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Thermoelectric Elements with Negative Temperature Factor of Resistance

Yuri Bokhan

Abstract

The method of manufacturing of ceramic materials on the basis of ferrites of nickel and cobalt by synthesis and sintering in controllable regenerative atmosphere is presented. As the generator of regenerative atmosphere the method of conversion of carbonic gas is offered. Calculation of regenerative atmosphere for simultaneous sintering of ceramic ferrites of nickel and cobalt is carried out. It is offered, methods of the dilated nonequilibrium thermodynamics to view process of distribution of a charge and heat along a thermoelement branch. The model of a thermoelement taking into account various relaxation times of a charge and warmth is constructed.

Keywords: thermoelement, ferrites, thermistor, nanoceramics, model

1. Introduction

Perspective direction of building of thermal cells with a high Z-factor is use nanomaterial's and nanocomposite [1].

The quantity of works, theoretical and experimental, devoted to research thermoelectric nanomaterial's, steadily grows. The received results are optimistically enough, at least, from the point of view of fundamental science.

The augmentation of thermoelectric quality factor in nanomaterial's is bound to two physical phenomena [2]:

- The thermal conductivity decreases, bound to presence of numerous borders of partition. And it is necessary to notice that basically such reduction is bound with *фононной* thermal conductivity and make small impact on electronic transport;
- Augmentation of width of the forbidden area in ceramic наноматериалах with simultaneous augmentation of density of states about Fermi's level. In this case there is an electric conductivity reduction. However thermal conductivity reduction, under certain conditions, can compensate such reduction and lead to quality factor augmentation.

For building of ceramic semi-conductor stuffs, instead of doping by certain impurities it is possible to use a furnacing method in a reducing atmosphere [3, 4]. Such method, together with use of stuffs with NTRC, will allow to raise quality

factor of thermoelectric stuffs and to raise efficacy of thermal cells, especially in the field of high temperatures where ceramic stuffs, are the steadiest. Such method probably building n - and p - phylum of conductivity a choice of composition of gas atmosphere and furnacing temperatures in one shot.

2. Material's

In thermoelectric nanocomposites the size of grain does not exceed several tens nanometers. It is obvious that for increasing of thermoelectric performance efficiency, the following condition is necessary: the size of grain should be less, than the average length of free run of phonons, but more than the average length of free run of charge carriers (electrons or holes). In this case phonons on intercrystallite borders, disperse more effectively and it leads to stronger reduction of thermal conductivity (at the expense of reduction of grid contribution), in comparison with electric conductivity reduction, providing total increase of thermoelectric quality factor.

It is obvious that in nanocomposites the lobe of intercrystallite borders will increase with the reduction of aggregate size, it will lead to consecutive depressing of thermal conductivity of the material. It is natural that dispersion of electrons on intercrystallite borders will take place leading to the reduction of their motility. However, the thermal conductivity reduction in volume nanocomposites can be more essential, than electric conductivity reduction. Thus, volume nanocomposites, consisting from nano the grains of the thermoelectric material that are divided by intercrystallite borders, can potentially possess high thermoelectric efficiency. They will have electric conductivity high and low thermal conductivity simultaneously.

Oxidic ceramic materials may be transferred into semiconductor state by means of process of operated valence. For this purpose, different methods are used, such as, a restoration method, i.e. ceramics furnacing in the regenerative medium [3, 4], univalent substitution are routinely used. In this case it is possible to receive comprehensible conductivity, at conservation of low thermal conductivity. In ceramic materials probably substantial growth of the dispersion mechanism, at low thermal conductivity, but it leads to quality factor augmentation.

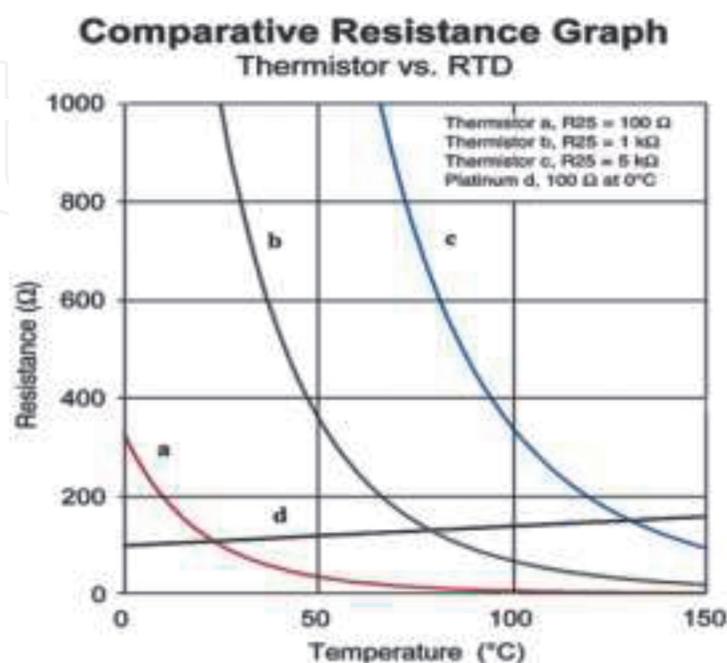


Figure 1.

Typical resistance dependence on the temperature for a thermistor with NTCR.

So, for example, some series of spinel's, at isomorphous substitution are transferred in to a state of the semi-conductor conductivity, possessing conductivity with NTRC (**Figure 1**) [5–8].

Oxide doping of nickel by lithium leads to sharp augmentation of conductivity at the expense of changing lithium ions into nickel ions in octahedral positions. The formation of the solid solution with uncompensated charge allows to create different types of conductivity by the variation of lithium concentration.



Similar reaction takes place when CO is replaced. If it is possible to omit superfluous oxygen, the solution of oxides receives the additional uncompensated charge in octahedrons spinel, and that process leads to conductivity augmentation. It follows that having combined doping with roasting in the recovery medium, it is possible to receive ceramic materials with adjustable conductivity. You should mind that thermal ceramic conductivity is defined by the phonon mechanism with characteristic wave length $\sim 5\text{--}10$ microns, and creating necessary grain frame of ceramics it is possible to achieve substantial increase of quality factor of the material.

Joint roasting in the recovery medium of ferrite on the basis of spinel and dielectrics, such as solid solutions on the basis of perovskite families of titanates of barium, strontium and lead, allows to create multilayered frames [3].

Let us consider as model of spinels recovery NiMn_2O_4 and CoMn_2O_4 in a gaseous medium received by conversion CO_2 and H_2O over Carboneum. The calculation shows that such reactions happen in some stages. It is difficult to analysis all reactions, we will illustrate calculation on the reactions defining composition of a gaseous environment (**Figure 2**).

Reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ takes place with $\Delta Z_0 = 43462 + 6,121T \lg T - 62,746 T$ – is potential change of Gibbs at temperature T and $\lg K_p = -9500 T^{-1} - 1,338 \lg T + 13,715$ – an equilibrium constant. Reaction $\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ has with $\Delta Z_0 = 35730 + 6,121T \lg T - 55,403 T$ and $\lg K_p = -7811 T^{-1} - 1,338 \lg T + 12,170$ accordingly [6]. The joint analysis of the received expressions shows that thermodynamically reactions are resolved with $T \approx 500\text{K}$, and kineticly proceed with sufficient speed with $T \approx 700\text{K}$.

