

On the heat equation for n-type semiconductors defective by dislocations

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Abstract

In a previous paper, in a geometrized framework for the description of simple materials with internal variables, the specific example of defective semiconductor crystals defective by dislocations was considered and a dislocation core tensor *à la* Maruszewski and its flux were introduced as internal variables in the state space. Moreover, the entropy function and the entropy 1-form, starting point to introduce a thermodynamical phase space, were derived. In this contribution Clausius-Duhem inequality for these media is exploited, and, using a Maugin technique, the laws of state, the extra entropy flux and the residual dissipation inequality are worked out. Also, following Maugin, the heat equation in a first and a second form is derived.

Keywords: Non-equilibrium thermodynamics, extrinsic semiconductor crystals, dislocation defects, internal variables.

1. Introduction

The models for semiconductors with defects of dislocations may have relevance in several fundamentals technological sectors: in applied computer science, in technology for integrated circuits VLSI (Very Large Scale Integration), in the field of electronic microscopy, in nanotechnology. Semiconductor crystals, as Germanium (Ge) and Silicon (Si), are tetravalent elements with electrical conductivity in between that of a conductor and that of an insulator. In Fig. 1_a we have the representation of a germanium crystal that has a behaviour of an insulator at a temperature of $0^\circ K$. But at room temperature, $300^\circ K$ (see Fig. 1_b), electrons of the crystal can gain enough thermal energy to jump to the conduction band. To modify the electrical properties of intrinsic semiconductors, impurity atoms adding one electron or one hole are introduced inside semiconductor crystals, using different techniques of “doping”. By pentavalent impurities, as antimony, an n-type extrinsic semiconductor is obtained, having more free flowing electrons (see

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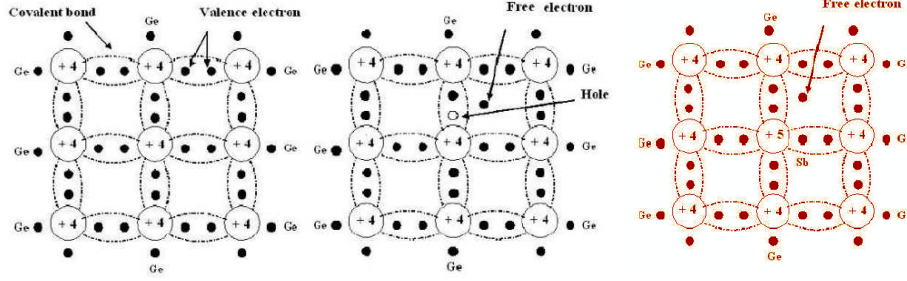


Fig. 1. A symbolic representation in 2-D of a Ge crystal structure: (a) at $0^\circ K$; (b) at $300^\circ K$ with a broken covalent bond and (c) doped by an atom of a pentavalent impurity (Antimony)

Fig. 1_c). In extrinsic semiconductor crystals with defects of dislocations the geometry of the internal structure of these materials can influence the physical fields occurring in the body. The dislocation lines form a network of infinitesimally capillary channels inside the elastic solid. Then, these defects, acquired during a process of fabrication, can self propagate, because of changed and favorable surrounding conditions. Thus, they can provoke a premature fracture. The dislocation lines disturb the periodicity of the crystal lattice [1]. A dislocation line can be created introducing an extra plane of atoms, as in Fig. 2. The interatomic distances are not conserved

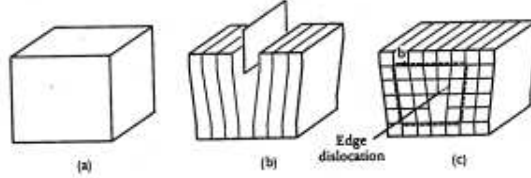


Fig. 2. A perfect crystal in (a) is cut and an extra plane of atoms is inserted; in (b) the bottom edge of the extra plane is an edge dislocation; in (c) a *Burgers vector* $\mathbf{b}$ is required to close a loop of equal atom spacings around the edge dislocation

in the direct neighborhood of the dislocation line which has a shape depending on the kind of dislocation. Thus, we introduce a dislocation core tensor à la Maruszewski [2] and its flux in the thermodynamical state space of independent variables for describing these defects. The definition and the introduction of the dislocation core tensor is based (see Fig. 3₁) on a Kubik's geometrical model. In [3] Kubik considers a representative elementary sphere volume Ω of structure of capillary porous channels (filled with fluid), large enough to provide a representation of all the statistical properties of the channel space Ω^{ch} . $\Omega = \Omega^s + \Omega^{ch}$, where Ω^s is the solid space. Since all the channels are considered to be interconnected the *effective volume*

