Generalized theory of thermoelectric figure of merit

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The fundamental equations of thermoelectricity are reviewed in a more general and rigorous context and the efficiency quotient of the thermoelements is derived, with emphasis on the relevance of the figure of merit parameter. The Joule–Lenz, thermoelectric and thermoconducted heat are identified, and the ideal situation of a perfectly homogeneous sample subjected to small temperature and voltage gradients is discussed. Thomson heat and the related Peltier effect arising at local inhomogeneities, such as junctions, are also analyzed. In this context, the efficiency quotient is derived for an ideal thermoelectric sample, which reveals a new figure of merit parameter. It is checked explicitly that the efficiency quotient is always lower than the Carnot efficiency quotient, and it is shown that the new figure of merit never exceeds unity. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2974789]

I. INTRODUCTION

It is well known that thermoelements, which may be used either as Seebeck electric generators or as Peltier electric coolers, are characterized by a figure of merit, according to which the Seebeck thermopower and the electric conductivity must be as high as possible, while the thermoconductivity must be as low as possible, in order to get a high efficiency quotient.[1–3] We limit ourselves to the classical way of operating the thermoelectric circuits, where the local thermodynamic equilibrium is ensured, while small and continuous temperature and voltage gradients are established along the sample. In addition, the sample is assumed to be homogeneous on the macroscopic scale, as for a stable thermodynamical phase. Under these circumstances, the electric flow $\mathbf{j}$ and heat flow $\mathbf{q}$, i.e., the electric charge and, respectively, heat flowing across the unit area of the cross section per unit time, are given by the basic equations of the thermoelectricity[4]

$$\mathbf{j} = \sigma\mathbf{E} - \sigma Q \ \text{grad} \ T \tag{1}$$

and

$$\mathbf{q} = \varphi\mathbf{j} + QT\mathbf{j} - K \ \text{grad} \ T, \tag{2}$$

where σ is the electric conductivity, $\mathbf{E}$ is the electric field, Q is the thermopower, T is the temperature, φ is the electric potential ($\mathbf{E} = -\text{grad} \ \varphi$), and, finally, K denotes the thermoconductivity; the gradient may be specialized to the x direction, i.e., $\text{grad} = \partial/\partial x$. One can see from Eq. (1) that a temperature gradient gives rise to an electric field $\mathbf{E} = -Q \ \text{grad} \ T$, controlled by the Seebeck thermopower coefficient Q; this is the Seebeck effect; while, from Eq. (2), the continuity of the flows across a junction leads to a released heat $-\Delta Q \cdot T\mathbf{j} = \Pi\mathbf{j} = -\Delta(K \ \text{grad} \ T)$ per unit time and per unit area of the junction, which is the Peltier effect, and $\Pi = -T\Delta Q$ denotes the Peltier coefficient. One can already notice

from Eqs. (1) and (2) that a high efficiency requires a high Q and σ and a low K.

II. JOULE–LENZ, THERMOELECTRIC AND THERMOCONDUCTED HEAT

Heat per unit volume and unit time is given by

$$- \text{div} \ \mathbf{q} = \mathbf{E}\mathbf{j} - \mathbf{j} \ \text{grad}(QT) + \text{div}(K \ \text{grad} \ T) \tag{3}$$

from Eq. (2) (since div $\mathbf{j} = 0$, as for a steady flow which conserves the charge), or, making use of Eq. (1),

$$- \text{div} \ \mathbf{q} = j^2/\sigma - T\mathbf{j} \ \text{grad} \ Q + \text{div}(K \ \text{grad} \ T). \tag{4}$$

