Effect of Inevitable Heat Leap on the Conversion Efficiency of Thermoelectric Generators

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Discrepancies between experimental and theoretical results in the study of thermoelectric generators (TEGs) have been a major long-standing problem in thermoelectric technology. In this Letter, we report that, besides interfacial resistance, the inevitable heat leap caused by the Peltier effect is the main factor affecting the conversion efficiency of TEGs. In fact, the heat leap is proven to have an impact of approximately 10% on the conversion efficiency of common TEGs. In addition, we enhance the formula for maximum conversion efficiency with heat leap from the classical expression to allow for the prediction of the performance of advanced materials in TEGs. For the first time, the experimental data from conversion efficiency corresponds exactly to that obtained theoretically by considering both the heat leap and interfacial resistivity.

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Introduction.—Thermoelectric (TE) materials can directly interconvert heat and electricity via internal carriers while enjoying the advantages of wide applicable temperature ranges, high power density, and rapid response, which occupy a leading position in the fields of low-grade heat recovery and microelectronics cooling [1–3]. The thermal-electric conversion efficiency is a primary index in evaluating the performance of TE technology, which firmly depends on the TE figure of merit $ZT[ZT = (\sigma S^2 T)/\kappa]$, where σ, S, κ, T are, respectively, the electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature [4]. Research on improving ZT values has endured for more than a century with significant improvement having been realized in classical materials such as Bi_2Te_3 [5], PbTe [6], GeTe [7], and SnSe [8].

TE materials must be fabricated into a thermoelectric generator (TEG) before practical use. However, the development of TEGs has been far less than that for TE materials. As the only commercially available TEG, the Bi_2Te_3-based TEGs have maximum conversion efficiencies of less than 6.6% [9]. Even using well-developed TE samples such as the GeTe, PbTe, and PbSe, the reported conversion efficiencies have been reported at no more than 12% [10–12]. The low conversion efficiency of TEGs has attracted the attention of researchers focused on revealing the mechanism of power generation [13,14]. Based on theoretical guidance, the conversion efficiencies of TEGs have been improved through methods of material selection [15,16], structure design [1,17], and interfacial optimization [18,19].

The precise representation of performance is the premise of the design and optimization of TEGs, but almost all of the theoretical results predict much higher values than the experimental data [9–12,15–19]. Interfacial resistivity was recognized as the primary factor that restricts the performance of TEG [20] and has thus attracted much attention recently [21–23]. However, theoretical results corresponding to conversion efficiency remain higher than the experimental data even when the error in output power induced by interfacial resistivity is neglected. This has motivated our attention to the study of heat conduction in TEGs.

In the experimental process, we have observed that the measured heat flow is always higher than the corresponding theoretical results when the TEG is connected to a closed loop, and that the error between experimental data and theoretical results will actually disappear in the case of an open circuit. With this in mind, we investigate the mechanism of heat conduction of a TEG through theoretical and experimental methods and prove that the heat leap caused by the Peltier effect is the main factor leading to the error between theoretical results and experimental data. With the aid of numerical and experimental examples, the effect of heat leap on the heat transfer and conversion efficiency of TEGs is discussed in detail. We anticipate that our results can provide a theoretical basis for evaluating TE materials and guide the optimization of TEGs.

Thermal-electric coupling in TE material.—The well-known formula that represents the maximum thermal-electric conversion efficiency of a homogeneous TE material is [4]

$$\eta_{\mathrm{TE}} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{\mathrm{ave}}} - 1}{\sqrt{1 + ZT_{\mathrm{ave}}} + \frac{T_c}{T_h}}, \tag{1}$$

where the subscripts h and c donate the qualities at the hot end and cold end of a TE material, respectively. Here, ZT_{ave} represents the average ZT value among T_c and T_h. Equation (1) can be derived from the governing equations of electric current density $\mathbf{J}$ and heat power density $\mathbf{Q}$ such that [4]

$$\begin{aligned}\mathbf{J} &= -\sigma\nabla\phi - \sigma S\nabla T,\\ \mathbf{Q} &= -\kappa\nabla T + TS\mathbf{J},\end{aligned} \tag{2}$$

where ϕ is the electric potential. In the process of derivation, the material parameters are assumed to be temperature independent. For an insulated TE material, the electrons and total power are transferred conservatively, yielding

$$\begin{aligned}\nabla\cdot\mathbf{J} &= 0,\\ \nabla\cdot\mathbf{U} &= 0,\end{aligned} \tag{3}$$