The recovery of nickel oxides and cobalt thermodynamically is possible with $T \approx 700\text{K}$. Thus, kineticly, recovery reactions take place in demanded atmosphere and there is no necessity of a pre-treatment of medium. Using diagrammes of Ellingem-Richardson-Dzheffez (**Figure 3**), we see that at the yielded temperatures cobalt and nickel recovery descends simultaneously. It allows to create simple adjustment of temperature necessary degree of restoration in spinels.

It is necessary to notice that at such temperatures there is a restoration to manganese metal. Calculation shows that manganese is reduced to the bivalent state and does not variate the position in a grid. At the same time nickel and cobalt, are restored to a monovalent state and provide n and p conductivity accordingly.

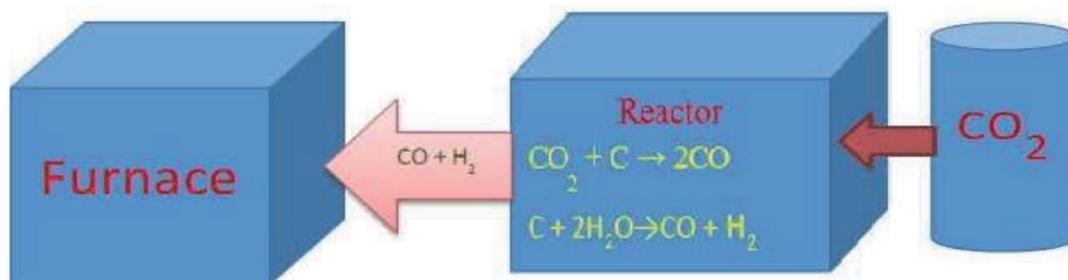


Figure 2.
 The schema of installation for roasting in a reducing atmosphere.

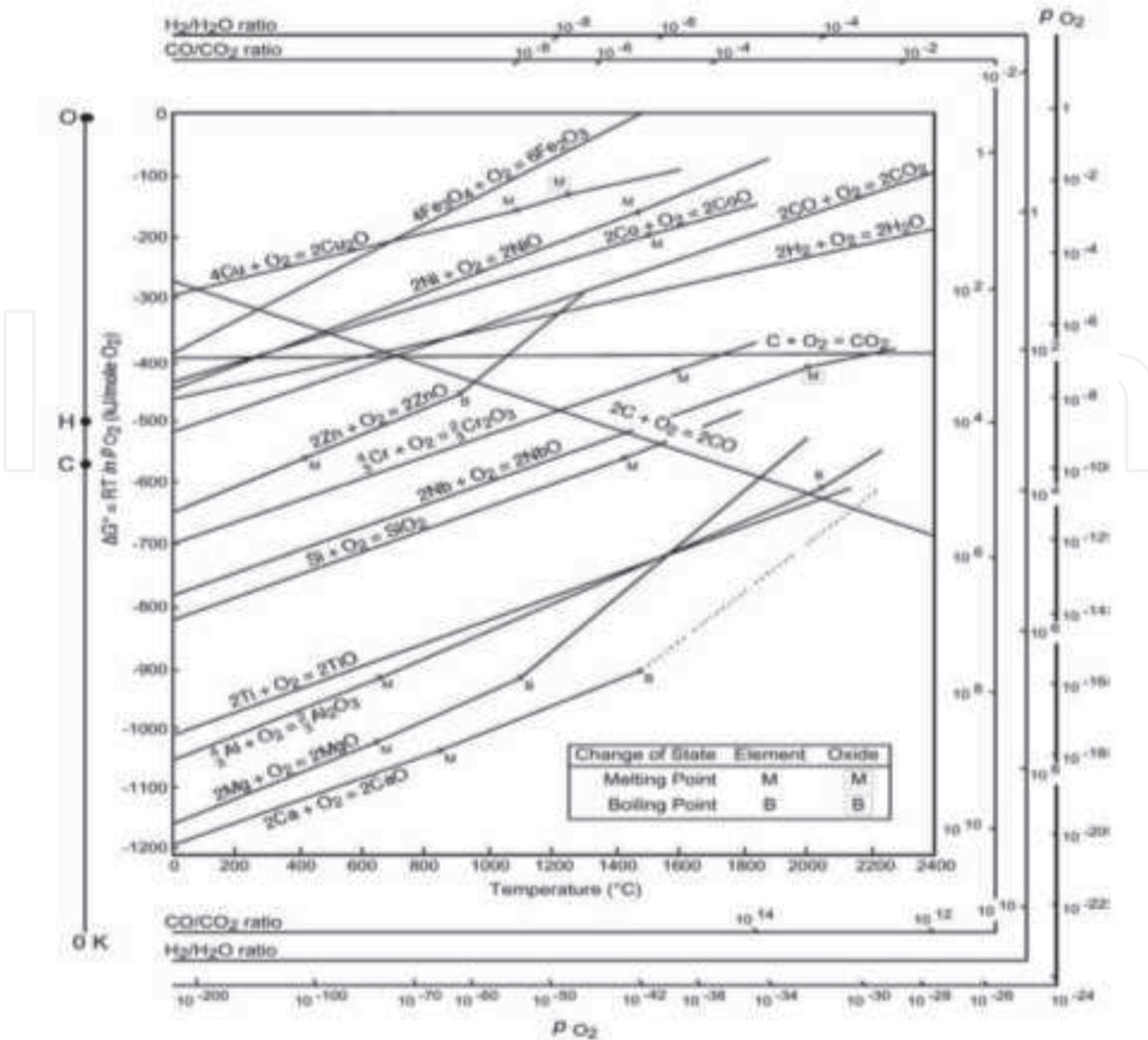


Figure 3. Diagramme of Ellingem-Richardson-Dzheffez for equilibriums metal - metal oxide: Points of M and I_n - temperatures of elements phase changes.

Thus, it is possible to create semi-conductor branches of thermal cells with various types of conductivity in one technological process is possible.

It is obvious that when the size of grain will decrease, the area of borders of grains will increase. It will lead to higher degree of restoration of a ceramic material on border of grains. Accordingly, conductivity of borders will differ from conductivity actually grains. Naturally, dispersion electron's in grain borders will take place, and their mobility will be reduced. However, on the average, change of conductivity of a material will not be so essential because of certain uniformity of a material. Thus, there is a possibility at the expense of essential reduction phonon's heat conductivity to raise good quality of a material. Therefore, use of ceramic materials with NTCR allows to create high-temperature thermoelements with good quality [9].

3. Microscopic model

Known microscopic models of thermoelectric effect in semiconductors, to some extent, are grounded on the solution of the equation of Boltzmann's.

Let us spot thermoelectromotive force (TEF) in the presence of a temperature lapse rate ($\nabla T \neq 0$) from the stationary kinetic equation of Boltzmann's in relaxation time approach:

$$(\bar{V}, \nabla_{\bar{r}} f) + \frac{1}{\hbar} (\bar{F}, \nabla_{\bar{r}} f) = -\frac{f - f_0}{\tau(\bar{k})} = -\frac{f^{(1)}(\bar{k})}{\tau(\bar{k})}. \quad (1)$$

were $f - f_0 = f^{(1)}(\bar{k})$, a F – exterior force, $\tau(\bar{k})$ – a relaxation time.