We note that Eq. (4) holds irrespective of the presence or absence of the external electric field $\mathbf{E}$. In the right hand side of Eq. (4) the first term is the dissipated Joule–Lenz heat, the second term is heat associated with thermoelectric effects, while the third contribution is the thermoconducted heat. Rigorously speaking, for an inhomogeneous sample there may be problems with establishing the thermodynamical equilibrium, so it is appropriate to restrict ourselves to homogeneous samples, as it was said above. For homogeneous samples at equilibrium σ, Q, and K are constant, and the conservation of steady charges div $\mathbf{j} = 0$ in neutral conductors, i.e., div $\mathbf{E} = -\Delta\varphi = 0$, requires grad $T = $const from Eq. (1), so the only heat is the dissipated heat j^2/σ. Under these circumstances there is no thermoelectric heat $-T\mathbf{j} \ \text{grad} \ Q$ and no volume contribution to the thermoconducted heat, div($K \ \text{grad} \ T$) = 0; both the thermoelectric heat and the thermoconducted heat are fully transported through the sample. It is also worth noting that Eqs. (1) and (2) correspond to small $\mathbf{j}$, $\mathbf{E}$, grad T, and $\mathbf{q}$; $\mathbf{j}$ and $\mathbf{E}$ are small in comparison with their counterpart on the atomic scale, since they are produced by macroscopic sources. Equations (1) and (2) should also be viewed as series expansions in grad T, which must be small in comparison with T; if not, the second-order contribution in grad T, which would lead to nonlinear thermoelectrics equations, may imply unphysical temperature gradients, according to material constants, by the same rea-

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son of charge conservation. It is also worth stressing the fact that the density of heat per unit time given by Eq. (3) or (4) is a second-order effect, so that T in the $QT\mathbf{j}$ term in Eq. (2) must be viewed as the local temperature, and, consequently, position dependent. This is related to Onsager's symmetry of kinetic coefficients, and ensures the increasing in the entropy with time;[5–7] indeed, the time variation of entropy is easily obtained from Eq. (4) as

$$\partial S/\partial t = -\int d\mathbf{r}\,\frac{\mathrm{div}\,\mathbf{q}}{T} = \int d\mathbf{r}\cdot[j^2/\sigma T + K(\mathrm{grad}\,T)^2/T^2] > 0,$$

(5)

and it is worth noting that the fully transported thermoconducted heat does not produce, in fact, entropy, since the volume term in Eq. (5) cancels out the surface contribution [the latter not written in Eq. (5)]. This assertion can also be verified directly by performing the integral $\int d\mathbf{r}\,\mathrm{div}(K\,\mathrm{grad}\,T)/T$ with grad T=const (and K=const). From such a standpoint, corresponding to a perfectly ideal situation, the only source of entropy, and the only true dissipation, is through the Joule–Lenz heat, as expected.

III. THOMSON HEAT

It is therefore appropriate to restrict ourselves to the linear equations of thermoelectricity (1) and (2) in the sense discussed above, which provide a consistent description of the thermoelectric phenomena in homogeneous samples; they imply also a small heat flow, in comparison with sample internal energy, as expected, and in agreement with the macroscopic nature of heat flows. Under these circumstances there is no internal (i.e., volume) thermoelectric or thermoconducted heat, as remarked before, and the only source of increasing the entropy is the Joule–Lenz dissipation. Nevertheless, in order to preserve some generality, though at the price of possible certain inconsistencies, it is customary to include the thermoconduction contribution to the increase in entropy in Eq. (5), and, similarly, one may admit localized inhomogeneities for material constants, as appropriate for junctions, for instance. In particular, Q may vary locally, as K may do as well (which does not mean that charge accumulates on, or disappear at junctions, as the normal components of the electric flow are continuous according to the boundary conditions). So, we are led to define the Thomson coefficient $\tau=T(\partial Q/\partial T)$, and get the Thomson thermoelectric heat in Eq. (4)

$$-T\mathbf{j}\,\mathrm{grad}\,Q = -T\mathbf{j}(\partial Q/\partial T)\mathrm{grad}\,T = -\tau\mathbf{j}\,\mathrm{grad}\,T,$$ (6)

per unit time; τ is, in fact, closely related to Peltier coefficient through $\Delta\tau=-T\partial(\Pi/T)/\partial T$. However, one must be aware, for instance, that negative-valued nonvanishing surface contributions may appear in the entropy variations through a position dependent Q, which are unphysical; in fact, the Thomson heat must be viewed as corresponding to Peltier heat, expressed, however, in terms of volume contributions and not as discontinuities at a junction which has a slight spatial extension.

