THERMOELECTRIC FIGURE OF MERIT OF THIN PLATES AND THIN FILMS

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The relations for the figure of merit of thin plates and thin films are derived. Thin plates and thin films are defined as samples of thickness comparable to or smaller than the mean free path of electrons and phonons. In this case the size of sample has a considerable influence upon some physical characteristics, e. g. electrical and thermal conductivity, Seebeck coefficient etc. It is therefore evident that the figure of merit, defined on the basis of this physical characteristics, depends on the thickness of the sample too. In the present paper it is shown that the *size* effect has in general a negative influence upon the thermoelectric figure of merit, but there are some cases in which the situation is more favourable.

INTRODUCTION

Mac Donald and Templeton [1] had pointed out the possibility of using the thermoelectric behaviour of materials for the construction of refrigerators at very low temperatures. It would be also possible to use these materials for the construction of thermogenerators acting at low temperatures. Ioffe [2] and other authors [3—7] had pointed out, that the efficiency of these devices is given by the Carnott efficiency and by the thermoelectric figure of merit, the latter defined by the relation:

$$Z = \frac{\alpha^2 \sigma}{\lambda} \tag{1}$$

where α is the Seebeck coefficient, σ the electrical conductivity and λ the thermal conductivity.

The maximum of the temperature change δT is given by the formula:

$$\delta T = \frac{1}{2} ZT. \tag{2}$$

It can be seen from this relation that for reaching a useful result it is necessary for the figure of merit to have the value of about 10^{-3} deg^{-1} at room temperature and the value of about 10^{-2}—10^{-1} deg^{-1} at very low temperatures.

In cases when the mean free path of electrons and phonons is greater than the thickness of the used materials (this case occurs at very low temperatures), all physical characteristics in the definition (1) depend on the geometry of the samples. It is therefore very important to find out whether this *size* effect has a positive or a negative influence upon the efficiency of the thermoelectric devices. For the solution of this problem the dependence of the electrical conductivity, the thermal conductivity and the Seebeck coefficient on the thickness of the sample must be known.

The foundations of the theory of electrical conductivity of thin plates and thin films were laid by Fuchs [8]. Sondheimer [9] and Dingle [10] used his theory for solving the problem of electrical conductivity of metal thin films and thin wires. The theory was applied to semiconducting thin films (with respect to the surface electric charge) by Schrieffer [11], Ciobanu and Croitoru [12].

Casimir [13] dealt with the problem of the influence of the geometrical delimitation upon the thermal conductivity of dielectric crystalline samples. From the modern standpoint (using the Boltzmann equation) the problem was solved by Ziman [14], Berman et al [15], Gurzhi [16], Gurzhi and Schewtchenko [17]. The influence of the substrate of thin film upon thermal conductivity was considered by Bezák and Krempaský [18].

The Seebeck coefficient of thin samples was theoretically investigated and experimentally dealt with by Justi, Kohler and Lautz [19—20]. We can apply this theory to the degenerate semiconducting thin plates where the electric field, due to the surface electric charge, is negligible. The problem of the Seebeck coefficient of thin plates of a semiconductor and thin semiconducting film has not been solved so far, but the necessary information can be found by using the method described in paper [19] and the results of paper [11].

In the present paper we consider only the metals and degenerate semiconductors, as there are only these two types of materials which can be used at very low temperatures (nondegenerate semiconductors are insulators at low temperatures).

INFLUENCE OF THE SAMPLE THICKNESS UPON THE THERMOELECTRIC FIGURE OF MERIT

1. *Basic equations*

We assume the sample to be homogeneous, its length in the directions of X and Y-axes to be infinit and its thickness to be h. The Seebeck coefficient, the electrical conductivity and the thermal conductivity of the sample are given by the relations:

$$\alpha = \alpha_\infty(1 - f_\alpha) \qquad (3a)$$

$$\sigma = \sigma_\infty(1 - f_\sigma) \qquad (3b)$$

$$\lambda = \lambda_\infty(1 - f_\lambda) \qquad (3c)$$

where α_∞, σ_∞ and λ_∞ are the characteristics of bulk materials. As the thermal conductivity has in general two components: the electron thermal conductivity and the phonon thermal conductivity, we can write

$$\lambda = \lambda_e + \lambda_m \qquad (4a)$$

$$\lambda_\infty = \lambda_{e\infty} + \lambda_{m\infty} \qquad (4b)$$

$$f_\lambda = \frac{\lambda_{e\infty} f_\sigma + \lambda_{m\infty} f_{\lambda m}}{\lambda_{e\infty} + \lambda_{m\infty}}\,. \qquad (4c)$$