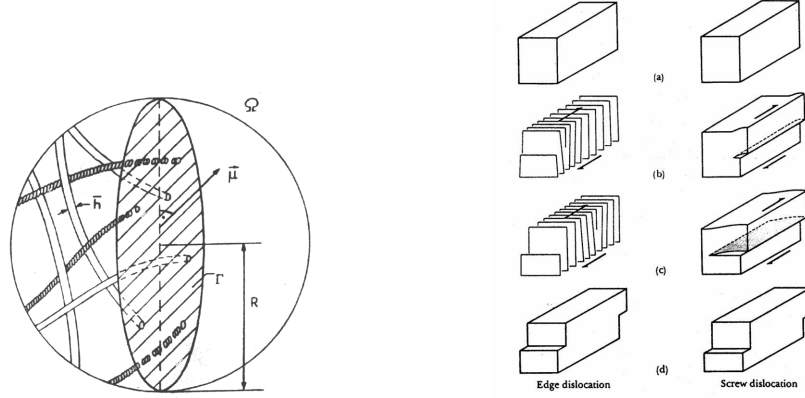


Fig. 3. (1) Characteristics of a channel-core structure ($\bar{h} \ll R$) (after [2]); (2) A shear force acting on a dislocation inside into a perfect crystal (a) causes the motion of the dislocation through the crystal until a step is created and (b) the crystal is now deformed [1]

porosity is completely defined as $f_v = \frac{\Omega^{ch}}{\Omega}$. The analysis is restricted to media which are homogeneous with respect to volume porosity f_v , i.e. f_v remains constant in the medium. Let $\alpha(\xi)$ be any scalar, spatial vector or second order tensor a quantity describing a microscopic property of the flux of some physical field flowing through the channel space Ω^{ch} and written with respect to a coordinate system ξ_i . We assume that such quantity is zero in the solid space Ω^s . The volume averaging procedures give

$$(1.1) \quad \hat{\alpha}(\mathbf{x}) = \frac{1}{f_v \Omega} \int_{\Omega^{ch}} \alpha(\xi) d\Omega, \quad \bar{\alpha}(\mathbf{x}) = \frac{1}{\Omega} \int_{\Omega^{ch}} \alpha(\xi) d\Omega,$$

where the quantities $\hat{\alpha}(\mathbf{x})$ and $\bar{\alpha}(\mathbf{x})$ (written with respect to the a coordinate system x_i) describe at macroscopic level the same property of the flux of the physical field. They are average quantities on channel-volume and on bulk-volume, respectively. Similarly, we define the average quantity of $\alpha(\xi)$ on channel-area as follows

$$(1.2) \quad \bar{\alpha}^*(\mathbf{x}, \boldsymbol{\mu}) = \frac{1}{\Gamma^{ch}} \int_{\Gamma} \alpha(\xi) d\Gamma,$$

where Γ is the central sphere section and Γ^{ch} represents the channel-area of Γ . The orientation of Γ in Ω is given by the normal vector $\boldsymbol{\mu}$. Furthermore, $\Gamma = \Gamma^s + \Gamma^{ch}$, where Γ^s is the solid area. By definition the quantity $\alpha(\xi)$ is zero on the solid surface Γ^s . In such a medium, following Kubik in [3], Maruszewski defines the so called *dislocation tensor*, as follows [2]

$$(1.3) \quad \bar{\alpha}(\mathbf{x})_i = \mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) \bar{\alpha}_j^*(\mathbf{x}, \boldsymbol{\mu}).$$

Eq. (1.3) gives a linear mapping between the bulk-volume average quantity $\bar{\alpha}(\mathbf{x})$ and the channel-area average of the same quantity $\bar{\alpha}^*(\mathbf{x}, \boldsymbol{\mu})$. In [3] Kubik gives an interpretation of $\mathcal{R}_{ij}$ considering the flux of a quantity $\bar{\alpha}(\mathbf{x})$ on a bulk-volume as a superposition of three unidimensional fluxes (along three mutually perpendicular channels) having average values $\bar{\alpha}_i^*(\mathbf{x}, \boldsymbol{\mu})$ on the orthogonal section areas of these channels. In [2] a new tensor, that refers $\mathcal{R}_{ij}$ to the surface Γ , is defined in the following way

$$\mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) = \Gamma a_{ij}(\mathbf{x}, \boldsymbol{\mu}).$$

a_{ij} is called *dislocation core tensor* and its unit is m^{-2} . The components of a_{ij} form a kind of continuous representation of the number of dislocations which cross the surface Γ . Investigations show that a_{ij} is also dependent on time.

In [4] a thermodynamical model for extrinsic semiconductors with defects of dislocations was developed in the framework of rational extended non-equilibrium thermodynamics with internal variables [5]. In fact, dissipative fluxes and gradients of the physical fields are included in the state space and additional rate equations for fluxes and internal variables are taken into consideration, so that the balance equations on such extended state space form a hyperbolic system of partial differential equations giving finite speeds of disturbances. Such finite velocity of propagation of physical fields is very important in nanotechnology where the signals have transmission velocity very high. In [4] the laws of state and the constitutive relations were deduced for defective semiconductors and wave propagations were investigated as applications. In [6] and [7] a geometrical model for these media was derived, in a geometrized framework for the description of simple materials with internal variables [8]. The dynamical system for a *simple material element* of extrinsic semiconductors was deduced and the entropy function and the entropy 1-form, as a starting point to introduce a thermodynamical phase space, were derived. In this contribution, within the model developed in [4], we exploit the Clausius-Duhem inequality for these media and, using a Maugin's technique [9], we work out the laws of state, the extra entropy flux and the residual dissipation inequality. Also, following Maugin [9], the heat equation in a first and a second form is obtained. Moreover, by means of the same methodology, dissipative processes were studied by us in perfect semiconductors with trivalent and pentavalent impurities [10].

