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SOME PROBLEMS OF PHYSICS OF THE THERMOELECTRIC PHENOMENA

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Термоэлектрик ҳодисалар (Зеегер, Пельтье ва Томсон) ҳақидаги ҳозирги кундаги, чизиқли номувозанат термодинамикага асосланган физикавий тасаввурлар кенг температуралар оралиғида ва турли материалларда (соф металлар, Si, Ge, интерметалл ва оксид бирикмалар, боридлар, силицидлар) олинган экспериментал натижаларга мос келмайди. Бу натижаларда термоЭЮК коэффициентининг кескин экстремумлари (100–10000 мартагача ошиши) ва ишораси ўзгариши кузатилади. Кузатилаётган натижаларни тушунтириш учун ночизиқли номувозанат термодинамикаси усуллари ва термоэлектрик материалларнинг тузилиши ҳақидаги тасаввурлардан фойдаланиш лозимлиги асосланган.

Показано, что существующие физические представления о природе термоэлектрических явлений (Зеебека, Пельтье и Томсона), основанные на линейной неравновесной термодинамике, не согласуются с экспериментальными данными, полученными в широком диапазоне температур на разных материалах (чистые металлы, Si, Ge, интерметаллические и оксидные соединения, бориды, силициды), где наблюдаются резкие экстремумы коэффициента термоЭДС (рост в 100–10000 раз) и смена его знака. Обоснована необходимость использования методов нелинейной неравновесной термодинамики, а также представлений о структуре термоэлектрических материалов для объяснения наблюдаемых особенностей термоэлектрических эффектов.

This paper shows inadequacy of contemporary conceptions of physics on nature of thermoelectric phenomena (Sebeck, Peltie and Thomson effects), based on linear nonequilibrium thermodynamics, to experimental data having in wide range of temperature and for various materials (pure metals, Si, Ge, intermetallic and oxide compounds, borides, silicides). Shape extrema of thermopower (increasing up to 100–1000 times) and change of its sign are observed experimentally. Reasons for use of methods of nonlinear nonequilibrium thermodynamics and structure conceptions of thermoelectric materials are motivated.

I. INTRODUCTION

Interest to the thermoelectric phenomena in various materials has dramatically increased in last two decades owing to: i) threat to exhaust reserves of fossil fuels (oil, gas, coal) so it is required to create an effective and cheap methods for use of renewable energy sources; ii) expansion of technical and technological possibilities of the humanity which leads to increase waste heat amount and environmental pollutes. This will deteriorate circumstances for human existence and compels to search for methods to use the waste heat; iii) creating the theory of «phonon glass, electronic crystal» [1] and disclosure of a new class of thermoelectric materials, oxide compound $NaCo_2O_4$ having high value of thermopower [2].

Scientific aspect of this interest is important as well because of thermoelectricity: i) lets to have information on state of an electronic subsystem in various materials;

ii) served and forms an experimental basis for verification of representations of nonequilibrium thermodynamics.

The existing theories of the thermoelectric phenomena starting from works of W. Thomson [3], are linear approximations for unknown function $\Delta U(T,\Delta T)$, while a lot of experimental data on temperature dependence of thermopower and on its absolute value in a wide range of temperatures are not agreed with results of these theories (received within a framework of linear nonequilibrium thermodynamics and the kinetic theory, including Onsager's reciprocity relations).

In this paper theoretical representations and experimental data on the thermoelectric phenomena in various materials differ in composition (metals and alloys, oxide and intermetallic compounds, borides and silicides, organic semiconductors) and structure (crystal and amorphous) are considered, and ways to eliminate mentioned above discrepancies between the theory and experiment in thermoelectricity are discussed.

II. THEORETICAL BASICS

There are three thermoelectric phenomena: 1) Seebeck effect – generation of thermoemf ΔU in material affected by temperature difference $\Delta T = T_H - T_C$ (discovered in 1821); 2) Peltye phenomenon – cooling ($Q_P<0$) or heating ($Q_P>0$) of contact of different conductors, connected in series, in accordance with direction of electrical current I (discovered in 1834); 3) Thomson phenomenon (1854) – emanation ($Q_T>0$) or absorption ($Q_T<0$) of additional heat amount in the uniform conductor affected simultaneously by temperature difference ΔT and electric current I. Here T_H and T_C are temperature of the hot and cold ends of a sample, respectively. Seebeck (generators of electric energy) and Peltye (refrigerators, heaters, thermal pumps) phenomena are most studied and used often, and they are considered mutually reversible, while Thomson phenomenon has scientific interest mainly because of small value of τ.