where the total power density $\mathbf{U}$ within a TE material consists of both heat and electric power densities, and can be expressed as

$$\mathbf{U} = \mathbf{Q} + \phi\mathbf{J}. \tag{4}$$

Consider a TE material with height L, which is subjected to the temperature fields T_h and T_c, respectively, at the hot and cold ends. The distributions of temperature and electric potential in a one-dimensional system along the x axis can be derived by substituting Eqs. (2) and (4) into Eq. (3) as

$$\begin{aligned}T &= -\frac{J^2}{2\sigma\kappa}x^2 + \left(\frac{LJ^2}{2\sigma\kappa} - \frac{T_h - T_c}{L}\right)x + T_h,\\ \phi &= \frac{SJ^2}{2\sigma\kappa}x^2 - \left[S\left(\frac{LJ^2}{2\sigma\kappa} - \frac{T_h - T_c}{L}\right) + \frac{J}{\sigma}\right]x.\end{aligned} \tag{5}$$

Here, the default electric potential at the point $x = 0$ is set to zero. The conversion efficiency of the TE material can be expressed as

$$\eta_{\mathrm{TE}} = \frac{P}{Q_h} = \frac{P}{P + Q_c}, \tag{6}$$

where P is the electric power density, Q_h and Q_c are the heat power densities at the hot and cold ends, respectively. From Eqs. (2) and (5), Q_c can be derived as

$$Q_c = \frac{\kappa(T_h - T_c)}{L} + T_c SJ + \frac{LJ^2}{2\sigma}. \tag{7}$$

Noting that $P = (\phi_c - \phi_h)J$, we have

$$P = S(T_h - T_c)J - \frac{LJ^2}{\sigma}, \tag{8}$$

and

$$\eta_{\mathrm{TE}} = \frac{S(T_h - T_c)J - \frac{LJ^2}{\sigma}}{\frac{\kappa(T_h - T_c)}{L} + T_h SJ - \frac{LJ^2}{2\sigma}}. \tag{9}$$

Since the conversion efficiency is a function of electric current density J, Eq. (1) can be obtained by seeking the maximum value of Eq. (9) with respect to J. It is clear that the thermal and electric fields are restricted to the TE material in the derivation process leading to Eq. (1). However, in practical applications, the electric power generated by the TE material should be exported via electrodes (usually copper or aluminum): this leads to the extra energy exchange on the interface between TE materials and electrodes.

Peltier effect and heat leap.—When TE materials are fabricated into TEGs, the interfacial energy exchange between TE materials and metallic electrodes is inevitable since the energy level of charge carriers is macroscopically uncontrollable at a constant temperature. Taking a p-type TE material as an example, the Fermi level of the TE material is the same as the connected metal. When the electric current flows from TE material to electrode, the holes (the charge carriers in the p-type material) in the valence band of the TE material transfer to the conduction band of the electrode: this is actually the transfer of electrons from metal to the TE material. Since the electrons in the conduction band of metal have higher energy than in the valence band of p-type TE material, the energy will be released on the interface between metal and the TE material, as shown in Fig. 1(a). The released heat is the well-known *Peltier heat*, which can be expressed as [24]

$$q = \Pi J, \tag{10}$$

where Π is the Peltier coefficient on the interface between the TE material and the metal, which can be derived as [25]

$$\Pi = \Delta S T, \tag{11}$$

where $\Delta S = S_{\mathrm{TE}} - S_{\mathrm{metal}}$ is the difference in Seebeck coefficients between the TE material and the metal. On the contrary, the interface will absorb heat when the electric current flows from metal to TE material. As a result, part of the heat will be directly transferred from the hot end to the cold end without any conversion from heat to electricity. The same effect also exists in a n-type TE material due to the different energy of electrons between the conduction band of n-type TE material and the conduction band of metal. We call this effect in TEG "heat leap."

