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Electro-magneto-thermo-elasticity of extrinsic semiconductors Extended irreversible thermodynamic approach

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AN EXTENDED irreversible thermodynamic approach to electro-magneto-thermo-elasticity of extrinsic anisotropic semiconductors is given. Basing on the above description, some new physical effects are shown. Starting from the residual entropy inequality, generalized kinetic relations for semiconductors are presented.

Przedstawiono rozszerzone, termodynamiczne podejście do opisu sprzężonych oddziaływań pól sprężystego i termicznego, dyfuzji nośników ładunku oraz elektromagnetycznego w niesamoistnym, anizotropowym półprzewodniku. Opierając się na powyższych rozważaniach, zasygnalizowano istnienie pewnych nowych efektów. Na podstawie residualnej części nierówności wzrostu entropii zaprezentowano uogólnione relacje kinetyczne.

Представлен расширенный, термодинаминамический подход для описания сопряженных взаимодействий упругого, термического, диффузии носителей заряда и электромагнитного полей в несобственном, анизотропном полупроводнике. Опираясь на вышеупомянутые рассуждения, обращено внимание на существование некоторых новых эффектов. На основе вычетной части неравенства роста энтропии представлены обобщенные кинетические зависимости.

Introduction

A VAST MAJORITY of methods which describe interactions between mechanical, electromagnetic, temperature and diffusion fields in solids of various electromagnetic, mechanical and thermal properties are based on classical irreversible thermodynamics [1]. The differential field equations obtained in that way, except equations of motion and equations of electromagnetic field, are of the parabolic type (equation of heat transfer, of transport of mass or charge carriers; in particular cases, also of electric or magnetic fields). Such a description allows for velocities of thermal and diffusive perturbations to be interpreted as infinite what, as one knows, is not true. In order to avoid such a paradox situation, instead of classical irreversible thermodynamics, we utilize in this paper the so-called extended irreversible thermodynamic description proposed by I. MÜLLER [2]. The main idea of that approach is based upon the postulate that a function of state can not only depend on parameters of state, but also on irreversible fluxes. The extension of the independent variables set is connected with the introduction of some new evolution equations which are responsible for time rates of the introduced new independent variables.

1. Evolution equations

We consider an extrinsic, polarizable, magnetizable, homogeneous, anisotropic and elastic semiconductor. The first evolution equation which we need in our further investigations is the evolution equation of mass, that is, the continuity equation

(1.1) $$\dot{\varrho}+\varrho v_{i,i} = 0.$$

The next basic equations are the evolution equations of momentum, i.e., balance of momentum (see also [3])

(1.2) $$\varrho\dot{v}_i-\tau_{ji,j}+\mathscr{E}_k P_{k,i}-\left(\frac{\partial \mathbf{P}}{\partial t}\times\mathbf{B}\right)_i+B_k\bar{M}_{k,i}-\varrho[p+\bar{p}-p_0-(n+\bar{n}-n_0)]\mathscr{E}_i - [(\mathbf{j}_n+\mathbf{j}_p)\times\mathbf{B}]_i-f_i = 0$$

and the evolution equation of internal energy or so-called energy balance [4].

(1.3) $$\varrho\frac{d}{dt}\left(\frac{v^2}{2}+U\right)+\frac{\partial U_e}{\partial t} = \varrho r+f_i v_i+[\tau_{ji}v_i-q_j-(\mathbf{E}\times\mathbf{H})_j]_{,j}.$$

Remark that the indices n and p refer only to electron and hole fields and there is not any summation over them.

The evolution equations of the electromagnetic field are the well-known Maxwell's equations

(1.4) $$\nabla\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t},\qquad \nabla\cdot\mathbf{D} = \varrho[p+\bar{p}-p_0-(n+\bar{n}-n_0)],$$
$$\nabla\times\mathbf{H} = \mathbf{j}'+\frac{\partial\mathbf{D}}{\partial t},\qquad \nabla\cdot\mathbf{B} = 0,$$

where $\mathbf{j}' = \mathbf{j}+\varrho[p+\bar{p}-p_0-(n+\bar{n}-n_0)]\mathbf{v}$, then the evolution equations of charge carriers are as follows:

(1.5) $$\varrho\frac{\partial p}{\partial t}+j_{pi,i}+\varrho v_i p_{,i} = g_p^+,$$
$$\varrho\frac{\partial n}{\partial t}-j_{ni,i}+\varrho v_i n_{,i} = g_n^+,$$
$$\varrho\frac{\partial\bar{p}}{\partial t}+\varrho v_i\bar{p}_{,i} = \bar{g}_p^+,$$
$$\varrho\frac{\partial\bar{n}}{\partial t}+\varrho v_i\bar{n}_{,i} = \bar{g}_n^+,$$

(1.6) $$g_n^++g_p^++\bar{g}_n^++\bar{g}_p^+ = 0.$$

The last system of evolution equations refers to the time rate of irreversible fluxes [5]

(1.7) $$\overset{*}{q}_i = Q_i(C),$$
$$\overset{*}{j}_{ni} = J_{ni}(C),$$
$$\overset{*}{j}_{pi} = J_{pi}(C);$$

finally we should add the evolution equation of entropy, i.e., entropy balance

(1.8) $$\varrho\dot{S}+\Phi_{i,i} = \sigma+s.$$

In the above mentioned evolution equations the following notations were introduced: ϱ — denotes mass density, τ_{ji} — electro-magneto-thermodiffusive stress tensor, $\mathscr{E}_k = E_k+(\mathbf{v}\times\mathbf{B})_k$ — the objective electric field intensity vector, P_k and M_k — polarization and magnetization vectors, respectively, n_0, p_0, n, p — mass densities of equilibrium and nonequilibrium charge of electrons and holes, respectively, $\bar{n}$, $\bar{p}$ — localized mass densities of impurity charges ($j_{\bar{n}i} = j_{\bar{p}i} = 0$ [6]), j_{ni}, j_{pi} — fluxes of electrons and holes, f_i — volume forces, U — internal energy, U_e — electromagnetic energy, r — heat production by the heat source distribution, q_i — heat flux, g_n^+, g_p^+, $\bar{g}_n^+$, $\bar{g}_p^+$ — charge source densities of electrons and holes and negative and positive charges of impurities, S — entropy, Φ_i — entropy flux, σ — entropy production, s — entropy supply, superimposed dot — the total time derivative and superimposed star — the objective Zaremba–Jauman's time derivative ($\overset{*}{a}_i = \dot{a}_i - w_{ik} a_k$) [7]. On the other hand the expressions below are connected with Eqs. (1.1)–(1.8):

