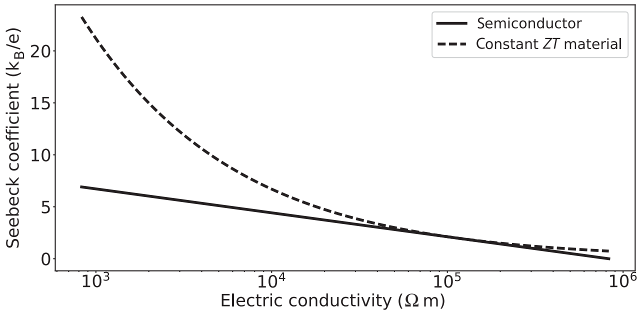

FIG. 2. The Seebeck coefficient as a function of the electric conductivity for a semiconductor (the solid line) and for a constant ZT material model (the dashed line). At any electrical conductivity, the Seebeck coefficient is higher in the case of a constant ZT material model having equality with the semiconductor model for a Seebeck value of $2k_B/e$, which corresponds to the value where the maximum ZT is reached for the semiconductor model. For low carrier density (low electric conductivity) in a real semiconductor, the Seebeck coefficient reaches a maximum. This effect is not present in our simple model.

IV. APPLICATION FOR A SEMICONDUCTOR

For the sake of simplicity, we apply the previous development to a nondegenerated Lorentz gas. It is possible to apply this relation to more-complex systems; however, the model we choose is a simple model for the thermoelectric properties of a semiconductor. The electrical conductivity and the Seebeck coefficient are functions of the doping n,

$$\sigma = ne\mu, \tag{15}$$

where μ denotes the electron mobility and e the elementary charge:

$$\alpha = -\frac{k_B}{e}\ln\left(\frac{n}{N_{\mathrm{eff}}}\right). \tag{16}$$

Using Eqs. (15) and (16), we obtain a relation between the electrical resistivity and the Seebeck coefficient, with N_{eff} denoting the effective density of states (as defined in Ref. [32]). This model is valid for a nondegenerated semiconductor,

$$\rho = \rho_0 \exp\left(\frac{e\alpha}{k_B}\right). \tag{17}$$

From Eq. (17) and the local criterion [Eq. (14)], we obtain the resistivity and the Seebeck coefficient as functions of the position x,

$$\rho(x) = \rho(0)\frac{1}{1-\frac{x}{L}}, \tag{18}$$

$$\alpha(x) = \alpha(0) + \frac{k_B}{e}\ln\left(\frac{1}{1-\frac{x}{L}}\right). \tag{19}$$

The obtained solution diverges at the hot side for both the electrical resistivity and the Seebeck coefficient. The electrical conductivity is a linear function of the position and takes the value zero on the hot side. This solution gives a hypothetical solution. However, for more-realistic situations, we investigate solutions where the electrical conductivity is a linear function of the position and is not equal to zero on the hot side.

Using Eqs. (18) and (19), we obtain Eq. (20), a solution for ΔT that depends on the properties of the material at the position 0:

$$\Delta T = \frac{T_0^2}{4\kappa\rho_0}\frac{[\alpha(0)+\frac{k_B}{e}]^2}{\exp(\frac{e\alpha(0)}{k_B})}. \tag{20}$$

The maximization of Eq. (20) gives

$$\alpha(0) = \frac{k_B}{e}, \tag{21}$$

which is the traditional prefactor value of any Seebeck expression.

From Eqs. (20) and (21), the maximal temperature difference in a graded thermoelectric semiconductor can be computed as

$$\Delta T_{\mathrm{graded}} = \frac{T_0^2}{\kappa\rho_0}\frac{(\frac{k_B}{e})^2}{\exp(1)}. \tag{22}$$

A comparison can be made between the graded system and a homogeneous system. The homogeneous case gives a temperature difference of

$$\Delta T_{\mathrm{homogeneous}} = \frac{T_0^2}{4\kappa\rho_0}\frac{\alpha^2}{\exp(\frac{e\alpha}{k_B})}. \tag{23}$$

The Seebeck coefficient that gives the maximum temperature in Eq. (23) is

$$\alpha_{\mathrm{homogeneous}} = 2\frac{k_B}{e}. \tag{24}$$

The graded system gives a theoretical 36% increase with respect to a classical system. This analytical calculation is coherent with numerical calculations based on experimental material properties [25,26] that yield a theoretical rise of 27% for $\mathrm{Bi_2Te_3}$ and 35% for Si. The analytical solution diverges at the position L, which corresponds to the hot side of the system. Based on Eqs. (2), (18), and (19), we compute the temperature as a function of the position in the optimal graded case,

$$\Delta T(x) = \frac{T_0^2(\frac{k_B}{e})^2 x}{\kappa\rho_0 \exp(1) L}. \tag{25}$$

Equation (25) shows that the temperature is a linear function of the position. At any position, the Peltier effect due to the graded material compensates for the Joule effect exactly. In this situation, the effective heat generation in the graded material is zero, and all of the heat sources are localized at the interfaces of the graded material.