In case of the undegenerated semiconductor the equilibrium distribution function for electrons is accepted in a view:

$$f_{on} = e^{\frac{E-\mu}{k_0 T}} \text{ for electrons,}$$

$$f_{op} = e^{\frac{\mu'-E}{k_0 T}} = e^{\frac{-E+\mu+\Delta E}{k_0 T}} \text{ for electron defects.}$$

$$\text{Here } \mu' = -\Delta E - \mu, E = \frac{2k^2}{2m_p^*}.$$

Approving of the allowance to equilibrium function $f^{(1)}(\bar{k})$ by a small, on the left of Eq. (1) exchange f на f_0 . Then we will have:

$$\nabla_{\bar{r}} f \approx \nabla_{\bar{r}} f_0 = \frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu = \frac{\partial f_0}{\partial E} \left(\frac{\mu - E}{T} \nabla T - \nabla \mu \right), \quad (2)$$

$$\nabla_{\bar{k}} f \approx \nabla_{\bar{k}} f_0 = \frac{\partial f_0}{\partial E} \nabla_{\bar{k}} E = \hbar \frac{\partial f_0}{\partial E} \bar{V}. \quad (3)$$

Substituting expressions (2) and (3) in the Eq. (1), and being restricted to a case when the electric field $\bar{E} = -\nabla \phi$, where ϕ - electrostatic potential, we will have for electrons operates only:

$$\bar{V}_n \frac{\partial f_0}{\partial E} \left\{ \frac{\mu - E}{T} \nabla T - \nabla \mu \right\} + e \frac{\partial f_0}{\partial E} \bar{V}_n \nabla \phi = -\frac{f^{(1)}(\bar{k})}{\tau_e(\bar{k})}. \quad (4)$$

From the Eq. (4) we will spot $f_n^{(1)}(\bar{k})$:

$$f_n^{(1)}(\bar{k}) = \tau_e(\bar{k}) \frac{\partial f_0}{\partial E} \left\{ \frac{\mu - E}{T} \nabla T - \nabla(\mu - e\phi) \right\} \bar{V}_n. \quad (5)$$

for electron defects:

$$f_p^{(1)}(\bar{k}') = \tau_p \frac{\partial f_0}{\partial E} \left\{ \frac{E + \mu + \Delta E}{T} \nabla T - \nabla(\mu - e\phi) \right\} \bar{V}_p. \quad (6)$$

From relations (2)–(6) it is visible that the equilibrium distribution function is supposed nonuniform, i.e. in an equilibrium state there are processes of transport of heat and particles, and transport of particles is carried out not only at the expense of an external field. Usually it is considered that the dispersion mechanism can be considered through a relaxation time.

For example, dispersion of charge carriers is carried out at interaction with ultrasonic oscillations of a crystalline lattice. In this case the free length $l = V\tau$ does not depend on energy of carriers, and it is possible to express a relaxation time through l :

$$\tau = \frac{l}{V} = \frac{m_n^* l}{\hbar} k^{-1}. \quad (7)$$

Having entered a label $E = k_0 T \alpha$, here $\alpha = \frac{d\varepsilon}{dT}$ – specific TEF, equal to the relation TEF to an individual difference of temperature.

Then

$$\bar{j}_n = nu_n \left\{ \nabla(\mu - e\phi) + \left(2k_0 - \frac{\mu}{T} \right) \nabla T \right\}, \quad (8)$$

$$\bar{j}_p = pu_p \left\{ \nabla(\mu - e\phi) - \left(2k_0 - \frac{\mu + \Delta E}{T} \right) \nabla T \right\}. \quad (9)$$

In this expression $\frac{4el}{3(2\pi m_n^* k_0 T)^{3/2}} = u_n(T)$ – Mobility of electrons.

The full density of a current we will spot expression:

$$\begin{aligned} \bar{j} = & nu_n \left\{ \nabla(\mu - e\phi) + \left(2k_0 - \frac{\mu}{T} \right) \nabla T \right\} + \\ & pu_p \left\{ \nabla(\mu - e\phi) - \left(2k_0 - \frac{\mu + \Delta E}{T} \right) \nabla T \right\} \end{aligned} \quad (10)$$

For a finding TEF it is necessary to spot a potential difference at a broken circuit. Having equated $\bar{j} = 0$, from (10) equality follows:

$$\nabla \left(\frac{\mu}{e} - \phi \right) = -\frac{k_0}{e} \left(2 - \frac{\mu}{k_0 T} \right) \nabla T.$$

Specific TEF α it is spotted as

$$\alpha = \frac{|\nabla(\phi - \frac{\mu}{e})|}{|\nabla T|}. \quad (11)$$

For the natural semiconductor $n = p = n_i$, $\mu = -\frac{\Delta E}{2}$ and the relation (11) will look like:

$$\alpha = \frac{k_0(b-1)}{e(b+1)} \left(2 + \frac{\Delta E}{2k_0 T} \right). \quad (12)$$

here $b = \frac{u_n}{u_p}, \frac{\Delta E}{2} = \mu$.

From the gained relation (12) it is visible that quantity TEF for the natural semiconductor is spotted only by forbidden band breadth ΔE and a relation of mobility of charge carriers.

Expression (4) is gained, actually, in approach, when derivative of function much less than the function. It means that times much major, then warmth and charge relaxation times are considered. During too time presence of dependence of temperature and potential from co-ordinates specify in presence of interior lapse rates. Therefore, it is not absolutely correct use of an equilibrium distribution function as it corresponds to concept of an equilibrium state of local approach.

Consecutive viewing of transport of a charge and heat for the systems which are in lapse rates of temperature and potential can be spent a method of the nonequilibrium statistical operator [10].

The method of the nonequilibrium statistical operator allows to write down a uniform fashion the equations featuring a kinetics, taking into account a principle of impairment of correlations, and to gain expressions for relaxation times.

As method bottom the combined equations - the dilated equations Neumann's background serves:

$$\frac{\partial \rho}{\partial t} + \frac{i}{\hbar} [H, \rho(t)] = -\epsilon (\rho(t) - \rho_{eq}(t)) \quad (13)$$

where H - a Hamiltonian of system's, $\rho_{eq}(t)$ - the quasi-equilibrium statistical f operator, and ϵ - the infinitesimal radiant providing irreversibility, which $\epsilon \rightarrow 0$ after thermodynamic transition.

Hamiltonian we will choose in a view [11]:

$$H = H_0 + H_1 + H_2, \quad (14)$$

$$H_0 = \sum_k E_k a_k^+ a_k + \sum_m E_m a_m^+ a_m + \sum_{mm'} J_{mm'} a_m^+ a_m + \sum_q \hbar \omega c_q^+ c_q,$$

$$H_1 = \sum_{kmq} (V_q + M_q a_m^+ a_m) e^{iqR_m} a_{k+q}^+ a_k$$

$$+ \frac{1}{2} \sum_{kk'q} \frac{4\pi e^2}{q^2} a_{k+q}^+ a_{k'} a_{k'-q}^+ a_k$$

$$+ \sum_{kk'mq}, \left(R_{mkq} a_m^+ a_{k'} a_{k'-q}^+ a_k + R_{mkq}^* a_k^+ a_{k'} a_{k'-q}^+ a_m \right),$$

$$H_2 = \sum_{kqm} V_{kqm} (c_q^+ + c_{-q}) (a_{k+q}^+ a_k + a_m^+ a_{m'} + a_{k+q}^+ a_m),$$

Here $a_{m(k)}^+$ ($a_{m(k)}$) - operators of a creation (annihilation) of electrons corresponding localized m (nonlocalized - k) to states, c_q^+ (c_{-q}) - operators of a creation (annihilation) of phonons with a wave vector q , $J_{mm'}$ - a matrix element of a jump between the localized states, V_q - potential of scatterers, $M_q \approx \frac{4\pi e^2}{q^2} \sum_q \Psi_0^*(p) \Psi_0(p+q)$, $R_{mkq} \approx \frac{4\pi e^2}{q^2} e^{i(k+q) \cdot R_m} \Psi_0(k+q)$, V_{kqm} - a matrix elements the interaction electron-phonon, obvious expression for which is spotted by the concrete mechanism of dispersion.