We define a TEG unit composed of a TE leg and the connected electrodes, as shown in Fig. 1(b). When the electric current flows from the TE leg to the electrode at the cold end, the Peltier heat $q_c = \Delta S T_c J$ will be generated on the interface. For an energy-conserved system, part of the Peltier heat will flow back to the TE leg, while the rest

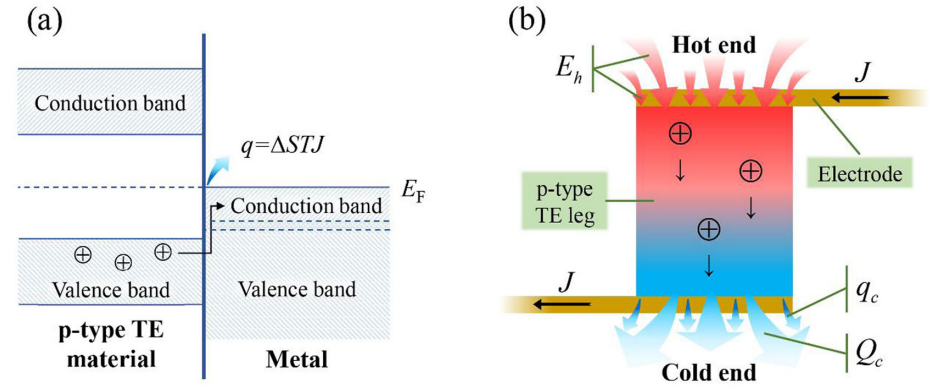

FIG. 1. (a) Energy band structure near the interface between p-type TE material and metallic electrode, and (b) schematic diagram of p-type TEG unit.

of the Peltier heat is released at the cold end beside the heat Q_c transferred by the TE leg. In order to build the temperature gradient (T_h, T_c) at two ends of the TEG unit, additional heat λq_c should be absorbed from the hot end, where the coefficient λ refers to the ratio of Peltier heat released at the cold end. According to the conservation of total energy, the required heat power density E_h at the hot end is

$$E_h = P + \lambda q_c + Q_c. \tag{12}$$

The heat leap can be directly observed in a TEG by measuring the heat power at the cold end. Figure 2 shows that the measured heat power density at the cold end of a Bi_2Te_3-based TEG equals the theoretical value of Q_c when the electric current $I = 0$ since the Peltier heat does not exist in an open circuit. With the increase of the electric current, the measured heat power densities increase rapidly versus the theoretical result of Q_c. The analysis of impact factors shows that the error between theoretical results and experimental data is mainly caused by the heat leap, which accounts for about half of the Peltier heat generated at the cold end of the TEG. Note that the heat power of the TEG is

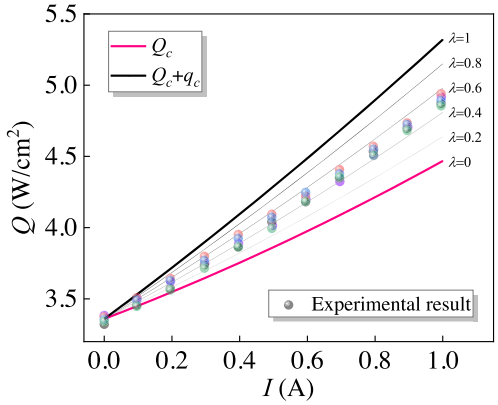

FIG. 2. Heat power density at the cold end of TEG versus electric current.

the sum of the values in both p-type and n-type TE legs. The fabricating process and measuring method of TEG, and the analysis of impact factors are illustrated in Supplemental Material [26].

Under the impact of heat leap, the conversion efficiency of the TEG unit should be expressed as

$$\eta_{\mathrm{TEG}} = \frac{P}{E_h}. \tag{13}$$

According to the detailed derivation process of the maximum conversion efficiency in Supplemental Material [26], we have

$$\eta_{\mathrm{TEG}} = \frac{T_h - T_c}{T_h + \lambda T_c} \frac{\sqrt{1 + Z\overline{T}_{\mathrm{ave}} + \lambda Z\overline{T}_c} - 1}{\sqrt{1 + Z\overline{T}_{\mathrm{ave}} + \lambda Z\overline{T}_c} + \frac{(1+\lambda)T_c}{T_h + \lambda T_c}}. \tag{14}$$

According to the experimental results in Fig. 2, the coefficient λ can be set as $\lambda = 0.5$ in predicting the conversion efficiency of a TEG unit. In comparison, the conversion efficiency of the TEG unit is inevitably decreased from the TE material since the heat leap leads to more heat assumption in generating the same electric power. It is worth pointing out that Eq. (14) applies equally to n-type TE materials since the opposite direction of electric current and the minus Seebeck coefficient will cancel each other in the derivation process.

