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Thermodiffusion and thermo-electric phenomena in condensed systems

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Abstract—The transport equations of irreversible processes such as thermodiffusion and thermo-electric phenomena are derived on the basis of modern nonequilibrium thermodynamics in the case of the reversible change of volume due to the thermal expansion. Priority was given to obtaining the generalized equation of heat conduction, which was further applied to metal systems and semiconductors. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

Modern nonequilibrium thermodynamics has worked out the methods which allow the formulation of the complete set of equations describing the broad class of irreversible processes. By formulation of these equations the modern thermodynamics of irreversible processes enables us to state clearly and explicitly the conditions of validity of the derived equations, which really is a large advantage in comparison with the older nonequilibrium thermodynamics, which uses more or less heuristic methods. Even recently, paper [1], in which the authors derive the equation of heat conduction in metal systems, taking into account the presence of an electric current, has appeared. The authors of this paper do not use those methods of modern nonequilibrium thermodynamics which are at present common and accepted. Therefore, the aim of the present paper is to derive the complete set of equations, which describe such irreversible processes as the thermodiffusion and thermo-electric phenomena in multi-component condensed systems. The results were obtained at first in a general form, and then they were applied for metal systems and semiconductors.

In monograph [2] there is a description of (i) the thermodiffusion in gases and liquids, which are enclosed in a vessel, so that the hydrodynamic velocity has zero value and (ii) the thermo-electric phenomena in electrolytes. The present paper deals with the irreversible processes in solids with the main emphasis on derivation of the equation of heat conduction, taking into consideration the thermal expansion of materials.

The present paper is divided into seven parts. In the second part the starting equations are briefly introduced. The aim of this part is to show the conditions under which the Gibbs's relation (9) is also valid for crystals. In connection with this condition, we explicitly make note of the fact that in the whole paper we consider only a reversible change of volume. That will be important especially in the third part, in which the internal energy is defined in a different way to that in monograph [2], and, similarly, the method of derivation of the entropy balance equation is different as well. In Section 4 the phenomenological equations for multi-component systems are formulated. The main contribution of the present paper is in Section 5, in which the generalized exact equation of heat conduction in the framework of linear nonequilibrium thermodynamics is derived. In Sections 6 and 7, the generalized equation of heat conduction is applied to metal systems and semiconductors. In these sections, the conditions under which some terms of the exact equation may be neglected without loss of sufficient accuracy are discussed.

2. STARTING EQUATIONS

By constructing the complete set of equations for describing the irreversible processes, the modern nonequilibrium thermodynamics starts partly from the relation of the entropy production and partly from Onsager reciprocal relations. For this reason, our first step will be to derive the entropy balance equation, from which the relation for the entropy production follows immediately.

To obtain the derivation of the entropy balance equation we will start with certain equations, which will be introduced in a short form. There exist two reasons for their introduction. The first one is, that in the case of solids and especially crystals, we meet some facts which are not taken into consideration in monograph [2]. The second one is the necessity of introducing the notation of quantities which will be used.

The basic equations for derivation of the entropy balance equation are as follows:

(a) Equation of motion of continuum

NOMENCLATURE

c_i	mass fraction of component i
c_{pi}	partial specific heat at constant pressure per unit mass of component i
c_{Vi}	partial specific heat at constant volume per unit mass of component i
$\mathbf{D}$	linear strain tensor
E_c, E_v	energy of band edge
E_D	donor energy
E_F	Fermi energy
e	density of energy
g_i	rate of generation per unit volume of component i
h	enthalpy per unit mass
h_i	partial specific enthalpy of component i
$\mathbf{I}$	unit tensor
$\mathbf{i}$	electrical current density
$\mathbf{i}_i$	contribution to the electric current density from component i
$\mathbf{J}_q$	heat current density
$\mathbf{J}_s$	entropy flux
$\mathbf{J}_i$	diffusion flow of component i
k_B	Boltzmann constant
m_i	mass of particle of component i
m_0	rest mass of electron
n	number of components of the system
n_i	intrinsic carrier density
N_i	particle number density of component i
$\mathbf{P}$	pressure tensor
$\mathbf{P}_{eq}$	equilibrium part of the pressure tensor
p	hydrostatic pressure
q_i	charge of particle of component i
r_i	rate of recombination-trapping per unit volume of component i
s	entropy per unit mass
s_i	partial specific entropy of component i
S	density of entropy
t_k	transference number of component k
T	temperature
u	internal energy per unit mass
U	density of internal energy
$\mathbf{v}$	hydrodynamic (barycentric) velocity
$\mathbf{v}_i$	velocity of component i
v	specific volume.
Greek symbols	
ε_0	permittivity of vacuum
ε_r	relative permittivity
η	Seebeck coefficient
η_i	Seebeck coefficient of component i
λ	thermal conductivity
μ_i	chemical potential of component i
μ_h	hole mobility
μ_e	electron mobility
π	Peltier coefficient
$\mathbf{\Pi}$	non-equilibrium part of the pressure tensor
ρ	density
ρ_i	density of component i
ρ_R	resistivity
ρ_{Ri}	resistivity of component i
ρ_e	electric charge density
$\sigma(s)$	entropy production
τ	Thomson coefficient
$\tilde{\tau}$	dielectric relaxation time
ψ_i	potential energy per unit mass of component i.

$$\rho\frac{d\mathbf{v}}{dt} = -\nabla\cdot\mathbf{P}+\sum_{i=1}^{n}\rho_i\mathbf{F}_i, \tag{1}$$

where

$$\rho = \sum_{i=1}^{n}\rho_i,\quad \mathbf{P} = \mathbf{P}_{eq}+\mathbf{\Pi},\quad \mathbf{v} = \sum_{i=1}^{n}c_i\mathbf{v}_i,$$

$$\mathbf{F}_i = -\nabla\psi_i,\quad \frac{d}{dt} = \frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla$$

is a substantial time derivative.

The isotropic part of $\mathbf{\Pi}$ is connected with the irreversible change of volume and the residium part is connected with a viscous flow.

(b) Mass balance equations

$$\frac{\partial\rho_i}{\partial t} = -\nabla\cdot\rho_i\mathbf{v}_i,\quad \text{for } i = 1,2,\ldots,n \tag{2}$$

or

$$\rho\frac{dc_i}{dt} = -\nabla\cdot\mathbf{J}_i,\quad \text{for } i = 1,2,\ldots,n, \tag{3}$$

where

$$\mathbf{J}_i = \rho_i(\mathbf{v}_i-\mathbf{v}),\quad v = \frac{1}{\rho},\quad c_i = \frac{\rho_i}{\rho}.$$

(c) Energy conservation law

$$\frac{\partial e}{\partial t} = -\nabla\cdot\left\{e\mathbf{v}+\mathbf{J}_q+\sum_{i=1}^{n}(\psi_i+\mu_i)\mathbf{J}_i+\mathbf{v}\cdot\mathbf{P}\right\}. \tag{4}$$

(d) Gibbs's relation

The energy balance equation in connection with the second law of thermodynamics has the following form:

$$T\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega(t)} S\,\mathrm{d}V = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega(t)} U\,\mathrm{d}V + \int_{\Omega(t)} \mathbf{P}_{\mathrm{eq}} : \frac{\partial \mathbf{D}}{\partial t}\mathrm{d}V + \sum_{i=1}^{n} \mu_i \oint \mathbf{J}_i \cdot \mathrm{d}\mathbf{S}. \quad (5)$$

By applying Gauss's theorem and auxiliary relation

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega(t)} f\,\mathrm{d}V = \int_{\Omega(t)} \left(\frac{\partial f}{\partial t} + \nabla \cdot f\mathbf{v}\right)\mathrm{d}V$$

and from equation (5) follows the equation

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = (U - TS)\nabla \cdot \mathbf{v} + \frac{\mathrm{d}U}{\mathrm{d}t} + \mathbf{P}_{\mathrm{eq}} : \frac{\partial \mathbf{D}}{\partial t} + \sum_{i=1}^{n} \mu_i \nabla \cdot \mathbf{J}_i. \quad (6)$$

Equation (6) follows from equation (5), because equation (5) is valid for the arbitrary domain $\Omega(t)$. Equation (6) represents the Gibbs relation for crystal. From the definition of the linear strain tensor, we can write

$$\frac{\partial \mathbf{D}}{\partial t} = [\tfrac{1}{2}(\nabla \mathbf{v} + \mathbf{v}\nabla) - \tfrac{1}{3}\nabla \cdot \mathbf{v}\mathbf{l}] + \tfrac{1}{3}\nabla \cdot \mathbf{v}\mathbf{l},$$

where $[\frac{1}{2}(\nabla \mathbf{v} + \mathbf{v}\nabla) - \frac{1}{3}\nabla \cdot \mathbf{v}\mathbf{l}]$ means the pure deformation and $\frac{1}{3}\nabla \cdot \mathbf{v}\mathbf{l}$ expresses the deformation connected with the change of volume.

