Journal of Optoelectronics and Advanced Materials, Vol. 3, No. 1, March 2001, p. 125 - 132

NON STEADY-STATE THERMOELECTRIC CONDUCTION

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It is shown that the figure of merit of a thermoelectric couple can be appreciably improved by using a pulsed current transferred from the thermoelectric circuit. In the frame of this theory un unusual drop of temperature in a thermoelectric circuit is possible. An ultrafast process of thermoelectric conduction is described, whose increased performance is realized by minimizing the effects of thermal dissipation.

(Received December 12, 2000; accepted February 9, 2001)

Keywords: Thermoelectricity, Seebeck and Peltier effect, Non-equilibrium transport

1. Introduction

The problem of the limit for the thermoelectric figure of merit and possible values of this limit for thermoelectric (TE) materials was studied in many works [1-6]. In papers [5-6], it is shown that the figure of merit, Z , and the dimensionless parameter, ZT, where T is the temperature, are confined within the following limits

$$\infty \geq Z \geq 0, \ \infty \geq ZT \geq 0$$

At present a detailed and comprehensive analysis of the problem on the possible limits for ZT has been given in paper [7]. Although Z and ZT have no thermodynamic limit, the maximum figure of merit, Z , obtained until today is somewhere around $Z = 3.3\ K^{-1}$. This paper shows that the figure of merit (which is proportional to the electric flow) may increase appreciably by a pulse-operating device, which enhances the electric flow through the concentration of the charge carriers over short lengths, while the rest of the sample is covered by the pulse moving with a high velocity, comparable with the Fermi velocity of charge carriers. The main point of such a device is the practical realization of a sudden drop of temperature over a short distance over the length of the sample.

Recently, new ideas have been advanced in order to increase the efficiency of the thermoelectric devices [8-13]. Such devices consist of an alternate sequence of p-n semiconducting junctions, subjected to an alternate sequence of temperature differentials, such as to create a serial battery of thermoelectric generators. The performance of the power supply output is improved by switching electric contactors. It has been noticed that the power output may greatly be increased for short and ultra-short pulses.

2. Results

The paper describes the transient, non stationary regime of an ultrafast process of thermoconduction. Under stationary external perturbation all relaxation mechanisms compatible with the law of conservation of energy are set to motion in the sample which results in stationary transport of energy and particles. A different situation arises under short pulse perturbations. If, for example, the pulse length is shorter than the characteristic mean-free path , stationary processes do not arise and the transition to equilibrium state takes place some time after the end of the pulse action. In the presence of several relaxation mechanisms the most intensive relaxation mechanism is involved, which is compatible with the law of conservation of energy and characterized by shortest relaxation time. The subsequent system evolution in time is accompanied by other, less intense and longer relaxation mechanisms.

It is worth mentioning that thermoelectric signal is formed only in the nonequilibrium subsystem of charged particles as a response to space and time inhomogeneous carrier temperature. The latter, however, is formed under the influence of boundary and initial conditions and by the nature of interaction with the other subsystems of quasi-particles. It is clear that thermoelectric signal carries information both on thermal parameters of quasi-particles and on various relaxation mechanisms.

Let

$$n(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\mu}{T}}+1} \tag{1}$$

be the Fermi-Dirac distribution of charge carriers with the Fermi level (chemical potential) μ at the temperature T. A local change δT in the temperature gives rise to a change

$$\begin{aligned} \delta n_T &= -\frac{2}{(2\pi\hbar)^3}\int dp(\partial n/\partial\varepsilon)\frac{\varepsilon-\mu}{T}\delta T = \\ &-\frac{\sqrt{2}m^{3/2}}{\pi\ \hbar^3}\int d\varepsilon(\partial n/\partial\varepsilon)\frac{\varepsilon^{3/2}-\mu\varepsilon^{1/2}}{T}(\delta T/T) \end{aligned} \tag{2}$$

in the electron density, where $\mathbf{v} = \partial\varepsilon/\partial\mathbf{p}$ is the quasi-particle velocity and m is the quasi-particle effective mass of the charge carriers (which may be taken as the base electron mass for practical purposes) and $\hbar$ denotes the Planck's constant [13]. According to the theory of slightly inhomogeneous electron liquid [14] the chemical potential μ may be taken as $\mu = p_F^2/2m$, where p_F is the Fermi momentum of a spherical Fermi surface. Integrating by parts in (2) and making use of the Fermi-Dirac integrals

$$\int n(\varepsilon)f(\varepsilon)d\varepsilon = \int_0^{\mu} f(\varepsilon)d\varepsilon + \frac{\pi^2}{6}T^2 f'(\mu) + \ldots \tag{3}$$

for $T/\mu << 1$ one obtains

$$\delta n_T = \frac{\pi 2}{4} n \frac{T\delta T}{\mu^2}, \tag{4}$$

where $n = p_F{}^3/3\pi^2\hbar^3$ is the electron concentration.The result may be generalized for non-spherical Fermi surfaces, and it may also be derived for relatively small concentrations of charge carriers, where equation (3) must be corrected. The numerical computations are carried out here as for electrons in simple metals. The general behavior of the results and the ensuing physical picture do not differ qualitatively with respect to various other practical situations.