From Eq. (18), we deduce that the electrical conductivity is a linear function of the position which corresponds [based on Eq. (15)] to a graded material where the doping level is a linear function of the position. For further analysis, we study the maximum cooling of a graded material with a linear doping level. This material will have a doping level of n_h on the hot side and n_c on the cold side, and the doping level is the linear function of the position given by Eq. (26),

$$n(x) = n_c + (n_h - n_c)\frac{x}{L}. \tag{26}$$

The ratio c can be defined as $c = n_h/n_c$, and this coefficient describes the amplitude of the doping gradient.

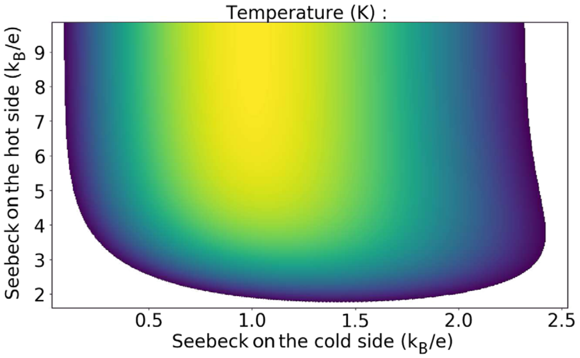

FIG. 3. Plot of the temperature difference as a function of the Seebeck coefficient at the cold side and the Seebeck coefficient at the hot side. $\kappa = 10\ \mathrm{W\,K^{-1}\,m^{-1}}$ and $\rho = 10^{-5}\ \Omega\,\mathrm{m}$. This plot corresponds to a semiconductor with a maximum ZT of 0.012. Only the cases where the temperature obtained is superior to the homogeneous optimal case are displayed. In this figure, we can notice that there is no particular need for a very high Seebeck coefficient on the hot side to obtain a fair improvement of the temperature difference.

The value $c = 1$ corresponds to a classical system with zero gradient. The electrical resistivity and the Seebeck coefficient can be written as functions of these values on the cold side ($x = 0$) and c,

$$\rho(x) = \rho(0)\frac{1}{1 - \frac{x}{L}(1 - c)}, \tag{27}$$

$$\alpha(x) = \alpha(0) + \frac{k_B}{e}\ln\left(\frac{1}{1 - \frac{x}{L}(1 - c)}\right), \tag{28}$$

The Seebeck coefficient on the hot side is

$$\alpha(L) = \alpha(0) - \frac{k_B}{e}\ln(c). \tag{29}$$

From Eqs. (27), (28), (29), (18), and (3), we can derive the temperature difference as a function of the Seebeck coefficient on the cold side and of the Seebeck coefficient on the hot side. In Fig. 3, we can see that maximum cooling is obtained when $\alpha_c = k_B/e$ and α_h is as large as possible.

For a real semiconductor, the optimal profile deviates from our solution on the cold side (due to the decrease in mobility at high carrier density) and on the hot side due to the saturation of the Seebeck coefficient (from bipolar and intrinsic conduction). In Fig. 4, the graded system is obtained for $c = 0.1$, which corresponds to a variation of carrier concentration between the hot and cold sides of a factor 10. For this variation of carrier concentration, a clear and fair improvement of the difference of temperature is obtained. These results highlight that there is no need for an important gradient, and therefore that deviation from the model at low and high carrier concentration will lead to only small consequences for the optimal profile.