Thermoelectric properties of material are characterized by coefficients Seebeck S (coefficient of thermoemf), Peltye π and Thomson τ:

$$\Delta U = S\Delta T\ , \tag{1}$$

$$Q_P = \pi I\ , \tag{2}$$

$$Q_T = \tau I \Delta T\ . \tag{3}$$

Additional quantity of heat Q_P and Q_T in expressions (2) and (3) is linear function of current I, unlike Joule's heat $Q_J = I^2 R$. Therefore emanation or absorption of Q_P and Q_T depends on the current direction. Thomson's effect is considered to be positive ($Q_T>0$) if the current I coincided in direction with the gradient T, causes heating of conductor. Samoylovich and Korenblit [4] have emphasised that emanation of heat, proportional to a current, is caused only by heterogeneity of system through which the current flows, and this heterogeneity has been connected not only with chemical nature (difference of composition). For example, thermoemf is located on interface of mechanically deformed and nondeformed (quenched and unquenched) parts of the homogeneous conductor [5].

Thomson's thermodynamic theory [3] has established intercorrelation of coefficients S, π and τ (the first and the second thermoelectric ratios, respectively):

$$\tau = T(dS/dT)\ , \tag{4}$$

$$\pi = TS\ . \tag{5}$$

Direct measurement of $S(T)$ in a homogeneous material is essentially impossible (Magnus law, 1851, [6]), and it is determined from measured $\tau(T)$ via the expression (4) [7-8]:

$$S(T) = \int_0^T \frac{\tau(T)}{T} dT \,. \tag{6}$$

Further development of thermodynamics of the thermoelectric phenomena has led to reciprocity relations [9] of kinetic coefficients $L_{12} = L_{21}$ in the generalized linear equations for charge flow $j(T, E)$ and heat flow $q(T, E)$:

$$j = -L_{11}\nabla\frac{\mu}{T} + L_{12}\nabla\frac{1}{T}, \tag{7}$$

$$q = -L_{21}\nabla\frac{\mu}{T} + L_{22}\nabla\frac{1}{T} - \mu j, \tag{8}$$

where $\mu = \mu_0 + e\varphi$ is the electrochemical potential consisting of chemical μ_0 and electric φ parts.

The linear equations (7) and (8) for the charge and heat flows, bringing to Onsager's reciprocity relations [9], deny possibility of thermoemf generation in the homogeneous isotropic conductor (Magnus's law, 1851; see also [4]). Thus Samoylovich and Korenblit [4] have emphasised that the assumption on convertibility of thermoelectric heat (Peltye and Thomson) does not follow from the second principle of thermodynamics and is the additional assumption. On the other hand, for developing formulae (4) and (5) W. Thomson considered the thermoelectric phenomena as reversible that is not rather reasonable. This moment of the Thomson's theory was criticised by Boltzmann, however, as authors [4] specify, discussion has lost urgency owing to numerous experimental confirmations of the Thomson's theory. Below we will see that the experimental data used for conformation almost do not containing nonlinearity and when such nonlinearity appeared (see, for example, [5]), it have been excluded from consideration as anomalies.

We must note here that in definition of Seebeck coefficient (1) $e\Delta U$ represents excess of electrons Coulomb energy on the cold end of a sample relative to hot end, created by their diffusion due to surplus of thermal energy $k_B\Delta T$ on the hot end rather cold (Fig. 1). Therefore it is reasonably to consider $e\Delta U \le k_B\Delta T$, that in a steady state without a current in an external circuit (an open-circuit mode) leads to the maximum value of Seebeck's coefficient: $|S| \le k_B / e = 86.25\,\text{muV/K}$. Here k_B is Boltzmann's constant. It is important that this limit does not depend both on studied substance and on a temperatures range.

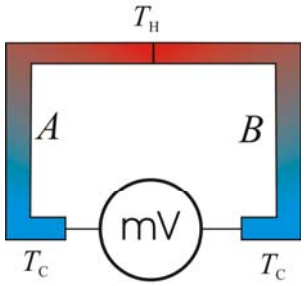


Fig. 1. Measurement scheme for thermopower (Seebeck phenomenon).

