Condensed Matter Physics.
Physics of Thermoelectric Phenomena

UDC 537.32+538.93

DOI: 10.33910/2687-153X-2020-1-2-74-77

Thermoelectric phenomena and thermodynamic laws

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For citation: Grabov, V. M., Komarov, V. A., Demidov, E. V. (2020) Thermoelectric phenomena and thermodynamic laws. *Physics of Complex Systems*, 1 (2), 74–77. DOI: 10.33910/2687-153X-2020-1-2-74-77

Received 17 April 2020; reviewed 27 April 2020; accepted 27 April 2020.

Funding: The research was supported by the Ministry of Science and Higher Education of the Russian Federation (project No. FSZN-2020-0026).

Abstract. The paper deals with thermoelectric phenomena from the standpoint of nonequilibrium thermodynamics of irreversible processes. The consideration is based on the fact that thermoelectric effects can occur if there is electrical and thermal contact of electrically conductive media. The necessary condition for the effect is the subsystems' different ordering degree of charge and heat carriers or different entropy and heat capacity per each carrier particle. The presented approach gives the possibility to understand physics of thermoelectric phenomena deeply. Its development can help to establish the theoretical limits of the efficiency of thermoelectric energy conversion imposed by fundamental physical laws.

Keywords: nonequilibrium thermodynamics, thermoelectricity, Seebeck effect, Peltier effect, entropy, heat capacity, heat transfer, order, disorder.

Introduction

Today we can see that thermoelectric phenomena and laws are attracting researchers because of their wide use in the field of small energy, electric power generation, or forced heat removal (thermoelectric cooling) from space and defense technology to household medicine. So it is very important to increase the efficiency of the developed thermoelectric energy converters and to develop the new thermoelectric materials with a high value of the thermoelectric efficiency parameter $Z = (\alpha^2\sigma/\kappa)$ (Gross 1961; Ioffe 1960), which includes material parameters α—thermoelectric coefficient (Seebeck), σ—electrical conductivity coefficient, κ—coefficient of specific thermal conductivity. Today, the best thermoelectric materials are characterized by the values of the dimensionless efficiency parameter ZT ≈ 1.5–1.8, as can be seen from Fig. 1.

Today, there are no studies that would allow us to conclude that there are fundamental limitations on the possibility to increase the ZT of thermoelectric materials. The authors believe that the thermoelectric phenomena analysis based on the fundamental laws of modern thermodynamics will help find ways to increase the ZT parameter of thermoelectric materials or to establish natural limitations of its magnitude. Significant progress in the analysis of thermoelectric phenomena can be achieved with the help of the following sections of modern physics: the fundamental laws of physical kinetics (Anselm 1978; Askerov 1985), the thermodynamics of irreversible processes, and the symmetry principle of the Onsager kinetic coefficients. The main issues of these sections are systematically presented by A.I. Anselm (Anselm 1973).

The initial system for describing thermoelectric phenomena in electrically conductive media based on the thermodynamics of irreversible processes and physical kinetics (Anselm 1973; 1978; Askerov 1985) usually has the following system of equations for electric charge flux density ($\boldsymbol{j}_q$) and heat ($\boldsymbol{j}_Q$):

$$j_q = \sigma E - \alpha\sigma gradT$$
$$j_Q = -kgradT + \pi j_q \tag{1}$$

Moreover, the symmetry condition for kinetic coefficients implies the Thomson relation between the Peltier coefficient (π) and the Seebeck coefficient (α): π = αT.

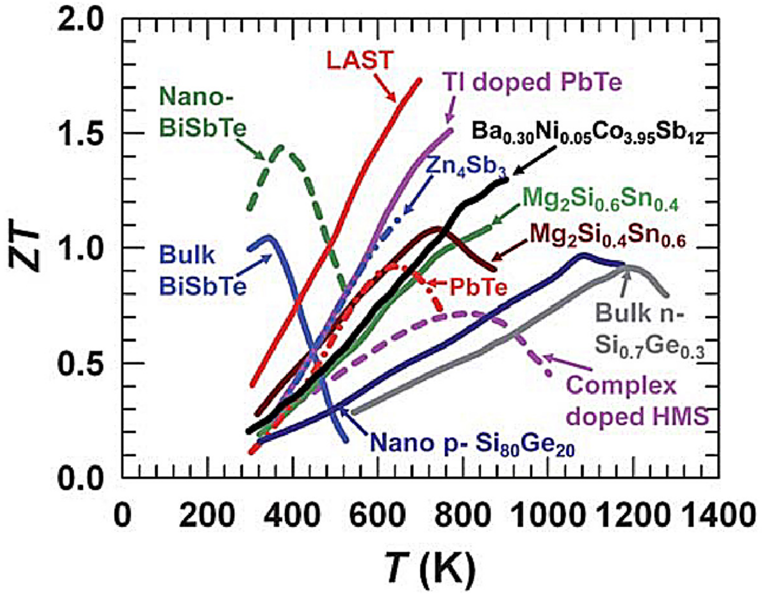

Fig. 1. State-of-the-art comparison of ZT in conventional bulk materials and nanostructured composite materials (Szczech, Higgins, Jin 2011). LAST (lead antimony silver telluride): $Ag_{1-x}Pb_{18}SbTe_{20.}$ HMS (higher manganese silicides): $MnSi_{1.7}$.

Thermoelectric phenomena in general thermodynamics

Let us see the Peltier effect on the contact of two different conductors (1) and (2) under the isothermal conditions *gradT = 0*. A continuous electric current with the density $(\boldsymbol{j_q})_1 = (\boldsymbol{j_q})_2 = (\boldsymbol{j_q})$ runs through the contact.