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \quad \mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \overline{\mathbf{M}}, \quad \overline{\mathbf{M}} = \mathbf{M} + \mathbf{M}^{eq}, \quad \mathbf{M}^{eq} = \mathbf{P}\times\mathbf{v},$$

$$\mathbf{v} = \dot{\mathbf{u}}, \quad \mathbf{j} = \mathbf{j}_n + \mathbf{j}_p, \quad \overset{*}{\overline{\underline{\mathscr{M}}}} = \frac{\gamma}{\mu_0}\overline{\underline{\mathscr{M}}}\times\mathbf{B}, \quad \overline{\mathbf{M}} = \varrho\overline{\underline{\mathscr{M}}},$$

$$\text{(1.9)} \qquad \mathbf{P} = \varrho\underline{\mathscr{P}}, \quad \overline{M}_k\overline{M}_k = \overline{M}^2 = \text{const}, \quad \overline{M}_{,i} = 0,$$

$$\overline{M}_k\overline{M}_{k,i} = 0, \quad \dot{\overline{M}} = 0, \quad \overline{M}_k\dot{\overline{M}}_k = 0,$$

$$w_{ik} = \frac{1}{2}(v_{i,k} - v_{k,i}),$$

$$\text{(1.10)} \qquad \tau_{ji} = \sigma_{ij} + (\mathscr{E}_k P_k + B_k \overline{M}_k)\delta_{ij},$$

$$\text{(1.11)} \qquad C = \{\varepsilon_{ij}, \mathscr{E}_i, B_i, n, p, T, q_i, j_{ni}, j_{pi}, \varepsilon_{kj,i}, n_{,i}, p_{,i}, T_{,i}\},$$

where $\mathbf{u}$ denotes the displacement vector, σ_{ij} — the thermodiffusive stress tensor, the expressions $(1.9)_{14-1}$ — magnetic saturation conditions [7], ε_0, μ_0 — dielectric constant and magnetic permeability of vacuum, γ — gyromagnetic ratio, ε_{ij} — elastic strain tensor

$$\text{(1.12)} \qquad \varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$$

and T — absolute temperature.

As we see now, from Eqs. (1.11) and (1.12) the following set of unknown fields results:

$$\text{(1.13)} \qquad \{u_i, \mathscr{E}_i, B_i, n, p, T, q_i, j_{ni}, j_{pi}\},$$

which can be found with the help of Eqs. (1.2), (1.3), $(1.4)_{1,3}$ $(1.5)_{1,2}$ and (1.7). The above set of equations stands for the basic system of equations of the theory.

In our further investigations it will be better to use the free energy instead of the internal energy. The latter we introduce in the way

$$\text{(1.14)} \qquad F = F(C),$$

$$\text{(1.15)} \qquad F = U - \mathscr{P}_i\mathscr{E}_i - \overline{\mathscr{M}}_i B_i - TS.$$

Finishing this section we should stress that both in the previous and in the further considerations we have used

1) the principle of equipresence stating that if an independent variable appears in one response function, it should appear in any response function unless contradicted by the laws of continuum thermodynamics;

2) the assumption that electron and hole fields do not influence each other;

3) the case of infinitesimal deformations about a natural undeformed configuration [7].

2. Entropy inequality

Let us consider now entropy balance (1.8) in details. Following [3] we admit that entropy supply s in linear approximation is

$$s = \frac{\varrho r}{T}, \tag{2.1}$$

then entropy production σ in semiconductor is nonnegative

$$\sigma \geqslant 0. \tag{2.2}$$

The above mentioned assumptions lead to the following entropy inequality:

$$\varrho\dot{S} + \Phi_{i,i} - \frac{\varrho r}{T} \geqslant 0, \tag{2.3}$$

in which the extended entropy flux $\Phi_i(C)$ is taken in the form [3, 5]

$$\Phi_i(C) = \frac{1}{T} q_i + \frac{1}{T}\mu_n j_{ni} - \frac{1}{T}\mu_p j_{pi} + \frac{1}{T}(\underline{\mathscr{E}} \times \overline{\mathbf{M}})_i + k_i(C), \tag{2.4}$$

where $k_i(C)$ denotes an extra entropy flux which could appear not to be equal to zero because of the assumed set of independent variables C (1.11).

Now, if we substitute Eqs. (1.1)–(1.5)$_{1\ 2}$, (1.9)–(1.12) and (1.15) into the inequality (2.3), it takes the form