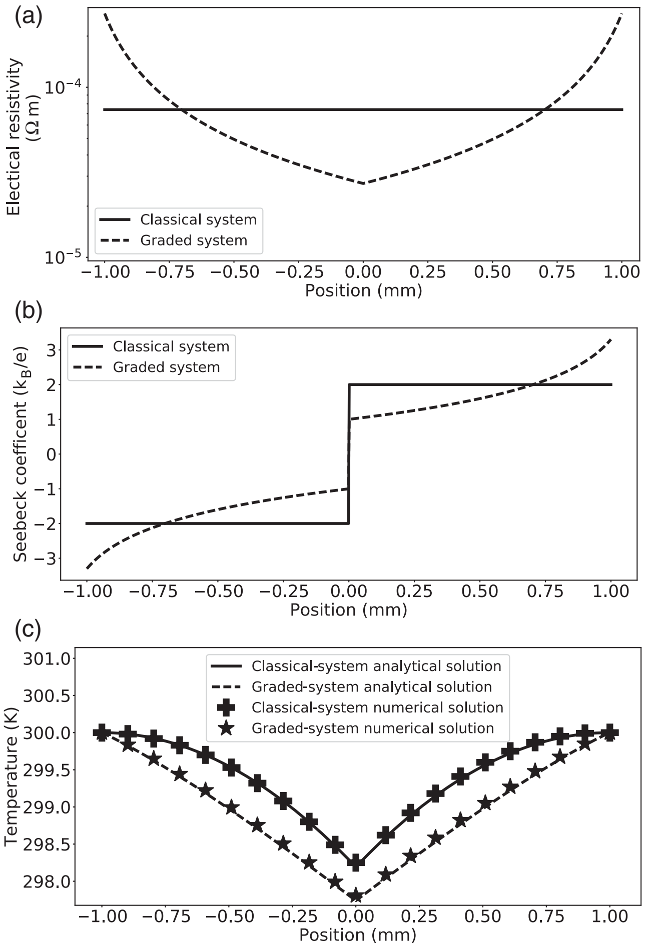

FIG. 4. For a Seebeck coefficient on the cold side of k_B/e where $c = 0.1$, we plot (a) the electrical resistivity, (b) the Seebeck coefficient, and (c) the temperature as functions of the position for the classical system (the solid line) and the graded system (the dashed line). The analytical and numerical solutions are compared. The numerical solution for the classical system (the graded solution) is plotted with crosses (stars).

V. NUMERICAL SOLUTION FOR A GRADED THERMOELECTRIC SYSTEM

A numerical resolution is used to confirm the analytical results without the approximations done for the analytical solution. The numerical solution of a graded material is obtain with the Dynamiques couplées (DYCO) solver, a numerical solver for coupled equations. This solver is based on a nodal approach, and we use it to solve the Onsager relations in a thermoelectric material. In this solver, a Millman approach and the conservation of the flux are used. A description of the theoretical background of the DYCO solver can be found in Chap. 3 of Ref. [33]. Classical systems and graded systems are solved analytically and numerically under the same conditions and results and are summarized in Table I.

For the sake of comparison between the analytical solution and the numerical solution, we choose $\kappa = 1$, 10, and 100 $\mathrm{W\,K^{-1}\,m^{-1}}$, $\rho_0 = 10^{-5}\ \Omega\,\mathrm{m}$, and $c = 0.1$.

TABLE I. In this table, we summarize results obtained with the resolution of graded and classical materials with both numeric and analytical resolution. $\kappa = 1$, 10, and 100 corresponds to $ZT = 0.12$, 0.012, and 0.0012, respectively.

Temperature (K)	Homogeneous system		Inhomogeneous system	
Solution	Analytical	Numeric	Analytical	Numeric
$\kappa = 1\ \mathrm{W\,K^{-1}\,m^{-1}}$	18.1	15.58	22.6	19.6
$\kappa = 10\ \mathrm{W\,K^{-1}\,m^{-1}}$	1.81	1.75	2.26	2.19
$\kappa = 100\ \mathrm{W\,K^{-1}\,m^{-1}}$	0.181	0.177	0.226	0.22

The analytical solution deviates from the numerical solution for high-ZT materials, which are able to impose a large temperature difference. This result is coherent with the approximation made to obtain an analytical solution (we suppose that the temperature stays close to the temperature of the hot side). Numerical solutions confirm that a graded system improves the maximum temperature that can be obtained.

The entropy flux can be evaluated from the solution of the temperature [34]. This approach can be used to evaluate the different sources of entropy in our system. In order to properly evaluate the entropy sources, a solution obtained with no hypothesis is needed. We use the computed numerical solution to perform this evaluation.

From Ref. [34], the entropy flux is given by

$$J_s = \alpha J - \kappa\left(\frac{\frac{\partial T}{\partial x}}{T}\right). \tag{30}$$

As we can separate the transport of heat from the convection and conduction [18], the entropy flux can be separated in convection [the first term of Eq. (30)] and conduction [the second term of Eq. (30)].