The chemical potential undergoes a change $\delta\mu$, given by

$$\delta n_{\mu} = -\frac{2}{(2\pi\hbar)^3}\int dp \cdot \frac{\partial n}{\partial \varepsilon}\delta\mu = \frac{3}{2} n \frac{\delta\mu}{\mu}, \tag{5}$$

such as to preserve the number of electrons. Therefore,

$$\delta n_T + \delta n_{\mu} = 0 \tag{6}$$

and

$$\delta\mu = -\frac{\pi^2}{6}\frac{T}{\mu}\delta T , \tag{7}$$

The change $\delta\mu$ in the chemical potential is equivalent with a change $-\delta\mu$ in the energy levels, and therefore, an electrical potential U appears, such as

$$-eU = -\delta\mu = \frac{\pi^2}{6}\frac{T}{\mu}\delta T , \tag{8}$$

or

$$U = -\frac{\pi^2}{6}\frac{T}{e\mu}\delta T , \tag{9}$$

where e is the electron charge. This is the origin of the thermoelectric effect and

$$-\frac{\pi^2}{6}\frac{T}{e\mu} = Q \tag{10}$$

Q being Seebeck coefficient or the termopower [15]. The change in energy per unit volume is

$$\delta E = c\delta T = \frac{\pi^2}{2\mu} nT\delta T \quad , \tag{11}$$

where $c = (\pi^2/2\mu)nT\delta T$ is the heat capacity of electrons (per volume unit).

The excited (quasi-) electrons in number of $\delta n = \delta n_T = -\delta n_{\mu}$ (per unit volume) move along the x-axis with the (average) velocity $v = v_F \cos\theta = v_F / 2$, where $v_F = p_F/m$ is the Fermi velocity. Here, we leave aside the finite-size and other geometric effects of the sample. The electronic quasi-particles have a finite lifetime τ, as due, for instance, to the electron-electron and electron-phonon interaction. During this short time τ they move along the mean free path Λ, so that their density $n(x,t)$ changes according to

$$n(x,t+\tau) - n(x,t) = n(x-\Lambda,t) - n(x,t), \tag{12}$$

or, as long as $\tau << t$ and $\Lambda << x$,

$$\frac{\partial n}{\partial t} = -v_0 \frac{\partial n}{\partial x} \tag{13}$$

This is the continuity equation, where $j = v_0 n$ is the density of particle flow. Its general solution is:

$$n = f(x - vt) \tag{14}$$

For the initial condition $n(x, t = 0) = V\,\delta n\ \delta(x)$, where V denotes the volume of the local heating, one obtains $f(x) = V\delta n\ \delta(x)$, so that

$$n(x, t) = V\delta n\ \delta(x - v_0 t), \tag{15}$$

The original perturbation propagates along the sample with the velocity v_0. The electric flow is therefore

$$I_0 = -e\, v_0 A\delta n, \tag{16}$$

where A is the area of the cross-section of the sample. Making use of (4) and (9) one may write Ohm's law for the electric resistence as

$$R = U / I_0 = \frac{4}{3}\frac{\mu}{e^2 v_F n}\frac{1}{\sigma}, \tag{17}$$

Since $\mu / v_F n = (3\pi^2 / 2)\ \hbar^3/p^2_F$ one obtains also

$$R = \frac{h}{e^2}(\pi a_e^2 / A), \tag{18}$$

where $a_e = 1 / k_F$ is the average inter-particle separation, $k_F = \hbar / p_F$ being the Fermi wavevector. It follows that the conductivity $R^{-1} = (e^2 / h) \times$ *number of current lines*, hence the quanta e^2/h for electric conductivity. It is worth emphasizing that the formation of δ-pulse through local heating is a highly idealized situation the volume V in (15) being given by $V = A \cdot l_0$ where l_0 is a length of the order of mean free path $(l_0 \cong \Lambda)$. It is worthwhile estimating the efficiency of this ultrafast thermoelectric conduction. According to the above equations the electric energy is given by