2. A non conventional model for n-type semiconductors

In [11], [12], thermodynamical models for semiconductors with impurities were developed. In [4] the behaviour of defective extrinsic semiconduc-

tors was studied. In this paper we use the model developed in [4], taking into account only n -type extrinsic semiconductors. We use the standard Cartesian tensor notation in a rectangular coordinate system and we refer the motion of our material system to a current configuration $\mathcal{K}_t$. We assume that in defective, extrinsic, thermoelastic semiconductors the following fields interact with each other: *the elastic field* described by the total stress tensor T_{ij} and the small-strain tensor ε_{ij} ; *the thermal field* described by the temperature θ and the heat flux q_i ; *the electromagnetic field* described by the electromotive intensity $\mathcal{E}_i$ and the magnetic induction B_i ; *the charge carrier fields* described by the densities of electrons n and holes p and their fluxes j_i^n and j_i^p ; *the dislocation field* described by the dislocation density tensor a_{ij} and the dislocation flux $\mathcal{V}_{ijk}$. The independent variables are represented by the set

$$(2.1) \quad C = \{\varepsilon_{ij}, \mathcal{E}_i, B_i, n, p, \theta, a_{ij}, \mathcal{V}_{ijk}, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i}, a_{ij,k}\}.$$

Now, in the following we present the laws that govern all the processes occurring in the considered body.

Maxwell's equations have the form

$$(2.2) \quad \varepsilon_{ijk} E_{k,j} + \frac{\partial B_i}{\partial t} = 0, \quad D_{i,i} - \rho Z = 0,$$

$$(2.3) \quad \varepsilon_{ijk} H_{k,j} - j_i^Z - \frac{\partial D_i}{\partial t} = 0, \quad B_{i,i} = 0,$$

where $\mathbf{E}$, $\mathbf{B}$, $\mathbf{D}$ and $\mathbf{H}$ denote the electric field, the magnetic induction, the electric displacement and the magnetic field per unit volume, respectively. Moreover, $H_i = \frac{1}{\mu_0} B_i$, $E_i = \frac{1}{\varepsilon_0} (D_i - P_i)$, v_i is the barycentric velocity of the body, ε_0 and μ_0 denote the permittivity and permeability of vacuum, respectively. $\mathbf{P}$ is the electric polarization per unit volume. The magnetization $\mathbf{M}$ is assumed to be zero, $\mathbf{M} = 0$. The total charge density Z and the density of the total electric current $\mathbf{j}^Z$ are defined as follows $Z = n - n_0 + p + \bar{p} - p_0$, $j_i^Z = \rho Z v_i + j_i^n + j_i^p$, where $n < 0$, $n_0 < 0$, $\bar{p} > 0$, $p > 0$, $p_0 > 0$ and $j_i^{n_0} = 0$, $j_i^{p_0} = 0$ and $j_i^{\bar{p}} = 0$. The following charge conservation law holds

$$(2.4) \quad \rho \dot{Z} + j_{i,i}^Z = 0.$$

n and p denote non equilibrium electron and positive charges, n_0 and p_0 denote the equilibrium electron and positive charges, $\bar{p}$ is the positive charge of ionized pentavalent impurities. $\rho Z v_i$ is the electric current due to convection, $j_i^n + j_i^p$, which is called the conduction current, is the electric current

due to the relative motion of the electrons and holes respect to the barycentric motion of the body (i.e. $j_i^n = \rho n(v_i^n - v_i)$ and $j_i^p = \rho p(v_i^p - v_i)$).

n are the negative electric charges coming from: the negative free charges created doping the semiconductor by pentavalent impurities, denoted by N (see Fig. 1_c), and the free electrons coming from the intrinsic base of the semiconductor, denoted by $\bar{n}$, (see Fig. 1_b). Thus we have $n = N + \bar{n}$. Furthermore, we have positive electric charges coming from: the fixed and positive ionized atoms of doping pentavalent impurities, denoted by $\bar{p}$, (see Fig. 1_c) and the holes coming from the intrinsic base of the semiconductor, denoted by p (see Fig. 1_b). The following charge conservation laws hold

$$\rho \dot{N} + j_{i,i}^N = g^N, \quad \rho \dot{\bar{n}} + j_{i,i}^{\bar{n}} = g^{\bar{n}}, \quad \rho \dot{n} + j_{i,i}^n = g^n,$$

where $n = N + \bar{n}$, $j_{i,i}^n = j_{i,i}^N + j_{i,i}^{\bar{n}}$ and $g^n = g^N + g^{\bar{n}}$.

Moreover, we have $\rho \dot{p} + j_{i,i}^p = g^p$, $\rho \dot{\bar{p}} = \bar{g}^p$, where $j_{i,i}^{\bar{p}} = 0$, since the fixed impurities ionized have velocity $\mathbf{v}$ (i.e. they are comoving with the body). Furthermore, we assume that the concentration $\bar{p}$ is practically constant. Hence, $\dot{\bar{p}} = 0$ and $\bar{g}^p = 0$. Moreover, g^n and g^p describe the recombination of electrons and holes and satisfy the equation $g^n + g^p = 0$, in virtue of the law of balance of the total charge. Now, we call non equilibrium conduction current the quantity $\rho z v_i = \rho(N + \bar{n} + p + \bar{p})v_i$, so that the following charge conservation law holds $\rho \dot{z} + j_{i,i}^z = g^z$, where $z = N + \bar{n} + p + \bar{p}$ and $g^z = g^n + g^p = 0$. Now, we consider a thermodynamical equilibrium state where the electromotive intensity $\mathcal{E}_i$, the deformation tensor ε_{ij} , the velocity $\mathbf{v}$ of the body and the fluxes of the physical fields assume the zero value, and all the other physical fields (indicated with the subscript "0") are constant. In such a state we have the following equilibrium charges $z_0 = N_0 + \bar{n}_0 + p_0 + \bar{p}_0$, (with $|n_0| = |p_0|$) and the balance equations $\rho \dot{n}_0 = 0$, $\rho \dot{p}_0 = 0$, $\dot{p}_0 = 0$. Thus, we can consider very small deviations with respect to the thermodynamical equilibrium state and for the charge carriers $Z = z - z_0$ we have the following charge conservation law $\rho \dot{Z} + j_{i,i}^Z = 0$ (see (2.4)). In fact, the Maxwell's equ.s (2.2) and (2.3) are equations in perturbation around the equilibrium state defined above. Moreover, also the balance equations, the rate equations and constitutive relations are equations in perturbation around the same equilibrium state. *The evolution equations for the electron, hole and heat fluxes have the form:*