We put $f_{\lambda e} = f_\sigma$. This fact results from the Franz-Wiedemann law $\lambda_e/\sigma = L\,T$, where L is the Lorentz number.

Using the relations (1) and (3), we can express the thermoelectric figure of merit in the form:

$$Z = Z_\infty \frac{(1 + K)(1 - f_\alpha)^2}{1 + K\dfrac{1 - f_{\lambda m}}{1 - f_\sigma}} \qquad (5)$$

where $K = \lambda_{m\infty}/\lambda_{e\infty}$ is the ratio of the phonon and electron thermal conductivity in the bulk material.

According to [8], [18] and [19] the functions f_σ, $f_{\lambda m}$ and f_α for the metal and degenerare semiconducting thin plates can be expressed by the formulas:

$$f_\sigma = \frac{3(1 - P_e)}{8a_e} + \frac{3(1 - P_e)}{4a_e} \sum_{m=1}^{\infty} P_e^{m-1} \left\{ \int_{ma}^{\infty} \frac{e^{-x}}{x}\, dx \left(a_e^2 m^2 - \frac{1}{12} a_e^2 m^2 \right) + e^{-ma_e} \left(\frac{1}{2} - \frac{5}{6} ma_e - \frac{1}{12} a_e^2 m^2 + \frac{1}{12} a_e^3 m^3 \right) \right\} \qquad (6a)$$

$$f_{\lambda m} = \frac{3a_f}{2} \int_0^1 u(1 - u^2)(1 - e^{-a_f/u}) \frac{1 - P_f - Qk_2/k_1}{1 - P_f e^{-a_f/u}}\, du \qquad (6b)$$

$$f_\alpha = -\frac{1}{n + 1} \left\{ 1 + n \left[\frac{1 - 3(1 - P_e)/8a_e + 3(1 - P_e)^2/4a_e \sum_{m=1}^{\infty} P_e^{m-1} G_1(m,\, a_e)}{1 - 3(1 - P_e)/8a_e + 3(1 - P_e)^2/4a_e \sum_{m=1}^{\infty} P_e^{m-1} G_2(m,\, a_e)} \right] \right\} \qquad (6c)$$

where

$$G_1 = \int_{ma_e}^{\infty} \frac{e^{-x}}{x} dx \left(-a_e^2 m^2 + \frac{1}{4} a_e^4 m^4\right) + e^{-ma_e}\left(\frac{1}{2} + \frac{1}{2} ma_e + \frac{1}{4} a_e^2 m^2 - \frac{1}{4} a_e^3 m^3\right)$$

$$G_2 = \int_{ma_e}^{\infty} \frac{e^{-x}}{x} dx \left(a_e^2 m^2 - \frac{1}{12} a_e^4 m^4\right) + e^{-ma_e}\left(\frac{1}{2} - \frac{5}{6} a_e m - \frac{1}{12} a_e^2 m^2 + \frac{1}{12} a_e^3 m^3\right).$$

Here $a_e = h/l_e$, $a_f = h/l_f$, where l_e and l_f are the mean free paths of electrons and phonons in the bulk material, P_e and P_f are the probabilities of the specular reflection of the electron and the phonon from the surface of the sample, Q is the probability of the *exchange* of phonons between the substrate and the sample, k_1 and k_2 are the thermal diffusivity of the substrate and of the bulk sample respectively, n is the exponent in the relation $l_e \sim E^n$, where E is the energy of the electron.