Increasing of $S(T)$ at low temperatures (Fig. 2) is usually explained by phonon drag [8, 10-12]; (see also Seeger [6]). This mechanism implies that phonons (thermal vibrations of atoms) move from hot end of sample to another end simultaneously with electrons. The first, colliding with electrons, pass them part of impulse, creating an additional charge flow and corresponding thermoemf.

The estimation of this additional thermoemf gives 400 mV/K upto 10 V/K [6]. However definition (1) of S assumes the independence of it on temperature (or weakly

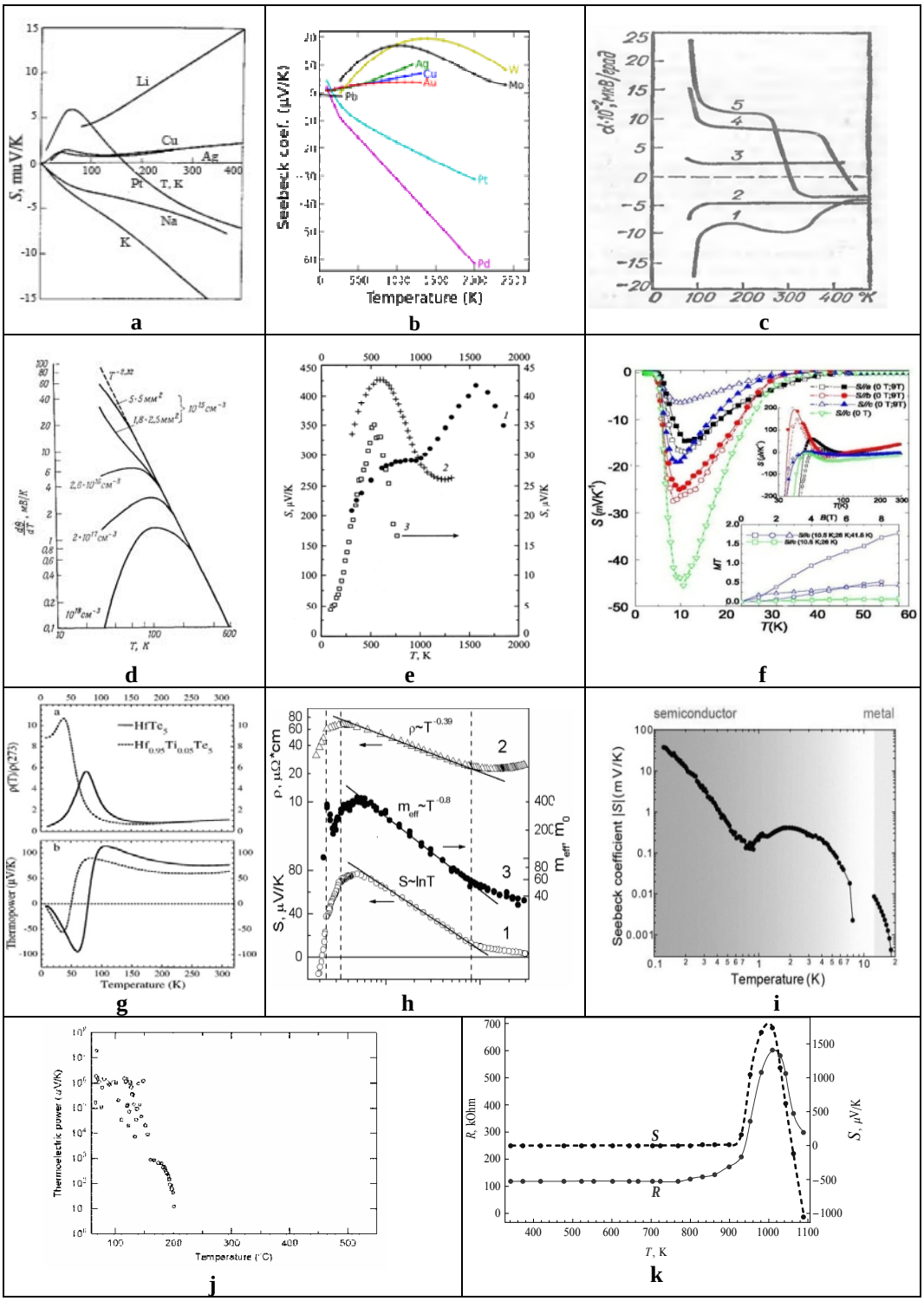


Fig. 2. Temperature dependence of thermopower in: metals at low (*a*) [14] and high temperatures (*b*) [15], (*c*) germanium [16], (*d*) silicon [17], (*e*) borides AlB_{12} (1), $B_{14}Si$ (2), FeB29:5 (3) [18], $FeSb_2$ (*f*) [19], $HfTe_5$ (*g*) and $Hf_{0.95}Ti_{0.05}Te_5$ monocrystals [20], (*h*) CeB_6 thermopower $S(T)$ (1), specific resistance $\rho(T)$ (2), effective mass $m^*(T)$ (3) [10], (i) $(TMTSF)_2PF_6$ [21], (*j*) $TlInSe_2$ [22], (*k*) the doped silicate glass [23].

dependence) and $\Delta T << T$ is required in experiment to provide applicability of (1). So ΔT should be about few K. But then average excess of phonon's energy $k_B \Delta T \approx 100$ μeV is essential less than Coulomb energy $e\Delta U \approx 0.4 - 10$ eV of electrons, so it is required to find out a source of their additional energy.

One more question to Thomson's theory arises from joint consideration of definition (1) of Seebeck coefficient S and Thomson's first relation (4). Definition (1) in fact can be considered as the first member of decomposition of unknown function $\Delta U(\Delta T)$ on degrees of argument ΔT (compare with definitions of temperature coefficients of linear expansion, electric resistance, capacities, inductance) when constancy of S (does not depend on T and ΔT: $dS/dT = 0$ and $dS/d\Delta T = 0$) is implicitly supposed. But then Thomson's phenomenon should be absent in accordance with (4): $\tau = TdS / dT = 0$.

Comparing distribution of energy flow in thermopile branches (Fig. 1) in framework of Thomson's theory and by results of computer modeling, Spry [13] concludes that Thomson's theory is based on the erroneous precondition, and for the description of the thermoelectric phenomena four parameters of a material (σ, κ, S and π) enough, it is not needed to introduce Thomson's phenomenon.