$$\dot{j}_i^n - J_i^n(C) = 0, \quad \dot{j}_i^p - J_i^p(C) = 0, \quad \dot{q}_i = Q_i(C),$$

where $\mathbf{J}^n$, $\mathbf{J}^p$ and $\mathbf{Q}$ are the electron, hole and heat flux sources.

Furthermore, we have: *the continuity equation* $\dot{\rho} + \rho v_{i,i} = 0$,

where ρ denotes the mass density. The mass charge carriers have been ne-

glected compared to ρ ;
the momentum balance:

$$(2.5) \quad \rho \dot{v}_i - T_{ji,j} - \rho Z \mathcal{E}_i - \varepsilon_{ijk} \left(j_j^n + j_j^p + \overset{\Delta}{P}_j \right) B_k - P_j \mathcal{E}_{i,j} = 0,$$

where $\overset{\Delta}{P}_i = \dot{P}_i + P_i v_{i,k} - P_k v_{i,k}$ and $\mathcal{E}_i = E_i + \varepsilon_{ijk} v_j B_k$ is the electric field referred to an element of the matter at time t (i.e. to the so called comoving frame $\mathcal{K}_c$);

the momentum of momentum balance:

$$(2.6) \quad \varepsilon_{ijk} T_{jk} + c_i = 0.$$

In [4] it was demonstrated that the couple c_i for unit volume is vanishing;

the internal energy balance: $\rho \dot{e} - T_{ji} v_{i,j} - \left(j_j^n + j_j^p \right) \mathcal{E}_j - \rho \mathcal{E}_i \dot{P}_i + q_{i,i} = 0$,
where e is the internal energy density, $\dot{P}_i = \rho \mathcal{P}_i$ and $v_{i,j}$ is the velocity gradient;

the evolution equation for the dislocation density and the dislocation fluxes:

$$\dot{a}_{ij} + \mathcal{V}_{ijk,k} - A_{ij}(C) = 0, \quad \dot{\mathcal{V}}_{ijk} - \mathcal{V}_{ijk}(C) = 0.$$

All the admissible solutions of the proposed evolution equations should be restricted by the following *entropy inequality*:

$$\rho \dot{S} + J_{k,k}^S - \frac{\rho r}{\theta} \geq 0,$$

where S denotes the entropy per unit mass and $\mathbf{J}^S$ is the entropy flux. $\mathbf{J}^S$ is defined by $\mathbf{J}^S = \frac{1}{\theta} \mathbf{q} + \mathbf{k}$, where $\mathbf{k}$ an additional term called *extra entropy flux density*. In [4] constitutive functions $\mathbf{Z} = \tilde{\mathbf{Z}}(C)$ with

$$(2.7) \quad \mathbf{Z} = \{ T_{ij}, P_i, c_i, e, g^n, g^p, A_{ij}, V_{ijk}, J_i^n, J_i^p, Q_i, S, J_i^S, \mu^n, \mu^p, \pi_{ij} \},$$

were obtained for extrinsic semiconductors with defects of dislocation in different cases to close the balance equation system. The entropy inequality was analyzed by Liu's theorem [13], using isotropic polynomial representations of proper constitutive functions satisfying the objectivity and material frame indifference principles (see Smith's theorem [14]). $\mu^n \equiv \frac{\partial \psi}{\partial n}$, $\mu^p \equiv \frac{\partial \psi}{\partial p}$, and $\pi_{ij} \equiv \rho \frac{\partial \psi}{\partial a_{ij,k}}$ are thermodynamical potentials, with $\psi = e - \theta S - \frac{1}{\rho} \mathcal{E}_i P_i$ the free energy density per unit volume. In [4], the following form was assumed for the quantities responsible for the dislocation field

$$(2.8) \quad a_{ij} = a \delta_{ij}, \quad A_{ij} = A \delta_{ij}, \quad \pi_{ij} = \pi \delta_{ij}, \quad \mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij}, \quad V_{ijk} = V_k \delta_{ij}, \quad \Pi_{ijk}^A = \Pi_k^A \delta_{ij},$$

and the following general representations were derived:

$$(2.9) \quad T_{ij} = \beta_\tau^1 \delta_{ij} + \beta_\tau^2 \varepsilon_{ij} + \beta_\tau^3 \varepsilon_{ik} \varepsilon_{kj} + \beta_\tau^4 \mathcal{E}_i \mathcal{E}_j + \beta_\tau^5 (\varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k + \varepsilon_{ik} \mathcal{E}_j \mathcal{E}_k) + \beta_\tau^6 (\varepsilon_{jk} \varepsilon_{ks} \mathcal{E}_i \mathcal{E}_s + \varepsilon_{ik} \varepsilon_{ks} \mathcal{E}_s \mathcal{E}_j),$$