The formal solution (13) we will write down in a view:

$$\rho(t) = \rho_{eq}(t) - \lim_{\epsilon \rightarrow +0} \int_{-\infty}^t dt' e^{-\epsilon(t-t')} e^{-\frac{i(t-t')H}{\hbar}} \left(\frac{\partial \rho_{eq}(t')}{\partial t'} + \frac{1}{i\hbar} [\rho_{eq}(t'), H] \right) e^{\frac{i(t-t')H}{\hbar}}. \quad (15)$$

Boundary conditions we will accept, in view of independence of a Hamiltonian of time, in a standard view [10]:

$$\text{Tr}(\rho_{eq} n_m) = \text{Tr}(\rho n_m) = \langle a_m^+ a_m \rangle,$$

$$\text{Tr}(\rho_{eq} n_k) = \text{Tr}(\rho n_k) = \langle a_k^+ a_k \rangle \quad (16)$$

At the initial moment of time $\langle a_{k,m}^+ a_{k,m} \rangle_{t=0} = (e^{(E(\mathbf{k})-\mu)/kT} + 1)^{-1}$ - an equilibrium distribution function of electrons with temperature T .

Expressions for streams of a charge and heat we will choose in a view:

$$j(\mathbf{r}, t) = -\frac{2e}{(2\pi)^3} \int v_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) d\mathbf{k}, \quad (17)$$

$$W(\mathbf{r}, t) = \frac{2}{(2\pi)^3} \int (E(\mathbf{k}) - \mu) v_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) d\mathbf{k}, \quad (18)$$

where μ - chemical potential. It is necessary to score that in an equilibrium state when $f(\mathbf{k}, \mathbf{r}, t) = f_0(\mathbf{k}, \mathbf{r},)$ - an equilibrium distribution function, streams are equal to zero. Thus, the problem solution consists in a finding and, after substitution, expressions for streams of a charge and warmth (17) and (18).

We choose a distribution function in a view:

$$f(\mathbf{k}, \mathbf{r}, t) = \langle a_k^+ a_k \rangle + \langle a_{m'}^+ a_m \rangle + \langle a_k^+ a_m \rangle + \langle a_m^+ a_k \rangle, \quad (19)$$

The select of a distribution function in the form of (19) is caused by majority carriers of a charge taking into account possibility of transition of electrons from non-local in the localized states. Actually, it means possibility of an interference of states in basic one-particle states [11]:

$$\mathbf{1} = \sum_m |m\rangle \langle m| + \sum_k |k\rangle \langle k|$$

Such select is caused by definition of dynamic variables in method nonequilibrium statistical operator as these variables spot charge and warmth transport. At the expense of a phonon subsystem it is difficult to express transport of heat in the form of a stream. However, the shape of a Hamiltonian (14) allows to express $\langle c_q^+ c_q \rangle$ through $\langle a_{k,m}^+ a_{k,m} \rangle$ in the second order on a constant an interaction electron-phonon.

As it is known [11] to write down the transport equations relation performance is necessary:

$$[P_k, H_0] = \sum_l c_{kl} P_l$$

Using commutation relations of pairs of fermi-operators we will gain for a $P_{11} = a_k^+ a_k, P_{22} = a_{m'}^+ a_m, P_{12} = a_k^+ a_m, P_{21} = a_m^+ a_k$ relation:

$$\begin{aligned} [P_{11}, H_0] &= 0; [P_{22}, H_0] = 0; \\ [P_{12}, H_0] &= -\sum_{m'} [(E_k - E_m) - J_{mm'} \delta_{mm'}] a_k^+ a_m; \\ [P_{21}, H_0] &= \sum_{m'} [(E_k - E_m) - J_{mm'}] a_m^+ a_k; \end{aligned} \quad (20)$$

Thus from (20) it is visible that in processes of transport the dominant role is played by $\langle a_k^+ a_m \rangle$, $\langle a_m^+ a_k \rangle$, $\langle a_k^+ a_k \rangle$ addends and serves as the tank having the temperature and chemical potential, depending on co-ordinates and time. Therefore, it is possible to spot from the kinetic equations and coefficients from (17) to (18).

Let us write down system of the kinetic equations for $\langle P_{12} \rangle$ and $\langle P_{21} \rangle$ in a view:

$$\begin{aligned} \frac{\partial \langle P_{12} \rangle}{\partial t} - \frac{1}{i\hbar} \sum_{m'} [(E_k - E_m) - J_{mm'} \delta_{mm'}] \langle P_{12} \rangle &= \\ = S_{12}^{(1)} + S_{12}^{(2)}; \\ S_{12}^{(1)} &= \frac{1}{i\hbar} \langle [P_{12}, H_{int}] \rangle; \\ S_{12}^{(2)} &= -\frac{1}{\hbar^2} \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \langle \left[H_{int}, [H_{int}, P_{12}] + i\hbar P_{12} \frac{\partial S_{12}^{(1)}}{\partial \langle P_{12} \rangle} \right] \rangle, \end{aligned} \quad (21)$$

Where $H_{int} = H_1 + H_2$. Similar equation registers and for $\langle P_{21} \rangle$ to within transposition of coefficients.

Carrying out commutated in collisional members, we will gain the kinetic equations for $\langle P_{12} \rangle$ and $\langle P_{21} \rangle$ in the second order on force constants and quadratic on $\langle P_{12} \rangle$, $\langle P_{21} \rangle$.

Thus writing down the kinetic equation for and carrying out integration on p we will gain the Eq. (21) in which the right part is spotted through.

Without giving bulky expressions for streams, taking into account dispersion mechanisms, we will give dependences of relaxation times for the elementary case of transfer in the first order.

As the free length usually, I use various relaxation times enters into relations for mobilities. At high temperatures i.e. when energy of a phonon $\hbar\omega_0$ is much less than energy of an electron k_0T dispersion it is possible to consider elastic. Considering that at dispersion on ultrasonic phonons $\hbar\omega_0 \ll k_0T$ also we will gain:

$$\tau = \frac{\sqrt{2}}{4\pi} \frac{Ma^3(\hbar\omega_0)^2 E^{1/2}}{Z^2 e^4 m^{*1/2} k_0 T}. \quad (22)$$

Free length

$$l = \tau V = \frac{V}{2\pi} \frac{M}{m^*} \left(\frac{\hbar\omega_0}{Ze^2/a} \right)^2 \frac{E}{k_0 T}, \quad (23)$$

Were V – velocity of an electron.