III. EXPERIMENTAL RESULTS

For almost two-centuries history of a thermoelectricity, the thermoelectric properties of the various materials have been investigated and agree of experimental data with expressions (1), (7) and (8) in some temperature intervals, assuming constancy (weakly changing) of values S, π and τ, as well as essential deviations from these expressions have detected especially at low T. Temperature dependence $S(T)$ of various materials is shown in Fig. 2.

Let's note some features of experimental data presented in Fig. 2: 1) sharp change of $S(T)$ at low temperatures; 2) change of a sign S in some cases; 3) the maximum value S in many materials essentially exceeds the limit 86 muV/K specified above. For example, in the compound $TlInSe_2$ $S \approx 10$ V/K at $T \leq 100$ K (Fig. 2*j*), and in the organic semiconductor $(TMTSF)_2PF_6$ $S(T)$ grows at $T \to 0$ K (Fig. 2*i*) instead of reduction according to the theory. Properties 1) and 2) have been found in metals more than 100 years ago [4]. Consequence of these features is strong temperature dependence of Peltye π and Thomson τ coefficients, defined by relations (4) and (5).

Zeeger [6] gives dependence of $S(T)$ in silicon (Fig. 2*d*) where $S(T) \approx 100$ mV/K is reached at $T = 30$ K, as confirmation of phonon drag. However there is a question what is a source of additional energy of electrons to carry out the energy conservation law.

The silicate glass doped by ruthenium oxide [23-25] stands by itself among the materials which thermoelectric properties have investigated. This glass has metallic properties ($S \approx 10$–20 μV/K) near room temperature, and the maximum of $S(T) \approx 1.7$ mV/K is observed not at low temperatures, but at $T \approx 970$–1000 K (Fig. 2*k*). Such behaviour, being accompanied similar change of resistance $R(T)$, is a consequence of structural transformations in silicate nanocrystals leading to change of location of the impurity band relative to valence band of glass [23, 26].

Unfortunately in known publications, there are not enough results of simultaneous measurement of $S(T)$ and $R(T)$ on the same samples so interpretation of features of $S(T)$ shown on Fig. 2 is quite complicated.