Theoretical and experimental results.—According to Eqs. (1) and (14), both the temperature loading and the value of Z are the main factors affecting the maximum conversion efficiencies of TE material and TEG unit. Figure 3 illustrates the error induced by heat leap in heat conduction and conversion efficiency under different temperature loading and values of Z, where the temperature at the cold end is $T_c = 300$ K. Results in Fig. 3(a) show that the Peltier heat at the cold end of TEG accounts for 15%–23% of the absorbed heat at the hot end for common TE materials, which decreases with the increase of temperature gradient and increases with the increase of the value of Z. When we set the coefficient $\lambda = 0.5$, the ratio of

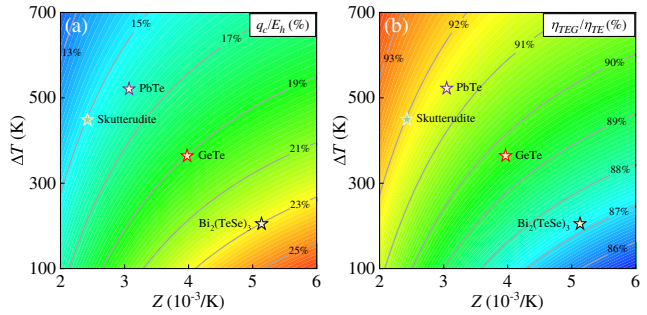

FIG. 3. (a) Ratio between Peltier heat q_c and total power density E_h and (b) ratio of efficiency between TEG unit and TE material versus Z and temperature gradient [5,7,27,28].

conversion efficiencies shown in Fig. 3(b) increases with the temperature gradient while decreasing with the value of Z, which motivates us to enlarge the temperature range of application in the design of TEGs. For the listed TE materials, the conversion efficiency of TEG units has about a 10% reduction from that of TE materials due to the heat leap.

To further reveal the effect of the heat leap on the conversion efficiency of TEGs, we investigate the performance of a Bi_2Te_3-based TEG by comparing the experimental data to the theoretical results. By adjusting the electric current density J in the theoretical derivation and adjusting the external loading in experimental measurement, the maximum conversion efficiency of a TEG can be found for each temperature gradient. Results in Fig. 4(a) show that the theoretical conversion efficiency of the TE material P/Q_h is 23% higher than the experimental data. From Fig. 4(b) we find that the heat leap increases the absorbed heat at the hot end of TEG, thus leading to the reduction of the theoretical value of P/E_h from the theoretical result of P/Q_h. On the other hand, Fig. 4(c) shows that the measured output power has a 10% decline from theoretical results due to the interfacial resistance between TE materials and electrodes, resulting in a further reduction of conversion efficiency from the theoretical value of P/E_h. As a result, the measured conversion

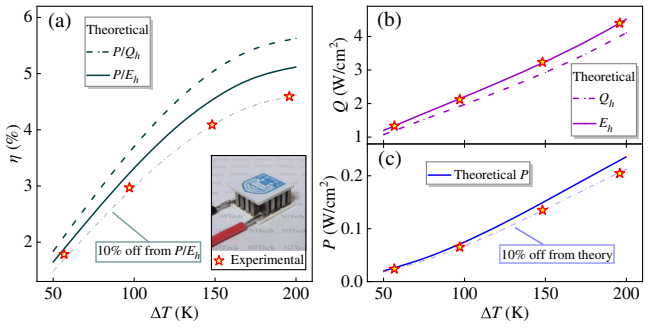

FIG. 4. (a) Conversion efficiency, (b) heat power density at the hot end, and (c) output power density of Bi_2Te_3-based TEG.

efficiency matches well with the theoretical result when considering the effects of both heat leap and interfacial resistance.

Conclusions.—In conclusion, the heat leap caused by the Peltier effect is clarified as an inevitable factor that affects the conversion efficiency of TEGs. The effect of heat leap on heat conduction and conversion efficiency is investigated through theoretical and experimental methods. Results show that the heat leap has an impact of about 10% on both heat conduction and conversion efficiency of TEGs made from common TE materials. Through the experimental method, we observe the heat leap by comparing the measured heat power at the cold end of TEG to the theoretical result, and upgrade the formula for the maximum conversion efficiency of a TEG unit when considering the heat leap. Taking the impacts of both heat leap and interfacial resistivity into consideration, the experimental data of conversion efficiency matches the theory for the first time. Our conclusions provide a theoretical basis for evaluating the TE materials and guide the optimization of TEGs.

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