If the deformation of crystal is connected only with the change of volume, then

$$\frac{\partial \mathbf{D}}{\partial t} = \tfrac{1}{3}\nabla \cdot \mathbf{v}\mathbf{l}. \quad (7)$$

After substituting relation (7) into equation (6), we obtain the equation

$$T\frac{\mathrm{d}S}{\mathrm{d}t} = (U - TS)\nabla \cdot \mathbf{v} + \frac{\mathrm{d}U}{\mathrm{d}t} + p\nabla \cdot \mathbf{v} + \sum_{i=1}^{n} \mu_i \nabla \cdot \mathbf{J}_i, \quad (8)$$

where $p = \frac{1}{3}Sp\mathbf{P}_{\mathrm{eq}}$.

For our purpose, it is suitable to transform equation (8) with the help of relations $S = \rho s$, $U = \rho u$,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{v}$$

and the equations of type (3) into the form

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t} - \sum_{i=1}^{n} \mu_i \frac{\mathrm{d}c_i}{\mathrm{d}t}. \quad (9)$$

Equation (9) is analogous to the Gibbs's relation for isotropic systems. This fact allows us to use those methods which are used in ref. [2] for formulating the equations of nonequilibrium thermodynamics. Equation (9) will be the last basic equation for derivation of the entropy balance equation.

3. ENTROPY BALANCE EQUATION

With the help of the equations of type (2), we can derive the potential energy balance equation, whose form follows from [2]

$$\frac{\partial \rho\psi}{\partial t} = -\nabla \cdot \left\{\rho\psi\mathbf{v} + \sum_{i=1}^{n} \psi_i \mathbf{J}_i\right\} - \sum_{i=1}^{n} \mathbf{J}_i \cdot \mathbf{F}_i - \mathbf{v} \cdot \sum_{i=1}^{n} \rho_i \mathbf{F}_i, \quad (10)$$

where $\psi = \Sigma_i^n c_i \psi_i$.

We substitute equation (10), together with the definition of internal energy

$$e = \rho\psi + \rho u,$$

into equation (4). After that, we obtain the internal energy balance equation

$$\frac{\partial \rho u}{\partial t} = -\nabla \cdot \left\{\rho u \mathbf{v} + \mathbf{J}_q + \sum_{i=1}^{n} \mu_i \mathbf{J}_i + \mathbf{v} \cdot \mathbf{P}\right\} + \sum_{i=1}^{n} \mathbf{J}_i \cdot \mathbf{F}_i + \mathbf{v} \cdot \sum_{i=1}^{n} \rho_i \mathbf{F}_i. \quad (11)$$

Kinetic energy $\frac{1}{2}\rho v^2$ in ref. [2] is taken from the internal energy. In our case, when we take into consideration the thermal expansion, the hydrodynamic velocity $\mathbf{v}$ is dependent on temperature and, therefore, we include the kinetic energy $\frac{1}{2}\rho v^2$ into the internal energy. The idea of the method of the entropy balance equation derivation is motivated by the assumption that the change of volume as a result of the thermal expansion is reversible.

We substitute equation (11) into equation (9), and making some changes, we obtain the entropy balance equation

$$T\frac{\partial \rho s}{\partial t} = -\nabla \cdot \left\{T\rho s\mathbf{v} + \mathbf{J}_q + \mathbf{v} \cdot (\mathbf{T} + \mathbf{\Pi})\right\} - \sum_{i=1}^{n} \rho_i \mathbf{v}_i \cdot (\nabla \mu_i - \mathbf{F}_i) + \mathbf{v} \cdot \left(\sum_{i=1}^{n} \rho_i \nabla \mu_i - \nabla p + \rho s \nabla T\right), \quad (12)$$

where

$$\mathbf{T} = \mathbf{P}_{\mathrm{eq}} - \tfrac{1}{3}Sp(\mathbf{P}_{\mathrm{eq}})\mathbf{l}.$$

By applying the Gibbs–Duhem's relation, equation (12) obtains the final form

$$\frac{\partial \rho s}{\partial t} = -\nabla \cdot \mathbf{J}_s - \frac{\mathbf{J}_s}{T} \cdot \nabla T - \frac{1}{T}\sum_{i=1}^{n} \rho_i \mathbf{v}_i \cdot (\nabla \mu_i - \mathbf{F}_i), \quad (13)$$

where

$$\mathbf{J}_s = \frac{\mathbf{J}_q + \mathbf{v} \cdot (\mathbf{T} + \mathbf{\Pi})}{\mathbf{T}} + \rho s \mathbf{v}.$$

If we introduce into equation (13) the relation

$$\nabla\mu_i = -s_i\nabla T + (\nabla\mu_i)_{\mathrm{T}},$$

then we obtain the modified entropy balance equation. Its form is as follows:

$$\frac{\partial\rho s}{\partial t} = -\nabla\cdot\mathbf{J}_{\mathrm{s}} - \frac{\mathbf{J}_q'}{T^2}\cdot\nabla T - \frac{1}{T}\sum_{i=1}^{n}\rho_i\mathbf{v}_i\cdot\{(\nabla\mu_i)_{\mathrm{T}} - \mathbf{F}_i\}, \tag{14}$$

where

$$\mathbf{J}_q' = \mathbf{J}_q + \mathbf{v}\cdot(\mathbf{T}+\boldsymbol{\Pi}) - T\sum_{i=1}^{n}\mathbf{J}_i s_i.$$

According to the Gibbs–Duhem's relation $\Sigma_{i=1}^{n}\rho_i[(\nabla\mu_i)_{\mathrm{T}} - \mathbf{F}_i] = 0$ is valid. From this relation we calculate the term $\rho_n[(\nabla\mu_n)_{\mathrm{T}} - \mathbf{F}_n]$ and introduce it into relation (14). After introducing we obtain the equation

$$\frac{\partial\rho s}{\partial t} = -\nabla\cdot\mathbf{J}_{\mathrm{s}} - \frac{\mathbf{J}_q'}{T^2}\nabla T - \frac{1}{T}\sum_{i=1}^{n-1}\rho_i(\mathbf{v}_i - \mathbf{v}_n)\cdot[(\nabla\mu_i)_{\mathrm{T}} - \mathbf{F}_i]. \tag{15}$$

From equation (15), the relation for the entropy production follows immediately

$$\sigma(s) = -\frac{\mathbf{J}_q'}{T^2}\cdot\nabla T - \frac{1}{T}\sum_{i=1}^{n}\rho_i(\mathbf{v}_i - \mathbf{v}_n)\cdot\{(\nabla\mu_i)_{\mathrm{T}} - \mathbf{F}_i\}. \tag{16}$$

4. PHENOMENOLOGICAL LINEAR EQUATIONS

For further progress, it will be necessary to specify quantities ψ_i. Quantity ψ_i will represent the electrostatic potential energy per unit mass of component i. In this case

$$\psi_i = \frac{q_i}{m_i}\varphi. \tag{17}$$

According to relation (17), we can write

$$\mathbf{F}_i = -\nabla\psi_i = \frac{q_i}{m_i}\mathbf{E}. \tag{18}$$

Introducing relation (18) into relation (16) and making some changes, we obtain the relation

$$\sigma(s) = -\frac{\mathbf{J}_q'}{T^2}\cdot\nabla T - \frac{1}{T}\sum_{j=1}^{n}\mathbf{i}_j\cdot\left\{\left(\nabla\frac{\bar{\mu}_j}{q_j}\right)_{\mathrm{T}} - \mathbf{E}\right\}, \tag{19}$$

where

$$\mathbf{i}_j = q_j N_j(\mathbf{v}_j - \mathbf{v}_n)$$

$$\bar{\mu}_j = m_j\mu_j.$$

Until now all relations are exact. The first approximation will presume that the system is close to the equilibrium state and, therefore, the thermodynamic fluxes are linear functions of the thermodynamic forces. In the first approximation, from the relation (19), the phenomenological linear equations follow

$$\mathbf{J}_q' = -\mathbf{L}_{qq}\cdot\frac{\nabla T}{T^2} - \sum_{j=1}^{n-1}\mathbf{L}_{qj}\cdot\frac{\left\{\left(\nabla\frac{\bar{\mu}_j}{q_j}\right)_{\mathrm{T}} - \mathbf{E}\right\}}{T} \tag{20}$$

$$\mathbf{i}_k = -\mathbf{L}_{kq}\cdot\frac{\nabla T}{T^2} - \sum_{j=1}^{n-1}\mathbf{L}_{kj}\cdot\frac{\left\{\left(\nabla\frac{\bar{\mu}_j}{q_j}\right)_{\mathrm{T}} - \mathbf{E}\right\}}{T}, \tag{21}$$

for $k = 1, 2, \ldots, n-1$.