The probabilities P_e, P_f and Q according to Ziman [14] and Bezák – Krempaský [18] are given by the functions:

$$P_e = \exp(-4p^2 k_e^2 \cos^2 \vartheta) \tag{7a}$$

$$P_f = R_{12}^2 \exp(-4p^2 k_{1f}^2 \cos^2 \vartheta) \tag{7b}$$

$$Q = (1 - R_{12}^2) \exp[-p^2(k_{1f} \cos \vartheta_1 - k_{2f} \cos \vartheta_2)^2] \tag{7c}$$

where

$$\frac{\sin \vartheta_1}{\sin \vartheta_2} = \frac{v_1}{v_2}, \quad R_{12} = \frac{\gamma_1 v_1 \cos \vartheta_1 - \gamma_2 v_2 \cos \vartheta_2}{\gamma_1 v_1 \cos \vartheta_1 + \gamma_2 v_2 \cos \vartheta_2}.$$

Here k_e and k_f are the wave numbers of the electrons and phonons respectively, v is the velocity of the phonon, γ the specific mass, ϑ the angle of the refraction, p the roughness coefficient. Index 1 denotes the sample, index 2 the substrate. Both surfaces of the considered sample are assumed to be equivalent (from the viewpoint of the refraction).

2. *Approximation for $h > l_e$ and $h > l_f$*

Using the relations (6) and (5) one obtains complicated expressions which cannot be easily expressed. Assuming that $a_e > 1$, $a_f > 1$ we can simplify the functions (6). In this case the thermoelectric figure of merit is determined by the relation:

$$Z = Z_\infty(1 + K)\left[1 - \frac{3}{8a_e}\frac{n}{n+1}(1 - P_e)\right]^2 \times$$

$$\times \left[1 + K \frac{1 - 3(1 - P_f - Qk_2/k_1)/8a_f}{1 - 3(1 - P_e)/8a_e}\right]^{-1}. \tag{8}$$

For the metal thin films, where $\lambda_{e\infty} \gg \lambda_{m\infty}$, i. e. $K \ll 1$ one could obtain the formula:

$$Z = Z_\infty\left[1 - \frac{3}{3a_e}\frac{n}{n+1}(1 - P_e)\right]^2. \tag{9}$$

It is seen that the thermoelectric figure of merit of thin metal plates is always smaller that that of the bulk material. In the ideal case, when $P_e = 1$, i. e. when all electrons are reflected from the surface, it is $Z = Z_\infty$. We would obtain the same result in the case of $P_e \neq 1$ under the assumption that $n = 0$, i. e. if the mean free path of the electron did not depend on the energy.

In degenerate semiconductors with $\lambda_{m\infty} > \lambda_{e\infty}$ (i. e. $K > 1$) we have for the figure of merit $[(1 - f_\alpha)^2 \approx 1 - 2f_\alpha]$

$$Z = Z_\infty\left[1 + \frac{1}{8a_f}(1 - P_f - Qk_2/k_1)\right]\left[1 - \frac{l_e(1 - P_e)(1 + 2n/(n+1))}{l_f(1 - P_f - Qk_2/k_1)}\right]. \tag{10}$$

This relation shows that under special conditions the thermoelectric figure of merit of thin plates can be greater than that of bulk material. The maximum occurs at $P_e = 1$, or $n = 0$ and $P_f = 0$, $Q = 0$ (or $k_2 \ll k_1$) and is determined by the formula:

$$Z = Z_\infty\left(1 + \frac{3}{8}\frac{\cdot l_f}{h}\right). \tag{11}$$

From the relation (7) it follows that this case can be realized. The ratio of the wavelengths of electrons and phonons in semiconductors and semimetals is at given temperatures approximately the same as the ratio of the velocity of electrons and the velocity of sound. So this approximate formula can be written for the ratio of the wave numbers:

$$\frac{k_f}{k_e} \doteq \frac{v_e}{v_z}.$$

This ratio has the value of about $10^2 - 10^3$ at room temperature. If the exponent in the relation (7a) is < 1 (and $P_e = 1$), the exponent in the relation (7b) and (7c) at the same value of the coefficient p can be > 1 and so $P_f \to \to Q \to 0$.