$$E = UI_0 t = \frac{\pi^4}{24} nV \frac{(T\delta T)^2}{\mu^3}, \tag{19}$$

while the heating energy δE is given by (11). It follows the efficiency quotient

$$\eta = E / \delta E = \frac{\pi^2}{12}\left(\frac{T}{\mu}\right)^2 \eta_C, \tag{20}$$

where $\eta_C = \delta T / T$ is the Carnot quotient. One can see that η is much smaller than η_C, since $T / \mu << 1$. The thermoelectric conduction is indeed a second-order effect, in the sense that both the voltage and the number of charge carriers are proportional to δT, so that the electric power goes like $(\delta T)^2$. In contrast with the heat given by (11) which is a first order effect (and which is transported by thermal conduction), while the main part of heat is spent for thermal disorder, only a small fraction of it is spent for thermoelectric conduction. For typical values $\mu \sim 1eV$, $v_F \sim 10^5 m/s$, $A \sim 1\ cm^2$, $\delta T \sim 100\ K$ and room temperature T, one obtains a rather small voltage $U \sim 10^{-4}\ V$, according to (9), but a high electric flux $I_0 \sim 10^7\ A$,from (16), i.e an electric power of the order of $\sim 1kW$. It is worth emphasizing that the electric flow as given by I_0 in (16) does not depend essentially on the electron concentration. We also note that the efficiency quotient derived above for an ideal δ-pulse is the same as the efficiency quotient corresponding to thermoelectric conduction at thermal equilibrium.

The lifetime τ_e of the electronic quasi-particles due to the electron-electron collisions is given by [14]

$$\frac{1}{\tau_e} \cong \frac{1}{\hbar} B^2 \frac{\rho^3}{n} T^2, \tag{21}$$

where $B \cong 4\pi e^2 / k_F^2$ and $\rho = mp_F / \pi^2 \hbar^3$ is the density of states at Fermi level. Making use of the atomic units of Bohr radius $a_H = \hbar^2 / me^2 = 0.53$ Å and $e^2 / a_H = 27.2\ eV$, one gets

$$1 / \tau_e \approx (a_e^2 / 27.2) * 10^7 T^2, \tag{22}$$

and for typical electronic densities at room temperature one obtains $1 / \tau_e \approx 10^{12}\ s^{-1}$, and the corresponding mean free path $\Lambda \approx 10^{-7}\ m = 10^3$ Å $= 0{,}1\ \mu m$. The electronic quasi-particle lifetime $\tau_{e\text{-}ph}$ caused by the electron-(acoustic) phonon collisions is given by [16]

$$\frac{1}{\tau_{e-ph}} \cong \frac{1}{\hbar}\frac{T}{F} = \frac{1}{\hbar}\frac{m}{M}\left(\frac{\mu}{\omega_D}\right)^2 T, \tag{23}$$

where M is the atomic mass and ω_D is the Debye frequency. For typical parameter values one gets $F \approx 10 - 100$ and $1/ \tau_{e\text{-}ph} \cong 10^9 - 10^{10}\ T$, which gives $1/ \tau_{e\text{-}ph} \cong 10^{11} - 10^{12}\ s^{-1}$ at room temperature. As one can see, it is comparable with the electron-electron lifetime of the electronic quasi-particles and the mean free path $l \cong 10^{-7}\ m = 10^3$ Å as given above. In fact, a comparison of the numerical factors in (22) and (23) shows that at room temperature the collision regime is usually dominated by the electron-phonon interaction.

It follows from the above considerations that the δ-pulse corresponding to the thermoelectric flux I_0 given by (16) is transported without dissipation over the length l of the sample with the velocite $v = v_F/2$. The time of flight is therefore $t_0 = 2l / v_F$. For $l = 1mm$, for instance, one obtains $t_0 \cong 2 \times 10^{-8}\ s$, i.e. a frequency $\nu_0 = 1/t_0 \cong 50\ MHz$. However, for longer times it begins to appear the dissipation of the electric flow, as due to the diffusion of the charge carriers. Indeed, already for an open circuit the electrons bounce on the ends of the sample, giving rise to thermal dissipation. Similarly, for a continuous operation in short circuit the electrons move repeatedly along the sample. For a motion proceeding in both directions equation (12) becomes

$$n(x,t + \tau) - n(x,t) = n(x + \Lambda,t) + n(x - \Lambda,t) - 2\, n(x,t), \tag{24}$$

or

$$\frac{\partial n}{\partial t} = \Lambda v_0 \frac{\partial^2 n}{\partial x^2}, \tag{25}$$