$$\begin{aligned}
(2.5)\quad & -\varrho\left(\frac{\partial F}{\partial T} + S\right)\dot{T} - \varrho\frac{\partial F}{\partial q_i} Q_i - \varrho\frac{\partial F}{\partial j_{ni}} J_{ni} - \varrho\frac{\partial F}{\partial j_{pi}} J_{pi} - \varrho\frac{\partial F}{\partial \varepsilon_{kj,i}}\dot{\varepsilon}_{kj,i} \\
& - \varrho\frac{\partial F}{\partial n_{,i}}\dot{n}_{,i} - \varrho\frac{\partial F}{\partial p_{,i}}\dot{p}_{,i} - \varrho\frac{\partial F}{\partial T_{,i}}\dot{T}_{,i} + \left\{T\frac{\partial k_i}{\partial T} - \frac{1}{T}[q_i + \mu_n j_{ni} - \mu_p j_{pi}\right. \\
& \left. + (\underline{\mathscr{E}} \times \overline{\mathbf{M}})_i]\right\} T_{,i} + T\frac{\partial k_i}{\partial \varepsilon_{kl}}\varepsilon_{kl,i} + T\frac{\partial k_i}{\partial \mathscr{E}_j}\mathscr{E}_{j,i} + T\frac{\partial k_i}{\partial B_j}B_{j,i} + T\frac{\partial k_i}{\partial n}n_{,i} \\
& + T\frac{\partial k_i}{\partial p}p_{,i} + T\frac{\partial k_i}{\partial q_k}q_{k,i} + T\frac{\partial k_i}{\partial j_{nk}}j_{nk,i} + T\frac{\partial k_i}{\partial j_{pk}}j_{pk,i} + T\frac{\partial k_i}{\partial \varepsilon_{lj,k}}\varepsilon_{lj,ki} \\
& + T\frac{\partial k_i}{\partial n_{,k}}n_{,ki} + T\frac{\partial k_i}{\partial p_{,k}}p_{,ki} + T\frac{\partial k_i}{\partial T_{,k}}T_{,ki} - \left(\varrho\frac{\partial F}{\partial \mathscr{E}_k}\mathscr{E}_i + \varrho\frac{\partial F}{\partial B_k}B_i + \sigma_{ki}\right)w_{ki} \\
& + j_{ni}(\mathscr{E}_i + \mu_{n,i}) + j_{pi}(\mathscr{E}_i - \mu_{p,i}) + (\underline{\mathscr{E}} \times \overline{\mathbf{M}})_{i,i} - \mu_n g_n^+ - \mu_p g_p^+ \geqslant 0.
\end{aligned}$$

As we see, the above inequality is linear in the variables $\dot{T}$, $\dot{\varepsilon}_{kj,i}$, $\dot{n}_{,i}$, $\dot{p}_{,i}$, $\dot{T}_{,i}$, $\mathscr{E}_{j,i}$, $B_{j,i}$, $q_{k,i}$, $j_{nk,i}$, $j_{pk,i}$, $\varepsilon_{ij,kl}$, $n_{,ki}$, $p_{,ki}$, $T_{,ki}$ and therefore we obtain the following relations and restrictions on free energy F and extra entropy flux k_i (we also require that free energy F is to be invariant under an infinitesimal rigid rotation of the body [17]):

(2.6) $$\frac{\partial F}{\partial T}+S=0,$$

(2.7) $$\frac{\partial F}{\partial \varepsilon_{kl,i}}=\frac{\partial F}{\partial n_{,i}}=\frac{\partial F}{\partial p_{,i}}=\frac{\partial F}{\partial T_{,i}}=0,$$

(2.8) $$\frac{\partial k_i}{\partial \mathscr{E}_j}=\frac{\partial k_i}{\partial B_j}=\frac{\partial k_i}{\partial q_k}=\frac{\partial k_i}{\partial j_{nk}}=\frac{\partial k_i}{\partial j_{pk}}=0,$$

(2.9) $$\frac{\partial k_i}{\partial \varepsilon_{lj,k}}+\frac{\partial k_k}{\partial \varepsilon_{lj,i}}=0,$$

(2.10) $$\frac{\partial k_i}{\partial n_{,k}}+\frac{\partial k_k}{\partial n_{,i}}=0,$$

(2.11) $$\frac{\partial k_i}{\partial p_{,k}}+\frac{\partial k_k}{\partial p_{,i}}=0,$$

(2.12) $$\frac{\partial k_i}{\partial T_{,k}}+\frac{\partial k_k}{\partial T_{,i}}=0,$$

(2.13) $$\sigma_{ik}-\sigma_{ki}=\varrho\frac{\partial F}{\partial \mathscr{E}_k}\mathscr{E}_i+\varrho\frac{\partial F}{\partial B_k}B_i-\varrho\frac{\partial F}{\partial \mathscr{E}_i}\mathscr{E}_k-\varrho\frac{\partial F}{\partial B_i}B_k,$$

(2.14) $$-\varrho\frac{\partial F}{\partial q_i}Q_i-\varrho\frac{\partial F}{\partial j_{ni}}J_{ni}-\varrho\frac{\partial F}{\partial j_{pi}}J_{pi}+\Big\{T\frac{\partial k_i}{\partial T}-\frac{1}{T}[q_i+\mu_n j_{ni}$$
$$-\mu_p j_{pi}+(\underline{\mathscr{E}}\times\overline{\mathbf{M}})_i]\Big\}T_{,i}+T\frac{\partial k_i}{\partial \varepsilon_{kl}}\varepsilon_{kl,i}+T\frac{\partial k_i}{\partial n}n_{,i}$$
$$+T\frac{\partial k_i}{\partial p}p_{,i}+j_{ni}(\mathscr{E}_i+\mu_{n,i})+j_{pi}(\mathscr{E}_i-\mu_{p,i})+(\underline{\mathscr{E}}\times\overline{\mathbf{M}})_{i,i}-\mu_n g_n^+-\mu_p g_p^+\geqslant 0.$$

From the relation (2.7) we see that free energy F does not depend on the gradients $\varepsilon_{kl,i}$, $n_{,i}$, $p_{,i}$, and $T_{,i}$. Hence

(2.15) $$F=F(\varepsilon_{ij},\mathscr{E}_i,B_i,n,p,T,q_i,j_{ni},j_{pi}).$$

Basing now on the relation (2.15) we can formulate Gibbs' equation in the form (see also [8–10])

(2.16) $$dF=\frac{1}{\varrho}\sigma_{ij}d\varepsilon_{ij}-\mathscr{P}_i\,d\mathscr{E}_i-\overline{\mathscr{M}}_i\,dB_i+\mu_n dn+\mu_p dp-SdT$$
$$-\frac{1}{\varrho}\Pi_i dq_i-\frac{1}{\varrho}\Pi_{ni}dj_{ni}-\frac{1}{\varrho}\Pi_{pi}dj_{pi},$$

where the following definitions were introduced:

(2.17) $$\sigma_{ij}=\varrho\frac{\partial F}{\partial \varepsilon_{ij}}$$ thermodiffusive stress tensor,

(2.18) $$\mathscr{P}_i=-\frac{\partial F}{\partial \mathscr{E}_i},$$

(2.19) $$\overline{\mathscr{M}}_i=-\frac{\partial F}{\partial B_i},$$

(2.20) $\mu_n = \dfrac{\partial F}{\partial n}, \quad \mu_p = \dfrac{\partial F}{\partial p}$ chemical potentials of electrons and holes,

$$\Pi_{qi} = \varrho \frac{\partial F}{\partial q_i}, \quad \Pi_{ni} = \varrho \frac{\partial F}{\partial j_{ni}}, \quad \Pi_{pi} = \varrho \frac{\partial F}{\partial j_{pi}} \tag{2.21}$$

vector potentials of thermal, electron and hole fields. Moreover, from Eq. (2.8) it results that extra entropy flux does not depend on $\mathscr{E}_j$, B_j, q_k, j_{nk}, j_{pk}.