In case of low temperatures, $\hbar\omega_0 \gg k_0T$, The electron–phonon interaction becomes inelastic. In this case processes of uptake of phonons are possible only, and to enter a relaxation time it is impossible. But in case of low temperatures if to consider a requirement $\hbar\omega_0 \gg k_0T$, the majority of the electrons immersing energy of a phonon, transfer in an energy interval from $\hbar\omega_0$ to $2\hbar\omega_0$. Such electrons will almost instantaneous let out phonons, since the relation of probability of emission to probability of uptake $\frac{N_q+1}{N_q} \approx \exp \frac{\hbar\omega_0}{k_0T} \gg 1$. As a result of such uptake energy of an electron does not change almost. It allows to view interaction of an electron with optical oscillations of a lattice at very low temperatures as elastic and to enter a relaxation time.

Calculation for a relaxation time gives view expression [12]:

$$\tau_{\text{opt}} = \frac{3\sqrt{2}}{4\pi} \frac{Ma^3(\hbar\omega_0)^{3/2}}{Z^2 e^4 m^{*1/2}} e^{\frac{\hbar\omega_0}{k_0 T}}. \quad (24)$$

From (15) it is visible that at low temperatures the relaxation time on optical phonons does not depend on energy, and on temperature depends exponentially.

Free length

$$l = \tau V = \frac{3a}{2\pi} \frac{M}{m^*} \left(\frac{\hbar\omega_0}{Ze^2/a} \right)^2 e^{\frac{\hbar\omega_0}{k_0 T}} \sqrt{\frac{E}{k_0 T}}. \quad (25)$$

It is necessary to score that because of presence $\exp \left(\frac{\hbar\omega_0}{k_0 T} \right)$ free length always more than interatomic distance, i.e. $l \gg a$.

From the presented analysis follows that charge relaxation times have essentially non-linear temperature dependence and the dispersion mechanism. All it demands the approach which is distinct from the traditional.

4. A method of the extended irreversible thermodynamics

In the standard approach of modeling of distribution of warmth in a thermoelement [4] as a rule, the classical equations of balance of transport of warmth are used:

$$q = \alpha j T - \frac{j^2 r L}{2} \quad (26)$$

where q - a specific heating capacity, T - temperature теплоотдающей mediums, α , r - TEF and a thermomaterial specific resistance, j - current density, L - thermobranch length.

Prominent feature of model (26) is lack of a time dependence q and temperature ρ . In case of use as a branch of a thermoelement of a material with NTCR [6], the temperature dependence is essential and demands the account at modeling of parameters of a thermoelement. The consecutive account of relaxation processes can lead to occurrence of waves of warmth and essentially changes character of distribution of heat at an initial stage of process.

Other feature of modeling is comparison of effects of model with experiment. Enough compound circuit of excitation and temperature measuring's is observationally used. The most attractive the plan with use as a radiant of warmth and a charge of an impulse of a current (**Figure 4**) looks.

In this case, measuring temperatures in points T_i , at excitation by a current impulse (point T_1) it is possible to realize the direct plan of distribution of warmth along a thermoelement branch.

As it was already specified earlier, use of classical thermodynamics invokes certain fundamental problems because of presence in system of a thermal cell of streams of heat and a charge. Therefore, the thermodynamic approach possesses intrinsic discrepancy. Such problems can be avoided, using the approach of extended irreversible thermodynamics [13]. Extended irreversible thermodynamics far from local balance uses as new explanatory variables dissipation streams, i.e. heat stream q , mass flux J and stress tensor P . Thus, in nonequilibrium system entropy S is function not only classical variable, but also dissipation streams:

$$S = S \{U(x, t), v(x, t), C(x, t), q(x, t), I(x, t)\}.$$

Introduction of streams as explanatory variables quite defensible from the physical point of view. Really, if in system there is any stream it means the directed

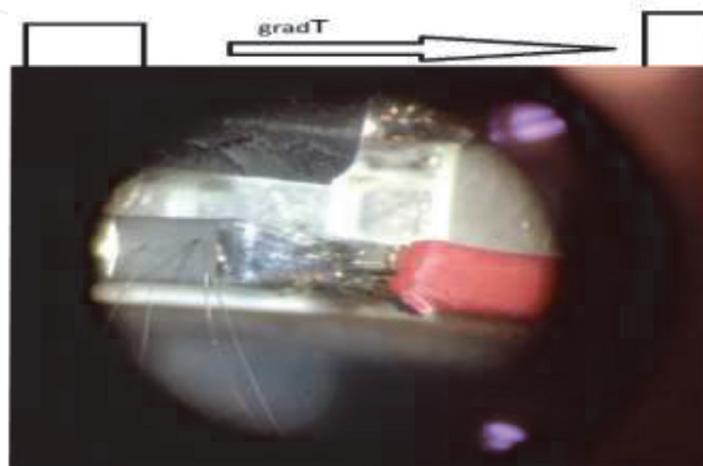


Figure 4.
Plan of modeling of a thermobranch.

locomotion of carriers of heat or mass. Hence, entropy which, as it is known, is a measure of affinity to an equilibrium state, specifies directions of locomotion of all system. Extended irreversible thermodynamics, in difference from classical is irreciprocal, introduces into processes time, as a variable that leads to the differential equations for dissipation streams of evolutionary (relaxation) phylum. In the elementary case relaxation times enter into such equations (Maksvela-Kataneo), in our case of heat and a charge.

Hence using methods of extended irreversible thermodynamics and the relaxation times, received from modeling representations about interactions in stuffs, it is possible to construct the consistent theory of the thermoelectric phenomena.

The initial combined equations can be written down in a view [13].

$$q + \tau_T \frac{\partial q}{\partial t} = -\lambda \nabla T + q_0(t, x) \quad (27)$$

$$\tau_e \frac{\partial i}{\partial t} = -(i - \sigma E') \quad (28)$$

where: $q_0(t, x)$ – source of heat, λ is the thermal conductivity coefficient, $E' = E - T \nabla(T^{-1} \mu_e)$, E is the electric field strength, μ_e is the chemical potential, τ_T , τ_e is the relaxation time of heat and charge, σ_e is conductivity, T is temperature.

Thus, the inclusion of dissipative flows in the series of independent variables leads to the fact that these flows are no longer determined by the gradient of the corresponding transfer potential, as in the classical local-equilibrium case, but they are solutions of the evolution Eqs. (27) and (28). These equations describe the process of relaxation of dissipative flows to their local-equilibrium values.

While analyzing the system of Eqs. (27) and (28), we use the following approximations. We assume that the coefficient of thermal conductivity and the relaxation time of the heat are constant and temperature is independent. Such assumption is correct in connection with the fact that the calculation of the heat relaxation time must be carried out taking into account the propagation of heat in the system. In other words, in the case of the heat propagation, the problem is self-consistent. Taking into account that the distribution of the heat and charge front may be considered in a single grain, we can assume that the spread of non-locality is rather weak, and the process describes the approach of the permanent τ_T and λ .

The τ_e - is an expression for the relaxation time of conduction electrons of a nondegenerate atomic semiconductor $\tau_e \sim \varepsilon^{-1/2} T^{-1}$ [12], where ε is an energy of the width order of the forbidden band of the semiconductor. Such an expression for the charge relaxation time is an approximation that has a temperature dependence. It is necessary to solve the kinetic equation for the charge propagation taking into account the dispersion law in the conduction mechanism [8]. However, in our case, such task is complicated by the fact that it is necessary to consider the flow of the charge along the grain surface. It complicates the solution of the kinetic equation, which must be solved taking into consideration the percolation flow model.