$$(2.10) \quad P_i = (\beta_{\mathfrak{P}}^1 \delta_{ik} + \beta_{\mathfrak{P}}^2 \varepsilon_{ik} + \beta_{\mathfrak{P}}^3 \varepsilon_{ij} \varepsilon_{jk}) \mathcal{E}_k,$$

$$(2.11) \quad S = \beta_s^1 n + \beta_s^2 p + \beta_s^3 \theta + \beta_s^4 \mathcal{E}_k \mathcal{E}_k + (\beta_s^5 \delta_{ij} + \beta_s^6 \varepsilon_{ij} + \beta_s^7 \varepsilon_{jk} \varepsilon_{ki} + \beta_s^8 \mathcal{E}_i \mathcal{E}_j + \beta_s^9 \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij},$$

$$(2.12) \quad \mu^n = \beta_n^1 n + \beta_n^2 p + \beta_n^3 \theta + \beta_n^4 a + \beta_n^5 \mathcal{E}_k \mathcal{E}_k + (\beta_n^6 \delta_{ij} + \beta_n^7 \varepsilon_{ij} + \beta_n^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_n^9 \mathcal{E}_i \mathcal{E}_j + \beta_n^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij},$$

$$(2.13) \quad \mu^p = \beta_p^1 n + \beta_p^2 p + \beta_p^3 \theta + \beta_p^4 a + \beta_p^5 \mathcal{E}_k \mathcal{E}_k + (\beta_p^6 \delta_{ij} + \beta_p^7 \varepsilon_{ij} + \beta_p^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_p^9 \mathcal{E}_i \mathcal{E}_j + \beta_p^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij},$$

$$(2.14) \quad \pi = \beta_\pi^1 n + \beta_\pi^2 p + \beta_\pi^3 \theta + \beta_\pi^4 a + \beta_\pi^5 \mathcal{E}_k \mathcal{E}_k + (\beta_\pi^6 \delta_{ij} + \beta_\pi^7 \varepsilon_{ij} + \beta_\pi^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_\pi^9 \mathcal{E}_i \mathcal{E}_j + \beta_\pi^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij},$$

where β_τ^α , $\beta_{\mathfrak{P}}^\gamma$, β_s^δ , β_n^ε , β_p^ε , β_π^ε , ($\alpha = 1, 2, \dots, 6$), ($\gamma = 1, 2, 3$), ($\delta = 1, 2, \dots, 9$), ($\varepsilon = 1, 2, \dots, 10$), can be functions of the following invariants

$$(2.15) \quad n, p, \theta, a, \mathcal{E}_i \mathcal{E}_i, \varepsilon_{kk}, \varepsilon_{ij} \varepsilon_{ij}, \varepsilon_{ij} \varepsilon_{jk} \varepsilon_{ki}, \varepsilon_{ij} \mathcal{E}_i \mathcal{E}_j, \varepsilon_{ij} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k.$$

The general representation for the affinities Π_i^n , Π_i^p , Π_i^Q and Π_i^A (defined in the last section) were given in the form

$$(2.16) \quad \Pi_i^n = \beta_N^1 \mathcal{V}_i + \beta_N^2 j_i^n + \beta_N^3 j_i^p + \beta_N^4 q_i, \quad \Pi_i^p = \beta_P^1 \mathcal{V}_i + \beta_P^2 j_i^n + \beta_P^3 j_i^p + \beta_P^4 q_i,$$

$$(2.17) \quad \Pi_i^Q = \beta_Q^1 \mathcal{V}_i + \beta_Q^2 j_i^n + \beta_Q^3 j_i^p + \beta_Q^4 q_i, \quad \Pi_i^A = \beta_A^1 \mathcal{V}_i + \beta_A^2 j_i^n + \beta_A^3 j_i^p + \beta_A^4 q_i,$$

where β_N^δ , β_P^δ , β_Q^δ , β_A^δ , ($\delta = 1, 2, \dots, 4$), can be depend on the invariants:

$$\mathcal{V}_i \mathcal{V}_i, j_i^n j_i^n, j_i^p j_i^p, \mathcal{V}_i j_i^n, \mathcal{V}_i j_i^p, \mathcal{V}_i q_i, j_i^n q_i, j_i^p q_i.$$

Approximated expressions for the evolution equations for the dislocation density, dislocation, electron, hole and heat fluxes were obtained in the form (see [4])

$$(2.18) \quad \dot{a} + \mathcal{V}_{k,k} = \delta_a^1 \varepsilon_{kk} + \delta_a^2 n + \delta_a^3 p + \delta_a^4 T + \delta_a^5 a + \delta_a^6 \mathcal{E}_i + \delta_a^7 a_{,i} + \delta_a^8 n_{,i} + \delta_a^9 p_{,i} + \delta_a^{10} \theta_{,i} + \delta_a^{11} \mathcal{V}_i + \delta_a^{12} j_i^n + \delta_a^{13} j_i^p + \delta_a^{14} q_i,$$

$$(2.19) \quad \dot{\mathcal{V}}_k = \delta_v^1 \mathcal{E}_k + \delta_v^2 a_{,k} + \delta_v^3 n_{,k} + \delta_v^4 p_{,k} + \delta_v^5 \theta_{,k} + \delta_v^6 \mathcal{V}_k + \delta_v^7 j_k^n + \delta_v^8 j_k^p + \delta_v^9 q_k,$$