IV. POSSIBLE WAYS TO SOLVE THE PROBLEMS IN THERMOELECTRICITY

Two directions are possible to look for solutions of problems of the thermoelectricity theory. **The first** direction consists in the accounting of nonlinear correlations of thermodynamic forces and flows in expressions (7) and (8) by including the highest order terms (at least - the second order):

$$j = -L_{11}\nabla\frac{\mu}{T} + L_{12}\nabla\frac{1}{T} + \frac{1}{2}L_{13}\nabla\frac{\mu}{T}\nabla\frac{1}{T} + \frac{1}{2}L_{14}\left(\nabla\frac{\mu}{T}\right)^2 + \frac{1}{2}L_{15}\left(\nabla\frac{1}{T}\right)^2, \qquad (9)$$

$$q = -L_{21}\nabla\frac{\mu}{T} + L_{22}\nabla\frac{1}{T} + \frac{1}{2}L_{23}\nabla\frac{\mu}{T}\nabla\frac{1}{T} + \frac{1}{2}L_{24}\left(\nabla\frac{\mu}{T}\right)^2 + \frac{1}{2}L_{25}\left(\nabla\frac{1}{T}\right)^2 - \mu j. \qquad (10)$$

Bakhareva [27] confirms that for coefficients of a linear parts of expressions (9) and (10) the Onsager's reciprocity relations is again carried out: $L_{12} = L_{21}$. The nonlinear terms cause bifurcation, turbulence and a hysteresis, complex chemical processes (for example, Belousov-Zhabotinsky reactions), self-organizing of various systems, including biological (up to emergence of life). These phenomena are considered in Prigogine's fundamental works [28], Bakhareva's [27] and Maksimov's [29] monographs, mainly with reference to chemical and biological processes.

Nonlinear properties in thermoelectricity were considered in a number of works [30-33] mainly as a result of the high gradients of temperature arising in nanostructures. Cimmelli et al. [30] note violation of Onsager's reciprocity relations because of nonlinear processes. But more detailed consideration of the problem compels one to admit impossibility of same gradients. Moreover the conception of temperature comes some undefined at nanoscale.

The second possible direction to eliminate the collected divergences of experiment and the theory of the thermoelectric phenomena, most likely, as supplementing previous, is based on the wave nature of thermal radiation. The matter is that in existing theories of the thermoelectric phenomena thermal influence is considered only as process of energy transmission from a heater to electronic gas (the thermal engine) and pressure of electronic gas $p = nk_{\text{Å}}T$ changes. In absence of temperature gradient the difference of pressure of electron gas in contacting conductors is counterbalanced by a difference of contact potential. Difference of temperatures in diverse conductors redistributes mobile charges and creates thermoemf [5].

Such consideration remains out of sight such phenomena as dispersion, resonance, the nonlinearity, caused by the wave nature of thermal radiation (Planck's formula) as a wide band electromagnetic oscillations, and gas of free electrons in conductors as oscillatory system (plasma or Langmuir oscillations) with own frequency $\omega_p = \sqrt{ne^2 / m^*\varepsilon\varepsilon_0}$, where m^* – effective mass of electrons, ε_0 – electric constant, ε – dielectric permeability of a material studied [34].

Probably, observable features of $S(T)$ in various materials (Fig. 2) are a consequence of temperature dependence of m^*, ε or n of thermoelectric materials, especially in thin transitional region of their contact where a strong dependence of properties of materials and forces operating on electrons on spatial coordinates take place.

Such approach to the thermoelectric phenomena enters into consideration, unlike linear nonequilibrium thermodynamics, their temporary characteristics.

V. CONCLUSION

Comparison of the theory of the thermoelectric phenomena and experimental data in various materials (metals and their alloys, oxides, borides, silicides, intermetallic compounds) with different structure shows that observed temperature dependence of Seebeck coefficient (and respectively Peltye and Thomson coefficients) has the features common for all materials (nonlinearity, an extremum, sign of change) and essentially differs from theoretical representations. It is shown that possible ways to eliminate these divergences are the accounting of temperature dependence of parametres of a material (an electrical conductivity, thermal conductivity, Seebeck, Peltye and Thomson coefficients) with simultaneous consideration of wave properties of thermal radiation. Also simultaneous experimental study of dependences of $S(T)$ and $R(T)$ as well as structural changes on the same sample is necessary.

From the experimental point of view it is required as well to find out where thermoemf arises – in a homogeneous part of a sample or on contacts – so far as Seebeck and Peltye phenomena are considered mutually reversible and appearance of the last on contact of two differing materials have unequivocally established.