The variation of the entropy flux is

$$\nu_f = \frac{\partial J_s}{\partial x} = J\frac{\partial \alpha}{\partial x} - \kappa\frac{\partial\left(\frac{\frac{\partial T}{\partial x}}{T}\right)}{\partial x}. \tag{31}$$

In a stationary condition, the produced entropy (ν_c) is equal to the variation of the entropy flux (ν_f). If we consider the heat equation [Eq. (1)], the entropy produced is given in Eq. (34). The entropy produced is composed of two terms, a term related to the Joule heating and a term related to the thermal gradient:

$$\nu_c = \nu_f, \tag{32}$$

$$\nu_c = J\frac{\partial \alpha}{\partial x} - \kappa\frac{\partial^2 T}{\partial x^2} + \kappa\frac{(\frac{\partial T}{\partial x})^2}{T^2}, \tag{33}$$

$$\nu_c = \frac{\rho J^2}{T} + \kappa\frac{(\frac{\partial T}{\partial x})^2}{T^2}. \tag{34}$$

In Fig. 5, we show that the produced entropy is lower on the cold side in the inhomogeneous case. This lower entropy production is mainly due to the lower Joule heating on the cold side in the inhomogeneous case.

The average entropy produced by the Joule effect is $122\ \mathrm{kW\,K^{-1}\,m^{-3}}$ for the homogeneous case and $140\ \mathrm{kW\,K^{-1}\,m^{-3}}$ for the inhomogeneous case. The average entropy produced by the thermal gradient effect is $0.45\ \mathrm{kW\,K^{-1}\,m^{-3}}$ for the homogeneous case and $0.56\ \mathrm{kW\,K^{-1}\,m^{-3}}$ for the inhomogeneous case. For both sources of entropy, the total entropy produced is higher in the inhomogeneous case.

The total entropy produced by the system is rejected in the thermostat on both hot sides. It can be obtained by integrating ν_c over the entire device:

$$V_c = \int_{-L}^{L}\left(\frac{\rho J^2}{T} + \kappa\frac{(\frac{\partial T}{\partial x})^2}{T^2}\right)dx, \tag{35}$$

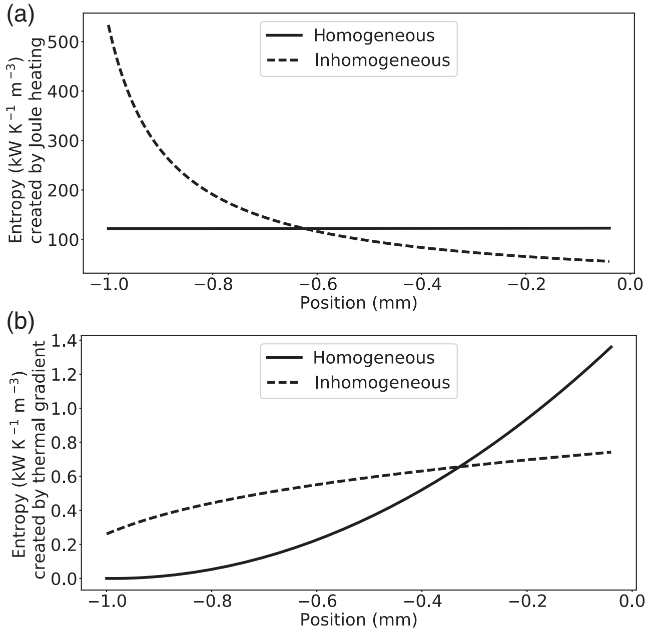

FIG. 5. Plot of the entropy produced between the hot side ($x = -1$ mm) and the cold side ($x = 0$). The entropy produced (a) by Joule heating is higher than the entropy produced (b) by the thermal gradient. For both entropy sources, the entropy produced is higher on the hot side for the inhomogeneous (dashed line) case and higher on the cold side for the homogeneous case (the solid line).

$$V_c = J[\alpha(L) - \alpha(-L)] - \kappa\left(\frac{\frac{\partial T}{\partial x}(L)}{T(L)} - \frac{\frac{\partial T}{\partial x}(-L)}{T(-L)}\right). \quad (36)$$

From Fig. 5, we observe that the produced entropy is due mainly to the Joule heating. In the graded system, the produced entropy is higher on the hot side due to higher Joule heating.