Now we should specify extra entropy flux k_i using the relations (2.9)–(2.12). The solution of Eq. (2.12) is as follows

$$k_i = \Omega_{ij}(\varepsilon_{ij}, n, p, T, \varepsilon_{ij,k}, n_{,k}, p_{,k})T_{,j} + \Omega_i(\varepsilon_{ij}, n, p, T, \varepsilon_{ij,k}, n_{,k}, p_{,k}), \tag{2.22}$$

where $\Omega_{ij} = -\Omega_{ji}$ and we have from Eq. (2.12) that both Ω_{ij} and Ω_i do not depend on $T_{,i}$. Substituting Eq. (2.22) into Eq. (2.10), we obtain

$$\frac{\partial \Omega_{ik}}{\partial n_{,j}} + \frac{\partial \Omega_{jk}}{\partial n_{,i}} = 0, \tag{2.23}$$

$$\frac{\partial \Omega_i}{\partial n_{,j}} + \frac{\partial \Omega_j}{\partial n_{,i}} = 0, \tag{2.24}$$

the solutions of which have the form

$$\Omega_{ik} = M_{ikl} n_{,l} + \tilde{\Omega}_{ik} \tag{2.25}$$

and

$$\Omega_i = A_{ik} n_{,k} + Y_i, \tag{2.26}$$

where M_{ikl}, $\tilde{\Omega}_{ik}$ and A_{ik} are skew-symmetric tensors and together with vector Y_i do not depend on $n_{,i}$. Hence we obtain

$$k_i = (M_{ikl} n_{,l} + \tilde{\Omega}_{ik}) T_{,k} + A_{ik} n_{,k} + Y_i. \tag{2.27}$$

Now, if we utilize the solution (2.27) in Eq. (2.11) and repeat the above calculations, we get

$$\frac{\partial M_{ikl}}{\partial p_{,j}} + \frac{\partial M_{jkl}}{\partial p_{,i}} = 0, \tag{2.28}$$

$$\frac{\partial \tilde{\Omega}_{ik}}{\partial p_{,j}} + \frac{\partial \tilde{\Omega}_{jk}}{\partial p_{,i}} = 0, \tag{2.29}$$

$$\frac{\partial A_{ik}}{\partial p_{,j}} + \frac{\partial A_{jk}}{\partial p_{,i}} = 0, \tag{2.30}$$

$$\frac{\partial Y_i}{\partial p_{,j}} + \frac{\partial Y_j}{\partial p_{,i}} = 0, \tag{2.31}$$

$$M_{ikl} = C_{ikls} p_{,s} + \tilde{M}_{ikl}, \tag{2.32}$$

$$\tilde{\Omega}_{ik} = G_{iks} p_{,s} + \tilde{\tilde{\Omega}}_{ik}, \tag{2.33}$$

$$A_{ik} = R_{iks} p_{,s} + \tilde{A}_{ik}, \tag{2.34}$$

$$Y_i = W_{,s} p_{,s} + \tilde{Y}_i, \tag{2.35}$$

where C_{ikls}, $\tilde{M}_{ikl}$, G_{iks}, R_{iks}, $\tilde{\tilde{\Omega}}_{ik}$, $\tilde{A}_{ik}$, W_{is} are skew-symmetric tensors and together with $\tilde{Y}_i$ do not depend on $p_{,i}$. Hence

(2.36) $k_i = \{(C_{ikls}p_{,s}+\tilde{M}_{ikl})n_{,l}+(G_{iks}p_{,s}+\tilde{\tilde{\Omega}}_{ik})\}T_{,k}+(R_{iks}p_{,s}+\tilde{A}_{ik})n_{,k}+W_{is}p_{,s}+\tilde{Y}_i.$

To obtain the final form of k_i, we substitute the solution (2.36) into Eq. (2.9). Then in the same way as in the above calculations we have

(2.37) $$\frac{\partial C_{ikls}}{\partial \varepsilon_{mr,j}}+\frac{\partial C_{jkls}}{\partial \varepsilon_{mr,i}}=0,$$

(2.38) $$\frac{\partial \tilde{M}_{ikl}}{\partial \varepsilon_{mr,j}}+\frac{\partial \tilde{M}_{jkl}}{\partial \varepsilon_{mr,i}}=0,$$

(2.39) $$\frac{\partial G_{iks}}{\partial \varepsilon_{mr,j}}+\frac{\partial G_{jks}}{\partial \varepsilon_{mr,i}}=0,$$

(2.40) $$\frac{\partial \tilde{\tilde{\Omega}}_{ik}}{\partial \varepsilon_{mr,j}}+\frac{\partial \tilde{\tilde{\Omega}}_{jk}}{\partial \varepsilon_{mr,i}}=0,$$

(2.41) $$\frac{\partial R_{iks}}{\partial \varepsilon_{mr,j}}+\frac{\partial R_{jks}}{\partial \varepsilon_{mr,i}}=0,$$

(2.42) $$\frac{\partial \tilde{A}_{ik}}{\partial \varepsilon_{mr,j}}+\frac{\partial \tilde{A}_{jk}}{\partial \varepsilon_{mr,i}}=0,$$

(2.43) $$\frac{\partial W_{is}}{\partial \varepsilon_{mr,j}}+\frac{\partial W_{js}}{\partial \varepsilon_{mr,i}}=0,$$