The tensors $\mathbf{L}_{qq}$, $\mathbf{L}_{qj}$, $\mathbf{L}_{jq}$ and $\mathbf{L}_{kj}$ are dependent on local state parameters and not on generalized thermodynamic forces. They satisfy the following Onsager reciprocal relations:

$$\mathbf{L}_{qq} = \tilde{\mathbf{L}}_{qq}, \quad \mathbf{L}_{qj} = \tilde{\mathbf{L}}_{jq}, \quad \mathbf{L}_{jk} = \tilde{\mathbf{L}}_{kj}.$$

When the system in an equilibrium state is isotropic or when the crystal has cubic symmetry, then the above-mentioned tensors are the trivial tensors.

In the following text, we will consider only the isotropic systems and crystals with cubic symmetry. In this case the equations (20) and (21) transform into the following form:

$$\mathbf{J}_q' = -L_{qq}\frac{\nabla T}{T^2} - \sum_{j=1}^{n-1}\frac{L_{qj}}{T}\left\{\left(\nabla\frac{\bar{\mu}_j}{q_j}\right)_{\mathrm{T}} - \mathbf{E}\right\} \tag{22}$$

$$\mathbf{i}_k = -L_{kq}\frac{\nabla T}{T^2} - \sum_{j=1}^{n-1}\frac{L_{kj}}{T}\left\{\left(\nabla\frac{\bar{\mu}_j}{q_j}\right)_{\mathrm{T}} - \mathbf{E}\right\}, \tag{23}$$

for $k = 1, 2, \ldots, n-1$.

The coefficients L_{qq}, L_{kq}, L_{qj} and L_{kj} satisfy the following Onsager reciprocal relations: $L_{qj} = L_{jq}$ and $L_{kj} = L_{jk}$.

The connection between the coefficients L_{qq}, L_{qj}, L_{kj} on the one hand and the measurable quantities on the other hand will be discussed in Sections 6 and 7.

The equations (22) and (23), together with the equations of type (2), the internal energy balance equation and Poisson's equation, form the complete set of equations for calculation of how the local state parameters of the system depend on space–time co-ordinates. Such information describes completely the irreversible process. However, the main aim of this paper is to derive the equation of heat conduction and to show the conditions under which it is valid.

5. GENERALIZED HEAT CONDUCTION EQUATION

The heat conduction equation is in fact the arranged internal energy balance equation (11). To arrange the internal energy balance equation we use the following relations:

$$h = u + pv \quad \frac{\partial h}{\partial p} = v - \frac{\partial v}{\partial T}$$

$$h_i = \mu_i + Ts_i \qquad \frac{\partial h}{\partial c_i} = h_i - h_n. \tag{24}$$

With the help of the above-mentioned relations, equation (11) obtains the form

$$\rho c_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} = -\nabla\cdot\mathbf{J}'_q + \mathbf{i}\cdot\mathbf{E} + \rho\frac{\partial v}{\partial T}\frac{\mathrm{d}p}{\mathrm{d}t} - \mathbf{v}\cdot\nabla p - \sum_{i=1}^{n}\mathbf{J}_i\cdot\nabla h_i. \tag{25}$$

If we introduce the relation (22) into equation (25) we obtain the equation of heat conduction, which is exact in the framework of linear approximation.

6. EQUATION OF HEAT CONDUCTION IN METAL SYSTEMS

In this section the results obtained in Section 5 will be applied for the binary system. As an example of the binary system we will consider the metal systems. In the metal systems the free electrons will be considered as the first component, and the positive ions of lattice as the second component. For the binary system, the set of equations (22) and (23) has the following form:

$$\mathbf{J}'_q = -L_{qq}\frac{\nabla T}{T^2} - \frac{L_{q1}}{T}\left\{\left(\nabla\frac{\mu_1}{q_1}\right)_{\mathrm{T}} - \mathbf{E}\right\} \tag{26}$$

and

$$\mathbf{i}_1 = -L_{1q}\frac{\nabla T}{T^2} - \frac{L_{11}}{T}\left\{\left(\nabla\frac{\mu_1}{q_1}\right)_{\mathrm{T}} - \mathbf{E}\right\}. \tag{27}$$

When we calculate the quantity $\nabla(\mu_1/q_1)_{\mathrm{T}} - \mathbf{E}$ from equation (27) and then introduce it into equation (26), we shall obtain the following equations:

$$\mathbf{E} - \left(\nabla\frac{\mu_1}{q_1}\right)_{\mathrm{T}} = -\eta\nabla T + \rho_{\mathrm{R}}\mathbf{i}_1 \tag{28}$$

and

$$\mathbf{J}'_q = -\lambda\nabla T + \pi\mathbf{i}_1, \tag{29}$$

where

$$\eta = -\frac{L_{1q}}{L_{11}}\frac{1}{T} \tag{30}$$

$$\pi = \frac{L_{q1}}{L_{11}} \qquad \rho_{\mathrm{R}} = \frac{T}{L_{11}} \qquad \lambda = \frac{L_{qq}L_{11} - L_{1q}L_{q1}}{T^2 L_{11}}. \tag{31}$$

From the Onsager relation $L_{q1} = L_{1q}$ and from the relations (30), (31), the relation follows

$$\pi = -\eta T.$$

There are three independent coefficients L_{qq}, L_{11}, L_{1q} which are determined by means of the measurable quantities η, λ and ρ_{R}.

Before writing the equation of the heat conduction we introduce some relations which will be used in the application of equation (25) for metal systems. With the help of the relation

$$q_1N_1 + q_2N_2 = \rho_e \tag{32}$$

we can write

$$\mathbf{i}_1 = q_1N_1(\mathbf{v}_1 - \mathbf{v}_2) = \mathbf{i} - \rho_e\mathbf{v}_2. \tag{33}$$

From the relations (33) immediately follows the relation

$$\mathbf{J}_1 = \frac{m_1}{q_1}\mathbf{i}_1 = \frac{m_1}{q_1}(\mathbf{i} - \rho_e\mathbf{v}_2). \tag{34}$$

If we multiply equation (28) by $\mathbf{i}$, we shall obtain the relation

$$\mathbf{i}\cdot\mathbf{E} = -\eta\mathbf{i}\cdot\nabla T + \rho_{\mathrm{R}}\mathbf{i}\cdot(\mathbf{i} - \rho_e\mathbf{v}_2) + \mathbf{i}\cdot\left(\nabla\frac{\mu_1}{q_1}\right)_{\mathrm{T}}. \tag{35}$$

Introducing the relations (29), (33), (34) and (35) into equation (25), we obtain the heat conduction equation which has the form

$$\begin{aligned}\rho c_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} &= \nabla\cdot\lambda\nabla T - \pi\nabla\cdot(\mathbf{i} - \rho_e\mathbf{v}_2)\\ &\quad - \tau\mathbf{i}\cdot\nabla T + \rho_e\mathbf{v}_2\cdot\nabla\pi + \rho_{\mathrm{R}}\mathbf{i}\cdot(\mathbf{i} - \rho_e\mathbf{v}_2)\\ &\quad - \frac{1}{\rho}\frac{\partial\rho}{\partial T}\frac{\mathrm{d}p}{\mathrm{d}t} - \mathbf{v}\cdot\nabla p - \frac{m_1}{q_1}(\mathbf{i} - \rho_e\mathbf{v}_2)\\ &\quad \cdot\nabla(h_1 - h_2) + \mathbf{i}\cdot\left[\left(\nabla\frac{\mu_1}{q_1}\right)_{\mathrm{T}} - (\nabla\pi)_{\mathrm{T}}\right],\end{aligned} \tag{36}$$

where the following relations have been used

$$\tau = \eta + \frac{\partial\pi}{\partial T} \tag{37}$$

$$\nabla\pi = (\nabla\pi)_{\mathrm{T}} + \frac{\partial\pi}{\partial T}\nabla T \tag{38}$$

and

$$\mathbf{J}_1 + \mathbf{J}_2 = 0.$$

We shall show that in certain special cases it is possible to express the equation of heat conduction in a simplified and approximate form, which in practical applications gives us sufficiently accurate results. These cases are as follows:

(a) Generally, in the case of solids, when the deformation is realized only by the reversible change of volume, the pressure tensors $\mathbf{T}$ and $\mathbf{\Pi}$ are zero tensors. To prove this we will continue in the following way,

we divide the tensor $\mathbf{\Pi}$ into two parts;

$$\mathbf{\Pi} = \mathbf{\Pi}^* + \tilde{\pi}\mathbf{I},$$

where

$$\tilde{\pi} = \tfrac{1}{3}Sp\mathbf{\Pi}.$$

From the thermodynamic point of view, the tensors **T** and **Π*** are function of the tensor $\frac{1}{2}(\nabla\mathbf{v}+\mathbf{v}\nabla)-\frac{1}{3}\nabla\cdot\mathbf{v}\mathbf{I}$, which is supposed to be zero and, therefore, the tensors **T** and **Π*** are zero tensors too. Analogously, the quantity $\tilde{\pi}$ has a zero value as well, due to the assumption that the irreversible change of volume is not realized. In such a case, equation (1) can be simplified to the form

$$\rho\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}=-\nabla p+\sum_{i=1}^{n}\rho_i\mathbf{F}_i. \tag{39}$$

If the forces have electrostatic origin (18), then equation (39) is transformed into the form

$$\rho\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}=-\nabla p+\varrho_e\mathbf{E}. \tag{40}$$

In the mechanical equilibrium ($\mathrm{d}\mathbf{v}/dt=0$), equation (40) can be simplified to the form

$$\nabla p=\varrho_e\mathbf{E}. \tag{41}$$

(b) We will consider the homogeneous metal systems. It is well-known [4] that in homogeneous systems with nonzero conductivity the charge density changes according to the relation

$$\rho_e=\rho_{e0}\,\mathrm{e}^{-t/\tilde{\tau}},$$

where $\tilde{\tau}=\varepsilon_r(\varepsilon_0/\sigma)$.

The conductivity in metal systems is about 10^6 S m^{-1} to 6.10^7 S m^{-1}, so that the dielectric relaxation time

$$\tilde{\tau}=(1.5\div 90)\cdot 10^{-19}\varepsilon_r[s].$$

The charge neutrality condition ($\rho_e=0$) is fulfilled if the change of the temperature during the dielectric relaxation time $\tilde{\tau}$ is not measurable and, therefore, only in this case we can consider that the heat conduction takes place at $\rho_e=0$. From this fact and from the relations (33) and (41) it follows that

$$\mathbf{i}_1=\mathbf{i} \tag{42}$$

$$\nabla p=0 \tag{43}$$

and

$$q_1N_1+q_2N_2=0. \tag{44}$$

From the law of conservation of charge $\partial\rho_e/\partial t+\nabla\cdot\mathbf{i}=0$ it follows that

$$\nabla\cdot\mathbf{i}=0. \tag{45}$$

(c) The relation (43) is valid for an arbitrary time and therefore $\partial p/\partial t$ is independent of space co-ordinates. If we assume that the pressure on the boundary of the metal systems is independent of time, then

$$\frac{\partial p}{\partial t}=0. \tag{46}$$

From relations (43) and (46) it follows that

$$\frac{\mathrm{d}p}{\mathrm{d}t}=\frac{\partial p}{\partial t}+\mathbf{v}\cdot\nabla p=0. \tag{47}$$

On the basis of relation (44) and the relation $c_1+c_2=0$, we can write

$$\nabla c_1=0. \tag{48}$$

If we choose T, p and c_1 as the local state parameters, then with the help of relations (43) and (48) we can write

$$\nabla(h_1-h_2)=\frac{\partial(h_1-h_2)}{\partial T}\nabla T+\frac{\partial(h_1-h_2)}{\partial p}\nabla p+\frac{\partial(h_1-h_2)}{\partial c_1}\nabla c_1=\frac{\partial(h_1-h_2)}{\partial T}\nabla T \tag{49}$$

$$\left(\nabla\frac{\bar{\mu}_1}{q_1}\right)_T=\frac{\partial\frac{\bar{\mu}_1}{q_1}}{\partial p}\nabla p+\frac{\partial\frac{\bar{\mu}_1}{q_1}}{\partial c_1}\nabla c_1=0 \tag{50}$$

and

$$(\nabla\pi)_T=\frac{\partial\pi}{\partial c_1}\nabla c_1+\frac{\partial\pi}{\partial p}\nabla p=0. \tag{51}$$

Introducing the relations (43), (45), (47), (49), (50) and (51) into equation (36), we obtain the final form of the equation of heat conduction which has the following form:

$$\rho c_p\frac{\mathrm{d}T}{\mathrm{d}t}=\nabla\cdot\lambda\nabla T-(\tau+\tau_1^*)\mathbf{i}\cdot\nabla T+\rho_R\mathbf{i}^2, \tag{52}$$

where the following relation has been used

$$\tau_1^*=\frac{m_1}{q_1}\frac{\partial(h_1-h_2)}{\partial T}=\frac{m_1}{q_1}(c_{p1}-c_{p2}).$$

The free electrons of metal represent a degenerate gas and, therefore, the parameter c_{p1} is expressed by the formula [7]

$$c_{p1}=\frac{\pi^2k_B^2T}{m_1E_F}.$$

We will consider that the temperature of the crystal is above the Debye temperature and, therefore, each degree of freedom of the atoms of the crystal contributes the value of k_BT to the average energy of vibrations. In this case the parameter c_{p2} can be written in the form

$$c_{p2}=R+c_{V2}=R+\frac{3k_BTN_2}{m_2N_2T}=R+\frac{3k_B}{m_2}.$$

Introducing the last two relations into the relation for τ_1^*, we obtain the relation

$$\tau_1^*=-\frac{3k_B}{e}\left(\frac{\pi^2k_BT}{3E_F}-\frac{m_1R}{3k_B}-\frac{m_1}{m_2}\right)\approx-\frac{\pi^2k_B^2T}{eE_F}$$

because $m_1/m_2 \approx 10^{-11}$, $m_1R/3k_B = 5.49 \cdot 10^{-7}$ and $\pi^2 k_B T/3E_F \approx 2 \cdot 10^{-2}$, where we consider $E_F \approx 5$ eV.

In order to compare the parameter τ with the parameter τ_1^*, we introduce the relation [3]

$$\tau = -\frac{\pi^2 k_B^2 T(\delta+1)}{3eE_F} \approx \frac{\delta+1}{3}\tau_1^*,$$

where the parameter δ depends on scattering mechanism of free electrons. For example, for scattering on the acoustic phonons $\delta = -\frac{1}{2}$. We see that τ_1^* is comparable with the parameter τ and, therefore, the term $-\tau_1^* i \cdot \nabla T$ represents the new result of this paper.

Within phenomenological thermodynamics, all quantities, such as λ, π, τ and τ_1^* can only be determined experimentally.

The second term on the right-hand side of the equation (52) corresponds to the Thomson heat per unit volume and time and to the heat per unit volume and time, due to the dependence of the partial specific enthalpy on the temperature. The third term corresponds to Joule's heat per unit volume and time.