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REFERENCES

1. G.A. Slack. In: CRC Handbook of Thermoelectrics. D.M. Rowe (editor) (CRC Press, Boca Raton, 1995).
2. I. Terasaki, Phys. Rev. B **56**, R12685 (1997).
3. W.K. Thomson. In: Mathematical and Physical Papers **1,** 174 (Cambridge University Press, London, 1882).
4. A.G. Samoylovich, L.L. Korenblit, UFN **49** (2), 243 (1953); **49** (3), 337 (1953).
5. O.D. Khvolson. Course of Physics (Rikker's publishing house, Petrograd, 1915). (In Russian).
6. K. Seeger. Semiconductor Physics (Springer-Verlag, Wien-New York, 2004).
7. Tables of physical quantities. I.K. Kikoin (ed) (Atomizdat, Moscow, 1977), page 462 (in Russian).
8. H.J. Goldsmid. Introduction to Thermoelectricity (Springer, Berlin-Heidelberg, 2010).
9. L. Onsager, Phys. Rev. **37**, 405 (1931); Phys. Rev. **38**, 2265 (1931).
10. M.I. Ignatov et al., J. Sol. St. Chem., **179**, 2805 (2006).
11. M.I. Ignatov. Thermoemf of Rare-Earth Compounds with Strong Electronic Correlations. PhD Thesis in physics (Moscow, Institute of General Physics of the Russian Academy of Sciences, 2006 (in Russian).
12. Y.V. Ivanov, M.V. Vedernikov, Yu.I. Ravich, Jetp Letters **69** (4), 317, https://doi.org/10.1134/1.568030.
13. M. Spry. Rethinking Thermoelectric Effects in Seebeck and Peltier Elements: Toward a Unifying Paradigm (Great Trout Press, Traverse City, 2015).
14. J.S. Dugdale. The Electrical Properties of Metals and Alloys (Edward Arnold, London, 1977).
15. J.W. Christian et al. doi:10.1098/rspa.1958.0078.
16. T.H. Geballe and G.W. Hull, Phys. Rev. **94**, 1134 (1954).
17. T.H. Geballe and G.W. Hull, Phys. Rev. **98**, 940 (1955).
18. O.A. Gudayev, V.K. Malinovsky, Physics of the Solid State **44** (12), 2120 (2002).
19. A. Bentien et al., Europhys. Letters, **80** 17008 (2007).
20. R.T. IV Littleton et al., Applied Physics Letters **72** (16), 2056 (1998).
21. Yo. Machida et al., Physical Review Letters **116** (8), 087003 (2016).

22. N. Mamedov et al., Thin Solid Films **499**, 275 (2006).
23. G. Abdurakhmanov, World J. Cond. Matter Phys. **4** (3), 166 (2014).
24. G. Abdurakhmanov and N.G. Abdurakhmanova, Phys. Stat. Sol. (a) **202**, 1799 (2005).
25. G. Abdurakhmanov, American J. Materials Science **1**, № 1, 12 (2011).
26. G. Abdurakhmanov and G.S. Vakhidova, American J. Materials Science **2** (1), 37 (2012).
27. I.F. Bakhareva. Nonlinear Nonequilibrium Thermodynamics (Saratov State University Publishing House, Saratov, Russia, 1976) (in Russian).
28. D. Kondepudi, I. Prigozhin. Modern Thermodynamics. From Heat Engines to Dissipative Structures (John Wiley and Sons, 1999).
29. A.I. Maksimov. Introduction to Nonlinear Physical Chemistry (Ivanovo State University of Chemical Technology, Ivanovo, Russia, 2014) (in Russian).
30. V.A. Cimmelli, A. Sellitto, D. Jou, Proc. of the Royal Society A **470,** № 2170 (2014). DOI: 10.1098/rspa.2014.0265.
31. T. Zhang, J. Computational Intelligence and Electronic Systems, **4** (1), 59 (2015).
32. O. Yamashita, Applied Energy **86,** 1746 (2009). DOI:10.1016/j.enconman.2009.04.019
33. G. Benenti et al. Colloquium: Fundamental Aspects of Steady State Heat to Work Conversion (2013), arXiv:1311.4430v1 [cond-mat.stat-mech].
34. L.A. Artsimovich, R.Z. Sagdeev. Plasma Physics for Physicists (Atomizdat, Moscow, 1979), page 10-15 (In Russian).