3. *Very thin plates (thin films)*

If the mean free path of electrons and phonons is substantially greater than the thickness of the sample, one can derive the following formula for the thermoelectric figure of merit (from the relation (5) using the functions (6)):

$$Z = Z_\infty(1+K)\left[1+\frac{n}{n+1}\frac{\ln a_e+0.58}{\ln a_e-0.42}\right]^2 \times$$

$$\times\left\{1+K\frac{1-P_e}{1+P_e}\frac{\dfrac{Qk_2}{(1-P_f)k_1}+\dfrac{3a_f}{4}(1-P_f-Qk_2/k_1)\left[\dfrac{1+P_f}{1-P_f}\right]^2(0.42-\ln a_f)}{a_e(0.42-\ln a_e)}\right\}^{-1}. \tag{12}$$

For the metal thin films (where $K \ll 1$) this complicated formula can be simplified to the form:

$$Z = Z_\infty\left(1+\frac{n}{n+1}\frac{\ln a_e+0.58}{\ln a_e-0.42}\right)^2 \approx Z_\infty\frac{1}{(n+1)^2}. \tag{13}$$

It is seen that, except in the case $n = 0$ and $P_e = 1$ respectively, the thermoelectric figure of merit of thin metal films increases when the thickness of the sample decreases.

An interesting case can be realized in degenerate semiconductors with $\lambda_{m\infty} > \lambda_{e\infty}$. When special conditions are fulfilled, i. e. $P_f \to 0$, $Q \to 0$ and $P_e = 1$, the phonon thermal conductivity decreases, but the electrical conductivity and the Seebeck coefficient do not change their value (or they change it only a little) when the thickness of thin film decreases. As a result the increase of the thermoelectric figure of merit of thin semiconducting films can occur. This increase is limited by a decrease of the phonon thermal conductivity below the value of the electron thermal conductivity. The maximum of the thermoelectric figure of merit, as it follows from the relation (12) or directly from the relation (5), is given by the formula:

$$Z_{\max} = Z_\infty\frac{\lambda_{m\infty}}{\lambda_{e\infty}}. \tag{14}$$

Taking into consideration the definition $Z_\infty = \alpha_\infty^2\sigma_\infty/\lambda_\infty$ we can rewrite the formula (14) in the form:

$$Z_{\max} = \frac{\alpha_\infty^2}{LT} \tag{15}$$

where $L = (\pi^2/3)(k^2/e^2)$ is the Lorentz number. This result is identical with the relation for the figure of merit of metal samples, for which we always have $\lambda_e > \lambda_m$. But the Seebeck coefficient of metal samples is very small (some units or tens μV/deg at room temperature or about 1—3 μV/deg at very low temperatures), therefore the value of figure of merit is very small too. Its value is about 10^{-5}—10^{-4} deg^{-1} at room temperature and can be a bit greater at very low temperatures. The Seebeck coefficient of degenerate semiconductores has a substantially greater value and the figure of merit of such semiconductors could acquire a value of practical importance at very low temperatures.

From this standpoint the semiconductor BiSb, the figure of merit of which in bulk material has the value of about 6×10^{-3} deg^{-1} at the temperature of 80 °K could have a great importance (see e. g. [21]).

CONCLUSION

Knowing the dependence of electrical conductivity, thermal conductivity and the Seebeck coefficient from the thickness of the sample at low temperatures the relation for the thermoelectric figure of merit is derived. The problem of the suitability of the metal and the semiconductors for the construction of thermoelectric devices at very low temperatures is discussed. It was shown that metal materials cannot be used for this purpose, because the *size* effect has a negative influence upon their figure of merit. As a convenient material a degenerate semiconductor was found. His figure of merit has a greater value than that of the metal and by fulfilling the special conditions the *size* effect can cause another increase of this value. In an ideal case the figure of merit of a thin semiconducting film can be $\lambda_{m\infty}/\lambda_{e\infty}$-times greater than that of the bulk material. It could be therefore convenient to use degenerate semiconducting materials in the form of thin plates or thin films for the construction of thermoelectric devices at very low temperatures.

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