$$(2.20) \quad \dot{j}_k^n = \delta_n^1 \mathcal{E}_k + \delta_n^2 a_{,k} + \delta_n^3 n_{,k} + \delta_n^4 p_{,k} + \delta_n^5 \theta_{,k} + \delta_n^6 \mathcal{V}_k + \delta_n^7 j_k^n + \delta_n^8 j_k^p + \delta_n^9 q_k,$$

$$(2.21) \quad \dot{j}_k^p = \delta_p^1 \mathcal{E}_k + \delta_p^2 a_{,k} + \delta_p^3 n_{,k} + \delta_p^4 p_{,k} + \delta_p^5 \theta_{,k} + \delta_p^6 \mathcal{V}_k + \delta_p^7 j_k^n + \delta_p^8 j_k^p + \delta_p^9 q_k,$$

$$(2.22) \quad \dot{q}_k = \delta_q^1 \mathcal{E}_k + \delta_q^2 a_{,k} + \delta_q^3 n_{,k} + \delta_q^4 p_{,k} + \delta_q^5 \theta_{,k} + \delta_q^6 \mathcal{V}_k + \delta_q^7 j_k^n + \delta_q^8 j_k^p + \delta_q^9 q_k,$$

where $\delta_a^\zeta, \delta_v^\eta, \delta_n^\eta, \delta_p^\eta, \delta_q^\eta$, ($\zeta = 1, 2, \dots, 14$), ($\eta = 1, 2, \dots, 9$), can depend on invariants built on the set C (2.1).

3. Clausius-Duhem inequality analysis

Now, taking into account the following set of independent variables $C = (F_{ij}, \mathcal{E}_i, B_i, n, p, \theta, a_{ij}, \mathcal{V}_{ijk}, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i}, a_{ij,k})$, where we have chosen the deformation gradient F_{ij} as ε_{ij} , we exploit the Clausius-Duhem inequality to derive the state laws, the entropy flux and the inequality governing the dissipative processes [9]. We consider the entropy inequality

$$(3.1) \quad \rho \theta \dot{S} + (\theta J_i^S)_{,i} - J_i^S \theta_{,i} \geq 0,$$

where $\theta > 0$ and J^S is the entropy flux. Then, we introduce the free energy per unit volume $\psi = e - \theta S - \frac{1}{\rho} \mathcal{E}_i P_i$. By the time derivation we obtain

$$(3.2) \quad \dot{\psi} = \dot{e} - \theta \dot{S} - \dot{\theta} S + \frac{1}{\rho^2} \dot{\rho} \mathcal{E}_i P_i - \frac{1}{\rho} \dot{\mathcal{E}}_i P_i - \frac{1}{\rho} \mathcal{E}_i \dot{P}_i.$$

Using the internal energy balance equation and taking into account the material derivative of the free energy ψ as a constitutive function of the independent variables, from the entropy inequality we obtain the following Clausius Duhem inequality:

$$(3.3) \quad \begin{aligned} & \left(T_{ji} F_{kj}^{-1} - \rho \frac{\partial \psi}{\partial F_{ik}} \right) \dot{F}_{ik} - \left(\rho \frac{\partial \psi}{\partial \mathcal{E}_i} + P_i \right) \dot{\mathcal{E}}_i - \rho \frac{\partial \psi}{\partial B_i} \dot{B}_i + \rho \mathcal{A}^n \dot{n} + \rho \mathcal{A}^p \dot{p} + \\ & + \rho \mathcal{A}_{ij} \dot{a}_{ij} - \rho \left(\frac{\partial \psi}{\partial \theta} + S \right) \dot{\theta} - \rho \frac{\partial \psi}{\partial \mathcal{V}_{ijk}} \dot{\mathcal{V}}_{ijk} - \rho \frac{\partial \psi}{\partial j_i^n} \dot{j}_i^n - \rho \frac{\partial \psi}{\partial j_i^p} \dot{j}_i^p - \rho \frac{\partial \psi}{\partial q_i} \dot{q}_i - \rho \frac{\partial \psi}{\partial \theta_{,i}} \dot{\theta}_{,i} + \\ & - \rho \left[\frac{\partial \psi}{\partial n_{,i}} \dot{n}_{,i} + \frac{\partial \psi}{\partial p_{,i}} \dot{p}_{,i} + B_{ijk} \dot{a}_{ij} - \frac{\theta}{\rho} k_i \right]_{,i} + (j_i^n + j_i^p) \mathcal{E}_i + \left(\frac{\theta}{\rho} k_i \right) \rho_{,i} - \theta_{,i} J_i^S \geq 0. \end{aligned}$$