7. EQUATION OF HEAT CONDUCTION IN SEMICONDUCTORS

In metals, the Peltier and Thomson heat in comparison with Joule's is small. These quantities may play a significant role in semiconductors, because the Seebeck coefficient is larger by about four orders than in metals. In this part we will study the transport phenomena in semiconductor systems. At first we will consider the pure semiconductor crystal. The pure semiconductor crystal by definition is one without any impurities and defects and, therefore, the concept of the pure semiconductor is some kind of idealization because it is difficult to purify the semiconductor completely so to remove all impurity atoms in the semiconductor crystal. It would be better to use the term of an intrinsic semiconductor. The intrinsic semiconductor is very pure and contains a negligibly small amount of impurities, so that the transport properties are the intrinsic properties of the semiconductor crystal and not due to extrinsic sources such as chemical impurities and physical defects. Due to covalent bonds between the host atoms, they can be considered as the neutral atoms. We will also consider an impurity semiconductor. There are two kinds of impurities. When an impurity atom sits at a lattice site and substitutes for a host atom, it is known as a substitution impurity. When it sits in the space between the host atoms (assuming all host atoms are situated at lattice sites), it is known as an interstitial impurity. There are two main types of substitutional impurities: donors and acceptors. The donors and the acceptors can occur in two states: in the neutral charge state and in the positive or negative charge state. The donors and the acceptors are very important because they control the transport phenomena and type of the semiconductor. The interstitial impurity atoms are also present in a semiconductor, but they are often electrically inactive (neutral atoms) and hence, they do not have as great an effect on the transport phenomena in the semiconductor as the donors and the acceptors have. Since the impurity diffusion coefficient at room temperature is about 10^{-48} m^2 s^{-1} to 10^{-18} m^2 s^{-1} [5], we can consider the average velocity of the impurity atoms to be the same as the average velocity of the host atoms.

In contradistinction of the metal systems, in semiconductor systems the generation and recombination process of the electrons and holes takes place. Due to that process, the mass balance equations of type (3) have to be modified into the following form:

$$\rho\frac{\mathrm{d}c_i}{\mathrm{d}t} = -\nabla \cdot \mathbf{J}_i + g_i - r_i,$$

for $i = 1, 2, \ldots, n$.

In this case, we meet with the two different types of the irreversible phenomena according to their 'tensorial character'. The first group of phenomena is formed by a 'vectorial process', such as heat conduction, diffusion, electrical conduction, and their cross-effects. The second group of irreversible phenomena is formed by 'scalar phenomena', such as the generation–recombination process, irreversible change of volume, and their cross-effects.

From the beginning of this paper, we assumed that it was possible to neglect the irreversible change of volume. Now we extend this assumption so that in the first approximation it is possible to neglect the 'scalar phenomena', but nevertheless, it would be interesting to study the effect of the 'scalar phenomena' on the semiconductor systems.

After an introductory description of the semiconductor systems we shall move on to particular cases.

7.1. *Intrinsic semiconductor crystal*

The intrinsic semiconductor will be considered as the ternary system. The electrons are considered as the first component, the holes as the second one and the host atoms with a negligible small amount of impurities as the third one. According to equations (22) and (23) we can write

$$\mathbf{J}'_q = -L_{qq}\frac{\nabla T}{T^2} - \frac{L_{q1}}{T}\left\{\left(\nabla\frac{\tilde{\mu}_1}{q_1}\right)_T - \mathbf{E}\right\} - \frac{L_{q2}}{T}\left\{\left(\nabla\frac{\tilde{\mu}_2}{q_2}\right)_T - \mathbf{E}\right\} \quad (53)$$

$$\mathbf{i}_1 = -L_{1q}\frac{\nabla T}{T^2} - \frac{L_{11}}{T}\left\{\left(\nabla\frac{\tilde{\mu}_1}{q_1}\right)_T - \mathbf{E}\right\} - \frac{L_{12}}{T}\left\{\left(\nabla\frac{\tilde{\mu}_2}{q_2}\right)_T - \mathbf{E}\right\} \quad (54)$$

and

$$\mathbf{i}_2 = -L_{2q}\frac{\nabla T}{T^2} - \frac{L_{21}}{T}\left\{\left(\nabla\frac{\bar{\mu}_1}{q_1}\right)_{\mathrm{T}} - \mathbf{E}\right\}$$

$$- \frac{L_{22}}{T}\left\{\left(\nabla\frac{\bar{\mu}_2}{q_2}\right)_{\mathrm{T}} - \mathbf{E}\right\}. \quad (55)$$

The Onsager reciprocal relations are as follows:

$$L_{q1} = L_{1q}$$

$$L_{q2} = L_{2q}$$

and

$$L_{12} = L_{21},$$

where [3]

$$\bar{\mu}_1 = E_{\mathrm{F}} - E_{\mathrm{c}}$$

and

$$\bar{\mu}_2 = E_{\mathrm{v}} - E_{\mathrm{F}}.$$

The above-mentioned relations can be used only if the electrons and holes are in equilibrium with each other.

We will further consider the homogeneous semiconductor systems. In this case $(\nabla E_{\mathrm{c}})_{\mathrm{T}} = (\nabla E_{\mathrm{v}})_{\mathrm{T}} = 0$. Considering this fact, the equations (53)–(55) can be simplified as

$$\mathbf{J}'_q = -L_{qq}\frac{\nabla T}{T^2} + \frac{L_{q1}+L_{q2}}{T}\left\{\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}} + \mathbf{E}\right\} \quad (56)$$

$$\mathbf{i}_1 = -L_{1q}\frac{\nabla T}{T^2} + \frac{L_{11}+L_{12}}{T}\left\{\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}} + \mathbf{E}\right\} \quad (57)$$

and

$$\mathbf{i}_2 = -L_{2q}\frac{\nabla T}{T^2} + \frac{L_{21}+L_{22}}{T}\left\{\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}} + \mathbf{E}\right\}, \quad (58)$$

where $q_2 = -q_1 = e$ has been used.

From equations (57) and (58), we calculate the term $[\nabla(E_{\mathrm{F}}/e)]_{\mathrm{T}} + \mathbf{E}$ and introduce it into equation (56). Using the Onsager reciprocal relations we obtain the following equations:

$$\mathbf{J}'_q = -\lambda\nabla T + \pi(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3) \quad (59)$$

$$\mathbf{i}_1 = -\beta\nabla T + t_1(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3) \quad (60)$$

$$\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}} + \mathbf{E} = -\eta\nabla T + \rho_{\mathrm{R}}(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3), \quad (61)$$

where

$$\lambda = \frac{L_{qq}(L_{11}+2L_{12}+L_{22}) - (L_{1q}+L_{2q})^2}{T^2(L_{11}+2L_{12}+L_{22})}$$

$$\pi = \frac{L_{1q}+L_{2q}}{L_{11}+2L_{12}+L_{22}}$$

$$\eta = -\frac{L_{1q}+L_{2q}}{T(L_{11}+2L_{12}+L_{22})} = -\frac{\pi}{T}$$

$$\rho_{\mathrm{R}} = \frac{T}{L_{11}+2L_{12}+L_{22}}$$

$$\rho_{\mathrm{R}1} = \frac{T}{L_{11}+L_{12}}$$

$$\eta_1 = -\frac{L_{1q}}{T(L_{11}+L_{12})}$$

and

$$\beta = \frac{1}{\rho_{\mathrm{R}1}}(\eta - \eta_1) \quad t_1 = \frac{L_{11}+L_{12}}{L_{11}+2L_{12}+L_{22}} = \frac{\rho_{\mathrm{R}}}{\rho_{\mathrm{R}1}}. \quad (62)$$

The quantities λ, η and ρ_{R} are measurable quantities. If we multiply equation (61) by **i**, we shall obtain the relation

$$\mathbf{i}\cdot\mathbf{E} = -\eta\mathbf{i}\cdot\nabla T + \rho_{\mathrm{R}}\mathbf{i}\cdot(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3) - \mathbf{i}\cdot\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}}. \quad (63)$$

Introducing the relations (59) and (63) into equation (25), we obtain the following equation:

$$\rho c_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} = \nabla\cdot\lambda\nabla T - \nabla\cdot\pi(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3)$$

$$-\eta\mathbf{i}\cdot\nabla T + \rho_{\mathrm{R}}\mathbf{i}\cdot(\mathbf{i} - \rho_{\mathrm{e}}\mathbf{v}_3) - \mathbf{i}\cdot\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}}$$

$$+\rho\frac{\partial v}{\partial T}\frac{\mathrm{d}p}{\mathrm{d}t} - \mathbf{v}\cdot\nabla p - \sum_{i=1}^{3}\mathbf{J}_i\cdot\nabla h_i \quad (64)$$

which is an exact equation of heat conduction in the framework of linear nonequilibrium thermodynamics.