Let us converse (28) considering communication of reciprocity coefficients of Onsager's with phenomenological relations [13]:

$$\nabla T^{-1} = \frac{1}{\lambda T^2} q - \frac{\mu_e - \alpha T}{\lambda T^2} i; \quad (29)$$

$$E - \nabla \mu_e = \frac{\alpha}{\lambda} q - \left(\alpha \frac{\mu_e - \alpha T}{\lambda} - r \right) i; \quad (30)$$

Here Thomson's relation is used $\alpha T = -P$, where P – coefficient of Pelte. As a result of (28) transfers in

$$\frac{\tau_T}{\tau_e} \frac{\partial i}{\partial \tau} = -\frac{\mu_e - \alpha T}{r\lambda T} q + \frac{(\mu_e - \alpha T)^2}{r\lambda T} i \quad (31)$$

Time scale in (31) we will choose concerning relaxation times [10]. Here in expression (31) replacement is yielded $t/\tau_e = \tau_T/\tau_e \tau$; $\tau = \frac{t}{\tau_T}$. Thus, the time dependence scale is spotted by the relation of relaxation times of warmth and a charge [12]. Conformity introduction between a return relaxation time and a thermal

conductivity $\tau_T^{-1} \sim \frac{\lambda}{\lambda_q^2}$, where $\lambda_q = 2l$ – the doubled path length $\lambda_q = \tau V =$

$\frac{3a}{\pi} \frac{M}{m^*} \left(\frac{\omega_0}{Ze^2/a} \right)^2 e^{\frac{\omega_0}{k_0 T}} \sqrt{\frac{E}{k_0 T}}$, λ – thermal conductivity. $E' = E - T\nabla(T^{-1}\mu_e)$, τ_e – charge relaxation time, σ – conductivity, μ_e – chemical potential, E – electric intensity, T – temperature, ε – energy of the order of breadth of a forbidden band of a material.

Similarly, we will converse the Eqs. (27) and (31). We use a relation (29) and having presented $\lambda\nabla T = -\lambda T^2(\nabla T^{-1})$, let us gain:

$$\tau_T \frac{\partial q}{\partial t} = -(\mu_e - \alpha T)i + q_0(t, x) \quad (32)$$

$$\frac{\tau_T}{\tau_e} \frac{\partial i}{\partial \tau} = \frac{\mu_e - \alpha T}{r} \frac{\nabla T}{T} \quad (33)$$

Further we use the law of conservation of energy and (32). It is as a result had:

$$\frac{1}{\tau_T} \frac{\partial^2 T}{\partial \tau^2} = -\frac{\alpha}{c_v \rho} i \nabla T + \frac{1}{c_v \rho} \frac{\partial}{\partial \tau} q_0(\tau, x) \quad (34)$$

were ρ – material density, c_v - specific heat capacity.

Thus, the Eqs. (33) and (34) feature distribution of a charge and temperature allocation to a thermoelement under the influence of a current impulse.

Warmth radiant we will choose in a view:

$$q_0(t, x) = r i^2 \quad (35)$$

I.e. a radiant is Joule heat. Thus, we consider that the current does not depend on co-ordinate and is spotted only by dependence from τ . Carrying out differentiation on τ and using (33), we will gain:

$$\frac{1}{\tau_T} \frac{\partial^2 T}{\partial \tau^2} = \frac{1}{c_v \rho} [\gamma \mu_e - (1 + \gamma) \alpha T] i \frac{\nabla T}{T} \quad (36)$$

were $\gamma = \tau_e / \tau_T$.

As a result, we gain the combined equations featuring model of allocation of temperature along the sample at excitation by an impulse of a current.

$$\frac{\partial i}{\partial \tau} = \gamma \frac{\mu_e - \alpha T}{r} \frac{\nabla T}{T} \quad (37)$$

$$\frac{1}{\tau_T} \frac{\partial^2 T}{\partial \tau^2} = -\frac{i}{c_v \rho} \left[\alpha \nabla T - \gamma (\mu_e - \alpha T) \frac{\nabla T}{T} \right]$$

Prominent feature of model (37) is presence of the addends proportional to the relation of relaxation times of a charge and heat γ which acts as natural parameter little. The system (37) looks like a series development on, to the first order though at its deduction of any guesses about little it was not supposed. Thus, in the equation for change of temperature the addend of the zero order on γ is spotted by a thermoelectric stream of warmth. It shows that in the course of warmth distribution, to the initial moment of time, there is a heating at the expense of a current, as the most prompt.

Initial and boundary conditions for system we will choose in a view

$$i(0) = I; \quad (38)$$

$$T(0, 0) = T_1; T(0, L) = T_2; \frac{\partial T}{\partial \tau}(0, 0) = 0. \quad (39)$$

The predominant model of the conductivity of thermistors with NTCR is a model of hopping conductivity in the approximation of the “nonadiabatic” polaron of a small radius leading to the temperature dependence of conductivity [6]:

$$\sigma = \pi^{\frac{3}{2}} \frac{e^2 l^2 J^2 E^{-1/2}}{h(kT)^2} \exp(-E/kT) \quad (40)$$

where: l is an effective hopping length, J is a parameter of jamping, E is an energy of hop activation, T is a temperature. Such nonlinear temperature dependence of electrical conductivity leads to a substantial nonequilibrium process of the heat and charge transfer in the branches of the thermoelement. It should be noted that in the case of a thermoelectric effect the process has a nonlocal character both in the coordinate and time. It is usually assumed that the chemical potential does not depend on temperature and is approximately equal to the Fermi energy. However, for a nondegenerate semiconductor with a temperature conductivity dependence (40), essentially nonlinear, it is necessary to consider the temperature dependence of the chemical potential [12], which has a logarithmic temperature dependence:

$$\mu_e = kT \ln \left[\frac{4}{3\sqrt{\pi}} \left(\frac{\varepsilon}{kT} \right)^{\frac{3}{2}} \right] < 0 \quad (41)$$

where k is a Boltzmann constant.

Thus, the problem of calculating the heat transfer in this system is nonstationary. To solve it, we assume the model to be one-dimensional, and dismiss the second-order terms in the temperature gradients. The initial and boundary conditions are assumed to be standard [14]. Such assumptions allow us to make a qualitative analysis of the nature of the propagation of heat and charge in the system. We examine the model at the distances of the grain size order. The generalization of the sample dimensions requires the establishment of an averaging procedure, which differs from the standard method i.e. the introduction of certain average or effective parameters requires additional considerations and cannot be carried out by simple averaging.

5. A construction and manufacturing of thermoelements

For manufacturing of structural thermoelements it is convenient to use the known production technology of chips-inductances.

Formation of structure of chips-thermoelements is carried out by level-by-level drawing ferrite and conductor layers. On a surface of a flat substrate superimpose thin (to several tens micron) a stratum of paste on the basis of the dielectric powder immixed with a binding material and solvents. On a surface of the dried stratum shape a printing expedient current-carrying (ferrite NiMn_2O_4 and CoMn_2O_4) drawing in the form of a semicoil, then superimpose the stratum coating 1/2 areas of preparation and leaving unclosed extremity of a semicoil. The following part of current-carrying drawing (semicoil) is superimposed so that the extremities of conductors were imposed against each other. Similar operations are iterated the necessary number of times that spending drawings in the form of semicoils were joined consistently, forming a spiral (**Figure 5**). Deficiencies of a “stage” expedient of manufacturing concern low reliability of switching of coils in places of transition of spending paste from the inferior plane on the upper.