(2.44) $$\frac{\partial \tilde{Y}_i}{\partial \varepsilon_{mr,j}}+\frac{\partial \tilde{Y}_j}{\partial \varepsilon_{mr,i}}=0,$$

and their solutions

(2.45) $$C_{ikls}=K_{iklsjmr}\varepsilon_{mr,j}+\tilde{C}_{ikls},$$

(2.46) $$\tilde{M}_{ikl}=O_{ikljmr}\varepsilon_{mr,j}+\tilde{\tilde{M}}_{ikl},$$

(2.47) $$G_{iks}=\Gamma_{iksjmr}\varepsilon_{mr,j}+\tilde{G}_{iks},$$

(2.48) $$\tilde{\tilde{\Omega}}_{ik}=\Lambda_{ikjmr}\varepsilon_{mr,j}+\bar{\Omega}_{ik},$$

(2.49) $$R_{iks}=\Pi_{iksjmr}\varepsilon_{mr,j}+\tilde{R}_{iks},$$

(2.50) $$\tilde{A}_{ik}=\Delta_{ikjmr}\varepsilon_{mr,j}+\tilde{\tilde{A}}_{ik},$$

(2.51) $$W_{is}=\mathscr{H}_{isjmr}\varepsilon_{mr,j}+\tilde{W}_{is},$$

(2.52) $$\tilde{Y}_i=Z_{ijmr}\varepsilon_{mr,j}+\tilde{\tilde{Y}}_i,$$

where $K_{iklsjmr}$, $\tilde{C}_{ikls}$, Q_{ikljmr}, Γ_{iksjmr}, $\tilde{\tilde{M}}_{ikl}$, $\tilde{G}_{iks}$, Λ_{ikjmr}, Π_{iksjmr}, $\tilde{R}_{iks}$, $\bar{\Omega}_{ik}$, Δ_{ikjmr}, $\mathscr{H}_{isjmr}$, $\tilde{\tilde{A}}_{ik}$, $\tilde{W}_{is}$, Z_{ijmr} are skew-symmetric tensors and together with the vector $\tilde{\tilde{Y}}_i$ do not depend on $\varepsilon_{mr,j}$.

In this way, the final form of extra-entropy flux is as follows:

$$(2.53)\qquad k_i = \{[(K_{iklsjmr}\varepsilon_{mr,j}+\tilde{C}_{ikls})p_{,s}+(O_{ikljmr}\varepsilon_{mr,j}+\tilde{\tilde{M}}_{ikl})]n_{,l} + [(\Gamma_{iksjmr}\varepsilon_{mr,j}+\tilde{G}_{iks})p_{,s}+(\Lambda_{ikjmr}\varepsilon_{mr,j}+\bar{\Omega}_{ik})]\}T_{,k}+[(\Pi_{iksjmr}\varepsilon_{mr,j}+\tilde{R}_{iks})p_{,s} + (\Delta_{ikjrm}\varepsilon_{mr,j}+\tilde{\tilde{A}}_{ik})]n_{,k}+(\mathscr{H}_{isjmr}\varepsilon_{mr,j}+\tilde{W}_{is})p_{,s}+Z_{ijmr}\varepsilon_{mr,j}+\tilde{\tilde{Y}}_i .$$

From the above mentioned considerations it results that all vectorial and tensorial coefficients in Eq. (2.53) depend only on ε_{ij}, n, p, T. If now we demand that vector k_i is to be objective, all the coefficients in Eq. (2.53) have to vanish, that is,

$$(2.54)\qquad K_{iklsjmr} = \tilde{C}_{ikls} = O_{ikljmr} = \tilde{\tilde{M}}_{ikl} = \Gamma_{iksjmr} = \tilde{G}_{iks} = \Lambda_{ikjmr} = \bar{\Omega}_{ik} = = \Pi_{iksjmr} = \tilde{R}_{iks} = \Delta_{ikjmr} = \tilde{\tilde{A}}_{ik} = \mathscr{H}_{isjmr} = \tilde{W}_{is} = Z_{ijmr} = \tilde{\tilde{Y}}_j = 0,$$

because there exist no objective vector and no skew-symmetric tensor depending on a single scalar and a single symmetric tensor [11]. Hence we have

$$(2.55)\qquad k_i = 0$$

and the entropy flux has the form

$$(2.56)\qquad \Phi_i = \frac{1}{T}[q_i+\mu_n j_{ni}-\mu_p j_{pi}+(\underline{\mathscr{E}}\times\bar{\mathbf{M}})_i].$$

On the other hand we have arrived at the final form of residual entropy inequality:

$$(2.57)\qquad -\Pi_{qi}Q_i-\Pi_{ni}J_{ni}-\Pi_{pi}J_{pi}-\frac{\psi_i}{T}T_{,i}+(\mathscr{E}_i+\mu_{n,i})j_{ni} +(\mathscr{E}_i-\mu_{p,i})j_{pi}-\varrho(\mu_n g_n^+ +\mu_p q_p^+)\geqslant 0,$$

where

$$\Phi_i = \frac{1}{T}\psi_i .$$

We should interpret the relation (2.13). If one utilizes Gibbs' equation (2.16), the expression (2.13) takes the form

$$(2.58)\qquad \sigma_{ik}-\sigma_{ki} = P_i\mathscr{E}_k+\bar{M}_i B_k-P_k\mathscr{E}_i-\bar{M}_k B_i,$$

which proves that the thermodiffusive stress tensor is nonsymmetric. This is an equivalent way to define the symmetry of tensor σ_{ij} instead of the common way based on the moment of the momentum balance [18].