The equation (64) may be simplified under the certain conditions. The charge neutrality condition in the intrinsic semiconductors in general need not be always fulfilled and, therefore, it has to be checked in each case. For example, the conductivity of pure silicon [6] at the liquid nitrogen temperature 77 K is so small ($\sigma_{\mathrm{Si}} = 10^{-38}$ S m^{-1}) that it is an insulator. But at the room temperature $\sigma_{\mathrm{Si}} = 3.2\cdot10^{-4}$ S m^{-1}. If we consider the relative permittivity for Si $\varepsilon_{\mathrm{r}} = 11.8$, then the dielectric relaxation time of this Si is at 77 K $\bar{\tau} = 10^{28}$ s and at 300 K $\bar{\tau} = 3.2\cdot10^{-7}$ s. For intrinsic *Ge* at $T = 300$ K ($\sigma_{\mathrm{Ge}} = 2.32\cdot10^{-1}$ S m^{-1}; $\varepsilon_{\mathrm{r}} = 16$) the dielectric relaxation time is $\bar{\tau} = 6.94\cdot10^{-10}$ s. Additionally, we will consider only those intrinsic semiconductors at which the charge neutrality condition is fulfilled. From the charge neutrality condition and from the assumption (c) in Section 6, as was shown, the relations (42), (43), (45), (47) and the relation

$$N_1 = N_2 \quad (65)$$

follow.

Now we shall direct our attention to an arrangement of the last term on the right-hand side of equation (64). From the relation $\Sigma_{i=1}^{3}\mathbf{J}_i = 0$ we obtain

$$\mathbf{v}_3-\mathbf{v} = -c_1(\mathbf{v}_1-\mathbf{v}_3)-c_2(\mathbf{v}_2-\mathbf{v}_3). \tag{66}$$

With the help of the relations (65) and (66), we can write the following relations:

$$\mathbf{J}_1 = \left[\frac{m_2}{e}\left(c_1(t_1-1)-t_1\frac{m_1}{e}(1-c_1)\right)\right]\mathbf{i} + \left[\frac{m_1}{e}(1-c_1)-\frac{m_2}{e}c_1\right]\beta\nabla T \tag{67}$$

and

$$J_2 = \left[\frac{m_1}{e}t_1c_2+\frac{m_2}{e}(1-t_1)(1-c_2)\right]\mathbf{i} + \left[\frac{m_2}{e}(1-c_2)-\frac{m_1}{e}c_2\right]\beta\nabla T, \tag{68}$$

where the relation (60) has been used.

Now for the ideal systems the parameter h_i depends on the state parameter T, p and therefore

$$\nabla(h_i-h_3) = \frac{\partial(h_1-h_3)}{\partial T}\nabla T, \tag{69}$$

where the relation (43) has been used.

When we introduce the relations (67)–(69) into the last term on the right-hand side of equation (64) we shall obtain the following relation:

$$\sum_{i=1}^{3}\mathbf{J}_i\cdot\nabla h_i = \sum_{i=1}^{2}\mathbf{J}_i\cdot\nabla(h_i-h_3) = \tau_2^*\mathbf{i}\cdot\nabla T+\gamma_2(\nabla T)^2, \tag{70}$$

where

$$\tau_2^* = \left[\frac{m_2}{e}c_1(t_1-1)-\frac{m_1}{e}t_1(1-c_1)\right]\frac{\partial(h_1-h_3)}{\partial T} + \left[\frac{m_1}{e}t_1c_2+\frac{m_2}{e}(1-t_1)(1-c_2)\right]\frac{\partial(h_2-h_3)}{\partial T} \tag{71}$$

and

$$\gamma_2 = \beta\left\{\left[\frac{m_1}{e}(1-c_1)-\frac{m_2}{e}c_1\right]\frac{\partial(h_1-h_3)}{\partial T} + \left[\frac{m_2}{e}(1-c_2)-\frac{m_1}{e}c_2\right]\frac{\partial(h_2-h_3)}{\partial T}\right\}. \tag{72}$$

For the further simplification of equation (64), we will assume that the following assumption is fulfilled.

(a) In the thermodynamic equilibrium, E_F is only a function of the temperature. If the system is homogeneous, but thermically inhomogeneous, then E_F is only the function of the temperature, and therefore

$$\left(\nabla\frac{E_F}{e}\right)_T = 0. \tag{73}$$

π is a function of the temperature and E_F, and therefore, according to the relation (73), the relation is valid

$$(\nabla\pi)_T = 0. \tag{74}$$

When we again assume that the assumption (c) in Section 6 and the assumptions in this section are fulfilled, then we substitute the relations (43), (45), (47), (70), (73) and (74) into equation (64). After substituting, we obtain the equation

$$\rho c_p\frac{dT}{dt} = \nabla\cdot\lambda\nabla T-(\tau+\tau_2^*)\mathbf{i}\cdot\nabla T+\rho_R\mathbf{i}^2-\gamma_2(\nabla T)^2. \tag{75}$$

In order to compare the parameter τ_2^* with the parameter τ, we shall present their numerical estimation. The mass-fractions c_1, c_2 are very small with respect to one. For example, for Si [5] ($T = 300$ K, $m_1 = 0.97m_0$, $m_2 = 0.5m_0$, $n_i = 2.10^{16}$ m^{-3}, $N_3 = 5\cdot10^{28}$ m^{-3}, $\rho_3 = 2.328\cdot10^3$ kg m^{-3}, $m_3 = 4.6\cdot10^{-26}$ kg) the mass-fractions $c_1 \approx m_1n_i/\rho_3 = 3.8\cdot10^{-18}$ and $c_2 \approx m_2n_i/\rho_3 = 1.96\cdot10^{-18}$. Due to the small values of the mass-fractions (without c_3), we can neglect all terms containing the mass-fractions c_1 and c_2 in the relations (71) and (72). In this case, relation (71) can be written in the following approximate form:

$$\tau_2^* = -\frac{m_1}{e}t_1\frac{\partial(h_1-h_3)}{\partial T}+\frac{m_2}{e}(1-t_1)\frac{\partial(h_2-h_3)}{\partial T}. \tag{76}$$

Additionally, we will consider electrons and holes as a nondegenerate gas and the temperature of the crystal to be above the Debye temperature. In this case, each degree of freedom of the electrons and holes contributes the value of $\frac{1}{2}k_BT$ to the average kinetic energy, and each degree of freedom of the host atoms contributes the values of K_BT to the average energy of vibrations and, therefore, relation (76) can be written as

$$\begin{aligned}
\tau_2^* &= -\frac{m_1}{e}t_1(c_{p1}-c_{p3})+\frac{m_2}{e}(1-t_1)(c_{p2}-c_{p3}) \\
&= -\frac{m_1}{e}t_1(c_{V1}-c_{V3})+\frac{m_2}{e}(1-t_1)(c_{V2}-c_{V3}) \\
&= -\frac{m_1}{e}t_1\left(\frac{\frac{3}{2}k_BTn_i}{m_1n_iT}-\frac{3k_BTN_3}{m_3N_3T}\right) \\
&\quad +\frac{m_2}{e}(1-t_1)\left(\frac{\frac{3}{2}k_BTn_i}{m_2n_iT}-\frac{3k_BTN_3}{m_3N_3T}\right) \\
&= -\frac{3k_Bt_1}{e}\left(\frac{1}{2}-\frac{m_1}{m_3}\right) \\
&\quad +\frac{3k_B(1-t_1)}{e}\left(\frac{1}{2}-\frac{m_2}{m_3}\right)\approx\frac{3k_B}{2e}(1-2t_1),
\end{aligned}$$

because $m_1/m_3 = 1.92\cdot10^{-5}$ and $m_2/m_3 = 10^{-5}$.