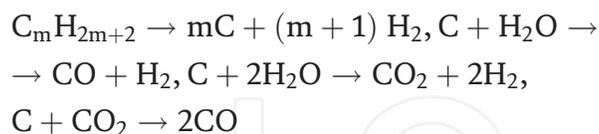
Other, simpler plan of switching of the extremities of semicoils through a hole in the dielectric stratum (**Figure 6**) is developed also.

As linking of semicoils is yielded each time on half of interturn distance that twice reduces probability of formation of flaws on this critical site, thanks to the free diffuence of paste linking of coils trustier, structural structure trustier.

Structural thermoelements devices are made by a group expedient, i.e. simultaneously agglomerated a considerable quantity of devices on a substrate by the area 100×100 mm. After the termination of the making up the group package is slited on separate devices which are exposed to sintering.

Making of regenerative atmosphere allows to spend formation of a firm solution to furnaces with not compensated charge that leads to various type of conductivity depending on an initial composition.

The intermixture of gases $\text{CO} - \text{CO}_2$ can be gained two expedients. The first is grounded on interaction of gases CO_2 and the prosir-butanovoj of an intermixture, the second expedient - on restoration CO_2 at its gear transmission through a stratum of the heated coal. According to the first variant regenerative medium gained by conversion the prosir-butanovoj of an intermixture and CO_2 . It occurs at temperature $800-1000^\circ\text{C}$. Formation of gases is accompanied by following responses:



The conducted examinations have shown that most full responses proceed at temperature 1000°C .

Advantage of the given method is that the rate of flux of gases is simply enough set with the help concentration of gas metter. However, enough high temperature is

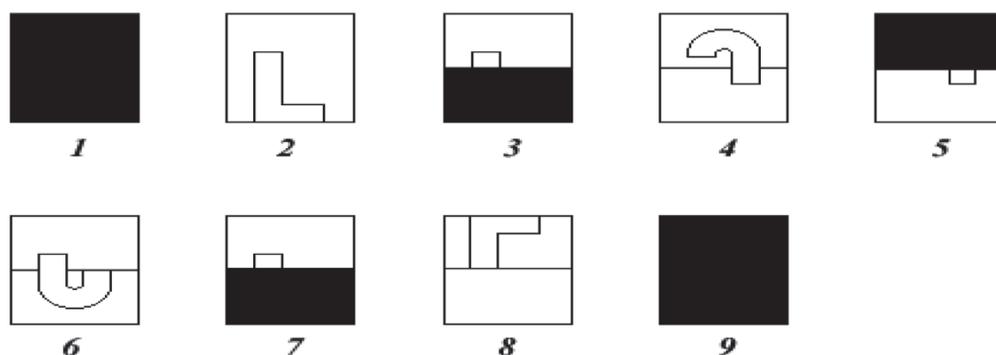


Figure 5.
The plan of the making up switching through a step.

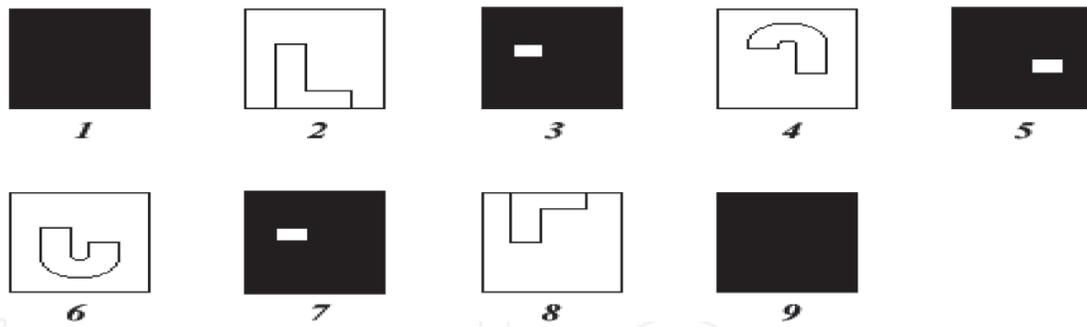


Figure 6.
 The plan of the making up switching through a hole.

necessary for making of demanded atmosphere with an optimum exit of gases $\sim 1000^{\circ}\text{C}$ and the materials applied at manufacturing of the converter, should possess ability to work in regenerative medium (the quartz, special high-temperature grades of a steel). Besides, in this case takes place many-stage chemical responses that demands application of the special data units checking a composition of atmosphere on an exit of the converter.

On the second expedient a gas intermixture gained by gear transmission CO_2 through the ceramic pipe filled with heated coal. There is an oxidizing of coal and restoration CO_2 on response:



In an equilibrium state at atmospheric pressure in a gas intermixture on a converter exit the following concentration CO in % contains: 2; 15; 58; 94; 99,3 accordingly at temperature 300, 500, 600, 700, 800°C . Advantage of this method is the low temperature at which there is a formation of regenerative medium. In our case it makes $650\text{--}700^{\circ}\text{C}$. Regulation of a composition of medium is carried out by change of temperature of the converter. It is necessary to carry necessity of a periodic fill of the converter to deficiencies coal.

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As builders it is possible to use restoration шпинелей NiMn_2O_4 and CoMn_2O_4 in the gas medium gained by conversion CO_2 and H_2O over carbon.

The offered procedure allows with sufficient repeatability to gain ceramic semiconductor materials with n and p conductivity types at simultaneous roasting.

6. Results and discussion

The results of numerical simulation are shown in **Figure 7**. The system analysis (37) was carried out for various relations τ_T/τ_e and the dimensionless time t/τ_T was used.

The result of the simulation is presented on **Figure 7a**, provided that the times of relaxation of heat and charge are close. In this case, the propagation of heat occurs almost simultaneously with the charge density. It has a character close to a solitary wave. Such result is quite obvious, since in this case Joule heat is released simultaneously with heat transfer and the increase of the charge current occurs with the velocity that is close to the velocity of propagation of heat V_1 . A characteristic

feature of such propagation is a formation of the wave on the length of the conductivity hop.

In the case when there is $\tau_T \gg \tau_e$ (**Figure 7b**), the break of propagation front happens and the Joule heat wave V_2 outpaces the actual heat transfer wave due to the temperature gradient. Thus, in this case two waves are formed, which are spatially separated. At the same time, the relaxation of the heat does not occur during the hopping of the charge, and the system is in a locally nonequilibrium state. In other words, charge transfer generates a locally nonequilibrium state in which the charge flow is a fast variable.

In the case when there is $\tau_T < \tau_e$ (**Figure 7c**), the heat relaxation occurs faster than the charge transfer, and a heat propagation front coinciding with the charge transfer is formed. It should be noted here that the steepness of the front is determined by the mechanism of hopping conductivity and the approximations in the calculation. When there is more correct calculation there will be no gaps on the front.

The mode of heat transfer will be especially manifested in functional gradient materials [3], especially along the grain boundaries. By creating a regular structure with the required relaxation time ratios, it is possible to achieve the wave character of the heat transfer and charge transfer. It will allow to create devices that simultaneously measure and regulate the temperature.

Investigating movement of a charging and temperature wave it is possible to estimate the relation of times of a relaxation. It will allow, at qualitative level to draw certain conclusions about the carrying over mechanism. Such possibility is very actual for ceramic materials.