The graded case allows higher performance for the thermoelectric cooler at the cost of higher entropy production. The improved performance is obtained through a redistribution of the entropy production. The graded system has a lower entropy production on the cold side at the cost of higher total entropy production.

VI. CONCLUSION

We analyze a functionally-graded-material-based Peltier cooler by both analytical and numerical means. Both yield an improvement of the temperature difference through the use of graded materials. The analytical solution of the heat equation shows that a local criterion can be found in order to maximize the temperature difference. This criterion is used within an analytical model of a thermoelectric semiconductor. This work shows that it should be possible to improve by 36% the maximum temperature with an optimized graded semiconductor, which corresponds to a cooling down of −88 K, as compared to only −65 K for a homogeneous material [35]. This improvement is equivalent to other theoretical evaluations based on real material properties [25,26].

The improvement of the temperature difference through graded materials has been confirmed with numerical calculations and shows that the hypothesis used for the analytical analysis yields an overestimation of the cooling effect. The overestimation of the cooling effect is due to the approximation made $[JT(x)[(\partial\alpha)/(\partial x)](x) = JT_0[(\partial\alpha)/\partial x](x)]$, which leads to an overestimation of the Thomson-Peltier effect since the temperature is lower than T_0.

The redistribution of the Joule and Peltier effects increases the maximum cooling. In the ideal case, the sum of the Peltier cooling due to the graded material and the Joule heating is zero. In this situation, the temperature displays a linear profile and the maximum cooling is reached. This improvement highly depends on the variation of the material properties with the doping, so other types of material might give higher possible improvements. An entropy-creation analysis through numerical computation shows that the Joule effect is the main source of entropy and that the entropy creation is lower on the cold side in the optimized graded case. The graded system forces the entropy production to be localized on the hot side, which increases the maximum cooling at the cost of a higher total entropy production (leading to a lower efficiency).

ACKNOWLEDGMENTS

The authors thank Association Nationale de la Recherche et de la Technologie (ANRT) (CIFRE) for the funding of doctoral studies by E. T., and STMicroelectronics Tours for their support.

[1] R. G. Moore, Exact computer solution of segmented thermoelectric devices, Adv. Energy Convers. **2**, 183 (1962).

[2] R. W. Ure and R. R. Heikes, Materials requirements for segmented thermoelectric materials, Adv. Energy Convers. **2**, 177 (1962).

[3] L. J. Ybarrondo and J. Edward Sunderland, Influence of spatially dependent properties on the performance of a thermoelectric heat pump, Adv. Energy Convers. **5**, 383 (1965).

[4] K. J. Kountz, A. D. Reich, and M. L. Stanley, Thermoelectric elements utilizing distributed Peltier effect, U.S. Patent No. 3,564,860 (23 February 1971).

[5] R. J. Buist, in *Proceedings of the XIV International Conference on Thermoelectrics, St. Petersburg, Russia, 1995*, edited by M. V. Vedernikov (A.F. Ioffe Physical-Technical Institute, St. Petersburg, Russia, 1995), p. 301.

[6] L. Helmers, E. Müller, J. Schilz, and W. A. Kaysser, Graded and stacked thermoelectric generators numerical description and maximisation of output power, Mater. Sci. Eng. B **56**, 60 (1998).

[7] J. Schilz, L. Helmers, W. E. Müller, and M. Niino, A local selection criterion for the composition of graded thermoelectric generators, J. Appl. Phys. **83**, 1150 (1998).

[8] G. D. Mahan, Inhomogeneous thermoelectrics, J. Appl. Phys. **70**, 4551 (1991).

[9] T. S. Ursell and G. J. Snyder, in *Proceedings of the 21st International Conference on Thermoelectrics (ICT '02), Long Beach, CA, 2002* (IEEE, New York, 2002), p. 412.

[10] G. J. Snyder, in *Proceedings of the 22nd International Thermoelectrics (ITC '03), La Grande Motte, France, 2003* (IEEE, New York, 2003), p. 443.

[11] G. J. Snyder, Application of the compatibility factor to the design of segmented and cascaded thermoelectric generators, Appl. Phys. Lett. **84**, 2436 (2004).

[12] G. J. Snyder and T. S. Ursell, Thermoelectric Efficiency and Compatibility, Phys. Rev. Lett. **91**, 148301 (2003).