which is the diffusion equation. It is worth emphasizing in this context the statistical nature of equations (12) and (24), as $1/ \tau$ is the quasi-particle probability, and Λ stands therefore for dissipation length [17]. For the same initial condition $n(x, t = 0) = V\delta n\, \delta(x)$ as the one used in (13) one may write for (25) the Fourier representation

$$n(x,t) = V\delta n \frac{1}{2\pi} \int dk \cdot e^{-ikx - \Lambda v_0 k^2 t}, \tag{26}$$

the integral can easily be estimated as

$$n(x,t) = V\delta n \frac{1}{\sqrt{4\pi\Lambda v_0 t}} e^{-x^2/4\Lambda v_0 t}, \tag{27}$$

which is the well-known solution of the diffusion equation. Similarly, equation (24) becomes for longer times

$$\frac{\partial n}{\partial t} = -v_0 \frac{\partial n}{\partial x} + \frac{1}{2} l v_0 \frac{\partial^2 n}{\partial x^2}, \tag{28}$$

whose solution is

$$n(x,t) = V\delta n \frac{1}{\sqrt{4\pi\Lambda v_0 t}} e^{-(x\ -v_0 t)^2/2\Lambda v_0 t} \ . \tag{29}$$

One can see that the peak of the charge carriers flattens gradually over a distance $\Delta x = 2\sqrt{l v_0 t},$ while moving with the velocity v_0. The electric flux

$$I = -e\int dx \cdot v_0 \frac{\partial n}{\partial x} \tag{30}$$

vanishes in the limit of the long times. For shorter times the electric flux is diminished to $I \sim I_0 l_0 / \sqrt{2\pi\Lambda v_0 t}$, where $l_0 \sim \Lambda$ is the original width of the ideal δ-pulse. The time after which the dissipation effect prevails upon the propagation is of the order of $t_1 \approx l^2/\Lambda v_0 \approx t_0 (l/\Lambda)$, corresponding to $\Delta x \approx l$. For $l = 1\ mm$ and $t_0 = 2 \times 10^{-8}\ s$ given above, and for the diffusion length $l \approx 10^3$ Å, one obtains $t_1 \approx 10^4\ t_0 \approx 2 \times 10^{-4} s$, corresponding to frequency $\nu_1 \approx 5\ kHz$. For any pulse- operating regime of frequency ν in the range ν_1 - ν_0 , i.e. $\nu_1 < \nu < \nu_0$, the electric flux is of the order of I given above, diminishing gradually for lower frequencies. For frequencies below the lower bound ν_1 the electric flux diminishes drastically, and the equilibrium-transport regime is reached. Of course, the finite duration of the electric contacts has the same damping effect.

The ideal pulse-operating regime described above is, therefore, limited by the extent of local heating, over which the heat dissipation acts. Let us assume that the local heating takes place over a length l', such as $\Lambda << l' << l$. Then, the heat $cl'\Delta T$ (per unit area) supplied for a temperature variation ΔT is given by $\kappa(\Delta T / l')t'$, where $\kappa \cong c v_F \Lambda$ is the electron thermoconductivity, which is independent of the temperature difference. The pulse formed over the distance l' moves with the velocity v_0 , so that the flight time is $t = (l-l')/v_0 \sim t_0$. One can see that the time t' needed for the formation of the pulse is much longer than the flight time (by the factor $l'^{\,2}/l\Lambda$). For an optimal operation the electric contacts should be maintened a duration t, and interrupted a duration t' , (while the thermal contacts must be maintened a time t', i.e. practically all the time). The operating frequency is therefore $\nu = 1/(t+t') \cong \nu_0(\Lambda l/l'^{\,2})$, and one can see that the ideal case $\nu = \nu_0$ is not attained, except for "microscopic engine" where $l' \sim l$ (the equality $l\Lambda = l'^{\,2}$ is difficult to be satisfied in practice. In fact, in order to preserve the width of the pulse durring its flight through the sample the condition $l\Lambda << l'^{\,2}$ must be satisfied, which is equivalent to $\nu << \nu_0$ and $t << t'$). The frequency ν can be also be written as $\nu = \nu_1 (l/l')^2$, where $\nu_1 = \nu_0(\Lambda/l)$ has been introduced above as the lower limit of the operating frequency. For the typical values given before ($\nu_1 = 5\ kHz$) and a reasonable ratio $l'/l = 1/2$ one obtains approximatelly $\nu = 20\ kHz$. The density of the charge carriers in the pulse formed at one end of the sample is given by (15) where now the volume V is given by $V = A \cdot l'$. The electric flux is of the order of I_0, and the electric energy is given by (19) (coresponding to $V = A \cdot \Lambda$). One can see that it increased in the same proportion as heat increased, so that the efficiency quotient given by (20) is left unchanged. However, the electric power is referred to the time $t' = (1/v_F)\ l'^{\,2} / \Lambda$ needed for formation of the pulse (as well as for its full relaxation), so that it is decreased by the factor l'/Λ, and the electric flux