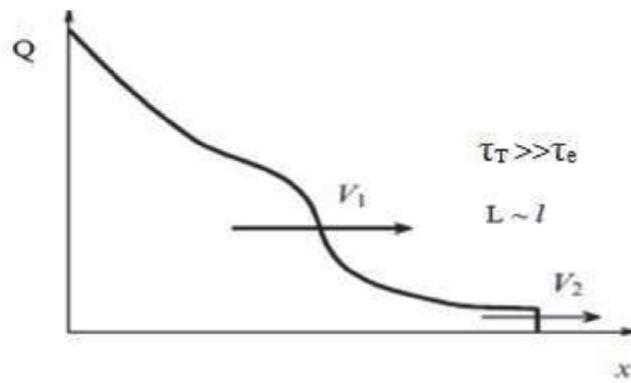
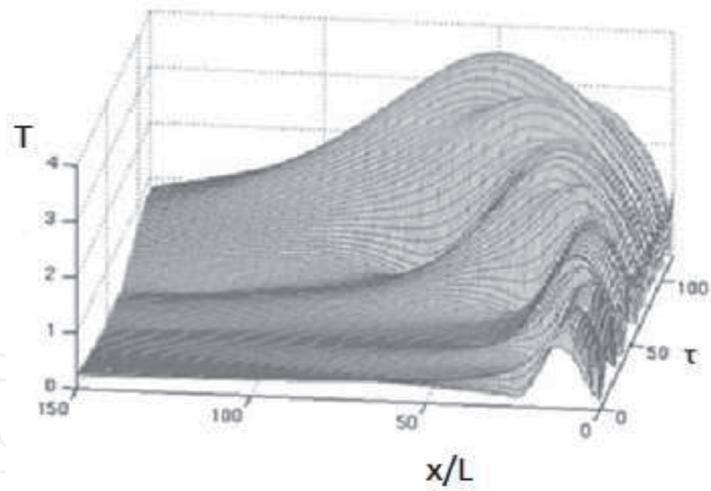
The first and obvious expedient of pinch of thermoelectric quality factor ZT of materials is optimization of their properties spotting thermoelectric efficiency. Such expedient allows to raise, though and is in most cases inappreciable, thermoelectric properties of traditional thermoelectric materials which are well studied and for which the physical analogues allowing purposefully to spot a direction of optimization of properties of materials are developed. As the basic directions of such optimization it is possible to ooze:

- Optimization of concentration of charge carriers;
- Optimization of breadth of a forbidden band;
- Optimization of a chemical compound of a material.

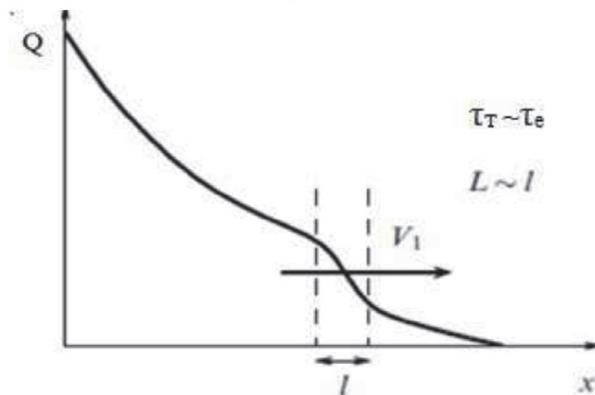
Optimum concentration of charge carriers (i.e., a select of an optimum level of a doping in the course of synthesis of a thermoelectric material) allows to provide the peak value of a thermoelectric quality factor. Physically, existence of optimum concentration of charge carriers is related by that at magnification of concentration the direct-current conductivity σ grows, and value termo-EDS, on the contrary, decreases. Dependence σ from concentration of charge carriers n is obvious and directly follows from direct-current conductivity definition.

Dependence termo-EDS from concentration of charge carriers is caused by a gas degeneracy of carriers at magnification of concentration of the item. For degenerated electronic gas Fermi level E_F gets to a conduction band (for the electronic semiconductor), and requirement $E_F - E_C > kT$, where E_C - energy of a bottom of conduction band, k - a Boltzmann constant is satisfied.

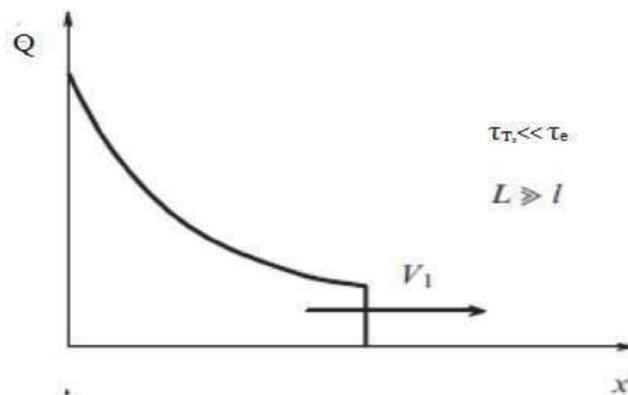
In this case energy and velocity of electrons are spotted by value of a Fermi level and practically do not depend on temperature. For such semiconductor, in the presence of a lapse rate of temperatures on its opposite extremities, streams of



a)



b)



c)

Figure 7.
 Distribution of heat in a thermoelements for various ratios τ_T , τ_e , L .

electrons from the cold and hot extremities feebly differ, hence, volume thermo-EDS will be inappreciable. Thermo-EDS, and, hence, and a thermoelectric quality factor, it is possible to achieve pinch in semiconductors and semimetals in requirements when there is the strong degeneration, but concentration of charge carriers is great enough.

Optimization of breadth of forbidden band E_g is fundamental parameter of an electronic spectrum of the semiconductors which change allows to optimize their thermoelectric properties. As a result of a series of examinations [15] it has been shown that from the point of view of reception of a material with the best thermoelectric performances (for the unregenerate semiconductor) performance of following requirements is necessary:

- The forbidden band breadth should surpass essentially thermal energy κT ,
- The Fermi level should settle down near to a bottom of an allowed band of majority carriers of a charge.

7. Conclusion

For the first time features of carrying over of warmth and a charge in semiconductor branches of a thermoelement are considered. The model of ceramic semiconductor branches is constructed of materials with negative temperature factor of resistance for thermoelements. Methods of the expanded irreversible thermodynamics spend modeling of distribution of temperature along the sample. On the basis of the spent modeling the technique of registration of impulses of temperature and definition of the relation of times of a relaxation in materials with negative temperature factor of resistance is offered. It is received that depending on a parity of times of a relaxation of processes of carrying over of a charge and warmth, various operating modes of a thermoelement can be realized.

It is offered to use by manufacture of thermobatteries the known production technology the chips-inductances. Feature of the specified technology is packing of separate elements in assemblage which then is divided into separate elements. Thus, instead of the semi-conductor materials containing rare and often ecologically dangerous materials, it is offered to use oxides ceramics. Roasting in regenerative atmosphere of the furnace allows to make layered thermoelements for one cycle of roasting.

Modeling of thermoelements from the ceramic materials possessing negative temperature in factor of resistance is spent.

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Author details

Yuri Bokhan
Vitebsk Branch Educational Establishment, The Belarus State Academy of
Communication, Vitebsk, Belarus

*Address all correspondence to: yuibokhan@gmail.com

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