In a similar way, we can approximate the relation (72). After approximation we obtain the relation

$$\gamma_2 \approx \beta\left[\frac{m_1}{e}(c_{p1}-c_{p3})+\frac{m_2}{e}(c_{p2}-c_{p3})\right]$$
$$= \beta\frac{3k_B}{e}\left[1+\left(\frac{m_1}{m_3}+\frac{m_2}{m_3}\right)\right] \approx \beta\frac{3k_B}{e}. \tag{77}$$

According to the second relation of equation (62) we can write

$$t_1 = \frac{\rho_R}{\rho_{R1}} = \frac{eN_1\mu_e}{eN_1\mu_e+eN_2\mu_h} = \frac{1}{1+b}. \tag{78}$$

Substituting the relation (78) into the relation for τ_2^* we obtain

$$\tau_2^* = -\frac{3k_B}{2e}\frac{1-b}{1+b}. \tag{79}$$

For the numerical estimation of the parameter τ we introduce the relation [3, 6]

$$\eta = \frac{k_B}{e}\left(\delta+\frac{5}{2}\right)\frac{1-b}{1+b}+\frac{E_c+E_v b-(1+b)E_F}{(1+b)eT}+\frac{1}{e}\frac{\partial E_F}{\partial T}, \tag{80}$$

where $b = \mu_h/\mu_e$ is independent of temperature and

$$E_F = \frac{E_c+E_v}{2}+K_B T\ln\left(\frac{m_2}{m_1}\right)^{3/4}. \tag{81}$$

If we substitute the relation (81) into the relation (80) we obtain the relation

$$\eta = \left[\frac{k_B}{e}\left(\delta+\frac{5}{2}\right)+\frac{E_c-E_v}{2eT}\right]\frac{1-b}{1+b}. \tag{82}$$

According to the relations (37) and (82), we can write the relation

$$\tau = -T\frac{\partial\eta}{\partial T} = \frac{(E_c-E_v)}{2eT}\frac{1-b}{1+b}. \tag{83}$$

For Si [5] ($E_c-E_v = 1.12$ eV, $b = \mu_h/\mu_e = \frac{2}{5}$, $T = 300$ K, $\rho_R = 3.1\cdot10^3$ Ωm) $\tau = 8.10^{-4}$ V K^{-1} and $\tau_2^* = -0.55\cdot10^{-4}$ V K^{-1}. We see that τ_2^* represents 6.9% of τ. For *Ge* [5] ($E_c-E_v = 0.803$ eV, $b = \frac{19}{39}$, $T = 300$ K, $\rho_R = 4.3$ Ωm) $\tau = 4.6\cdot10^{-4}$ V K^{-1} and $\tau_2^* = -0.44\cdot10^{-4}$ V K^{-1}. The τ_2^* represents 10% of τ. The term $-\tau_2^*\mathbf{i}\cdot\nabla T$ in equation (75) represents the new result of this paper.

For the comparison of the second and third term on the right-hand side of equation (75) we will present their ratio. According to the first relation (62) we can write

$$\beta = \frac{\eta-\eta_1}{\rho_{R1}} = -\frac{2b}{(1+b)^2\rho_R}\left[\frac{k_B}{e}\left(\delta+\frac{5}{2}\right)+\frac{E_c-E_v}{2eT}\right], \tag{84}$$

where η_1 follows from the relation (82), if we put $b = 0$ and

$$\rho_{R1} = \rho_{R1}(1+b).$$

Now we give the numerical results of the second, third and fourth term on the right-hand side of equation (75). For Si ($|\nabla T| = 10^3$ K m^{-1}) according to the relations (77)–(79), (83) and (84) we can write for $i = 10^{-1}$ A m^{-2}. $\gamma_2(\nabla T)^2 = -6.92\cdot10^{-3}$ J m^{-3} s^{-1}, $(\tau+\tau_2^*)i|\nabla T| = 7.44\cdot10^{-2}$ J m^{-3} s^{-1}, $\rho_R i^2 = 3.1\cdot10$ J m^{-3} s^{-1}, but for *Ge* [5] ($E_c-E_v = 0.803$ eV, $b = \frac{19}{39}$) we can write for $i = 10^{-1}$ A m^{-2}: $\gamma_2(\nabla T)^2 = 2\cdot10^{-2}$ J m^{-3} s^{-1}, $(\tau+\tau_2^*)i|\nabla T| = 3.5\cdot10^{-3}$ J m^{-3} s^{-1}, $\rho_R i^2 = 4.3\cdot10^{-2}$ J m^{-3} s^{-1}. In the first case, the second and fourth term on the right-hand side of equation (75) can be neglected according to the third term. In the second case, all terms on the right-hand side of equation (75) have to be considered.

7.2. *Impurity semiconductors*

The composition of the impurity semiconductors was described at the beginning of Section 7. The donors and the acceptors can either be in the neutral charge state or in the positive (donor) or in the negative (acceptor) charge state. The charge state is realized in this way: the electron can jump from a valence band to an acceptor ground state or from a donor ground state to a conduction band. The result of that process is in the first case the generation of a valence hold (delocalized) and a localized electron on the acceptor, and in the second case the generation of a conduction (delocalized) electron and a localized hole on the donor. According to these facts, the impurity semiconductor is composed of five components. The conduction electrons will be considered as the first component, the valence holes as the second one, the localized holes on donors as the third one, the localized electrons on the acceptors as the fourth one and finally the donors and acceptors with the host atoms as the fifth one. The average velocity of the donors, acceptors, localized electrons and holes is the same as the average velocity of the host atoms.

Considering this composition of the impurity semiconductors, the entropy production according to the relation (19) has the following form:

$$\sigma(s) = -\frac{\mathbf{J}_q'}{T^2}\cdot\nabla T-\frac{1}{T}\sum_{j=1}^{2}\mathbf{i}_j\cdot\left\{\left(\nabla\frac{\mu_j}{q_j}\right)_T-\mathbf{E}\right\}. \tag{85}$$

From the relation (85) in the framework of the linear nonequilibrium thermodynamics we obtain the phenomenological equations (56)–(58). Proceeding in the same way as in Section 7.1, we obtain the following equations:

$$\mathbf{J}_q' = -\lambda\nabla T+\pi(\mathbf{i}-\rho_e\mathbf{v}_5) \tag{86}$$

$$\mathbf{i}_1 = -\beta\nabla T+t_1(\mathbf{i}-\rho_e\mathbf{v}_5) \tag{87}$$

$$\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}}+\mathbf{E}=-\eta\nabla T+\rho_{\mathrm{R}}(\mathbf{i}-\rho_{\mathrm{e}}\mathbf{v}_5),\tag{88}$$

where relation (62) has been used.

Multiplying equation (88) by $\mathbf{i}$, we obtain the relation

$$\mathbf{E}\cdot\mathbf{i}=-\eta\mathbf{i}\cdot\nabla T+\rho_{\mathrm{R}}\mathbf{i}\cdot(\mathbf{i}-\rho_{\mathrm{e}}\mathbf{v}_5)-\mathbf{i}\cdot\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}}.\tag{89}$$

As a rule, the charge neutrality condition in impurity semiconductors is fulfilled. For example, for n-type Si [6] ($T=300$ K, $\varepsilon_{\mathrm{r}}=11.8$, $\rho_{\mathrm{R}}=8.8\cdot10^{-1}$ Ωm). In this case we find out that the dielectric relaxation time $\bar{\tau}=9.2\cdot10^{-12}$ s. If we consider that the assumptions (a), (b) and (c) in Section 6 are fulfilled, then we can introduce the relations (43), (45), (47) and (89) into equation (25). We then obtain the following equation

$$\rho c_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t}=\nabla\cdot\lambda\nabla T-\tau\mathbf{i}\cdot\nabla T+\rho_{\mathrm{R}}\mathbf{i}^2-\mathbf{i}\cdot\left[\left(\nabla\frac{E_{\mathrm{F}}}{e}\right)_{\mathrm{T}}+(\nabla\pi)_{\mathrm{T}}\right]-\sum_{i=1}^{4}\mathbf{J}_i\cdot\nabla(h_i-h_5),\tag{90}$$

where the relation $\Sigma_{i=1}^{5}\mathbf{J}_i=0$ and the relation (42) have been used. From the relation $\Sigma_{i=1}^{5}\mathbf{J}_i=0$ the relation

$$\mathbf{v}_5-\mathbf{v}=-c_1(\mathbf{v}_1-\mathbf{v}_5)-c_2(\mathbf{v}_2-\mathbf{v}_5)\tag{91}$$

follows.

The electric current density is expressed by the relation

$$\mathbf{i}=\sum_{j=1}^{4}q_jN_j\mathbf{v}_j=q_1N_1(\mathbf{v}_1-\mathbf{v}_5)+q_2N_2(\mathbf{v}_2-\mathbf{v}_5),\tag{92}$$

where the charge neutrality condition

$$\sum_{j=1}^{4}q_jN_j=0$$

has been used.