3. Kinetic relations

It seems to be necessary now to take care of kinetic reciprocal relations for Π_{qi}, Π_{ni}, Π_{pi}, ψ_i, j_{ni}, j_{pi}, i.e. for irreversible fluxes: generalized heat flux and fluxes of charge carriers, respectively, and response thermodynamic forces Q_i, J_{ni}, J_{pi}, $T_{,i}T^{-1}$, $\mathscr{E}_i+\mu_{n,i}$, $\mathscr{E}_i-\mu_{p,i}$. The solution of the above problem is based on residual inequality (2.57). It is well known that the above inequality can be written in the form (omitting for simplicity the source-like terms)

$$(3.1)\qquad \mathscr{J}_a X_a \geqslant 0,$$

where

$$\mathcal{J}_a = L_{ab} X_b, \tag{3.2}$$

L_{ab} denote phenomenological coefficients.

Now, basing on the inequality (2.57) and the relations (3.1) and (3.2), we choose the generalized forces and fluxes in the following way:

$$\mathcal{J}_a = \begin{Bmatrix} \psi_i \\ j_{pi} \\ j_{ni} \\ \Pi_{qi} \\ \Pi_{pi} \\ \Pi_{ni} \end{Bmatrix}, \quad X_a = \begin{Bmatrix} -\frac{1}{T} T_{,i} \\ \mathcal{E}_i - \mu_{p,i} \\ \mathcal{E}_i + \mu_{n,i} \\ -Q_i \\ -J_{pi} \\ -J_{ni} \end{Bmatrix}, \tag{3.3}$$

and the matrix of tensorial phenomenological coefficients will now be as follows:

$$L_{ab} = \begin{Bmatrix} T\varkappa_{ij} & Tm^p_{ij} & Tm^n_{ij} & TA^Q_{ij} & TA^P_{ij} & TA^N_{ij} \\ Tm^p_{ij} & \varrho p \xi^p_{ij} & 0 & B^Q_{ij} & B^P_{ij} & 0 \\ Tm^n_{ij} & 0 & \varrho n \xi^n_{ij} & C^Q_{ij} & 0 & C^N_{ij} \\ TA^Q_{ij} & B^Q_{ij} & C^Q_{ij} & D^Q_{ij} & D^P_{ij} & D^N_{ij} \\ TA^P_{ij} & B^P_{ij} & 0 & D^P_{ij} & E^P_{ij} & 0 \\ TA^N_{ij} & 0 & C^N_{ij} & D^N_{ij} & 0 & F^N_{ij} \end{Bmatrix}. \tag{3.4}$$

From the matrix (3.4) we deduce that the symmetry of matrix L_{ab} coincides with Onsager's reciprocity relations $L_{ab} = L_{ba}$. $\varkappa_{ij}$ is the heat conduction tensor, ξ^n_{ij}, ξ^p_{ij} — the tensors of mobilities of charge carriers and m^n_{ij}, m^p_{ij} — the tensors of Peltier–Seebeck's effects referred to electron and hole currents. Now, from Eq. (3.2)–(3.4) the kinetic relations take the form

$$\psi_i = -\varkappa_{ij} T_{,j} + Tm^p_{ij}(\mathcal{E}_j - \mu_{p,j}) + Tm^n_{ij}(\mathcal{E}_j + \mu_{n,j}) - TA^Q_{ij} Q_j - TA^P_{ij} J_{pj} - TA^N_{ij} J_{nj}, \tag{3.5}$$

$$j_{pi} = -m^p_{ij} T_{,j} + \varrho p \xi^p_{ij}(\mathcal{E}_j - \mu_{p,j}) - B^Q_{ij} Q_j - B^P_{ij} J_{pj}, \tag{3.6}$$

$$j_{ni} = -m^n_{ij} T_{,j} + \varrho n \xi^n_{ij}(\mathcal{E}_j + \mu_{n,j}) - C^Q_{ij} Q_j - C^N_{ij} J_{nj}, \tag{3.7}$$

$$\Pi_{qi} = -A^Q_{ij} T_{,j} + B^Q_{ij}(\mathcal{E}_j - \mu_{p,j}) + C^Q_{ij}(\mathcal{E}_j + \mu_{n,j}) - D^Q_{ij} Q_j - D^P_{ij} J_{pj} - D^N_{ij} J_{nj}, \tag{3.8}$$

$$\Pi_{pi} = -A^P_{ij} T_{,j} + B^P_{ij}(\mathcal{E}_j - \mu_{p,j}) - D^P_{ij} Q_j - E^P_{ij} J_{pj}, \tag{3.9}$$

$$\Pi_{ni} = -A^N_{ij} T_{,j} + C^N_{ij}(\mathcal{E}_j + \mu_{n,j}) - D^N_{ij} Q_j - F^N_{ij} J_{nj}. \tag{3.10}$$

The above relations differ from the previous ones [12] by vector-potential-like terms. The tensorial coefficients A^Q_{ij}, A^P_{ij}, A^N_{ij}, B^Q_{ij}, B^P_{ij}, B^N_{ij}, C^Q_{ij}, C^N_{ij}, D^Q_{ij}, D^P_{ij}, D^N_{ij}, E^P_{ij}, F^N_{ij} describe new effects connected with rates of irreversible fluxes. And now it appears that adding irreversible fluxes to the set of independent variables widens kinetic relations by "fluxes" Π_{qi}, Π_{ni}, Π_{pi} and "forces" Q_i, J_{ni}, J_{pi}. It is very interesting to note that, using the description presented here, thermal and diffusion fields have both scalar (T, μ_p, μ_n) and vector (Q_i, J_{pi}, J_{ni}) potentials. This is a new result in comparison to the existing theories.

4. Constitutive relations

The general problem to be solved is the determination of the field variables u_i, $\mathscr{E}_i$, B_i, n, p, T, q_i, j_{ni}, j_{pi} as functions of space and time. These quantities are obtained from the balance equations (1.2), (1.3) and $(1.5)_{1\ 2}$ complemented by Maxwell's equations (1.4) and evolution equations (1.7). Since balance and Maxwell's equations contain new unknown quantities σ_{ij}, P_i, $\overline{M}_i$, μ_n, μ_p, S, Π_{qi}, Π_{ni}, Π_{pi}, it is necessary to express the latter in terms of the above set of variables through constitutive equations.