$$I \sim I_0\,(\Lambda/l') \tag{31}$$

is also reduced to the same extent. One can see that the ideal situation is approached for heating lengths l' as short as posible. For $l'/l = 1/2$ and for the typical values given above the electric flux is reduced to $I \sim 10^3$ A. It is also worth nothing that the extent of pulse is now $\Delta x \sim \sqrt{\Lambda v_0 t'} = l'$, as expected, and t' is precisely the time needed for formation of pulse tail $\sqrt{\Lambda v_F t'}$ of the order of l', i.e. $t' \sim (1/v_F)\, l'^2/\Lambda$.

In general, the high-performance device operation requires high-quality electric contacts, a sharply-defined operating pulse frequency ν, obeing as close as possible the contact interruption $t' = (1/v_F)\, l'^2/\Lambda$ and contact duration $t = (l - l')/v_0$, good thermal isolation, and good thermal contacts. The latter are necessary since the thermal conduction is always present (including that due to the phonon transport), and a decrease of temperature as abrupt as possible must be ensured over short distances l'. Under the conditions described above the heat injection into the sample is an equilibrium process, its rate being of the order of $v_F(\Lambda/l')$ (while the heating time is $t' \sim (1/v_F)\, l'^2/\Lambda$). A similar rate holds for the lattice heat, where the Fermi velocity is replaced by the sound velocity v_s. Usually, long after the dissipation is fully developed, a stationary drop of temperature is realized over the sample length, of small, constant gradient, which is the usual condition under which the transport experiments (like thermoconduction, electric conduction, thermopower, etc.) are conducted [15]. In contrast to the situation described above (which is a non-stationary, transient, and non-equilibrium one), such cases correspond to stationary, equilibrium transport.

It is worth noting that for equilibrium transport the electric conductivity σ is given by $I = \sigma UA/l$ and the thermoconductivity $k = KA\delta T/l$, the electric power is therefore $P_e = U\cdot I = \sigma Q^2 A\,(\delta T)^2/l$, where $Q = U/\delta T$ is the thermopower (Seebeck coefficient), while the caloric power is $P_{cal} = \partial\delta E/\partial t$, one can write therefore the efficiency quotient as

$$\eta = \frac{T\sigma}{K} Q^2 \eta_C, \tag{32}$$

the ratio $K/T\sigma = L$ is the Lorenz number, which is independent of temperature, according to Wiedemann-Franz law. For ideal conditions $L = \pi/3e^2$. On the other hand, the ideal thermopower is given by

$$Q = -\frac{\pi^2}{6e}\frac{T}{\mu}, \tag{33}$$

for $T/\mu << 1$, so that the efficiency quotient above becomes $\eta = \frac{\pi^2}{12}\left(\frac{T}{\mu}\right)^2 \eta_C$, as that given by (20).

3. Conclusions

The electric flux through the sample is given by $I \approx I_0\,(\Theta/T)^2$ or $I \approx I_0\,[\Theta^2/T(T+\Theta_2)]$, at room temperatures, as corresponding to electron-electron or electron-electron plus electron-phonon relaxation processes, where the scale temperatures are typically $\Theta \approx 1$ K (for 1 cm^2 an area of cross-section) and $\Theta_2 \approx 10^2$ K. Both I_0 and the voltage U are the same as those computed above [16]. One can see that the equilibrium processes reduce the electric flow by a factor of $\approx 10^5$ at least, leading to $I \approx 10^2$ A for typical sample employed here. It corresponds very closely to a reduction factor of the order Λ/l, $(\Theta^2 \sim \Lambda/l)$, where l is the mean transverse size of the sample, and stands for the local heating length l' introduced above. As long as this length l is replaced by the much shorter length l', through the pulse-operating regime described here, the performance of such devices is much improved. In this difference resides the distinction between the equilibrium electric transport employed in the usually operated thermoelectric devices and the non-equilibrium electric transport in the fast pulse-operating devices.

In fact it was demonstrated that an ultrafast process with increased thermoelectric performances can be realised by minimizing the thermal dissipation. It is described a "pulse operating regime" of a new "cold" thermoelectric device.

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