[13] W. Seifert, E. Müller, and S. Walczak, Local optimization strategy based on first principles of thermoelectrics, Phys. Status Solidi (a) **205**, 2908 (2008).

[14] W. Seifert, V. Pluschke, and N. F. Hinsche, Thermoelectric cooler concepts and the limit for maximum cooling, J. Phys. Condens. Matter **26**, 255803 (2014).

[15] W. Seifert and V. Pluschke, Exact solution of a constraint optimization problem for the thermoelectric figure of merit, Materials **5**, 528 (2012).

[16] W. Seifert, G. J. Snyder, E. S. Toberer, C. Goupil, K. Zabrocki, and E. Müller, The self-compatibility effect in graded thermoelectric cooler elements, Phys. Status Solidi (a) **210**, 1407 (2013).

[17] G. J. Snyder, E. S. Toberer, R. Khanna, and W. Seifert, Improved thermoelectric cooling based on the Thomson effect, Phys. Rev. B **86**, 045202 (2012).

[18] Y. Apertet, H. Ouerdane, C. Goupil, and P. Lecæur, Internal convection in thermoelectric generator models, J. Phys. Conf. Ser. **395**, 012103 (2012).

[19] L. N. Vikhor and L. I. Anatychuk, Generator modules of segmented thermoelements, Energy Convers. Manage. **50**, 2366 (2009).

[20] L. I. Anatychuk, L. N. Vikhor, L. T. Strutynska, and I. S. Termena, Segmented generator modules using Bi_2Te_3-based materials, J. Electron. Mater. **40**, 957 (2011).

[21] L. N. Vikhor and L. I. Anatychuk, Theoretical evaluation of maximum temperature difference in segmented thermoelectric coolers, Appl. Therm. Eng. **26**, 1692 (2006).

[22] E. M. J. Hedegaard, S. Johnsen, L. Bjerg, K. A. Borup, and Bo. B. Iversen, Functionally graded $Ge_{1-x}Si_x$ thermoelectrics by simultaneous band gap and carrier density engineering, Chem. Mater. **26**, 4992 (2014).

[23] E. Muller, G. Karpinski, L. M. Wu, S. Walczak, and W. Seifert, in *Proceedings of the 25th International Conference on Thermoelectrics (ICT '06), Vienna, 2006* (IEEE, New York, 2006), p. 204.

[24] Z. Bian and A. Shakouri, Beating the maximum cooling limit with graded thermoelectric materials, Appl. Phys. Lett. **89**, 212101 (2006).

[25] Z. Bian and A. Shakouri, in *Proceedings of the 25th International Conference on Thermoelectrics (ICT '06), Vienna, 2006* (IEEE, 2006), pp. 264.

[26] Z. Bian, H. Wang, Q. Zhou, and A. Shakouri, Maximum cooling temperature and uniform efficiency criterion for inhomogeneous thermoelectric materials, Phys. Rev. B **75**, 245208 (2007).

[27] P. J. Price, Theory of transport effects in semiconductors: Thermoelectricity, Phys. Rev. **104**, 1223 (1956).

[28] K. Wu, L. Rademaker, and J. Zaanen, Bilayer Excitons in Two-Dimensional Nanostructures for Greatly Enhanced Thermoelectric Efficiency, Phys. Rev. Applied **2**, 054013 (2014).

[29] S. Walia, S. Balendhran, H. Nili, S. Zhuiykov, G. Rosengarten, Q. H. Wang, M. Bhaskaran, S. Sriram, M. S. Strano, and K. Kalantar-zadeh, Transition metal oxides—Thermoelectric properties, Prog. Mater. Sci. **58**, 1443 (2013).

[30] T. E. Humphrey and H. Linke, Reversible Thermoelectric Nanomaterials, Phys. Rev. Lett. **94**, 096601 (2005).

[31] Q. Li, L. Cruz, and P. Phillips, Granular-rod model for electronic conduction in polyaniline, Phys. Rev. B **47**, 1840 (1993).

[32] F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Refrigeration* (Infosearch, London, 1960).

[33] C. Goupil, *Continuum Theory and Modelling of Thermoelectric Elements* (Wiley, New York, 2016).

[34] C. Goupil, W. Seifert, K. Zabrocki, E Müller, and G. J. Snyder, Thermodynamics of thermoelectric phenomena and applications, Entropy **13**, 1481 (2011).

[35] B. J. Huang, C. J. Chin, and C. L. Duang, A design method of thermoelectric cooler, Int. J. Refrig. **23**, 208 (2000).