In equ.(3.3) we have introduced the following notations:

$$B_{ijk} = \frac{\partial \psi}{\partial a_{ij,k}} \quad \mathcal{A}_{ij} = \left[-\frac{\partial \psi}{\partial a_{ij}} + \left(\frac{\partial \psi}{\partial a_{ij,k}} \right)_{,k} \right] = -\frac{\delta \psi}{a_{ij}},$$

$$\mathcal{A}^n = \left[-\frac{\partial \psi}{\partial n} + \left(\frac{\partial \psi}{\partial n_{,i}} \right)_{,i} \right] = -\frac{\delta \psi}{\delta n} \quad \mathcal{A}^p = \left[-\frac{\partial \psi}{\partial p} + \left(\frac{\partial \psi}{\partial p_{,i}} \right)_{,i} \right] = -\frac{\delta \psi}{\delta p}.$$

where $\frac{\delta \psi}{\delta n}$, $\frac{\delta \psi}{\delta p}$ and $\frac{\delta \psi}{\delta a_{ij}}$ are the “space” Euler-Lagrange derivative respect to n , p and $\mathbf{a}$, respectively [9]. As $T_{ji}F_{kj}^{-1}$, P_i , $\frac{\partial \psi}{\partial B_i}$, S and $\frac{\partial \psi}{\partial \theta_{,i}}$ are assumed not to depend on $\dot{F}_{ik}$, $\dot{\mathcal{E}}_i$, $\dot{B}_i$, $\dot{\theta}$ and $\dot{\theta}_{,i}$, while the remaining coefficients may in general depend on their respective factors, from inequality (3.3) we obtain the following laws of state

$$(3.4) \quad \rho \frac{\partial \psi}{\partial F_{ik}} = T_{ji}F_{kj}^{-1}, \quad \frac{\partial \psi}{\partial B_i} = 0, \quad \rho \frac{\partial \psi}{\partial \theta_{,i}} = 0, \quad \rho \frac{\partial \psi}{\partial \mathcal{E}_i} = -P_i, \quad \frac{\partial \psi}{\partial \theta} = -S.$$

Moreover, since in non-equilibrium thermodynamics the residual dissipation inequality has the standard bilinear form $\sum_{\beta} X_{\beta} Y_{\beta} \geq 0$, (with $\mathbf{X}$ and $\mathbf{Y}$ fluxes and associated forces), the divergence term is assumed to be equal to zero and by physical reasons the vector, to which the divergence operator is applied, is taken to be equal to zero (see [9])

$$\left(\frac{\partial \psi}{\partial n_{,i}} \dot{n} + \frac{\partial \psi}{\partial p_{,i}} \dot{p} + B_{ijk} \dot{a}_{ij} - \frac{\theta}{\rho} k_i \right)_{,i} = 0, \quad k_i = \left(\frac{\partial \psi}{\partial n_{,i}} \dot{n} + \frac{\partial \psi}{\partial p_{,i}} \dot{p} + B_{ijk} \dot{a}_{ij} \right) \frac{\rho}{\theta},$$

so that Clausius-Duhem inequality reduces itself to the following *residual dissipation inequality*

$$(3.5) \quad \rho \mathcal{A}^n \dot{n} + \rho \mathcal{A}^p \dot{p} + \rho \mathcal{A}_{ij} \dot{a}_{ij} - \rho \frac{\partial \psi}{\partial \mathcal{V}_{ijk}} \dot{\mathcal{V}}_{ijk} - \rho \frac{\partial \psi}{\partial j_i^n} \dot{j}_i^n +$$

$$- \rho \frac{\partial \psi}{\partial j_i^p} \dot{j}_i^p - \rho \frac{\partial \psi}{\partial q_i} \dot{q}_i + (j_i^n + j_i^p) \mathcal{E}_i + \left(\frac{\theta}{\rho} k_i \right) \rho_{,i} - J_i^S \theta_{,i} \geq 0.$$

Very often the residual dissipation inequality is split in two parts [9]

$$(3.6) \quad \Phi_{intr} = \rho \mathcal{A}^n \dot{n} + \rho \mathcal{A}^p \dot{p} + \rho \mathcal{A}_{ij} \dot{a}_{ij} - \rho \frac{\partial \psi}{\partial \mathcal{V}_{ijk}} \dot{\mathcal{V}}_{ijk} - \rho \frac{\partial \psi}{\partial j_i^n} \dot{j}_i^n +$$

$$- \rho \frac{\partial \psi}{\partial j_i^p} \dot{j}_i^p - \rho \frac{\partial \psi}{\partial q_i} \dot{q}_i + (j_i^n + j_i^p) \mathcal{E}_i + \left(\frac{\theta}{\rho} k_i \right) \rho_{,i} \geq 0$$

and $\Phi_{th} = -J_i^S \theta_{,i} \geq 0$, where, in some sense, we recognize the different qualitative nature of the two classes of dissipative processes. Φ_{intr} and Φ_{th} are the intrinsic and thermal dissipations, respectively [9].

4. Heat equation

Now, in order to obtain the heat equation, we observe that it is none other than a form of energy balance equation. Indeed, on using the free energy expression $\psi = e - \theta S - \frac{1}{\rho} \mathcal{E}_i P_i$, its time derivative and the laws of state in the energy balance equation or, equivalently, “just comparing entropy inequality (3.1) and the residual inequality” (3.6) (see [9]), we deduce *a first general form of the heat equation*

$$(4.1) \quad \rho \theta \dot{S} + (\theta J_i^S)_{,i} = \Phi_{intr},$$

where the intrinsic dissipation acts like a body source of heat. Now, taking into account the state laws (3.4)₂, (3.4)₃ and (3.4)₅ and the following material derivative of the entropy S as a constitutive function of the independent variables