Hence, expanding free energy (2.15) about the equilibrium and denoting by

$$\theta = T-T_0, \quad \left|\frac{\theta}{T_0}\right| \ll 1, \quad N = n-n_0, \tag{4.1}$$
$$\left|\frac{N}{n_0}\right| \ll 1, \quad P = p-p_0, \quad \left|\frac{P}{p_0}\right| \ll 1$$

the small deviations of thermal and diffusion fields with respect to the equilibrium, one obtains (with the subscript "o" referring to the equilibrium and requiring an invariance condition under time reversal):

$$\begin{aligned} F-F_0 = & -\frac{c}{2T_0}\theta^2 - \frac{1}{\varrho}\lambda^T_{ij}\theta\varepsilon_{ij} + p^{TE}_i\theta\mathscr{E}_i + p^{TB}_i\theta B_i - \alpha_p\theta P - \alpha_n\theta N \\ & + \frac{1}{2\varrho}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \frac{1}{\varrho}h^E_{ijk}\varepsilon_{ij}\mathscr{E}_k - \frac{1}{\varrho}h^B_{ijk}\varepsilon_{ij}B_k - \frac{1}{\varrho}\lambda^P_{ij}\varepsilon_{ij}P \\ & - \frac{1}{\varrho}\lambda^N_{ij}\varepsilon_{ij}N - \frac{1}{2\varrho}\chi^E_{ik}\mathscr{E}_i\mathscr{E}_k - \frac{\Sigma_{ik}}{\varrho}\mathscr{E}_iB_k + p^{PE}_i\mathscr{E}_iP + p^{NE}_i\mathscr{E}_iN - \frac{1}{2\varrho}\chi^B_{ik}B_iB_k \\ & + p^{PB}_iB_iP + p^{NB}_iB_iN + \frac{\delta_p}{2p_0}P^2 + \frac{\delta_n}{2n_0}N^2 + \frac{1}{2\varrho}a^Q_{ik}q_iq_k \\ & + \frac{1}{\varrho}a^{QIN}_{ik}q_ij_{nk} + \frac{1}{\varrho}a^{QIP}_{ik}q_ij_{pk} + \frac{1}{2\varrho}a^{IN}_{ik}j_{ni}j_{nk} + \frac{1}{2\varrho}a^{IP}_{ik}j_{pi}j_{pk}. \end{aligned} \tag{4.2}$$

In Eq. (4.2) the following notations were introduced:

1. For known effects, c — the specific heat coefficient, λ^T_{ij}, λ^P_{ij}, λ^N_{ij} — the tensors of thermal and diffusion stress coefficients, p^{TE}_i, p^{PE}_i, p^{NE}_i, p^{TB}_i, p^{PB}_i, p^{NB}_i — the pseudovectors of pyroelectric, pyromagnetic and pyrodiffusive constants, α_p, α_n — the thermodiffusive constants c_{ijkl} — the tensor of elastic constants, h^E_{ijk}, h^B_{ijk} — the piezoelectric and piezomagnetic constant tensors, χ^E_{ik}, χ^B_{ik} the electrical and magnetic susceptibility tensors, δ_n, δ_p — the diffusive constants, Σ_{ik} — the magnetoelectric constant tensor

2. For unknown effects, a^Q_{ik}, a^{QIN}_{ik}, a^{QIP}_{ik}, a^{IN}_{ik}, a^{IP}_{ik} — the tensors describing linear interactions between nonequilibrium fluxes.

Coming back to the remarks presented at the beginning of this section, we can now specify the following constitutive relations for dependent variables with the help of Eqs. (2.6), (2.17)–(2.21) and (4.2) (we admit that the equilibrium values of all dependent variables are conventionally taken equal to zero),

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl} - h^E_{ijk}\mathscr{E}_k - h^B_{ijk}B_k - \lambda^N_{ij}N - \lambda^P_{ij}P - \lambda^T_{ij}\theta, \tag{4.3}$$

$$P_i = h^E_{ikl}\varepsilon_{kl} + \chi^E_{ik}\mathscr{E}_k + \Sigma_{ik}B_k - \varrho p^{NE}_iN - \varrho p^{NE}_iP - \varrho p^{PE}_i\theta, \tag{4.4}$$

(4.5) $$\bar{M}_i = h^B_{ikl}\,\varepsilon_{kl} + \Sigma_{ik}\mathscr{E}_k + \chi^B_{ik}B_k - \varrho p_i^{NB}N - \varrho p_i^{PB}P - \varrho p_i^{TB}\theta,$$

(4.6) $$\mu_n = -\frac{1}{\varrho}\lambda^N_{kl}\,\varepsilon_{kl} + p_k^{NB}\mathscr{E}_k + p_k^{NB}B_k + \frac{\delta_n}{n_0}N - \alpha_n\theta,$$

(4.7) $$\mu_p = -\frac{1}{\varrho}\lambda^P_{kl}\,\varepsilon_{kl} + p_k^{PE}\mathscr{E}_k B_k + \frac{\delta_p}{p_0}P - \alpha_p\theta,$$

(4.8) $$S = \frac{1}{\varrho}\lambda^T_{kl}\,\varepsilon_{kl} - p_k^{TE}\mathscr{E}_k - p_k^{TB}B_k + \alpha_n N + \alpha_p P + \frac{c}{T_0}\theta,$$

(4.9) $$\Pi_{qi} = a^Q_{ik}q_k + a^{QIN}_{ik}j_{nk} + a^{QIP}_{ik}j_{pk},$$

(4.10) $$\Pi_{ni} = a^{QIN}_{ik}q_k + a^{IN}_{ik}j_{nk},$$

(4.11) $$\Pi_{pi} = a^{QIP}_{ik}q_k + a^{IP}_{ik}j_{pk}.$$

The last quantities should be specified here by constitutive relations are rates of recombination of electrons and holes. According to the principle of equipresence we can write them in the form

(4.12) $$g_n^+ = g_n^+(C),$$

(4.13) $$g_p^+ = g_p^+(C).$$

Now, if we expand them into Taylor's series with respect to the equilibrium, we get