IV. EFFICIENCY QUOTIENT AND FIGURE OF MERIT

The critical analysis made above is meant to point out the kinds of difficulties which may be encountered in practical operation of the thermoelements, as the practitioners are well aware of.

According to the above discussion we limit ourselves to the perfectly ideal situation, where the only volume heat is the dissipated Joule–Lenz heat j^2/σ per unit time and unit volume. This heat may, in principle, be used, as heat produced by thermoelectric effects. Indeed, in addition, we assume that there is no external electric field, such that $\mathbf{j}=-\sigma Q\,\mathrm{grad}\,T$. Actually, as it is well known, only half of this amount of heat may, in fact, be used in an external electric circuit, at most; however, in principle, the whole amount j^2/σ may be used in an ideal situation where the thermoelement is at the same time both source and user of electricity. The same amount of energy is consumed by the thermoelement for establishing the electric flow; in addition, the thermoconducted heat injected at the hot end of the sample, and integrally recuperated at the cold end, is also a consumed energy; it is given from Eq. (4) by $K\,\mathrm{grad}\,T$ per unit area of the cross section and per unit time. It follows that the transformed energy can be written as $j^2/\sigma\cdot lA = Q^2\sigma(\Delta T)^2\cdot A/l$ per unit time, where l is the length of the sample, A is the area of its cross section and ΔT is the temperature drop along the sample. Similarly, the consumed thermoconduction heat is $K|\mathrm{grad}\,T|\cdot A = K\Delta T\cdot A/l$ per unit time. In addition, according to Eq. (2), the Peltier heat $-QT\mathbf{j}=Q^2\sigma T|\mathrm{grad}\,T|$ per unit area of the cross section and per unit time is also consumed; it can be written as $Q^2\sigma T|\mathrm{grad}\,T|\cdot A = Q^2\sigma T\Delta T\cdot A/l$. Consequently one may write down successively the efficiency quotient

$$\eta = \frac{j^2/\sigma\cdot lA}{j^2/\sigma\cdot lA + Q^2\sigma T|\mathrm{grad}\,T|\cdot A + K|\mathrm{grad}\,T|\cdot A}$$

$$= \frac{Q^2\sigma(\Delta T)^2\cdot A/l}{Q^2\sigma(\Delta T)^2\cdot A/l + Q^2\sigma T\Delta T\cdot A/l + K\Delta T\cdot A/l}$$

$$= \frac{\Delta T}{\Delta T + T + K/Q^2\sigma} = \frac{\eta_c}{\eta_c + 1/ZT}$$

(7)

of this perfect, ideal thermoelectric "machine," where $\eta_c = \Delta T/T$ is the efficiency quotient of a perfect Carnot engine, and

$$ZT = Q^2\sigma T/(K + Q^2\sigma T)$$ (8)

is the figure of merit of the thermoelement; it can also be written as

$$ZT = \frac{Q^2}{L + Q^2},$$ (9)

where $L = K/\sigma T$ is the Lorenz number.

V. DISCUSSION

Usually, $Q^2\sigma T/K$ is called figure of merit,[8] but the definition (8) employed here is more appropriate. From Eqs. (8) and (9) we can see that ZT can never exceed unity, $ZT<1$.[9]

Since η must be smaller than η_c, i.e., $\eta < \eta_c$, it follows also $ZT < 1/(1-\eta_c) = 1/(1-\Delta T/T)$ for any ΔT, which shows again that

$$ZT < 1. \tag{10}$$

Accordingly, the maximal value of the efficiency coefficient is $\eta = \eta_c/(1+\eta_c)$, which can never be attained. It is worth noting that, in contrast to the dissipated Joule–Lenz heat, any other amount of heat, like the Thomson heat, or heat arising from thermoconduction are not utilizable in a thermoelectric thermal engine. It is worth noting that previous work[10–12] focused on Joffe's definition of the figure of merit $ZT = Q^2 \sigma T/K$.

In conclusion, a detailed analysis has been developed herein with special emphasis on the range of values taken on by the efficiency quotient and the figure of merit, and its implications were discussed.

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