$$\dot{S} = - \left[\frac{\partial^2 \psi}{\partial \mathbf{F} \partial \theta} \cdot \dot{\mathbf{F}} + \frac{\partial^2 \psi}{\partial \boldsymbol{\mathcal{E}} \partial \theta} \cdot \dot{\boldsymbol{\mathcal{E}}} + \frac{\partial^2 \psi}{\partial n \partial \theta} \dot{n} + \frac{\partial^2 \psi}{\partial p \partial \theta} \dot{p} + \frac{\partial^2 \psi}{\partial \theta^2} \dot{\theta} + \frac{\partial^2 \psi}{\partial \mathbf{a} \partial \theta} \cdot \dot{\mathbf{a}} + \frac{\partial^2 \psi}{\partial \boldsymbol{\mathcal{V}} \partial \theta} \cdot \dot{\boldsymbol{\mathcal{V}}} + \frac{\partial^2 \psi}{\partial \mathbf{j}^n \partial \theta} \cdot \dot{\mathbf{j}}^n + \frac{\partial^2 \psi}{\partial \mathbf{j}^p \partial \theta} \cdot \dot{\mathbf{j}}^p + \frac{\partial^2 \psi}{\partial \mathbf{q} \partial \theta} \cdot \dot{\mathbf{q}} + \frac{\partial^2 \psi}{\partial \nabla p \partial \theta} \cdot \nabla \dot{p} + \frac{\partial^2 \psi}{\partial \nabla \mathbf{a} \partial \theta} \cdot \nabla \dot{\mathbf{a}} \right],$$

setting

$$\begin{aligned} \mathcal{C} &= -\rho \theta \frac{\partial^2 \psi}{\partial \theta^2}, & \boldsymbol{\tau} &= \rho \frac{\partial^2 \psi}{\partial \mathbf{F} \partial \theta}, & \mathbf{l} &= \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{a}}, & \mathbf{g} &= \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial \boldsymbol{\mathcal{E}}}, & \boldsymbol{\pi} &= \rho \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{a}}, \\ \boldsymbol{\nu} &= \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{q}}, & h^n &= \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial n}, & h^p &= \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial p}, & \mathbf{n} &= \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial \nabla \mathbf{a}}, \end{aligned}$$

$$\mathbf{z} = \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{q}}, \quad \mathbf{p} = \rho \theta \frac{\partial^2 \psi}{\partial \mathbf{j}^p \partial \theta}, \quad \mathbf{r} = \rho \theta \frac{\partial^2 \psi}{\partial \nabla n \partial \theta}, \quad \boldsymbol{\eta} = \rho \theta \frac{\partial^2 \psi}{\partial \nabla p \partial \theta}, \quad \mathbf{m} = \rho \theta \frac{\partial^2 \psi}{\partial \theta \partial \nabla \mathbf{a}},$$

and using the definitions of affinities: $\boldsymbol{\Pi}^n = \rho \frac{\partial \psi}{\partial \mathbf{j}^n}$, $\boldsymbol{\Pi}^p = \rho \frac{\partial \psi}{\partial \mathbf{j}^p}$, $\boldsymbol{\Pi}^Q = \rho \frac{\partial \psi}{\partial \mathbf{q}}$, we obtain the *second form of the heat equation*

$$(4.2) \quad \mathcal{C} \dot{\theta} + \nabla \cdot (\theta \mathbf{J}_S) = \Phi_{te} + \Phi_{td} + \Phi_{intr} + \Phi_{tel} + \Phi_{tc} + \Phi_q + \Phi_{ch} + \Phi_{elc} + \Phi_\rho,$$

where $\Phi_{te} = \theta (\boldsymbol{\tau} \cdot \dot{\mathbf{F}})$, $\Phi_{td} = \mathbf{l} \cdot \mathbf{a} + \boldsymbol{\nu} \cdot \boldsymbol{\mathcal{V}} + \mathbf{m} \cdot \nabla \mathbf{a}$,

$$\Phi_{intr} = \rho \boldsymbol{\mathcal{A}} \cdot \mathbf{a} - \boldsymbol{\Pi}^A \cdot \boldsymbol{\mathcal{V}}, \quad \Phi_{tel} = \mathbf{g} \cdot \dot{\boldsymbol{\mathcal{E}}}, \quad \Phi_q = (\mathbf{z} - \boldsymbol{\Pi}^Q) \cdot \dot{\mathbf{q}},$$

$$\Phi_{tc} = h^n \dot{n} + h^p \dot{p} + \mathbf{n} \cdot \dot{\mathbf{j}}^n + \mathbf{p} \cdot \dot{\mathbf{j}}^p + \mathbf{r} \cdot \nabla \dot{n} + \boldsymbol{\eta} \cdot \nabla \dot{p}, \quad \Phi_\rho = \left(\frac{\partial \psi}{\partial \rho} \right) \cdot \nabla \rho,$$

$\Phi_{ch} = \rho \mathcal{A}^n \dot{n} + \rho \mathcal{A}^p \dot{p} - \boldsymbol{\Pi}^n \cdot \dot{\mathbf{j}}^n - \boldsymbol{\Pi}^p \cdot \dot{\mathbf{j}}^p$, $\Phi_{elc} = (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\mathcal{E}}$. The dissipation terms in above equations are coming from the interaction among the different physical fields inside the body. The non negativity of the specific heat follows from the concavity of ψ with respect to θ . In semiconductor crystals ρ is practically constant, so that the terms $\left(\frac{\partial \psi}{\partial \rho} \right) \cdot \nabla \rho$, $\frac{1}{\rho} \dot{\rho} \mathcal{E}_i P_i$ and $\frac{1}{\rho} \dot{\rho} P_i$ can be neglected in previous equations. A special choice of the constitutive equations and effects to take into consideration allow to consider and solve analytically and/or numerically particular problems, describing dissipative processes in real situations.

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