With the help of the relations (87), (91) and (92) we can write the following relations:

$$\mathbf{J}_1=\left[t_1\frac{m_1}{q_1}(1-c_1)+t_1\frac{m_2}{q_2}c_1-\frac{m_2}{q_2}c_1\right]\mathbf{i}-\left[\frac{m_1}{q_1}(1-c_1)+c_1\frac{m_2}{q_2}\right]\beta\nabla T\tag{93}$$

$$\mathbf{J}_2=\left[\frac{m_2}{q_2}(1-c_2)(1-t_1)-t_1\frac{m_1}{q_1}c_2\right]\mathbf{i}+\left[\frac{m_1}{q_1}c_2+\frac{m_2}{q_2}(1-c_2)\right]\beta\nabla T\tag{94}$$

$$\mathbf{J}_3=c_3\left[(t_1-1)\frac{m_2}{q_2}-t_1\frac{m_1}{q_1}\right]\mathbf{i}-c_3\left(\frac{m_2}{q_2}-\frac{m_1}{q_1}\right)\beta\nabla T\tag{95}$$

$$\mathbf{J}_4=c_4\left[(t_1-1)\frac{m_2}{q_2}-t_1\frac{m_1}{q_1}\right]\mathbf{i}-c_4\left(\frac{m_2}{q_2}-\frac{m_1}{q_1}\right)\beta\nabla T.\tag{96}$$

For the ideal systems the parameter h_i depends on the state parameters T, p and therefore

$$\nabla(h_i-h_5)=\frac{\partial(h_i-h_5)}{\partial T}\nabla T,\tag{97}$$

where relation (43) has been used.

We will consider that assumption (a) in Section 7.1 is fulfilled, then we can introduce the relations (93)–(96) into equation (90). After doing this we obtain the equation

$$\rho c_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t}=\nabla\cdot\lambda\nabla T-(\tau+\tau_3^*)\mathbf{i}\cdot\nabla T+\rho_{\mathrm{R}}\mathbf{i}^2-\gamma_3(\nabla T)^2,\tag{98}$$

where

$$\tau_3^*=\left[t_1\frac{m_1}{q_1}(1-c_1)+c_1\frac{m_2}{q_2}(t_1-1)\right]\frac{\partial(h_1-h_5)}{\partial T}+\left[(1-t_1)(1-c_2)\frac{m_2}{q_2}-t_1c_1\frac{m_1}{q_1}\right]\frac{\partial(h_2-h_5)}{\partial T}+\left[(t_1-1)\frac{m_2}{q_2}-t_1\frac{m_1}{q_1}\right]\left[c_3\frac{\partial(h_3-h_5)}{\partial T}-c_4\frac{\partial(h_4-h_5)}{\partial T}\right]\tag{99}$$

and

$$\gamma_3=\beta\left\{\left[\frac{m_1}{q_1}(c_1-1)-c_1\frac{m_2}{q_2}\right]\frac{\partial(h_1-h_5)}{\partial T}+\left[c_2\frac{m_1}{q_1}+(1-c_2)\frac{m_2}{q_2}\right]\frac{\partial(h_2-h_5)}{\partial T}-c_3\left(\frac{m_2}{q_2}-\frac{m_1}{q_1}\right)\frac{\partial(h_3-h_5)}{\partial T}-c_4\left(\frac{m_2}{q_2}-\frac{m_1}{q_1}\right)\frac{\partial(h_4-h_5)}{\partial T}\right\}.\tag{100}$$

In order to compare the parameter τ_3^* with the parameter τ, we shall give their numerical estimation. The mass-fractions $c_1\div c_4$ are very small with respect to one. For example, for n-type Si [5] ($m_1=1.065m_0$, $N_1=10^{24}$ m^{-3}, $N_5=5\cdot10^{28}$ m^{-3}, $\rho_5=2.328\cdot10^3$ kg m^{-3}) the mass-fraction $c_1\sim m_1N_1/\rho_5=4.16\cdot10^{-10}$. The mass-fractions c_2, c_3 and c_4 are either of the same order, or less than c_1. Due to the small values of the mass-fractions (without c_5), we can neglect all terms containing the mass-fraction in the relations (99) and (100). In this case, the relations (99) and (100) are the same as relations (76) (for $t_1 = 1$) and (77), therefore we can write

$$\gamma_3 \approx \beta \frac{3k_B}{e} \tag{101}$$

and

$$\tau_3^* = -\frac{3k_B}{2e}. \tag{102}$$

We again consider electrons and holes as a non-degenerate gas and the temperature of the crystal to be above the Debye temperature.

The quantity η for an n-type semiconductor is expressed by the relation [3]

$$\eta = \frac{k_B}{e}\left(\delta + \frac{5}{2}\right) + \frac{1}{eT}\left(\frac{E_c - E_D}{2} - k_B T \ln \sqrt{\frac{N_D}{2A_c}}\right) + \frac{1}{e}\frac{\partial E_F}{\partial T}, \tag{103}$$

where

$$E_F = \frac{E_c + E_D}{2} + k_B T \ln \sqrt{\frac{N_D}{2A_c}} \tag{104}$$

$$A_c = 2\left(\frac{2\pi m_1 k_B T}{h^2}\right)^{3/2}. \tag{105}$$

Substituting the relations (104) and (105) into the relation (103), we obtain the relation

$$\eta = \frac{k_B}{e}\left(\delta + \frac{7}{4}\right) + \frac{E_c - E_D}{2eT}. \tag{106}$$

From the relation (37) and (107) it follows:

$$\tau = -T\frac{\partial \eta}{\partial T} = \frac{E_c - E_D}{2eT}.$$

For n-type Si [5] ($E_c - E_D = 0.01$ eV) we obtain $\tau = 1.7 \cdot 10^{-5}$ V K^{-1} and $\tau_3^* = -1.3 \cdot 10^{-4}$ V K^{-1}. The term $-\tau_3^* \mathbf{i} \cdot \nabla T$ on the right-hand side of the equation (98) represents the new result of this paper.

According to the first relation of (62) for n-type semiconductor $\eta \approx \eta_1$ and therefore $\beta \approx 0$ and also $\gamma_3 \approx 0$. In this case, the equation (99) simplifies into the following form:

$$\rho c_p \frac{\mathrm{d}T}{\mathrm{d}t} = \nabla \cdot \lambda \nabla T - (\tau + \tau_3^*)\mathbf{i} \cdot \nabla T + \rho_R \mathbf{i}^2. \tag{107}$$

Analogous discussion can be carried out also for a p-type semiconductor if we consider the holes as the first component. For n-type Si [6] ($\rho_R = 8.8 \cdot 10^{-1}$ Ωm, $|\nabla T| = 10^3$ K m^{-1}, the numerical values on the second and third term of the right-hand side of the equation (107) are as follows: for $i = 1$ A m^{-2}: $-(\tau + \tau_3^*)i|\nabla T| = 1.13 \cdot 10^{-1}$ J m^{-3} s^{-1}, $\rho_R i^2 = 8.8 \cdot 10^{-1}$ J m^{-3} s^{-1}. We see that both terms are of the same order, but for $i = 10$ A m^{-2}: $-(\tau + \tau_3^*)i|\nabla T| = 1.13$ J m^{-3} s^{-1}, $\rho_R i^2 = 8.8 \cdot 10$ J m^{-3} s^{-1}. In the last case the term $(\tau + \tau_3^*)i|\nabla T|$ is only 1.2% of $\rho_R i^2$ and, therefore, it can be neglected.

8. CONCLUSION

This paper gives the following results:

- derivation of the equation of heat conduction for multi-component condensed systems;
- application of that equation of heat conduction to metal systems and semiconductors;
- the conditions at which the equation of heat conduction is valid have been shown;
- the equation of heat conduction contains the term which represents the new result.

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REFERENCES

1. J. Spišiak and F. Righini, Differential equations for a dynamic thermal conductivity experiment, *Int. J. Thermophys.* **13,** 29–37 (1992).
2. S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics*, pp. 15–16, 30–41, 367–371. North-Holland, Amsterdam (1969).
3. P. S. Kireev, *Physics of Semiconductor* (2nd Edn), pp. 287, 296. Vysch. skola, Moskva (1975) (in Russian).
4. J. A. Stratton, *Electromagnetic Theory*, p. 29. McGraw-Hill, New York (1941).
5. S. M. Sze, *Physics of Semiconductor Devices*, pp. 31, 43, 57, 58. Wiley, New York (1969).
6. Chih-Tang Sah, *Fundamentals of Solid-State Electronics*, pp. 159, 253. World Scientific, London (1991).
7. L. D. Landau and E. M. Lifschitz, *Statistical Physics* (2nd Edn), p. 194. Nauka, Moskva (1964) (in Russian).