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Thermoelectric energy conversion: Assessment of limiting capabilities

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Abstract. Based on a thermodynamic ratio between the thermopower coefficient and entropy of the electrically conducting medium, we obtained an estimated value of the thermoelectric efficiency parameter ZT for an electronic system of fully ionised plasma. An example of such a system, which is in the most disordered state, is the electron-nuclear plasma of the Sun. The resulting universal value $ZT = (25/6)$ can be considered as an assessment of the limiting capabilities of thermoelectric energy conversion.

Keywords: thermoelectricity, the most disordered state of an electronic system, solar plasma, dimensionless parameter of thermoelectric efficiency ZT, limit value of ZT

Introduction

As already noted (Grabov et al. 2020), thermoelectric energy converters are widely used in instrument engineering and technology, making the task of increasing the thermoelectric efficiency parameter particularly interesting. Thermoelectric efficiency is expressed as $ZT = \left(\alpha^2\sigma/\kappa\right)$, where α is the thermopower coefficient (Seebeck coefficient), σ is the conductivity coefficient, and κ is the heat conductivity coefficient (Gross 1961; Ioffe 1960). Currently, the best thermoelectric materials are characterized by the values of the dimensionless efficiency parameter $ZT \approx 1.5$–1.8 (Szczech et al. 2011). Materials demonstrating higher values of $ZT > 2.4$ have not exhibited stable reproducibility so far and still remain laboratory results with no practical applicability (D'Angelo et al. 2023). Intensive research to find ways to increase the ZT of thermoelectric materials is now underway, but there is a lack of studies investigating fundamental restrictions on a possible increase in the ZT of thermoelectric materials. We consider it possible to approach an assessment of the limiting capabilities of thermoelectric energy conversion on the basis of an analysis of thermoelectric phenomena from the standpoint of modern physical kinetics and thermodynamics (Anselm 1978; Askerov 1985; Grabov et al. 2020; Szczech et al. 2011).

On the theory of thermoelectric phenomena

The following system of equations for the density of electric charge (j_q) and heat (j_Q) fluxes is usually used as a starting point for describing thermoelectric phenomena in electrically conducting substances based on the thermodynamics of irreversible processes and physical kinetics (Anselm 1973; 1978; Askerov 1985):

$$j_q = \sigma E - \alpha\sigma \mathrm{grad} T ,$$

$$j_Q = -\kappa \mathrm{grad} T + \pi j_q . \tag{1}$$

The Thomson relation between the Peltier coefficient (π) and the Seebeck coefficient (α) follows from the symmetry condition of the Onsager kinetic coefficients, (Anselm 1973):

$$\pi = \alpha T . \tag{2}$$

Based on the thermodynamics of irreversible processes, it is shown that the thermopower coefficient α represents the entropy transferred by one charge carrier s_i, related to the value of this charge q_i. It is true for the electronic system (Anselm 1973; Grabov et al. 2020):

$$\alpha = {}^{S_\mathrm{i}}\!/_{e} . \tag{3}$$

Assessment of the limiting capabilities of thermoelectric energy conversion

In its physical meaning, entropy is a measure of a system's disorder (Anselm 1973). Therefore, we can expect that the highest efficiency of thermoelectric energy conversion will correspond to an electrically conducting substance with the highest degree of disorder. From this point of view, let us consider a system of electrons in various conducting substances. Since the entropy of a system is related to its heat capacity, it is obvious that the state of the electronic system described by the Maxwell distribution (for which $C_V = \left({}^{3}\!/_{2}\right)k$) is characterized by the highest entropy. In nature, a state in which the electron system is described by the Maxwell distribution is the one of a fully ionised electron-ion plasma — for example, the electron-nuclear plasma of the Sun (Kotelnikov 2013). According to (Kotelnikov 2013), in a stationary electron-ion plasma, in the presence of a temperature gradient and absence of an electric current, and as a result of the thermal diffusion of the system of electrons relative to the system of nuclei, an electric field is formed, the intensity vector $\vec{E}$ of which is determined by the following condition:

$$eE = \frac{5}{2}k\frac{dT}{dx} ,$$

$$E = \frac{5}{2}\frac{k}{e}\frac{dT}{dx} = \alpha\frac{dT}{dx} . \tag{4}$$

Thus, plasma thermopower is determined mainly by electrons, with the thermopower coefficient expressed through the ratio of ») universal constants, such as the Boltzmann constant, to the electron charge:

$$\alpha = \frac{5}{2}\frac{k}{e} . \tag{5}$$

According to (Kotelnikov 2013), thermal and electrical conductivity of a plasma is also determined by a system of electrons that complies with the Maxwell distribution. The ratio of contributions of the system of electrons and ions to transport phenomena in a fully ionised plasma is proportional to the square root of the ratio of the masses of ions and electrons $\sqrt{{}^{m_i}\!/_{m_e}}$ (Kotelnikov 2013). So, the contribution of ions to these phenomena can be neglected, and the problems of electronic transfer phenomena can be solved relative to the stationary ion system (Kotelnikov 2013). In this case, as shown in the classical Drude–Lorentz theory of metals (Ashcroft, Mermin 1976), the ratio of the coefficients of thermal conductivity κ and electrical conductivity σ of the electronic system is determined by the universal Lorentz number L, also expressed through the same universal constants (5) (Ashcroft, Mermin 1976):

$$\frac{\kappa}{\sigma} = \frac{3}{2}\left({}^{k}\!/_{e}\right)^2 T = LT\,,$$

$$L = \frac{3}{2}\left({}^{k}\!/_{e}\right)^2\,. \tag{6}$$

For the dimensionless indicator of thermoelectric efficiency ZT of an electronic system in the most disordered state, characterized by the highest entropy, we obtain the following relation:

$$ZT = \frac{\alpha^2\sigma}{\kappa}T = \frac{\alpha^2}{L} = \frac{25}{6} \approx 4.17\,. \tag{7}$$

Thus, the ZT value, determined by expression (7) for the electronic system in the most disordered state characterised by the highest entropy, can be considered as an approximate estimate of the limiting value of the dimensionless efficiency coefficient of thermoelectric energy conversion. It is also interesting that for the extremely disordered state of the electronic system, the universal constants included in Z are reduced, which gives simply the universal number (7) for the ZT parameter: $ZT = (25/6)$. Based on the modern achievements of $ZT \approx 1.5–1.8$ (Szczech et al. 2011) and as follows from (7), developers of thermoelectric materials still have something to strive for.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Vladimir Grabov — research concept development, discussion, preparation of the manuscript, editing and supervision; Vladimir Komarov — discussion, preparation of the manuscript and editing; Vasilisa Gerega — discussion and editing; Anton Suslov — discussion and editing. All the authors have read and agreed on the published version of the manuscript.

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