(4.14) $$g_n^+ - g_{n0}^+ = b^{TN}\theta + g^{\varepsilon N}_{ij}\varepsilon_{ij} + l_i^{EN}\mathscr{E}_i + l_i^{BN}B_i - \frac{1}{\tau_n^+}N + \gamma_i^{QN}q_i + \nu_i^N j_{ni},$$

(4.15) $$g_p^+ - g_{p0}^+ = b^{TP}\theta + g^{\varepsilon P}_{ij}\,\varepsilon_{ij} + l_i^{EP}\mathscr{E}_i + l_i^{BP}B_i - \frac{1}{\tau_p^+}P + \gamma_i^{QP}q_i + \nu_i^P j_{pi}.$$

In equilibrium we assume that $g_{n0}^+ = g_{p0}^+ = 0$. Then τ_n^+, τ_p^+ denote the relaxation times of linear coupled recombination (life-times of charge carriers) [13]. The coefficients b^{TN}, b^{TP}, $g^{\varepsilon N}_{ij}$, $g^{\varepsilon P}_{ij}$ and l_i^{EN}, l_i^{EP} describe effects of direct influence of temperature, elastic strain, electric field intensity and magnetic induction on recombination processes, respectively. In the framework of the theory proposed here it appears that the same kind of influence on the above processes have also irreversible fluxes (coefficients γ_i^{QN}, γ_i^{QP}, ν_i^N, ν_i^P). That fact seems to be unparalleled till now.

Finally, we shall focus on the expressions of evolution equations for the heat flux and the charge flow currents (1.7). Expanding, therefore, the above expressions into Maclaurin's series with respect to the equilibrium and confining them only to the linear approximation, we obtain

(4.16) $$\tau^q_{ij}\dot{q}_j = -q_i - \varkappa_{ij}T_{,j} + Tm^p_{ij}(\mathscr{E}_j - \mu_{p,j}) + Tm^n_{ij}(\mathscr{E}_j + \mu_{n,j}),$$

(4.17) $$\tau^n_{ij}\dot{j}_{nj} = -j_{ni} - m^n_{ij}T_{,j} + \varrho n\xi^n_{ij}(\mathscr{E}_j + \mu_{n,j}),$$

(4.18) $$\tau^P_{ij}\dot{j}_{pj} = -j_{pi} - m^P_{ij}T_{,j} + \varrho p^P_{ij}\xi(\mathscr{E}_j - \mu_{p,j}).$$

In Eqs. (4.16)–(4.18) τ^q_{ij}, τ^n_{ij} and τ^P_{ij} denote relaxation time tensors associated to the heat, electron and hole fluxes. Remark that in the phenomenological theory investigated in the paper we shall state that the recombination relaxation times of electrons and holes quoted in Eqs. (4.14) and (4.15) are much more than components of relaxation time tensors associated to the heat, electron and hole fluxes. These strong inequalities denote the so-called diffusion approach to processes occurring inside the considered semiconductor [13] and make obtained rules true in the above framework. Equation (4.16) generalizes Vernotte–Cattaneo's relation [14, 15] by including the effects of charge carriers and having anisotropic form while expressions similar to Eqs. (4.17) and (4.18) in isotropic form can be found in magnetohydrodynamics [16] and in the semiconductor theory [13]. Finally we have to underline the fact that when we pass in Eqs. (4.16)–(4.18) with $\tau^q_{ij} \to 0$, $\tau^n_{ij} \to 0$ and $\tau^p_{ij} \to 0$ we obtain classical kinetic relations for fluxes q_i, j_{ni} and j_{pi} (see isotropic form in [12]).

Finally we can write equations for temperature and diffusion fields which suggest that velocities of their signals have finite values. Therefore basing on Eqs. (1.3), $(1.5)_{1,2}$ and (4.16)–(4.18), utilizing the relations (4.1), we obtain in the case of isotropy

$$(4.19)\quad \varkappa\theta_{,ii} - \tau^q \varrho T_0 \ddot{S} - \varrho T_0 \dot{S} - T_0 m^p(\mathscr{E}_i - \mu_{p,i})_{,i} - T_0 m^n(\mathscr{E}_i + \mu_{n,i})_{,i} - \left(\tau^q \frac{d}{dt} + 1\right) \times (-\mu_n j_{ni,i} + \mu_p j_{pi,i}) - \left(\tau^q \frac{d}{dt} + 1\right)(Q_i \Pi_{qi} + J_{ni}\Pi_{ni} + J_{pi}\Pi_{pi}) + \left(\tau^q \frac{d}{dt} + 1\right)(\varrho r + \mu_n g_n^+ + \mu_p g_p^+) = 0,$$

$$(4.20)\quad \varrho n_0 \xi^n(\mathscr{E}_i + \mu_{n,i})_{,i} - \tau^n \varrho \ddot{N} - \varrho \dot{N} - m^n \theta_{,ii} + \left(\tau^n \frac{d}{dt} + 1\right) g_n^+ = 0,$$

$$(4.21)\quad -\varrho p_0 \xi^p(\mathscr{E}_i - \mu_{p,i})_{,i} - \tau^p \varrho \ddot{P} - \varrho \dot{P} + m^p \theta_{,ii} + \left(\tau^p \frac{d}{dt} + 1\right) g_p^+ = 0.$$

For the sake of simplicity, the above expressions do not concern any constitutive relations (4.3)–(4.11) and (4.14), (4.15).

5. Final remarks

Summing up, we should like to make two important remarks,

1) the information about the signs and the relations between the coefficients appearing in the kinetic expressions (3.5)–(3.10) can be derived from the fact that the phenomenological coefficients L_{ab} have to satisfy such weak inequalities

$$L_{aa} \geqslant 0, \quad L_{aa}L_{bb} - \frac{1}{4}(L_{ab} + L_{ba})^2 \geqslant 0, \quad \det L_{ab} \geqslant 0;$$

2) basing on the theory proposed in the paper we can work out the remaining coupled differential equations referring to distributions of u_i, $\mathscr{E}_i$, B_i, N, P, θ fields in the following way:

from balance of momentum together with kinetic and constitutive relations — equations of motion,

from Maxwell's equations together with constitutive and kinetic relations — equations of the electromagnetic field coupled with other fields.

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