The corresponding heat fluxes will be different $(j_Q)_1 = \pi_1(\boldsymbol{j_q})$, $(j_Q)_2 = \pi_2(\boldsymbol{j_q})$ and Peltier heat will be generated or absorbed at the contact, depending on the electric current direction:

$$\frac{dQ}{dt} = (\pi_1 - \pi_2)(j_q). \tag{2}$$

In the calculation of the transition through the contact of one electron, Peltier heat will be released or absorbed

$$\frac{dQe}{dt} = (\pi_1 - \pi_2)e. \tag{3}$$

On the other hand, the amount of heat can be expressed through the entropy $Q = TS$. When one electron passes through the contact, heat equal to the difference in the entropy transferred by the electron will be released or absorbed.

$$\frac{dQe}{dt} = (s_1 - s_2)T\ . \tag{4}$$

Comparison of (3) and (4) leads to the following relations for each conductor: $\pi_i e = s_i T$, or, $s_i = \frac{\pi_i e}{T}$, taking into account the Thomson relation π = αT, which leads us to the relation $s_i = \alpha_i e$.

Let us take into account that entropy is related to the heat capacity ($\boldsymbol{c}_{ei}$) per charge carrier as $s_i = \int_0^T \left(\frac{c_{ei}}{T}\right) dT$.

Thus, the difference between the magnitude of the thermoelectric coefficients of two contacting conductors is determined by the difference in the entropy or heat capacity per charge carrier. The analysis shows that the Peltier effect can be considered similar to magnetic cooling—the method of getting low temperatures by adiabatic demagnetization of paramagnetic substances. In this case, heat transfer is carried out by changing the entropy and heat capacity, which is carried out by applying and removing an external magnetic field to the system of paramagnetic ions (Anselm 1973).

The method analysis to change conductor's entropy value or heat capacity gives the possibility to determine the limits in changes conductor's value of thermoelectric parameters in the of electrically conducting media.

On the other hand, the analysis of heat transfer processes from the standpoint of Peltier effect theory allows, in some cases, to deepen the physical understanding of the essence of heat transfer processes. Let's discuss, for example, the bipolar mechanism of heat transfer in intrinsic semiconductors in the presence of two sign charge carriers—electrons and holes. For the thermal conductivity due to bipolar diffusion of charge carriers (k ±), the solution of the kinetic equation leads to the expression (Askerov 1985):

$$k^{\pm} = \frac{\sigma^+ \sigma^-}{\sigma^+ + \sigma^-} T \left(\alpha^+ - \alpha^-\right)^2 . \tag{5}$$

The thermoelectric field is formed in the semiconductor with charge carriers of the same sign, if there is the temperature gradient and the electric current density of zero, this field prevents diffusion of charge carriers from a warmer to a less heated face, which limits the thermal conductivity of charge carriers. If there are charge carriers of two signs, electrons in the conduction band and holes in the valence band, the total electric current is zero, but there is an electric current carried by the electrons in the conduction band $j_q^- = \sigma^- \alpha^- gradT$ and holes in the valence band $j_q^+ = \sigma^+ \alpha^+ gradT$ for $j_q^- = -j_q^+$

The created partial electric currents are equivalent to the closed electric current in the sample. And the current direction in the conduction band coincides with the temperature gradient direction, and in the valence band it is opposite to it.

Based on the solution of the kinetic equation (Askerov 1985), one can obtain the expression for this closed electric current:

$$j_q^{\pm} = j_q^+ = -j_q^- = -\frac{\sigma^+ \sigma^-}{\sigma^+ + \sigma^-} \left(\alpha^+ - \alpha^-\right) gradT. \tag{6}$$

In this case, on the verge with a higher temperature, when an electron transfers from the valence band to the conduction band (the creation of an electron-hole pair), heat will be absorbed, and on the verge with a lower temperature when the electron transfers from the conduction band to the valence band (electron-hole pair recombinations) the heat of a peculiar "interband Peltier effect" $\frac{dQ}{dt} = \left(\pi^+ - \pi^-\right) j_q^{\pm}$ will be released.

Taking into account the relation for the partial kinetic coefficients $\pi^{\pm} = \alpha^{\pm} T$, we obtain:

$$j_Q = \left(\alpha^+ - \alpha^-\right) T j_q^{\pm} = -\frac{\sigma^+ \sigma^-}{\sigma^+ + \sigma^-} T \left(\alpha^+ - \alpha^-\right)^2 gradT. \tag{7}$$

Bipolar thermal conductivity in intrinsic semiconductors can also be given a different physical interpretation. This interpretation is based on the action of the so-called heat pipe, in which heat of phase transition (heat of evaporation) is absorbed on the face with high temperature, and heat of condensation is released on the face with low temperature. For such consideration, the heat of formation of an electron-hole pair and the heat of recombination of an electron-hole pair must be represented as the heat of some phase transition.

 DOI: 110.33910/2687-153X-2020-1-2-74-77

Conclusions

From the standpoint of modern thermodynamics, thermoelectric phenomena manifest themselves when charge carriers pass through the boundary of systems with different degrees of ordering, different entropy, and specific heat per each charge carrier.

This approach in combination with the traditional interpretation gives the possibility to understand deeply the physics of thermoelectric phenomena, which provides more opportunities for analyzing the prospects for increasing the efficiency of thermoelectric energy conversion and for determining the possible limits and restrictions on these processes imposed by fundamental physical laws.

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